Structure et propriétés des solutions et gel de cellulose-NaOH-Eau et leurs matériaux régénérés

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T H E S E

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STRUCTURE AND PROPERTIES OF CELLULOSE / NaOH AQUEOUS SOLUTIONS, GELS AND REGENERATED OBJECTS

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La cellulose est un polymère naturel de la famille des polysaccharides. Elle est formée lors de la photosynthèse. La cellulose est le principal constituant des parois cellulaires des végétaux et peut donc être extraite de l'herbe, des feuilles, des tiges (essentiellement la paille), des arbres. Le coton est très pur en cellulose, jusqu'à 98% de la composition totale. Pour la préparation des pâtes de cellulose, le bois reste la source majoritaire d'autant plus que les arbres sont aussi exploités dans ce but. La cellulose est biodégradable sous l'action des bactéries.
Mais la cellulose est difficile à mettre en oeuvre. Elle ne peut être fondue car elle se dégrade avant d'avoir atteint une fusion. Pour fabriquer des fibres, des films ou des objets tridimensionnels, la cellulose doit être soit dissoute dans des solvants directs, soit transformée chimiquement et être ensuite mise en forme.

Actuellement, le procédé industriel le plus couramment utilisé pour mettre en forme des objets en cellulose pure est le procédé dit « viscose ». La cellulose est d'abord activée par une solution aqueuse de 18-20% d'hydroxyde de sodium (NaOH) afin de faciliter la pénétration du solvant. Le sulfure de carbone (CS_2) réagit alors avec les chaînes de cellulose et forme le xanthate de cellulose, soluble dans NaOH dilué. Le mélange ainsi obtenu est appelé « viscose » et peut être mis en forme. La viscose est ensuite régénérée afin de retrouver la cellulose. Des objets variés sont ainsi obtenus : fibres, films minces et objets tridimensionnels. Ce procédé est très efficace et totalement maîtrisé. Cependant, l'utilisation du CS_2 et le dégagement des composés soufrés issus des réactions chimiques le rendent fortement polluant. A l'heure actuelle, les rejets en phase aqueuse (oxydes de soufre) sont totalement recyclés tandis que les rejets atmosphériques (H_2S) ne représentent plus que 10% du CS_2 utilisé. Mais les réglementations environnementales deviennent de plus en plus contraignantes et les techniques de traitement de la pollution sont coûteuses.

Pour des raisons à la fois économiques et environnementales, les fabricants de produits finis cellulosiques cherchent des alternatives pour mettre en forme la cellulose, le but étant de supprimer l'étape de transformation de la cellulose par le CS_2 et de trouver un solvant direct de la cellulose non polluant et peu coûteux.

Depuis le XIX^{e} siècle, les industriels utilisent des solutions aqueuses d'hydroxyde de sodium, à différentes concentrations, afin de modifier l'aspect et les propriétés des fibres de cellulose. Dans l'industrie textile, par exemple, les traitements à la soude permettaient d'améliorer la brillance des tissus ou l'absorption des colorants.
En 1939, Sobue [SOB1939] montra que 7-10% de NaOH/eau pouvait être un solvant direct de la cellulose. De nos jours, plusieurs équipes de recherche dissolvent directement la cellulose dans des solutions aqueuses d'hydroxyde de sodium (7-10%NaOH/eau, en dessous de 0°C) mais les propriétés des produits finis sont souvent inférieures à celles obtenues par le procédé « viscose ». Le problème est que ni la dissolution de la cellulose dans 7-10%NaOH/eau, ni les propriétés des solutions cellulose/NaOH/eau ne sont bien comprises.

Deux partenaires industriels ont participé à ce projet de recherche. Innovia Films Ltd, en Grande-Bretagne, qui fabrique des films cellulosiques pour l'emballage et Spontex, en France, produisant des éponges cellulosiques.

Le but de ce travail est d'explorer la possibilité de préparer des films et éponges cellulosiques par le procédé soude tout en approfondissant les aspects plus fondamentaux de la dissolution de la cellulose dans les solutions aqueuses peu concentrées d'hydroxyde de sodium. Le premier objectif était donc de comprendre la structure des solvants de la cellulose – solution d'hydroxyde de sodium avec ou sans oxyde de zinc ou urée – et la structure des solutions de cellulose dans ces mêmes solvants. Ensuite, nous avons étudié les propriétés rhéologiques des solutions de cellulose en déterminant leur comportement à l'écoulement et les conditions de gélification, en temps et en température. L'influence des additifs, ZnO et urée, fut également étudiée. Pour finir, nous avons testé mécaniquement des objets de cellulose régénérée et étudié l'influence des conditions de préparation des échantillons et notamment l'influence de l'étape de congélation (solution de cellulose restant 20 heures à -20°C) et des bains de régénération.

- *Problématique 1* : Les films obtenus à partir du procédé « soude » sont moins résistants que les films produits à partir du procédé « viscose ». Au cours des essais expérimentaux sur le procédé « soude », il apparaît que seulement une assez faible quantité de cellulose peut être dissoute dans les solutions NaOH/eau. Pour des raisons liées à la fois aux propriétés mécaniques et à la faisabilité économique du procédé, il faut augmenter la quantité de cellulose mise en solution. La question est donc de déterminer la concentration maximale de cellulose qui peut réellement être dissoute dans une solution donnée de NaOH/eau.

  Etude expérimentale : L'étude des propriétés thermiques des solutions de cellulose permettra de mieux comprendre la structure des solutions de cellulose et les interactions qui interviennent

au cours de sa dissolution entre les chaînes de cellulose, les molécules de NaOH, l'eau et les additifs.

- *Problématique 2* : Pour la fabrication des films, les solutions de cellulose doivent être les plus homogènes possible, toutes particules – fibres non dissoutes, impuretés – d'un diamètre supérieur à ~8µm doivent être filtrées pour éviter la déchirure du film au moment de son étirage. En outre, il se pose un problème de gélification lors du procédé pour la fabrication des films, et ce d'autant plus que la concentration en cellulose est élevée. Les solutions de cellulose dans la soude sont des systèmes instables qui gélifient, d'autant plus rapidement que la température est élevée au dessus de la température ambiante. De ce fait, si un début de gélification se produit avant la mise en forme du film, le morceau de gel devient alors un point de rupture du film.

  Plan d'expérience : Nous étudierons en détail les propriétés rhéologiques des solutions de cellulose afin de (i) connaître leur comportement à l'écoulement, (ii) déterminer les conditions de gélification et (iii) étudier l'influence d'additifs tels que oxyde de zinc et urée sur la rhéologie des solutions de cellulose/NaOH/eau.

- *Problématique 3* : Les éponges préparées à partir du procédé « soude » doivent être congelées plusieurs heures à -20°C pour avoir des propriétés assez proches de celles des éponges « viscose ». Un procédé avec un séjour prolongé à très basse température n'est pas viable économiquement. Il est donc nécessaire d'étudier l'influence de la congélation sur les propriétés finales d'objets de cellulose régénérée.

  Plan d'expérience : Une éponge cellulosique est en fait un composite poreux ayant une matrice de cellulose régénérée et des fibres de renfort de cellulose naturelle (coton, lin, bois). L'étude de la résistance à la rupture et de l'influence de la congélation sur les propriétés mécaniques se fera étape par étape, c'est-à-dire sur la matrice de cellulose régénérée seule, puis sur le composite matrice+fibres et pour finir sur le produit fini matrice+fibres+porophores, créant la macroporosité nécessaire aux propriétés d'absorption.

Ces trois problématiques industrielles structurent notre thèse, ainsi que ce résumé, en constituant les chapitres III, IV et V. Le chapitre I est consacré à l'étude bibliographique tandis que le chapitre II présente les matériaux et méthodes utilisés tout au long de cette étude.

Une brève description des expériences réalisées et des résultats obtenus est présentée ci-dessous.

I- LITTERATURE : LA CELLULOSE ET SA DISSOLUTION DANS LES SYSTEMES HYDROXYDE ALCALIN/EAU

La cellulose est un polymère linéaire constitué d'unité anhydroglucose (AGU). Les groupes hydroxyles présents sur chaque motif, et donc tout au long de la chaîne, sont facilement accessibles pour créer des liaisons hydrogène intra- et intermoléculaires. Par ces liaisons hydrogène, les chaînes de cellulose ont une forte tendance à s'agréger pour former des arrangements cristallins très ordonnés. Ils sont au nombre de quatre : la cellulose I, ou cellulose native, la cellulose II, la cellulose III et la cellulose IV. Les structures cristallines II, III et IV s'obtiennent par traitement chimique, seule la cellulose I se trouve dans les membranes des cellules végétales à l'état natif. Les chaînes de cellulose native s'organisent d'abord sous forme de micro fibrilles qui s'agglomèrent à leur tour dans les macro fibrilles pour donner finalement la fibre de cellulose.
L'organisation des fibrilles (diamètre, densité, texture) varie suivant l'origine de la cellulose (coton, bois…), ce qui explique des différences de comportement au contact des solvants [CUI2006] par exemple. Lors de l'extraction de la cellulose, des traitements chimiques et mécaniques sont également appliqués pour séparer la cellulose des autres constituants du bois (lignine, hémicelluloses…). Ces traitements modifient la structure des fibres de cellulose et influent donc sur les propriétés de ces dernières.

Comme nous l'avons exposé dans le contexte de l'étude, la soude, relativement concentrée, est utilisée depuis de très nombreuses années pour modifier les propriétés des textiles (brillance, absorption des colorants), et ce, grâce au gonflement des fibres de cellulose puis à leur transformation de la cellulose I à la cellulose II : c'est le phénomène appelé mercerisation [MER1903]. Il apparaît également que la mercerisation peut se produire à plus faible concentration en NaOH (~9%) si la température est faible. Davidson [DAV1934] et Sobue [SOB1939] montrent que la cellulose peut être dissoute dans la soude mais dans un domaine de température et de concentration en NaOH très étroit (7-10%NaOH/eau, en dessous de 0°C). Les solutions de cellulose obtenues ne sont pas stables et gélifient dans le temps et en fonction de la température [ROY2003]. D'autres systèmes alcalins comme KOH/eau et LiOH/eau sont également étudiés. Si le premier ne permet qu'une faible solubilité de la cellulose, le deuxième est très efficace mais beaucoup plus cher que la soude. La plupart des études se consacreront donc à la dissolution de la cellulose dans la soude, solvant alcalin efficace et peu onéreux.

Peu de temps après la découverte de la mercerisation, l'ajout d'additifs fut étudié pour améliorer l'action de NaOH sur les fibres de cellulose. L'oxyde de zinc est déjà mentionné à cette époque [MER1903] et apparaît dans la littérature de façon sporadique [DAV1937] [WO 02/22924]. Par contre, aucune explication sur son rôle n'est proposée. L'ajout d'urée est étudié depuis seulement quelques années [LAS1998] [ZHO2000] mais de façon très détaillée. Non seulement il est montré que l'urée améliore nettement la dissolution de la cellulose et la stabilité des solutions [ZHO2000] mais certains auteurs tentent également d'expliquer ces phénomènes [CAI2005] [CAI2006].

II- MATERIAUX ET METHODES EXPERIMENTALES

La dissolution de la cellulose dans NaOH/eau, avec ou sans additif, s'effectue à -6°C pendant deux heures sous agitation. Une fois préparée, les solutions peuvent être gardées un mois environ à +5°C. Néanmoins, avant chaque prélèvement, elles devront être re-homogénéisées car les fibres non dissoutes sédimentent.

L'étude des propriétés thermiques des solutions peut se diviser en deux parties, l'étude des solvants – NaOH/eau, urée/eau, NaOH/urée/eau et NaOH/ZnO/eau – et celle des solutions de cellulose. Afin de déterminer les température et enthalpie de fusion de chaque composant présent dans la solution, nous avons utilisé un appareil DSC 7 (PERKIN-ELMER) permettant de descendre à basse température (-65°C), les vitesses de refroidissement et de chauffe utilisées étant de 1°C/min. La corrosivité des solutions (présence de soude) a nécessité l'utilisation de capsule inox plaquée en or. Dans la plupart des cas, les températures et enthalpies de fusion ont été calculées directement par le logiciel de DSC. Dans le cas de pics superposés, une déconvolution de pics étant nécessaire, nous avons utilisé le logiciel PeakFit 4.12.
Pour déterminer la structure des solvants, nous avons également effectué des analyses de diffraction de rayons X (XPERT-PRO de PANalytical) et des analyses de RMN. Ces dernières ont été réalisées à l'Institut Fraunhofer à Gölm, en Allemagne.

Les propriétés rhéologiques des solutions semi diluées de cellulose (de différents DP, traitements et origines) dans 7,6NaOH/eau, avec ou sans additif (oxyde de zinc et l'urée, à différentes concentrations) ont largement été étudiées à l'aide d'un rhéomètre Gemini (BOHLIN) équipé d'outils cône plan et d'une platine Peltier. Cette dernière permettant des variations rapides de la température, nous avons pu déterminer le point de gélification en fonction de la température et du temps. Le comportement à l'écoulement a également été étudié par des mesures de viscosité en fonction du taux de cisaillement.
Quant à l'étude des solutions diluées de cellulose, elle a été effectuée en utilisant un viscosimètre capillaire Ubbelohde équipé d'une burette automatique de dilution (Lauda).

La résistance à la rupture de films de cellulose régénérée, de composites cellulose régénérée + fibres de renfort et de produits finis (cellulose régénérée + fibres de renfort + porophores créant la porosité) a été mesurée à l'aide d'une machine ZWICK Z2.5, en mode de traction. Les échantillons sont dans leur état humide et la mesure s'effectue à l'air ambiant.

Pour finir, tout au long de cette étude, des observations microscopiques ont été réalisées que ce soit au microscope optique ou au microscope électronique à balayage (MEB, SEM en anglais).

III- STRUCTURE DES SOLUTIONS DE CELLULOSE ET LIMITE DE DISSOLUTION

Nous présentons tout d'abord quelques aspects théoriques sur les diagrammes de phase binaires et ternaires et l'utilisation des thermogrammes de DSC pour les construire. Une construction très précise des diagrammes de phase à partir des pics de fusion obtenus par DSC nécessite de très nombreux essais – variation de la masse *m* de l'échantillon et de la vitesse de chauffe *v* – afin de pouvoir extrapoler les résultats à *m=0* et *v=0*. Le but de notre étude étant seulement de connaître les phases présentes dans le système, leur composition et leur proportion, nous avons réalisé les mesures pour une seule vitesse de chauffe et une seule masse.

L'étude de structure des solvants et des solutions de cellulose a essentiellement été basée sur des analyses de DSC. Les systèmes ont été refroidis à très basse température (-65°C) afin qu'ils soient totalement cristallisés, puis remontés lentement (+1°C/min) à température ambiante en enregistrant les pics de fusion des différents composants.

Dans un premier temps, nous avons analysé des solutions aqueuses d'hydroxyde de sodium contenant entre 0 et 20% en poids de NaOH. A partir des thermogrammes de fusion, nous avons pu tracer la partie du diagramme de phase 0-20%NaOH/eau qui correspond parfaitement à celui trouvé dans la littérature [PIC1893] [ROL1964]. Dans ce domaine de concentrations en NaOH, le système forme un mélange eutectique composé d'un hydrate de sodium $NaOH,5H_2O$ et de quatre molécules d'eau. Cette adéquation entre l'expérience et la littérature nous a permis d'utiliser une méthode de calcul, basée sur les enthalpies de fusion, permettant de déterminer la proportion de chaque phase en solution.
Pour une solution de 7,6%NaOH/eau on aura tout d'abord cristallisation de l'eau libre puis du mélange eutectique $NaOH,5H_2O+4H_2O$ quand la température diminue, les températures de fusion étant respectivement -4°C/-5°C et -33,4°C.

L'analyse du système 0-100%urée/eau montre un comportement eutectique simple, le mélange eutectique étant composé de $1urée+8H_2O$.
L'addition de 0-25% d'urée dans une solution de 7,6%NaOH/eau ne modifie ni la température ni l'enthalpie de fusion de l'eutectique $NaOH,5H_2O+4H_2O$: l'urée ne réagit pas avec NaOH. Par ailleurs, quand la concentration en urée augmente, le pic de fusion du composé urée se décale vers les plus hautes températures, tandis que celui de l'eau libre se décale vers les basses températures. Les deux pics se rejoignent pour une concentration totale en urée de 18%. Un tel système est en fait composé de l'eutectique $NaOH,5H_2O+4H_2O$ et de l'eutectique $urée+8H_2O$. Il n'y a plus d'eau libre. Tant qu'il y a suffisamment d'eau pour les deux mélanges eutectiques, ils se forment indépendamment. Si l'eau vient à manquer, chaque NaOH s'entoure de ses 9 molécules d'eau puis l'eau restante entoure l'urée, l'urée en excès restant dans son état pur.

Lors de sa dissolution en milieu fortement basique, l'oxyde de zinc réagit avec OH^- pour former des hydroxydes de zinc. Ces réactions chimiques provoquent donc une modification des solutions et par conséquent des changements au niveau du diagramme de phase NaOH/eau. Plus la quantité en ZnO augmente, plus les température et enthalpie de fusion de l'eutectique

« NaOH » diminuent. On a ainsi déterminé que trois NaOH pour un ZnO ne participent plus à l'eutectique et que les composés de zinc formés lors de la dissolution sont fortement hydratés (jusqu'à $25H_2O$).

La structure des solvants NaOH/eau, NaOH/urée/eau et NaOH/ZnO/eau étant désormais connue, nous y avons ajouté la cellulose afin de déterminer quelles interactions ont lieu lors de sa dissolution.

L'ajout de 0,5-7,6% de cellulose dans une solution de 7,6-9% de NaOH/eau n'entraîne pas de diminution de la température de fusion de l'eutectique « NaOH » : la présence de cellulose ne modifie pas le diagramme de phase du solvant NaOH/eau. Par contre, l'enthalpie diminue proportionnellement à la quantité de cellulose ajoutée et atteint zéro quand la quantité de cellulose est égale à la quantité de NaOH présent en solution. Nous en avons donc déduit que (i) la dissolution de cellulose dans NaOH nécessite au moins quatre molécules de NaOH qui se lient à une unité anhydroglucose (AGU) et (ii) la limite de dissolution de la cellulose est atteinte quand $m_{cell}=m_{NaOH}$.
Quant à la température de fusion de la glace libre, elle augmente légèrement avec la cellulose, ce qui s'explique par un changement de l'environnement moléculaire de l'eau dû à la présence de cellulose. L'enthalpie de l'eau libre reste constante quand la concentration en cellulose augmente ce qui signifie que la quantité d'eau libre en solution est constante. Nous en avons donc conclu que les NaOH liés à la cellulose sont entourés des 9 molécules d'eau formant initialement le mélange eutectique.

Des analyses DSC similaires ont été réalisées sur des solutions de cellulose dans NaOH/eau contenant 6% d'urée. Les valeurs d'enthalpie de fusion de l'eutectique NaOH suivent la même courbe que celles obtenues précédemment pour des solutions de cellulose dans NaOH/eau, sans urée. La présence d'urée ne permet pas d'augmenter la limite de dissolution de la cellulose qui reste telle que $m_{cell}=m_{NaOH}$, chaque AGU s'entourant au minimum de 4 NaOH et 36 molécules d'eau.
Quant au pic de l'eutectique « urée », il ne change ni en intensité, ni en température. Nous en concluons donc que les chaînes de cellulose ne réagissent pas avec l'urée.

Nous avons vu que l'ajout de ZnO dans le solvant diminue ou supprime la température de fusion de l'eutectique « NaOH ». Lors de l'ajout de cellulose, ce pic n'apparaît pas, il n'est donc pas possible de déterminer ni la concentration limite en cellulose pouvant être dissoute dans une solution donnée de NaOH/ZnO/eau, ni la quantité de NaOH lié à chaque AGU.

La dernière section de ce chapitre concerne l'influence de la congélation sur la structure des solutions, modification structurale pouvant être détectée par une analyse thermique.
Après un séjour prolongé à -28°C, un pic apparaît à 0°C, température de fusion de la glace. Ceci signifie qu'une certaine quantité d'eau a cristallisé de manière tout à fait indépendante. D'un point de vue thermodynamique, cette eau pure ne peut provenir ni du mélange eutectique

$NaOH,5H_2O+4H_2O$ libre en solution ni de l'eau initialement libre. La seule possibilité est que cette eau pure provienne de l'eau liée à la cellulose. A partir des enthalpies de fusion, nous avons pu calculer qu'une molécule d'eau par AGU a été détachée. Mais étant donné que cette eau est dégagée dans un système en équilibre thermodynamique, elle cristallise immédiatement et indépendamment des autres constituants du système, donnant ainsi un pic à la température de fusion de l'eau pure.
Des résultats tout à fait équivalents ont été observés pour des solutions de cellulose/NaOH/ZnO/eau.

IV- ECOULEMENT ET GELIFICATION DES SOLUTIONS AQUEUSES DE CELLULOSE/NAOH. INFLUENCE DES ADDITIFS

L'étude bibliographique a montré que d'une part la cellulose ne se dissout que dans des conditions précises de concentration en NaOH et de température [SOB1939] et que d'autre part, une fois dissoute, les solutions ne sont pas stables et gélifient en fonction du temps et de la température [ROY2003]. Il apparaît également que l'ajout d'additifs tels que urée et oxyde de zinc améliore la dissolution de la cellulose et la stabilité des solutions [ZHO2000]. Le but de ce chapitre est donc d'étudier le comportement des solutions à l'écoulement ainsi que déterminer les conditions de gélification, et ce en faisant varier de nombreux paramètres tels que DP, concentration et origine de la cellulose, température et additifs.
Les solutions ont été étudiées (i) en régime semi dilué en mode continu afin de mesurer la viscosité des solutions en fonction du taux de cisaillement, (ii) en mode dynamique pour déterminer le point de gélification et (iii) en régime dilué pour mesurer la viscosité intrinsèque de la cellulose dans différents solvants. Parallèlement aux résultats rhéologiques, de nombreuses observations microscopiques (microscope optique) ont été effectuées pour avoir des données qualitatives sur la dissolution des fibres de cellulose.

Par les mesures de viscosité en fonction du taux de cisaillement, nous avons montré que le comportement à l'écoulement des solutions de cellulose explosée à la vapeur est identique dans les trois systèmes de solvant étudiés – 7,6%NaOH/eau, 7,6%NaOH/6%urée/eau et 7,6%NaOH/0,7%ZnO/eau. Ce ne sont pas des solutions moléculairement dispersées. Leur comportement se rapproche plutôt de celui d'une suspension. Ce résultat concorde bien avec le résultat précédent à savoir qu'en solution les chaînes de cellulose sont entourées d'une grande quantité de molécules d'hydroxyde de sodium et d'eau.

Les observations microscopiques ont montré que la présence d'oxyde de zinc ou d'urée améliore la dissolution de la cellulose puisque la quantité de fibres non dissoutes diminue. Les mesures de viscosité intrinsèque dans les différents solvants ont révélé que cette amélioration de la dissolution des fibres est due à une amélioration de la qualité de solvant de la façon suivante 7,6%NaOH/eau est moins bon que 7,6%NaOH/6%urée/eau qui est moins bon que 7,6%NaOH/0,7%ZnO/eau.

Par ailleurs, quel que soit le solvant utilisé, la viscosité intrinsèque de la cellulose diminue quand la température augmente. Ceci signifie que les chaînes de cellulose se contractent et que la qualité du solvant diminue. Par conséquent les interactions cellulose-cellulose sont favorisées ce qui conduit à la gélification des solutions en régime semi dilué et à la compactisation des molécules en régime dilué.
Pour des solutions de même concentration en cellulose et en NaOH, la détermination du point de gélification en fonction de la température donne nécessairement l'ordre suivant T_{gel}(cellulose/NaOH/eau) < T_{gel}(cellulose/NaOH/urée/eau) < T_{gel}(cellulose/NaOH/ZnO/eau).

L'ajout de ZnO dans 7,6%NaOH/eau est d'autant plus efficace (augmentation de la température de gélification) que sa concentration est élevée, jusqu'à 1,5% qui correspond à la limite de solubilité de ZnO dans 7,6%NaOH/eau. Au-delà de cette valeur, les propriétés restent constantes. Nous en concluons donc que ZnO améliore la dissolution de la cellulose et la stabilité des solutions seulement s'il a d'abord été dissout dans NaOH. Ceci signifie que ce sont les complexes formés entre NaOH, ZnO et l'eau qui permettent d'améliorer la dissolution des fibres de cellulose et de retarder la gélification. Par ailleurs le mécanisme de gélification semble être le même avec ou sans ZnO, qui agit donc uniquement en empêchant les interactions cellulose-cellulose qui apparaissent à plus haute température.
En ce qui concerne l'ajout d'urée dans 7,6%NaOH/eau, nous avons constaté que nos résultats ne correspondaient pas à ceux trouvés dans la littérature. Nous avons donc préparé des solutions de cellulose de différentes origines (différence d'essence d'arbre, de traitement des fibres, de DP) dans 7.6NaOH/eau contenant de 6 à 20% d'urée. Nous avons alors mesuré les modules G' et G" en fonction de la température afin de déterminer le point de gel. La température de gélification et la concentration optimale en urée varient suivant la cellulose utilisée. Une solution de cellulose explosée à la vapeur atteint sa température maximale de gélification à 40°C pour une concentration en urée de 6% tandis qu'une solution de cellulose irradiée par un faisceau d'électron atteint sa température maximale à presque 60°C pour une concentration en urée de 12-15%. La stabilité des solutions dépend donc fortement de l'origine de la cellulose.
A l'heure actuelle, les raisons de telles différences restent une question ouverte mais ces résultats expliquent pourquoi nous trouvons des résultats différents de ceux rapportés dans la littérature.

V- PROPRIETES MECANIQUES D'OBJETS REGENERES A PARTIR DE SOLUTIONS DE CELLULOSE/NAOH/EAU

Ce chapitre concerne la fabrication d'objets cellulosiques par dissolution directe de la cellulose dans des solutions aqueuses d'hydroxyde de sodium. Nous présentons tout d'abord le procédé « viscose » actuel puis le nouveau procédé « soude ». Ce dernier nécessite une étape de congélation des blocs d'éponge afin d'obtenir des propriétés du produit fini proches de celles obtenues pour les éponges « viscose ». Etant donné que ce séjour prolongé à basse température rend ce procédé économiquement non viable, il est important d'étudier l'influence de la

congélation sur les propriétés des éponges et de savoir sur quel élément du produit (matrice, fibres…) elle intervient.

L'essentiel de cette étude porte sur des tests de traction permettant de mesurer la résistance à la rupture des éponges. Une éponge est en fait un matériau composite constitué d'une matrice de cellulose avec des fibres de renfort et de trous. La matrice est composée de cellulose régénérée, provenant de la solution de cellulose dans NaOH/eau, et de fibres de renfort, ensemble de fibres de coton, de lin et/ou de bois. Les trous sont formés suite à la fusion de cristaux de sel Na_2SO_4,$10H_2O$.
Afin de comprendre où et quand agit la congélation, nous avons préparé puis testé des échantillons (i) de matrice de cellulose régénérée seule, (ii) de matrice de cellulose régénérée+fibres de renfort et (iii) de matrice+fibres+porophores créant la porosité.

Les tests de traction sur la matrice de cellulose régénérée seule montrent que les conditions utilisées initialement (congélation à -20°C et régénération dans l'eau à +70°C) sont très défavorables à la résistance à la rupture. Les meilleures propriétés mécaniques sont obtenues lorsque la solution de cellulose/NaOH/eau est traitée à température ambiante que ce soit au moment de la gélification mais également lors de la régénération dans l'eau. Nous remarquons toutefois qu'une régénération en milieu acide donne de bonnes propriétés mécaniques mais ce mode de régénération convient essentiellement lors de la fabrication de film mince et non lors de la fabrication d'objet tridimensionnel telles que les éponges. La congélation n'agit donc pas sur la résistance mécanique de la matrice de cellulose régénérée. Les échantillons congelés de cellulose régénérée révèlent de nombreuses empreintes en forme d'aiguille dues à la cristallisation puis à la fusion de l'eau.

L'ajout de fibres de renfort augmente la contrainte à la rupture mais le résultat reste médiocre. L'adhésion entre la matrice et les fibres est donc à améliorer. Les observations microscopiques ont montré qu'au cours de la congélation, les fibres de renfort, de DP élevé, ont gonflé au contact de la soude. Dans un premier temps, nous avons pensé que ce gonflement pouvait permettre une certaine pénétration de la solution de cellulose et donc améliorer l'adhésion fibres/matrice. Cette hypothèse s'est révélée fausse, la congélation n'intervenant pas au niveau de l'adhésion fibres/matrice.
L'ajout de promoteur d'adhésion n'a pas donné de résultats satisfaisants.

Finalement, nous avons préparé et testé les produits finis : matrice de cellulose régénérée + fibres de renfort + porophores créant la porosité. C'est à ce stade seulement que nous avons vu l'influence de la congélation sur les propriétés des éponges. Outre l'amélioration de la résistance à la rupture, la congélation des éponges entraîne également une augmentation de l'absorption en eau et une diminution du rétrécissement des éponges, comparé à des éponges équivalentes n'ayant pas subit d'étape de congélation. Ceci est en adéquation avec les observations microscopiques qui révèlent une porosité plus importante des éponges congelées, conduisant à une meilleure absorption.

Nous avons également observé que, après un premier séchage à l'air ambiant, un grand nombre de pores se sont fermés ce qui explique un retrait non négligeable des échantillons congelés ou non.

Le manuscrit se termine par des conclusions générales et des annexes qui donnent une description détaillée de quelques techniques et résultats expérimentaux.

INTRODUCTION

Cellulose is a natural polymer which is the structural substance present in all plants, allowing their stalk and their protection. This polysaccharide is created by the photosynthesis from carbon dioxide and water, using the sunlight as the energy source. Cellulose can be extracted from grass, leaves, stems, tree trunks and brunches. Wood is the most often used source since trees are planted especially for this purpose. Nevertheless, properties of the wood pulp strongly vary as a function of age and growing conditions of trees and these parameters are difficult to control when timber comes from the wild. Moreover, it is interesting to note that pulp manufacturers plant sufficient trees to at least replace what they use.
At the end of the life cycle, cellulose degrades readily under bacterial action forming compost or peat and ultimately degrades further producing methane, carbon dioxide and water. The loop is closed.

The major problem of cellulose is that it is degrading before melting. Consequently, to process cellulose and make fibres, films or 3D objects, cellulose has to be either dissolved in direct solvents or derivatised and then processed.

The most common industrial process of making shaped pure cellulose objects is called the "viscose" process: after cellulose activation with aqueous 18-20%NaOH, the carbon disulfide (CS_2) is reacting with cellulose chains to form the cellulose xanthate which is then dissolved in dilute sodium hydroxide. At this stage, the mixture is named the "viscose" and can be shaped. Finally, cellulose is regenerated and various final products can be obtained: fibres, films or tri-dimensional objects. This process is very efficient and totally mastered, but it is very polluting: because of the use of CS_2 and the numerous chemical reactions, sulphured products are released creating pollution in atmosphere and in aqueous phases. Although the major part of the pollution is treated in the plant some pollutants are still released. Moreover, technologies for pollution treatments are very expensive. Thus for economical and for environmental reasons, manufacturers of pure cellulose products have been trying to find alternative routes to shape cellulose. There is a continuous search on environmentally friendly cellulose processes.

NMMO, for example, is a good cellulose solvent, but these solutions are not easy to prepare and to process in the case of film and tri-dimensional object. This solvent is now used in the fibre manufacture, called the Lyocell process.

For a long time, sodium hydroxide aqueous solutions at various concentrations were used in cellulose processing, especially to change aspects and properties of cellulose fibres: in the textile industries. For example, NaOH was largely used to increase the degree of lustre and to improve the absorption of dyes. In 1939 Sobue showed [SOB1939] that (7-10)%NaOH aqueous solutions can be a direct solvent of cellulose. Nowadays, several research teams directly dissolve cellulose in sodium hydroxide aqueous solutions (7-10%NaOH below 0°C) but the properties of final products are often inferior to the ones of similar products made from "viscose" process. One of the problem is that neither cellulose dissolution in 7-10%NaOH, nor the properties of cellulose/NaOH/water solutions are well understood.

This work has two different goals, the first is the fundamental understanding of the behaviour of the mixing of cellulose in NaOH-based aqueous solutions, and the second is to apply this knowledge to the manufacturing of films and sponges.

The first goal of the work was to understand the structure of cellulose solvent – aqueous solution of sodium hydroxide with and without ZnO or urea and of cellulose solution in these solvents, and then to determine how NaOH reacts with the polymer chains. From this fundamental aspect we can determine the maximal cellulose concentration that can be dissolved in NaOH/water. The study of the rheological properties of cellulose solutions by determining the flow behaviour and the conditions of the occurrence of gelation, in time and in temperature, gave information on the gelation. The influence of additives on rheological properties was also investigated.

The second goal was to investigate two aspects of the manufacturing of objects from this process. In the case of the preparation of films, the difficulty lies in the amount of cellulose that can be dissolved in the cellulose solution. The higher is the better, but this causes extreme difficulties during processing due to gelation. The results obtained above explained why. The second process is the manufacturing of sponges where a freezing step was shown to be important. We thus studied the mechanical properties of regenerated objects and the influence of preparation conditions and especially the influence of the freezing step (keeping cellulose solution at -20°C for 20 hours) and the influence of regeneration baths.

Two industrial partners supported this thesis. Innovia Films Ltd, in Great Britain, is a manufacturer of cellulose films for wrapping and packaging and Spontex, in France, is a company producing cellulose sponges.

The thesis is divided into five chapters.

The first one gives generalities on cellulose as well as a description of the different techniques used for its extraction and its activation. We also present the state of the art concerning the swelling and the dissolution of cellulose in sodium hydroxide/water and the influence of additives – such as zinc oxide or urea – on the cellulose solubility.

In the second chapter, materials (cellulose, solvents and additives) and methods (DSC, rheology, optical and electron microscopy, rheology, viscometry, x-ray scattering) used in this work are described.

The next three chapters concern the results and their discussion.
Chapter III investigates, using DSC analysis, the structure of the various solvents used in this study as well as the structure of cellulose solutions in these solvents. As the NaOH/water binary system is described in details in literature, it enables to check the validity of the methodology used to calculate NaOH/water phase diagram below 0°C at NaOH concentrations used for cellulose dissolution. The same methodology was applied on other solvents – urea/water, NaOH/ZnO/water and NaOH/urea/water – and on cellulose solutions. We also determine the amount of cellulose that can be dissolved in sodium hydroxide/water and we study the influence of additives on this limit of cellulose dissolution.

Chapter IV focuses on the rheological properties of cellulose/NaOH/water solutions with and without additives. The experiments in steady state mode were used to describe the behaviour of cellulose/NaOH/water solutions under shear. The oscillatory mode allows examination of the conditions for the occurrence of gelation.

Chapter V tackles the mechanical properties of regenerated wet cellulose samples. The tensile tests were performed on regenerated pure cellulose and cellulose with the reinforcing fibres and porophores. The influence of regenerating bath parameters and of the freezing step on the mechanical properties was studied. We investigated how to improve the sponge manufacture process while keeping in mind the necessity to have costs as low as possible.

Finally, a general conclusion summarizes the main results of this work and presents some prospective aspects.

RESUME DU CHAPITRE I

ETAT DE L'ART: LA CELLULOSE ET SA DISSOLUTION DANS DES SOLUTIONS AQUEUSES D'HYDROXYDE DE SODIUM

Les polysaccharides sont des matériaux naturels, renouvelables et biodégradables. Par conséquent leur utilisation dans l'industrie, en tant que matière première ou en tant qu'additif, se développe. La cellulose, par exemple, est le constituant principal des végétaux ; sa production naturelle est donc considérable. Par contre, elle est difficile à mettre en œuvre et doit subir de nombreux traitements avant de se retrouver dans le produit fini.
La cellulose ne peut pas être fondue comme la plupart des polymères et ne peut être dissoute ni dans l'eau ni dans la plupart des solvants. Sa dissolution nécessite l'emploi de solvants forts, souvent dangereux et polluants. De nombreux travaux de recherche portent donc sur la mise en solution de la cellulose dans des solvants peu coûteux, efficaces et non dangereux pour l'environnement.

Le but de ce chapitre est de faire un état de l'art sur la cellulose et sa dissolution en milieu alcalin.

Dans un premier temps, nous présenterons la cellulose du point de vue de son organisation moléculaire et structurale. L'important réseau de liaisons hydrogènes permet non seulement de nombreuses combinaisons donnant ainsi quatre structures cristallines différentes mais également une très forte cohésion entre les chaînes, rendant difficile la pénétration des solvants. Nous verrons que l'organisation supramoléculaire des chaînes de polymère dépend de l'origine de la cellulose (coton ou bois par exemple). Il existe également différentes méthodes d'extraction, de traitement et d'activation des fibres pour préparer les pulpes de cellulose. Tous ces aspects influençant sur les propriétés des pulpes de cellulose rendent difficile l'universalité des résultats et des interprétations.

La deuxième partie de ce chapitre aborde deux techniques de dissolution de la cellulose.
La première intervient dans le procédé « viscose », procédé actuel de fabrication de films minces ou d'objets tridimensionnels à base de cellulose. Il s'agit d'une dissolution indirecte : la cellulose est d'abord transformée chimiquement avant d'être dissoute puis mise en forme et enfin régénérée (retour à la structure de la cellulose). La succession de réactions chimiques et l'utilisation de sulfure de carbone (CS_2) comme solvant de la cellulose le rendent très polluant. Ceci a conduit les industriels à trouver une alternative à ce procédé.

Une deuxième méthode de dissolution des fibres de cellulose est alors étudiée. Il s'agit, cette fois, d'une dissolution directe de la cellulose dans une solution peu concentrée (7-10%) d'hydroxyde de sodium/eau. La soude fut d'abord utilisée comme agent de gonflement des fibres de cellulose avant d'être utilisée comme un solvant direct de la cellulose. Nous rapportons dans cette partie de nombreux travaux effectués sur les solutions de cellulose/NaOH/eau. Si les premiers traitent essentiellement des conditions de dissolution de la cellulose (concentration en NaOH, température, additifs…), les suivants cherchent davantage à expliquer les phénomènes observés (gonflement irrégulier des fibres, mécanisme de transformation de la cellulose I à la cellulose II, gélification des solutions de cellulose, rôle des additifs sur la dissolution des fibres et leur influence sur la gélification).

CHAPTER I

STATE OF THE ART: CELLULOSE AND ITS DISSOLUTION IN ALKALINE HYDROXIDE AQUEOUS SOLUTIONS

The general goal of our work is to determine the structure of cellulose solutions in aqueous sodium hydroxide and to understand the mechanisms of cellulose dissolution and gelation of solutions. So flow behaviour and gelation properties were investigated as well as the influence of additives (urea and zinc oxide) on cellulose dissolution and kinetics of gelation. In order to understand all this, it is necessary to know and understand the structure and properties of cellulose itself and to review what is known in literature about cellulose behaviour in aqueous alkaline solutions. Thus, there will be two main parts in this chapter: "Cellulose: structure, morphology and treatment" and "Cellulose dissolution in aqueous alkali hydroxide solutions".

In the first part, the structure of cellulose and its polymorphs are briefly presented in order to describe the crystalline structure of cellulose and to better understand specificities of cellulose materials. For example, we will see how the network of hydrogen bonding changes depending on polymorph of cellulose I and II which explains differences in stability and reactivity. The supra-molecular structure of cellulose of different origins is shown to emphasize the complexity of fibre arrangement. These two points have a great interest because supra-molecular structure and hydrogen bonding have to be broken to dissolve cellulose. Finally, different treatments of cellulose are described because we will use microcrystalline cellulose and steam exploded cellulose and thus we must know what their specificities are.

In the second part, the first section concerns the current industrial process to dissolve cellulose: the viscose process. It is still used by our partners but as this process generates some pollution,

an alternative route to dissolve cellulose must be found. The others sections deal with another cellulose solvent based on NaOH aqueous solution. Varying the nature of alkali, the concentrations, and the temperature enables to better understand what happens when alkali hydroxide aqueous is added to cellulose fibres. Some explanations on mercerisation mechanism are given. Finally, the action of some additives to improve cellulose dissolution will be described.

I.1- CELLULOSE: STRUCTURE, MORPHOLOGY AND TREATMENT

Cellulose is one of the many polysaccharides present in nature (part I.1.1-). Its chemical structure is relatively simple (part I.1.2-) but the arrangement of chains in crystalline (part I.1.3-) and in supra-molecular structures is very complex and depends on the origin of cellulose (part I.1.4-). The synthesis of cellulose is difficult; nowadays only chains with about ten units can be obtained. So native cellulose is used as a raw material, after treatments to extract it from plants and activate it (part I.1.5-).

I.1.1- Generalities

Polysaccharides are the most abundant organic polymers available world-wide. Photosynthesis produces approximately 1.5 10^{12} tonnes of cellulose, starch and other natural polymers, whereas the annual production of petroleum polymers is 7-8 times lower. The economical interest of cellulose as a raw material is thus evident. Humans use 5.10^{8} tonnes per year of cellulose as wood, cotton, paper, textile, wrapping films…

Plants are natural composite materials and chemical complexes of cellulose, lignin, hemicelluloses, and other chemicals. The main ingredients are as follows:

- Cellulose is the main component of plant cell walls. It is the structural substance, which allows protecting and stalking. Cellulose content varies from 30% to 50% depending on the source, for example, in straws, hard- and softwood, early- and latewood, algae. Cotton is the purest natural form of cellulose that reaches more than 98% of the whole composition. Cellulose represents around 50% of the whole biomass. It can also be produced by some bacteria and found in skeleton of sea animals (tunicin).
- Lignin is the encrusting substance solidifying the cell wall since lignin resists strongly to compression. One of its important chemical properties is hydrophobicity. Consequently, cells become impermeable and can transport water and mineral salts. Lignin is a group of chemical compounds formed by carbon rings. The proportion of lignin varies from 15% to 30% depending on species and represents about 20% of the whole biomass.
- Hemicelluloses are the matrix substances and provide a linkage between cellulose and lignin. Hemicelluloses are shorter chains of polysaccharides. They can be divided into 3 groups: xylans, mannans, and galactans. Their contents vary from 20% to 30%.
- Other compounds consist of a wide variety of chemicals as resins, fats, silica crystals, proteins… In spite of their small content, extraneous compounds significantly influence the final properties and characteristics of cellulosic materials.

People have used cellulose in a natural state for several thousand years. However, its processing and use as a raw material in the chemical industry started 150 years ago, with the discovery of cellulose derivatives, and has ever since been studied. Although the chemical structure of cellulose is well-known, there are still many debates concerning its crystalline structure, i.e. the

way in which the cellulose molecules are packed in crystals and how these crystals are assembled into microfibrils, fibres, cell walls or other cellulose morphologies.

I.1.2- Chemical structure of cellulose

Cellulose is a linear syndiotactic homopolymer of β-(1→4)-D-glucopyranose units in $^4C_1$ conformation (Fig.I.1-1).

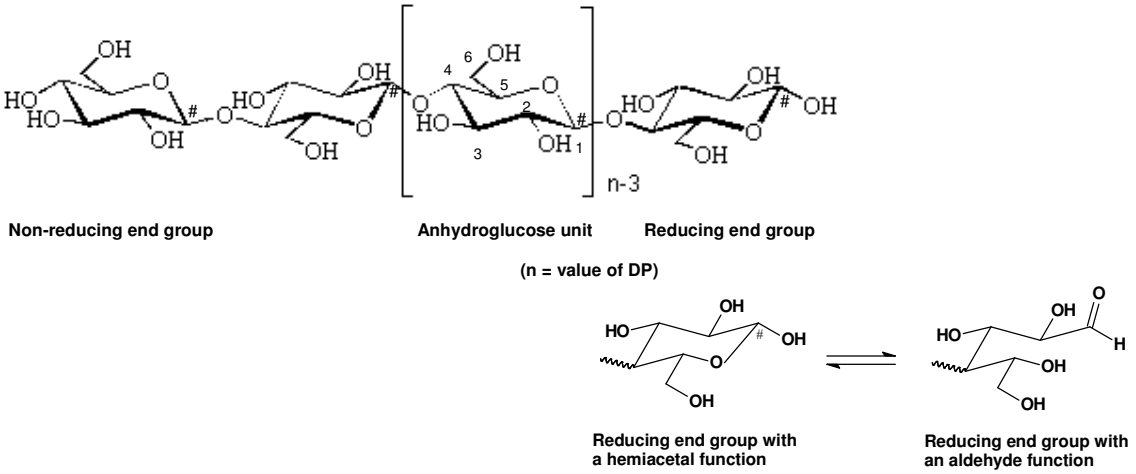

Fig.I.1-1: Molecular structure of cellulose (on the top) and the reaction occurring on the reducing end group (on the bottom) # indicates the anomeric carbon –C(OR)(OR')

Cellulose is based on glucose units having taken the shape of 6-membered rings, called pyranoses or glucopyranoses. They are connected by a single oxygen atom (acetal linkages) between the C1 of one pyranose ring and the C4 of the next ring. During the chemical reaction forming the acetal linkage, a molecule of water is given off. Consequently, the glucose units in the cellulose polymer are referred to as anhydroglucose units. The spatial arrangement, or stereochemistry, of these acetal linkages is very important: when the hydroxyl group at C1 is on the same face of the ring as the C6 carbon, it is said to be in the β configuration where all functional groups are in equatorial positions. This causes an extended conformation cellulose molecular chain (a semi-rigid conformation), making it a good fibre-forming polymer.

Each of the anhydroglucose units possesses hydroxyl groups at C2, C3 and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols. Because of these reactions, a lot of cellulose derivatives, such as methylcellulose (-CH_3 groups substitute -OH groups), can be obtained.
The two chain ends are chemically different. The non-reducing end has a D-glucopyranose unit in which the anomeric carbon atom (indicated by # in the Fig.I.1-1) is involved in a glycosidic linkage, whereas the reducing end has a D-glucopyranose unit in which the anomeric carbon atom is free. The cyclic hemiacetal function is in equilibrium with an aldehyde function (as shown Fig.I.1-1), which gives rise to reducing properties, so that the cellulose chain has a chemical polarity. Determination of the relative orientation of cellulose chains in the three-dimensional structure has been and remains one of the major problems in the study of cellulose.

Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule. This positioning makes them readily available for hydrogen bonding with the ring oxygen atoms. This hydrogen bonding has a strong tendency to aggregate chains and to form highly ordered structural entities. Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between. The inter-chain hydrogen bonds in the crystalline regions are strong, giving the resultant fibres good strength and insolubility in most solvents. They also prevent cellulose from melting. In the less ordered regions, the chains are further apart and more available for hydrogen bonding with other molecules, such as water. Most cellulose structures can absorb large quantities of water.

I.1.3- Crystalline structures of cellulose

The hydroxyl groups present in the cellulose macromolecule are likely to be involved in a number of intra- and intermolecular hydrogen bonds, which may give rise to various ordered crystalline arrangements. Four main polymorphs of cellulose have been found and they are named as cellulose I, II, III and IV. Their brief description is given in the following sections and their crystalline parameters are shown in Tab.I.1-1.

Type	Chains number in a unit cell	Unit cell (Å, °)					
		a	b	c	α	β	γ
I_α	1	6,74	5,93	10,36	117	113	81
I_β	2	7,85	8,27	10,38	90	90	96,3
II	2	8,10	9,05	10,31	90	90	117,1
III_1	2	10,25	7,78	10,34	90	90	122,4
IV_1	2	8,03	8,13	10,34	90	90	90
IV_2	2	7,99	8,10	10,34	90	90	90

Tab.I.1-1 [ZUG2001]: The parameters of crystalline unit cell of cellulose polymorphs 'a', 'b' and 'c' correspond to the axes of unit cell; 'α', 'β', 'γ' are the angles between 'b' and 'c', 'a' and 'c', 'a' and 'b' , respectively.

I.1.3.1. Native cellulose or cellulose I

Studies on crystalline structure of cellulose started almost one century ago and have generated many debates. In his recent paper, Zugenmaier [ZUG2001] reported a historical development of the structure determination of native cellulose. By various techniques, such as X-ray and electron diffractions, NMR, molecular modelling studies, the global structure has been defined and only the fine structure is expected to be improved.

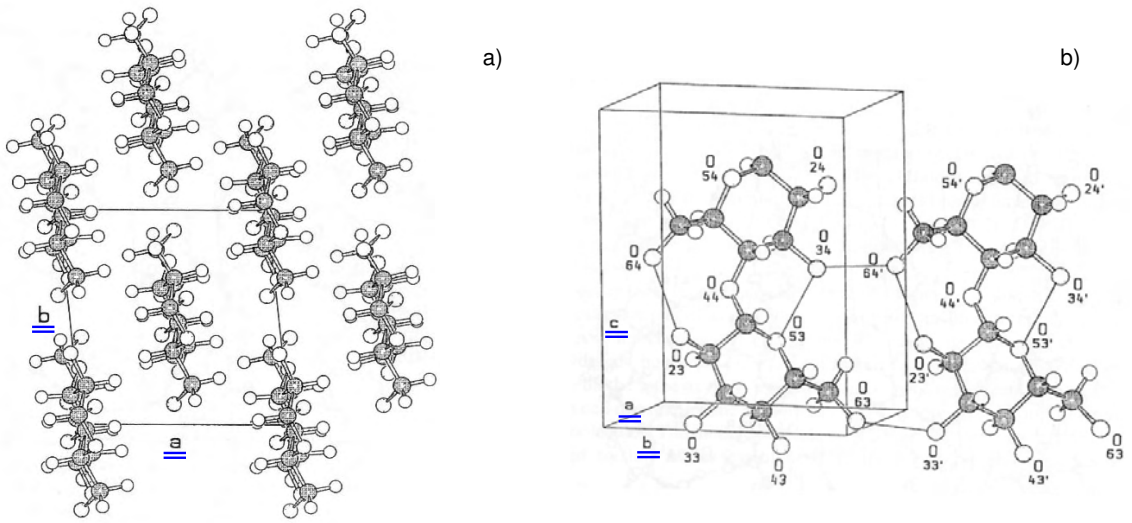

Fig.I.1-2 [ZUG2001]: Representation of the model of cellulose I_β a) onto the a-b plan, b) intrasheet (100) of molecules through the centre of the unit cell to demonstrate the hydrogen bonding.
'a' and 'b' axes represent the unit cell vectors as 'a'<'b'; 'c' is the third axis of the unit cell and corresponds to the fibre axis; 'γ' is the angle between 'a' and 'b'

The natural cellulose crystal is metastable and called cellulose I. Cellulose I has a parallel crystalline structure [ELL1962][GAR1974][SAR1974][MAC1990] and is composed of two distinct crystalline forms I_α and I_β [ATA1984], the latter being thermodynamically more stable. Cellulose can also be a composite of I_α, which has a triclinic unit with one chain, and of I_β, which has a monoclinic unit with two chains. Fig.I.1-2 represents (a) the typical arrangement of parallel chains of cellulose I composed of the monoclinic unit of cellulose I_β, and (b) O3-H…O5' and O2-H…O6' intramolecular and O6-H…O3' intermolecular hydrogen bonds. Between two molecular layers, only Van der Walls forces occur, there are no hydrogen bonds. The proportion between the two crystalline phases I_α and I_β depends on the cellulose origin [ATA1999]. Cellulose produced by primitive organisms (bacteria, algae etc.) is enriched with the I_α phase whereas cellulose of higher plants (woody tissues, cotton, ramie etc.) consists mainly of the I_β phase.

I.1.3.2. Cellulose II

The crystalline structure of cellulose II is obtained when the native cellulose is either mercerised (alkaline treatment) or regenerated (dissolution and then precipitation). Cellulose II has an antiparallel crystalline structure organised in a monoclinic unit with two chains (Fig.I.1-3a) [SAR1974][KOL1976][STI1976]. After many controversies, in 90's, Isogai *et al.* [ISO1989] and Raymond *et al.* [RAY1995] demonstrated that all hydroxyl groups of cellulose II (in C6) are oriented *gauche-trans* (*gt*), e.i. O61-C61 is positioned *gauche* to O51-C51 and *trans* to C41-C51 (Fig.I.1-3b). They also revealed that the central chain is shifted as compared with the cellulose chains at the origin of the unit cell [RAY1995]. Moreover, cellulose II has a complex network of hydrogen bonds inside and between molecular layers, which was precisely analysed by Langan *et al.* [LAN1999]. These numerous hydrogen bonds induce a greater stability of cellulose II as compared with cellulose I.

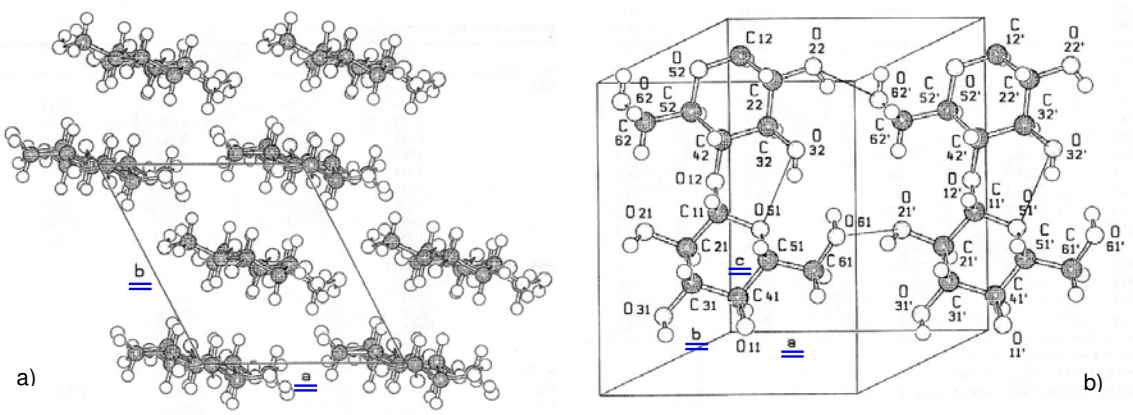

Fig.I.1-3 [ZUG2001]: Representation of the model of cellulose II a) onto the a-b plan, b) intrasheet (010) of molecules through the origin of the unit cell.
'a' and 'b' axes represent the unit cell vectors as 'a'<'b'; 'c' is the third axis of the unit cell and corresponds to the fibre axis; 'γ' is the angle between 'a' and 'b'

I.1.3.3. Cellulose III

Liquid ammonia treatment of cellulose gives another polymorph: cellulose III. It can be divided into cellulose III_I and III_{II} obtained from cellulose I and cellulose II respectively. The transformation of cellulose I to III_I and of cellulose II to III_{II} is reversible. The unit cell for both cellulose III_I and III_{II} structures is the same but the meridional reflections differ. The chains arrangement corresponds to the one of the initial cellulose, that is to say parallel for cellulose III_I and antiparallel for cellulose III_{II} [SAR1976]. In 2001, Wada *et al.* [WAD2001] reported that the unit cell of cellulose III_I contains one chain and has a volume twice as small as the one of the model proposed by Sarko *et al.* [SAR1976].

I.1.3.4. Cellulose IV

Heating of cellulose III produces the crystalline structure of cellulose IV, thermodynamically stable. As well as for cellulose III, the two allomorphs IV_I and IV_{II} originate from cellulose I and cellulose II respectively. The unit cell is orthogonal [GAR1985].

I.1.4- Supra-molecular structure of cellulose

I.1.4.1. Micro-fibrils

The chemical structure of cellulose (part I.1.2-), with a significant network of intra- and intermolecular hydrogen bonds, generates chain aggregations and highly ordered structures.
In the plasma membrane of cells, enzymes – called 'cellulose synthetases' – synthesise cellulose molecules by glucose addition, the degree of polymerisation *DP* (= number of anhydroglucose units) reaching several thousand units. As several molecules are synthesised simultaneously in the same area, they grow in a parallel way [Web site 1]. These parallel cellulose molecules create hydrogen bonds between them to form the basic crystalline arrangement of cellulose into the micro-fibrils (Fig.I.1-4). Micro-fibrils have a diameter in the range of 2-20 nm depending on

cellulose origin, and are agglomerated into fibrils. The latter have diameters in the range of 60-360 μm and the arrangement of micro-fibrils also depends on cellulose source.

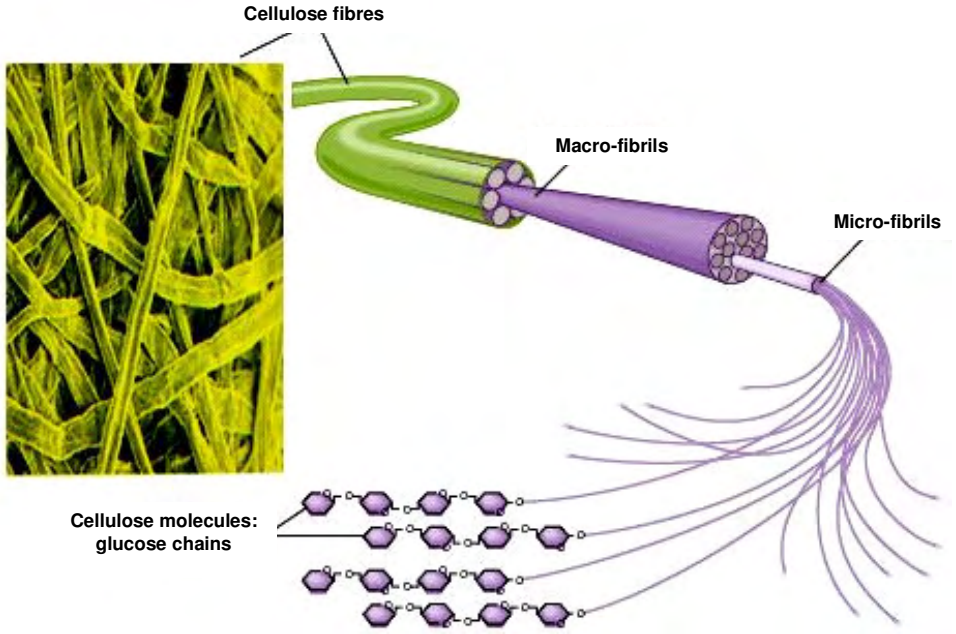

Fig.I.1-4 [Web site 2]: Supramolecular structure of cellulose

I.1.4.2. Wood and cotton cellulose fibres

Wood can be divided into two main classes: hardwood (or deciduous wood) that is generally composed of packed cells with thick walls (Fig.I.1-5) and softwood (or coniferous wood) usually composed of large cells with thin walls. As we saw previously (part I.1.1-), cells contain cellulose and also high proportions of lignin, hemicelluloses, etc.
Cotton is a seed "hair", unicellular and thus very pure in cellulose. The cotton hair is practically cylindrical and contains a central canal known as lumen (Fig.I.1-6). When the hair has been removed from the seed, the cell collapses into a flat ribbon which twists into an irregular spiral band [MAR1941].

Despite the differences in their origin, the morphological architecture of fibres presents some similarities: the organisation in layers of fibrils (Fig.I.1-7). On the other hand, the fibrillar texture and density change according to species [KLE1998].

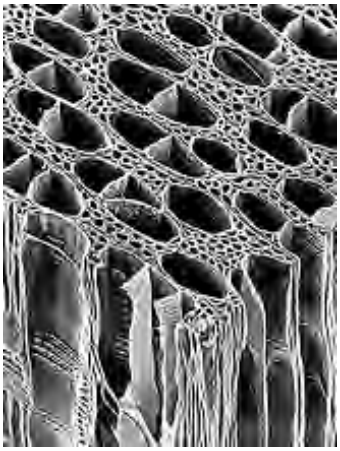

Fig.I.1-5: Wood is composed of dead cells. Cellular walls are a composite material of cellulose fibres and lignin.

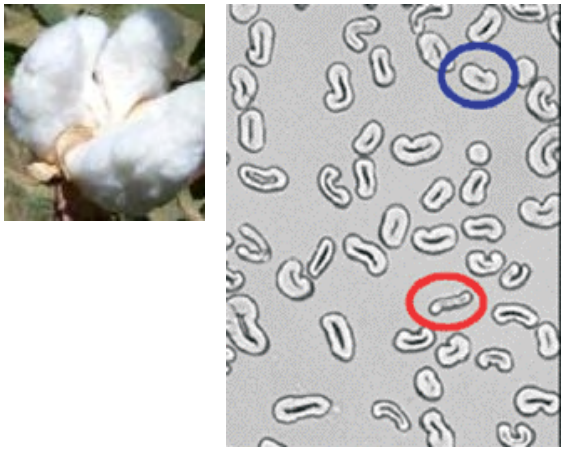

Fig.I.1-6: Cotton flower and cotton fibre cross-section. The blue circle shows a mature cotton fibre, with a thick and well-developed wall. The red circle shows an immature cotton fibre with a thin and poorly developed wall.

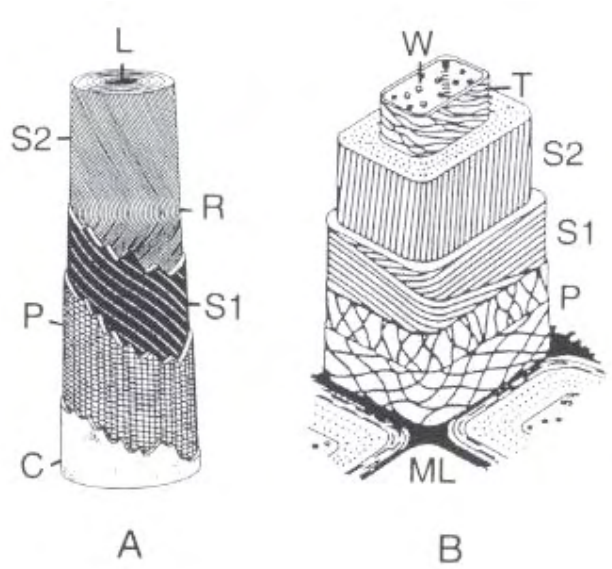

Fig.I.1-7 [KLE1998]: Scheme of the "morphological architecture" of a cotton and delignified spruce fibres:

(A) cotton fibre	**(B) delignified spruce wood fibre**
C = cuticle (rich in pectins and waxes)	ML = middle lamella (mainly lignin)
P = primary wall	
S1 = secondary wall (winding layer)	
S2 = secondary wall (main body)	
R = reversal of the fibril spiral	T = tertiary wall
L = lumen	W = wart layer

The so-called primary wall (*P*) forms when cells are individualised and it follows their growth [AIT1988]. In this primary wall, fibrils of about 10nm in diameter are positioned crosswise to a layer of about 50nm thickness. In his review, Klemm *et al.* [KLE1998] reported that this crosswise positioning possibly impedes a swelling of the inner secondary wall (*S*).

When the cell has reached its definitive size, the secondary wall grows with fine lamellae inside the cell. The secondary wall consists of many lamellae of cellulose, which are not separated from one another by non-cellulosic substances but represent dense and less dense areas of a cellulose fibre. This wall can be divided into two layers S_1 and S_2.

- The thickness of the S_1 layer is about 100nm and 300nm in the case of cotton and spruce pulp fibre respectively. The fibrils are aligned parallel and densely packed. The angle between the microfibril and the cell axis is large (50-70°), and the direction of helix may be opposite in subsequent S_1 layers. This structure in S_1 is called "crossed fibrillar texture". Moreover, the S_1 layer can strongly impede swelling of the S_2 layer.
- The S_2 layer is the thickest within the layers of secondary wall and contains most of the cellulose mass. It is a compact region in which a high degree of parallelism of microfibrils exists. The S_2 has a small microfibrils angle to the cell axis (10-30°). In wood, despite this microfibrillar orientation in S_2, there are lamellae transitions on its inner and outer surfaces. Several lamellae show a gradual shift of microfibril angles between S_1 and S_2 and between S_2 and S_3 [HON2001]. In cotton, there are some areas in the secondary wall where cellulose fibrils change from right-hand to left-hand, and vice-versa, at frequent intervals. One type of reversal (*R*) is that in which one set of spiral strands ends and a second system running in the opposite direction begins (Fig.I.1-7A); the ends of the strands overlap at the reversal [MAR1941].
- The inner layer, closest to the fibre lumen, named S_3 for cotton or *T* for wood, is comparably thin and has the fibrils aligned in a flat helix as in the layer S_1.

I.1.5- Extraction of cellulose and activation

I.1.5.1. Manufacture of cellulosic pulp

The manufacture of cellulosic pulp consists of extracting cellulose fibres from the biomass. All methods induce a progressive impoverishment of the cell wall, i.e. a decrease of the amount of lignin, hemicelluloses and other compounds, in order to obtain a high proportion of cellulose. As a result, individualised cellulose fibres are obtained with given morphological, optical and mechanical characteristics, depending on the source. Pulps can be classified according to the extraction technique.

- Mechanical pulps

Wood is crushed in order to tear out fibres. With this technique, the yield is significant since pulp keeps all components of wood – lignin, cellulose and hemicelluloses. The use of steam, high pressure or chemical agents allows obtaining pulps with different properties. As the resistance of these mechanical pulps is relatively low, they are especially used for newspapers and magazines.

- Chemical pulps

In this technique, only chemical products are added to separate fibres by dissolving lignin. According to the compound used, different types of pulp are obtained:

- The two alkaline processes: (i) the so-called sulphate or Kraft process and (ii) soda process. These two processes are relatively similar but the former is cheaper and thus more often used.
- The acid process: so-called sulphite process.

These processes are suitable for soft- and hardwood. The main principle consists in cooking chips in a chemical reactor with "white liquor", a liquid composed of chemicals. Cooking is occurring from 130°C to 180°C, under pressure, during 2-5 hours depending on wood species. After this treatment, chips are in suspension in "black liquor", a liquid containing chemicals and dissolved lignin. After defibration, fibres become individualised and flexible. Then, washing and bleaching steps are following.
An important feature of the alkaline processes is the recovery and the re-utilisation of the chemicals in the digester liquor and washings after digestion. This serves the double purpose of economy and elimination of the trouble of disposing of a polluting effluent [GRA1958]. Pulps obtained from alkaline process have a good mechanical resistance and thus can be used as they are in wrapping. Despite of a difficult bleaching, these alkaline pulps are also used for printing paper.
From sulphite process, pulps have lower mechanical properties, especially in tear strength, but they are light and easy to bleach. However, for environmental reasons, they are rarely used, except for very refined papers.

- Mi-chemical pulps

Fibres are obtained from moderate chemical and mechanical treatments. They are especially used in flute papers since fibres are individualised but some lignin is still present. The presence of lignin rigidifies fibres and induces a high quality of compression resistance.

Other than from wood, pulps can be made of:

- Straw: in specific papers with high transparency and rigidity
- Cotton and flax: in very resistant papers as bank notes and cigarette papers
- Recycled cellulosic fibres: in newspapers and cardboards.

I.1.5.2. Activation of cellulose

As we saw previously, the density of hydroxyl groups in cellulose molecules is quite high. In this sense, it should not be surprising if cellulose were completely water-soluble. However, this has never been realised owing to a very high intra- and intermolecular hydrogen bonds in natural cellulose. These bonds prevent the dissolution of cellulose fibres in aqueous solvents. A so-called activation of cellulose improves its dissolution by breaking down intramolecular hydrogen bonds, by decreasing the DP (degree of polymerisation) of cellulose molecules, by removing some layers

of cellulose fibres and by purifying cellulose. Two examples of treatments to activate cellulose are given below.

- Microcrystalline cellulose

Microcrystalline cellulose (MCC) is a purified and partially depolymerised cellulose. This cellulose is obtained by a controlled hydrolysis with a diluted mineral acid solution, at ~105°C. The fibrous structure is thus broken and gives a particular structure. In addition, the DP is lowered down to 200. This change of morphology is due to the preferential hydrolysis of cellulose chains in amorphous region. So MCC cellulose has a high degree of crystallinity. Further filtration of cellulose suspension enables to purify the sample. The process is schematically shown in Fig.I.1-8

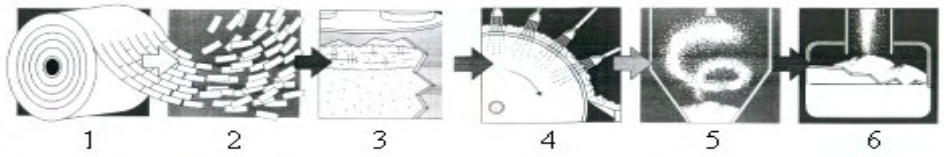

Fig.I.1-8: Process to obtain microcrystalline cellulose
1- Roll of α-cellulose; 2- Chipping; 3- Acid hydrolysis;
4- Filtration and washing to remove impurities and chemicals;
5- Drying on a fluidised bed; 6- packaging

Conditions to produce microcrystalline cellulose, which stay trade secrets, considerably influence the quality of the final cellulose pulp.

- Steam exploded pulp

The steam explosion method has the potential ability to destroy the inner and outer structure of any material. The destruction of the inner structure of cellulose corresponds to the breakdown of O3-H…O5' intramolecular hydrogen bonds, which seems to be the key for producing alkali-soluble cellulose, as demonstrated by Kamide *et al.* [KAM1984] with solid-state cross-polarisation/magic angle sample spinning ^{13}C NMR (CP/MAS/^{13}C NMR). The destruction of the outer structure corresponds to the removing of primary wall of cellulose fibres, which prevents swelling of secondary wall and thus fibre dissolution.

The steam explosion apparatus was originally designed by Sawada [SAW1985] and the explosion process is schematised Fig.I.1-9 [YAM1990].

- *Stage 1*: Cellulose is stored at room temperature.
- *Stage 2*: In order to obtain a weight ratio water/cellulose of 1/1, one weight part of cellulose is immersed in 20 weight parts of distilled water at 25°C for 15h; then the excess water is removed by centrifuging (2000rpm, 5min)
- *Steam explosion*: 200g (dry base) of the so-prepared cellulose is put into the vessel heated at a desired temperature. The vessel is closed. Then a saturated water vapour controlled to a given steam pressure P is introduced into the vessel for a given treatment time t (15-300s). Controlling the time enables to control the final DP.
- *Stage 3*: The vapour input valve is closed and the valve connected to the discharging nozzle is abruptly opened. Thus the treated cellulose is discharged.
- *Stage 4*: Treated sample is thoroughly washed with water.

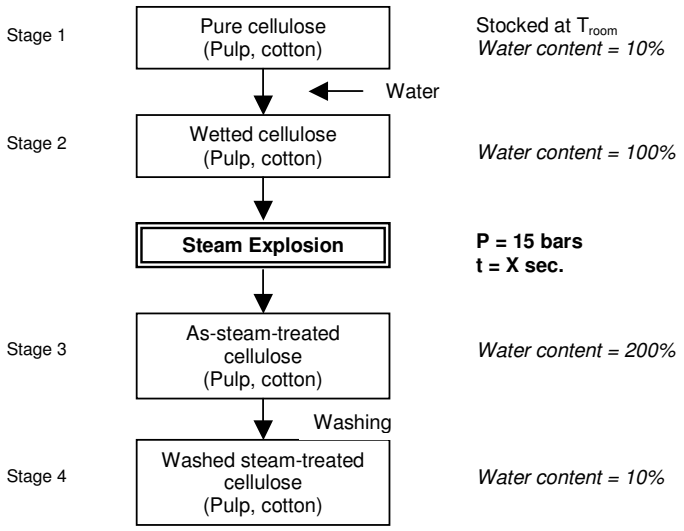

Fig.I.1-9 [YAM1990]: Schematic representation of the steam explosion process.

Yamashiki *et al.* [YAM1990] reported that soft wood pulp is very sensitive to steam explosion treatment because of the high porosity of fibres. On the other hand, hard wood pulp necessitates higher pressure to be completely soluble in 9%NaOH/water. Finally, the morphology and solubility of cotton linter do practically not change after steam explosion treatment.

I.2- CELLULOSE DISSOLUTION IN ALKALINE HYDROXIDE AQUEOUS SOLUTIONS

Cellulose is not a thermoplastic polymer. Thus, cellulose melting is not possible and dissolution is a necessary step to process cellulose. Because of intra- and intermolecular hydrogen bonds, the penetration of solvent is difficult and it has to be "strong" enough to break them. Different types of solvent can be used; they are largely described and classified by Klemm *et al.* [KLE1998]. The oldest process to dissolve cellulose is named "viscose process": cellulose is chemically transformed before being dissolved, this is the xanthation step. But as this process is polluting, an alternative route is to dissolve cellulose in alkali hydroxide aqueous solutions. After describing the current industrial process (part I.2.1-), we will present the first studies on this new solvent of cellulose (part I.2.2.1). Our work was based on these data concerning experimental conditions: concentrations, temperature, additives. Several authors investigated cellulose/alkali hydroxide aqueous solutions (parts I.2.2.2 and I.2.2.3) in order to understand the dissolution mechanism. Some hypotheses are given concerning the mechanism at the level of fibres and microfibrils (part I.2.2.4), but there are practically no literature dealing with the mechanism at the molecular level. Concerning additives, it will be shown that the influence of the proportion between NaOH and urea or thiourea or zinc oxide was studied in details (part I.2.3-). However, the mechanism of the action of these additives still remains unclear, despites a rather large amount of publications.

I.2.1- Xanthation in viscose process

The viscose process was discovered in 1892 by Cross, Bevan and Beadley and allowed spinning of viscose fibres. Still nowadays, the step of xanthation of this process is a method widely used in industry to dissolve cellulose. This process can be divided into three main chemical steps, which are identical in most of the industrial viscose processes (Fig.I.2-1).

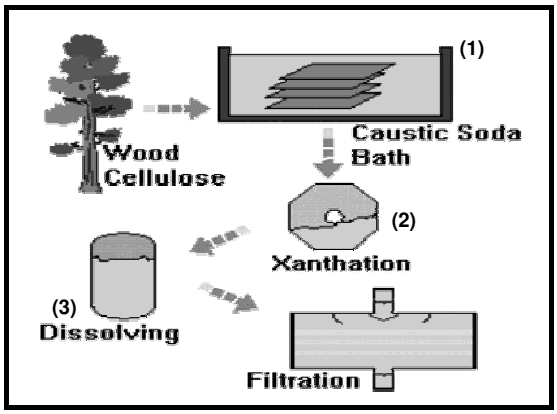

Fig.I.2-1: Scheme of viscose process
(1) formation of alkali-cellulose, (2) xanthation (3) dissolution

(1) Cellulose, prepared from either wood pulp or, less commonly, cotton linters, is treated with 17-20% sodium hydroxide (NaOH), at a temperature in the range of 18-25°C, to convert cellulose to alkali-cellulose.

$$\text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell-O}^-,\text{Na}^+ + \text{H}_2\text{O}$$

Cellulose fibres are swelling and become more accessible to other reactants. Then the alkali cellulose is aged under controlled conditions of time and temperature (between 18 and 30°C) in order to depolymerise the cellulose to the desired degree of polymerisation (DP). The molecular weight obtained determines the viscosity of viscose solution and cellulose concentration.

(2) After this maturing step, carbon disulfide (CS_2), in gas or liquid state, is added to the solution of alkali-cellulose to react with hydroxyl groups and generate the xanthation reaction:

$$\text{Cell-O}^-,\text{Na}^+ + \text{CS}_2 \rightarrow \text{Cell-O-C}(=\text{S})\text{-S}^-,\text{Na}^+$$

The resulting product is a substance called 'cellulose xanthate'.

(3) Then this alkaline cellulose xanthate is dissolved in dilute sodium hydroxide (~2.7 wt%) and forms a viscous solution called 'viscose'.

$$\text{Cell-O-C}(=\text{S})\text{-S}^-,\text{Na}^+ + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Cell-O-C}(\text{S}^-,\text{Na}^+)(\text{OH})\text{-S}^-,\text{Na}^+ + \text{H}_2\text{O}$$

The large xanthate substituents on the cellulose force the chains apart, reducing the interchain hydrogen bonds and allowing water molecules to solvate and separate the chains.

After obtaining viscose, industrial processes vary. The next steps can be: filtration and then spinning to obtain fibres or thin films, addition of reinforcing fibres and porophores then moulding to obtain sponges (see Chapter V), etc.
The last step of processes is called coagulation: cellulose is precipitating in regeneration baths (water, acid or base). The final regenerated cellulose is obtained and CS_2 and sulphured compounds formed during chemical reactions are going out.

However, "viscose process" involves some pollution: in the atmosphere, because of CS_2 and H_2S, and in water, because of the reducing agents (containing sulphur compounds) which decrease the oxygen amount in water. Optimisation and improvement in the viscose process result in a total recycling of the pollutant compounds in the aqueous phase and in a decrease of pollutant compounds in the atmosphere. Nowadays the quantity of the latter is "only" 10% of CS_2 used initially. Unfortunately, technologies for pollution treatment are very expensive. Thus for economical and for environmental reasons, it is very important to find new cellulose solvents. The purpose of research laboratories is to step away from the chemical modifications of cellulose by CS_2. NMMO, for example, is a good cellulose solvent, but these solutions are not very easy to prepare and to process. That is why it is interesting to look for alternative routes.

I.2.2- Action of alkaline hydroxide solutions on cellulose fibres

For a long time, it was known that strong alkaline aqueous solutions act on cellulose. Indeed, at the end of 19th century, Mercer [MER1903] discovered that cellulose fibres are swelling in aqueous solutions of sodium hydroxide and that was drastically changing the properties of the fibres. Several years later, in 1939, Sobue showed that cellulose can be dissolved in a narrow range of temperature and concentration of NaOH [SOB1939].

I.2.2.1. Introduction on mercerisation process and cellulose dissolution

Mercerisation is a process, which John Mercer developed between 1844 and 1850. Cotton cloth is immersed in a strong caustic alkaline solution, and then washed, in order to improve the lustre and smoothness, for example. Mercerisation also increases the ability to absorb dye, improves the reactions with a variety of chemicals, the strength and elongation of fibres and the stability of form. This type of cotton is often compared to silk and is especially used to produce high-quality fabrics. But this process tended to shrink the cotton cloth. In 1889, Horace Lowe improved this technique by keeping the material under tension whilst being mercerised and he applied a more thorough washing process to remove the caustic soda. Thus the mercerisation became a viable textile process.

During mercerisation, alkaline solution acts on cellulose chains by changing the fine structure, morphology and conformation of cotton. The native cellulose I crystalline form is transformed

into cellulose II, resulting in a variation in fibre strength and lustre as well as adsorption properties. In addition, soda fills up almost entirely the central cavity (the lumen) of cotton fibres. So, the ribbon-like cotton fibres become perfectly cylindrical and loose their convolutions inducing a smoother and shinier texture [MAR1941]. In mercerising, a decrease in length of cotton hair is accompanied by an increase in diameter: cellulose fibres are swelling.

According to Mercer [MER1903], mercerisation also occurs at low NaOH concentration (~9%NaOH) and the properties of cotton are improved. The lower the temperature, the more effectively the soda acts on the fibrous material. This reveals that the term of mercerisation was very wide and corresponded to all changes in cellulose fibres due to the action of alkaline hydroxide aqueous solutions. Several conditions of temperatures and NaOH concentrations are reported depending on material (cotton, ramie, flax, yarn or cloth…) and on process. The most often used conditions are 18-32% NaOH concentrations at 25-40°C. It is important to note that hardly few minutes (from 20s to 3min) are enough to obtain mercerisation of cellulose. Nowadays, the term of mercerisation essentially represents the action of concentrated alkali hydroxides on cellulose.

The NaOH concentration and temperature conditions to swell cellulose fibres are relatively well determined and slightly change depending on cellulose origin. In 30's, Davidson defined optimal conditions to dissolve modified cotton. As illustrated Fig.I.2-2, a decrease of temperature improves "hydrocellulose" dissolution in sodium hydroxide solutions [DAV1934] ("hydrocellulose" was obtained by cellulose hydrolysis with strong acids).

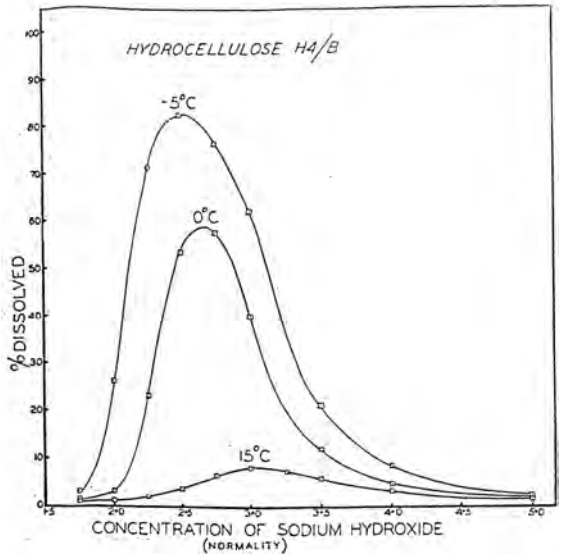

Fig.I.2-2 [DAV1934]: Hydrocellulose solubility versus NaOH concentration and solution temperature

The maximum solubility is 80% and it occurs at NaOH concentration of 10%, at –5°C. Moreover, the solubility increases when the chain length decreases. Consequently, authors concluded that unmodified cellulose cannot be dissolved because of the large length of the macromolecules. But, in 1939, Sobue *et al* [SOB1939] showed that it is possible to dissolve

cellulose, from natural ramie fibres, in a narrow range of phase diagram: between NaOH concentrations of 7% and 10% at low temperature (-5°C/+1°C).

In the 80's-90's, cellulose dissolution in 7-10%NaOH/water was largely studied. Kamide *et al.* [KAM1984] revealed that regenerated cellulose can be dissolved in NaOH/water and that the dissolution depends on the degree of breakdown in O3-H…O5' intramolecular hydrogen bonds. They also showed that the cellulose solubility depends on the DP, the concentration and the crystallinity of cellulose samples. Some years later [KAM1990], the authors also compared the X-ray diffraction peak intensities of cellulose I (ΔI_1) and Na-Cell I (ΔI_2) as a function of cellulose concentration in 9%NaOH/water. Fig.I.2-3 represents the results obtained. It appears that up to 9% of steam exploded cellulose (DP being ~340), there is no peak of cellulose I and no peak of Na-cell I. This means that 9%NaOH/water totally dissolves cellulose when its concentration is inferior to 9% and that the total dissolution of cellulose I (C_{cell} < 9%) in 9%NaOH aqueous solution gives a solution without conversion of cellulose I to Na-Cell I.

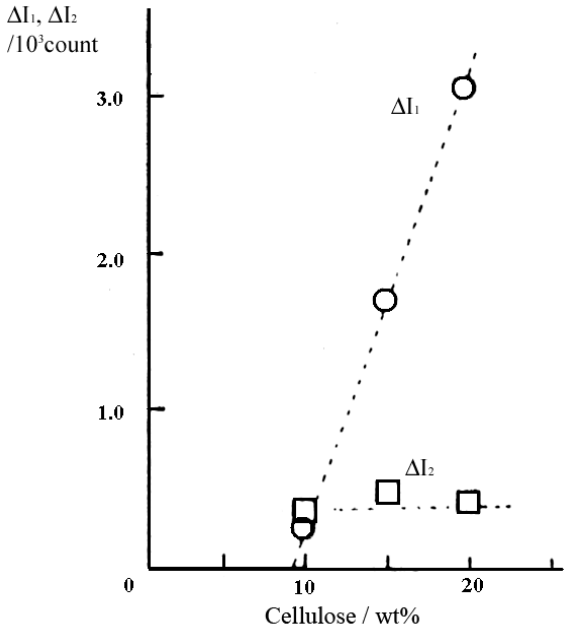

Fig.I.2-3 [KAM1990]: The cellulose concentration dependence of ΔI_1 and ΔI_2 for cellulose/9%NaOH aqueous system at 4°C.

More recently, it was shown that a ground Borregaard cellulose with a DP of 550 is swelling in a heterogeneous way in contact with a 9%NaOH/water solution [ROY_PhD]: some cellulose fibres remain non-swollen and non-dissolved, some others are partly dissolved and some others are swollen with balloons. The formation and the reason of the appearance of these balloons were largely studied in our laboratory these three past years, on different native cellulose fibres (cotton, wood…) in mixtures of NMMO/water [CUI2006a] and in NaOH/water with or without additives (ZnO and urea) [CUI2006b]. In good solvent of cellulose, the dissolution is occurring in four phases. First, the cellulose fibre swells by ballooning, with cellulose being totally dissolved inside the balloons. This phase gives the beaded structure often observed in relatively bad cellulose solvent. Secondly, the balloons continue to swell until the burst of the membrane.

Then the unswollen sections (between two balloons) are dissolved from the surface to the centre of the fibre. Finally, the scraps of the membrane are then dissolved. At this stage, all cellulose is dissolved [CUI2006a]. In a worse cellulose solvent, the dissolution of cellulose fibres is stopping at one of these phases. This is the case when 7.6%NaOH/water is used at -5°C to dissolve native cellulose fibres; the balloons are formed but do not burst [CUI2006b]. This paper also revealed that the presence of urea increases the quality of the alkaline solvent by a faster balloon formation, with a larger expansion. On the other hand, the presence of ZnO increases the swelling kinetics but decreases the size of balloons.
When cellulose is dissolved, even partly, in 9%NaOH/water, the solutions obtained are not stable. Gelation is occurring and the gel time decreases when the temperature increases [ROY2003].

I.2.2.2. Formation of alkali-celluloses

Mercer [MER1903] listed the influence of NaOH concentrations on cellulose fibre swelling:

- 3.2% NaOH is without action
- 6.5% NaOH acts only very slightly and at very low temperature
- 10% NaOH increases the effect which remains most marked at the lowest temperature
- 18.8% NaOH greatly increases the effect on cellulose.

This seems to be the outline of the cellulose/NaOH/H_2O phase diagram (**Erreur ! Source du renvoi introuvable.**) plotted by Sobue *et al* [SOB1939]. Fig.I.2-4 shows the presence of five different forms of alkali celluloses, or Na-Cell (I, II, III, IV or Q and V).

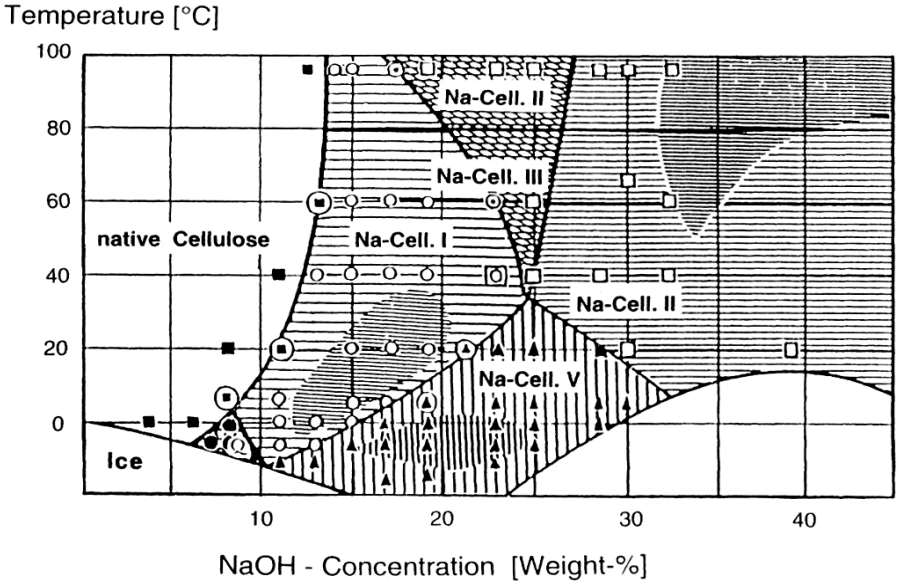

Fig.I.2-4 [SOB1939]: Phase diagram of the system cellulose/NaOH/water, cellulose being natural ramie fibres.
This graph reveals zones of different sodium celluloses as a function of NaOH concentration and temperature.
The unbroken hatching indicates the regions in which the sodium cellulose concerned is optimally formed.

The formation of these Na-Cell compounds depends on the temperature (from -20°C to 100°C) and NaOH concentration (from 0% to 45% by weight) but the boundaries of the various regions

are defined more or less distinctly. For example, below 0°C and at about 8 wt% NaOH concentration, is the location of what the authors called the alkali cellulose Na-Cell Q, Q as Quellung ("swelling" in German). Its X-Ray diffraction pattern is very characteristic and reveals a highly disordered state and a swelling in layers [SOB1939].

Sobue *et al.* [SOB1939] also investigated the composition of alkali celluloses from the correlation between two methods: the solid-phase analysis and the examination of volumes. The latter is based on the difference between the volumes of Na-Cellulose unit cell, determined from X-ray diffraction patterns, and of cellulose unit cell. This difference in volume can be used as a measurement for the quantity of the substance incorporated into the lattice by substituting the required volume for NaOH (32.6Å^3) and for H_2O (29.7Å^3). Their conclusions are reported Tab.I.2-1.

Sodium celluloses	Most probable composition	Molecular weight	Density
Na-Cell I	$C_6H_{10}O_5 – 1NaOH – 3H_2O$	256	1.51
Na-Cell III	$C_6H_{10}O_5 – 1NaOH – 2H_2O$	238	1.51
Na-Cell II	$C_6H_{10}O_5 – 1NaOH – 1H_2O$	220	1.6
Na-Cell V	$C_6H_{10}O_5 – 1NaOH – 4.5\text{-}5H_2O$	283-292	1.41-1.46
Na-Cell IV	$C_6H_{10}O_5 – 1H_2O$	180	1.48

Tab.I.2-1 [SOB1939] : Most probable compositions of sodium celluloses and the molecular weights and densities calculated therefrom.

I.2.2.3. Hydration of alkali ions

In 1941, Marsh [MAR1941] published a review of different works concerning cellulose swelling in aqueous solutions of alkaline hydroxides as lithium, sodium, and potassium but also rubidium and caesium. It appears that all alkaline hydroxides can act on cotton hairs and that the maximum of swelling is reached at a certain hydroxide concentration depending on the nature of metallic ion (Fig.I.2-5).

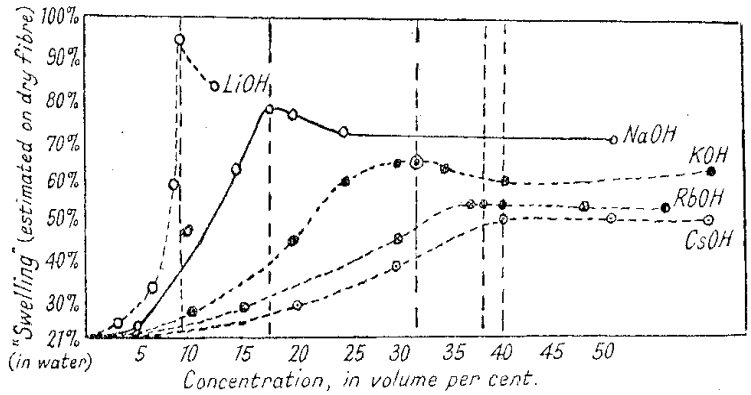

Fig.I.2-5 [HEU1925]: Change in volume of cotton hairs in five alkalis
Swelling is measured in terms of volume percentage between swollen and dried fibres.

An increase of the atomic force of the metallic ion – Li < Na < K < Rb < Cs – leads to a decrease of swelling. Bigger is the alkali ion, more difficult is its penetration into cellulose fibres [PET1948] but more uniform is the swelling [SRE1993]

The shape of the swelling versus alkali concentration curves can be explained by the size of hydrates [FRE1983]. For low alkaline hydroxide concentrations, a lot of water molecules form hydrated ion pairs (Fig.I.2-6). The hydrodynamic diameter of this system is too large to easily penetrate into the macromolecular structure of cellulose. Thus the swelling is relatively low. When ion concentration increases, the number of water molecules decreases to form solvated dipole hydrates. The hydrodynamic diameter decreases and ions can penetrate into amorphous and then well-organised domains. The maximum of swelling is reached.

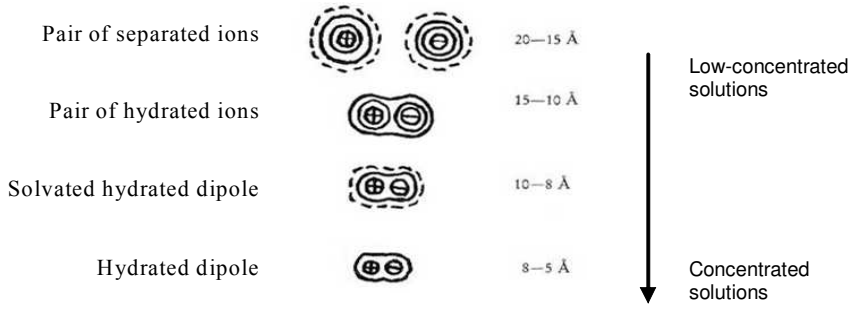

Fig.I.2-6: Various forms and the corresponding hydrodynamic diameter of hydrates as a function of ion concentration

Another explanation is based on the necessity of the presence of water to swell cellulose [LEG1952]. If NaOH concentration is too low, the number of Na^+ is insufficient to bring water molecules into cellulose chain in order to cleave hydrogen bonding. If the NaOH concentration is too high, the hydration of alkali ions is insufficient to break hydrogen bonding [KUO2005].

Investigating the solubility of "oxycellulose" ("Oxycellulose" being obtained after the action of an oxidant agent on cellulose) in these alkaline hydroxides, Davidson [DAV1936] showed that they follow the same order as previously for swelling: KOH < NaOH and LiOH, solubility being less than 5% and 85-90% respectively (Fig.I.2-7).

Due to considerations of cost and efficacy, only caustic soda is used as alkali in mercerisation, to change the aspect of cellulose fibres, and is considered for a potential use to dissolve cellulose.

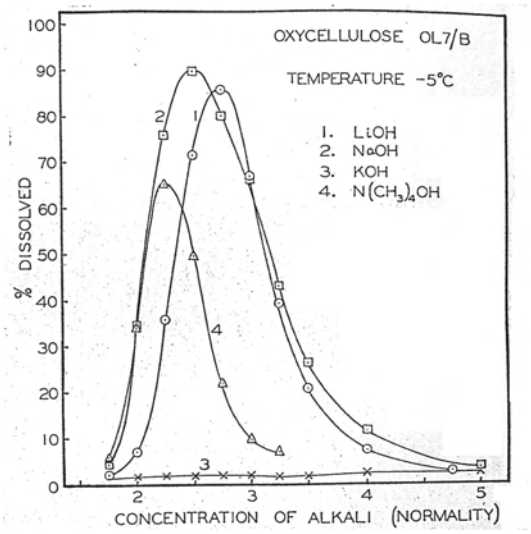

Fig.I.2-7 [DAV1936]: "Oxycellulose" solubility versus alkali concentration and type of ion, at –5°C.

I.2.2.4. Mechanism of mercerisation

It is known that the sodium hydrate size depends on the NaOH concentration [PIC1893] and that the cellulose dissolution region is very narrow (Fig.I.2-4). In 1990, from an X-Ray diffraction analysis, Kamide *et al.* [KAM1990] proved that NaOH penetrates into the cellulose chains inducing swelling of fibres. Thus we can think that there is an optimal size of sodium hydrate at which it can penetrate into cellulose fibres. This hypothesis has been mentioned by Yamashiki *et al.* [YAM1988], but the problem with this paper is that the molar ratios do not seem correct. Nevertheless, according to them, Na^+ does not play an important role in the dissolution of cellulose. The main parameter is to have a specific structure of alkali hydroxide, which is formed at 9%NaOH. Na^+ and OH^- ions, surrounded by their solvation cages, break the intra- and intermolecular hydrogen bonds in the solid structure of the cellulose. Sodium hydrates interact with the cellulose chains and give various Na-Cell compounds depending on the experimental conditions as it appears on the phase diagram (Fig.I.2-4) [SOB1939]. If sodium hydroxide is then removed from the mixture, the alkali cellulose transforms into cellulose II.

As we saw previously (partI.2.2.1), the irreversible transformation from cellulose I, with a parallel crystalline structure, to cellulose II, with an antiparallel crystalline structure, at room temperature, is named mercerisation. Okano, Sarko and Nishimura [OKA1984] [OKA1985] [NIS1987a] [NIS1987b] studied in details the mechanism and the molecular changes of this transformation and mentioned the complex Na-Cell I as the first intermediate component. This complex has an antiparallel structure [OKA1985], very similar, in the chain conformation, to the structure of cellulose II [NIS1991a]. The structure of Na-Cell Q, mentioned by Sobue [SOB1939], was not analysed extensively because of temperature conditions (below 0°C).

A proposed mechanism of mercerisation is schematised on the Fig.I.2-8.

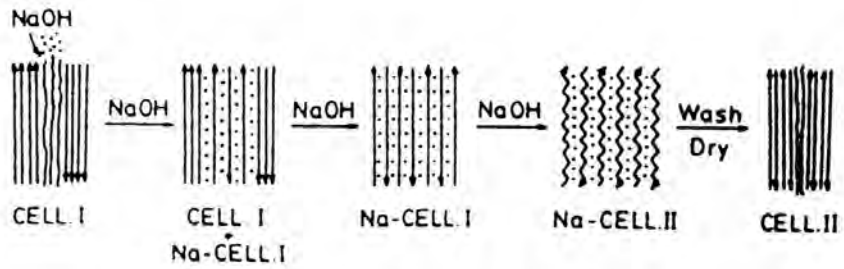

Fig.I.2-8 [OKA1985]: Possible mechanism of mercerisation

- The raw material is native cellulose, or cellulose I, which has a parallel crystalline structure. In a fibre of cellulose, there are a large number of crystallites in which the chain directions are parallel but the crystallites are distributed along the fibre axis with equal probability for "up" and "down" directions, as represented in the Fig.I.2-8 – 1st pattern. French *et al.* [FRE1987] reported that the convention used by the most authors is that the cellulose chain direction is defined by the vector from C4 to C1, i.e. from the non-reducing to the reducing ends. If the angle between the vector C4-C1 and the 'c'-direction (fibre axis) of the unit cell is acute, the chain is called "up", if not, it is called "down". Let us note that Gardner and Blackwell [GAR1974], for example, interchanged this notation.

- It was demonstrated that the accessibility of –OH groups depends on the crystallinity of cellulose [TAS1994]. Consequently, highly crystalline cellulose is difficult to mercerise [CHA1976]. Thus, to begin the mercerisation it is necessary to have an amorphous phase in the cellulose or some imperfections in the crystalline morphology. During the first step of the mercerisation, the alkali solution enters the amorphous regions that exist as the interface regions between the crystallites, where the polymer chains are arranged along both directions "up" and "down". The penetration of $NaOH/H_2O$ causes swelling of cellulose fibres [OKA1984] and in these swollen regions, the polymer chains are expected to be relatively mobile. Thus very little lateral movements of chain segments enable the formation of an antiparallel soda-cellulose, the Na-Cell I [OKA1985]. In terms of energy and entropy, the formation of Na-Cell I is favoured and thus the crystalline regions of cellulose I gradually diminish in size while the crystallites of Na-Cell I increase simultaneously [PET1948] [NIS1987a]. Furthermore, as the amount of amorphous regions does not increase during the conversion steps, the authors concluded on a crystal-to-crystal phase transition occurring without an intervening amorphous state [OKA1984]. This shows that the conversion from the parallel cellulose I to antiparallel Na-Cell I proceeds through a side slip of polymer chains and not a reversal of those.

- Na-Cell I contains one NaOH molecule per anhydroglucose unit (AGU) and has a twofold helical chain conformation with a repeat unit of 10.1Å. Fig.I.2-9 schematises the various possibilities of interactions between the cellulose chains and the Na^+ ions. Practically all authors [KAM1985] [NIS1991a] [TAK1991] [FIN1995] [ISO1997] agree that Na^+ breaks the intermolecular hydrogen bonds O2_H…O6' and that the most probable location of the Na^+ ion is on the –OH at C2. The carbon C3 is more resistant to the complexation with the sodium hydroxide.

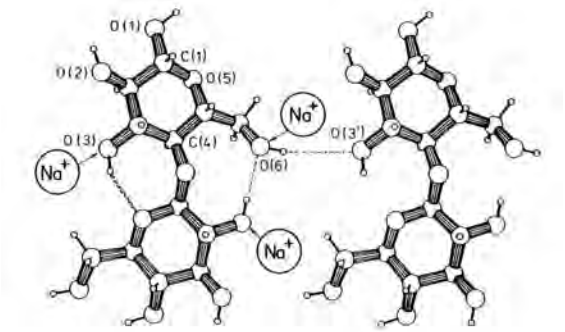

Fig.I.2-9 [FIN1995]: Interaction between Na^+ and the cellulose chain.

- When the initial conversion step is completed, the Na-Cell I is free to absorb more NaOH and convert to Na-Cell II, with a threefold helical chain conformation with a repeat unit of 15.4Å.

- Finally, after NaOH has been washed out of the structure, the cellulose chains again revert to a twofold helical conformation (lower energy structure without NaOH), cellulose II polymorphic form. Later, Nishimura and Sarko [NIS1991b] added the Na-Cell IV as an intermediate compound between the Na-Cell II and the cellulose II.

I.2.3- Influence of additives on cellulose dissolution

I.2.3.1. Influence of zinc oxide (ZnO)

Mercer [MER1903] reported that the mercerisation can begin at low NaOH concentrations (8.5%-9%NaOH) when the temperature is decreased below 0°C. He added: *"It is a remarkable fact, however, that the addition of zinc oxide to a lye containing 9%NaOH will enable it to mercerise at ordinary temperature. (…) it is ineffective if the solution is heated".*

In the last part of his article, Davidson [DAV1937] showed that ZnO improves "oxycellulose" dissolution and that unmodified cotton can be dissolved at –5°C, at a relatively high ZnO/NaOH ratio (Fig.I.2-10 and Tab.I.2-2). He added that precipitation of zinc oxide takes place if the ZnO/NaOH ratio is too high and especially for concentrated-cellulose solutions.
The last paper talking about the addition of ZnO into cellulose/alkali hydroxide aqueous solutions is a Polish patent [WO02/22924]. It revealed that in order to improve the stability of cellulose solutions, zinc oxide content has to be at least 0.1wt% (0.01N), NaOH concentration being inferior to 10wt%.

Davidson [DAV1937] also investigated the influence of ZnO on cellulose dissolution in potassium hydroxide (KOH). As ZnO is difficult to dissolve in KOH, only one ZnO/KOH ratio was studied and was equal 0.14. Author showed that the addition of ZnO increases the percentage of "oxycellulose" dissolved but dissolution remains very low.

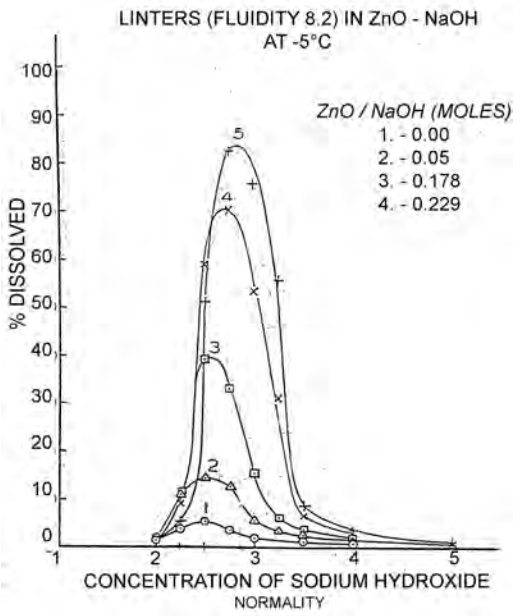

Fig.I.2-10 [DAV1937]: Cotton linter solubility, at -5°C, as a function of NaOH concentration and the ZnO/NaOH ratio

Maximum dissolution

ZnO/NaOH (moles)	NaOH (N)	NaOH (%)	ZnO (%)	% dissolved
0.0	2.5	10	0	5.2
0.05	2.5	10	1.0	14.5
0.10	2.5	10	2.0	39.2
0.178	2.75	11	4.0	70.1
0.229	2.75	11	5.1	82.6

Tab.I.2-2: Values of NaOH and ZnO concentrations obtained at the maximum dissolution of cotton linter for a given ZnO/NaOH ratio, from Erreur ! Source du renvoi introuvable..

Unfortunately, no article gives any explanation concerning the action of ZnO on cellulose dissolution. We only know that when ZnO is dissolved in alkaline solution, new compounds are formed. In the literature, it is stipulated that, depending on NaOH concentration, the dissolution of ZnO in NaOH gives several zinc hydroxides. The determination of the compounds formed between NaOH and ZnO is not easy and the conclusions differ from one paper to the other. But most of authors agree that at high pH (~12), the main species are $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$ and $Zn_2(OH)_6^{2-}$ [DIR1954] [REI1975].

I.2.3.2. Influence of urea and thiourea

In 1998, Laszkiewicz [LAS1998] reported that the addition of 1% urea in 8.5% NaOH at –5°C improves the solubility of bacterial cellulose having an initial DP of 680. The fraction of dissolved cellulose is 48.6% with 1% urea and 17.8% without urea. Some years later, a research group in Wuhan University in China reported that cellulose is "totally dissolved" in NaOH with urea [ZHO2000] [ZHO2002a] [ZHO2004] or thiourea [ZHA2002] [WEN2004] and both additives are removed out completely from the cellulose during the coagulation and washing.

Zhou *et al.* [ZHO2000] investigated the influence of NaOH/urea solvent composition on cellulose dissolution. They concluded that the optimal NaOH/urea/water ratios to dissolve cellulose at 0°C are 6/4/90 and 8/2/90. According to them, cellulose solutions in these solvents are stable and did not form a gel with temperature increase. They also studied the influence of cellulose molecular weight on the dissolution for different NaOH/urea solvent compositions and for different cellulose samples (Fig.I.2-11). From their papers, we calculated the DP of each sample with $M_\eta/162$, where M_η is the cellulose molecular weight given in the article and 162 is

the molar mass of the anhydroglucose unit (AGU); the DP are also shown in Fig.I.2-11. Solubility S_a (in percentage) of cellulose was calculated by:

$$S_a = [w_1/(w_1 + w_2)] \times 100$$

We plotted the best solubility results – NaOH/urea = 6/4, 8/2, 6/0 and 8/0 (see selected columns in Fig.I.2-11) – versus DP (Fig.I.2-12). It is clear that the solubility decreases when the DP of cellulose samples increases: a result that should be expected.

Table I. Solubility (S_a) of celluloses in NaOH / urea aqueous solution

Cellulose	S_a/%									
	S6-0	S6-2	S6-4	S6-6	S6-8	S8-0	S8-2	S8-4	S8-6	S8-8
Linter-1	44.7	50.5	48.4	43.3	36.1	40.6	48.5	40.5	28.3	23.7
Linter-2	21.0	26.8	30.2	30.8	17.6	24.2	27.8	25.9	18.9	12.2
Bagasse-1	53.4	58.0	69.3	63.3	49.5	51.4	54.0	53.4	52.8	46.2
Bagasse-2	56.0	61.7	74.3	68.6	54.0	62.8	64.0	62.7	58.1	56.1
Alkali-soluble cellulose	Gel	100	100	100	100	100	100	100	100	100
Bemliese[8]	Gel	100	100	100	100	100	100	100	100	99

Table II. Crystallinity χ_c, solubility (S_a) and viscosity-average molecular weight (M_η) of dissoluble and indissoluble parts of cellulose in the solvent of S6-4

Cellulose	χ_c	$M_\eta \times 10^{-4}$			S_a/%
		Initial cellulose	Indissoluble cellulose	Dissoluble cellulose	
Linter-1	0.73	10.0	12.8	5.57	48
Linter-2	0.74	15.9	17.4	6.70	30
Bagasse-1	0.64	8.32	15.4	2.97	69
Bagasse-2	0.61	7.26	16.2	2.25	74
Alkali-soluble cellulose	0.76	4.75	—	4.54	100

Linter-1	**DP 617**
Linter-2	**DP 981**
Bagasse-1	**DP 514**
Bagasse-2	**DP 448**
Alkali-soluble cellulose	**DP 293**

Fig.I.2-11 [ZHO2000]: Data on 5% cellulose solubility in different NaOH+urea mixtures

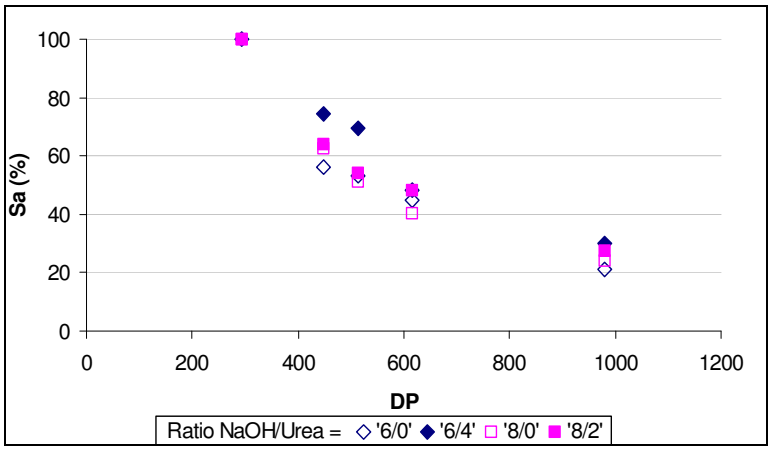

Fig.I.2-12: Solubility of cellulose in pure 6%NaOH, in 6%NaOH+4%urea, in pure 8%NaOH and in 8%NaOH+2%urea as a function of DP, based on literature data from [ZHO2000].

Some years later, the same team studied the influence (i) of the nature of alkali hydroxide and (ii) of the process to dissolve cellulose [CAI2005]. They classified the solvents according to their dissolution power on cotton linter: LiOH/urea/water > NaOH/urea/water >> KOH/urea/water. Moreover, the best NaOH/urea/water solvent composition was found to be 7/12/81.
On one hand, they showed [ZHO2004] [CAI2005] with ^{13}C NMR studies that (i) NaOH/urea is a direct solvent of cellulose and (ii) urea and NaOH interact, this interaction probably playing an important role in the solvation of cellulose. On the other hand, DSC experiments described in [CAI2005] mentioned "urea hydrates" and "NaOH hydrates", no "new" NaOH/urea compound was found. They added that only NaOH hydrates are linked to cellulose and that the interactions between urea and cellulose decrease the self-association of cellulose chains and thus enhance the stability of solution. But the nature and mechanism of cellulose/urea interactions was not explained and is not revealed by NMR. Finally, from viscometry in dilute state, they concluded that in such aqueous solutions, cellulose exists as semi-flexible chains [ZHO2004].

Zhang *et al.* [ZHA2002] studied the influence of thiourea on cellulose dissolution. They determined that the best dissolution occurs when the NaOH/thiourea/water composition is 6/5/89. Cellulose solutions obtained are transparent and colourless. This new direct solvent of cellulose is better than 6%NaOH/4%urea/water. Indeed, for cotton linter DP620, the solubility in the "thiourea" solvent is 2 or 3 times superior to the solubility in the "urea" solvent and the intrinsic viscosity is also higher in 6%NaOH/5%thiourea (245g.cm^{-3}) than in 6%NaOH/4%urea (150g.cm^{-3}). They also concluded that thiourea prevents the self-association of cellulose molecules in NaOH aqueous solutions leading to improve cellulose solubility.

This group of researchers essentially investigated regenerated cellulose membranes prepared from NaOH/urea or NaOH/thiourea aqueous solutions. Consequently, the influence of coagulation conditions on pore size, water permeability and mechanical properties was largely studied. Whatever the nature of regeneration baths is, adjusting the acid concentration and the coagulation time enable to control properties of the membranes [ZHO2002a][ZHO2002b]. However, only few papers concern mechanism of cellulose dissolution or solutions gelation.
Weng *et al.* [WEN2004] studied gelation of 4-6%cellulose/6%NaOH/5%thiourea aqueous solutions, as a function of temperature. They noted that after gelation, G' always increases and never reaches a plateau. Consequently, the gelation process does not involve chemical cross-links but probably results from the formation of a condensed network, accompanied by a micro-phase separation. Moreover, increasing cellulose concentration shifts gelation point towards lower temperatures by increasing the chance of "collision" of the cellulose chains. Another evidence of physical interactions is that ^{13}C NMR spectra of solution and gel states are similar indicating that there is no change in macromolecular structure during the sol-gel transition.
They proposed the following dissolution and gelation mechanisms of cellulose/NaOH/thiourea (or urea) aqueous solutions (Fig.I.2-13). Because of strong intra- and intermolecular hydrogen bonds, cellulose has a high tendency to aggregate and self-associate (Fig.I.2-13a). The addition of NaOH/thiourea (or urea)/water solution allows breaking these intermolecular hydrogen bonds to create a significant ion-pair interaction. Then water or thiourea (or urea) molecules can form

hydrogen bonds with the released –OH groups on the cellulose chains leading to a high swelling of cellulose fibres in alkaline aqueous solution (Fig.I.2-13b) and then dissolution. All solvent molecules surround the cellulose chains to prevent its self-association (Fig.I.2-13c). At a lower temperature, this system is relatively stable whereas increasing temperature breaks the overcoat layer. So the hydroxyl groups of cellulose are exposed to each other inducing the gel formation caused by the self-association force of cellulose macromolecules.

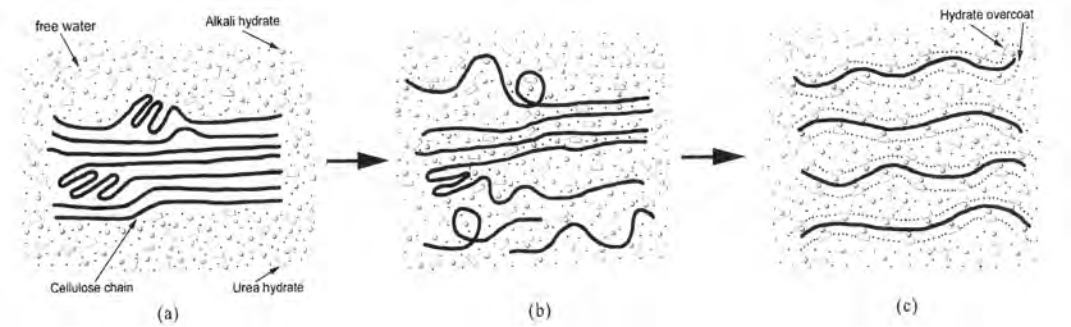

Fig.I.2-13 |CAI2005]: Schematic dissolution process of the cellulose in LiOH/urea and NaOH/urea aqueous solutions pre-cooled to -10℃ : (a) cellulose bundle in the solvent, (b) swollen cellulose in the solution, (c) transparent cellulose solution

I.2.3.3. Other additives

In his works, Mercer reported the use of some additives to prevent shrinkage of cellulose fibres as silicate or aluminate of soda, ethylic or methylic alcohol, oxalic acid [MER1903]. But at that time, only findings were published and no explanation of the action of additives on cellulose solutions was given.

At room temperature and at low NaOH concentrations (<10%NaOH), Legrand [LEG1952] investigated the influence of alcohol addition on Na-Cellulose formation. It appears that when the alcohol concentration increases, and thus the water amount decreases, the Na-Cell formation is favoured. But on the other hand, if no water is present in the solution, native cellulose is not transformed: this seems to confirm the significant role of water in cellulose swelling, mercerisation and dissolution.
Moreover, gelatine, glycol, glycerol decrease the swelling of cotton [MAR1941] and penalize the Na-Cell formation [LEG1952], whereas acetone and ethylenediamine favour it.

I.3- CONCLUSION

In the part I.1-, the structure of cellulose was described with its dense network of intra- and intermolecular hydrogen bonding which explains the difficulties to dissolve cellulose in most of solvents. There is a large diversity of cellulose samples:

- the crystals with four possible structures,
- the supra-molecular arrangements depending on origin of cellulose (various species of wood, cotton…),
- the treatment to extract pure cellulose (alkaline or acid processes) that is changing the physical and chemical nature of the fibres,
- the treatment to activate cellulose fibres.

In the part I.2-, we reviewed literature concerning cellulose dissolution in alkali hydroxide aqueous solutions. Sodium hydroxide is the cheapest and the most effective alkali hydroxides and thus has been largely studied for many years. It appears that NaOH can act as a swelling agent of cellulose in a large domain of NaOH concentrations and temperatures. But, in a narrow range of NaOH concentrations (7-10wt%) and temperatures (-6°C-+4°C), NaOH is a direct solvent of cellulose. The mechanism of cellulose mercerisation was described in terms of chain arrangement and formation of Na-Cell intermediates, the latter containing some NaOH and water molecules.

A large amount of publications reveal that cellulose/NaOH/water solutions are not stable in time, even after the addition of zinc oxide, urea or thiourea. But in these papers, the best conditions to improve cellulose dissolution and increase the stability of solutions are investigated but no clear explanation on the reasons of gelation and action of additives are given.

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RESUME DU CHAPITRE II

MATERIAUX ET METHODES EXPERIMENTALES

Ce chapitre décrit les produits, les dispositifs et les méthodes utilisés dans ce travail.

Différentes celluloses ont été utilisées, les deux principales étant une cellulose microcristalline et une cellulose de bois explosée à la vapeur afin de diminuer le DP et de faciliter sa dissolution dans la soude. Quel que soit le type de cellulose utilisé, la dissolution s'effectue de la même manière : deux heures de mélangeage à -5°C dans une solution aqueuse de 7,6%-9% d'hydroxyde de sodium préalablement refroidie à -5°C. Au cours de l'étude bibliographique, nous avons vu que l'ajout d'additif peut améliorer la dissolution des fibres de cellulose. Nous avons donc travaillé avec de l'oxyde de zinc et de l'urée mais également avec quelques surfactants.
Une éponge cellulosique est un composite poreux constitué d'une matrice de cellulose régénérée, provenant de la solution cellulose/NaOH/eau décrite précédemment, et de fibres de renfort naturelles (généralement du coton, du lin ou des fibres de bois). Des cristaux de sulfate de sodium (Na_2SO_4,$10H_2O$) sont incorporés en grande quantité dans le mélange, leur fusion créant la macro porosité des éponges. Nous donnons une description rapide des fibres de renfort utilisées au laboratoire et des cristaux de sel. La méthode de préparation des éponges est également présentée et reprend les données fournies et utilisées au laboratoire pilote Spontex.

Nous verrons dans les chapitres suivant que de nombreuses techniques d'analyse physico-chimique ont été utilisées que ce soit pour déterminer les propriétés thermique, rhéologique, mécanique et autres. Dans ce chapitre, nous présentons à la fois leur principe de base et les conditions expérimentales appliquées à nos échantillons.

Les propriétés thermiques des solvants utilisés dans cette étude ainsi que celles des solutions de cellulose ont été analysées par un appareil de DSC (Differential Scanning Calorimetry). Les thermogrammes nous ont permis de mesurer les température et enthalpie de fusion de chaque phase présente dans le système et ainsi déterminer la structure des solutions, en dessous de 0°C.

La rhéologie des solutions a été étudiée sur de nombreuses solutions de cellulose. Nous avons fait varier le DP, la concentration et l'origine de la cellulose, mais également les systèmes de solvant en modifiant la nature et la concentration des additifs. Le but de l'étude rhéologique est de mieux comprendre le comportement des solutions de cellulose à l'écoulement (mesure de viscosité en fonction du taux de cisaillement), et ce pour différentes températures. Les solutions n'étant pas

stables thermodynamiquement, nous avons déterminé les conditions de gélification des solutions en temps, en température et en fonction des additifs présent dans le système de solvant. Le point de gel est défini comme étant le point d'intersection des deux modules G' et G". La rhéologie en mode dilué a été réalisée à plusieurs températures et nous a permis de classer les différents solvants en fonction de leur pouvoir de solvant sur la cellulose d'une part et d'étudier l'influence de la température sur cette qualité de solvant d'autre part.

Les produits de cellulose régénérée ont été analysés mécaniquement par des tests de traction allant jusqu'à rupture de l'éprouvette. Le but de ces essais est de comparer les différentes conditions de gélification et de régénération de la cellulose sur la résistance mécanique afin d'améliorer les propriétés finales des éponges.

Des observations microscopiques, que ce soit à l'aide d'un microscope optique ou d'un microscope électronique à balayage (MEB – SEM en anglais), ont été réalisées tout au long du projet pour étudier qualitativement la solubilité de la cellulose en fonction du solvant, l'influence de la congélation sur l'aspect des fibres de renfort et de la porosité des éponges finales. Le microscope optique relié à une camera nous a permis de visualiser l'action de la soude sur les fibres de cellulose.

CHAPTER II

MATERIALS AND METHODS

In the first chapter, the diversity of cellulose pulps was shown as well as the numerous studies on the optimal concentrations of the different components (cellulose, sodium hydroxide, additives). Consequently, in order to minimize misinterpretations in the discussion of results, a well-detailed description of all experimental conditions is given. This second chapter is divided in three main parts "Materials", "Solution preparation" and "Methods".

The first part deals with the materials used: cellulose pulps, solvent and additives. We will give some details about the origin of cellulose and its DP, the suppliers of each components, and their purity.

The second one presents the procedure to dissolve cellulose in NaOH/water, NaOH/ZnO/water and NaOH/urea/water solutions. Some results are given to explain our choice in sample preparation. This concerns the drying of initial cellulose pulp to avoid the problem of humidity, the storage conditions and the necessity, or not, to filter solutions before rheological measurements.

The last one describes the various methods used in this study. As DSC (Differential Scanning Calorimetry) analyses were largely performed, not only the conditions of sample preparation are described but also the principle of DSC apparatus and the method used to determine melting temperature and enthalpy. For the other techniques (X-ray diffraction analyses, rheology, microscopic observations, mechanical tests), essentially details on sample preparation are presented.

II.1- MATERIALS

II.1.1- Cellulose samples

In this study, several types of cellulose were used (Tab.II.1-1). The main ones were microcrystalline cellulose Avicel from FMC Corporation and steam exploded cellulose Borregaard prepared by Innovia Films Ltd (B342, B389, B407 and B500). Some work (Chapter IV) was also performed on non-steam exploded cellulose from Borregaard and cellulose samples provided by Lenzing: L307 sample obtained with electron beam degradation and L198 sample obtained from cellulose regeneration from alkali solutions. A detailed description of each cellulose type is given in the following sections.

Name	Type of cellulose (Appendix I)	Origin	Treatment	DP
Avicel	Cellulose I	Wood but origin is unknown	MCC	170
B342	Cellulose I	Spruce and pine	Steam explosion	342
B389	Cellulose I	Spruce and pine	Steam explosion	389
B407	Cellulose I	Spruce and pine	Steam explosion	407
B500	Cellulose I	Spruce and pine	Steam explosion	500
B530	Cellulose I	Spruce and pine	Elemental Chlorine Free bleaching (ECF)	530
L307	Cellulose I	Eucalyptus	Degradation by electron beam	307
$L198_{II}$	Cellulose II	Eucalyptus	Alkali cellulose	198

Tab.II.1-1: Main data concerning the pulps of cellulose used in this study.
Names consist of the supplier initial and the DP value.

II.1.1.1. Avicel cellulose

Avicel cellulose is a microcrystalline cellulose (MCC). This cellulose is very pure; there is no lignin and no hemicelluloses and it consists of pure cellulose micro-crystals (see more details in Chapter I, part I.1.5.2). Such a cellulose sample has a relatively low degree of polymerisation (DP).
Here the grad used was Avicel PH101 with a DP of 170.

II.1.1.2. Borregaard cellulose

Cellulose extraction from spruce and pine softwood was performed in Borregaard ChemCell:

- Steam-exploded samples: The steam explosion treatment had been made by Innovia Films Ltd. As we saw previously (Chapter I, part I.1.5.2), this treatment enables to activate cellulose fibres by decreasing the DP of cellulose. Consequently, cellulose dissolution is improved as compared with untreated samples. In this study samples of different DPs were used: 342, 389, 407 and 500. They will be named B342, B389, B407 and B500 respectively.
- Non-steam exploded samples: The B530 cellulose sample was treated using the sulphite pulping process and ECF bleaching (Elemental Chlorine Free bleaching using chlorine dioxide as chemical). It is a high quality dissolving pulp containing around 92% of cellulose, the rest being moisture and very low level impurities (hemicelluloses…). Its DP is 530.

II.1.1.3. Other cellulose samples

Two other cellulose pulps used were kindly provided by Lenzing. The initial pulp was Solucell 1175 with DPv=412. It was treated in two ways:

- By electron beam irradiation (60kGy), which gave cellulose I with DP307 (sample L307).
- Regenerated from alkali solution, which gave cellulose II with DP198 (sample $L198_{II}$).

II.1.2- Solvents and additives

Cellulose was dissolved in alkali hydroxide aqueous solutions, with or without additives.

II.1.2.1. Alkali hydroxides

The main alkali used was sodium hydroxide NaOH; potassium hydroxide KOH was also tested for some experiments. NaOH and KOH were pellets from the supplier VWR; purities were 98% and 85% respectively. Water was distilled in the lab.

II.1.2.2. Additives

Two main additives were added to solutions in order to improve cellulose dissolution. They were zinc oxide ZnO and urea $CO(NH_2)_2$. ZnO was powder from the supplier VWR; its purity was 98%. Urea was pellets from Fisher; its purity was 99%.

II.1.2.3. Surfactants

In the process of sponge fabrication, surfactants are added to improve properties of final product. The surfactants used are non-ionic and can be dissolved in water. Two of them are fluoropolymers – Zonyl FS and Zonyl FSN – and the third one is an alkylpolyol, named AP in the following.
The exact structure of these surfactants is not known.
In cellulose solutions, the surfactant concentration is 1% of cellulose content, which corresponds to 0.05% in a 5% cellulose solution.

II.1.3- Other components used in sponge manufacture

II.1.3.1. Reinforcing fibres

The fibres were either cotton fibres, with a length of 20mm, or fluff. The latter is a short wood fibre which is cheaper than cotton. Fluff is a wood pulp as the one for paper manufacturer, with some differences in order to make easier the defibration.
The fluff fibres provided by Weherhauser under the reference CF416, with a DP of 1100.
These two fibres should not be dissolved in 7.6NaOH/water, even at -6°C. According to Yamashiki [YAM1990], cellulose can be dissolved in 8-9%NaOH if its DP is inferior to 400. In

our case, we partly dissolved cellulose with DP of 500, but cellulose with higher DP, as the Raywhite HJ cellulose with a DP of 1044 (provided by the supplier Rayonier), are effectively not dissolved in 7.6NaOH/water (Fig.II.1-1).

Fig.II.1-1: non-dissolved fibres of Rayonier DP1044 cellulose in a 5cellulose/7.6NaOH/water solution.
Scale bar represents 100µm

II.1.3.2. Adhesion promoters

Three DYNASYLAN® adhesion promoters, from Hüls France, were used:

- 0.5% and 1% of GLYMO (Glycidyloxypropyltrimethoxysilane)
- 1% AMEO (Aminopropyltriethoxysilane)
- 1% CPTMO (Chloropropyltrimethoxysilane)

II.1.3.3. $Na_2SO_4,10H_2O$ crystals

The $Na_2SO_4,10H_2O$ crystals are used as porophores in the sponges. The size of these crystals is between less than 1mm and 4mm. The distribution of diameters generates different porosities which are adjusted as a function of properties of the final product.
The $Na_2SO_4,10H_2O$ crystals added at the beginning of the industrial process are recycled at the end and re-introduced in the process.

II.2- SOLUTIONS PREPARATION

The description of the proportions between the components in the solutions that will be studied and the corresponding notations used in the following chapters will be presented. The reason of such a notice is that systems studied are of a complex composition, like a mixture of cellulose, NaOH, urea, zinc oxide and water, and confusions in concentration determination should be avoided.

The notion of concentrations will be used only for binary solvents, like NaOH/water or urea/water. In all other cases we shall use and show in the notations the amount of grams of the substance in 100 g of solution. In other words, Xcellulose/YNaOH/water means that in 100 g of solution there are X grams of cellulose, Y grams of NaOH and (100–X–Y) of water. Another example is as follows: Xcellulose/YNaOH/Zurea/water means that in 100 grams of solution there are X grams of cellulose, Y grams of NaOH, Z grams of urea and (100-X-Y-Z) grams of water. For the binary systems "concentration" in weight per cent, calculated as $Y = \frac{M_i}{M_i + M_{water}} 100\%$ **(M_i and M_{water} being component "i" and water weights, respectively), coincides with the amount of grams Y of this component in 100 g of solution: Ycomponent/water.**

II.2.1- Drying of steam exploded cellulose

Steam exploded cellulose was provided in a wet state. The water content was from 10% for B500 to 47% for B342. Moreover, because of changes in the humidity in the lab, water content in given wet cellulose pulp could vary. To avoid any mistake in the cellulose concentration when preparing solutions, cellulose was dried in an oven at +60°C during 10 hours in order to obtain a dry pulp.

Two solutions were prepared. The first one consists in 5 dry B342 cellulose/7.6NaOH/water, the second one in 5 wet B342 cellulose/7.6NaOH/water. It is clear that in the wet cellulose solution, water content is taken into account when weighting cellulose.

Quick tests were performed to study the influence of cellulose drying on rheological properties of 5 B342 cellulose/7.6NaOH/water solutions. On one hand, viscosity measurements (Fig.II.2-1) reveal that drying slightly increases viscosity of solutions, for the three temperatures studied. On the other hand, moduli versus temperature measurements (Fig.II.2-2) show that gelation point is reached later with wet cellulose (T_{gel}=31°C) than with dry cellulose (T_{gel}=28°C). It seems that water content in cellulose pulp influences results of rheological tests, even slightly. Thus, in order to remove this parameter, cellulose was dried in all our experiments.

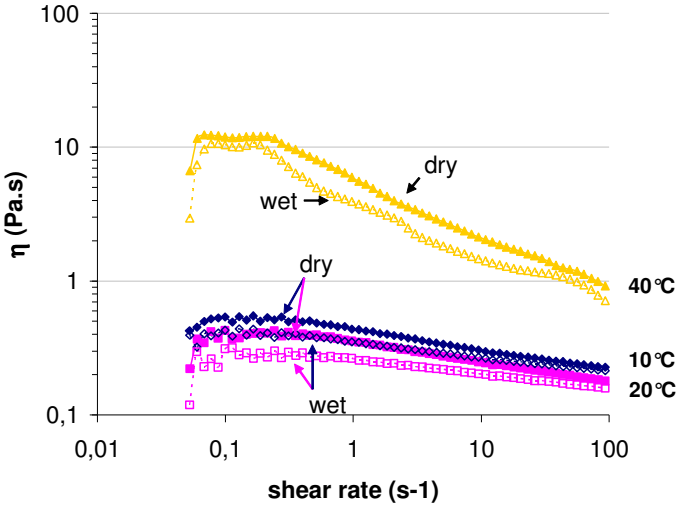


Fig.II.2-1: Viscosity versus shear rate, at 10°C, 20°C and 40°C, for 5 B342 cellulose/7.6NaOH/water, with dry (full symbols) and wet cellulose (open symbols)

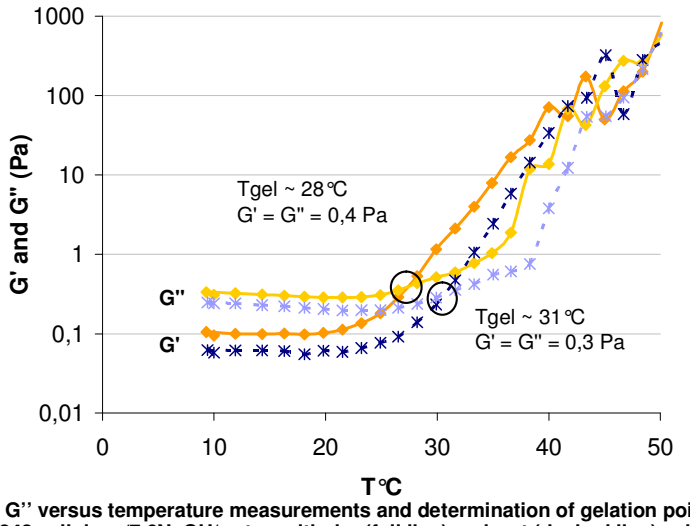


Fig.II.2-2: G' and G'' versus temperature measurements and determination of gelation point when G'=G'' for 5 B342 cellulose/7.6NaOH/water, with dry (full line) and wet (dashed line) cellulose

II.2.2- Dissolution procedure

Cellulose content was varied from 0.5g to 7.6g in 100g of solution depending on experiments. The content of alkali will be in the middle of the region of the phase diagram where there is dissolution, i.e. 7.6NaOH/water. 7.6KOH/water was also tested as cellulose solvent using the same procedure as for cellulose/NaOH dissolution, described below. Zinc oxide, urea or surfactants were added to 7.6NaOH/water to improve cellulose dissolution.

The dissolution process was as follows:

1. Preparation of solvent: Three concentrated solvents were prepared to be further mixed with swollen-in-water cellulose. The content of NaOH was 7.6g in most of cases; details will be given in each part.

   - *NaOH/water:* 12%NaOH/water and 20%NaOH/water solutions were prepared. The first solution was used to dissolve cellulose in NaOH/water and in NaOH/ZnO/water. The second was used to dissolve cellulose in the presence of urea.
   - *NaOH/ZnO/water*: Zinc oxide was added to the alkali hydroxide (12%) and it has to be fully dissolved. ZnO content in 100g of the finale cellulose solution was varied from 0.4g to 3.9g.
   - *Urea/water*: a 50%urea/water solution was prepared. Urea content in 100g of the finale cellulose solution was varied from 2g to 20g.

2. Water was added to dry cellulose to make fibres slightly swollen. Water content was adjusted to obtain 100g of solution.

3. Solvents and swollen-in-water cellulose were cooled down:
   - Cellulose/water to +5°C
   - NaOH/water and NaOH/ZnO/water to -6°C
   - Urea/water to +5°C

4. When the components are cooled, NaOH/water (or NaOH/ZnO/water) was added to the swollen-in-water cellulose and mixed thoroughly with a spatula. In the case where urea was used, 50%urea/water solution was added to cellulose/NaOH/water mixture.

5. Mixtures were placed into the thermobath at -6°C and mixed at ~1000 RPM using a rotary overhead mixer, for 2 hours.

6. Ready solutions were stored at +5°C.

As we will see in the next chapter, cellulose/NaOH/water solutions are complex: some cellulose fibres are not dissolved and gelation occurs. Thus a procedure of storage and treatment of solutions before measurements has to be clearly determined in order to have reproducible results. Because of gelation of solutions, the storage conditions must be studied. And because of the presence of non-dissolved fibres, the influence of filtration must be investigated. Both aspects are described in sections II.2.3 and II.2.4; the most suitable conditions for having reproducible results will be selected.

II.2.3- Storage

It is known [YAM1996] [ROY2003] that cellulose/NaOH solutions are gelling in time and with temperature increase. Consequently, it was important to check if there is any influence of the storage time on the viscosity of solutions. The aim of this section was to determine the time for which cellulose solutions remain stable at +5°C.

To do this, viscosity versus shear rate measurements were performed on a StressTech rheometer (see part II.3.3.1) on 5 B500 cellulose/7.6NaOH/water solutions kept at +5°C during different storage time: t=0 (fresh solution), t=1, 2, 4 and 28 days. Temperatures of viscosity measurements were 0°C and 20°C.
An example of this test at 0°C is shown Fig.II.2-3. The results show that if solutions are stored at +5°C, there is no storage time influence on their viscosity (within the experimental errors) during at least one month. Nevertheless, the solutions need to be homogenised because of sedimentation of non-dissolved fibres. Otherwise results become not reproducible.

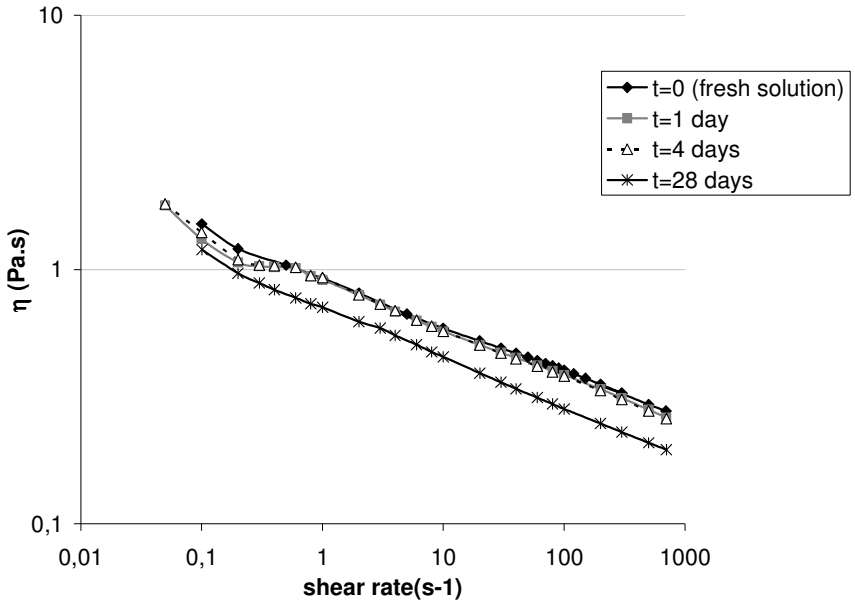


Fig.II.2-3: Influence of storage time at +5°C on the viscosity of 5 B500 cellulose/7.6NaOH/water solution. Measurements have been performed at 0°C
(at 20°C the viscosity values are very close and do not appear for a better visibility)

Conclusion: Cellulose/NaOH/water solutions were stored at +5°C and used within one month.

II.2.4- Filtration

We will see in the following that cellulose is rarely totally dissolved in NaOH/water: a small amount of non-dissolved fibres often remains after dissolution. The question is if the presence of non-dissolved fibres influences properties of solutions. Cellulose solutions were filtered and the rheological properties of filtered or not solutions were compared. The objective was to decide if filtration is needed before detailed rheological studies.

As the Borregaard cellulose solutions are the ones containing the larger amount of non-dissolved fibres, filtration tests were performed on these Borregaard cellulose solutions.
⇒ The first question was if the presence of non-dissolved fibres changes the results of intrinsic viscosity. Does the presence of non-dissolved fibres influence the intrinsic quality of solvent of cellulose?

Firstly, a 0.5 B342 cellulose/7.6NaOH/water solution was prepared by diluting an initial 5 B342 cellulose/7.6NaOH/water solution with 7.6NaOH/water. Secondly, the dilute cellulose solution was filtered using a Schott filter n°3 with pore size = 17-40µm. A water pump helped the solution to go through the filter.
Dilute filtered or not cellulose solutions were introduced in a capillary viscometer to determine intrinsic viscosity of solutions. Results are shown on Fig.II.2-4. This fine filtration induces a slight decrease in reduced viscosity but the intrinsic viscosity is approximately the same for filtered or not cellulose solutions.

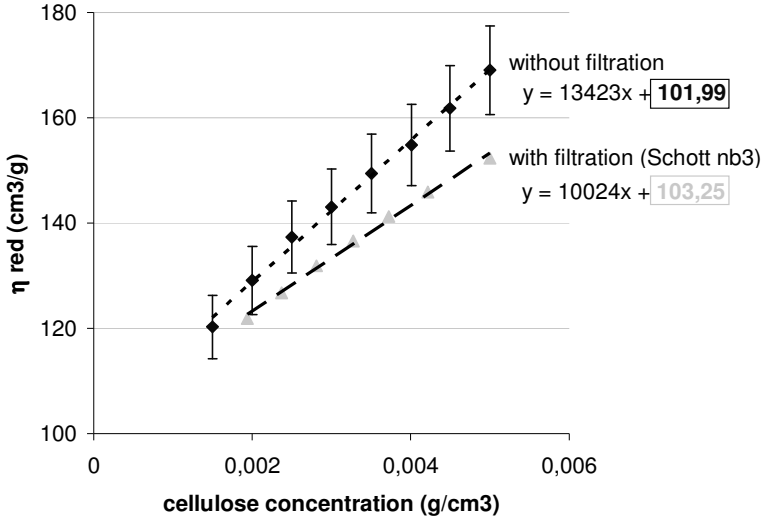


Fig.II.2-4: Reduced viscosity versus cellulose concentration to determine the intrinsic viscosity, at +25°C, of a B342 cellulose/7.6NaOH/water solution, without filtration (in blue) and with a fine filtration (in yellow)
Intrinsic viscosities are indicated on the graph (circled values)
Error bars correspond to 5%.

⇒ The second question was if the presence of non-dissolved fibres influences gelation: faster kinetics or increase of the gel modulus. Consequently, gel points were determined for filtered or not solutions and results were compared.

5 B342 cellulose/7.6NaOH/water and 5 B342 cellulose/7.6NaOH/0.7ZnO/water solutions are rather viscous and cannot be filtered with the Schott filters because of the jamming of pores. Indeed, it seems that the low pressure in the flask induces gelation and jams the filter. Thus a special set-up for filtering concentrated solutions was provided by Innovia Films Ltd.
G' and G" moduli versus temperature were measured for filtered or not 5 B342 cellulose/7.6NaOH/water and 5 B342 cellulose/7.6NaOH/0.7ZnO/water solutions. Results of

gel points were compared and are summarised in the Tab.II.2-1. The gel point is defined as being the intersection point of both moduli, when G'=G". Thus at the gel point corresponds two coordinates (x,y) where x corresponds to the gelation temperature T_{gel} and y to G' value at gel point (more details on determination of T_{gel} and G'_{gel} will be precise in section II.3.3.1).
Whatever the system is, the gel point is the same with or without filtration of the non-dissolved fibres.

	in NaOH	in NaOH/0.7%ZnO
without filtration	30°C ; 2.8 Pa	46°C ; 1.9 Pa
with filtration	31.5°C ; 3.4 Pa	45°C ; 1.9 Pa

Tab.II.2-1: Summarised results of the rheological measurements versus temperature on 5 B342 cellulose/7.6NaOH/water solutions with or without 0.7ZnO, with or without filtration of non-dissolved fibres.

From these results, the presence of non-dissolved fibres does not influence either the "intrinsic viscosity" (filter pores varied from 17 to 160 μm) or the gelation and its kinetics.

Thus, in the forthcoming experiments, the solutions will not be filtered.

II.3- METHODS

II.3.1- Differential Scanning Calorimetry (DSC)

The instrument used was a PERKIN-ELMER DSC-7 composed of two thermally insulated ovens, in an inert atmosphere (N_2). The sample was placed in a stainless steel screwed capsule, gold-plated or not (the nature of capsule will be given depending on cases but the procedure is the same). The reference consists of an identical empty capsule.
The main principles of DSC measurements and determination of important characteristics (melting temperature, melting enthalpy) are given below.

II.3.1.1. Main principles

In a material, first order chemical or physical transformations, such as changes of phase or of crystalline structure, induce temperature variations: either heat absorption (endothermic phenomenon) or heat emission (exothermic phenomenon). Calorimetric techniques can measure these heat exchanges.

Differential Scanning Calorimetry (DSC) is a technique for measuring the necessary energy to establish a nearly zero temperature difference between a substance and an inert reference material, which follow the same temperature control program. In this study, we used a power-compensation DSC (Fig.II.3-1): the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

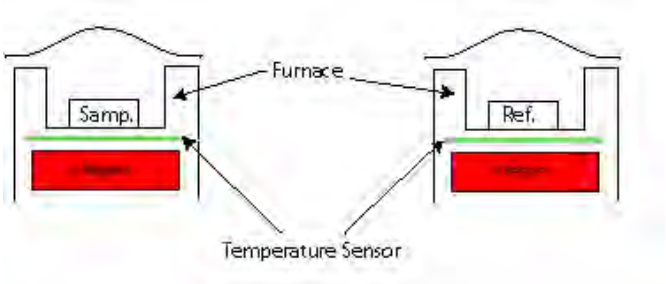


Fig.II.3-1: Diagram of a power-compensated DSC

The basic principle of this technique is that when the sample undergoes a physical transformation, the sample needs more (or less) heat than the reference to maintain both at the same temperature. For example, during an endothermic process, such as melting, the sample absorbs a certain amount of heat. Consequently, the sample requires a more significant heat flow than the reference to increase its temperature at the same rate as the one of reference. By observing the difference in heat flow between the sample and reference, Differential Scanning Calorimeters are able to measure the amount of energy absorbed or released during such transitions. DSC can thus be used to determine the temperature range and/or measure the enthalpies of glass transitions, first order transitions, calorific capacity. DSC gives information to build phase diagrams, to investigate kinetic of crystallisation, and in some cases to measure the purity of samples.

The heating elements are kept very small (weighing less than 1 gram) in order to ensure that heating, cooling, and thermal equilibration can occur as quickly as possible. The sample and reference are located above their respective heaters. The temperatures of sample *Ts* and the one of reference *Tr* are monitored using electronic temperature sensors located just beneath them. Generally platinum resistance thermometers are used due to its high melting point.

Electronically, the instrument consists of two temperature control circuits [DEA1995] (Fig.II.3-2)

1) The average temperature control circuit (*in blue*) is used to monitor the progress of the temperature control program set by the operator.
   - The average temperature *(Ts+Tr)/2* is compared with the programmed temperature *Tp*.
   - A power generator sends an electrical power *P* to the sample and reference heaters so that *(Ts+Tr)/2=Tp*. This power *P* maintains the two heaters in the given temperature program.

2) The differential temperature control circuit (*in red*) is used to determine the relative temperatures of the sample and reference, and to adjust the power going to the respective heaters so as to maintain both at the same temperature, when a disequilibria appears (exothermic or endothermic phenomenon) in the sample. This adjustment is continuous and automatic.
   - The difference between temperatures *Ts* and *Tr* is controlled.

- The second power generator sends an auxiliary power ΔP to the heater with the lower temperature so that $Ts=Tr$ (in reality, the generator sends $+\Delta P/2$ in one hand and $-\Delta P/2$ in other hand to decrease the response time of the apparatus).

3) The output of the differential temperature control circuit (*in green*) is used to generate the DSC curve:
   - X-axis represents the average temperature $Tp=(Ts+Tr)/2$
   - Y-axis represents the power ΔP

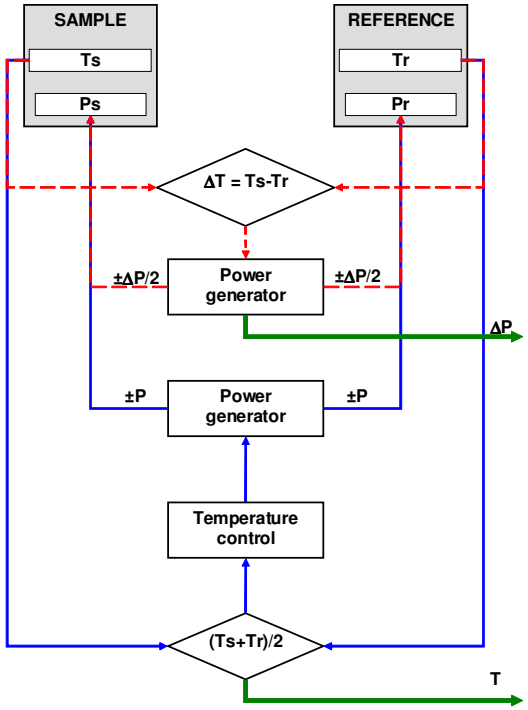


Fig.II.3-2 [NAV1980]: Electrical diagram of DSC instruments

II.3.1.2. Temperature measurement

Measuring the temperature difference between the sample and the platinum resistance thermometer located in the heater allows determining the sample temperature. This difference is due to various thermal resistances present in the heater-sample-outer system. These thermal resistances induce heat leakage (shown on Fig.II.3-3) and thus temperature variations.

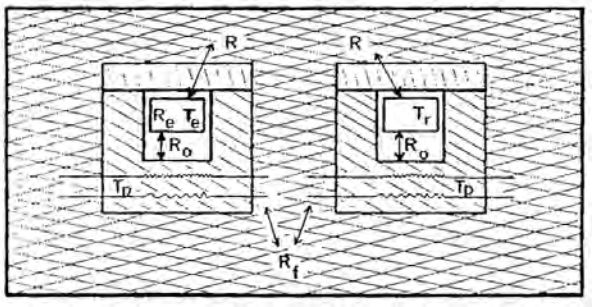


Fig.II.3-3: Various thermal resistances present in DSC

The various thermal resistances, which influence the system, are:

- *Re*: the sample thermal resistance
- *Rf*: the leakage thermal resistances due to thermometer wires
- *R*: the heater/outer thermal resistance
- *Ro*: the sample/heater thermal resistance

R and *Rf* are identical for the two ovens and, if the sample weight is low, *Re* << *Ro*. Consequently, *Ro* is the only one thermal resistance to consider. *Ro* is the sum of two thermal resistances, which are the sample/caps and caps/heater thermal couplings. The ΔP power, sent through the *Ro* thermal resistance, generates a temperature difference ΔT between terminals of *Ro*. This can be written as follows:

$$\Delta T = Ro.\Delta P = Ro.(dW/dt) = Ro.(dW/dT).(dT/dt)$$

$$\Delta T = Ro.Cp_E.\dot{Tp}$$

Cp_E represents the sample calorific capacity. 'E' = 'S' or 'L' if the sample is in solid or liquid state respectively.

II.3.1.3. Melting temperature measurement

A melting thermogram reveals the melting temperature *Tf* and gives the melting enthalpy ΔH.

In the case of a pure substance, melting is isothermal. *Tf* is determined at the onset of the peak and corresponds to the intersection between the straight line $\Delta P = Cp_S.\dot{Tp}$ (Cp_S is the calorific capacity of the sample in solid state) and the straight line of peak increase. The melting thermogram of distilled water is an example (Fig.II.3-4).

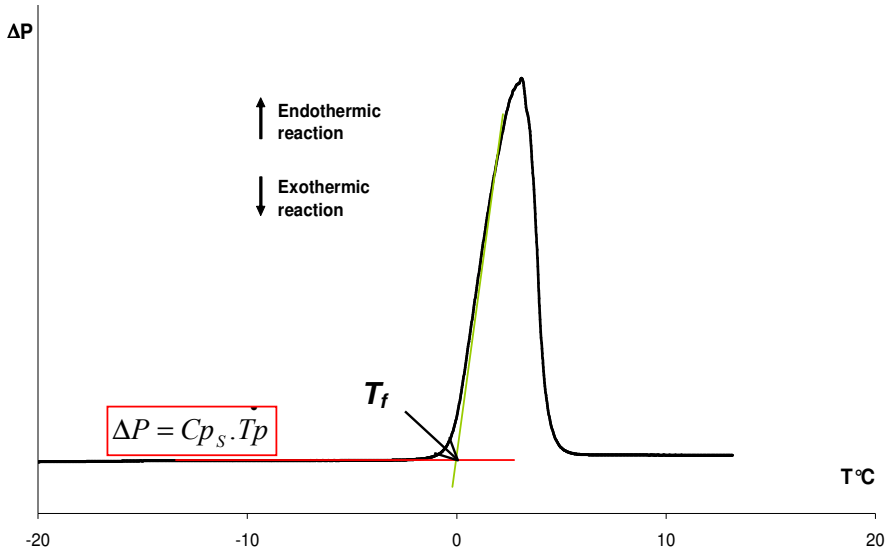


Fig.II.3-4: Melting thermogram of distilled water
Heating rate = +1 °C/min

In the case of a binary system where the two components are not miscible, the DSC thermograms reveal two peaks. The first one allows defining the solidus, it is sharp and the melting temperature is determined as in the case of a pure substance: at the onset of the peak. The second peak allows defining the liquidus, the melting occurs in a range of several degrees and *Tf* is determined at the end of the peak and corresponds to the intersection between the straight line $\Delta P = Cp_L.Tp$ (Cp_L is the calorific capacity of sample in liquid state) and the straight line of peak decrease. The melting thermogram of 7.6% NaOH aqueous solution is an example (Fig.II.3-5).

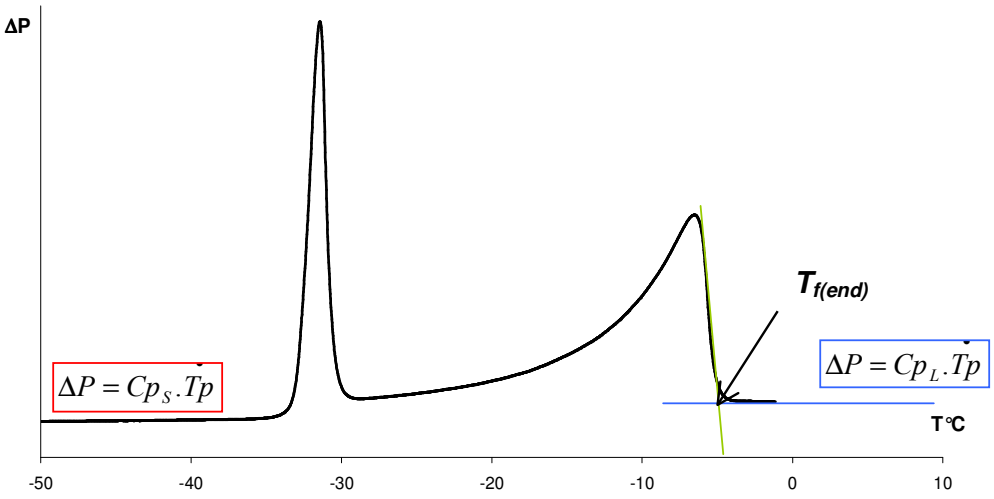


Fig.II.3-5: Melting thermogram of 7.6%NaOH aqueous solution
Heating rate = +1 °C/min

II.3.1.4. Melting enthalpy measurement

Integrating the melting peak gives the melting enthalpy. It can be shown that the enthalpy of transition can be expressed as follows:

$$\Delta H = KA$$

ΔH is the enthalpy of transition
A is the area under the curve
K is the calorimetric constant

The calorimetric constant K varies from instrument to instrument and depends on experimental conditions. K can be determined by analyzing a well-characterized sample with known enthalpies of transition [PUN1994].

II.3.1.5. Calibration and experimental conditions

Before quantitative measurement, the calorimeter has to be calibrated to obtain the calorimetric constant K and to determine an exact temperature scale. This calibration is performed by using very pure substances with well-known melting enthalpies and with melting temperatures near the experimental conditions.

$$K = \frac{\Delta H_s}{A_s}$$

ΔH_S is the melting enthalpy of the well-characterized pure substance
A_S is the area of DSC melting peak of this well-characterized pure substance

In studies of an "ordinary" polymer or metal, indium is the most often used as a reference; its melting temperature is 156.6°C. As our experiments are performed between -60°C and +20°C, it is better to use a reference substance with a melting temperature below 0°C. Moreover, calibration has to be performed in more or less the same conditions as the experiments, that is to say in the same capsules and with the same heating rate.

Stainless steel gold-plated screwed capsules have been used because of the corrosive action of high concentrated NaOH-water solutions on aluminium capsules. These stainless steel capsules (Perkin-Elmer B018-2901 and B018-2902) withstand an internal pressure of 150 atmospheres and temperature up to +400°C. To carry out a perfect capsule "locking", a gold-plated copper seal is added and capsule is locked with wrenches.
The stainless steel capsules have a high thermal resistivity: heat flows are slow. Thus, in order to be near the thermodynamical equilibrium, it is necessary to apply low heating and cooling rates. So heating and cooling rates were equal to 1°C/min for all experiments of this work.

DSC apparatus was calibrated with n-decane (to determine K) and distilled water (to fix the temperature scale). The melting temperature of n-decane is -29.66°C; its melting enthalpy is 202.090J/g. The melting temperature of distilled water is naturally considered as being 0°C. Moreover, in order to check the temperature scale, n-dodecane with a melting temperature at -9.65°C was analysed.

II.3.1.6. Software for peaks deconvolution: "PeakFit 4.12"

Each solid phase present in a system gives a melting peak when its melting temperature is reached. As enthalpy is a function of weight (enthalpy unit = J/g), each melting peak depends on the amount of the corresponding solid phase. Thus, we can deduce that measurement of melting enthalpies gives information on the contribution of each phase in the system.

In the case of a mixture, several peaks may appear and each of it has to be characterised. Fig.II.3-5 shows the melting peaks of the NaOH/water eutectic mixture and of water in 7.6%NaOH/water solution (such thermograms will be explained in chapter III); here both peaks are well separated from each other and can be easily characterised. For the case of urea/water solution, the situation becomes more complicated (Fig.II.3-6a) and with the increase of urea concentration, water peak is practically "hidden" inside melting peak of urea/water eutectic mixture (Fig.II.3-6b). In order to obtain melting enthalpies of each peak, a peak deconvolution program was used: PeakFit 4.12 from Systat. An example of similar thermograms treatment with this program can be found in literature [PRA1995].

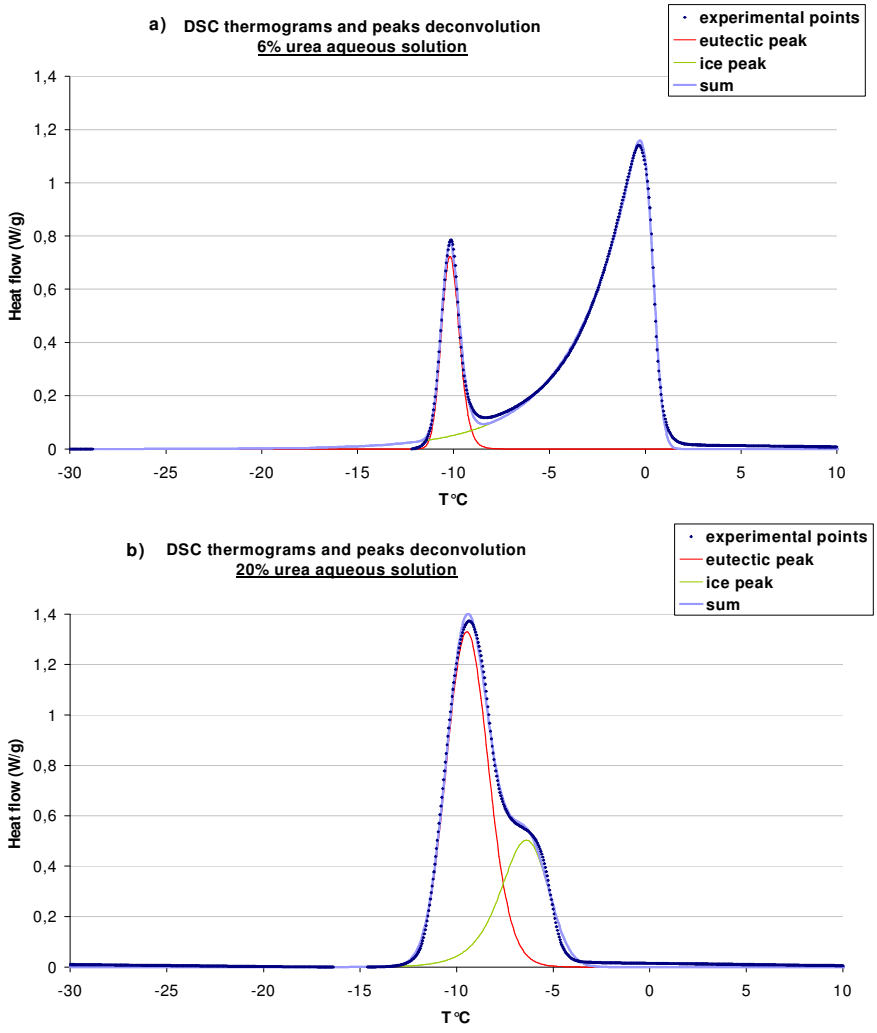


Fig.II.3-6: DSC melting thermograms and peaks deconvolution for a) 6% urea + H_2O and b) 20%urea + H_2O

First of all, the equations describing the peak shape must be chosen. On DSC thermograms (Fig.II.3-6a), the melting peak of water (at higher temperature) is very asymmetric and can not be defined by simple Gaussian or Lorentzian functions. Several functions were tested and an Exponentially Modified Gaussian function (EMG) was chosen because of the best fit and possibility to vary the asymmetric coefficient (Eq.1).

$$y = \frac{a_0}{2a_3}\exp\left(\frac{{a_2}^2}{2{a_3}^2} + \frac{a_1 - x}{a_3}\right)\left[erf\left(\frac{x - a_1}{\sqrt{2}.a_2} - \frac{a_2}{\sqrt{2}.a_3}\right) + \frac{a_3}{|a_3|}\right] \qquad \textbf{Eq. 1}$$

Where x corresponds to the temperature and where the coefficients a_0, a_1, a_2 and a_3 are adjustable parameters:

a_0 is the peak area
a_1 is the peak centre
a_2 is the peak width (>0)
a_3 is the distortion (≠0)

Fig.II.3-6 reveals the comparison between experimental points and calculated curves. The fit is good, the same result was obtained for other thermograms. Thus, the choice of the EMG function is correct and will be used in the following for peaks deconvolution.
Such deconvolutions were performed for all experiments. After having fitted the four variables, the software calculates the percentage of each peak in comparison with the total area. As DSC analysis gives the total enthalpy, we can determine the contribution of each phase and calculate the melting enthalpies of the different compounds.

II.3.2- XR diffraction

In our study, X-rays diffraction was only used to check:

- If the solid phase, which crystallises in binary system containing more than 30% of urea + water (see Chapter III), is pure urea.
- The nature of cellulose samples tested in this work. Are they cellulose I or cellulose II?

The diffractometer system was a XPERT-PRO (from PANalytical). The electron voltage was 40kV, the current was 30mA and the anticathode was made of Cu, so the wavelength K_{α_1} was 1.5406 Å. The diffraction patterns were obtained by a continuous single scan from 5° to 60° with 0.04° steps.

The preparation of samples consisted in deposing the material (in liquid or solid state) on the holder. Pure urea and cellulose samples were in solid state – pellets and fibres respectively. Moreover, as experiments were carried out at room temperature, the 70%urea+water sample was a mixture of crystals and solution. It was the only sample for which the surface was difficult to prepare. The surface has to be very smooth and in the continuity of the borders of the support.

When the surface is irregular, the diffraction peaks can be slightly shifted in comparison with the theoretical ones. If the studied sample is unknown, translation of some peaks can induce serious mistakes in the determination of nature, crystallographic structure, and elementary unit of crystal. In our case, the components present in the samples were known, so the irregularity on surface of the 70%urea+water sample was not a problem.

The diffraction spectrum consists in a network of peaks or spots (depending on the detector nature). Each trace corresponds to a series of lattice planes (*hkl*), which is characteristic of the crystallographic structure. So, the crystalline parameters can be determined from the Bragg's law:

$$2d_{hkl}\sin\theta = n\lambda$$

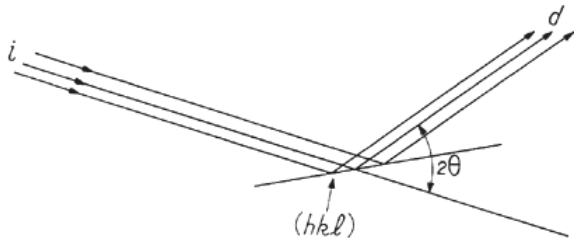
d_{hkl} is the length between two consecutive lattice plane and $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

h, *k* and *l* represent the Miller indexes of the considered lattice plane and *a*, *b* and *c* represent the parameters of crystalline unit.

θ is the angle between the sample surface and the incident ray.

λ is the wavelength of X-rays used.

n diffraction order



i	**incident radiation**	***(hkl)***	**lattice plane**
d	**scattered radiation**	***θ***	**Bragg's angle**

For native cellulose and cellulose II, the lattice parameters are given in Appendix I.

II.3.3- Rheology

The flow and gelation of semi-dilute and dilute cellulose solutions were studied using different rheological methods. They are briefly described in this section.

II.3.3.1. Semi-dilute cellulose solution

Rheological measurements of semi-dilute cellulose solutions were performed on a:

- StressTech rheometer (Reologica Instruments) equipped with a thermobath to control the temperature. The tested solutions were equilibrated at a given temperature for 30 minutes before starting the viscosity versus shear rate measurements.
  The geometry used was a Couette double gap, it is made of two concentric cylinders (both gaps = 2mm). The volume of cellulose solution was about 24ml.

- Gemini 150 rheometer (Bohlin Instruments) equipped with a Peltier temperature control. With such a temperature control, temperatures can vary in a quick and accurate way, up to 60 degrees per minute in the interval from -30°C to 180°C. The sample remained 60s at temperature before measurement.
  The geometry used was a cone and plane (60/2°), made of stainless steel. About 3ml of solution was placed on the plate in order to fill the gap perfectly (Fig.II.3-7). A solvent trap was used to avoid evaporation.

Fig.II.3-7: Scheme to fill the gap between cone and plate correctly

Steady state mode

The measurements of viscosity (Pa.s) versus shear rate (s^{-1}) were performed in isothermal mode at different temperatures from 0°C to +40°C. The shear rate varied from $0.05s^{-1}$ to $100s^{-1}$.

Oscillatory mode

The storage modulus G' and the loss modulus G" were measured as a function of time or of temperature.

- The kinetics of gelation was studied at various constant temperatures from +10°C to +40°C. To be in linear regime (Appendix 2), the frequency was fixed at 0.1Hz and the stress at 0.01Pa.
- The gelation temperature was determined from a sort of an "express method" where G' and G" were measured as a function of temperature. Keeping the experimental conditions always the same, this method allows a quick comparison of the gelation process of different cellulose solutions.
  Temperature varied from +10°C to +80°C with a heating rate of +5°C per minute. We chose a rapid heating rate in order to neglect the influence of time.
  The rheometer was in the auto-stress mode: it fits stress during the measurement to maintain a constant strain of 1%.
  The frequency was fixed at 1Hz.

II.3.3.2. Dilute cellulose solution

The intrinsic viscosities of cellulose solutions were studied using an Ubbelohde capillary viscometer equipped with an automatic dilution burette (from Lauda). The viscometer was immersed in a water bath at different constant temperatures from +12°C to +40°C.
The initial concentration of a cellulose solution was 0.5% obtained with 10 times dilution of a 5% cellulose solution. In order to obtain the viscosity versus cellulose concentration dependence, 7 or 8 dilutions were made. The relative viscosity η^{rel} is calculated as a ratio between the kinematic viscosities of the solution $\eta_{Solution}$ and the solvent $\eta_{Solvent}$ (Eq. 3):

$$\eta^{rel} = \frac{\eta_{Solution}}{\eta_{Solvent}} \qquad \textbf{Eq.2}$$

The intrinsic viscosity $[\eta]$ is determined as follows:

$$[\eta] = \lim_{c \to 0}\left(\frac{\eta^{rel} - 1}{c}\right) \qquad \textbf{Eq.3}$$

where c represents the polymer concentration.

The intrinsic viscosity is the viscosity of solution at infinite dilution and is usually obtained when plotting $\eta_{red} = \left(\frac{\eta^{rel} - 1}{c}\right)$ dependence as a function of concentration. Graphically, the intrinsic viscosity corresponds to the point of intersection between the straight line passing through the reduced viscosity points 'η_{red}' and the y-axis

For a given polymer in a given solvent, a decrease of the intrinsic viscosity means that the intramolecular links are favoured and the solvent quality decreases.

II.3.4- Microscopy

II.3.4.1. Optical Microscopy (OM)

The observations of cellulose solutions were performed with a transmission optical microscope Leitz Metallux 3 with unpolarised light in order to observe the swelling of cellulose fibres and the state of cellulose dissolution.

- Qualitative observations of cellulose solutions were carried out at room temperature. Cellulose + solvent (solvent being 7.6NaOH/water or 7.6NaOH/0.7ZnO/water or 7.6NaOH/6urea/water) fresh solution was placed between two glass plates. In this case, solution had been prepared before the observation and the results were time-independent.
- The study of cellulose dissolution mechanism was performed at -6°C: the optical microscope is equipped with a LINKAM TMS 91 hot stage. A few dry cellulose fibres were placed between two glass plates slightly shifted (Fig.II.3-8). The solvent contained in a pipette was introduced by capillary forces between the two plates. The whole process of swelling and dissolution was recorded with CCD camera on DVD recorder and then analysed.

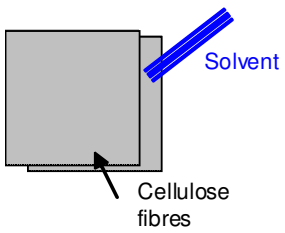


Fig.II.3-8: Samples preparation for optical microscopy at -6°C.

II.3.4.2. Scanning Electronic Microscopy (SEM)

Scanning Electronic Microscopy (SEM) was used to observe the porosity of regenerated cellulose samples and the reinforcing fibres (cotton and fluff) in their initial state and after treatment in NaOH solutions. SEM has two main advantages in comparison with optical microscopy: to obtain greater magnification (up to 150000 times instead of ~1000 with OM) and to observe irregular samples because of an important depth of field.

Electron gun sends an electron beam to the sample surface. When the electron beam strikes the target, it is reflected and the resulted incident radiation is picked up by the SEM sensors. This is repeated very rapidly on several points until covering the whole sample surface. In other words, the electron beam scans the whole sample and data are analysed to build the picture.

A non-conducting material reflects very badly the electron beam and it is very difficult to obtain a picture. So, either the sample is covered by very fine gold particles or the microscope is used with the environmental mode. Indeed, the latter allows observing non-conducting samples due to the presence of a gaseous atmosphere in the microscope chamber. A Peltier temperature control is used for monitoring the relative humidity in the microscope chamber.

The instrument used was a Philips XL-3000 Scanning Electron Microscope.

<u>Environmental mode</u>
The temperature was fixed at +8°C and the chamber pressure at 2.5 mbar, giving a relative humidity around the sample of approximately 30%. The voltage was fixed at 15kV and a GSE detector was used.
The samples were placed in the vacuum chamber, without other treatment.
The problem of environmental mode is a relatively low resolution.

<u>High vacuum mode</u>
This mode allows obtaining greater magnification with a good resolution because of high vacuum in the microscope chamber. Samples have to be metallised with gold particles.
SE detector was used and voltage was fixed at 12kV or 15kV depending on experiments.

II.3.5- Mechanical property: tensile test

The mechanical properties of regenerated cellulose films, of regenerated cellulose + reinforcing fibres and of final product (regenerated cellulose + re-enforcing fibres + porophores) were studied using the tensile mode on a ZWICK Z2.5 machine (Fig.II.3-9).

The experiments were performed at room temperature. The sample was fixed between two holders or "grips" (see Fig.II.3-9b). The lower grip stayed immobile and the higher grip moved until rupture. The tensile force was measured. The rupture force F was considered as being 80% of maximal tensile force. On the forthcoming graphs, one point corresponds to 3-4 measurements at least. Error bars show the standard deviations.

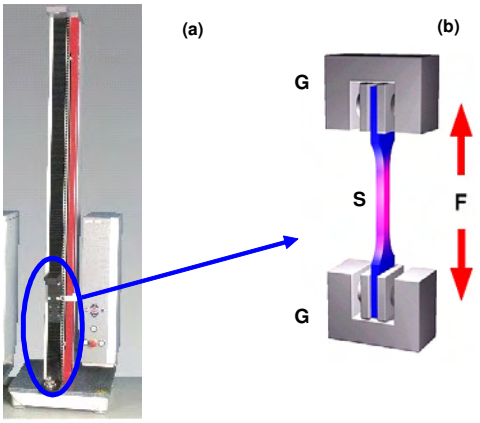


Fig.II.3-9: Picture of the Zwick Z2.5 machine and scheme of the tensile test.
G: grips; S: specimen of regenerated cellulose; F: the tensile force.

The rupture stress F_R is determined as follows:

$$F_R = \frac{F}{S}$$

F_R is the rupture stress (daN/cm²)
F is the tensile force when rupture appears (daN)
S is the initial specimen section (cm²)

Units were chosen to easily compare with the Spontex values.

II.3.5.1. Tensile test on films of regenerated cellulose

Tensile tests were performed on films of regenerated cellulose. This means that cellulose solutions were prepared from the previous procedures (part II.2-), then underwent various thermal treatments and finally they were placed in a regeneration bath to obtain the final products. After regeneration, cellulose has the crystalline structure of cellulose II, as expected.

The procedure was as follow:

1. Cellulose solution was prepared from the procedure described above (part II.2-). Cellulose was the B389 or B407 pulp and the solutions consisted in 5cellulose/7.6NaOH/water, 5cellulose/7.6NaOH/0.7ZnO/water or 5cellulose/7.6NaOH/6urea/water.

2. Cellulose solution was stored at +5°C up to the disappearance of air bubbles.

3. About 10g of the solution was poured in a plastic Petri box (∅=10cm).

4. Petri box was kept at various temperatures:
   - 20 hours at +25°C
   - 1.5 hours at +70°C
   - 1.5 hours at +70°C, then 20 hours at +25°C
   - 20 hours at -20°C
   - 20 hours at -20°C, then 20 hours at +25°C.

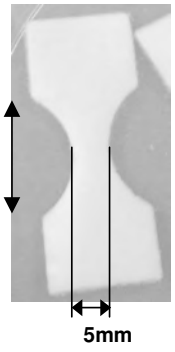
5. Immediately after the thermal treatment, a non-solvent was added (water or 1N acetic acid) into the Petri box at the temperature of regeneration (+5°C, +25°C or +70°C for water and +25°C for acetic acid).
   NB: In order to make the regenerated sample as homogeneous as possible (in terms of thickness, surface, without holes, etc), the non-solvent was carefully added ON the sample. Putting the sample in the regeneration bath induced cracks and holes.

6. Regeneration bath was changed several times until it becomes pH neutral (checked with a pH-paper).

After regeneration, tensile dumbbell-like specimens were cut. The dimensions were:

- Effective length = 17mm
- Width = 5mm
- Thickness = 1-1.5mm

After the preparation of the specimen, it was immediately put back into regeneration bath to avoid drying in the air. The specimens were removed from the bath just before performing the tensile test. As the experiment lasted for about one minute, it was not necessary to take into account the humidity of ambient air.
The speed of the top grip is fixed at 5mm/min.



II.3.5.2. Tensile test on regenerated cellulose + reinforcing fibres

In order to approach industrial conditions, but varying different parameters, reinforcing fibres were added to cellulose solution. The fibres were either cotton with a length of 20mm or fluff. Reinforcing fibres, cotton and fluff, have high DP (>1100). The dissolved cellulose + reinforcing fibres system was regenerated in water before mechanical tests.

The sample preparation was as follows:

1. Cellulose solution was prepared from the procedure described above (part II.2-). Cellulose was the B389 or B407 pulp and the solutions consisted in 5cellulose/7.6NaOH/water.
   NB: Stirring lasts 1.5 hour instead of 2 hours, according to the Spontex procedure.

2. 0.2g of AP surfactant was added to the 100g cellulose solution and mixed 10 minutes.

3. 2g of reinforcing fibres (cotton or fluff) were impregnated with 8%NaOH/water at T_{room} or at -6°C (20 hours). These fibres were added to the 100g solution (still at -6°C) and mixed for 1.5 hour, at -6°C.

4. The system of dissolved cellulose + fibres was poured in a mould and different thermal treatments were applied:
   a. 2 hours ageing at +5°C and then 20 hours freezing at -20°C
   b. 20 hours freezing at -20°C (without ageing)
   c. 20 hours gelation at +25°C
   d. 2 hours gelation at +70°C

5. Immediately after the thermal treatment, water at 70°C or 25°C was added on the cellulose system.

6. Regeneration bath was changed several times until it becomes pH neutral.

After regeneration, two types of specimens were cut:
- tensile dumbbell-like specimens, as previously
- tensile parallelepiped specimens (for practical purposes). The dimensions were:
  - Effective length = 20mm
  - Width = 10mm
  - Thickness = 2-2.5mm

The speed of testing is also fixed at 5mm/min

II.3.5.3. Tensile test on sponges (regenerated cellulose + fibres + porophores)

To reproduce the Spontex conditions, porophores were added to the previous system. The porophores are crystals of $Na_2SO_4 10H_2O$, which melt above +40°C.
A large quantity of crystals was included to the cellulose system in the amount of 3 to 4 times of the weight of cellulose/fibres/NaOH/water system. In order to avoid an important temperature increase of cellulose during the addition of porophores, Na_2SO_4 was cooled down at +5°C, before being added to the system.

In this study, only fluff was used because of a better homogenisation with solution. Cotton fibres are enrolling and sticking around the mixer.

The sample preparation was as follows:

1. Solution of cellulose + fluff fibres was prepared as previously: steps from 1 to 3.

2. Na_2SO_4 crystals were pre-cooled at +5°C, added to cellulose solution + reinforcing fibres and mixed about 15 minutes.

3. The system of cellulose solution + fibres + porophores was poured in a mould and different thermal treatments were applied:
    a. 20 hours freezing at -20°C (without ageing)
    b. 20 hours gelation at +25°C

4. Immediately after the thermal treatment, water at +70°C was added on the cellulose system.

5. Regeneration bath was changed several times until it becomes pH neutral.

After regeneration, tensile parallelepiped specimens were cut. The dimensions were:

- Effective length = 20mm
- Width = 25mm
- Thickness = 10mm

The speed of testing is fixed at 300mm/min, to be near the Spontex procedure.

II.3.6- Other methods

Several methods were used to analyse the properties of sponges. Thus regenerated samples consisted of cellulose + fluff fibres + Na_2SO_4 crystals.

II.3.6.1. Density measurement

The density is one of the main properties of sponges since it influences all their properties (rupture stress, water absorption…). The density is in g/dm^3.

$$d = \frac{m_d}{V_w}$$

d represents the density of the sponge (g/dm^3)
m_d is the weight of the dry sample (g)
V_w is the volume of the wet sample (dm^3)

To determine the density, a piece of wet sponge was cut and the volume was measured. The sample was placed in an oven at 105°C during 2 hours until a constant weight and then in a dessicator during 15 minutes to cool down without trapping the ambient humidity. Finally, the sample weight was measured.

II.3.6.2. Water absorption

The absorption capacity represents the quantity of water that a sponge can absorb.

$$Abs. = \frac{(m_w - m_d)}{m_d}$$

Abs. is the absorption capacity
m_w represents the weight of wet sample
m_d is the weight of dry sample

The sample weight in dry state was measured and then it was placed in distilled water at room temperature during a few minutes. The sample was taken at an extremity and drained during 1 minute. Finally the sample was weighted to obtain the wet weight.

II.3.6.3. Shrinkage

Shrinkage represents the percentage of surface loss between a wet sample, which has never been dried, and a sample dried for 2 hours in the oven and then swollen in water again.

$$Shr. = \frac{A_w - A_{dw}}{A_w}$$

Shr. is the shrinkage of the sponge sample
A_w is the surface of a never-dried-wet sample
A_{dw} is the surface of a dried-and-swollen again sample.

To determine the shrinkage, the surface areas of never-dried-wet and of dried-and-swollen samples were measured.

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RESUME DU CHAPITRE III

STRUCTURE DES SOLUTIONS AQUEUSES DE NAOH ET DE CELLULOSE/NAOH AVEC ET SANS ADDITIFS. LIMITE DE DISSOLUTION DE LA CELLULOSE

Ce chapitre présente une étude détaillée des propriétés thermiques des solvants d'une part et des solutions de cellulose d'autre part, étude basée essentiellement sur des analyses de DSC. L'obtention des thermogrammes de fusion allant de -65°C à +10°C permet de déterminer les températures et enthalpies de fusion de chaque phase présente dans le système, de tracer les diagrammes de phase et de déterminer les interactions ayant lieu dans les solutions.

La première partie de cette étude a porté sur l'analyse de solutions NaOH/eau ayant des concentrations en NaOH comprise entre 0 et 20%. Le tracé du diagramme de phase dans ce domaine de concentrations en NaOH a été effectué à partir des températures de fusion obtenues par DSC et correspond parfaitement à celui rapporté dans la littérature [PIC1893] [ROL1964]. Entre 0 et 20%NaOH, quand tout le système est solide (T<-33,4°C), nous sommes en présence (i) d'un mélange eutectique comprenant un hydrate de sodium $NaOH,5H_2O$ et 4 molécules d'eau et (ii) de glace libre. La température de fusion de l'eutectique est constante (-33,4°C) pour toute concentration en NaOH tandis que celle de l'eau diminue quand la concentration en NaOH augmente. Quant à l'enthalpie d'un composant X, sa valeur est proportionnelle à la quantité de composant X cristallisé dans le système. En effet, les fractions d'eutectique et de glace déterminées à partir du diagramme de phase par la règle des segments inverses correspondent aux fractions calculées à partir des enthalpies de fusion ($f_{eut}=\Delta H_{eut,\ X\%NaOH}/\Delta H_{eut,\ pure}$ et $f_{ice}=\Delta H_{ice,\ X\%NaOH}/\Delta H_{ice,\ pure}$). Cette méthode de calcul à partir des enthalpies de fusion étant validée par l'étude des systèmes binaires NaOH/eau, elle sera utilisée non seulement pour les autres systèmes de solvant mais également pour les solutions de cellulose.

Avant d'étudier le système ternaire NaOH/urée/eau, il nous a fallu déterminer le comportement du système binaire urée/eau et tracer son diagramme de phase. Il s'avère que ce dernier a un comportement de mélange eutectique simple. L'eutectique est constitué de 1 urée et 8 molécules d'eau, ce qui correspond à une concentration en urée de 29,4%, il fond à -11,4°C.
Dans le système ternaire, la concentration en NaOH est fixée à 7,6% et celle de l'urée varie entre 0 et 25%. Il apparaît que la température de fusion de l'eutectique « NaOH » ne diminue que très légèrement et que son enthalpie de fusion est constante quelle que soit la concentration en urée. Ceci signifie que l'urée ne réagit pas avec les molécules de NaOH. Une augmentation de la

concentration en urée entraîne un décalage du pic de fusion de l'urée vers les plus hautes températures et celui de la glace libre vers les plus basses températures. Ils se rejoignent pour un système constitué de 7,6%NaOH et 18%urée, ce qui signifie qu'il n'y a plus d'eau libre en solution. En effet, à cette composition, il y a tout juste assez d'eau pour former simultanément et de façon indépendante les deux mélanges eutectiques NaOH+9H_2O et urée+8H_2O. Au-delà de cette concentration, il n'y a plus suffisamment d'eau pour les deux eutectiques qui rentrent alors en compétition. Le pic de l'eutectique « NaOH » étant toujours constant pour des concentrations en urée supérieures à 18%, ceci signifie qu'il est prioritaire sur l'urée, probablement du fait de sa forte polarité. L'urée en excès cristallise donc dans sous forme pure.

Nous avons trouvé dans la littérature [DIR1954][REI1975][BEN1999] que la dissolution de l'oxyde de zinc a lieu en milieu basique par réaction des ions OH^- avec ZnO pour former des hydroxydes de zinc. Ces réactions chimiques entraînent une modification de la solution et il n'est donc pas étonnant de constater que la présence d'oxyde de zinc dans le système NaOH/eau modifie le diagramme de phase : les température et enthalpie de fusion de l'eutectique « NaOH » diminuent proportionnellement à la quantité de ZnO présente en solution. Nous en avons conclu que chaque ZnO réagit avec 3 NaOH qui ne participent plus à l'eutectique. Les complexes ainsi formés sont fortement hydratés puisqu'ils peuvent être entourés jusqu'à 25 molécules d'eau, valeur déterminée à partir du pic de glace libre.

L'ajout de cellulose dans NaOH/eau ne modifie pas les températures de fusion du mélange eutectique NaOH+eau et de la glace libre : la présence de cellulose ne modifie pas le diagramme de phase du solvant NaOH/eau.
Par contre, l'enthalpie de fusion du mélange eutectique diminue proportionnellement à la concentration en cellulose et atteint zéro quand la masse de cellulose est égale à la masse d'hydroxyde de sodium. Nous en avons donc conclu que la limite de dissolution de la cellulose dans NaOH/eau est atteinte quand $m_{cell}=m_{NaOH}$ et que la dissolution de la cellulose nécessite au moins quatre molécules de NaOH qui se lient à chaque motif de polymère (AGU). Le rapport entre l'enthalpie de fusion de l'eutectique déterminée pour une concentration en cellulose donnée et l'enthalpie de fusion de l'eutectique pur ($\Delta H_{eut,\ Y\%cell}/\Delta H_{eut,\ pur}$) permet de calculer la fraction d'eutectique qui a cristallisé dans le système et d'en déduire la quantité de NaOH lié à la cellulose, et ce, pour chaque concentration de cellulose. Les résultats montrent que pour des concentrations en cellulose supérieures à 1,5-2%, le rapport NaOH/AGU est égal à 4. Par contre, pour de faibles concentrations en cellulose, le rapport NaOH/AGU peut atteindre 20, ou encore 50 à partir de mesures de turbidité [KUO2005]. Cette transition autour de 2% de cellulose correspond à la transition régime dilué / régime semi-dilué rapportée dans la ref. [ROY2003]. Il n'est certes pas étonnant de trouver des valeurs un peu plus importantes en régime dilué dû à la diminution de l'encombrement stérique mais un tel écart entre les deux « types » de solutions (4/20 ou encore 4/50) reste, à l'heure actuelle, une question ouverte.
En ce qui concerne le pic de fusion de la glace libre, son enthalpie reste constante quelle que soit la teneur en cellulose. La quantité d'eau libre en solution n'est pas modifiée par la présence de

cellulose, ce qui signifie que les 9 molécules d'eau cristallisant dans le mélange eutectique NaOH+eau sont également liées à la cellulose.
Chaque AGU est donc entourée d'un minimum de 4NaOH et $36H_2O$.

Une analyse similaire a été effectuée sur des solutions de cellulose dans 7,6NaOH/6urée/eau. Les thermogrammes de DSC ainsi obtenus donnent des résultats tout à fait semblables aux précédents, à savoir (i) pas de diminution des températures de fusion (eutectique NaOH, eutectique urée et glace libre), la présence d'urée ne modifie le diagramme de phase du solvant, dans les domaines de concentrations étudiés, (ii) pas de variation des enthalpies de fusion de la glace libre et de l'eutectique de l'urée, la quantité d'eau libre en solution reste constante et la cellulose ne se lie pas avec l'urée mais (iii) diminution de l'enthalpie de fusion du mélange eutectique NaOH+eau proportionnelle à la teneur en cellulose, la cellulose piège une certaine quantité de NaOH. De plus, la courbe « enthalpie de l'eutectique en fonction de la concentration en cellulose » pour des solutions de cellulose dans 7,6NaOH/6urée/eau se superpose à celle obtenue pour des solutions de cellulose dans 7,6NaOH/eau. Ceci signifie que la limite de dissolution de cellulose est atteinte pour $m_{cell}=m_{NaOH}$, que la dissolution de la cellulose nécessite au moins quatre NaOH entouré de ses 9 molécules d'eau. L'urée ne permet pas d'augmenter la quantité de cellulose pouvant être dissoute dans un système NaOH/eau donné.

Nous avons vu que la présence d'oxyde de zinc diminue la température de fusion du mélange eutectique NaOH+eau, il y a donc modification du système de solvant. Les thermogrammes de fusion des solutions de cellulose/NaOH/ZnO/eau ne révèlent pas le pic de fusion de l'eutectique, il n'est donc pas possible de déterminer la quantité de NaOH lié à la cellulose. Par ailleurs, l'enthalpie du pic de fusion de la glace libre reste constant même après ajout de cellulose : comme précédemment pour les solutions de cellulose/NaOH/eau et cellulose/NaOH/urée/eau, les solutions de cellulose/NaOH/ZnO/eau ont la même quantité d'eau libre quelle que soit la concentration en cellulose.

Pour finir, nous avons étudié l'influence d'une étape de congélation sur les propriétés thermiques des solutions de cellulose/NaOH/eau, avec ou sans ZnO. Dans les deux cas, un séjour prolongé à -28°C entraîne la cristallisation d'eau pure, dont la température de fusion est de 0°C. D'un point de vue thermodynamique, ces molécules d'eau ne peuvent pas se détacher du mélange eutectique NaOH/eau. De plus, étant donné que l'eau libre a déjà cristallisé dans le système, la seule possibilité est que cette eau pure soit « détachée » de la cellulose. A partir des rapports d'enthalpies de fusion, nous avons pu déterminer que dans les deux cas, cellulose/NaOH/eau et cellulose/NaOH/ZnO/eau, une molécule d'eau par AGU est détachée lors d'un séjour prolongé à -28°C.

Cette analyse approfondie nous a permis de déterminer la structure des solvants – NaOH/eau, urée/eau, NaOH/urée/eau et NaOH/ZnO/eau – et celle des solutions de cellulose dans ces mêmes solvants.

CHAPTER III

STRUCTURE OF AQUEOUS NAOH AND CELLULOSE/NAOH SOLUTIONS WITH AND WITHOUT ADDITIVES. LIMIT OF CELLULOSE DISSOLUTION.

Chapter III is devoted to a detailed study of the structural organisation of cellulose in the aqueous sodium hydroxide solutions with and without additives. The main goal is to understand what are the proportions between cellulose and solvent molecules linked to it and, as a consequence, what is the limit of cellulose dissolution in aqueous sodium hydroxide solutions. The role of additives like ZnO and urea that are known to "help" cellulose dissolution is investigated. The changes in cellulose/NaOH solutions induced by freezing are also considered. Most of the study is performed using DSC technique accompanied by viscometric measurements. This chapter is divided into four main parts.

In the first part, entitled "Bibliography: phase diagram of aqueous sodium hydroxide solution", we will first describe some theoretical aspects concerning binary and ternary phase diagrams, and especially how to build them from DSC analyses. Then, we will review the literature on the structure of NaOH/water: it is known that several sodium hydrates can be formed depending on NaOH concentration. The number of water molecules surrounding sodium hydroxide ions increases when the NaOH concentration decreases. The authors of two papers [PIC1893] [COH1960] gave the composition of sodium hydrates and the melting temperatures of different compounds formed.

The second part concerns the structure of cellulose solvents: NaOH/water, NaOH/urea/water and NaOH/ZnO/water. As the NaOH/water system was known, we shall compare our DSC results obtained in the region of 0-30%NaOH with the literature and thus validate the

methodology used. Then urea/water binary system will be studied and its phase diagram will be built. This was the necessary step in the understanding of the structure of NaOH/urea/water ternary system. Finally, the influence of zinc oxide on NaOH/water solutions will be investigated.

The third part concerns the structure of cellulose solutions in NaOH/water, NaOH/urea/water and NaOH/ZnO/water. We will study the influence of the addition of cellulose in the solvents studied in the previous part. This will allow us to understand the structural organisation of cellulose solutions and to determine the limit of cellulose dissolution in NaOH/water and in NaOH/urea/water. A large part of this study is performed on Avicel cellulose; other cellulose samples will be tested to study the influence of cellulose origin on the structure of solutions.

The last part deals with the influence of freezing on the thermal properties of cellulose/NaOH mixtures.

III.1- BIBLIOGRAPHY: PHASE DIAGRAM OF AQUEOUS SODIUM HYDROXIDE SOLUTION

III.1.1- Phase diagrams

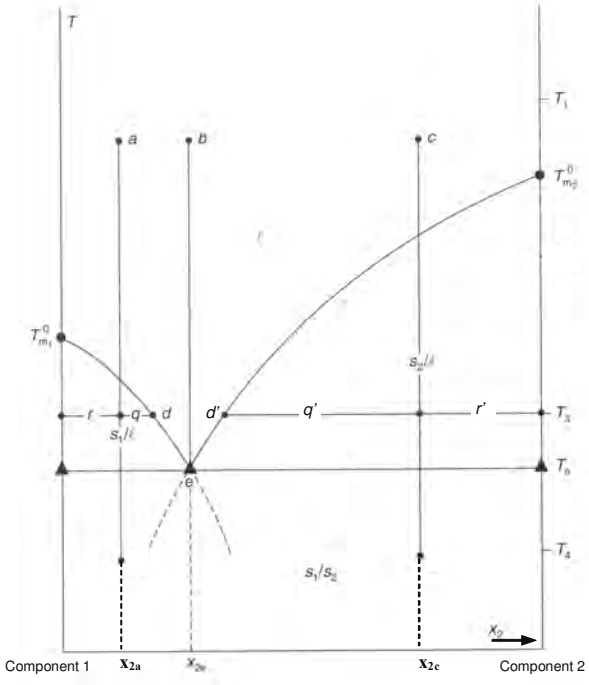
III.1.1.1. Binary phase diagram

Let us consider two components that are completely miscible in the liquid state but with their solid phase fully immiscible [KON2001]. The melting point of the first component is always lowered when adding a second one. This can be shown on a temperature versus mixture composition diagram (Fig.III.1-1, graph). From such a binary phase diagram, at constant pressure, the following parameters can be measured:

- the compositions of solid and liquid phases from solidus and liquidus curves, respectively
- the relative amounts of each phase in the whole system from 'level rule' or 'level principle'.

Three examples are given on Fig.III.1-1 for 'a', 'b' and 'c' systems.

The eutectic point, named 'e', is where the two solubility/melting curves of the solid phases meet (Fig.III.1-1, graph). The composition x_{2e} of the eutectic point is fixed at a given pressure. The eutectic crystal is a mixture of the crystals of both components that were formed simultaneously. Its morphology is very fine.
At either side of 'e' and below T_e, there are the crystals of the eutectic mixture plus an excess of pure 1 or 2 crystals (depending on the composition of the initial mixture – see Fig.III.1-1, table) that have slowly crystallised upon cooling.



X-axis corresponds to component 2 fraction in the mixture.

$T°_{m1}$ = melting temperature of a pure first component
$T°_{m2}$ = melting temperature of a pure second component
Te = melting temperature of eutectic component
x_{2e} = eutectic composition

Explanation

System	a	b	c
Composition	**x_{2a}**	**x_{2e}**	**x_{2c}**
Temperature			
T_1	The whole system is a liquid (*l*) with the composition x_{2a}	The whole system is a liquid (*l*) with the composition x_{2e}	The whole system is a liquid (*l*) with the composition x_{2c}
T_3	There are two phases: A liquid phase (*l*) – composition *d*, quantity r/(r+q) A solid phase (s_1) – pure component 1, quantity q/(r+q)	"	There are two phases: A liquid phase (*l*) – composition *d'*, quantity r'/(r'+q') A solid phase (s_2) – pure component 2, quantity q'/(r'+q')
T_e		The liquid (*l*) crystallises to form the eutectic compound, composition x_{2e}, very fine crystals of pure components 1 and 2	
T_4	Two crystals: Pure solid 1, eutectic compound composed of fine crystals of components 1 and 2	only eutectic compound	Two crystals Pure solid 2, eutectic compound

**Fig.III.1-1 [KON2001]: Binary phase diagram under constant pressure (left-hand graph)
Explanation on how to read such a diagram (right-hand table)**

III.1.1.2. Ternary phase diagram

The representation of the equilibrium diagrams of a ternary system needs a three dimensional model. Two dimensions are required to show the variation in composition, and a third dimension is needed for the temperature variable. The latter is often drawn on the vertical axis and the former on the horizontal plane (Fig.III.1-2). The three-dimensional model is a right-angled prism, the sides representing the three binary systems [HUM1953].
Generally, isothermal cross-sections are useful to study the equilibrium of a ternary system. But vertical cross-sections are interesting to reveal how a binary system is affected by the addition of a third component.

Fig.III.1-2 represents the liquidus surface of a ternary phase diagram of three components A, B, and C. These components are fully miscible in the liquid state and making two by two eutectic mixtures. We can see that the addition of a component to the binary liquid phase decreases the melting temperatures of the binary eutectic.

Example:
In the front of this figure, the diagram of the binary system containing the components A and B is represented; the component C is not present, C_C = 0%.
When the component C is added at a constant concentration C_C=X%, the binary phase diagram of components A and B is determined by the red plane. We can see that all the melting temperatures decrease, even the eutectic one: T^0_{mA} becomes T_{mA}, T^0_{mB} becomes T_{mB}, and Te_{AB} becomes $Te_{AB}(C_C=X)$.

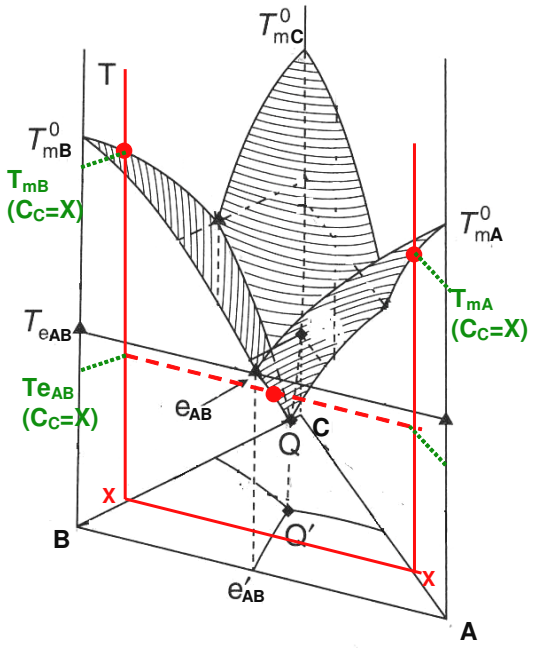


Fig.III.1-2 [KON2001]: Ternary isobaric phase diagram showing the melting-point depressions of each of the components caused by the addition of the other two to the liquid phase.

T^0_{mA}, T^0_{mB}, and T^0_{mC}: melting temperatures of pure components A, B, and C respectively;
e_{AB}: the eutectic mixture of components A and B; Te_{AB} its melting temperature; e'_{AB} its projection on the base triangle;
T_{mA} and T_{mB}: the melting temperatures of components A and B, when X% of the component C is added;
$Te_{AB}(C_C=X)$: the melting temperature of eutectic e_{AB} when X% of the component C is added to A and B components;
Q: the quadruple point for the considered pressure; Q' its projection on the base triangle.

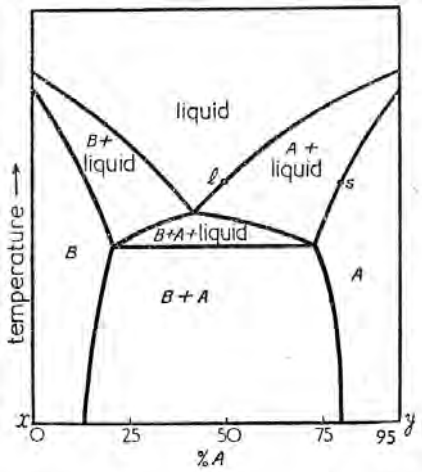


Fig.III.1-3 [HUM1953]: Vertical cross-section of a ternary phase diagram containing the components A, B and C.
The concentration of C is constant and equals 5%,
A and B concentrations vary from 0 to 95%.

Fig.III.1-3 is a vertical cross-section of a ternary phase diagram, where the concentration of C remains constant (here C_C=5%) and where A and B concentrations change. Consequently, the points *x* and *y* represent two systems containing 5%C+95%B and 5%C+95%A respectively. The point *l* on the liquidus curve shows that a system containing 5%C+50%A is exactly on the liquidus surface at the temperature concerned. However, the point *s* is not the solidus point corresponding to the liquidus point *l*. The reason for this is that all points on this figure represent systems containing 5%C, but there is no reason why a liquid containing 5%C should be in equilibrium with a solid containing the same percentage of C.
Thus, such a diagram only shows the phases present in the system at different temperatures. This is the aspect which is interesting in our study of solvent systems. But such a diagram cannot be used to deduce the compositions of mixtures in equilibrium with one another. Vertical sections are thus easily misleading, because after working with binary phase diagram, there is an instinctive tendency to imagine that horizontal lines may be drawn to give the compositions of various phases.
In ternary systems, compositions of different phases can be determined by studying the isothermal sections. This will not be described because a complete investigation of ternary solvent system is not our topic.

III.1.1.3. Methods for building phase diagrams. The limits of the DSC analysis

The building of phase diagrams can be divided into two parts:

A) The first one consists in plotting the liquidus and solidus curves.

For example, the liquidus can be easily determined by solubility measurements.
Another classical method is the use of calorimetry, where a large amount of material is slowly heated or cooled in order to be always in equilibrium conditions. Temperatures and heat

exchanges are then used to build the phase diagram. It is a very slow method requiring a lot of sample, but it is the only exact manner to plot the phase diagrams.

Differential Scanning Calorimetry (DSC) is often used to measure enthalpies of phase transitions and their corresponding temperatures (part II.3.1) and thus to build phase diagram (Fig.III.1-4). It is a very fast method, using only a very small amount of material. The drawback of it is that several corrections must be applied if one wishes to have correct temperature values. Outside the classical calibration corrections, one major difficulty is to obtain a correct temperature for the melting of material phases like crystalline ones. To be correct, all measurements should be done by extrapolating the data to zero heating or cooling rate and to zero mass. This is very time consuming and usually it is not done. However, without such measurements there are some difficulties in exploiting the DSC data. We give below (Fig.III.1-5) one example where we show that we are making an error when using DSC to plot the liquidus if we are not using the extrapolation at zero mass and zero heating rate.

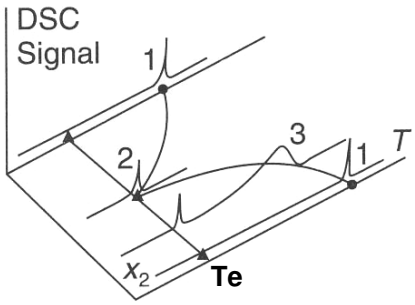


Fig.III.1-4: Solid/liquid equilibrium in a binary eutectic-forming system as observed by DSC.
Curve 1: **Melting of pure components 1 and 2;** *Curve 2*: **Eutectic melting;**
Curve 3: **Melting of a mixture with an excess of solid 2 (in comparison with the eutectic composition)**

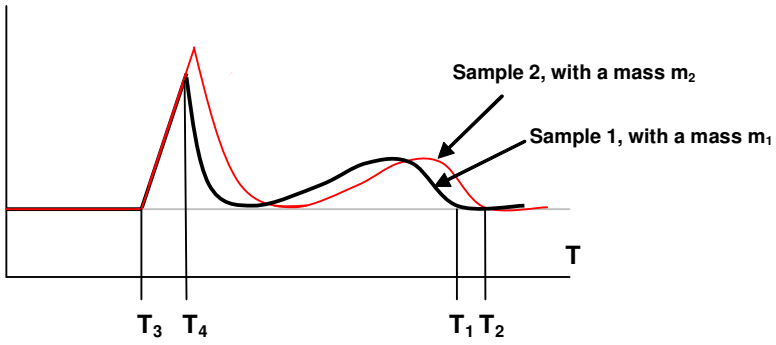


Fig.III.1-5: Example of DSC traces showing the error when the extrapolation at zero mass and heating rate is not used

For the samples of two different masses ($m_2 > m_1$), the end of the melting peaks is shifted towards higher temperatures for a higher-mass sample, both for a pure substance melting at a single temperature or for a substance having a large melting peak. This is due to the time needed for heat transfer inside the sample, considering that on a DSC trace such as the one shown here (Fig.III.1-5), the horizontal axis that is usually labelled as the temperature axis is in reality a time

axis. Each time that a substance is melting at a single temperature, the temperature is constant, while time is flying. In the Fig.III.1-5, while points T_3 and T_4 are given in the DSC trace as two different temperatures, the sample is in fact staying for a certain time between these two points at the temperature T_3, which is the melting temperature.

This will have a small impact on our data since it will slightly shift all temperatures of the liquidus at high water content of the mixtures by less than 1°C. The lower is the water content, the smaller is the peak of the melting of ice, and the smaller is the error. The real and DSC-determined liquidus shapes are as shown below in Fig.III.1-6.
It must be noted that the values of the enthalpy of the peaks measured by DSC do not depend on mass or heating rates.

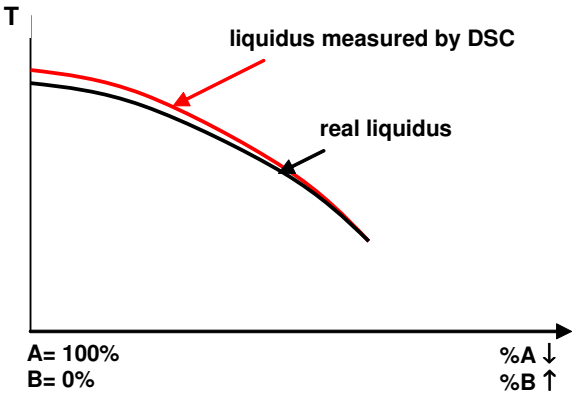


Fig.III.1-6: Real and DSC-determined liquidus, when the extrapolations at zero mass and heating rate are not used

In our study, the goal was not to plot very exact phase diagrams that would have taken a lot of time, but to understand the structure of cellulose solutions and proportions between the components. For this reason, we did not use the extrapolation technique to measure precisely temperature, but we always used the same range of heating rates and masses. As we will see later, this had no influence on our work.

B) The second one consists in determining the nature of the crystalline solid phases; X-Ray diffraction analysis is the most often used method.

III.1.2- State of the art on the structure of NaOH aqueous solutions

III.1.2.1. Pure sodium hydroxide

Anhydrous sodium hydroxide is a white and translucent solid, strongly hygroscopic. Thus it easily catches the humidity of atmosphere and, in that case, also absorbs carbon dioxide. Also called lye or caustic soda, sodium hydroxide is a strong chemical base and, thus, its aqueous solutions violently react with acid.
We saw previously (part I.2.2) that cellulose can be dissolved in relatively low NaOH concentrated solutions, at low temperature.

The anhydrous sodium hydroxide has two crystalline structures α and β, at low and high temperature respectively. However, as far as NaOH is strongly hygroscopic, NaOH is essentially found as hydrated forms. In the forthcoming, crystalline structures of anhydrous sodium hydroxide will not be described, only the sodium hydroxide hydrates will be detailed.

III.1.2.2. Sodium hydroxide hydrates

Several papers [PIC1893][COH1960][ROL1964] report the formation of stable sodium hydrates in which the number of water molecules depends on the NaOH concentration and on the solution temperature.
In 1893, Pickering [PIC1893] identified 8 hydrates of sodium hydroxide:

- The monohydrate ($NaOH,H_2O$)
- The dihydrate ($NaOH,2H_2O$)
- The trihydrate ($9NaOH,28H_2O$ which can also be written $NaOH,3.11H_2O$). Pickering [PIC1893] as well as Rollet and Cohen [ROL1964] are doubtful concerning this formula but experiment of solubility for the former and thermal analyses for the latter do not allow to make a choice between the $NaOH,3H_2O$ and $NaOH,3.11H_2O$ formulae.
- The 3.5hydrate ($NaOH,3.5H_2O$)
- Two tetrahydrates ($NaOH,4H_2O$ α and $NaOH,4H_2O$ β)
- The pentahydrate ($NaOH,5H_2O$)
- The heptahydrate ($NaOH,7H_2O$)

Pickering [PIC1893] also investigated other alkaline hydroxides as KOH and LiOH and plotted the liquidus curves for these three binary systems.
Some years later, Antropoff and Sommer [ANT1926] added the part of liquidus concerning the anhydrous sodium hydroxide.
From thermal analyses and solubility studies, Cohen-Adad [COH1960], Rollet *et al.* [ROL1964] checked the Pickering results, which turned out to be very precise [PIC1893]. They added the solidus curves and thus completed the binary phase diagrams for NaOH/water, KOH/water, LiOH/water, RbOH/water, and CsOH/water.

Fig.III.1-7 represents the NaOH/water binary phase diagram, plotted by Rollet and Cohen-Adad, with the well-determined NaOH hydrates in crystallised states.

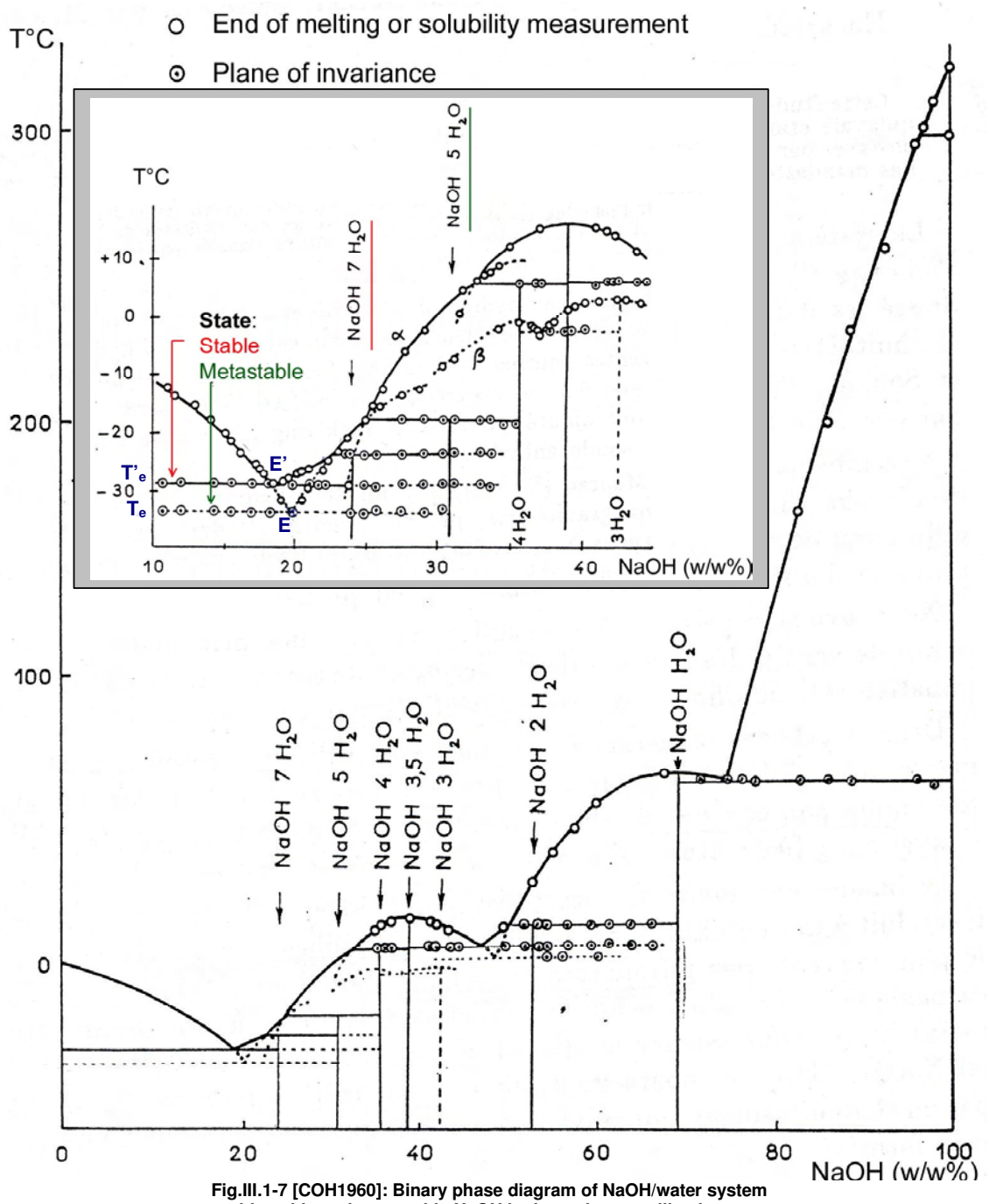


Fig.III.1-7 [COH1960]: Binary phase diagram of NaOH/water system with stable and metastable NaOH hydrates in crystallised state.

Y-axis corresponds to the temperature and X-axis to the mixture composition given in NaOH weight percentage (x=0% corresponds to **pure water** – on the left of the graph)

As we can see, this phase diagram is complex: it contains stable and metastable hydrates and several eutectic mixtures. We can note that:

- x=24% corresponds to the stable crystalline sodium hydrate **$NaOH,7H_2O$**
- x=31% corresponds to the metastable crystalline sodium hydrate **$NaOH,5H_2O$**

The points E' and E (in the detailed part of the Fig.III.1-7) correspond to eutectic mixtures, formed by ice and sodium hydrates $NaOH,7H_2O$ and $NaOH,5H_2O$, respectively. According to Rollet and Cohen-Adad [ROL1964], $NaOH,7H_2O$ is a stable hydrate obtained after a rapid drop in temperature, in liquid air or dry ice, followed by an isothermal step at a higher temperature, and $NaOH,5H_2O$ is a metastable hydrate, obtained when the temperature decreases relatively slowly and that the thermal analysis is performed just after the crystals formation. They also reported that the NaOH/water binary system forms the metastable equilibria very easily.

When ions are in solution, they have different solvated forms depending on their concentration: in a concentrated solution, the two ions form a hydrated dipole, whereas in a dilute solution, they are separated (Fig. I.2-6).
In the case of sodium hydroxide in water, Bartunek [BAR1954] determined the existence of separated ions for NaOH concentrations inferior to 6% and Yamashiki [YAM1988] observed separated ions for NaOH concentration around 9%. But whatever the concentration limits are, the ions Na^+ and OH^- are surrounded by a "cage" of water molecules. In 1949, Bockris [BOC1949] defined a primary and a secondary cage of solvation. In the primary cage of solvation, water molecules are strongly linked to the ions Na^+ and OH^- (but it is not a covalent link). In the secondary cage of solvation, water molecules are less linked to the ions and thus can be easily exchanged with the free solvent molecules.

Different techniques (NMR, ultrasonic velocity, ionic mobility…) were used to measure the number of water molecules in different cages but the results are not in agreement. According to Yamashiki [YAM1988], from ^{23}Na and ^{1}H NMR and ultrasonic velocity measurements at +4°C, for a 9% NaOH solution, the primary and secondary cages contain 8 and 23 water molecules respectively (Fig.III.1-8), that is to say 31 water molecules on the whole. From ^{23}Na NMR, Kunze [KUN1985] determined a total of 22 water molecules for a 9% NaOH concentration at 30°C. The comparison between these two figures is not totally possible because the temperature is very different and we know that the structure of hydrates is strongly dependent of temperature. But these results give an idea on the significant hydration state of Na^+ and OH^- ions.

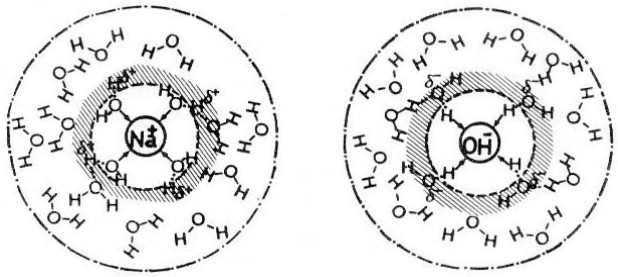


Fig.III.1-8 [YAM1988]: Schematic representation of a 9% (w/w) NaOH aqueous solution at +4°C
Na^+ and OH^- ions are in the centre of the cage,
the grey part represents the primary solvation cage
and the white part is the secondary cage.

The cage structure and the number of water molecules linked to the ions determine the diameter of the sodium hydrate. This parameter has been thought to be important for the cellulose dissolution since the sodium hydrates must penetrate into the cellulose fibres.

III.2- STRUCTURE OF CELLULOSE SOLVENTS: NAOH/WATER, NAOH/UREA/WATER AND NAOH/ZNO/WATER

The goal of this part is to precisely investigate the structure of solvent systems and to plot their phase diagrams. Binary systems – NaOH/water and urea/water – will be first studied and then ternary systems – NaOH/urea/water and NaOH/ZnO/water – will be investigated in order to observe the influence of the addition of a third component. The knowledge of phases present in solution and of the proportions between the species in this or that phase allows a better understanding of the interactions between urea and NaOH and/or water, and between ZnO and NaOH and/or water.

We should like to remind here (see also part II.2) how the proportions between the components will be given in the following.
The notion of concentrations will be used only for binary solvents, like NaOH/water or urea/water. In all other cases we shall use and show in the notations the amount of grams of the substance in 100 g of solution. In other words, Xcellulose/YNaOH/water means that in 100 g of solution there are X grams of cellulose, Y grams of NaOH and (100–X–Y) of water. Another example is as follows: Xcellulose/YNaOH/Zurea/water means that in 100 grams of solution there are X grams of cellulose, Y grams of NaOH, Z grams of urea and (100-X-Y-Z) grams of water. For the binary systems "concentration" in weight per cent, calculated as $Y = \frac{M_i}{M_i + M_{water}} 100\%$ **(M_i and M_{water} being component "i" and water weights, respectively), coincides with the amount of grams Y of this component in 100g of solution: Ycomponent/water.**

III.2.1- NaOH/water binary system

The binary phase diagram of NaOH/water system has been largely studied in literature (part III.1.2.2). This part revisits it in order to validate our experimental results as well as the methodology used to calculate the composition of each phase.

III.2.1.1. DSC melting thermograms of NaOH/water solutions

Thermal analyses with DSC consist in determining melting peaks for pure NaOH/water solutions ('pure' means without urea, without ZnO and without cellulose). We used a concentration of NaOH varying from 7.6wt% to 20wt%. The DSC thermograms are given on

Fig.III.2-1; the corresponding melting temperatures are reported in Tab.III.2-1 and the melting enthalpies in Tab.III.2-2 and Tab.III.2-3.

The phase diagram of NaOH/water solutions (Fig.III.1-7 and Fig.III.2-2) shows that at low sodium hydroxide concentration (<30%NaOH in water) a eutectic mixture and ice should melt at lower and higher temperatures, respectively [PIC1893][COH1960]. In the following sections, each peak is analysed in order to find the type of the melting compound and its composition.

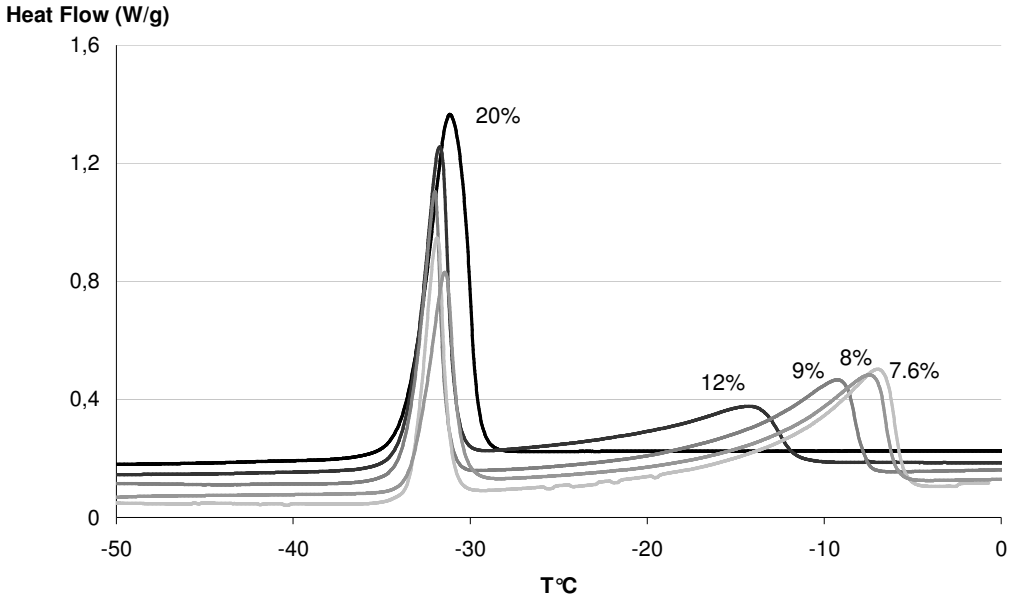


Fig.III.2-1: DSC melting thermograms of NaOH/water solutions.
C_{NaOH} = 7.6%, 8%, 9%, 12% and 20%
Curves are shifted vertically for a better visibility.

NaOH, %	Tm (onset) eutectic peak, °C	Tm (end) ice peak, °C
7.6	-33.2	-5.4
8	-33.2	-5.9
9	-33.6	-7.7
12	-33.5	-11.7
20	-33.3	no peak

Tab.III.2-1: Melting temperatures determined from DSC thermograms (Fig.III.2-1)

III.2.1.2. Peak at lower temperature: melting of the eutectic mixture

The melting temperature of the peak at low temperature is around -33.4°C. The temperature variation with the NaOH concentration is not negligible, but it is due to the inherent difficulty of finding the proper beginning of melting with the DSC technique (part II.3.1). In addition, the melting temperatures have not been measured at heating or cooling rates and mass of sample extrapolated to zero, which induces a small temperature error (see part III.1.1.3). The peak corresponds to the melting of the eutectic mixture. It is in the range of temperatures given in the literature (-34°C [COH1960]).

A) What is the molecular composition of the eutectic mixture which crystallises during the DSC experiments?

The peak at higher temperature disappears when the NaOH concentration is 20%. This means that only eutectic is present in the solution, in agreement with the NaOH/water phase diagram described in ref. [PIC1893][COH1960]. Fig.III.2-2 also represents NaOH/water phase diagram and indicates the terms used in this report. Thus **20%NaOH/80%H_2O in weight per cent** is the composition of the pure eutectic. Taking into account the molar weight of water and sodium hydroxide, 18 and 40, respectively, we can also write:

$$m_{NaOH} = 20\% \ (m_{NaOH} + m_{H2O})$$
$$40 = 0.2(40 + n_{H2O} * 18)$$
$$n_{H20} \sim 9$$

Thus, the eutectic mixture, melting at -33.4°C, has a total composition of **1NaOH and 9H_2O in moles**.

B) What is the structure of this eutectic mixture?

Let us consider the detailed structure of the eutectic, which is a mixture of two crystals.
In a recent paper [ROY2001], it is reported that the eutectic mixture is composed of the stable crystalline sodium hydrate NaOH,7H_2O and water. But, in fact, the melting temperature of the eutectic containing the stable hydrate + water is -29°C whereas the melting temperature of the eutectic containing the metastable crystalline hydrate NaOH,5H_2O + water is -34°C [COH1960], see Fig.III.1-7. In addition, Rollet and Cohen-Adad [ROL1964] reported that a low decrease of temperature leads to the formation of metastable sodium hydrates. Because we used stainless steel capsule, the temperature decrease rate is low (part II.3.1.5) which confirms the formation of the eutectic metastable crystalline hydrate NaOH,5H_2O + water**.**
From X-Ray diffraction pattern obtained by Roy [ROY_PhD], it is not possible to discriminate both hydrate crystals since the experimental diffracting angle was 16.4°, value very close to literature data: NaOH,7H_2O at 16.22° and NaOH,5H_2O at 16.26° and 16.53 [MOO1994].

We conclude that the peak at low temperature corresponds to the melting of the eutectic mixture composed of two crystals: the crystalline hydrate NaOH,5H_2O and ice, the composition being **NaOH,5H_2O + 4H_2O**, in order to obtain the ratio 1NaOH/9H_2O.

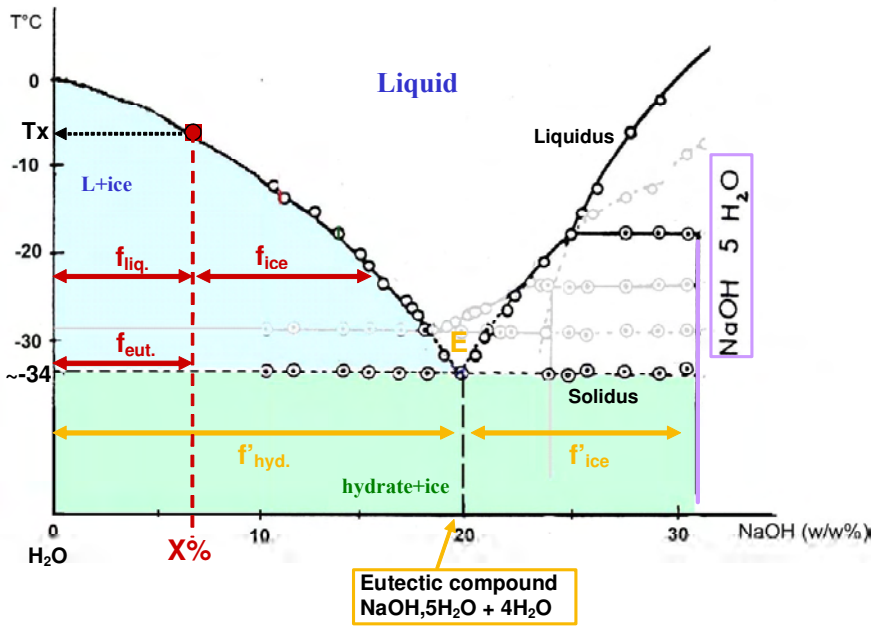


Fig.III.2-2: Detailed part of NaOH/water phase diagram (Fig.III.1-7 [COH1960]) for 0-31% NaOH concentrations
f_{ice} : fraction of "free" ice, f_{liq}: fraction of liquid
at T~-34°C, $f_{liq} = f_{eut}$ with f_{eut}: fraction of the eutectic compound, function of the NaOH concentration
f'_{hyd} and f'_{ice} fractions of sodium hydrate and ice, respectively, in the eutectic compound

On the Fig.III.2-2, the left-hand axis of the phase diagram corresponds to water. At the right-hand side, the vertical line corresponds to the crystalline pentahydrate $NaOH,5H_2O$ having a molar weight of 130g/mol. The composition of this crystalline hydrate is 30.8%NaOH and 69.2% water, in weight per cent.

For information, the level rule applied on this part of the binary NaOH/water phase diagram enables to determine the proportion of each phase present in the eutectic mixture. Knowing that the NaOH concentration at the eutectic point is 20%, we obtain:

- Hydrate fraction = $f'_{hyd} = 20/30.8 = 65\%$
- Ice fraction = $f'_{ice} = (30.8-20)/30.8 = 35\%$

The eutectic compound is a mixture of **35% ice and 65% crystalline $NaOH,5H_2O$ hydrate, in weight per cent**.

To conclude, the eutectic mixture can be defined:

- By the nature of crystals: **$NaOH,5H_2O$ and ice, with one mole of $NaOH,5H_2O$ and four moles of water**
- By the proportion of crystals: **65% sodium hydrate + 35% H_2O**
- By the proportion of components: **20% NaOH + 80% H_2O**

Its melting temperature is **~33.4°C.**

III.2.1.3. Peak at higher temperature

The melting peak at higher temperature changes with NaOH concentration (Fig.III.2-1). Higher is the NaOH concentration; lower are the melting temperature and the intensity of the peak. This peak disappears at 20% NaOH. It corresponds to the melting of free ice. In agreement with the phase diagram, this peak is very large because of the gradual melting of crystallised water.

III.2.1.4. Proportions between NaOH and water

The peak at low temperature (-33.4°C) corresponds to the melting of the eutectic mixture containing 20% NaOH. Thus the DSC thermogram of the 20%NaOH solution gives the melting enthalpy of pure eutectic: $\mathbf{\Delta H_{eut,\,pure} = 187\ J/g}$ (Tab.III.2-2).
The peak at higher temperature corresponds to the melting of free ice. The melting enthalpy of pure crystallised water: $\mathbf{\Delta H_{ice,pure} = 358\ J/g}$ (Tab.III.2-3) was measured with distilled water. This value is in the acceptable agreement with the data of literature (333.5 J/g [WEA1983]).
Applying the level rule on the NaOH/water phase diagram, it is possible to calculate the fraction of eutectic mixture $f_{eut,\,calc.}$ and the fraction of free ice $f_{ice,\,calc.}$ at any NaOH concentration (X% on the graph Fig.III.2-2). When the NaOH concentration C_{NaOH} is lower than 20%, we obtain:

$$f_{eut,calc.} = \frac{C_{NaOH}}{20} \qquad \textbf{Eq. 1}$$

$$f_{ice,calc} = \frac{20 - C_{NaOH}}{20} \qquad \textbf{Eq. 2}$$

Since we know the melting enthalpies of the pure eutectic $\Delta H_{eut,pure}$ and pure ice $\Delta H_{ice,pure}$, it comes that the experimental fractions of eutectic $f_{eut,exp.}$ and ice $f_{ice,pure}$, at any NaOH concentration, are:

$$f_{eut,\exp.} = \frac{\Delta H_{eut,\exp.}(C_{NaOH})}{\Delta H_{eut,pure}} \qquad \textbf{Eq. 3}$$

$$f_{ice,\exp.} = \frac{\Delta H_{ice,\exp.}(C_{NaOH})}{\Delta H_{ice,pure}} \qquad \textbf{Eq. 4}$$

The fractions, determined from DSC thermograms and calculated from the phase diagram, are compared Tab.III.2-2 and Tab.III.2-3 for the eutectic and ice peaks, respectively.

C_{NaOH} %	$\Delta H_{eut,exp.}(C_{NaOH})$, J/g *DSC*	$f_{eut,exp.}$ *Eq.3*	$f_{eut,calc.}$ *Eq.1*
7.6	72	0.39	0.38
8	73	0.39	0.40
9	83	0.44	0.45
12	111	0.59	0.6
20	187 = $\Delta H_{eut,pure}$	1	1

Tab.III.2-2: Melting enthalpy of eutectic mixture $\Delta H_{eut,exp.}(C_{NaOH})$ determined from DSC thermogram (Fig.III.2-1; fractions of eutectic in NaOH+water solution at a given NaOH concentration C_{NaOH} from 7.6% to 20%, determined from DSC $f_{eut,exp.}$ and calculated from phase diagram level rule $f_{eut,calc.}$

C_{NaOH} %	$\Delta H_{ice,exp.}(C_{NaOH})$, J/g *DSC*	$f_{ice,exp.}$ *Eq.4*	$f_{ice,calc.}$ *Eq.2*	≠%
0	358 = $\Delta H_{ice,pure}$	1	1	
7.6	197	0.55	0.62	*11*
8	188	0.53	0.60	*12*
9	173	0.48	0.55	*13*
12	133	0.37	0.4	*7*

Tab.III.2-3: Melting enthalpy of free ice $\Delta H_{ice,exp.}(C_{NaOH})$ determined from DSC thermogram (Fig.III.2-1); fractions of free ice in NaOH+water solution at a given NaOH concentration C_{NaOH} from 0% to 13%, determined from DSC $f_{ice,exp.}$ and calculated from phase diagram level rule $f_{ice,calc.}$. Column 5 is the relative difference between the two experimental and calculated values.

Tab.III.2-2 and Tab.III.2-3 show that fractions calculated from phase diagram level rule and determined from DSC thermograms coincide within the experimental errors, in agreement of the phase diagram plotted in Fig.III.2.2. The NaOH and water mixtures behave as normal eutectic-type mixtures. All the components are fully identified, at all concentrations under consideration; their state (crystalline or liquid) and fractions are known from the phase diagram.
Thus the experimental data obtained and methodology used can be applied for the analysis of urea/water binary system as well as for the analysis of ternary phase diagrams – NaOH/urea/water, NaOH/ZnO/water, cellulose/NaOH/water solutions and we will apply the same consideration to four-body mixtures (cellulose/NaOH/water/urea).

Revision of the previous work

In the previous work on NaOH/water solutions [ROY_PhD][ROY2001], the comparison of experimental and calculated ice fractions gave differences superior to 20%, even reaching 64%. In order to explain this discrepancy, the presence of a third phase – amorphous water – was suspected.

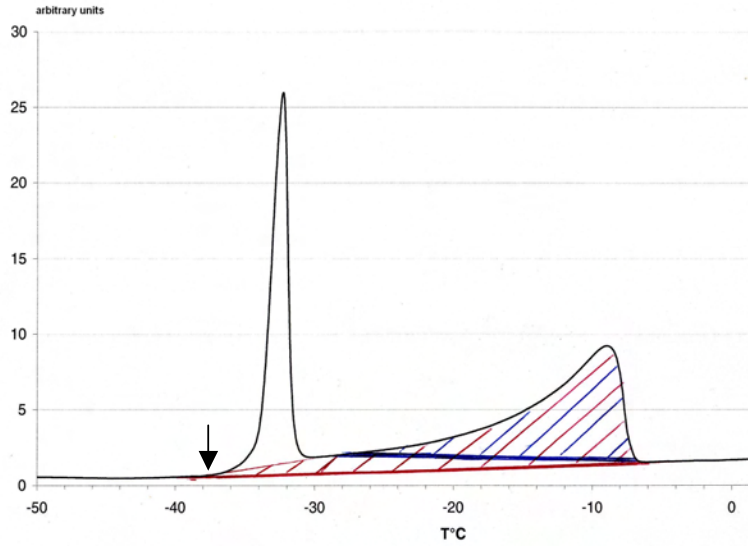


Fig.III.2-3: Scheme of two different calculations of melting enthalpy of ice. The red area is the correct one.

However, from the phase diagram (Fig.III.2-2), it is not possible to have three phases and the thermograms used by Roy [ROY_PhD][ROY2001] were re-examined. It turned out that the peak area of the ice was strongly underestimated due to error on the base line. The enthalpy was calculated as a blue area shown on Fig.III.2-3 while the peak is larger: it starts at low temperature (shown by ↓ on Fig.III.2-3), just at the beginning of the peak of the eutectic mixture, in accordance with the phase diagram. The real enthalpy values are greater than the ones measured by Roy (area in red is larger than in blue).
We can note that in our case (Tab.III.2-3), the relative difference between experimental and measured values is about 10%. The fraction of free ice calculated from phase diagram and determined from enthalpy measurements are in good agreement, within the experimental errors. This means that there is no third component like "amorphous water".

III.2.1.5. Conclusion on the phase diagram and structure of NaOH/water solutions

The mixture of sodium hydroxide and water in the 0-31%NaOH range is a simple solution of two components: NaOH and water. They are miscible in liquid state and immiscible in solid state. In our experimental conditions, sodium hydroxide and water form a eutectic mixture composed of the sodium pentahydrate and water molecules in the following proportions: $NaOH,5H_2O+4H_2O$. This eutectic mixture crystallises around –33.4°C.
Consequently, at very low temperature (T<-33.4°C), the $NaOH/H_2O$ mixture is composed of two crystalline phases (Fig.III.2-4):

- The crystalline hydrate: $NaOH,5H_2O$
- Ice in two locations:
  - free ice forming rather large crystals (if $C_{NaOH} < 20\%$)
  - ice with the crystalline hydrate in the form of tiny crystals to form the eutectic mixture.

From the phase diagram, the calculations of the fractions of the various components presented at a given composition and temperature show a good agreement with the experimental data. The system is at equilibrium at all moment in the experimental conditions that have been used.
It is thus possible to schematically represent the structure at temperatures below -33.4°C as below:

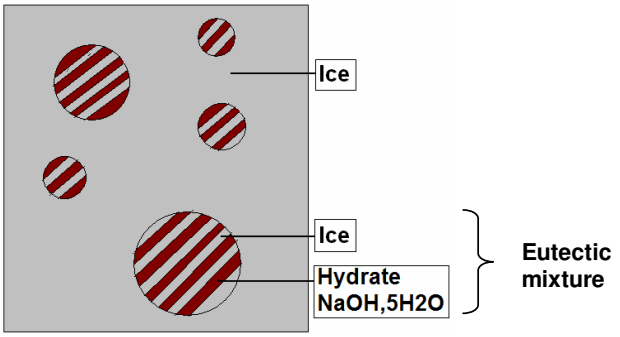


Fig.III.2-4: Scheme of the structure of crystallised NaOH/water system at C_{NaOH}<20% and temperature below -33.4°C.
Note that the shape of the eutectic crystals is not known. It is presented here in the form of spheres for the sake of drawing.

III.2.2- NaOH/urea/water ternary system

The aim of this section is to understand how NaOH and urea are reacting when they are mixed in aqueous solutions. Firstly, we will determine the 0-100%urea/water binary phase diagram. Secondly, NaOH/urea/water ternary system will be investigated: NaOH concentration being fixed at 7.6wt% and urea concentrations varying from 0% to 25%. A section of the phase diagram will be drawn.

III.2.2.1. Urea/water binary phase diagram

DSC experiments consist in determining melting peaks for urea/water solutions, urea concentrations varying from 0% to 100%. This study is divided into two parts: from 0% to 30% of urea and from 30% to 100%.

From 0% to 30% of urea

DSC melting thermograms of 0-30%urea aqueous solutions are represented on the Fig.III.2-5. The melting temperature and enthalpy of each peak are reported in the Tab.III.2-4 and Tab.III.2-5, respectively. In the Tab.III.2-4, the term 'solidus (DSC)' corresponds to the onset of the peak at low temperature and the term 'liquidus (DSC)' to the end of the peak at higher temperature, both determined with our DSC analyses. The measurements of the liquidus are reported in literature from the data on urea solubility in water [RAB1978][WEA1983]. We can note that 'DSC values' and 'Handbook values' are relatively close and differ because of the difference in the method of determination.

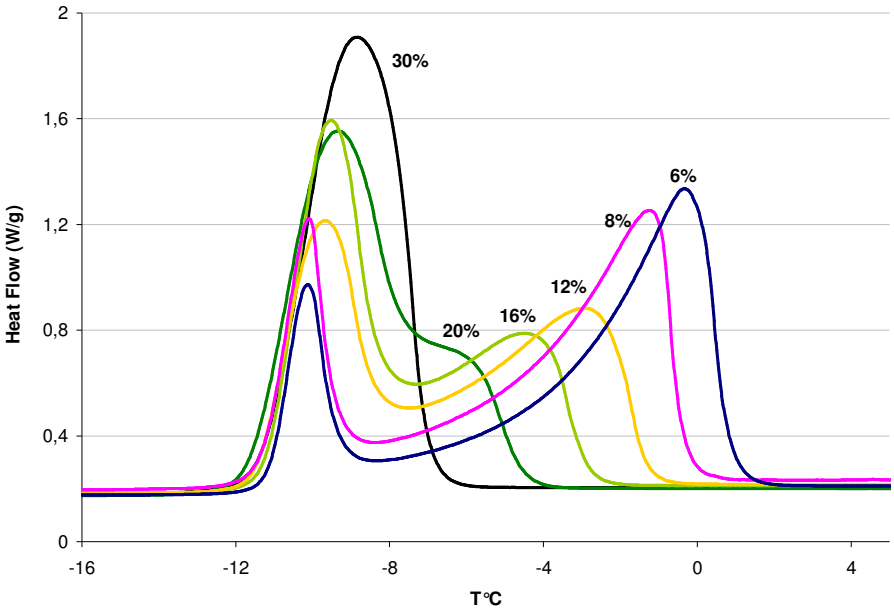


Fig.III.2-5: DSC melting thermograms of urea/water solutions
C_{urea} = 6%, 8%, 12%, 16%, 20%, and 30%

%urea	solidus	liquidus	
	(DSC)	(DSC)	(Handbook)
6	-11,3	0,8	-1,9
8	-11,3	-0,4	-2,6
12	-11,4	-1,3	-4,0
16	-11,2	-2,9	-5,4
20	-11,6	-4,5	-7,0
30	-11,2		-11,4
40	-11,4		0
50	-11,4		
60	-11,4	39	35
70	-11,5	64	56
80		85	80
100		137	135

Tab.III.2-4: Temperatures of solidus and liquidus curves.
'DSC values' correspond to the melting temperatures obtained by DSC experiments.
'Handbook values' correspond to solubility temperatures reported in handbooks [RAB1978][WEA1983]

The urea/water DSC thermograms (Fig.III.2-5) are similar to the NaOH/water DSC thermograms (Fig.III.2-1). Apart for 30% urea, all DSC thermograms reveal two melting peaks more or less well-separated:

- The first one, at low temperature, has the same position whatever is the urea concentration from 6% to 30%. At the onset of the melting peak, the temperature is about -11.3°C (Tab.III.2-4, column 2). This peak should correspond to the melting of a eutectic mixture.
- The second one, at higher temperatures, is shifted towards low temperatures when urea content increases (Tab.III.2-4, column 3 and 4). We deduced that this peak probably corresponds to the gradual melting of free ice.

The peak of free ice disappears at about 30% of urea. This means that the eutectic mixture should contain 30% of urea in the whole.
From these data, the 0-30%urea part of the phase diagram can be drawn.

We can see here the effect of the phenomena described in part III.1.1.3 concerning the influence of using non-zero heating rate and mass. The peak at high water content is finishing above 0°C. The error here is about 1°C.

30% of urea

As the molar masses of urea – $CO(NH_2)_2$ – and water are 60g/mol and 18g/mol respectively, 30% of urea in weight corresponds to a molar ratio n_{H2O}/n_{urea} = 7.8. Thus, the total eutectic composition is probably **1 urea and 8 H_2O**. This can be checked using the above-described methodology in the case of NaOH/water binary system.
Melting enthalpies of urea eutectic mixture and ice are reported in Tab.III.2-5. Since the two peaks overlap, the enthalpy of each peak was deconvoluted with PeakFit software, described in the part II.3.1.6. All the thermograms with their deconvolution treatment are shown in the Appendix 3.

	Enthalpies		
	DSC	PeakFit	
% urea	**Total**	**eutectic**	**ice**
0	358 = $\Delta H_{ice,pure}$		
6	325	51	275
8	323	67	256
12	319	111	208
16	311	155	156
20	308	212	96
29,4	290 = $\Delta H_{eut,pure}$		
30	291		

Tab.III.2-5: Melting enthalpies of eutectic mixture and free ice.
The total enthalpy was determined with DSC software from the thermogram.
Eutectic and ice enthalpies were calculated with PeakFit software as described in part II.3.1.6

The calculated and measured fractions of eutectic mixture and free ice are compared in order to check the existence and the composition of the urea/water eutectic mixture. Calculations were performed with the hypothesis that eutectic mixture is reached at 29.4% urea, which corresponds to the composition 1 urea + 8 water molecules.
The equations are described below and values are reported in the Tab.III.2-6.

$$f_{eut,calc.} = \frac{C_{urea}}{29.4} \qquad \textbf{Eq. 5}$$

$$f_{eut,\exp.} = \frac{\Delta H_{eut,\exp.}(C_{urea})}{\Delta H_{eut,pure}} \qquad \textbf{Eq. 6}$$

$$f_{ice,calc.} = \frac{29.4 - C_{urea}}{29.4} \qquad \textbf{Eq. 7}$$

$$f_{ice,\exp.} = \frac{\Delta H_{ice,\exp.}(C_{urea})}{\Delta H_{ice,pure}} \qquad \textbf{Eq. 8}$$

% urea	$f_{eut,exp.}$ *Eq.6*	$f_{eut,calc}$ *Eq.5*	*≠%*	$f_{ice,exp.}$ *Eq.8*	$f_{ice,calc.}$ *Eq.7*	*≠%*
6	0,17	0,20	*15*	0,77	0,80	*4*
8	0,23	0,27	*16*	0,72	0,73	*2*
12	0,38	0,41	*6*	0,58	0,59	*2*
16	0,53	0,54	*2*	0,44	0,46	*4*
20	0,73	0,68	*8*	0,27	0,32	*16*

Tab.III.2-6: Comparison of fractions of eutectic mixture and free ice, determined from DSC thermograms $f_{eut,exp.}$ and $f_{ice,exp.}$ and calculated from phase diagram level rule (eutectic having 29.4%urea) $f_{eut,calc.}$ and $f_{ice,calc.}$

Tab.III.2-6 shows that fraction of eutectic mixture and free ice calculated from phase diagram and measured from DSC thermograms are similar within the experimental errors. This is validating the hypothesis of a eutectic mixture containing 29.4wt% of urea, which corresponds to a molar urea/water ratio of 1/8. This eutectic melts at -11.4°C. But knowing the exact structure of eutectic mixture needs an X-Ray diffraction analysis, as we will see below.

From 30% to 100% of urea

DSC analyses were also performed on 30-100%urea/water solutions. Typical thermogram is represented on the Fig.III.2-6 and the melting temperatures are reported in the Tab.III.2-4.
For urea aqueous solutions, two peaks are seen. The first one is still at -11.4°C, as in the case of 0-30%urea/water solutions; thus corresponding to the melting of the same eutectic mixture. The second one is shifted towards higher temperature. Pure urea gives a single peak at 137°C.

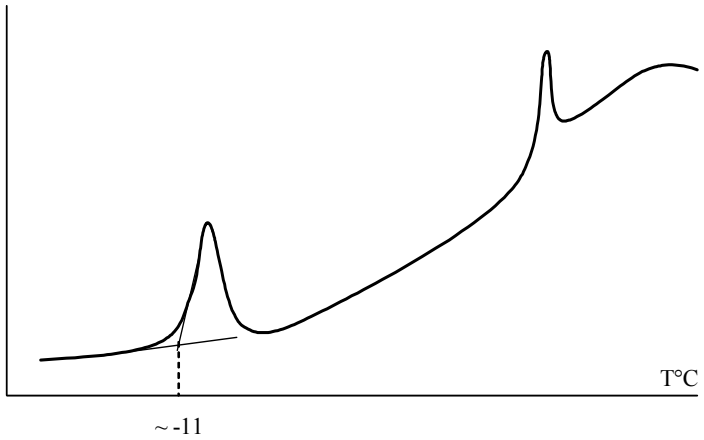


Fig.III.2-6: Scheme of DSC melting thermograms for urea aqueous solutions with 30% < C_{urea} < 100%.

In order to check the crystalline structure of the component which melts at high temperature for an aqueous solution containing more than 30% of urea, and thus the composition of the eutectic mixture, we carried out X-Ray diffraction analyses.
We tested pure urea and the 70%urea/water system. X-ray diffraction patterns were compared and are represented on the Fig.III.2-7.

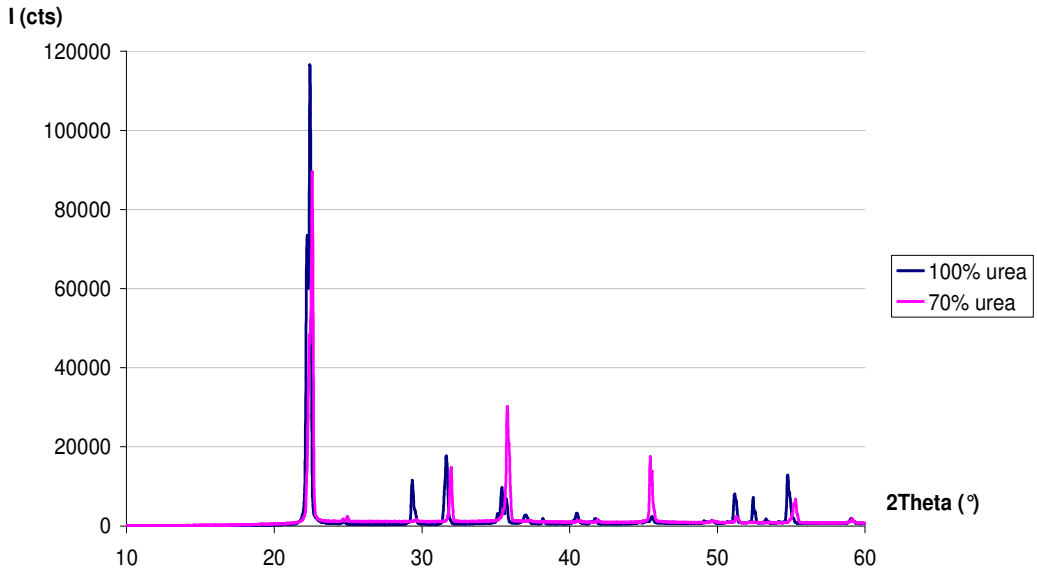


Fig.III.2-7: X-Ray diffraction patterns for pure urea and for a 70%urea aqueous solution.

The two patterns of 100%urea and 70%urea show the same diffraction peaks. Nevertheless, we can note a slight shift of some peaks, especially at high value of 2 Theta. This could be explained by an irregular surface of the 70%urea/water sample. We concluded that the peak at higher temperature corresponds to the melting of **pure urea**.
Consequently, the eutectic mixture contains two crystals: pure urea and ice, without crystalline hydrate. The urea/water binary system has a simple eutectic behaviour.

Conclusion on the urea/water binary phase diagram

DSC and X-Ray scattering enable us to draw the whole urea/water binary phase diagram (Fig.III.2-8).

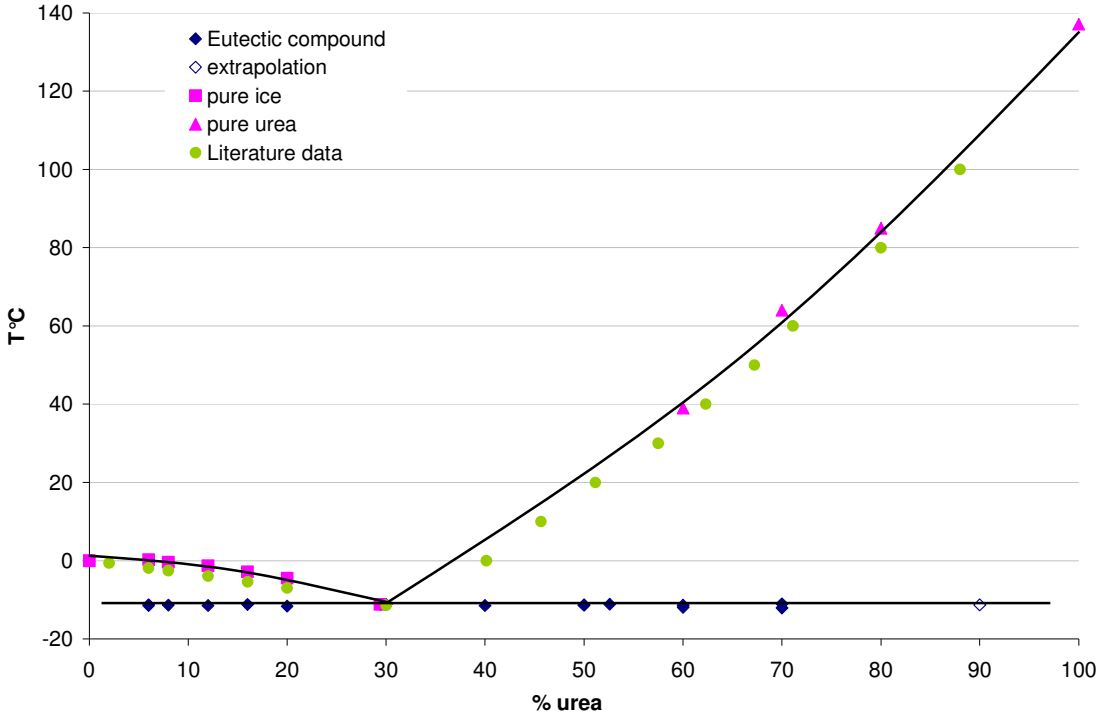


Fig.III.2-8: Binary phase diagram of urea/water system

The urea/water system has a typical eutectic behaviour:

- The eutectic compound is a mixture of two crystals: **pure urea + ice**. Its melting temperature is **-11.4°C** and its composition is **1 urea + 8H_2O**.
- From 0% to 29.4% of urea, the liquidus corresponds to the melting of pure ice.
- From 29.4% to 100% of urea, the liquidus corresponds to the melting of pure urea.

At low temperature (<-11.4°C), the system has two crystalline phases but the structure and the size of urea and ice crystals depends on the urea concentrations.

- Below 29.4%urea, the system is composed of pure urea and ice in two locations: free ice and ice with pure urea to form the eutectic mixture (Fig.III.2-9a).

- 29.4% is the eutectic composition; the system only contains the eutectic mixture, i.e. crystals of pure urea and crystals of ice (Fig.III.2-9b).
- Above 29.4%urea, the system is composed of ice and urea in two locations: free urea and urea with ice to form the eutectic mixture (Fig.III.2-9c).

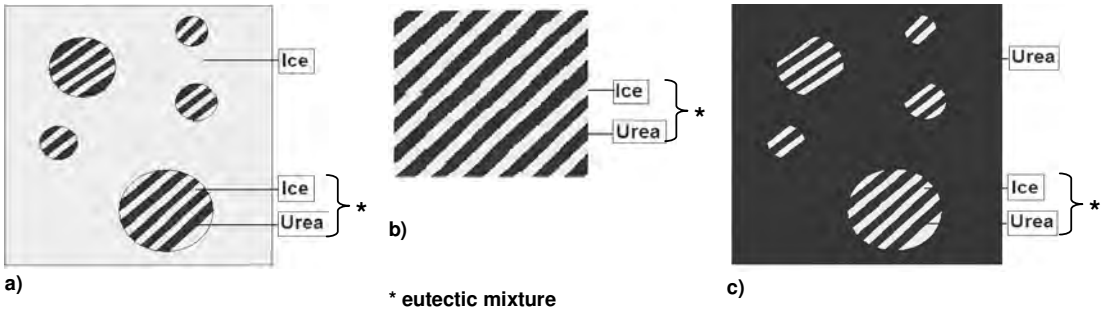


Fig.III.2-9: Schematic structure of crystallised urea/water system below -11.4°C, a) C_{urea}<29.4% ; b) C_{urea}=29.4% ; c) C_{urea}>29.4%

III.2.2.2. NaOH/urea/water ternary phase diagram

Now, as NaOH/water and urea/water binary phase diagrams are known, the NaOH/urea/water ternary system can be investigated. The compositions of mixtures studied were in the range from 7.6NaOH/**6urea**/water to 7.6NaOH/**25urea**/water. In other words, 100g of solution 7.6NaOH/Zurea/water contained 7.6g of NaOH, from Z = 6 to 25 g of urea and from 86.4 to 69.4 g of water, respectively. DSC melting thermograms were plotted and are represented on the Fig.III.2-10. In this range of urea concentrations, five melting peaks are seen. A given NaOH/urea/water system reveals some of them depending on the urea concentration.

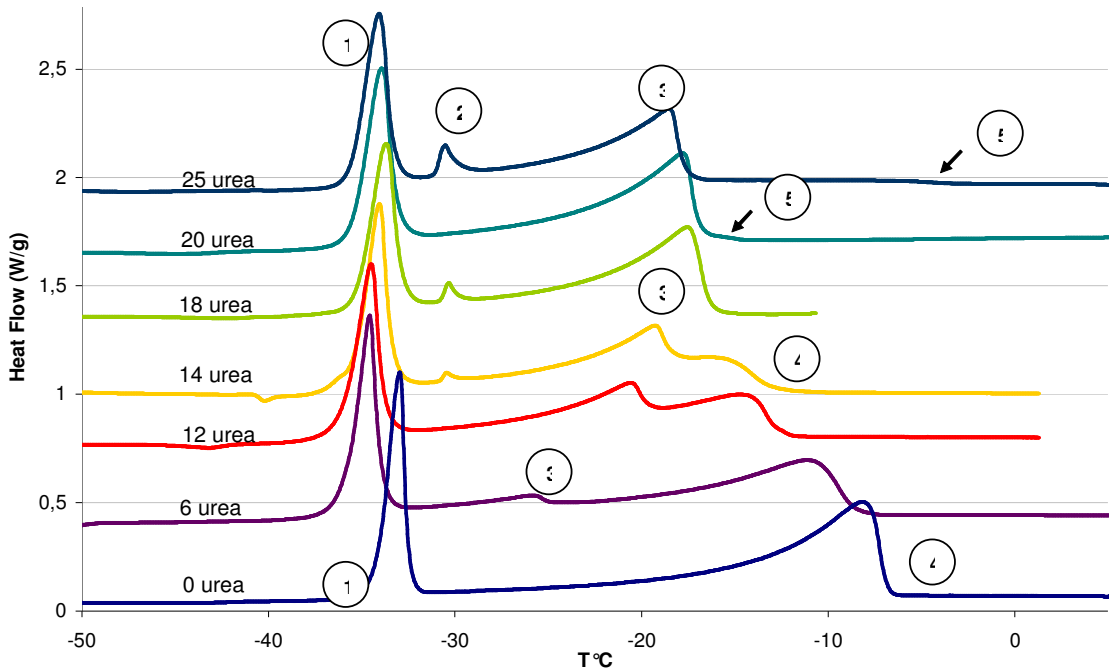


Fig.III.2-10: DSC melting thermograms for 7.6NaOH/Z urea/water solutions (Z= 0, 6, 12, 14, 18, 20 and 25).
DSC traces were shifted for a better visibility

Appendix 4 shows the DSC thermograms for 7.6NaOH/Z urea/water solutions (Z= 6, 12, 14, and 18) with deconvolution treatment.

Peak n°1

The peak n°1 corresponds to the melting of the metastable eutectic mixture NaOH,5H_2O+4H_2O (named NaOH eutectic mixture in the following). Tab.III.2-7 column 3 shows that as soon as urea is added, the melting temperature is depressed from about -33.4°C – in binary NaOH/water solution, without urea – to about -35.6°C with urea. This slight decrease of eutectic melting temperature in ternary system compared with a binary system is due to the presence of the third component (part III.1.1.2). On the other hand, we can note that this melting peak remains constant for all urea concentrations studied because the NaOH/water eutectic mixture is never crystallizing in presence of a liquid.

Peak n°2

This peak appears at about -30°C but it is not always present. This one corresponds to the melting of the stable eutectic mixture NaOH,7H_2O+2H_2O studied previously (part III.1.2.2). It seems, but we do not know why, that the presence of urea in a 7.6NaOH/water makes easier the crystallisation of this stable eutectic.

With the DSC7, it is not possible to obtain only a stable NaOH eutectic mixture. Consequently, its pure melting enthalpy is unknown. In the next parts, we will use the same enthalpy for both eutectic melting, i.e. 187J/g. The low intensity of the peak of the stable eutectic in comparison with the one of metastable eutectic mixture (Fig.III.2-10 for 7.6NaOH/water solutions containing 14, 18 and 25 grams of urea) will not bring a lot of error.

7.6NaOH/ Z urea/water	$\Delta H_{eut\ NaOH}$, J/g	T_m $NaOH_{eut}$ (onset)	T_m $urea_{eut}$ (peak)	T_m free comp (end)	
0	72	-34.2	-	-6.9	
6	72	-35.9	-25.7	-8.6	free
12	71	-36.0	-20.6	-12.5	ice
14	70	-35.5	-19.2	-12.9	
18	71	-35.3	-17.3	-16.3	
20	74	-35.5	-17.8	-14.1	free
25	69	-35.6	-18.5	-6.2	urea

Tab.III.2-7: Melting enthalpy of NaOH eutectic and melting temperatures of NaOH eutectic, urea eutectic, free compounds (ice and urea) for 7.6NaOH / Z urea / water solutions (Z= 0, 6, 12, 14, 18, 20, and 25)

The melting temperature of the NaOH eutectic is taken at the onset of the peak, the one of the urea eutectic at the maximum of the peak (the onset is impossible to be measured) and the one of ice at the end of the peak to determine the liquidus (with the same comments concerning the drawback of using a finite mass of sample and a finite heating rate).

As the melting enthalpy and the melting temperature of NaOH eutectic mixtures (Tab.III.2-7 column 2 and 3) remain constant with an increase of urea concentration, **we can conclude that urea neither disrupt the formation of NaOH eutectic nor modify its composition, which is still 1NaOH+9H_2O. During the time of experiment, urea does not react with NaOH.** Consequently, the species in solution are:

- NaOH eutectic mixtures, in metastable and/or stable state.
- Urea compounds which remain to be determined
- and water

Peaks n°3 and n°4

The peak n°3 appears as soon as urea is added but its location changes depending on urea concentration. This peak should correspond to the melting of a urea compound whose the nature has to be determined.
The temperature of the melting peak n°4 decreases when urea concentration increases from 0 to 14 g of urea in 100 g of solution. This peak could be attributed to the gradual melting of free ice.

From DSC data obtained we may assume that urea does not react with NaOH molecules and does not modify the NaOH eutectic. Thus we can expect that in solution in the presence of NaOH urea and water behave as in the binary system: they form a eutectic mixture containing 1 urea and 8 water molecules. In that case, the peaks n°3 and n°4 should represent the melting of urea eutectic mixture and the melting of free ice, respectively.

Plotting the melting temperature of the peaks as a function of urea concentration (Fig.III.2-11) shows that these two peaks n°3 and n°4 are joining at 7.6NaOH/18urea/water. If our hypothesis is correct, this means that at this composition there are the two NaOH and urea eutectic mixtures coexisting but there is no free water in solution.

Calculation to determine the nature of the urea compound

Let us consider a solution containing 7.6g NaOH + 18g urea + 74.4g water. For 100g of mixture, we have:

- *M_{H2O}=18g/mol; 74.4 g H_2O → 4.13moles of water in the whole solution*
- *M_{NaOH}=40g/mol; 7.6 g NaOH → 0.19 moles of NaOH which corresponds to 0.19 moles of NaOH eutectic mixture.*
- *M_{urea}=60g/mol; 18 g urea → 0.3 moles of urea in the solution*

The NaOH eutectic mixture is not modified by the addition of urea and it contains 1NaOH and 9H_2O molecules

- *0.19*9 = 1.71 moles of water molecules are trapped in the NaOH eutectic mixture.*
- *It remains 4.13-1.71 = 2.42 moles of free water.*

(i) The urea eutectic mixture is composed of 1urea and 8H_2O molecules

- *0.3*8 = 2.4 moles of water are trapped in the urea eutectic*
- *It only remains 0.02 moles of free water in the whole solution.*

(ii) After the formation of NaOH eutectic mixture, 100g of solution contains:

- *18 g of urea*
- *2.42 mol*18 = 43.56g of free water*
- *Consequently, the local concentration of urea is [18/ (18+43.56])*100 = 29.2g which corresponds to the composition of the urea eutectic mixture.*

These calculations allow concluding that:

- Both NaOH and urea eutectic mixtures are formed independently and thus are competing for water
- At 7.6NaOH/18urea/water there is no free water, only NaOH and urea eutectic mixtures.

Peak n°5

For a 7.6NaOH/20urea/water solution, we can observe a small peak at the end of the eutectic peak. For a 7.6NaOH/25urea/water solution, we can guess that there is a peak at about -6°C. These two phenomena are reproducible. Since this peak cannot be due to NaOH, it is due to the melting of strongly depressed urea. This is the clear sign that upon competing with water, NaOH is winning over urea.

Conclusion on the 7.6NaOH/urea/water ternary phase diagram

From the melting temperatures reported in the Tab.III.2-7, we can draw a part of the ternary phase diagram of the 7.6NaOH/urea/water system (Fig.III.2-11).

The figure shows the crystalline phases present in the system at a given temperature and a given urea concentration, with 7.6g of NaOH in 100g of solution. It is not possible to calculate the proportion of each phase from such a phase diagram, as we saw in the theoretical part of this chapter (part III.1.1.2).

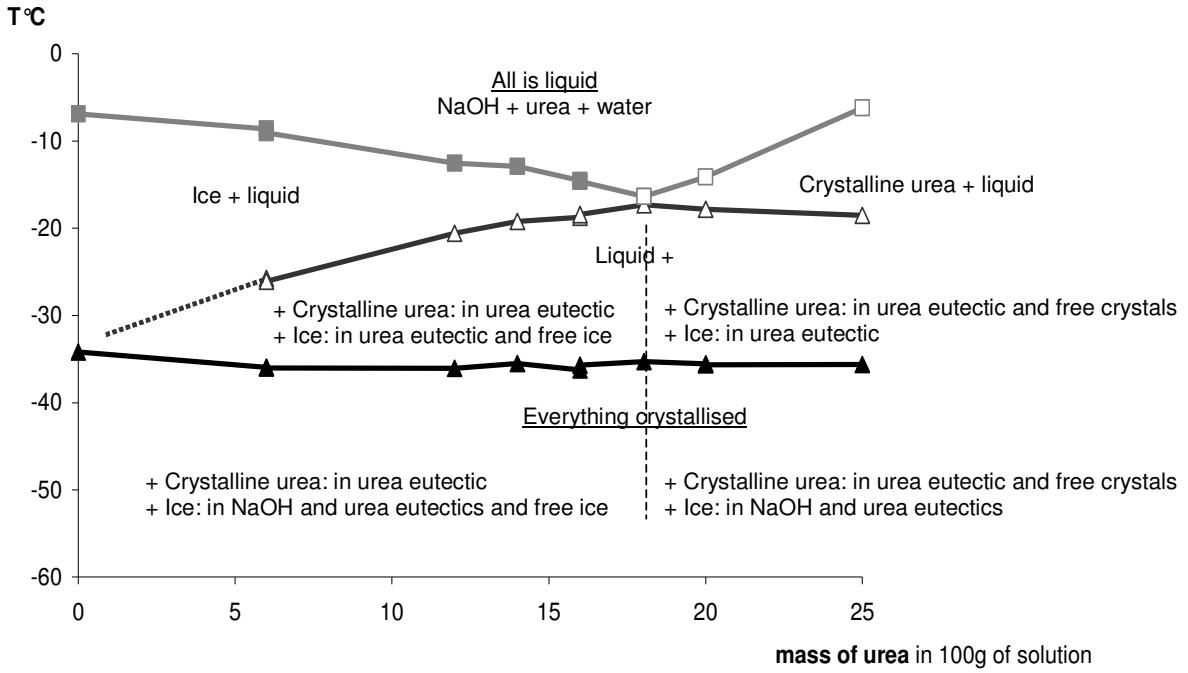


Fig.III.2-11: Ternary phase diagram for 7.6NaOH / (0-25)urea / water solution
full triangle: melting of NaOH eutectic mixture; open triangle: melting of the urea eutectic mixture;
full square: melting of free ice; open square: melting of free urea

We saw that NaOH and urea are forming both their normal eutectic mixture with water – $NaOH,5H_2O$+$4H_2O$ and urea+$8H_2O$ respectively. This means that they are not interacting but they are competing for water. In 100 g of solution:

- at $m_{urea} < 18$ g, there is enough water for both compounds to feel independent.
- at $m_{urea} = 18$ g, there is no free water in solution, all water molecules are linked either to the NaOH eutectic mixture or to the urea eutectic mixture.
- at $m_{urea} > 18$ g, there is not enough water for both eutectics. Because of a strong polarity of NaOH (pairs of ions), the water molecules surrounding the Na^+ and OH^- ions in solution are more strongly linked to NaOH molecules than water molecules surrounding urea molecules. Consequently, the NaOH eutectic mixture is thermodynamically easier to form than the urea eutectic mixture. This explains that the melting peak of NaOH eutectic mixture appears for all the urea concentrations studied and that, at urea concentrations higher than 18 g in 100 g of solution, pure urea is present in the system.

NaOH, urea and water behave as in their binary situations.

III.2.3- NaOH/ZnO/water ternary system

The goal of this section is to understand how sodium hydroxide and zinc oxide are reacting when they are put together in water.

From literature [LIU1998], we know that ZnO can be dissolved in acid or strongly basic aqueous solutions (Fig.III.2-12). Moreover, dissolving ZnO, in solid state (s), induces some reactions with OH^- to form zinc hydroxyl ions; the major species at high alkalinity are $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ (Fig.III.2-13) [DIR1954] [REI1975] [BEN1999], according to the following equilibrium equations:

$$ZnO_{(s)} + H_2O + OH^- \rightleftharpoons Zn(OH)_3^-$$

$$ZnO_{(s)} + H_2O + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$$

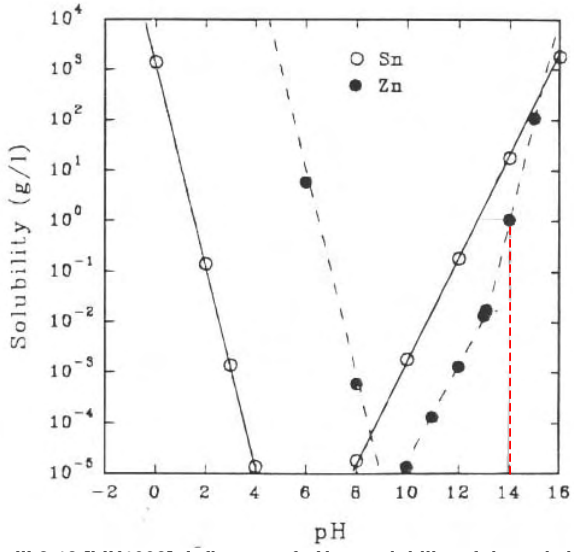


Fig.III.2-12 [LIU1998]: Influence of pH on solubility of tin and zinc

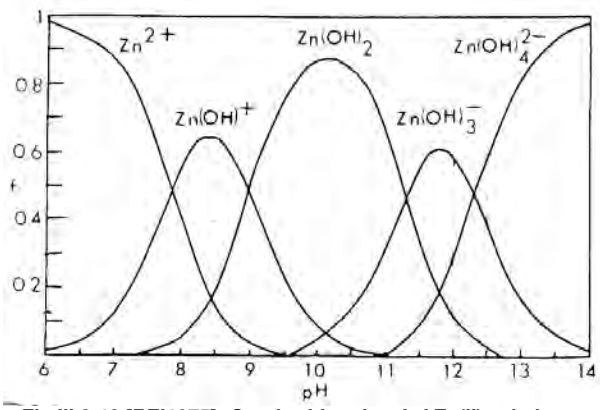


Fig.III.2-13 [REI1975]: Graph of fraction *f* of Zn(II) existing as Zn^{2+}, $Zn(OH)^-$, $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$ over a range of *pH* at 25°C.

As soon as ZnO is added to a NaOH/water solution, the above reactions occur to totally dissolve ZnO crystals. Consequently, the structure of the alkaline solutions should be modified

by the presence of ZnO. In the forthcoming sections, we will compare the two aqueous solvents – NaOH/water and NaOH/ZnO/water – by viscosimetry, NMR, and DSC.
The mixtures that we used contained up to 20 g of NaOH (without ZnO, this corresponds to the eutectic mixture) and up to 1.84 g of ZnO in 100 g of solution.

III.2.3.1. Viscosity of dilute NaOH/ZnO/water solutions

We measured the viscosity of the NaOH/water and NaOH/ZnO/water solutions during their dilution with water with an Ubbelohde capillary viscometer (see description in II.3.3.2). The initial compositions were 12 g of NaOH and 1.1 g of ZnO in 100 g of solution. As water is the solvent, ZnO concentration decreases upon dilution in the same way as NaOH concentration and the ratio ZnO/NaOH is constant. That is why, on Fig.III.2-14, the relative viscosity is plotted versus NaOH concentration.

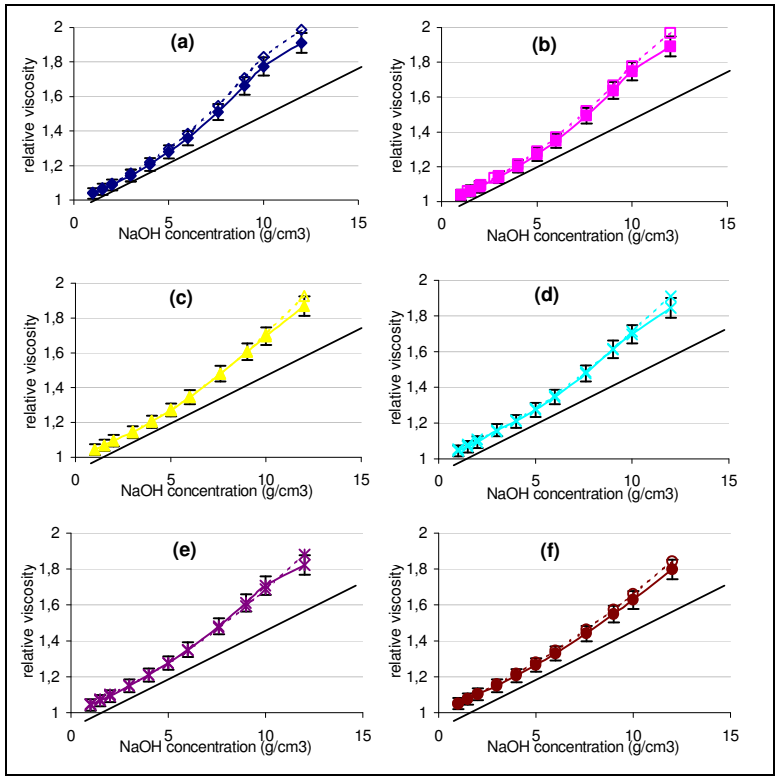


Fig.III.2-14: Relative viscosity versus NaOH concentration, comparison of NaOH/water solution (—) and NaOH/ZnO/water solution (----) (a) 12°C; (b) 15°C; (c) 20°C; (d) 25°C; (e) 30°C and (f) 40°C.
Initial compositions: 12NaOH/water and 12NaOH/1.1ZnO/water where NaOH/ZnO=cst for all measurements.

Whatever the temperature is, from +12°C to +40°C, the relative viscosities of the mixtures versus NaOH concentration curves are not linear. This means that the solvents are not simple solutions but that some intermolecular associations and interactions take place, in agreement with the fact that there is a complex solvation of the NaOH ions [BAR1954] [KUN1985] [YAM1988].
We can note that the relative viscosity of NaOH/water is the same as NaOH/ZnO/water, within the experimental errors. We can conclude that the formation of zinc hydroxyls, during

ZnO dissolution in NaOH/water, does not significantly influence the main non linear effect of viscosity due to the interactions between NaOH and water.

III.2.3.2. NMR study

This work was performed in the group of Dr Hans-Peter Fink in the Fraunhofer Institute in Gölm, Germany. The full report is in Appendix 5.

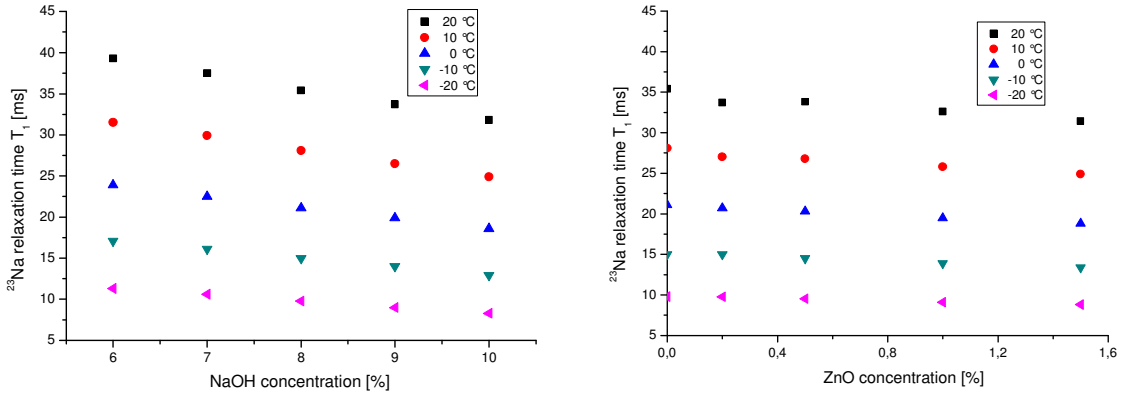
^{1}H and ^{23}Na nuclei were analysed by NMR in NaOH/water with compositions of (6-10)NaOH/water, with or without the addition of (0.2-1.5)g of ZnO. Temperature was varied between -20°C and 20°C. Two parameters were studied, the chemical shift and the spin lattice time T1 which expresses the mobility of the nuclei, influenced by the environment.

The purpose of the work was to investigate the hydration behaviour of the Na^{+} ions influenced or not by temperature variation and the presence of ZnO.

^{23}Na

The relaxation time T1 of ^{23}Na decreases with temperature due to the variation of viscosity and with NaOH concentration (also due to the viscosity increase). Addition of ZnO is slightly decreasing the relaxation time, this effect being more pronounced with increasing ZnO concentration and solution temperature (Fig.III.2-15 and Appendix 5).

The chemical shift for ^{23}Na is increasing with decreasing temperature or increasing NaOH, also due to viscosity changes. The chemical shift is not affected by the presence of ZnO.



for the lyes **for 8% lye with ZnO**

Fig.III.2-15: Results of ^{23}Na relaxation times

^{1}H

The experiments with ^{1}H show that the relaxation time T1 decreases with increasing NaOH concentration, which may reflect either a change of viscosity/mobility or a difference in the free/bound water mole fraction. There is no influence of the addition of ZnO.

Conclusion on the NMR analysis

The conclusion of the authors is that there is no change in the hydration of Na^+ ions in the temperature/concentration range explored since any change should give non linear characteristic of the relaxation times or the chemical shifts as a function of NaOH concentration. Only linear regimes were found.
As far as ZnO is concerned, the experiments do not show any influence of the addition of this compound. There is no major change like the formation of a complex between ZnO and NaOH. This is in agreement with the viscosity measurements reported above.

III.2.3.3. DSC results

As ZnO reacts with OH^- to form zinc hydroxyl ions and as ZnO is not soluble in water, the number of Na^+/OH^- ion pairs should decrease. Consequently, the formation of the NaOH eutectic mixture should be disrupted by the addition of ZnO and DSC thermograms should reveal a smaller melting peak of NaOH eutectic than the one of NaOH solutions without ZnO.
Fig.III.2-16 shows DSC thermograms for 20NaOH/(0-1.84)ZnO/water solutions. Without ZnO, this NaOH concentration corresponds to the eutectic mixture and there is no free water crystallising. This figure shows a constant decrease of melting temperature (measured at the onset of the peak) and of melting enthalpy of the NaOH eutectic peak when ZnO concentration increases (Tab.III.2-8), and no melting of ice.

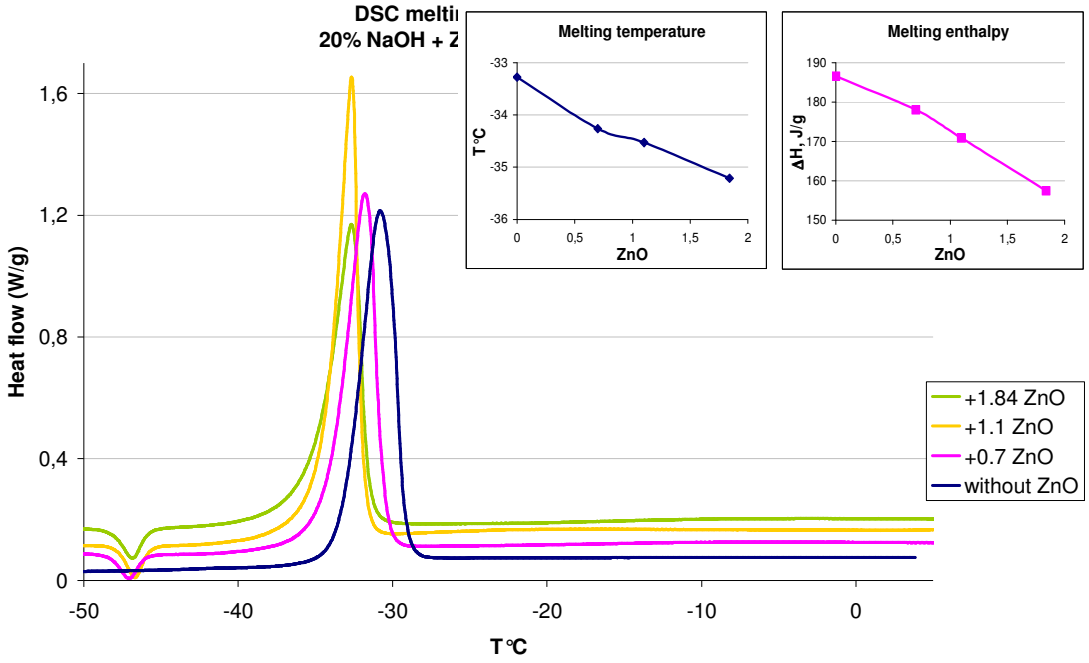


Fig.III.2-16: DSC melting thermograms for 20NaOH /x ZnO/water solutions (x= 0, 0.7, 1.1, and 1.84). This melting peak corresponds to the melting of the metastable NaOH eutectic mixture. The changes of this NaOH eutectic peak (melting temperature and melting enthalpy) versus ZnO concentration are represented on inset graphs.

Peak of the NaOH eutectic mixture

Melting temperature

If we look at the melting temperature of the eutectic peak (Fig.III.2-16 and Fig.III.2-8), we can note that the decrease is constant when ZnO concentration increases. This means that the NaOH eutectic mixture is crystallising in the presence of liquid which contains at least ions involving Zn. According to the equilibrium reactions of ZnO dissolution in alkali solutions and Fig.III.2-13, these ions could be $Na^+/Zn(OH)_3^-$ and $2Na^+/Zn(OH)_4^{2-}$.

Melting enthalpy

The constant decrease of melting enthalpy (Fig.III.2-16 and Tab.III.2-8) confirms that some NaOH molecules react with ZnO. According to the literature [DIR1954] [REI1975] [BEN1999], at pH>12, the major species in solution are $Zn(OH)_3^-,Na^+$ and $Zn(OH)_4^{2-},2Na^+$ (Fig.III.2-13), thus one or two NaOH should be linked to ZnO.

The number of NaOH having participated to the ZnO dissolution can be determined from the decrease of the peak since these NaOH molecules cannot participate to the crystallisation of the eutectic mixture $NaOH,5H_2O+4H_2O$:

$$f_{NaOH\,.not\cdot in\cdot eut} = 1 - f_{eut} = 1 - \frac{\Delta H_{eut,\exp.}(m_{ZnO})}{\Delta H_{eut,pure}}$$

$$NaOH/ZnO = f_{NaOH\cdot not\cdot in\cdot eut} \times \frac{m_{NaOH} \times M_{ZnO}}{M_{NaOH} \times m_{ZnO}} \qquad \textbf{Eq. 9}$$

where m_{NaOH}=20g, m_{ZnO} is the mass of ZnO in solution, M_{NaOH}=40g/mol and M_{ZnO}=81.4g/mol.

The results are reported in the Tab.III.2-8.

xZnO in 20NaOH/water	**Tm_{eut} (°C)**	**ΔH_{eut} (J/g)**	***NaOH/ZnO*** Eq.9	***H_2O/ZnO*** Eq.11
0	-33.3	187=$\Delta H_{eut\ pure}$		
0.7	-34.3	178	2.8	14
1.1	-34.5	171	3.2	20
1.84	-35.2	157	3.5	25

Tab.III.2-8: Melting temperature and enthalpy of the NaOH eutectic peak (columns 2 & 3) as a function of ZnO concentration in 20NaOH/xZnO/H_2O solutions (x= 0, 0.7, 1.1, and 1.84), columns 4 & 5 give the calculated ratios *NaOH/ZnO* and *H_2O/ZnO* necessary to dissolve ZnO.

We see that about 3NaOH are linked to each ZnO whereas the literature is suggesting a value of one and two.

From these values, an extrapolation of the eutectic melting enthalpy to zero gives a limit of ZnO dissolution in 20NaOH/water at about 12g ZnO in 100g of solution. This concentration corresponds to a calculated molar ratio (eq.9) $NaOH/ZnO$=3.4. This result does not correspond to our solubility experiments since we measured that ZnO can be dissolved in NaOH up to a

maximal molar ratio NaOH/ZnO=10 (i.e. about 4g of ZnO in 100g of solution containing 20g of NaOH).

Peak of free ice

We know that the 20NaOH/water solution without ZnO is only composed of the NaOH eutectic and that there is no free water. In that case, the DSC melting thermogram has just one melting peak at -33.4°C.
Dissolving ZnO in highly basic solution induces reaction with NaOH. So water molecules initially surrounding NaOH should be released and thus should crystallise as free water. This is not the case since no melting peak of free ice appears on the DSC thermograms of solutions containing ZnO (Fig.III.2-16). All the water molecules present in solution are linked to other species that prevented them to freeze as ice.

We also studied mixtures with a lower NaOH content (12NaOH/water), where the melting peak of free ice was observed when ZnO is added. For the 12NaOH/ZnO/water solutions, the NaOH eutectic could not crystallise most probably because the lowest temperature of the DSC oven was not low enough to induce crystallisation. Consequently, only the melting peak of free ice appears (Fig.III.2-17) and we can note that its melting temperature and enthalpy remain constant at all ZnO concentrations. This means that the quantity of free water is always the same, even after ZnO addition.

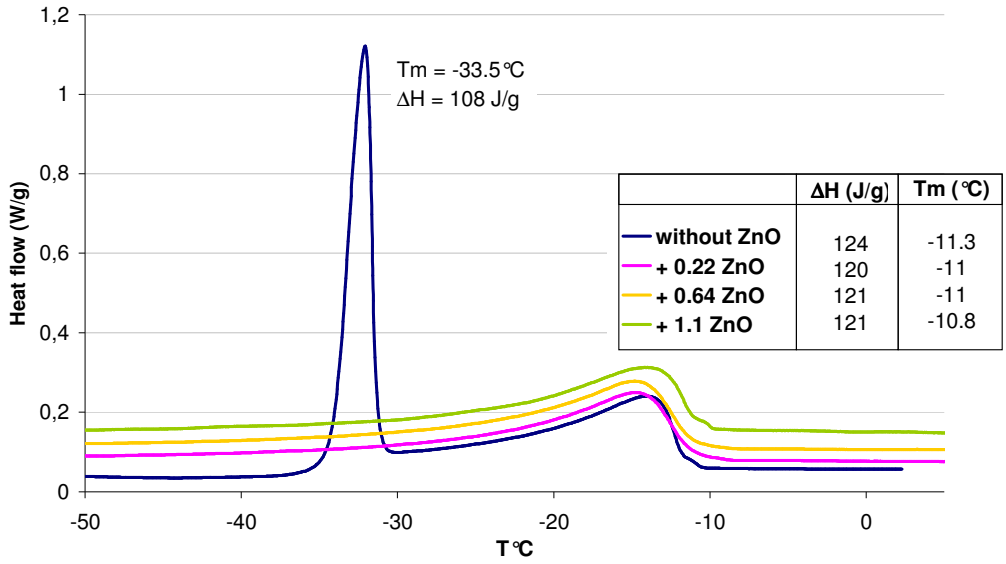


Fig.III.2-17: DSC melting thermograms of 12NaOH/xZnO/water solutions (x=0, 0.22, 0.64, 1.1) with melting enthalpy and temperature of free ice.
The melting peak of NaOH eutectic does not appear because the temperature of the cooler was not low enough.

We will calculate in the following how many water moles are surrounding the ions involving ZnO. This calculation will be performed for the 20NaOH/ZnO/water solution since it was the only one showing a decrease of the NaOH eutectic peak, thus allowing calculating the number of NaOH moles involved in a reaction with ZnO.

The total number of moles of water '$n_{tot.w}$' in solution is:

$$n_{tot.w} = \left(\frac{100 - m_{NaOH} - m_{ZnO}}{M_{H2O}} \right) = \frac{80 - m_{ZnO}}{18}$$

The number of moles of water linked to NaOH to form the eutectic mixture '$n_{eut.w}$' is:

$$n_{eut.w} = \left(f_{eut} \times \frac{m_{NaOH}}{M_{NaOH}} \right) \times 9 = \frac{\Delta H_{eut,\exp.}(m_{ZnO})}{\Delta H_{eut,pure}} \times 4.5$$

where m_{NaOH}=20g, m_{ZnO} is the mass of ZnO in solution, M_{H2O}=18g/mol, M_{NaOH}=40g/mol and M_{ZnO}=81.4g/mol.

According to the dissolution reactions, whatever the zinc hydroxyl ion formed is, one water molecule reacts with one ZnO and thus cannot participate to the eutectic crystallisation:

$$n_{dissol.w} = n_{ZnO} = \frac{m_{ZnO}}{M_{ZnO}}$$

Thus we can determine how many water molecules '$n_{surr.w}$' are surrounding the ion pairs. These water molecules are not free and can not participate to the melting peak of free ice.

$$n_{surr.w} + n_{dissol.w} = n_{tot.w} - n_{eut.w}$$

$$n_{surr.w} + n_{ZnO} = \frac{80 - m_{ZnO}}{18} - \frac{\Delta H_{eut,\exp.}(m_{ZnO})}{\Delta H_{eut,pure}} \times 4.5 \qquad \textbf{Eq. 10}$$

Thus, if Eq.10 is divided by n_{ZnO}, the ratio H_2O/ZnO is obtained and corresponds to the quantity of water necessary to dissolve ZnO in alkali solutions.

$$H_2O/ZnO = \frac{n_{surr.w} + n_{ZnO}}{n_{ZnO}} \qquad \textbf{Eq. 11}$$

The values are reported in the Tab.III.2-8. We can note that the number of moles of water linked to ZnO increases with ZnO content.

If we assume that 25 moles of water per ZnO is necessary for the ZnO dissolution in NaOH/water, it is possible to calculate the dissolution limit since the number of water molecules surrounding ZnO has to be equalled to the number of water molecules not crystallised in NaOH eutectic mixture. We obtain the following equation:

$$n_{tot.w} - n_{eut.w} = n_{ZnO.w} \qquad \textbf{Eq. 12}$$

where $n_{ZnO.w}$ is the number of water molecules involved in ZnO dissolution $= 25 \times \frac{m_{ZnO}\lim}{M_{ZnO}}$ and $n_{eut.w}$ the number of water molecules crystallised in NaOH eutectic mixture $= 9 \times n_{NaOH.eut}$ $= 9 \times (n_{NaOH.tot} - n_{NaOH.with..ZnO}) = 9 \times \left(\frac{m_{NaOH}}{M_{NaOH}} - 3.4 \times \frac{m_{ZnO}\lim}{M_{ZnO}} \right)$, where $n_{NaOH.with.ZnO}$ represents the number of NaOH molecules involved in ZnO dissolution, 3.4 being the ratio $NaOH/ZnO$ determined from the extrapolation of melting enthalpy.

Substituting these expressions in the Eq.12 gives:

$$\frac{100 - m_{NaOH} - m_{ZnO}\lim}{M_{H2O}} - 9\times\left(\frac{m_{NaOH}}{M_{NaOH}} - 3.4\times\frac{m_{ZnO}\lim}{M_{ZnO}}\right) = 25\times\frac{m_{ZnO}\lim}{M_{ZnO}}$$

$$m_{ZnO}\lim\left(\frac{5.6}{M_{ZnO}} - \frac{1}{M_{H2O}}\right) = 9\times\frac{m_{NaOH}}{M_{NaOH}} - \frac{100 - m_{NaOH}}{M_{H2O}}$$

Thus, $\boxed{m_{ZnO}\lim = 4.2g}$ in 100g of 20NaOH aqueous solution.

This calculation suggests that ZnO can be dissolved in 20NaOH/water solution up to about 4.2g. This concentration corresponds to a 0.052mol of ZnO in 0.5mol NaOH. The calculated limit of ZnO dissolution is reached when NaOH/ZnO=10 which corresponds to our experimental data, with the assumption that 25 moles of water are necessary for dissolving ZnO.

III.2.3.4. Conclusion on the NaOH/ZnO/water system

Intermolecular interactions take place in NaOH/water and NaOH/ZnO/water systems which are reflected by the non-linear dependence of the relative viscosity upon dilution. It seems that ZnO does not influence the structure of the NaOH/water complexes, at least seen from viscometric measurements and NMR analyses.

On the other hand, DSC analyses reveal significant changes in NaOH/water system when ZnO is added:

- During dissolution, ZnO reacts with NaOH to form zinc hydroxides, $NaZn(OH)_3$ and $Na_2Zn(OH)_4$ according to literature. As a consequence, some NaOH molecules are not anymore able to form the NaOH eutectic mixture and its melting peak decreases. About 3NaOH/ZnO is involved in the dissolution.
- The quantity of water crystallizing as free ice does not change with the addition of ZnO: the melting enthalpy of free ice remains constant. Some water molecules are involved in the dissolution reactions – $1H_2O$/ZnO – and some other are surrounding the ions in solution. The total ratio H_2O/ZnO increases up to 25, when ZnO concentration increases from 0 to 1.8g in 100g of solution.

From these results we also determined that ZnO needs not only Na^+/OH^- ions but also a large quantity of water to be dissolved. With the assumption that 25 water molecules are needed for dissolving one molecule of ZnO, the limit of ZnO dissolution is reached for a NaOH/ZnO molar ratio equals to 10, value in agreement with our solubility experiment.

Finally, the NaOH eutectic mixture is crystallising in presence of a liquid containing zinc hydroxides, some sodium hydroxide and water molecules. That is why the NaOH eutectic melting temperature decreases when ZnO content increases. This may also explain why, in some cases, the NaOH eutectic peak does not appear when we analyse solutions containing ZnO.

III.2.4- Conclusions on the structure of cellulose solvents: NaOH/water, NaOH/urea/water and NaOH/ZnO/water

The NaOH/water binary phase diagram obtained from DSC experiments is in agreement with the ones reported in literature [PIC1893] [COH1960] [ROL1964].

The NaOH/water and urea/water binary systems have both typical eutectic behaviours:

- Below the eutectic composition (NaOH content lower than 20g and urea content lower than 29.4g, in 100g of solution), free ice is crystallising and its melting temperature decreases with the increase of NaOH or urea concentrations.
- The eutectic mixture is melting at a constant temperature for all concentrations. For sodium hydroxide aqueous solutions, the eutectic mixture is composed of $NaOH,5H_2O$ and $4H_2O$ and melts at -33.4°C. For urea aqueous solutions, the eutectic compound is a mixture of 1urea and $8H_2O$, it melts at -11.4°C.
- At concentrations higher than the eutectic composition, the components that are crystallising are $NaOH,5H_2O$ and urea for sodium hydroxide aqueous solutions (from 20g NaOH to 31g NaOH in 100g of solution) and for urea aqueous solution (higher than 29.4g of urea in 100g of solution) respectively. Their melting temperature increases with the increase of NaOH and urea concentrations.

The 7.6NaOH/urea/water ternary system has a particular behaviour. Actually, the two NaOH and urea eutectic mixtures are forming independently and are competing for water molecules. Because of the strong polarity of sodium hydroxide, NaOH is attracting water more than urea.

In the NaOH/ZnO/water ternary system, some NaOH and water molecules react with ZnO to dissolve it and to form zinc hydroxides. The NaOH molecules not involved in ZnO dissolution are crystallising in eutectic mixture. Its' melting temperature decreases with the increase of ZnO content because the NaOH eutectic is crystallising in presence of liquid containing zinc hydroxides and its surrounding molecules (water and probably NaOH).
We determined that during dissolution ZnO is trapping about 3NaOH and 25 water molecules.

III.3- STRUCTURE OF CELLULOSE SOLUTIONS IN NAOH/WATER, NAOH/UREA/WATER AND NAOH/ZNO/WATER

III.3.1- Cellulose/NaOH/water ternary solutions

III.3.1.1. DSC results on Avicel/NaOH/water

The goal of this part is twofold: (i) to determine the concentration limit of cellulose that can be dissolved in sodium hydroxide and (ii) to propose a mechanism of cellulose dissolution by determining the amount of NaOH and H_2O linked to cellulose. To do this, we will use microcrystalline cellulose, pure and of low DP.

In part III.2.1-, we studied the NaOH/water solvent from DSC analyses. We described the methodology used to determine the fraction of each compound present in the system from its melting enthalpy and we plotted the phase diagram. We will base our research on the same technique and approach.

Most of the studies were performed on cellulose/7.6NaOH/water systems. Cellulose content was varied from 0 to 7.6g in 100g of solution. In order to check the influence of NaOH concentration, cellulose/8NaOH/water solutions were also tested. In all cases studied the condition of being inside the domain of the phase diagram [SOB1939] where cellulose can be dissolved in NaOH/water was fulfilled.

An example of DSC melting thermograms for solutions of different cellulose concentrations is given in Fig.III.3-1. Melting temperature and enthalpy of each peak for the curves shown and for some other cellulose concentrations are presented in Tab.III.3-1. The analysis of the peak at lower and higher temperatures is discussed below.

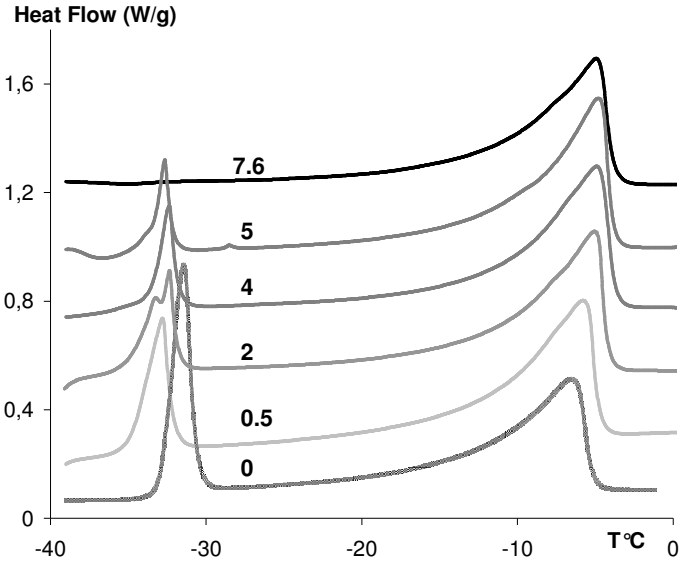


Fig.III.3-1: DSC melting thermograms of Avicel cellulose/7.6NaOH/water solutions.
Cellulose content is indicated on the graph. 0 corresponds to a 7.6NaOH/water solution without cellulose.
Curves are shifted vertically for a better visibility.

Avicel	"eutectic" peak		"ice" peak	
X g in a 100g solution	T_m (onset), °C	ΔH_{eut}, J/g	T_m (end), °C	ΔH_{ice}, J/g
0	-32.9	72	-5.1	195
0.5	-34.9	50	-4.8	205
1	-33.7	43	-4.1	200
2	-33.5	41	-4.3	205
3	-33.2	30	-3.9	210
4	-33.4	29	-3.7	209
5	-33.5	22	-3.9	217
7.6	No peak	-	-3.8	178

Tab.III.3-1: Melting temperatures and enthalpies of the peaks at lower and higher temperatures for Avicel/7.6NaOH/water solutions.

Avicel	"eutectic" peak		"ice" peak	
X g in a 100g solution	T_m (onset), °C	ΔH_{eut}, J/g	T_m (end), °C	ΔH_{ice}, J/g
0	-33.2	74	-5.9	187
1	-34.6	52	-5.9	180
3	-33.9	34	-5.2	175
5	-33.8	25	-4.7	178

Tab.III.3-2: Melting temperatures and enthalpies of the peaks at lower and higher temperatures for Avicel/8NaOH/water solutions.

III.3.1.2. Peak at low temperature. Limit of cellulose dissolution

Whatever are the concentrations of Avicel cellulose and of the solvent, the melting temperature of the peak at lower temperature is constant (Tab.III.3-1 and Tab.III.3-2), within the experimental errors. It practically coincides with the melting temperature of the eutectic mixture in pure aqueous sodium hydroxide solution of 7.6NaOH/water and 8NaOH/water (without cellulose) but with a systematic shift of about 1°C towards lower temperatures. This means two things. First, the same eutectic mixture – $NaOH,5H_2O + 4H_2O$ – is present in cellulose/sodium hydroxide aqueous solutions in this region of temperatures and cellulose concentrations, in (7.6-8)NaOH/water, owing to the fact that the temperature shift is very small. The presence of cellulose is not perturbing the composition of solvent system. Second, because of the addition of cellulose, the molecular environment of the NaOH eutectic mixture has changed, even slightly. Consequently, crystallization and melting of the eutectic mixture are disrupted which induces a slight shift in the melting temperature. A similar behaviour was observed after the addition of urea in NaOH/water solution (see part III.2.2.2). Moreover, we will see in the next paragraph that this change due to the presence of cellulose is also visible in the melting peak of pure water.

The results obtained mean that we are not here in the presence of a ternary phase diagram where each of the components makes eutectic mixtures two by two. Cellulose does not form either covalent bond or eutectic mixture with water and NaOH. Nevertheless, the presence of cellulose

is drastically changing the amount of the NaOH/water eutectic mixture. The influence of cellulose concentration on the eutectic peak can be seen from the variation of enthalpy values: the enthalpy decreases down to zero with the increase of cellulose concentration (see Fig.III.3-1 – curve in bold corresponding to m_{cell}=7.6g does not show any eutectic peak at -33.4°C). This means that cellulose interacts with sodium hydroxide. The higher is the cellulose concentration, the smaller is the amount of eutectic mixture that can crystallise and then melt at -33.4°C. Since NaOH is present only in the eutectic mixture, the decrease of its melting enthalpy allows the calculation of the number of NaOH molecules linked to cellulose and thus not able to participate to $NaOH,5H_2O$ crystal fraction of the eutectic mixture.

The eutectic melting enthalpies (Tab.III.3-1 and Tab.III.3-2) enable (i) to determine the limit of cellulose dissolution and (ii) to calculate how many NaOH are linked to the cellulose, for all the cellulose concentrations.

Limit of cellulose dissolution

Fig.III.3-2 represents the dependence of eutectic melting enthalpy on cellulose concentration, for cellulose/7.6NaOH/water solutions.

The fact that ΔH_{eut} is reaching zero at a certain Avicel cellulose concentration means that all sodium hydroxide molecules have been trapped by the cellulose chains. This corresponds to the dissolution limit since there is no more NaOH molecules able to solvate any additional cellulose chain that could be brought in the mixture. At this dissolution limit, we can calculate the proportion between cellulose anhydroglucose unit (AGU) and NaOH molecules. In this case, in 100g of cellulose/NaOH/water solution, there are 7.6g of cellulose and 7.6g of NaOH when the eutectic peak disappears. As the molar mass of NaOH is 40 while the molar mass of an anhydroglucose unit is 162, it gives that four NaOH molecules are associated to each AGU.

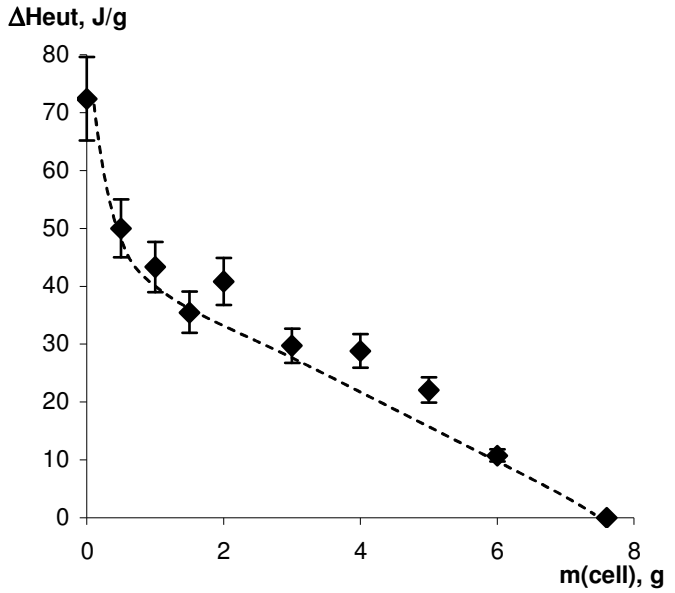


Fig.III.3-2: Eutectic melting enthalpy (J/g) versus cellulose concentration for the Avicel cellulose/7.6NaOH/water system.
The dashed line is given to guide the eyes.

The other data obtained for Avicel/8NaOH/water solutions (Tab.III.3-2) as well as the ones reported in the ref. [ROY2001], where Avicel cellulose was dissolved in 9%NaOH/water, give very similar results. In order to compare the results for all these systems and to avoid the influence of NaOH concentration, we plotted reduced melting enthalpy versus reduced cellulose concentration (Fig.III.3-3). The reduced eutectic enthalpy corresponds to the enthalpy of the eutectic peak at X% of cellulose, $\Delta H_{eut,X\%cell}$, divided by the one at m_{cell} =0, $\Delta H_{eut,0cell}$. The reduced cellulose concentration corresponds to the cellulose weight divided by the one of NaOH.

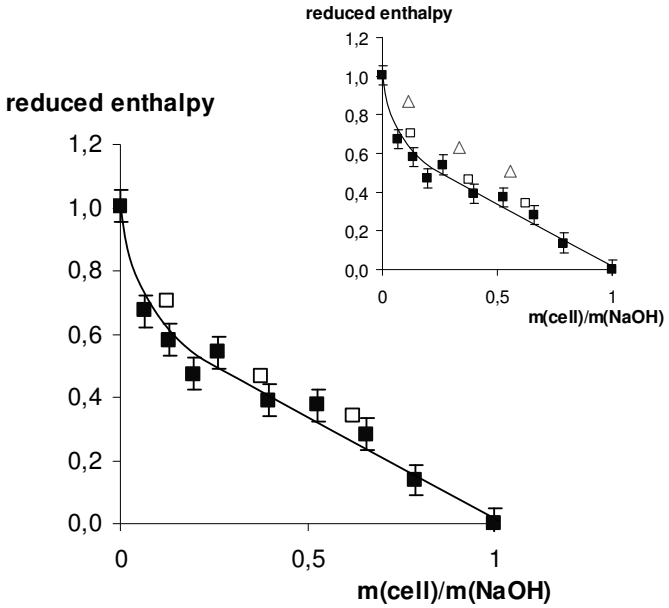


Fig.III.3-3: Reduced melting enthalpy versus reduced cellulose concentration m_{cell}/m_{NaOH} for Avicel/7.6NaOH/water (■) and for Avicel/8NaOH/water (□).
***Inset:* the results for Avicel in 9%NaOH/water from [ROY2001] were added (△)**
The lines are given to guide the eyes

For the three systems studied, the decrease of the reduced melting enthalpy is reaching zero at m_{cell}/m_{NaOH}=1.

- This means that the maximum Avicel cellulose concentration for having a proper dissolution is equal to the sodium hydroxide concentration in weight per cent. At this concentration, all the NaOH molecules are associated with the cellulose. Consequently, the dissolution of further added cellulose should not be possible. Above this concentration, cellulose can not fully dissolve and could form cellulose aggregates.

Number of NaOH and H_2O molecules linked to cellulose

Tab.III.3-1 and Tab.III.3-2 allow the calculation of the proportion between AGU and NaOH for the other cellulose concentrations. The fraction of eutectic linked $f_{eut.linked}$ to cellulose is as follows:

$$f_{eut\cdot linked} = \frac{\Delta H_{eut,0\%cell} - \Delta H_{eut,X\%cell}}{\Delta H_{eut,0\%cell}} \qquad \textbf{Eq. 13}$$

Thus the amount of eutectic (or NaOH) linked to cellulose, in moles, is given by

$$n_{NaOH} / AGU = f_{eut,linked} \frac{m_{NaOH}}{M_{NaOH}} \frac{M_{AGU}}{m_{cell}} \qquad \textbf{Eq. 14}$$

The amount of NaOH molecules linked to one anhydroglucose unit as a function of reduced cellulose concentration m_{cell}/m_{NaOH} for the system Avicel/7.6NaOH/water and for Avicel/8NaOH/water is shown in Fig.III.3-4. At $m_{cell}/m_{NaOH} > 0.4$ the proportion between AGU and NaOH molecules is constant and equal to the limit of cellulose dissolution which is four NaOH per AGU. At low cellulose concentrations, $m_{cell}/m_{NaOH} < 0.25$, up to 20 NaOH molecules seem to be linked to one anhydroglucose unit. The change of the slope in Fig.III.3-4 as well as in Fig.III.3-3 may be caused by the transition of cellulose solution from the dilute to semi-dilute state. In ref. [ROY2003], the overlap concentration for Avicel in 9%NaOH/water was reported to be $C_{cell} \approx 1\%$. Fig.III.3-4 shows that the slope changes at $C_{cell} \approx 1.5\text{-}2\%$ (here $C_{cell}=m_{cell}$). It may be possible that due to the sterical hindrance caused by the transition from dilute to the semi-dilute state, the number of NaOH molecules linked to cellulose strongly decreases.

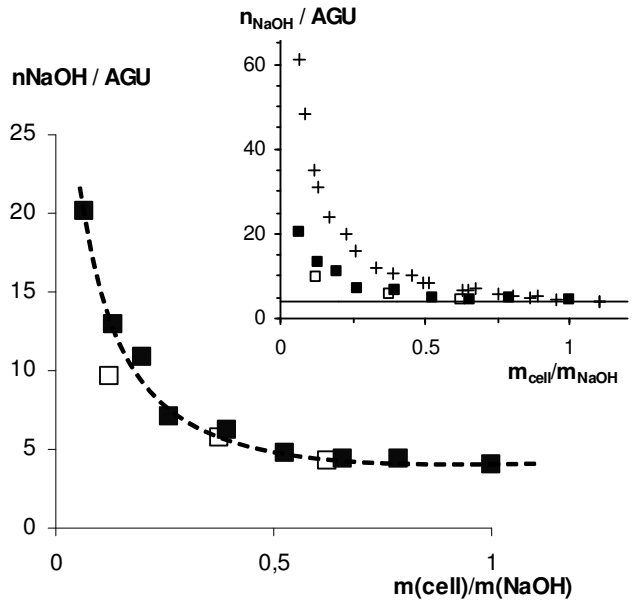


Fig.III.3-4: Number of NaOH molecules linked to one anhydroglucose unit (AGU), calculated from melting enthalpy data, versus cellulose/NaOH weight ratio for cellulose/7.6NaOH/water (■) and cellulose/8NaOH/water (□)
Inset: the same data (squares) and the ones from ref. [KUO2005] for NaOH concentrations of 4.5, 6.2 and 7.9%.
The dashed line is given to guide the eyes.

The same proportion between NaOH and anhydroglucose unit corresponding to the limit of cellulose dissolution, four NaOH per AGU, can be obtained from the study of Avicel solubility in NaOH aqueous solutions of different concentrations [KUO2005]. Using turbidimetry, authors

measure the amount of undissolved cellulose as a function of cellulose and NaOH concentration. We recalculated their data as the weight of NaOH per one gram of dissolved cellulose, converted the obtained figures into mole ratios and plotted together with our data as a function of m_{cell}/m_{NaOH}. The result is presented in the inset of Fig.III.3-4 : at higher cellulose concentrations, the results of ref. [KUO2005] coincide with the ours' and show that at least 4 NaOH molecules are needed to dissolve one AGU. At low cellulose concentrations, $m_{cell}/m_{NaOH} < 0.25$, the amount of NaOH linked to one anhydroglucose unit calculated from ref. [KUO2005] is twice higher than obtained by us using DCS technique. In general, it is not clear how and why so many NaOH molecules can be bound to one anhydroglucose unit. However, this is not an artefact since the proportion (20-50)NaOH per one AGU at cellulose concentrations around 1-2% was obtained independently by different methods.

III.3.1.3. Peak at high temperature

Fig.III.3-1, Tab.III.3-1 and Tab.III.3-2 show that the temperature of the melting peak at higher temperatures is slightly increasing when increasing the cellulose concentration. Again, this change is small, as in the case of the eutectic peak. This increase of the melting temperature of ice with increasing cellulose concentration reflects the fact that the molecular environment of the crystallizing water is changed when cellulose is trapping NaOH.

The proportion between water, NaOH and cellulose molecules can be calculated as follows. In cellulose/NaOH/water solutions, H_2O is present in three forms or compounds:

- as a free water frozen to ice below the liquidus curve,
- in the eutectic mixture that is not linked to cellulose and
- in the mixture linked to cellulose through NaOH.

As far as the amount of free water is not changing with adding cellulose (see ΔH_{ice} in Tab.III.3-1 and Tab.III3.-2), it means that the number of water molecules linked to NaOH that are bound to cellulose is the same as in the eutectic mixture. The number of water molecules linked to one anhydroglucose unit is then straightforward to calculate: it is a product of n_{NaOH} x 9; n_{NaOH} calculated according to Eq.14 and nine being the amount of water molecules in the eutectic mixture.

III.3.1.4. Influence of cellulose origin on the structure of cellulose/NaOH/water solutions

This part is a preliminary quantitative study on the influence of cellulose origin on the structure of cellulose/NaOH/water solutions. The nature of cellulose pulp highly influences the cellulose dissolution and the stability of solutions. Using DSC analysis with the methodology described previously, it should be possible to determine the limit of cellulose dissolution and thus how many NaOH and water molecules are linked to the cellulose chain for other cellulose than Avicel.

The cellulose samples used in this part are:

- steam-exploded Borregaard cellulose with a DP of 407 (B407)

- irradiated Lenzing cellulose with a DP of 307 (L307), before the irradiation treatment it is called Solucell 1175 (part II.1.1)
- regenerated Lenzing cellulose II with a DP of 198 ($L198_{II}$), this cellulose also comes from the Solucell 1175.

Fig.III.3-5 represents the DSC melting thermograms of 5cellulose/7.6NaOH/water solutions, cellulose being $L198_{II}$, L307 and B407. The results were compared with the one of Avicel cellulose (DP170), described above. The values of melting temperatures and enthalpies are listed in Tab.III.3-3.

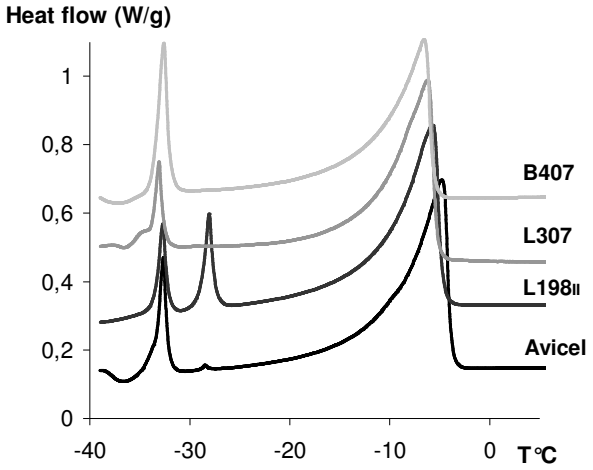


Fig.III.3-5: DSC melting thermograms of 5cellulose/7.6NaOH/water solutions. Cellulose origins are indicated on the graph.
Curves are shifted vertically for a better visibility.

5cellulose/7.6NaOH/water	"eutectic" peak		"ice" peak	
	T_m (onset), °C	ΔH_{eut}, J/g	T_m (end), °C	ΔH_{ice}, J/g
Avicel	-33.5	22	-3.9	217
$L198_{II}$	-33.7 / -29.2	33	-4.7	187
L307	-34.1	24	-5.3	226
B407	-33.8	30	-5.6	189

Tab.III.3-3: Melting temperatures and enthalpies of the peaks at lower and higher temperatures for cellulose of various origins in 5cellulose/7.6NaOH/water system.

First of all, we can note that a peak appears at -29.2°C, especially for the $L198_{II}$ cellulose solution. This peak corresponds to the melting of the stable $NaOH,7H_2O+2H_2O$ eutectic mixture (see part III.1.2.2 above). We assume that the melting enthalpies of the stable and the metastable eutectic mixtures are relatively close which enables to determine the total melting enthalpy, ΔH_{eut}, of eutectic mixtures, stable and/or metastable.

Each DSC melting thermogram reveals a peak at low temperature, -33°C/-34°C, corresponding to the melting of the metastable $NaOH,5H_2O+4H_2O$ eutectic mixture. The temperature is approximately the same for each cellulose pulp. On the other hand, its enthalpy is changing from one cellulose origin to another. According to the enthalpy values, it seems that cellulose pulps can

be divided into two groups: Avicel/L307 and $L198_{II}$/B407. At the same cellulose concentration, the former is trapping more sodium hydroxide (lower enthalpy) than the latter. It clearly means that $L198_{II}$ and B407 are not dissolved well.

Concerning the peak at higher temperature, we can see that the melting temperature of ice decreases when the cellulose DP increases. Let us note that for pure 7.6NaOH/water solution, without cellulose, the ice melting temperature is -5.1°C. This decrease is again the sign that cellulose of higher DP are not fully dissolving (for Avicel, the higher the cellulose concentration, the lower the melting temperature of the ice).
Moreover, regarding the values of enthalpies, the two previous cellulose groups are appearing again.

It would have been very interesting to perform the same analyses as previously for Avicel/NaOH/water solutions on cellulose of different origins, treatments and DP. We could determine:

- If some cellulose is more or less easily accessible to fix NaOH and water.
- If the amount of linked and free NaOH and water molecules is a significant parameter influencing the dissolution, solution properties and gelation.

III.3.1.5. Conclusions

DSC experiments and careful analyses of experimental data allowed understanding the thermodynamic behaviour and structure of cellulose/sodium hydroxide aqueous solutions at temperatures below 0°C, in the region of cellulose dissolution.

It was possible to determine the limit of cellulose dissolution in NaOH/water as being at least four NaOH molecules per one anhydroglucose unit (corresponding to equal cellulose and NaOH concentrations in weight). Water molecules forming the eutectic mixture in solution are still around the NaOH linked to the cellulose. If the concentration of cellulose is higher than this limit, it will not be dissolved. Because cellulose can be dissolved only in a narrow range of sodium hydroxide concentrations, from 7 to 10%, this means that maximal amount of cellulose that can be dissolved in NaOH/water solutions is 10%.

This result is compatible with what is found experimentally when trying to prepare cellulose/NaOH/water solutions for processing. It is a strong limitation if one wishes to use such a solvent in commercial applications since the amount of polymer is rather low. It has two bad side effects. One is the cost of processing. The second is the fact that the properties of the final products are strongly correlated with the amount of polymer material in the solution. In addition, this dissolution limit in NaOH/water was determined for a low DP cellulose sample. Increasing the molecular weight is decreasing the ability to dissolve cellulose. As shown in the Chapter IV, a lot of insoluble parts are present in the solutions with higher DP pulps.

III.3.2- Cellulose/NaOH/urea/water solutions

III.3.2.1. DSC results on Avicel/NaOH/6urea/water

Let us first recall the main conclusions of the ternary NaOH/urea/water mixtures:

- When adding urea to a NaOH/water mixture, both the melting of water and the melting of the urea/water eutectic that is crystallizing are changed because of the presence of the NaOH/water liquid mixture that will form the NaOH eutectic.
- At a certain urea concentration (18g in 100g of solution), the melting peaks of urea eutectic and ice are joining. There is no more free ice; there are only NaOH and urea eutectic mixtures.
- NaOH and urea are both forming their normal eutectic mixture meaning that the components are not interacting.

In this part, we will investigate a set of Avicel cellulose solutions in 7.6NaOH/6urea/water, cellulose concentrations being from 0 to 5g in 100g of solution. In other words, a 100g solution contains X g of cellulose (X varying from 0 to 5), 7.6g of NaOH, 6g of urea and the rest being water. An example of DSC melting thermograms is represented on Fig.III.3-6 and melting temperatures and enthalpies are reported on Tab.III.3-4. The main features of these DSC melting curves are similar to the ones reported in literature [CAI2005]

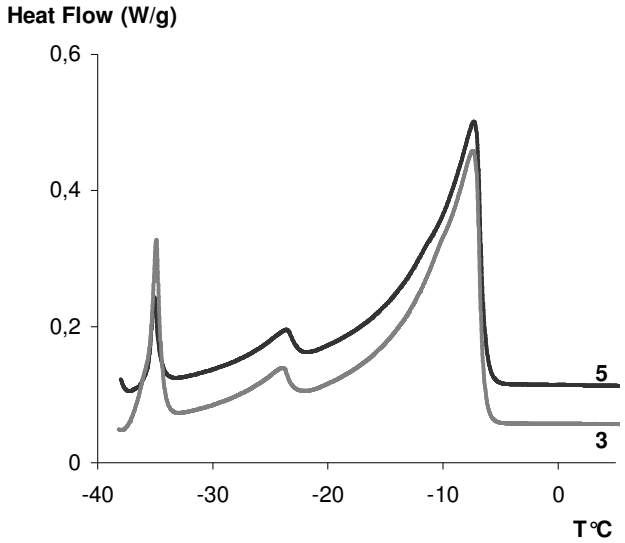


Fig.III.3-6: DSC melting thermograms of Avicel cellulose/7.6NaOH/6urea/water solutions. Cellulose content is indicated on the graph.
Curves are shifted vertically for a better visibility.

The addition of cellulose does not change the shape of the thermograms as compared to the case without cellulose. The DSC melting curves present three peaks. They were described in part III.2.2.2:

- The peak at the lowest temperature, at about -35°C, corresponds to the melting of the NaOH/water eutectic mixture,

- The next one, at about -25°C, corresponds to the melting of the urea/water eutectic mixture,
- The peak at the highest temperature, at about -7°C, corresponds to the melting of free ice.

As far as the melting peaks are not well separated, the PeakFit software (see details part II.3.1.6) was used to determine the melting enthalpy of each compound crystallised and melted in the system.

Avicel, X g in	"NaOH eutectic" peak		"urea eutectic" peak		"ice" peak	
100g of solution	T_m (onset), °C	ΔH_{eut}, J/g	T_m (peak), °C	ΔH_{urea}, J/g	T_m (end), °C	ΔH_{ice}, J/g
0	-35.9	72	-25.7	30	-8.6	160
1	-35.8	41	-24.8	34	-7.2	176
3	-35.7	35	-24.0	29	-6.5	175
5	-35.6	22	-23.7	26	-6.4	172

Tab.III.3-4: Melting temperatures and enthalpies of the peaks for different contents of cellulose in 7.6NaOH/6urea/water

In order to calculate the proportions between the interacting compounds, each peak will be considered separately.

III.3.2.2. Peak of NaOH eutectic

Taking into account the experimental errors, we can say that whatever the concentration of cellulose is, the melting temperature of the NaOH/water eutectic mixture is similar to the one obtained for a pure 7.6NaOH/6urea/water (without cellulose). This means that the addition of cellulose into an aqueous solution of sodium hydroxide and urea does not disrupt the formation of the NaOH/water eutectic mixture, as it was in the case of cellulose/NaOH/water solutions.
As previously seen for cellulose/NaOH/water solutions without additives, there is a decrease of the eutectic melting enthalpy with cellulose concentration: during the dissolution process, cellulose is trapping some NaOH molecules that can not participate anymore to the crystallisation of the eutectic mixture. Fig.III.3-7 represents reduced melting enthalpy versus reduced cellulose concentration for cellulose/7.6NaOH/water (taken from Fig. III.3.2) and for cellulose/7.6NaOH/6urea/water solutions.

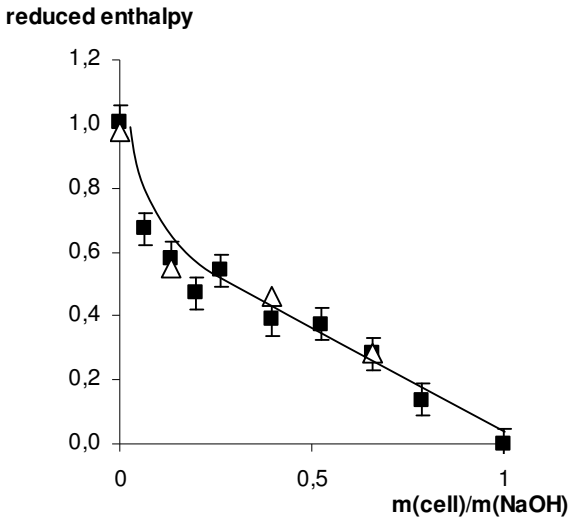


Fig.III.3-7: Reduced melting enthalpy of the NaOH eutectic versus reduced cellulose concentration for Avicel / 7.6NaOH / water (■, Fig.III.3-2) and for Avicel / 7.6NaOH / 6urea / water (△)
The full line is given to guide the eyes.

Whatever the solvent system is, the decrease of the eutectic melting enthalpy is the same.
The addition of urea does not change the interactions between cellulose and NaOH. This is a very important result.

III.3.2.3. Peak of urea eutectic

Whatever the concentration of cellulose is, the peak of the urea/water eutectic mixture is seen (Fig.III.3-6). We can note that the melting temperature of urea eutectic is increasing with cellulose content (Tab.III.3-4). An explanation of this increase of melting temperature is a change in the molecular environment of urea and water due to the addition of cellulose.

The values of the melting enthalpy of the urea eutectic are scattered, but we can assume that there is no influence of the cellulose content on the melting enthalpy of the urea eutectic peak.
The enthalpy of the urea eutectic does not depend on cellulose concentration. The addition of cellulose does not change the urea-water interactions and cellulose does not interact with urea.

III.3.2.4. Peak of free ice

We can note that the melting temperature of ice is increasing with cellulose content (Tab.III.3-4). An explanation of this increase of melting temperature is a change in the molecular environment of water due to the addition of cellulose.
Since the melting enthalpy of free ice is approximately constant for all cellulose concentrations, we conclude that the amount of free ice remains the same with and without cellulose.

III.3.2.5. Conclusions

Three main facts are obtained from these series of experiments and their interpretations:

1. NaOH and urea do not interact when mixed together with water; their eutectic mixtures are independent (part III.2.2.2).
2. Urea and cellulose do not interact when mixed with NaOH and water (urea-water eutectic is not changed).
3. The interactions between NaOH hydrates and cellulose are not changed by the addition of urea (the decrease of the eutectic peak of NaOH with cellulose content is the same with or without urea)

This clearly challenges the use of urea as a promoter for cellulose dissolution and, as will be seen in the next chapter, as a retardation agent for solution gelation. We will elaborate hypothesis on the influence of urea in the Conclusion part of this chapter.

III.3.3- Cellulose/NaOH/ZnO/water solutions

As far as we did not have enough time to test all cellulose concentrations in 7.6NaOH/0.7ZnO aqueous solutions, we only performed experiment on solution containing 5g of cellulose Avicel. The DSC thermograms are represented on Fig.III.3-8 and melting temperatures and enthalpies are reported in Tab.III.3-5.

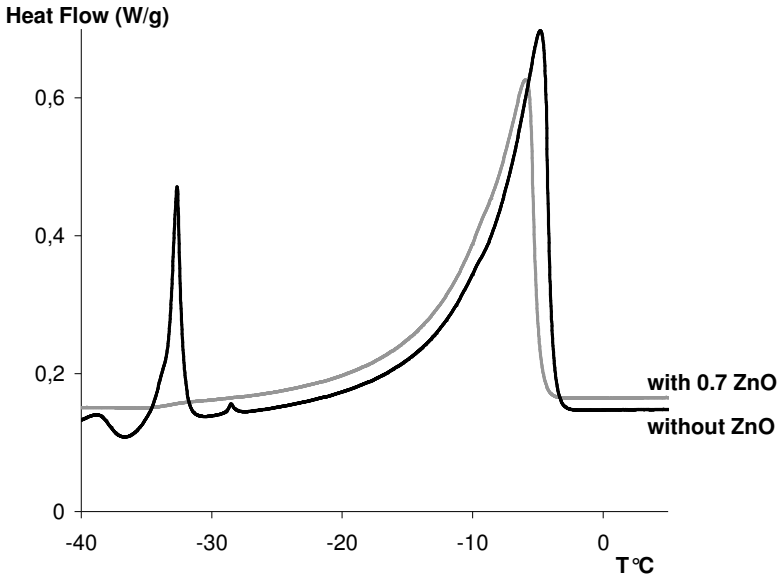


Fig.III.3-8: DSC melting thermograms of 5Avicel /7.6NaOH/water and of 5Avicel /7.6NaOH/0.7ZnO/water solutions.
Curves are shifted vertically for a better visibility

	"NaOH eutectic" peak		"ice" peak	
	T_m (onset), °C	ΔH_{eut}, J/g	T_m (end), °C	ΔH_{ice}, J/g
7.6NaOH/water	-32.9	72	-5.1	195
5Avicel/7.6NaOH/water	-33.5	22	-3.9	217
7.6NaOH/0.7ZnO/water	-	-	-5.5	186
5Avicel/7.6NaOH/0.7ZnO/water	-	-	-4.9	181

Tab.III.3-5: Melting temperatures and enthalpies of the melting peaks for 5Avicel/7.6NaOH/water and for 5Avicel /7.6NaOH/0.7ZnO/water.

As far as the temperature of DSC apparatus does not decrease enough to obtain the melting peak of the NaOH eutectic in the presence of ZnO (Fig.III.3-8), we cannot conclude either on the amount of NaOH linked to cellulose or on the limit of cellulose dissolution when ZnO is present in the solvent system.

Nevertheless, the DSC thermogram shows the melting peak of free ice.
As in the case of cellulose/NaOH/water solution, the melting temperature of free ice slightly increases when cellulose is added. This was previously explained by some changes in the molecular environment of the crystallizing water when cellulose is trapping NaOH.
Regarding the melting enthalpy of free ice, we can see that it does not change within the experimental error. This means that the amount of free water remains the same with and without cellulose and, thus, that cellulose traps NaOH surrounded by the water molecules forming the eutectic mixture.

III.3.4- Conclusions on the structure of cellulose solutions in NaOH/water with and without additives

In NaOH/water and in NaOH/urea/water, the addition of cellulose does not change the melting temperatures of the eutectic mixtures and of free ice, or very slightly only showing some changes in the molecular environment due to the presence of cellulose. Cellulose does not modify the phase diagrams of solvent systems.
On the other hand, the enthalpy of the NaOH eutectic is decreasing proportionally to the cellulose concentration and is reaching zero when the ratio $m_{cell} = m_{NaOH}$. This means that cellulose can be dissolved in 7-9NaOH/water as well as in 7.6NaOH/6urea/water if at least four NaOH are linked to each anhydroglucose unit. Consequently, in these two solvents the limit of cellulose dissolution is reaching when $m_{cell} = m_{NaOH}$.
For all the cellulose contents from 0 to 7.6, the melting enthalpy of free ice remains constant. The amount of free water does not change with the addition of cellulose and thus each anhydroglucose is surrounded by at least 36 water molecules initially forming the NaOH eutectic.

We saw in the study of solvents that the addition of ZnO in NaOH/water decreases the melting temperature of the NaOH eutectic. As we work in the limit of the DSC apparatus, the addition of cellulose leads to the disappearance of this peak. Thus it is possible neither to determine the limit of cellulose dissolution nor the amount of NaOH linked to each AGU.

For cellulose/NaOH/ZnO/water, only the melting peak of free ice appears and its enthalpy remains constant, within the experimental errors, when cellulose is added. The amount of free water stays the same whatever the cellulose content is.

III.4- INFLUENCE OF FREEZING ON THE THERMAL PROPERTIES OF THE CELLULOSE/NAOH MIXTURES

In his PhD thesis, Roy [ROY_PhD] showed that after freezing of cellulose/NaOH/water solution at -20°C for 8 hours, a pure substance melting around 0°C appeared after thawing. Freezing seems to be an important step in the preparation of sponges from cellulose/NaOH aqueous solutions, as it will be shown in details in Chapter V. That is why the transformations occurring in the solution during freezing should be studied and understood.

The temperature of the "new" melting peak at 0°C suggests that pure water appears in the system during freezing. The enthalpy value of this peak varied from experiment to experiment and was not reproducible. We decided to examine again this phenomenon, trying to find a way to obtain reproducible results. We know that non-dissolved fibres or at least non dissolved parts of fibres are present in cellulose/NaOH/water solutions and that these fibres precipitate relatively rapidly after the solution preparation. This is varying cellulose concentration in the supernatant. In order to always have the same cellulose solutions in the measuring cell, we homogenised the mixture right before all the experiments and solution was taken and immediately put into the DSC cell.

5g B342 cellulose was dissolved in 7.6NaOH/water and in 7.6NaOH/0.7ZnO/water as described in Chapter II, total solution weight being 100g. After homogenisation, about 20mg of the solution were put into DSC caps. Three thermal treatments were performed:

- The temperature decreased down to -28°C, there was no isothermal step and the temperature immediately increased up to 10°C.
- The temperature decreased down to -28°C, a 2 hours isothermal step was performed at -28°C, and then the temperature increased up to 10°C.
- The temperature decreased down to -28°C, a 20 hours isothermal step was performed at -28°C, and then the temperature increased up to 10°C.

The results obtained after freezing and thawing were reproducible (Fig.III.4-1 and Fig.III.4-2).

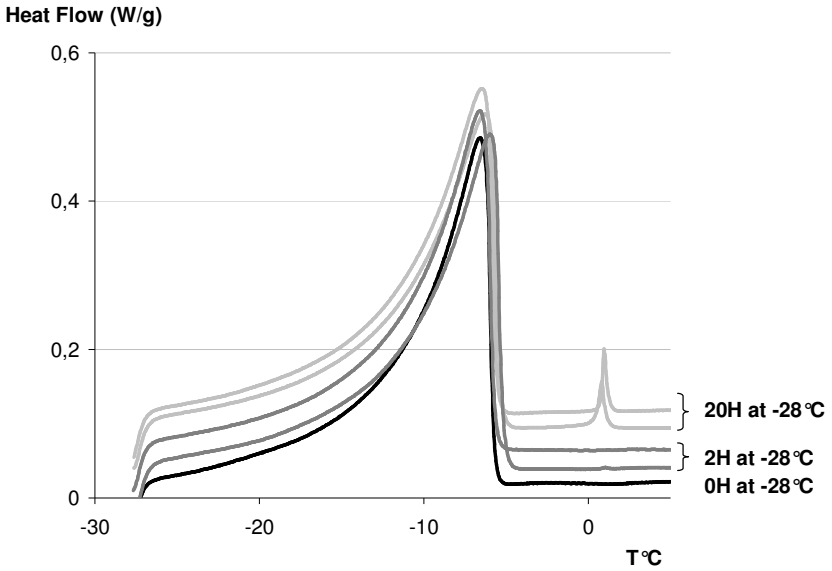


Fig.III.4-1: Melting DSC thermograms for 5B342 cellulose/7.6NaOH/water solutions after freezing at -28°C and immediate thawing (0H) and after keeping solution at -28°C for 2 hours (2H) and 20 hours (20H)
(each experiment was performed twice on different solutions)

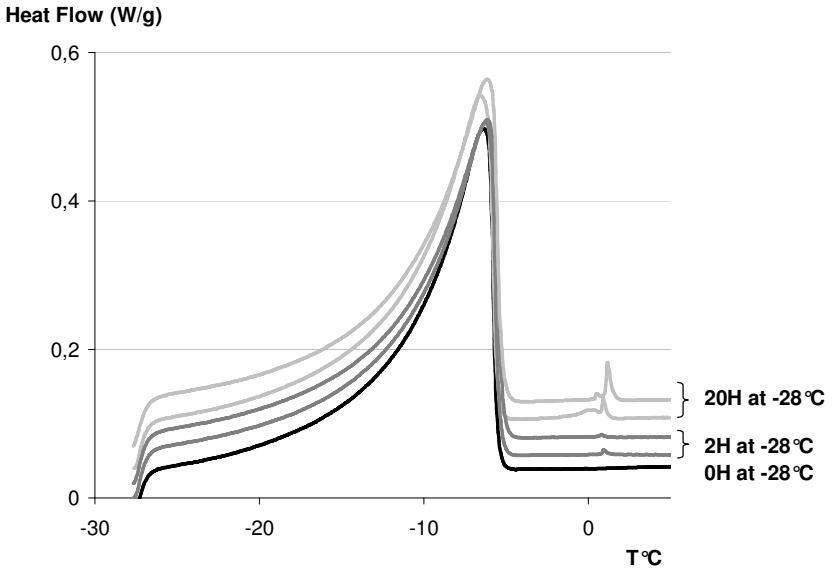


Fig.III.4-2: Melting DSC thermograms for 5B342 cellulose/7.6NaOH/0.7ZnO/water solutions after freezing at -28°C and immediate thawing (0H) and after keeping solution at -28°C for 2 hours (2H) and 20 hours (20H)
(each experiment was performed twice on different solutions)

Time at -28°C, hours	Tm_1, °C of free ice	ΔH_1, J/g of free ice	Tm_0, °C of water released	ΔH_0, J/g of water released
0	-5.5	156	-	-
2	-5.0	160	-	-
2	-5.2	162	-	-
20	-5.5	144	0.7	1.8
20	-5.4	147	0.2	2.3

Tab.III.4-1: Temperatures and enthalpies of melting peaks of free ice and of water "released" for a 5B342 cellulose /7.6NaOH/water solution, after freezing and keeping for 0, 2 and 20 hours at -28°C.

Time at -28°C, hours	Tm_1, °C of free ice	ΔH_1, J/g of free ice	Tm_0, °C of water released	ΔH_0, J/g of water released
0	-5.5	155	-	-
2	-5.5	156	0.6	Very low
2	-5.2	153	0.8	Very low
20	-5.6	147	-1.3 / 0.7	1.8
20	-5.4	145	0.4 / 1.0	1.9

Tab.III.4-2: Temperatures and enthalpies of melting peaks of free ice and of water "released" for a 5B342 cellulose/7.6NaOH/0.7ZnO/water solution, after freezing and keeping 0, 2 and 20 hours at -28°C.

During freezing and keeping the solution at -28°C for several hours, a phase separation is occurring.

- A 5B342 cellulose/7.6NaOH aqueous solution left at -28°C for 20 hours reveals a single and sharp peak at 0°C (Fig.III.4-1). We can say that pure water appeared. These results are in agreement with the ones obtained by Roy [ROY_PhD].
  We can note that this peak is not present after 2 hours at -28°C.
- A 5B342 cellulose/7.6NaOH/0.7%ZnO aqueous solution left at -28°C for 20 hours reveals two melting peaks, at -1.3°C and 0.7°C in the first experiment and at 0.4°C and 1°C in the second experiment (Fig.III.4-2). The presence of ZnO does not prevent the phase separation but it seems that two liquids are released separately: probably pure water, as in the case of cellulose in pure NaOH/water, and a very dilute liquid containing NaOH and/or ZnO in water.
  Moreover, after only 2 hours at -28°C, we can see that the phase separation is also occurring since the melting peaks are present but the enthalpies are too low to be quantified. It seems that the presence of ZnO in the solvent system makes easier the occurrence of phase separation.

In the case of cellulose/7.6NaOH/water, we determined that a 20hours isothermal step at -28°C induces a release of pure water. Consequently, using the melting enthalpies of the released water (Tab.III.4-1) and of pure crystallised water ($\Delta H_{ice\ pure}$ = 358J/g), the amount of released water per one AGU can be calculated.

$$n_{water.released} / n_{AGU} = \frac{f_{water.released} \times 162}{18 \times \frac{m_{cell}}{100}}$$

where $f_{water.released} = \frac{\Delta H_{water.released}}{\Delta H_{ice.pure}}$ is the fraction of water released and m_{cell} is cellulose weight in 100g of solution.

The result is that one water molecule per AGU is released. The reason that there is water molecule that is "detached" from water-linked-to-AGU is as follows. The water crystallizing in time under cooling at -28°C could come, in general, from three places in solution where water

molecules are present: free eutectic mixture, eutectic mixture linked to cellulose and non-frozen water (according to the phase diagram, at this temperature there is a small amount of a non-frozen water). On one hand, according to thermodynamic reasoning, water belonging to free eutectic cannot be "detached", so the "released" water cannot come from eutectic mixture. On the other hand, as far as the addition of cellulose does not perturb NaOH/water phase diagram, water in non-frozen water is not modified. The only possibility is thus water-bound-to-cellulose together with the NaOH ions. We have shown above that there are at least 36 such water molecules surrounding each AGU. About one is leaving to form the ice melting at 0°C. There is no depression of the melting temperature probably because this water is diffusing in a system in thermodynamic equilibrium. We may suppose that because cellulose/NaOH/water is not a very stable organisation, water molecules are "detaching" from cellulose and moving towards ice that serves as nuclei for new crystals. Because of low temperatures this diffusion is slow, that is why several hours are needed for free water to form crystals.

During the freezing step, 1 H_2O/AGU is released, which is not much in comparison with the 36 H_2O molecules surrounding AGU initially. The addition of ZnO does not change the amount of water released

III.5- CONCLUSIONS

We performed an extended investigation, mainly based on DSC technique, of the thermodynamic behaviour of cellulose in NaOH/water solutions with and without additives. This study allowed understanding the structure and proportions between the components interacting in the system and determination and explanation of the limit of cellulose dissolution in NaOH/water and in NaOH/urea/water solutions.

Cellulose in NaOH/water

The phase diagram of NaOH/water in the 0-30% region is of the eutectic type. Our DSC experiments are in agreement with the phase diagram reported in the literature.

According to the known phase diagram of cellulose/NaOH/water system [SOB1939], cellulose can be dissolved when mixed with NaOH/water in the 6-10% of NaOH/water below 0°C. DSC experiments reveal that the addition of Avicel cellulose does not change either the temperature of the NaOH eutectic mixture or the temperature of melting ice. This means that cellulose does not disrupt the formation of the NaOH eutectic and does not directly interact with water. Nevertheless, the intensity of the NaOH eutectic peak decreases when cellulose concentration increases. Thus, it is possible to calculate the amount of NaOH molecules linked to each AGU and to deduce the maximal amount of cellulose that can be dissolved in a given NaOH/water solution: at least four NaOH should be bound to one AGU to provide dissolution. This proportion expressed in weight ratio gives $m_{cell}/m_{NaOH} \leq 1$ as a limit of cellulose dissolution. In these limiting conditions, about 36 water molecules are bound to one AGU.
An interesting feature is that the amount of NaOH that is not able to participate to the eutectic due to the presence of cellulose is increasing when decreasing the cellulose concentration, or in other words, the amount of NaOH linked to AGU increases with the decrease of cellulose concentration. We do not have a simple explanation of this phenomenon, and it is not an artefact since the same can be deduced from turbidity experiments on cellulose dissolution [KUO2005].

As far as cellulose can be dissolved in 6% - 10% aqueous NaOH, the maximum of Avicel cellulose that can be dissolved in sodium hydroxide is 10%, which can be a blocking point for solutions processing.

For 5cellulose/7.6NaOH/water solutions, the melting enthalpy of the NaOH eutectic depends on the cellulose origin. The most difficult to dissolve was cellulose B407 and $L198_{II}$.

Cellulose in NaOH/urea/water

Urea/water forms a simple eutectic phase diagram.
When mixed with NaOH/water, urea and NaOH do not interact. They each behave as if they were alone, when enough water is present in the system: both NaOH and urea form their eutectic mixture with water, $NaOH,5H_2O$+$4H_2O$ and urea+$8H_2O$. As soon as the concentrations are such that water is missing, NaOH is attracting water at the expense of urea.

When cellulose is added to NaOH/urea/water, the interaction between NaOH and cellulose is the same as if urea were not present. This means that urea is not linked to cellulose. The question is why urea is efficient for helping the dissolution and delaying gelation (see Chapter IV). A possible hypothesis is that cellulose dissolution is possible when the NaOH hydrates have a given size and structure that is found in the region of 6-10%NaOH below 0°C. In these conditions, a lot of liquid water is present in NaOH/water solution. The role of urea is to bind a part of this water which is not favourable for the cellulose dissolution.

Cellulose in NaOH/ZnO/water

ZnO reacts with NaOH to form zinc hydroxides, $NaZn(OH)_3$ and $Na_2Zn(OH)_4$. As a consequence, some NaOH molecules are linked to ZnO and the melting temperature of the peak NaOH/water eutectic mixture decreases and becomes not measurable when ZnO is added. The limit of ZnO dissolution is reached when NaOH/ZnO molar ratio becomes equal to 10.

As far as there is no NaOH/water eutectic peak in cellulose/7.6NaOH/0.7ZnO/water and free ice peak is not influence by the presence of either cellulose or ZnO, the analysis of the proportions between the components was not possible. The role of ZnO in cellulose dissolution is supposed to be the same as the one of urea.

Influence of freezing on the thermal properties of the cellulose/NaOH mixtures

The addition of cellulose in NaOH/water does not change the NaOH/water binary phase diagram, plotted by Pickering [PIC1893] and Rollet *et al.* [ROL1964]. Consequently, at -20°C, with or without cellulose, a large amount of water (f_{ice} ~ 0.49) is crystallised decreasing the amount of liquid water in the system and thus increasing the NaOH concentration of the liquid up to 15%NaOH. The fact to be outside the domain of cellulose dissolution [SOB1939] may explain why after freezing the cellulose solution is a weak gel (see Chapter IV).

Secondly, when keeping cellulose/NaOH/water solution below -20°C for several hours, free water appears that crystallises and then melts at 0°C. If freezing occurs for short time, no peak appears at 0°C. Approximately one water molecule per one AGU is "detached" from cellulose and crystallises.

The influence of the freezing step on the final properties of regenerated cellulose is more probably due to the large amount of crystallised water (crystallisation following the NaOH/water binary phase diagram), which changes the environment of cellulose (decreasing of liquid water and increasing of NaOH concentration), than the very low amount of released water.

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RESUME DU CHAPITRE IV

ECOULEMENT ET GELIFICATION DES SOLUTIONS AQUEUSES DE CELLULOSE/NAOH : INFLUENCE DES ADDITIFS.

Le but de ce chapitre est d'étudier le comportement à l'écoulement des solutions de cellulose, de déterminer les conditions de gélification. Nous étudierons également l'influence des additifs tels que oxyde de zinc et urée sur les propriétés rhéologiques des solutions de cellulose. Pour finir, nous verrons brièvement l'influence d'une étape de congélation à -20°C sur l'état du système.

Dans la première partie, nous avons réalisé des mesures de viscosité en fonction du taux de cisaillement sur des solutions de cellulose/7,6NaOH/eau et cellulose/7,6NaOH/0,7ZnO/eau essentiellement, et ce, pour différents DP et concentrations en cellulose et pour des températures comprises entre 0°C et 40°C. Quelques mesures ont également été effectuées sur des solutions aqueuses de cellulose/7,6NaOH/6urée.
Nous avons ainsi déterminé que, pour les trois systèmes alcalins étudiés, les solutions de cellulose n'ont pas un comportement de solutions moléculairement dispersées mais que leur comportement se rapproche de celui d'une dispersion. Ce résultat n'est pas étonnant puisque nous avons vu dans le chapitre III que chaque unité anhydroglucose de la chaîne de polymère est entourée, au minimum, de 4 NaOH et 36 molécules d'eau.

Par des mesures de viscosité intrinsèque, nous avons pu classer les solvants en fonction de leur qualité de solvant de la cellulose. Il s'avère que 7,6NaOH/eau est moins bon que 7,6NaOH/6urée/eau qui est à son tour moins bon solvant que 7,6NaOH/0,7ZnO/eau. Ce résultat est en adéquation avec les observations microscopiques que nous avons réalisées.
Une augmentation de la température d'essai conduit à une diminution de la viscosité intrinsèque et donc une diminution de la qualité du solvant. Quand la température augmente, les interactions cellulose-cellulose sont donc favorisées au détriment des interactions cellulose-solvant, ce qui entraîne la gélification des solutions, phénomène déjà rapporté dans la littérature [ZHO2000] [ROY2003].

Les solutions de cellulose ne sont pas stables et gélifient avec le temps et la température. Les conditions de gélification étant mal connues, nous avons déterminé le point de gel des solutions de cellulose en variant de nombreux paramètres (température, DP et concentration en cellulose) et notamment la présence ou non d'additifs.
Une augmentation rapide de la température donne un point de gel des solutions de cellulose aux alentours de 30°C. La présence d'oxyde de zinc ou d'urée augmente cette température de

gélification de plusieurs degrés suivant la nature et la concentration de l'additif et la nature de la cellulose.
En ce qui concerne la présence d'oxyde de zinc, la température de gélification augmente quand la teneur en ZnO augmente jusqu'à une concentration limite de 1,5ZnO dans 7,6NaOH/eau. Le rapport NaOH : ZnO est alors de 10 et correspond à la limite de solubilité de ZnO dans NaOH. De plus, l'ajout de ZnO solide après mélangeage de la cellulose avec la soude donne la même température de gélification que des solutions de cellulose ne contenant pas du tout de ZnO. Ceci signifie que ZnO n'est efficace que s'il est préalablement dissout dans NaOH/eau avant d'être ajouté à la cellulose. Etant donné que ZnO et NaOH réagissent pour former des hydroxydes de zinc, nous pensons que la formation de ces complexes NaOH-ZnO-eau est favorable à la dissolution des fibres de cellulose et à la stabilité des solutions.
Quant à l'urée, nous avons vu que sa présence augmente nettement la température de gélification des solutions. Par contre, sa teneur optimale dans 7,6NaOH/eau dépend de la cellulose (origine, traitement). A l'heure actuelle, les raisons de telles différences restent une question ouverte.
Dans tous les cas, quels que soient les mécanismes qui interviennent, urée et ZnO retardent la gélification des solutions.

Pour finir, nous avons réalisé quelques mesures rhéologiques sur des solutions congelées de cellulose/NaOH/eau. Si on compare une solution ayant subit un séjour prolongé à -20°C et une solution fraîchement préparée, on constate que la congélation diminue la qualité de solvant de NaOH/eau (diminution de la viscosité intrinsèque) en favorisant les interactions cellulose-cellulose allant jusqu'à la gélification des solutions (augmentation de la viscosité et du module G'). Par contre, la présence d'oxyde de zinc minimise considérablement ces effets. Après congélation, G' a certes augmenté mais très faiblement tandis que la viscosité reste pratiquement inchangée sur tout le domaine de taux de cisaillement étudié.
Comme pour la gélification par hausse de la température, ZnO retarde également la gélification à basse température.

CHAPTER IV

FLOW AND GELATION OF AQUEOUS CELLULOSE/NAOH SOLUTIONS: INFLUENCE OF ADDITIVES

As shown in Chapter I [SOB1939], sodium hydroxide can be a solvent of cellulose in a narrow range of temperature (-6°C-0°C) and NaOH concentration (6%-10%). Moreover, according to the literature [YAM1990], the DP of cellulose samples that can be dissolved in NaOH has to be inferior to about 400 for steam exploded wood pulp but this value also depends on the cellulose origin. These very restrictive conditions show the difficulties of cellulose processing. In addition, even after dissolution, cellulose solutions are not stable and gelation occurs as a function of time and temperature [ROY2003] [ROY_PhD]. Gelation kinetics and influence of temperature were studied for microcrystalline Avicel cellulose dissolved in 9%NaOH/water [ROY2003]. Gelation can be either an advantage or a drawback depending on the industrial process.

Literature reveals that the addition of some compounds such as urea and ZnO improves cellulose dissolution and stability of solutions [WO 02/22924] [ZHO2000]. The goal of this chapter is to study the influence of ZnO and urea on the flow and gelation of cellulose/NaOH/water solutions and to understand the mechanisms of solution gelation. This chapter is divided into four parts "Influence of ZnO and urea on the flow behaviour of cellulose/NaOH aqueous solutions", "Gelation and dissolution of cellulose in the presence of ZnO", "Gelation and dissolution of cellulose in the presence of urea. Comparison between urea and ZnO", and "Tests on gelation and dissolution of cellulose in other alkali solvents: KOH and NaOH with other additives"

The first part corresponds to the study of the flow behaviour of semi-dilute cellulose solutions. Viscosity versus shear rate measurements were performed on cellulose/NaOH aqueous

solutions, with or without ZnO or urea, by changing parameters as DP and concentration of cellulose, and solution temperature.

The second and third parts investigate the influence of additives – ZnO and urea – as well as the influence of cellulose origin on (i) cellulose dissolution by microscopic observations and (ii) gelation of solutions by rheological measurements in dynamic mode. The optimal concentration of both additives for cellulose dissolution was determined. Finally, the role of these two additives on gelation and dissolution of cellulose is discussed.

The fourth part is devoted to the analysis of other additives, like $ZnSO_4$, $MgCl_2$, and $CaSO_4$ on the gelation of a 5cellulose/7.6NaOH/water solution and on cellulose dissolution.

IV.1- INFLUENCE OF ZNO AND UREA ON THE FLOW BEHAVIOUR OF CELLULOSE/7.6NAOH/WATER SOLUTIONS

The goal of this section is to investigate the flow behaviour of cellulose/7.6NaOH/water solutions with and without additives (a detailed study on ZnO presence in the solvent and a few tests on the presence of urea). Viscosity-shear rate dependence was measured on cellulose solutions in which many parameters were varied:

- The temperature: from 0°C to 40°C.
- The DP of cellulose: DP 342 and DP 500 (Borregaard steam exploded pulp, B342 and B500, respectively)
- The cellulose content: from 0.8g to 5g in 100 g of solution.
- The solution composition: cellulose/7.6NaOH/water, cellulose/7.6NaOH/0.7ZnO/ water.

- Two other cellulose samples were tested – B407 and Avicel – but only at 10°C and with a content of 5g. The solutions were Avicel/7.6NaOH/water, B407/7.6NaOH/water, and B407/7.6NaOH/4urea/water.
  4g of urea in a 100g solution containing 7.6g of NaOH was the optimal urea content to dissolve cellulose in 6-8NaOH/urea/water reported in the ref. [ZHO2000].

IV.1.1- Influence of the presence of ZnO or urea in the solvent on the flow of cellulose/7.6NaOH/water solutions

This section is devoted to the influence of the presence of additives in the solvent on the flow behaviour of cellulose/7.6NaOH/water solutions. The main results compare cellulose/7.6NaOH/water and cellulose/7.6NaOH/0.7ZnO/water solutions, only few results concern the presence of urea in the system. The solutions were sheared in steady-state mode in a Couette double gap rheometer.

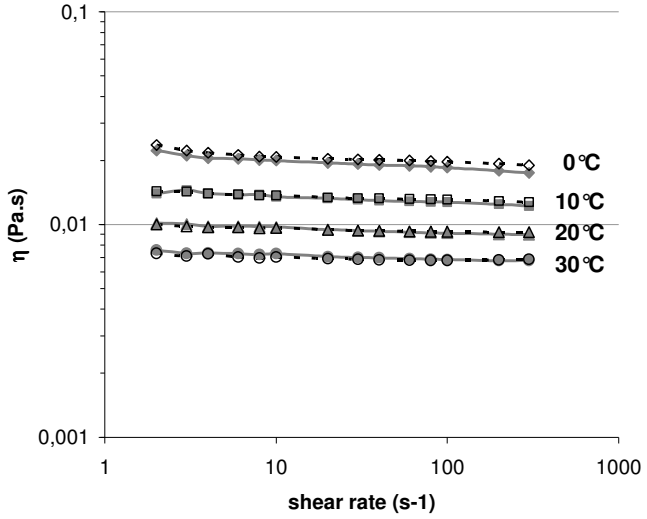


Fig.IV.1-1: Viscosity-shear rate dependence of 1.7 B342 cellulose/7.6NaOH/water solutions (full symbols) and 1.7 B342 cellulose/7.6NaOH/0.7ZnO/water solutions (open symbols) at 0°C, 10°C, 20°C, and 30°C

At low cellulose concentrations (Fig.IV.1-1), the viscosity-shear rate curves of B342 cellulose/7.6NaOH/water and B342 cellulose/7.6NaOH/0.7ZnO/water coincide.
The viscosity is constant when the shear rate increases: at low cellulose concentration the flow is Newtonian. The small increase of viscosity at low shear rate is due to the effect of the rheometer which reaches its maximum sensitivity. The temperature increase leads to a viscosity decrease (at least from 0°C to 30°C). This phenomenon can be explained by an increase of chain mobility and is classically observed for most other systems. It is quantified through the activation energy, which is determined from the Arrhenius law in the following way:

$$\eta = A.\exp^{(E_a/RT)}$$

$$\ln\eta = \ln A + \frac{E_a}{RT}$$

Where η: the viscosity (Pa.s); it was arbitrarily measured at $\dot{\gamma} = 10s^{-1}$

A: a constant

E_a: the activation energy (J/mol)

R: the constant of perfect gas = 8.32 J/mol/°K

T: the absolute temperature (°K)

The activation energy can be calculated from the slope E_a/R of the lines $\ln\eta$ versus 1/T.
Fig.IV.1-2 shows the results for pure water, for aqueous sodium hydroxide solutions, with or without 0.7ZnO, and for cellulose solutions – 1.7 B342 cellulose/7.6NaOH/water, 1.7 B342 cellulose/7.6NaOH/0.7ZnO/water and 2.8 B342 cellulose/7.6NaOH/0.7ZnO/water. Let us note that it is not possible to determine E_a for 2.8 B342 cellulose/7.6NaOH/water solution since the flow is not Newtonian anymore. This second behaviour will be discussed in the forthcoming.
Nevertheless, if we compare 1.7 B342 cellulose/7.6NaOH/water (Fig.IV.1-2, full symbols) with 1.7B342 cellulose/7.6NaOH/0.7ZnO/water (Fig.IV.1-2, open symbols), the presence of 0.7ZnO in the solvent does not change the viscosity-temperature dependence, within the experimental error (Fig.IV.1-2, table).

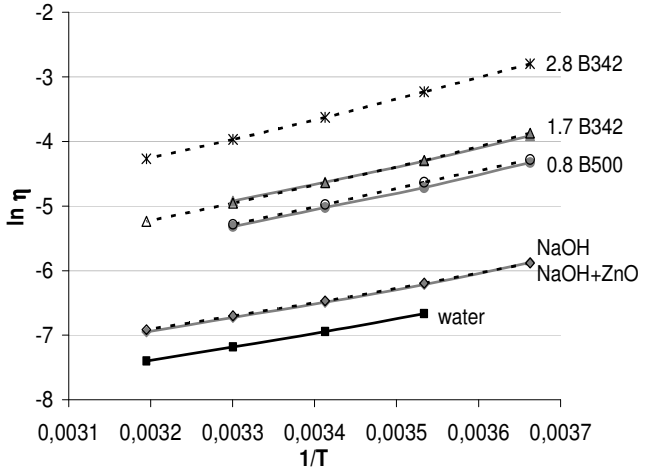


Fig.IV.1-2: Viscosity versus inverse temperature for water, pure solvents (7.6NaOH/water and 7.6NaOH/0.7ZnO/water) and for cellulose/7.6NaOH/water, cellulose/7.6NaOH/0.7ZnO/water.
Solid lines correspond to solutions in 7.6NaOH/water, dashed lines to solutions in 7.6NaOH/0.7ZnO/water.
Content and DP of cellulose are indicated on the graph
The values of the corresponding activation energy E_a (kJ/mol) are given in the Tab.IV.1-1.

	Cellulose content			
	0 cellulose pure solvent	**0.8 B500**	**1.7 B342**	**2.8 B342**
water	18.0			
7.6NaOH/water	19.0	22.6	23.1	
7.6NaOH/ 0.7ZnO/water	18.4	23.0	24.2	26.2

Tab.IV.1-1: Values of activation energy E_a (kJ/mol) determined from Fig.IV.1-2

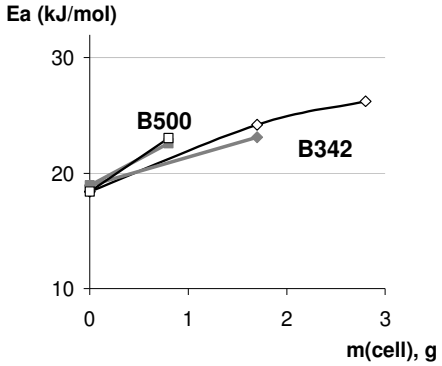


Fig.IV.1-3: Activation energy E_a versus cellulose content for B342 (◇) and B500 (□) cellulose in 7.6NaOH/water (full symbols) and in 7.6NaOH/0.7ZnO/water (open symbols)

An increase of cellulose concentration as well as of DP of cellulose leads to an increase of the activation energy E_a. As the activation energy is expressing the difficulty of motions of polymer chains and so is connected with the density of entanglements, the increase of the activation energy with concentration and DP of cellulose was an expected result. This phenomenon observed for steam exploded cellulose solutions is in contradiction with the results obtained for Avicel cellulose solutions [ROY2003]. There, the authors showed that the activation energy was independent on the cellulose concentration and concluded that cellulose/NaOH aqueous solutions are not real solutions.

Comparing 1% DP950 cellulose in NMMO/water [GAV2005] with 0.8 B500 (DP500) cellulose in 7.6NaOH/water shows a large difference with respectively 48kJ/mol and 22.6kJ/mol. This latter value is close to the one of the solvent (19kJ/mol). It suggests either that NMMO/water is a complexing solvent that is hampering strongly the motion of the cellulose chains or that the interactions between the solvent and cellulose in the case of NaOH solutions are weak, leading to a collapsed state, in a sense similar to what [ROY2003] found.

With the increase of cellulose concentration and, as we will see, temperature, the cellulose solutions behave in a different way. The flow is non-Newtonian; the shear rate increase leads to a more or less pronounced decrease of viscosity (Fig.IV.1-4) which is characteristic of a pseudoplastic behaviour. The flow index *'n'* was calculated in the shear-thinning region as follows:

$$\eta = A.\dot{\gamma}^{n}$$

Where $\dot{\gamma}$: the shear rate (s^{-1})

η: the viscosity (Pa.s)

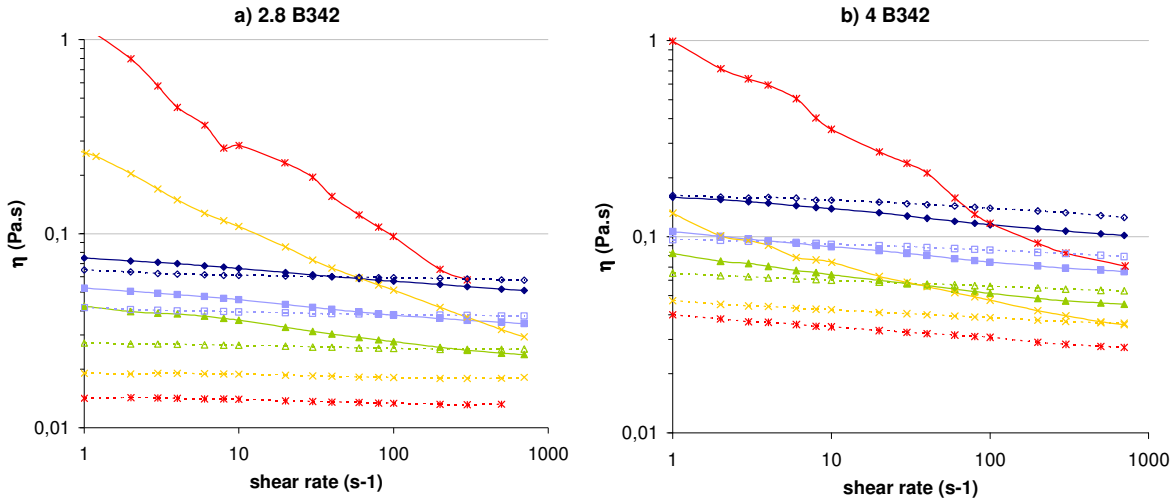
n: the flow index

A: a constant

For each cellulose solutions, the flow index *'n'* was calculated and the results are reported in Tab.IV.1-2 and in Tab.IV.1-3.

Viscosity-shear rate curves of cellulose/7.6NaOH/water, cellulose/7.6NaOH/0.7ZnO/water solutions are represented on Fig.IV.1-4. Viscosity measurements were performed as a function of temperature and content and DP of cellulose; the trend is similar in all cases.
At low temperatures (0-20°C), the viscosity is decreasing with shear rate. The non-linearity is more pronounced with increasing either content or molar mass of cellulose, as should be expected.
Then, at a certain temperature (~30°C) and at low shear rate, there is a sudden increase of the viscosity. As far as we know that cellulose solutions are gelling with temperature increase [ROY2003], we can say that this sudden increase of viscosity is a direct indication of solution gelation. Simultaneously, an indirect indication of the gelation is a strong shear thinning of cellulose solutions, quantified by the flow index *'n'* (Tab.IV.1-2). At a low shear rate, the characteristic time of the flow is large and the gel is reforming easily leading to a thick suspension of very large elastic gel particles. This induces a high viscosity. At high shear rates, the characteristic time of the flow is small and the gel is not reforming easily, i.e. is broken in small pieces. Consequently, the system behaves as a suspension and the viscosity is low.

Moreover, we can note that the direct and indirect indicators of gelation – the sudden increases of viscosity (Fig.IV.1-4) and flow index *'n'* (Tab.IV.1-2) respectively – appear at higher cellulose concentration and temperature for a solution containing ZnO compared with the same cellulose solution without ZnO. For example, a 4 B342 cellulose/7.6NaOH/0.7ZnO/water solution is not forming a gel, even at 40°C, whereas the same solution in 7.6NaOH/water is gelling at 30°C. We can thus conclude that the presence of ZnO in the NaOH/water solvent delays the occurrence of gelation.
The cellulose/7.6NaOH/0.7ZnO/water systems have Newtonian flow for higher cellulose concentrations than cellulose/7.6NaOH/water systems (Tab.IV.1-2), we can thus conclude that the presence of ZnO in sodium hydroxide improves cellulose dissolution.



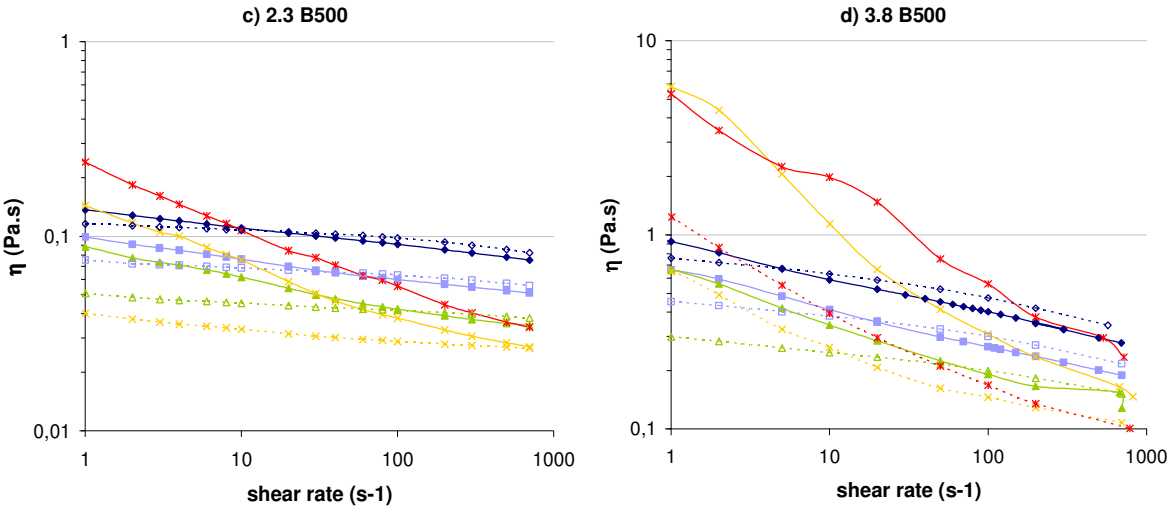


Fig.IV.1-4: Viscosity-shear rate dependence of cellulose/7.6NaOH/water (solid lines) and cellulose/7.6NaOH/0.7ZnO/water (dashed lines), at 0℃ (◇), 10℃ (□), 20℃ (△), 30℃ (×) and 40℃ (∗). Cellulose concentrations and DP are a) 2.8 B342, b) 4 B342, c) 2.3 B500, and d) 3.8 B500.

	x B342 /7.6NaOH/water			x B342 /7.6NaOH/0.7ZnO/water		
T℃	**X=1.7**	**x=2.8**	**x=4**	**x=1.7**	**x=2.8**	**x=4**
0	0.04 (N)	0.07 (PP)	0.08 (PP)	0.03 (N)	0.02 (N)	0.04 (N)
10	0.03 (N)	0.07 (PP)	0.07 (PP)	0.02 (N)	0.01 (N)	0.03 (N)
20	0.03 (N)	0.09 (PP)	0.12 (PP)	0.02 (N)	0.01 (N)	0.03 (N)
30	0.03 (N)	0.33 (G)	0.22 (G)	0.01 (N)	0.006 (N)	0.05 (PP)
40		0.52 (G)	0.43 (G)	0.003 (N)	0.008 (N)	0.07 (PP)

	x B500 /7.6NaOH/water			x B500/7.6NaOH/0.7ZnO/water		
T℃	**X=0.8**	**x=2.3**	**x=3.8**	**x=0.8**	**x=2.3**	**x=3.8**
0	0.05 (N)	0.10 (PP)	0.18 (PP)	0.03 (N)	0.05 (PP)	0.11 (PP)
10	0.03 (N)	0.11 (PP)	0.19 (PP)	0.03 (N)	0.05 (PP)	0.12 (PP)
20	0.04 (N)	0.15 (PP)	0.23 (G)	0.03 (N)	0.06 (PP)	0.11 (PP)
30	0.008 (N)	0.27 (G)	0.53 (G)	0.005 (N)	0.07 (PP)	0.36 (G)
40	0.01 (N)	0.31 (G)	0.54 (G)	0.02 (N)	-	0.48 (G)

Tab.IV.1-2: Values of the flow index *'n'*, which quantifies the shear thinning, for B342-B500 cellulose /7.6NaOH/water and B342-B500 cellulose/7.6NaOH/0.7ZnO/water solutions, at different cellulose contents and temperatures.
The values followed by (N) correspond to a Newtonian flow, (PP) to a pseudoplastic behaviour and (G) to solution in gel state

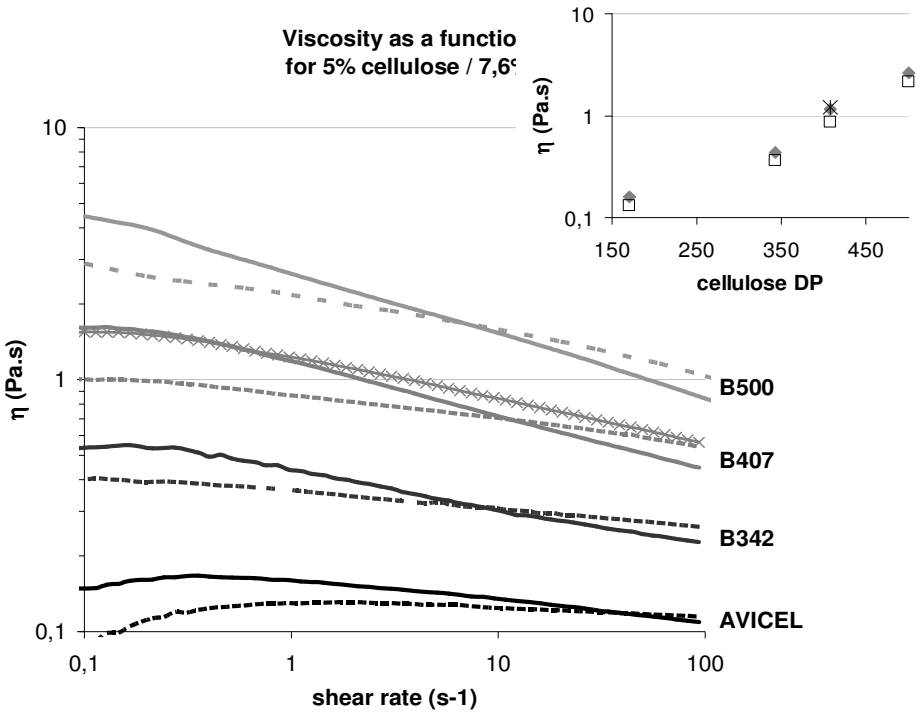


Fig.IV.1-5: Viscosity-shear rate dependence, at 10°C, of 5cellulose/7.6NaOH/water (solid lines), 5cellulose/7.6NaOH/0.7ZnO/water (dashed lines) and 5cellulose/7.6NaOH/4urea/water (full line with crosses)
Inset: **Viscosity, arbitrarily measured at 1s^{-1}, versus DP of cellulose for 5cellulose/7.6NaOH/water (◆), 5cellulose/7.6NaOH/0.7ZnO/water (□) and for cellulose/7.6NaOH/4urea/water (∗)**
The names (including the DP) of cellulose samples are directly indicated on the graph

Cellulose	In NaOH	In NaOH +ZnO	In NaOH +urea
Avicel (DP170)	0.08	0.03	-
B342	0.15	0.07	-
B407	0.22	0.10	0.17
B500	0.25	0.16	-

Tab.IV.1-3: Values of the flow index *'n'*, at 10°C for cellulose/7.6NaOH/water, cellulose/7.6NaOH/0.7ZnO/water and cellulose/7.6NaOH/4urea/water solutions with cellulose having different DP
Cellulose content is 5g in 100g of solution.

Fig.IV.1-5 represents the viscosity-shear rate dependence, at 10°C, for 5cellulose/7.6NaOH/water, 5cellulose/7.6NaOH/0.7ZnO/water and 5cellulose/7.6NaOH/ 4urea/water solutions with cellulose having different DP. 10°C was chosen because at this temperature gelation is very slow (more than 300 hours, [ROY2003]) and thus can be neglected as compared with the duration of experiment. As expected, a DP increase induces a viscosity increase. Indeed, a DP increase involves an increase in the size of macromolecules and of functional groups and thus an increase of molecular interactions in the solution and thus a decrease of the motion of polymer chain.

The shear thinning was quantified and the values of flow index *'n'* are reported on Tab.IV.1-3.

Tab.IV.1-2 and Tab.IV.1-3 show that the flow index *'n'* depends on the DP and concentration of cellulose, the temperature and the solvent. When the cellulose solutions are neither Newtonian nor in gel state, the flow index *'n'* remains between 0.05 and 0.25, depending on cellulose concentration and DP, and on solvent and temperature. These values correspond to the ones found in literature for Avicel cellulose/9%NaOH/water solutions [ROY2003].

IV.1.2- Conclusions

The flow of two cellulose samples – B342 and B500 – dissolved in 7.6NaOH/water and in 7.6NaOH/0.7ZnO/water was studied for cellulose contents from 0.8g to 5g in 100g of solution, at temperatures from 10°C to 40°C. The flow of two other cellulose samples – Avicel and B407 – was studied but only for 5g of cellulose at 10°C. B407 cellulose was also dissolved in 7.6NaOH/4urea/water.

At low cellulose contents, m_{cell} < 2g in 100g of solution, the flow is Newtonian whatever the solvent is. The increase of solution temperature leads to the decrease of viscosity reflecting a classical solution behaviour.
The increase of cellulose content leads to a weak shear thinning that is less pronounced when cellulose is dissolved in 7.6NaOH/0.7ZnO/water than in 7.6NaOH/water. In other words, the presence of ZnO shifts the Newtonian behaviour towards higher cellulose concentration. We relate this with the improvement of cellulose dissolution in the presence of ZnO that will be discussed together with the influence of additives on cellulose gelation and will be confirmed in the next section by microscopic observations.

The increase of solution temperature at cellulose contents higher than ≈2g leads to a sharp increase in solution viscosity and strong shear thinning, when cellulose is dissolved in 7.6NaOH/water. As it will be shown in the following, it is related to solution gelation and gel breaking under flow, respectively. This phenomenon is much less pronounced for cellulose dissolved in 7.6NaOH/0.7ZnO/water: the increase of viscosity followed by the shear thinning occurs at higher cellulose concentrations and higher temperatures. This will be studied in details with oscillatory measurements. Higher the cellulose concentration, lower the temperature of gelation.

The activation energy values reported above for Borregaard steam-exploded cellulose correspond to the ones in ref [ROY2003], where a weak influence of Avicel cellulose concentration was noticed. On the contrary, with Borregaard steam-exploded cellulose, it appears that the activation energy increases with Borregaard cellulose concentration as well as with the presence of ZnO in NaOH/water.
The fact that at low concentration the flow is Newtonian, reaching a non-Newtonian regime at high concentration, is typical of polymer solution, despite that the flow index is very small. Nevertheless, the fact that the activation energy of rather concentrated cellulose solutions is very close to the ones of the solvent is suggesting that the cellulose chain is not participating a lot to the flow as a single chain undergoing internal conformational changes. This suggests a

"suspension-like" behaviour, as was also noted by [ROY2003]. We can make the assumption that the polymer chains are aggregating as soft nano gel-like objects, giving rise to a weak non-Newtonian behaviour (no strong conformational changes during flow) and a small contribution to the activation energy of the mixture.

IV.2- GELATION AND DISSOLUTION OF CELLULOSE IN THE PRESENCE OF ZNO

Gelation is due to the formation of more or less strong links between polymer chains in order to form an infinite structure. Two types of gel can be defined, chemical gel (formation of covalent connections) and physical gel (formation of a network using secondary forces like hydrogen, ionic or hydrophobic bonds, helical formation…). With the former, gelation is irreversible. The latter are easy to form but they are thermodynamically stable only in a given range of conditions.
A gel is a solid state body. During gelation, the material is going from a liquid state to a solid state. Gelation is a continuous process which can be studied with rheological measurements. The steady-state mode [WIN1986] enables to determine the gel point but not the properties of the final gel since it is breaking under shear. The dynamic mode [TUN1982] [WIN1986] [FRE1996], which will be used in this work, allows not only to determine the gel point but also to study in details the gelation kinetics, the mechanical properties of the gel, and the eventual changes occurring in time.

The time-moduli dependence as well as the temperature-moduli dependence will be the most often used experiments to investigate the gel formation of cellulose solutions. The gel point will be considered to correspond to the intercept point between both moduli, in time or in temperature.

In this section the influence of ZnO on gelation will be studied in details using dynamic rheology. Gelation kinetics, temperature of gel formation and gel strength at the gel point are investigated as a function of the dissolution procedure and ZnO concentration. The optimal concentration of ZnO in cellulose alkali solutions for delaying gelation in time and temperature is determined. The rheological results are accompanied by visual observations of the dissolution of cellulose fibres, performed by optical microscopy.

IV.2.1- Influence of the preparation conditions on gelation of cellulose/ 7.6NaOH/water solutions in the presence of ZnO

In order to quantify the influence of additives on gelation, the gelation temperature T_{gel} was determined from G' and G" measurements as a function of temperature (see details in Chapter II), and is defined as being the intercept point of both moduli.
First of all, different methods of solution preparation were tested to dissolve B342 cellulose. 100g of solution contains 5g of cellulose, 7.6g of NaOH, 0.7g of ZnO and water; the preparation methods were as follows:

Method 'a' – Innovia Films Procedure – the main method used in this work (see details in Chapter II):

- 1.1%ZnO is dissolved in 12%NaOH/water; 63.33g of this NaOH/ZnO/water system is cooled down at -6°C.
- 31.67g of water is added to 5g of cellulose pulp; the cellulose/water system is cooled down at 5°C.
- The solvent system is added to the cellulose pulp, mixing thoroughly with a spatula
- The system is placed at -6°C and mixed with a rotary overhead mixer, for 2 hours

Method 'b':

- 63.33g of 12%NaOH/water are cooled down at -6°C and then added to the cellulose pulp (5g cellulose + 31.67g water), mixing thoroughly with a spatula
- 0.7g of ZnO is put in 5cellulose/7.6NaOH/water, at 20°C
- The system is placed at -6°C and mixed with a rotary overhead mixer, for 2 hours

Method 'c':

- 63.33g of 12%NaOH/water are cooled down at -6°C and then added to the cellulose pulp (5g cellulose + 31.67g water), mixing thoroughly with a spatula
- 0.7g of ZnO is put in 5cellulose/7.6NaOH/water, at –6°C
- The system is mixed with a rotary overhead mixer, for 2 hours, at -6°C.

The gelation temperature for these different preparation methods are shown in Fig.IV.2-1 and compared with 5cellulose/7.6NaOH/water solution prepared from the Innovia Films procedure (noted 'NaOH' on the graph).

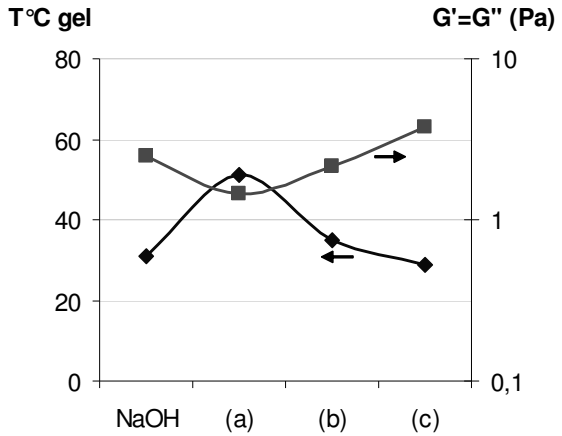
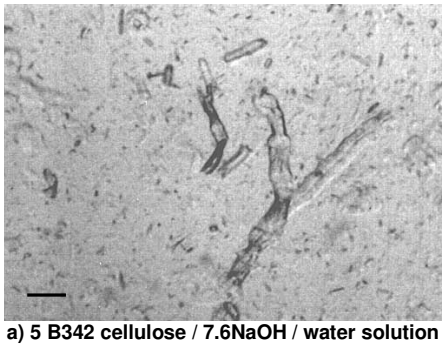


Fig.IV.2-1: Gelation temperature *Tgel* (◆) and strength of the gel when G'=G'' (■) of 5 B342 cellulose/7.6NaOH/0.7ZnO/water mixture for three methods to add ZnO, compared to the case without ZnO noted 'NaOH' on the graph

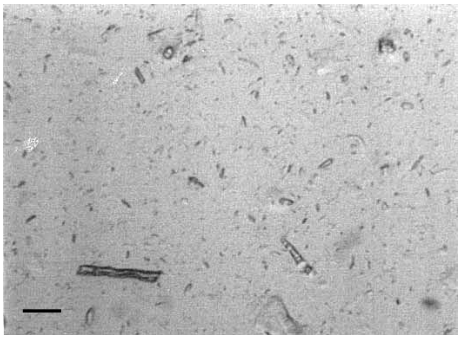
Gelation temperature and strength of gel obtained in methods 'b' and 'c' are approximately the same as cellulose/7.6NaOH/water without ZnO ('NaOH' on the graph). This means that the addition of ZnO in cellulose/NaOH/water solutions does not improve their stability with these 'b' and 'c' methods. On the other hand, gelation is delayed if using method 'a'. ZnO must be dissolved in 12%NaOH solution and then this solvent added to cellulose to influence the properties of cellulose solutions. The microscopic observations (Fig.IV.2-2) showed that in 'b'

procedures ZnO is not well dissolved and the ZnO particles stay in suspension, while in method 'a' all ZnO was dissolved.

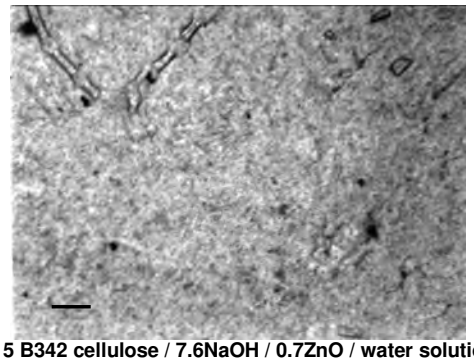
Let us try to explain the influence of the preparation method on gelation temperature. It must be linked to ZnO degree of dissolution. It should be noted that the dissolution of ZnO in aqueous solutions is rather difficult and strongly depends on pH values [LIU1998]. It is not soluble at all in water and the dissolution increases with the medium becoming either strongly basic or acid. Since all the four mixtures of Fig.IV.2-1 have the same pH (about 12), pH is not the reason explaining the reported differences. Most probably these differences can be explained by a competition of different components during dissolution, for example, the competition between ZnO and cellulose for water or for NaOH. The competition for NaOH seems to be the most probable since we have seen in the previous part (Chapter III) that the dissolution of ZnO in alkali solution forms zinc hydroxides.



a) 5 B342 cellulose / 7.6NaOH / water solution



b) 5 B342 cellulose / 7.6NaOH / 0.7 ZnO / water solution
Method 'a': ZnO dissolved in NaOH/water



c) 5 B342 cellulose / 7.6NaOH / 0.7ZnO / water solution
Method 'b': ZnO added to cellulose/NaOH/water

Fig.IV.2-2: Observations with optical microscope of 5 B342 cellulose / 7.6NaOH / water (a), 5 B342 cellulose/7.6NaOH/0.7ZnO/water, prepared from method 'a' (b), and from method 'b' (c)
Scale bar represents 100µm

When cellulose is added first to NaOH/water, it dissolves with a coating of hydrated ions around the cellulose chain. Adding ZnO in this solution is not changing the organisation of Na ions around the chain, and thus not changing the dissolution state. On the contrary, the addition of ZnO to NaOH/water before the introduction of cellulose is creating new chemical species, as seen in Chapter III with the temperature decrease or the disappearance of the NaOH/water eutectic peak. This new solvent is better for dissolving cellulose than pure NaOH/water.
In the following, the Innovia Films dissolution procedure (method 'a') will be used.

IV.2.2- Influence of ZnO concentration on gelation and cellulose dissolution

In this section, the influence of ZnO content on the stability of cellulose solution (or shift of gelation temperature) and cellulose dissolution is studied. In 100g of solution, NaOH and B342 cellulose contents were fixed at 7.6g and 5g. ZnO amount varied from 0g to 3.9g.

As in the previous section, G' and G" were measured as a function of temperature and gelation temperature and G' at gel point were plotted versus ZnO concentration (Fig.IV.2-3).

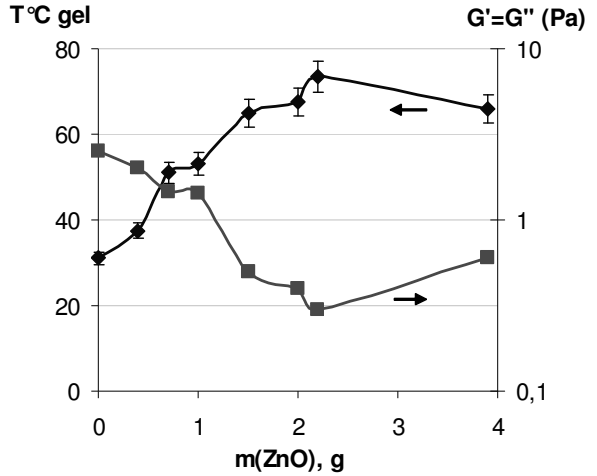


Fig.IV.2-3: Influence of ZnO content on gelation temperature *Tgel* (◆) and strength of the gel when G'=G" (■) of 5 B342 cellulose/7.6NaOH/X ZnO/water solutions (X = 0, 0.4, 0.7, 1, 1.5, 2.2 and 3.9)

This graph shows that there are two regions of ZnO content:

- The first one, from 0 to around 1.5g ZnO, reveals an increase of the gelation temperature with the increase of ZnO content. For example, the gelation temperature of 5 B342 cellulose/7.6NaOH/water without ZnO is about 30°C whereas with 1.5g ZnO it is 65°C. Simultaneously, the gel strength decreases by a factor 5.
- Above around 1.5g ZnO, the gelation temperature is constant (65-70°C) whatever the ZnO content is.

Let us compare the results obtained with cellulose dissolution in the presence and absence of ZnO and also with ZnO solubility.

The solutions were observed with an optical microscope and the following pictures were obtained (Fig.IV.2-4).

The first picture (Fig.IV.2-4a) corresponds to the solution of 5 B342 cellulose/7.6NaOH/water without ZnO and on the others pictures the quantity of ZnO is increased. If we look at the pictures from a) to c), it is clear that the number of non-dissolved fibres or parts of fibres decreases with the increase of ZnO concentration. Pictures 'c' and 'd' are very similar, showing a good dissolution of cellulose. Picture 'd' has more dark points that are non-dissolved ZnO

aggregates. Whatever the ZnO concentration is, the cellulose dissolution is not complete. Fig.IV.2-4 shows that small cylinder-like parts of the fibres remain non-dissolved and un-swollen. These probably correspond to the "un-swollen sections" of the fibres as described in [CUI2006a] and [CUI2006b] (see Chapter I).

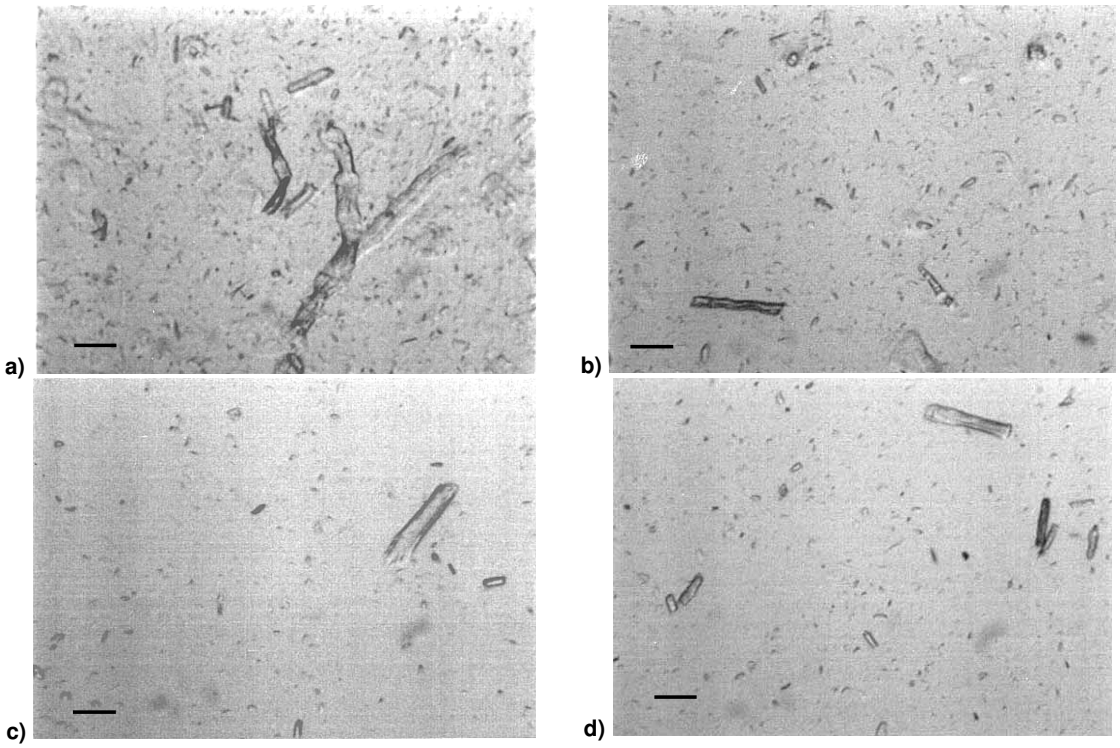


Fig.IV.2-4: Observation with optical microscope of 5 B342 cellulose/7.6NaOH/water solutions containing a) 0g ZnO, b) 0.7g ZnO, c) 1.5g ZnO, and d) 2.2g ZnO
Scale bar represents 100µm

From these microscopic observations, we can say that the cellulose dissolution is better when adding ZnO. But it seems that there is a threshold ZnO content above which the cellulose dissolution is not improved anymore (Fig.IV.2-4 c and d). This limit is around 1.5g of ZnO. In addition, we can note that in 7.6NaOH/1.5ZnO/water, the ratio NaOH/ZnO is 10, which corresponds to the limit of ZnO solubility determined in Chapter III. Experimentally, we observed that above 1.5g of ZnO in 7.6NaOH/water, some ZnO particles are not dissolved and stay in suspension.

If correlating visual observations with the results obtained on gelation temperature, one can conclude that with the increase of ZnO content up to 1.5, zinc oxide is completely dissolved in 7.6NaOH/water and higher is the ZnO content, higher the gelation temperature and lower the gel strength. Above 1.5ZnO, zinc oxide is not fully dissolved and thus the gelation temperature remains constant. The non-dissolved ZnO is not playing any role.

To conclude, we can say that the optimum ZnO content giving the maximum of cellulose dissolution and the best solution stability (highest gelation temperature) is linked to the maximum of ZnO solubility in the NaOH/water mixture.

IV.2.3- Dissolution of cellulose in a solvent with a constant molar ratio ZnO:NaOH = 1:10

As demonstrated in the previous section, the best dissolution of Borregaard cellulose is reached with the 7.6NaOH/1.5ZnO/water solvent, which corresponds to a ZnO:NaOH molar ratio of 1:10. The goal of this section is to increase ZnO concentration keeping the optimal ratio ZnO:NaOH = 1:10, hoping that this could improve cellulose dissolution because of keeping ZnO dissolved. To do this, we fixed the ratio ZnO:NaOH = 1:10 and increased NaOH and ZnO concentrations simultaneously.

The results were not satisfactory since 15NaOH/3ZnO/water did not dissolve cellulose at all even at –6°C. The reason is that as soon as NaOH concentration is higher than 10% it reaches the upper limit of the cellulose dissolution domain [SOB1939]. The presence of ZnO does not increase the range of NaOH concentration able to dissolve cellulose.

IV.2.4- Influence of the presence of ZnO on gelation kinetics

In the previous sections, the evolution of G' and G" as a function of temperature was studied in order to rapidly determine gelation temperature and thus to compare the solvents of cellulose in terms of solutions stability (gelation). In this section, the gelation kinetics of 5cellulose/7.6NaOH/water and of 5cellulose/7.6NaOH/0.7ZnO/water solutions was investigated at different temperatures (Fig.IV.2-5). Frequency and stress were fixed at 0.1Hz and 0.01Pa, respectively, in order to be in the linear visco-elastic regime. The gel point is defined as being the intercept between the G' and G" curves [WIN1986].

Fig.IV.2-5 is an example of curves obtained. The gel point is directly indicated on the graphs. The results on gelation time as a function of temperature and solvent used are summarised in Fig.IV.2-6.

The most common trends of moduli evolutions are as follows.
At the beginning of the experiment, at +10°C/+20°C, the viscous component, G", is higher than the elastic one, G'. This reflects a classical liquid-like behaviour of a polymer solution. At a certain time, depending on temperature and presence of ZnO, both moduli start to increase. G' is increasing faster than G", the two parameters G' and G" crossing at a certain time. This time defines the gelation time t_{gel}. At this time, the solution is a mixture of a gel phase and a sol phase. Above this gelation time, the solution is more elastic than viscous.

With gelation proceeding further, a strong data scattering of the elastic and viscous components can be seen. The scattering of the viscous component G" is more pronounced and appears at a shorter time than the scattering of G'. This scattering is probably due to a phase separation during gelation.

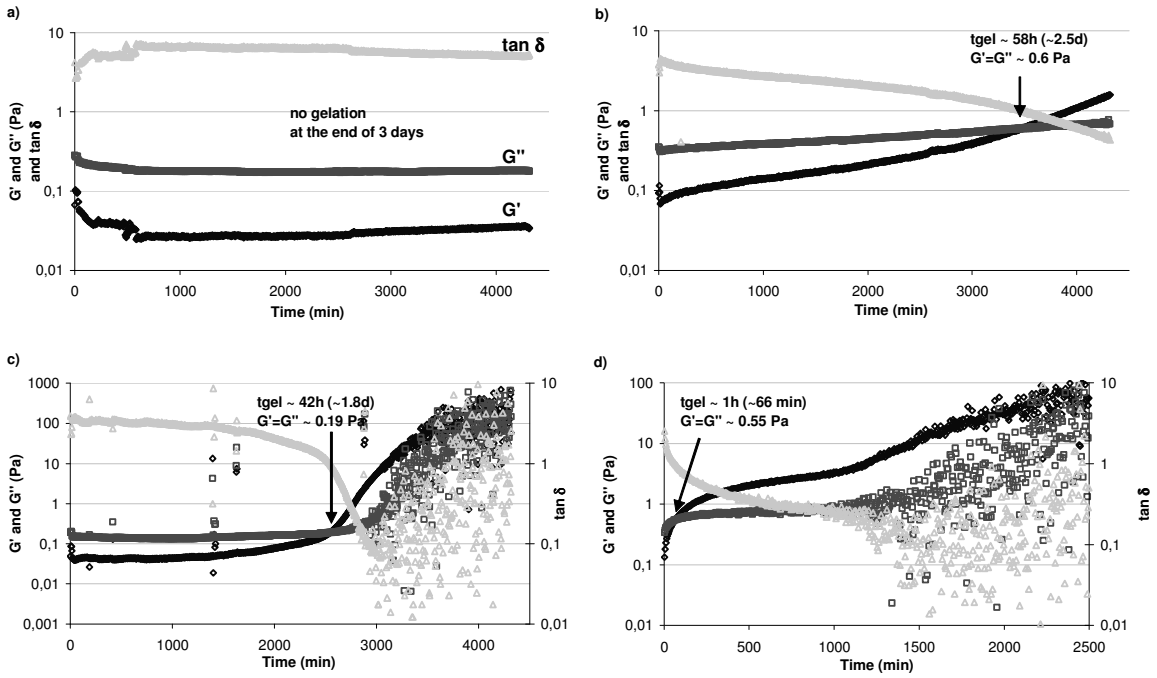


Fig.IV.2-5: Rheological measurement – G' (◇), G'' (□) and tan δ (△) – as a function of time for a) 5 B342 cellulose/7.6NaOH/0.7ZnO/water, at 10°C; b) 5 B342 cellulose/7.6NaOH/water, at 10°C; c) 5 B342 cellulose/7.6NaOH/0.7ZnO/water, at 20°C; d) 5 B342 cellulose/7.6NaOH/water, at 20°C
f = 0.1 Hz and σ = 0.01 Pa

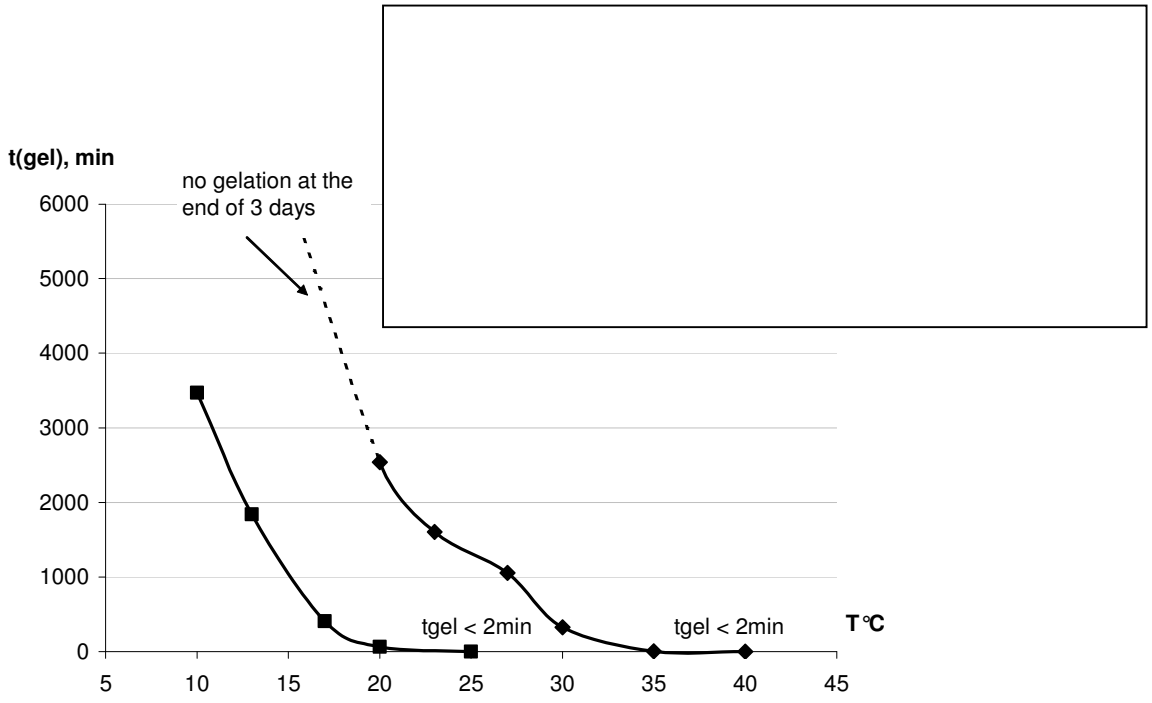


Fig.IV.2-6: Gelation time versus temperature and values of the gel point for 5 B342 cellulose/7.6NaOH/water (■) and 5 B342 cellulose/7.6NaOH/0.7ZnO/water (◆) solutions

Without ZnO, the increase of G' starts right at the beginning of the experiment, even at 10°C (Fig.IV.2-5, b). The solution is gelling very quickly at 20°C and higher. The presence of ZnO delays the start of gelation. At 10°C, 20°C and 30°C, there is a noticeable period of time from the beginning of the experiment where the solution is still in its liquid state. With time, even in the presence of ZnO, gelation starts. Gelation time decreases with the temperature increase for both solvents (Fig.IV.2-6). It was not possible to measure gelation time of this cellulose solution in the presence of 0.7ZnO at +10°C because of a very slow kinetics. The values of G' at the gel point is much lower when ZnO is present, see table on the Fig.IV.2-6.

The similar shape of the two curves in Fig.IV.2-6 will be discussed together with the other results in the Discussion section concerning the mechanism of cellulose solution gelation.

IV.2.5- Influence of ZnO on cellulose intrinsic viscosity

Intrinsic viscosity is an important molecular parameter that reflects the size of the macromolecule in a certain solvent and thus gives the information on solvent thermodynamic quality. The intrinsic viscosity of Avicel microcrystalline cellulose dissolved in 9%NaOH/water as a function of temperature was studied in ref [ROY2003]. In this section the intrinsic viscosity of a steam exploded cellulose (B342) was measured in 7.6NaOH/water with and without 0.7ZnO, also as a function of temperature.

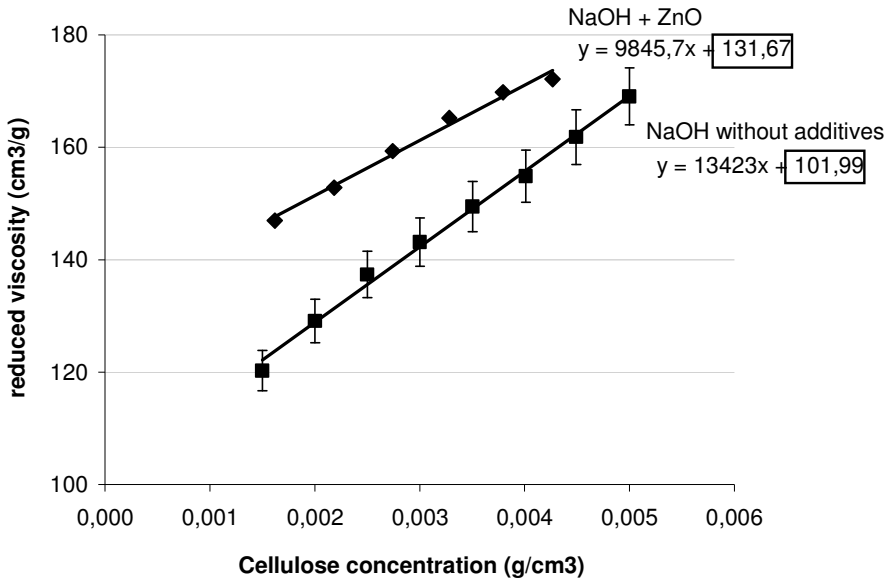


Fig.IV.2-7: Determination of intrinsic viscosity, at 25°C, for B342 cellulose/7.6NaOH/water (■) and B342 cellulose/7.6NaOH/0.7ZnO/water (◆)
The nature of solvent is indicated close to the curve, intrinsic viscosity is the value in the rectangle.

First, the reduced viscosity (see details in Chapter II) of cellulose solutions was measured as a function of cellulose concentration during dilution with the corresponding solvent, 7.6NaOH/water or 7.6NaOH/0.7ZnO/water, at different temperatures. An example is shown in

Fig.IV.2-7 for 25°C together with the equation corresponding to the least square approximation for each solution. The intrinsic viscosity is the value of the reduced viscosity at $C_{cell} \rightarrow 0$. Fig.IV.2-8 represents the intrinsic viscosity-temperature dependence for solutions in NaOH/water, in NaOH/ZnO/water and in NaOH/urea/water.

For a given polymer in a given solvent, a decrease of the intrinsic viscosity means that the polymer chain is decreasing its hydrodynamic radius. Intramolecular links are favoured and the solvent quality decreases. On the Fig.IV.2-7, we can see that at 25°C the intrinsic viscosity of a cellulose solution containing ZnO is higher (132cm^3/g) than the one of cellulose solution in pure NaOH (102cm^3/g). This indicates that NaOH/ZnO/water is a better cellulose solvent than NaOH/water.

The dependence of the intrinsic viscosity of cellulose/7.6NaOH/water in the presence and absence of 0.7ZnO is plotted as a function of temperature in Fig.IV.2-8. At all temperatures, the intrinsic viscosity of solutions in the presence of ZnO is higher than the one of solutions without it. On the same figure, data for cellulose/7.6NaOH/6urea/water solutions are also shown. They will be discussed in the section dealing with the influence of urea on cellulose gelation and dissolution.

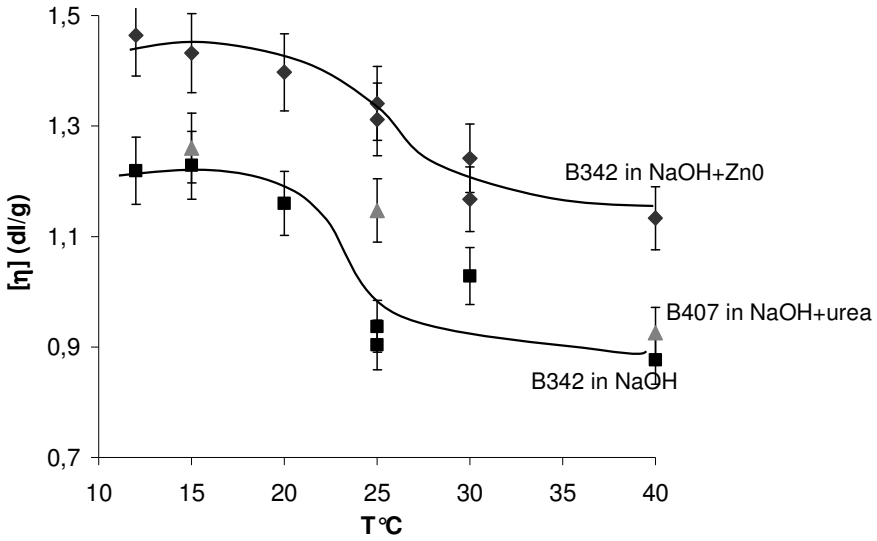


Fig.IV.2-8: Intrinsic viscosity (dl/g) versus temperature for B342 cellulose/7.6NaOH/water (■), B342 cellulose/7.6NaOH/0.7ZnO/water (◆) and B407 cellulose/7.6NaOH/6urea/water (▲)

With or without additives, the intrinsic viscosity decreases when temperature increases. The same result has already been obtained for Avicel/9%NaOH/water solutions [ROY2003]. This is compatible with the fact that upon increasing temperature, gelation occurs (Fig.IV.2-6). The solvent is thermodynamically worse when temperature increases. We can also see that the trend of intrinsic viscosity versus temperature curves is the same for the three studied solvents.

IV.2.6- Discussion on the influence of ZnO on gelation of steam exploded cellulose in 7.6NaOH/water solutions

The purpose of this part is to summarise the results obtained on the role of zinc oxide on gelation of cellulose/7.6NaOH/0.7ZnO/water solutions and to compare them with the gelation of cellulose solutions without ZnO.

The intrinsic viscosity (Fig.IV.2-8) and gelation time (Fig.IV.2-6), both as a function of temperature, show that the curves with and without ZnO have the same shape. It is thus possible to plot master curves, i.e. to translate by a certain temperature shift the intrinsic viscosity and the gelation time to have the curves with and without ZnO coinciding. The master plots are shown on Fig.IV.2-9 and Fig.IV.2-10.

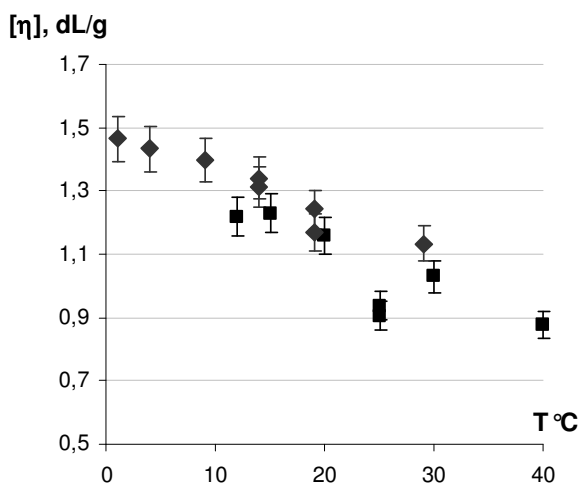


Fig.IV.2-9: same as Fig.IV.2-8 but with a -11°C shift of the intrinsic viscosity of cellulose/7.6NaOH/0.7ZnO/water (◆); the reference being the cellulose/7.6NaOH/water solution (■).

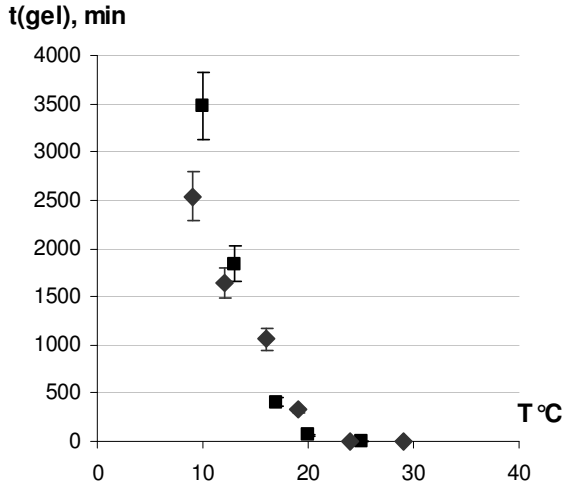


Fig.IV.2-10: same as Fig .IV.2-6 but with a -11°C shift of the gelation time of cellulose/7.6NaOH/0.7ZnO/water (◆); the reference being the cellulose/7.6NaOH/water solution (■).

The remarkable effect is that these two different phenomena need the same shift factor. When ZnO is present in the solution there is a high energy barrier to overcome for the chains to start cross-linking. This is due to the ZnO-NaOH-water complexes that are surrounding the chains of cellulose and that are slowly weakening with increasing temperature. It is this same effect that is controlling the main conformation of the cellulose chain, expanding more and having a larger intrinsic viscosity in the presence of ZnO. It is thus understandable that it is the same shift factor that is found in the variations of both the gel point and the intrinsic viscosity to bring the results of cellulose/NaOH/ZnO/water coinciding to the ones of cellulose/NaOH/water.

As G' and G" moduli depend on the frequency of the measurements, Frey *et al.* [FRE1996] proposed to plot the tan δ versus time dependence at various frequencies for a 12%cellulose/ammonia/ammonium thiocyanate solution. Thus they determined the gel point as the intercept point of all the curves. Consequently, the gel point is independent of the frequency used in the experiment and only depends on the materials.

We performed similar experiments: the tan δ versus time dependence at various oscillation frequencies was measured for 5 B342 cellulose/7.6NaOH/water solution at 20°C and for 5 B342

cellulose/7.6NaOH/0.7ZnO/water solution, at 35°C, with a stress of 0.01Pa. The temperature difference between the two experiments is due to the difference of the gelation kinetics for cellulose solutions with and without ZnO.

Using this method, the gel point is obtained in less than 1 minute which does not correspond to the reality. Moreover, there is no distinction between the two solvent systems. This test is not exploitable in this way. On the other hand, if we determine the gel time as the intersection of both G' and G" moduli, it is possible to draw the gel time *t gel* (Fig.IV.2-11a), as well as the gel strength *G' when G'=G"* (Fig.IV.2-11b), versus the frequency of the test. Fig.IV.2-11 'a' and 'b' represent the experimental results while 'c' and 'd' correspond to the master plot. The gelation time obtained for cellulose/NaOH/ZnO/water was multiplied by 9 to coincide with the one obtained for cellulose/NaOH/water. Similarly, the strength of the gel at the gel point (G' value when G'=G") for solution containing ZnO was multiplied by 1.5 to join the one of solution without ZnO. This could also be helpful to understand the gelation mechanisms.

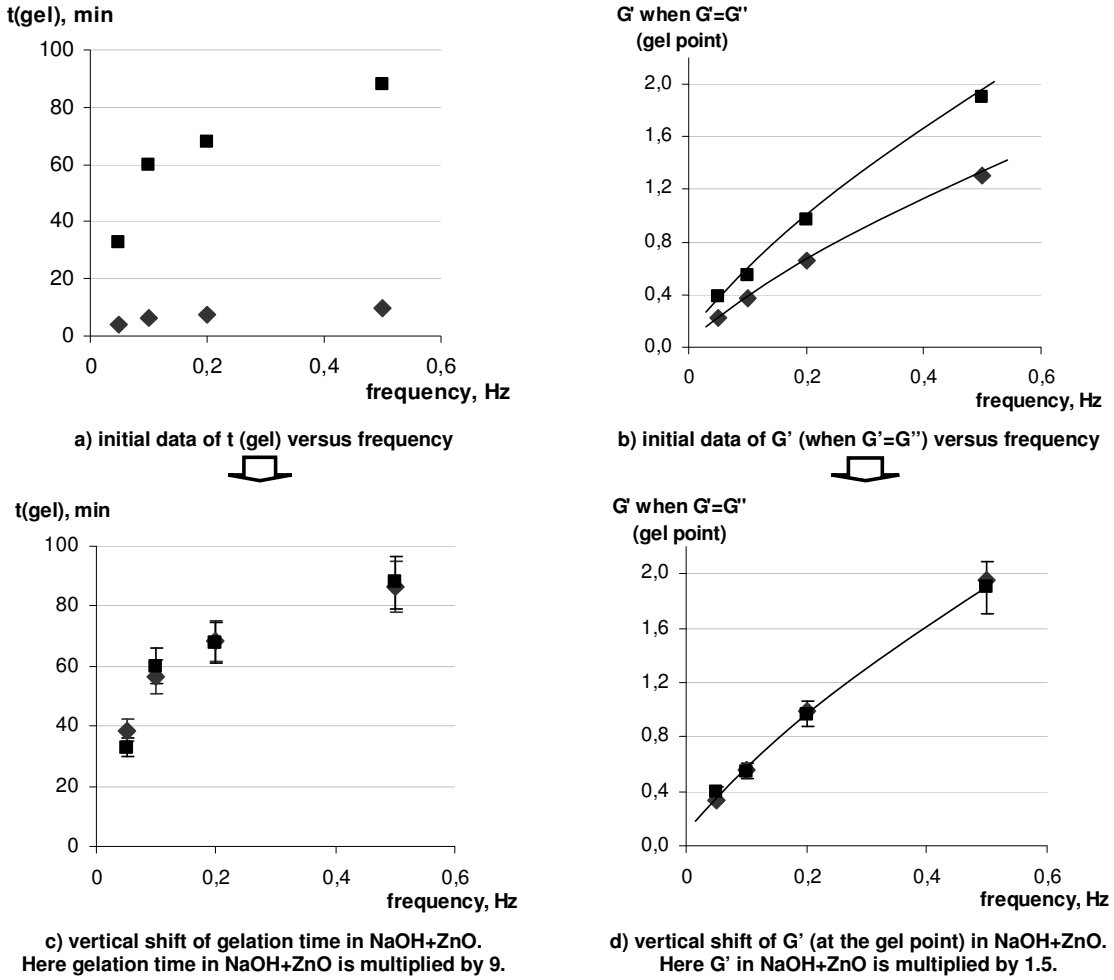


Fig.IV.2-11: Comparison of gelation time (on the left-hand side) and strength of the gel when G'=G'' (on the right-hand side) obtained from G' and G'' versus time measurements at different frequencies (σ=0.01Pa) for 5 B342 cellulose/7.6NaOH/water at 20°C and for 5 B342 cellulose/7.6NaOH/0.7ZnO/water at 35°C

The master plots (Fig.IV.2-11 c and d) show that the evolution of the gel point (gelation time and G' at G'=G") versus frequency is similar in the two cases, cellulose/7.6NaOH/0.7ZnO/ water and cellulose/7.6NaOH/water. This means that ZnO delays gelation but that the gelation mechanism is the same one with or without ZnO. The way cellulose chains cross-linked by most probably forming hydrogen bonds does not depend on the presence of ZnO.

IV.2.7- Conclusions

Summarising the results obtained in Sections IV.2.1 – IV.2.6 on the influence of the presence of ZnO on cellulose dissolution and solution stability (gelation), we can conclude that the increase of ZnO content from 0 to the limit of ZnO solubility (around 1.5 in 7.6NaOH/water which corresponds to a ZnO:NaOH molar ratio of 1:10), leads to the following phenomena:

- the gelation temperature is shifted towards higher temperatures (+ 30-40°C),
- gelation time occurs several hours later
- and cellulose dissolution is improved.

The higher is the ZnO content up to 1.5g in 100g of solution containing 7.6g of NaOH, the better is its effect to delay cellulose gelation. Above a ZnO content of 1.5, the excess of zinc oxide particles are not dissolving. They stay in suspension and ZnO does not influence anymore either cellulose dissolution or gelation. However, even at the optimal ZnO concentration steam-exploded cellulose is not completely dissolved.
The improvement of cellulose dissolution is thus effective only if ZnO is completely dissolved in sodium hydroxide/water, having formed ions such as $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$. We saw in Chapter III that the formation of these ions changes the quantity of free water present in solution: higher ZnO concentration, higher the number of water molecules surrounding zinc hydroxide ions (up to a limit of 25 water molecules per one ZnO).

At the same time the mechanism of cellulose gelation in the presence of ZnO is the same as solution without ZnO (7.6NaOH/water). The fact that the shift factor for gelation time and intrinsic viscosity is the same suggests that ZnO complexes are coating the cellulose chains in the same way as NaOH alone is doing. It is just more effective.

The following hypothesis can be made:
The amount of free water molecules present in solution is an important factor influencing cellulose dissolution. Keeping the NaOH concentration in cellulose dissolution range defined by Sobue in 1939, lower is the quantity of free water, better are the cellulose solubility and the solution stability.

IV.3- GELATION AND DISSOLUTION OF CELLULOSE IN THE PRESENCE OF UREA. COMPARISON BETWEEN UREA AND ZNO

In this section the influence of urea on gelation will be studied using dynamic rheology. The gelation temperature is determined as a function of the dissolution procedure and urea concentration. As previously, the rheological results are accompanied by visual observations of cellulose dissolution in the same solvent performed by optical microscopy.
The optimal concentration of urea in cellulose alkali solutions for delaying gelation is determined as a function of DP and origin of the cellulose pulp. Results are compared with the one obtained for cellulose/NaOH/ZnO aqueous solution, described above.

In 100g of solution, the NaOH and cellulose contents were fixed at 7.6g and 5g, respectively; the urea content was varied from 0 to 20g.

IV.3.1- Influence of the preparation conditions on cellulose dissolution and gelation in the presence of urea, and of urea concentration

Literature described several procedures allowing a total cellulose dissolution in NaOH/urea/water and stable solutions, not gelling with the temperature increase [ZHO2000] [CAI2005] (see part I.2.3). The aim of this section is to find the best procedure of solution preparation in terms of cellulose dissolution and delay of gelation. The results are compared with cellulose dissolution and gelation in the presence of 0.7ZnO.

Four methods (see description in the first column of Fig.IV.3-1) were tested to prepare 5 B407 cellulose/7.6NaOH/6-12urea/water solutions. Optical microscopy was used to visualise the amount of non-dissolved fibres. In the first line of this figure, cellulose solutions prepared with Innovia Films procedure (IF in the following) without urea are shown as a reference: 5cellulose/7.6NaOH/water (photo a), 5cellulose/7.6NaOH/0.7ZnO/water (photo b) and 5cellulose/7.6NaOH/1.5ZnO/water (photo c). Photos from d to i show cellulose solutions in the presence of 6g or 12g of urea as a function of the procedure used.

The following conclusions can be made:

- Qualitatively, there is no significant improvement in cellulose dissolution with the presence of urea whereas ZnO clearly decreases the amount of non-dissolved cellulose fibres.
- "Zhang" and "Caï" procedures (photos g-i) seem to be the least effective: more cellulose fibres remain non-dissolved as compared with "IF" and "Cemef" procedures (photos d-f).
- Cellulose solutions with the presence of 12g of urea are gelling immediately at -6°C whatever is the dissolution procedure (photos e, h, and i). That is why the background on the photos is blurred.

According to the results obtained, "Caï procedure" was immediately abandoned.

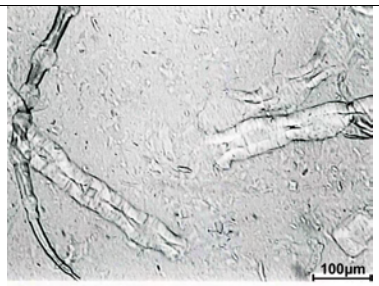
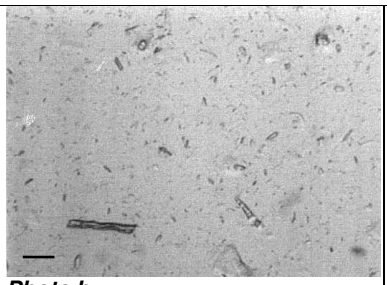
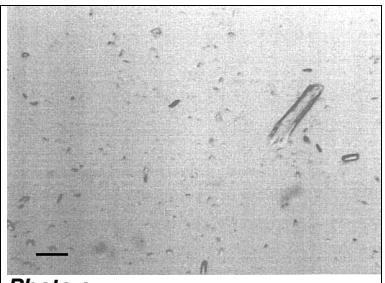
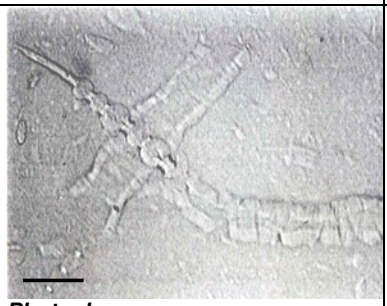
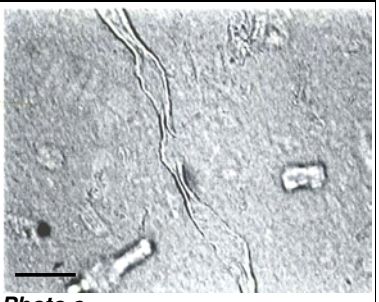
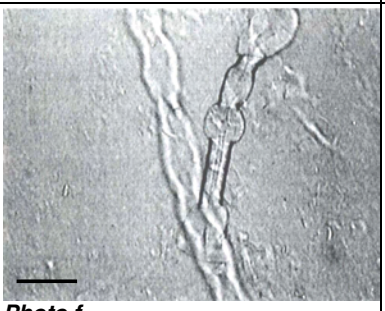
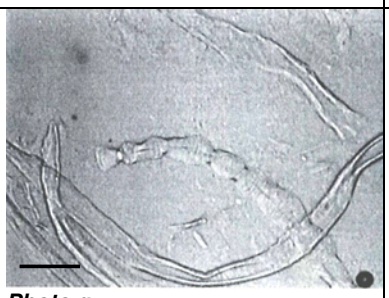
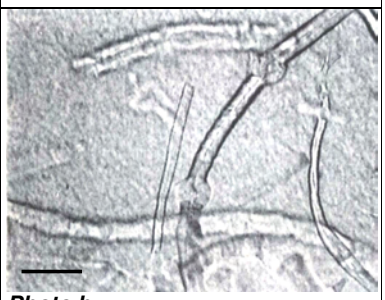
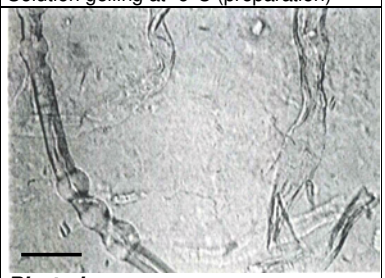
 ***Photo a*** **5 B407 cellulose/7.6NaOH/water** (IF procedure)	 ***Photo b*** **5 B407 cellulose/7.6NaOH + 0.7ZnO/water** (IF)	 ***Photo c*** **5 B407 cellulose/7.6NaOH + 1.5ZnO/water** (IF)
	5 B407 cellulose/ 7.6NaOH/6urea/water	**5 B407 cellulose/ 7.6NaOH/12urea/water**
Innovia Films (IF) procedure (described in Chapter II) ❑ *2h pre-cooling:* NaOH/urea aqueous solution, -6°C Cellulose/water, +5°C ❑ *Mixing all the components* ❑ *2h stirring at -6°C, ~1000rpm*	 ***Photo d***	 ***Photo e***
Cemef procedure ❑ *2h pre-cooling:* NaOH aqueous solution, -6°C Urea aqueous solution, +5°C Cellulose/water, +5°C ❑ *Mixing all the components: first, cellulose/water with NaOH aqueous solution and then adding urea aqueous solution* ❑ *2h stirring at -6°C, ~1000rpm*	 ***Photo f***	
Zhang procedure [ZHA2002] ❑ *Mixing:* Cellulose/NaOH/urea/water at room temperature for 5min ❑ *4h storage, -6°C* ❑ *1h stirring at +4°C, ~1000rpm*	 ***Photo g***	 ***Photo h*** Solution gelling at -6°C (preparation)
Caï procedure [CAI2005] ❑ *2h pre-cooling: NaOH/urea aqueous solution, -10°C* ❑ *Mixing with cellulose* ❑ *30min stirring at room temperature, ~1000rpm*		 ***Photo i*** Solution gelling at -6°C (preparation)

Fig.IV.3-1: Optical micrographs of 5 B407 cellulose/7.6NaOH/water solutions, with ZnO or urea, prepared with various procedures
Scale bar represents 100µm

In order to decide between the three other procedures (IF, Cemef and Zhang procedures), G' and G" of cellulose/7.6NaOH/water solutions in the presence of urea of different contents versus temperature were measured and gelation temperature T_{gel} was determined. The goal is to choose the preparation procedure that leads to the highest gelation temperature to be used in the following. Fig.IV.3-2 shows the gelation temperature T_{gel} versus urea content for the three procedures mentioned above: IF, Cemef and Zhang

First of all, the measurement of gelation temperature shows that the addition of urea improves the stability of solution up to 6g of urea. From "Cemef" and "IF" procedure, the solution turns into a gel at 40°C with 6g of urea instead of 30°C without it. Moreover, taking into account the experimental errors, the gelation temperatures are identical for cellulose solutions prepared from "Innovia films" or from "Cemef" procedure.
If using "Zhang" procedure, urea also increases the gelation temperature. However all values of gelation temperatures are lower than the ones obtained with IF and Cemef methods. Thus "Zhang" procedure was also abandoned.

Secondly, if adding 12g of urea, the solution is gelling immediately after the preparation, for the three dissolution procedures. In this case the gelation temperature is noted as being -6°C.

With 8g of urea, some lumps of non-dissolved cellulose remain after the preparation. Filtration of such a solution should lead to a significant decrease in cellulose concentration and thus the gel point was not measured.

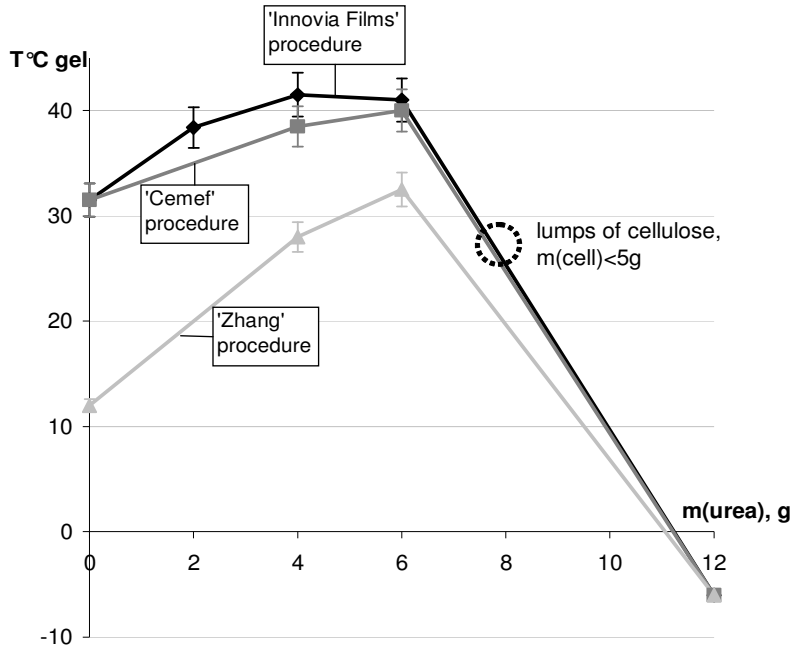


Fig.IV.3-2: Influence of urea content and dissolution procedure on gelation temperature for 5 B407 cellulose / 7.6 NaOH / urea aqueous solutions
Error bars correspond to 5%

- In the following sections, the solutions containing urea will be prepared using "Cemef" procedure, that is to say that NaOH aqueous solution is pre-cooled at –6°C, urea aqueous solution and cellulose/water are pre-cooled at +5°C. All the components are mixed (cellulose/water with NaOH/water and then with urea/water) and then stirred for 2 hours at –6°C.

IV.3.2- Influence of cellulose DP and origin on the dissolution and gelation in the presence of urea and ZnO

Because of a significant difference between literature and our experiments obtained on cellulose dissolution in the presence of urea ("Cai" and "Zhang" procedures not effective), we tested cellulose from various origins and different DP. In addition, several urea contents from 0 to 20g were also used, NaOH content being always fixed at 7.6g. To characterise the cellulose solutions, G' and G" versus temperature were measured to determine the gelation temperature. The results obtained were compared with those of 5cellulose/7.6NaOH/water and 5cellulose/7.6NaOH/0.7ZnO/water solutions.

Gelation temperature was plotted versus DP for several solvent systems (Fig.IV.3-3) and various cellulose origins (Fig.IV.3-5).

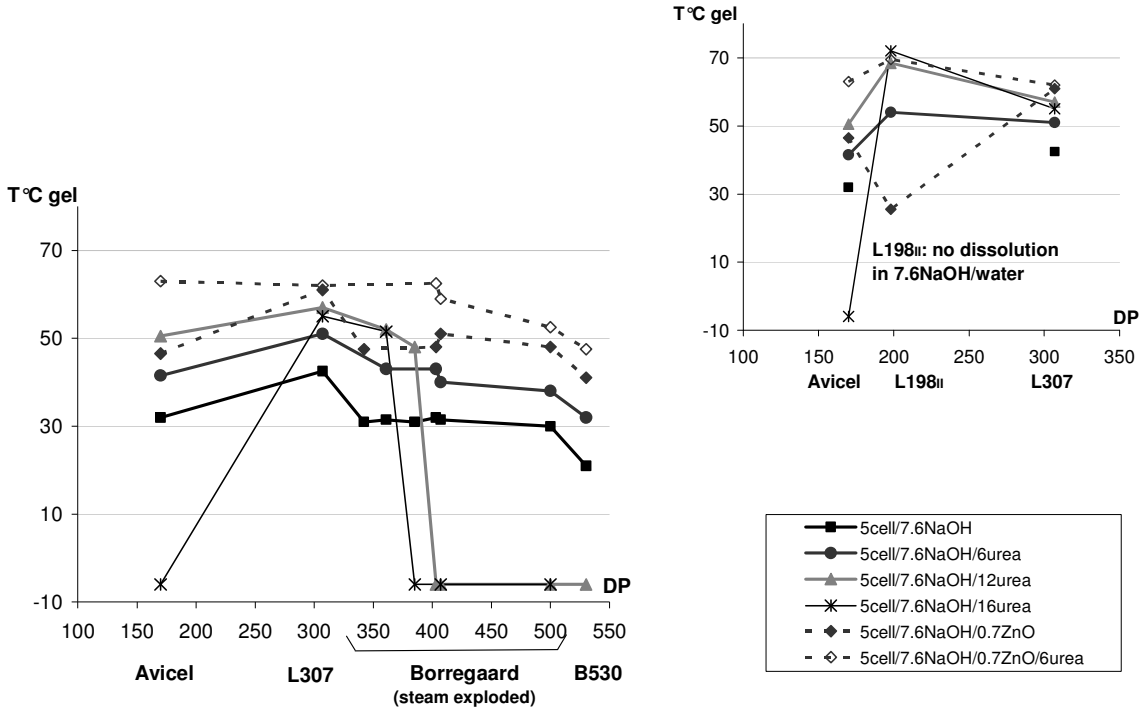
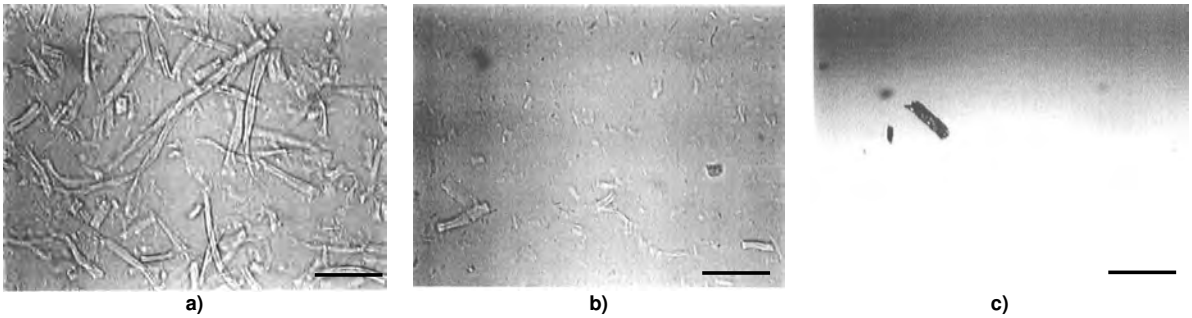


Fig.IV.3-3: Gelation temperature versus cellulose DP for various solvent systems.
Details of cellulose are indicated on the graph.

Several conclusions can be made from the analysis of this graph:

- In NaOH/water, NaOH/6urea/water, NaOH/0.7ZnO/water, NaOH/0.7ZnO/6urea/water:
  - Solutions of Avicel microcrystalline cellulose and of all the Borregaard steam exploded cellulose (from B342 to B500) are reaching the same gelation temperature: the DP does not influence the occurrence of gelation and gelation temperature increases when additives are added. The best solution stability (highest gelation temperature) is reached when cellulose is dissolved in 7.6NaOH/0.7ZnO/6urea/water.
  - Solutions with non-steam exploded Borregaard cellulose (B530) turn into a gel at lower temperatures than those with steam exploded cellulose. The B530 pulp was treated using a standard pulping process and elemental chlorine free (ECF) bleaching; this difference in treatment of initial pulp may explain the results. Moreover, the fibres of this sample are relatively long and thus more difficult to dissolve than small cellulose fibres.
  - Solutions of Lenzing cellulose I (L307) demonstrate higher gelation temperature than the one obtained with steam exploded cellulose.
- Solutions of cellulose with DP higher than 370 and containing 12g or 16g of urea are gelling immediately at –6°C during the preparation step. Moreover, it seems that the threshold of DP, for which gelation is occurring or not during the preparation, depends on the cellulose origin.
- Lenzing cellulose II ($L198_{II}$) has an opposite behaviour as compared with the other pulps studied here. On one hand, 7.6NaOH/water does not dissolve this cellulose (see optical micrograph 'a' in Fig.IV.3-4) and 0.7ZnO improves cellulose dissolution but gelation temperature is lower as compared with the other solutions in the same solvent. On the other hand, higher is the urea content (up to 16g), better the cellulose dissolution is (see Fig.IV.3-4 picture 'b': less non-dissolved fibres in 7.6NaOH/6urea/water, and picture 'c': solution is translucent and no fibres remain non-dissolved in 7.6NaOH/12urea/water) and higher the gelation temperature is. This significantly different behaviour is not explained yet but the results obtained are close to some found in literature [CAI2005]. It is reported that 4% of a cotton linter of DP700 (cellulose from Hubei Chemical Fiber Co Ltd – Xiangfan, China – but there is no detail concerning the treatment of fibres) is not dissolved at all in 7%NaOH/water and is totally dissolved (the solution is transparent) in 7%NaOH/12%urea/water after 60s.



a) b) c)

Fig.IV.3-4: Optical micrographs of a) 5 $L198_{II}$ cellulose/7.6NaOH/water, b) 5 $L198_{II}$ cellulose/7.6NaOH/6urea/water, c) 5 $L198_{II}$ cellulose/7.6NaOH/12urea/water. Scale bar represents 100µm

Fig.IV.3-5 represents the same data on gelation temperature as shown in Fig. IV.3-3 but versus urea concentration, for different cellulose origins. This way to show the results allows focusing on other details. We can identify three groups of curves: the first one is including all Borregaard cellulose samples (Steam exploded or not), the second one is the Avicel cellulose and the last one is Lenzing celluloses. The latter cellulose samples show very high gelation temperatures. At least two reasons can be given: cellulose origin and/or treatment – eucalyptus origin and electron beam irradiation treatment in order to decrease the DP. In general, steam exploded treatment may give more acidic medium that would change the total pH of the solvent and thus the action of NaOH and urea on cellulose. This hypothesis could be checked by preparing steam exploded samples from eucalyptus cellulose, with various DP.

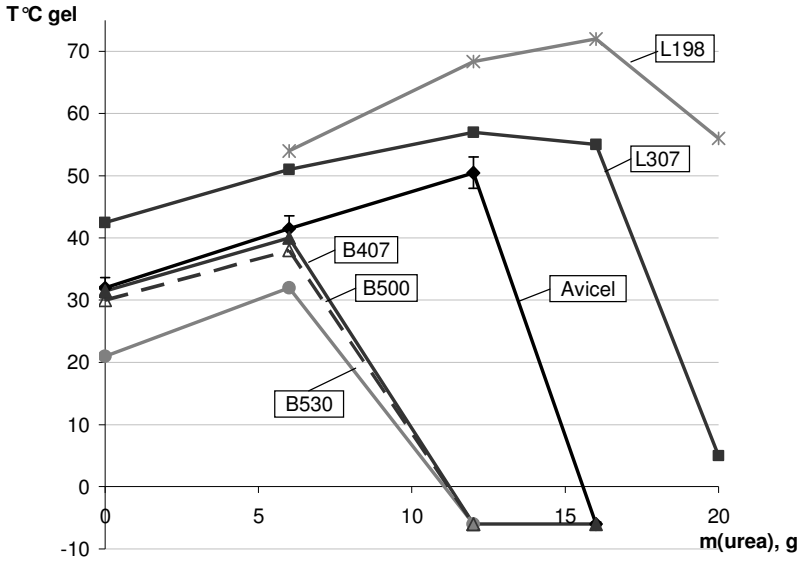


Fig.IV.3-5: Influence of urea content and origin of cellulose on gelation temperature for 5 cellulose/7.6NaOH/Y urea/water solutions (Y = 0, 6, 12, 16 and 20)

The results presented in Fig.IV.3-3 and Fig.IV.3-5 showed that gelation noticeably depends on cellulose origin and pulp treatment. Unfortunately, for the time being, we are not able to explain these differences. As it will be shown in the following paragraphs, dissolution of different celluloses also occurs in different ways. Nevertheless, this rheological study demonstrated why our results on the stability/gelation of steam exploded cellulose solutions are different from literature data: the results strongly depend on cellulose origin and treatment.

The difference in gelation of celluloses was then correlated with the swelling and dissolution of the same cellulose fibres in the presence of urea and ZnO with the exception of Avicel that is not composed of fibres.

Dissolution of cellulose was directly observed in time with an optical microscope equipped with a CCD camera and a DVD recorder. The duration of each experiment was about 5 minutes; the details are given in Chapter II. This investigation is qualitative since kinetics depends on the concentration of cellulose fibres that was not controlled and the degree of dissolution was not measured. Results are summarised in the Tab.IV.3-1 and main pictures, picked up from movies, are shown (Fig.IV.3-6).

Solvent / Cellulose	Experimental test	7.6NaOH/water	7.6NaOH/0.7ZnO / water	7.6NaOH/6urea/ water	7.6NaOH/12urea / water
B530 Cellulose I	Visual observation	Partial dissolution	Partial dissolution		
	Rheology	Tgel~21°C	Tgel~41°C		
	Microscopy	**Swelling**	**Twisting Quick swelling**		
B500 Cellulose I Steam exploded	Visual observation	Partial dissolution	Partial dissolution	Partial dissolution	Gelation
	Rheology	Tgel~30°C	Tgel~48°C	Tgel=38°C	Tgel~-6°C
	Microscopy	**Twisting Swelling**	**Twisting Quick swelling Dissolution**	**Twisting Quick swelling Dissolution**	**Weak swelling**
L307 Cellulose I	Visual observation	Partial dissolution	Dissolution	Dissolution	Dissolution
	Rheology	Tgel~43°C	Tgel~61°C	Tgel=51°C	Tgel=57°C
	Microscopy	**Swelling with ballooning**	**Swelling Quick dissolution**	**Swelling with ballooning**	**Slow dissolution**
L198 Cellulose II	Visual observation	No dissolution			Complete dissolution
	Rheology	-			Tgel=68°C
	Microscopy	**Nothing observed**			**Slow dissolution**

Tab.IV.3-1: Summary of the observations of cellulose dissolution at +4°C for 4 different cellulose pulps and 4 solvents Movies started to be recorded just before the addition of solvent and were stopped at the end of about 5min.

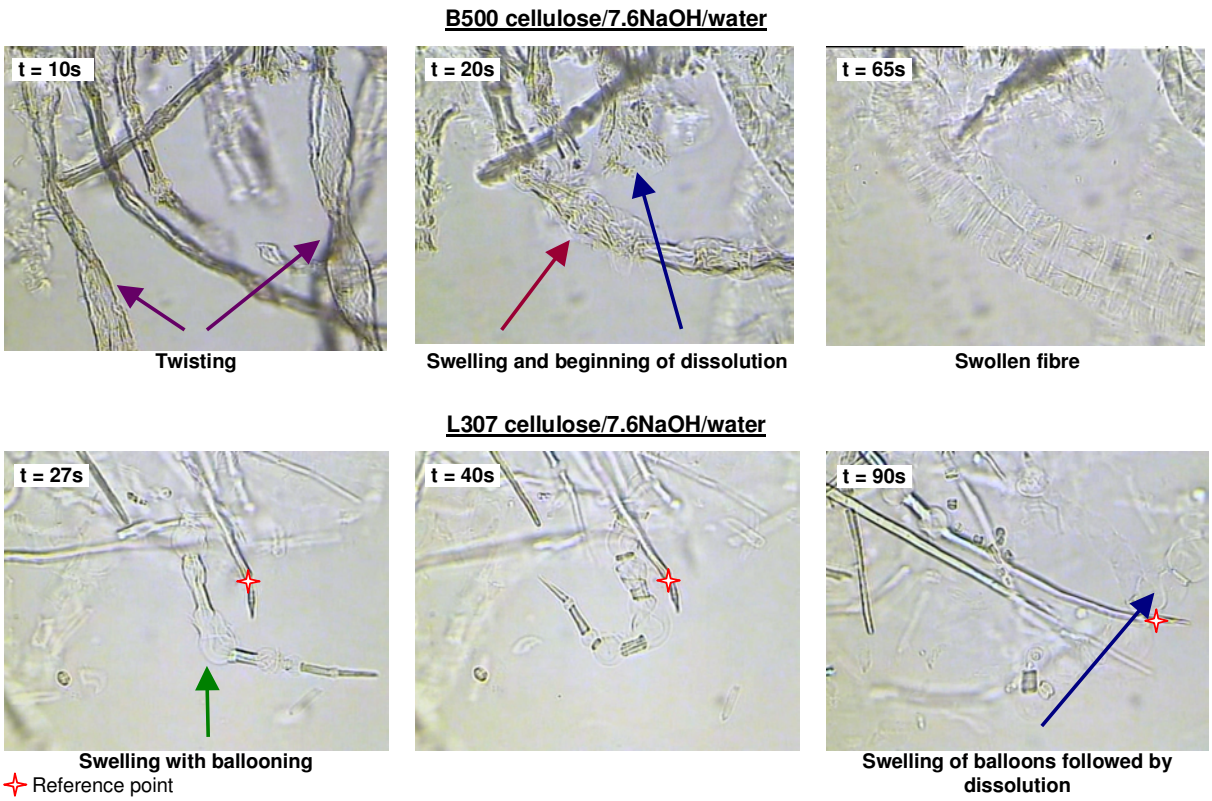


Fig.IV.3-6: Two examples of cellulose dissolution observed with optical microscope

The results presented in Tab.IV.3-1 and Fig.IV.3-6 show that there is a certain difference in the swelling behaviour between Borregaard and Lenzing celluloses. Steam exploded Borregaard cellulose fibres twist and swell before dissolution and Lenzing cellulose fibres form balloons that are swelling and breaking followed by dissolution.
Even qualitatively, it is difficult to compare the kinetics of dissolution of different fibres.

As far as the influence of solvent on swelling and dissolution is concerned, all fibres studied dissolve better and quicker in the presence of 0.7ZnO. Urea is acting on cellulose in different ways depending on cellulose origin:

- Borregaard fibres are hardly swelling in the presence of 12urea but the presence of 6urea seems to increase the cellulose dissolution, at least qualitatively.
- Lenzing L307 fibres in 7.6NaOH/12urea/water are swelling slowly (we do not know at what time the swelling begins, but after 5min, duration of observation, nothing is observed) but are completely dissolving in the same solvent at the end of 2 hours (visual observation).
- Cellulose $L198_{II}$ is swelling differently from all samples: it is not swelling in 7.6NaOH/water and not dissolving at all (this was already mentioned in the previous paragraphs concerning the study on gelation time), and its swelling is very slow (nothing is observed during the 5 first minutes in contact with the solvent) in 7.6NaOH/12urea/water whereas the dissolution of fibres is complete at the end of 2 hours (Fig.IV.3-4c).

Despite the differences observed in the dissolution of fibres of different origins, the general mechanism of their swelling is the same: fibres are first swelling with ballooning or not, then breaking into pieces that are then dissolving. The difference observed between steam exploded and Lenzing fibres is caused by their treatment: the surface of steam exploded fibres is damaged and thus balloons that are "preserved" by the primary wall which plays a role of a membrane [CUI2006a] [CUI2006b] cannot be formed. The qualitative difference in the swelling kinetics can also be explained by the presence of a "membrane" on the fibre surface: if it is intact, swelling and dissolution is slower as compared with the case of "broken" membranes in steam exploded cellulose.

What remains unclear in cellulose dissolution, as well as in cellulose gelation, is why urea is acting in a different way on fibres of different origins. The results obtained on swelling and dissolution of sample $L198_{II}$ are very different from all the other ones since these fibres were not swelling and dissolving in 7.6NaOH/water. Gelation temperatures of this cellulose in different solvent also did not follow the main trend observed for the other samples.

IV.3.3- Discussion on the influence of urea on gelation and dissolution of steam exploded cellulose in 7.6NaOH/water solutions and comparison with the role of ZnO

The results obtained on gelation of cellulose/7.6NaOH/water solutions in the presence of ZnO or urea and on the dissolution of fibres in these solvents show a lot of similarities. In both cases

ZnO and urea of certain content shift the gelation temperature towards higher values which means that these additives make aqueous cellulose/NaOH solutions more stable. Steam exploded fibres are dissolving in the presence of 0.7ZnO or 6urea in a similar way: with homogeneous swelling followed by breaking into pieces and dissolution.

Another proof of the similar action of ZnO or urea on cellulose can be seen in Fig.IV.2-8 where the intrinsic viscosity of cellulose as a function of temperature in 7.6NaOH/water, in 7.6NaOH/0.7ZnO/water and in 7.6NaOH/6urea/water is presented. The presence of ZnO improves solvent quality (see Part IV.2.5-) and so does urea. The shape of the curves for all three solvents is also very similar: the intrinsic viscosity decreases with the increase of solution temperature. One can thus conclude that the reason of cellulose/7.6NaOH/water solutions gelation, with or without additives like ZnO or urea, is the decrease of solvent thermodynamic quality: higher is solution temperature, worse is the solvent quality leading to cellulose-cellulose and not cellulose-solvent preferential interactions.

What is the mechanism of the action of ZnO or urea on cellulose/NaOH aqueous solutions? In Chapter III, we studied the structure of NaOH/urea aqueous solutions (without cellulose) and we demonstrated the formation of a eutectic mixture containing 1urea+8water molecules. This means that when urea is present in the solvent, some water molecules are trapped by urea decreasing the amount of free water in the system. A similar effect was observed for ZnO: it can « keep » up to 25 water molecules. The hypothesis made at the end of Section IV.2- is compatible with the results obtained for solutions in the presence of urea: the presence of free water molecules in cellulose/NaOH aqueous solutions could decrease their stability.

One hypothesis to explain the delay of gelation is as follows. In 7.6NaOH/water, without or with 6urea, the limit of cellulose dissolution is the same and is reached when $m_{cell}=m_{NaOH}$. Thus we can say that urea does not modify the cellulose/NaOH phase diagram, but just « take » « bad » water molecules. The area of cellulose dissolution in NaOH on the phase diagram is very narrow; this means that solvent has a bad thermodynamic quality and that the solution is not stable. Free water molecules may act as nuclei to start phase separation. Urea, and maybe ZnO, may improve solution stability by keeping water molecules. But if these complexes $ZnO+25H_2O$ and $urea+8H_2O$ are not very stable with the increase of temperature, they are broken and free water appears inducing gelation/phase separation.

Another explanation of the role of urea in 4%cellulose/7%NaOH/12%urea/water is presented in literature [CAI2005]: urea being surrounded by 8 water molecules locates between cellulose chains and thus prevents their aggregation. But this hypothesis may not apply to ZnO in sodium hydroxide aqueous solution. Although the size of zinc compounds surrounded by 25 water molecules is probably higher than the one of urea+8water, their amount is much too low to prevent polymer chain aggregation by locating between all chains.

IV.3.4- Conclusions

The addition of urea to NaOH/water improves the quality of cellulose solvent. This explains a slight increase in cellulose solubility and a shift of gelation temperature towards higher values. However, the dissolution of steam-exploded cellulose fibres is not complete: parts of fibres remain non-dissolved.

The optimal urea content to shift the gelation temperature towards the highest values possible depends on cellulose origin. For Borregaard steam exploded pulp, it is around 6g while for eucalyptus pulp treated by Lenzing it is around 12-16g. The best solution stability (highest gelation temperature) was obtained in the presence of both urea and ZnO.

The mechanism of gelation of aqueous cellulose/NaOH solutions in the presence or absence of urea or ZnO seems to be the same. The additives slightly increase the thermodynamic quality of the solvent thus enlarging the temperature interval of solution stability by shifting the beginning of cellulose-cellulose preferential interactions towards higher temperatures. The role of urea or ZnO could be to bind water molecules, up to a certain temperature, that serve as a driver for the phase separation.

IV.4- INFLUENCE OF FREEZING ON RHEOLOGICAL PROPERTIES OF CELLULOSE/NAOH AQUEOUS SOLUTIONS

In ref. [ISO1998][KUO2005], it is reported that freezing is used to dissolve microcrystalline cellulose in NaOH and thus that freezing improves cellulose dissolution and makes NaOH a thermodynamically better solvent. In order to check these data, we performed some experiments.

First of all, we prepared steam exploded cellulose solution following the method with freezing [ISO1998]: "*One g of microcrystalline cellulose was suspended in 26.9ml of water. 2.5g of NaOH was then added, and the mixture was shaken to dissolve the NaOH at room temperature, resulting in a suspension of the cellulose in an 8.5%NaOH solution. The suspension was cooled at -20°C and held at temperature until it became a solid frozen mass. The frozen liquid was then allowed to thaw at room temperature, and was transformed into a gel-like mass. Water (20.6ml) was added to the gel-like material and, with gentle shaking, a clear cellulose solution was obtained. The resulting solution contained 2% cellulose in 5% aqueous NaOH".*
But proceeding as above-described leads to a system with a precipitate of cellulose. In our case, we cannot say that the freezing step improves the steam exploded cellulose dissolution.

Then we compared the rheological properties of steam exploded cellulose solutions prepared with our standard procedure (described in the Chapter II) with and without freezing.
The first experiment is the determination of intrinsic viscosity for frozen and non-frozen cellulose solutions. The results are shown on the Fig.IV.4-1. We can see that the intrinsic viscosity of a non-frozen solution is higher than the one of a frozen solution: the freezing step does not increase the solvent quality of NaOH/water.

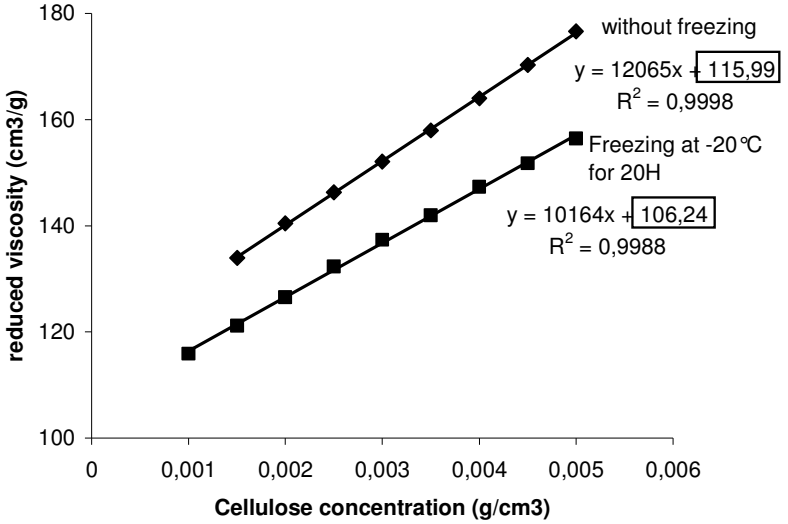


Fig.IV.4-1: Determination of intrinsic viscosity (values in rectangles), at 20°C, for B342 cellulose/7.6NaOH/water solutions without freezing (◆) and after freezing at -20°C for 20H (■).

To study the influence of the freezing step on the state of solution, we measured (i) the viscosity versus shear rate, at 20°C, for frozen and non-frozen cellulose/NaOH aqueous solutions, without or with 0.7ZnO (Fig.IV.4-2) and (ii) the moduli as a function of time, at 15°C (Tab.IV.4-1).

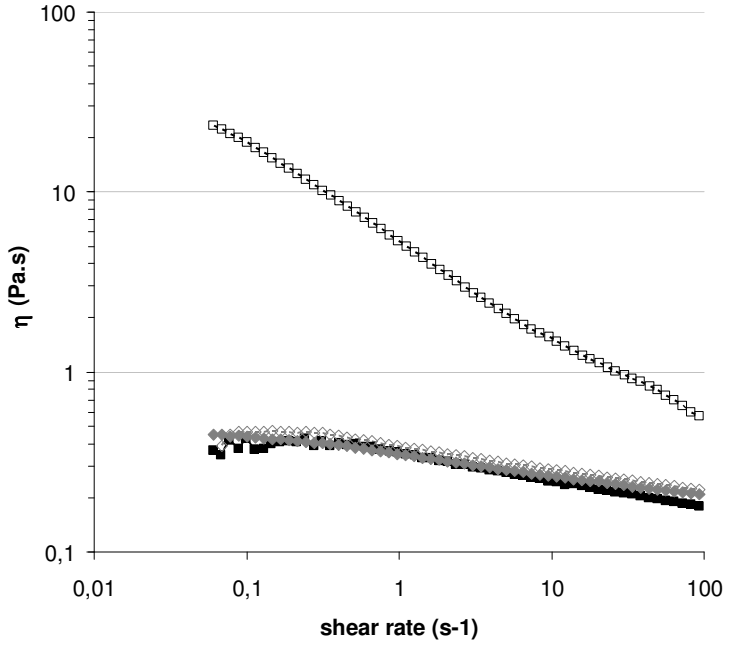


Fig.IV.4-2: Viscosity versus shear rate at 20°C for 5B342 cellulose/7.6NaOH/water (■) and for 5B342 cellulose/7.6NaOH/0.7ZnO/water (◆) just after the preparation (full points) and after a freezing step at -20°C for 20H (open points)

	5B342 cellulose/7.6NaOH/water		5B342 cellulose/7.6NaOH/0.7ZnO/water	
Freezing at -20°C	**0H**	**20H**	**0H**	**20H**
G'	0.15	70	0.05	10
G''	0.40	16	0.2	3

Tab.IV.4-1: Values of G' and G'' moduli for non-frozen (0H) and frozen (20H) 5B342 cellulose/7.6NaOH/water and 5B342 cellulose/7.6NaOH/0.7ZnO/water

After the freezing step, we can note that cellulose/NaOH aqueous solutions are in the gel state: G' is largely superior to G" and the gel is relatively strong (G'=70Pa) (see Tab.IV.4-1). The measurement in steady-state mode reveals an important shear thinning (Fig.IV.4-2). This result is in agreement with the decrease of the solvent quality after freezing (Fig.IV.4-1).
On the other hand, the presence of ZnO in NaOH/water delays gelation not only after heating (see part IV.2) but also after freezing: the viscosity versus shear rate curve of frozen solution almost superimposes the one of non-frozen solution and the strength of gel is relatively low (G'=10Pa with ZnO instead of 70Pa without ZnO)

We can conclude that the freezing step does not improve the cellulose dissolution but induces the gelation of solutions. As in the case of heating, the presence of 0.7ZnO in 7.6NaOH/water delays the occurrence of gelation.

IV.5- TESTS ON GELATION AND DISSOLUTION OF CELLULOSE IN OTHER ALKALI SOLVENTS: KOH AND NAOH WITH OTHER ADDITIVES

This last section describes the results obtained on cellulose dissolution and gelation in other alkali solvents (KOH) and in 7.6NaOH/water in the presence of other additives (surfactants and salts). Some of these compounds were cited in literature as possible cellulose solvents. The goal was to scan different compounds in order to find if indeed they improve the dissolution of steam-exploded cellulose and shift gelation temperature towards higher values.

IV.5.1- Testing cellulose dissolution in potassium hydroxide

7.6KOH/water was tested as a solvent of 5 B342 cellulose and compared with 7.6NaOH/water. The procedure to dissolve cellulose in potassium hydroxide is exactly the same as the one used to dissolve cellulose in sodium hydroxide (see Chapter II), sodium is replaced by potassium. Microscopic observations were performed to qualitatively investigate dissolution of cellulose fibres. The pictures obtained are shown on the Fig.IV.5-1.

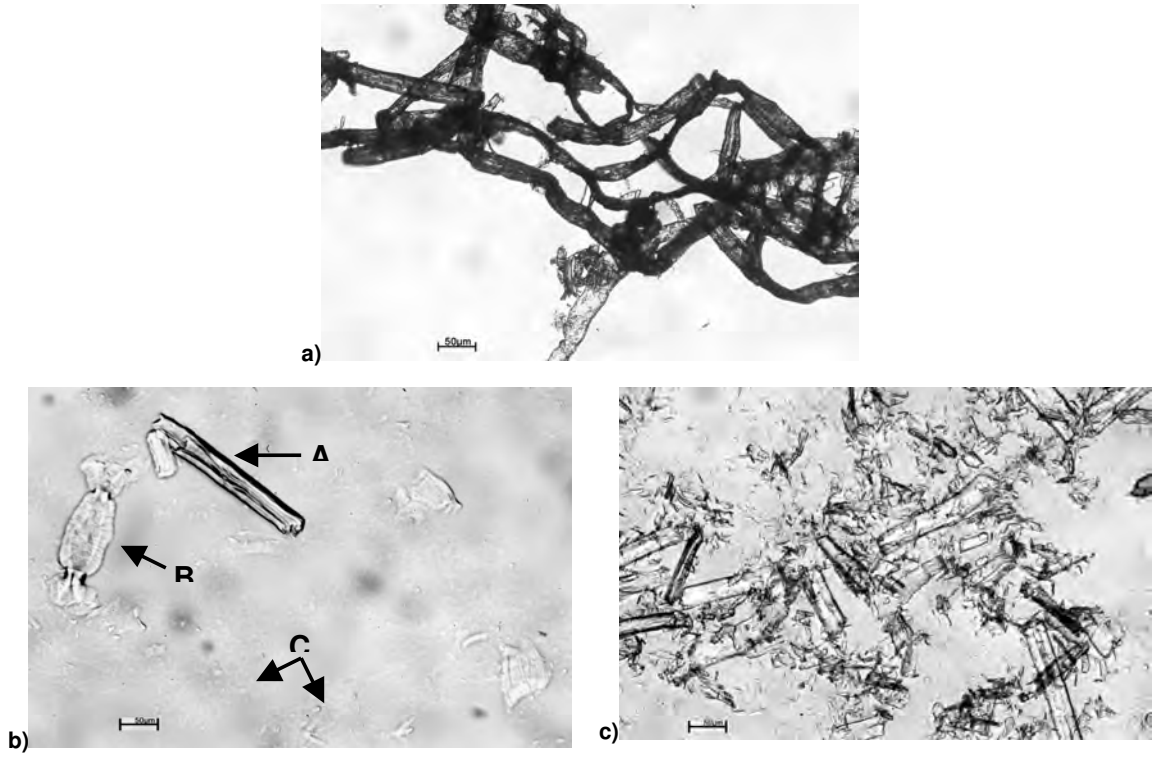


Fig.IV.5-1: Observation with optical microscope of
a) 5 B342 cellulose in water; b) 5 B342 cellulose/7.6NaOH/water; c) 5 B342 cellulose/7.6KOH/water
Scale bar represents 50µm

Picture 'a' on the Fig.IV.5-1 represents cellulose fibres in pure water. As at room temperature and standard pressure water does not dissolve cellulose at all, this is the reference to qualitatively determine the solvent quality.

After the preparation of cellulose in alkali solutions (2 hours mixing at -6°C), we can immediately note that sodium hydroxide is a better cellulose solvent than potassium hydroxide. Indeed, the aspect and the morphology of solutions are different (Fig.IV.5-1 b and c).

- First of all, 5cellulose/7.6NaOH/water solutions are translucent and the microscopic observation (Fig.IV.5-1b) reveals that only a few non-dissolved fibres remain (A). Most of them have undergone swelling (B) or start of dissolution, which corresponds to the more or less fuzzy zones (C).
- On the contrary, 5cellulose/7.6KOH/water solutions are opaque and after a few minutes a noticeable sedimentation can be observed. The solution was homogenised and then observed using optical microscope (Fig.IV.5-1c). The aspect of the fibres is very different from the initial fibres since they have been broken. No swollen fibre was seen.

We know from literature that a small fraction of cellulose can be dissolved [DAV1936] [MAR1941] (see part I.2.2): swelling and dissolution of cellulose fibres are lower in KOH than in NaOH. Even if we only tested one condition of temperature and alkali concentration, literature stipulates that this is true for all alkali concentrations.

IV.5.2- Addition of surfactants

A surfactant is added during the sponges fabrication to the cellulose solution. Empirically, the final properties of sponges were shown to be improved in the presence of surfactant. The aim of this section is to study cellulose dissolution and gelation in 7.6NaOH/water in the presence of surfactants (AP, Zonyl FS and Zonyl FSN) in order to better understand their role.
The three surfactants used in this study are soluble in water. They were mixed with the NaOH/water solvent (as in the case of NaOH/ZnO/water) before being added to the cellulose pulp. The preparation of solutions remains the same as in pure NaOH/water.

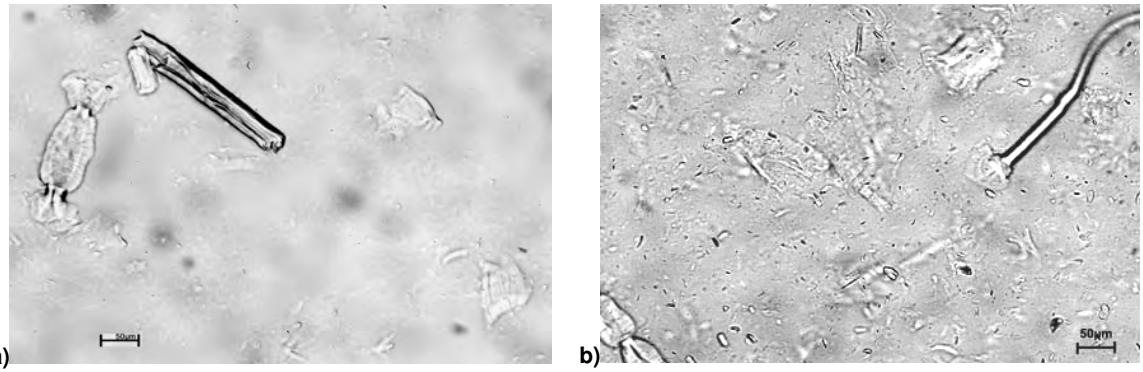


Fig.IV.5-2: Observation with optical microscope of
a) 5 B342 cellulose/7.6NaOH/water; b) 5 B342 cellulose/7.6NaOH/0.05AP/water
Scale bar represents 50µm

Microscopic observations (Fig.IV.5-2) reveal that the addition of 0.05g AP surfactant does not improve cellulose dissolution. It even seems that the solubility of cellulose slightly decreases.
In order to quantify the influence of surfactants on cellulose dissolution, intrinsic viscosity of cellulose/7.6NaOH/water in the presence of 0.05ZonylFSN and of 0.05AP was measured at 25°C (Fig.IV.5-3). The intrinsic viscosity values were calculated according to a least square approximation of experimental data by a straight line; they are indicated in the rectangles on Fig.IV.5-3.

We can see that for cellulose/NaOH/water solutions with or without surfactant, the intrinsic viscosity is about 100g/cm^3. This confirms the previous results: the addition of surfactant does not improve the quality of solvent.

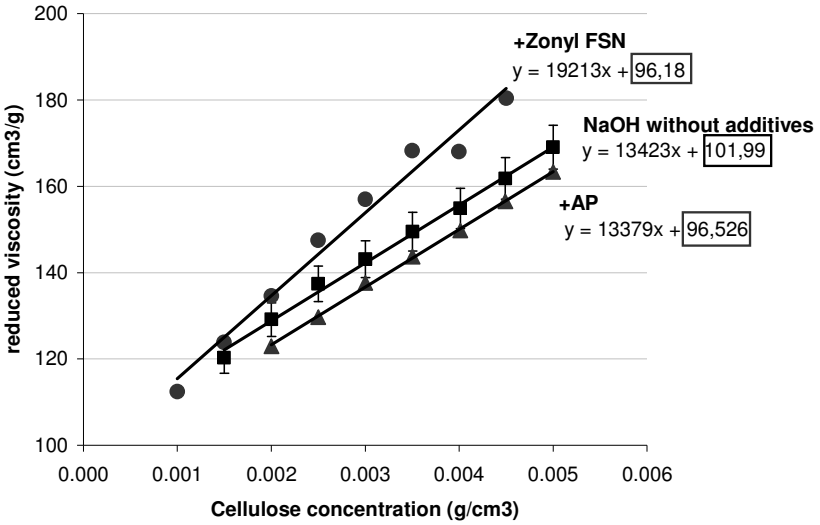


Fig.IV.5-2: Determination of intrinsic viscosity, at 25°C, for B342 cellulose/7.6NaOH/water (■), B342 cellulose/7.6NaOH/0.05ZonylFSN/water (●), and B342 cellulose/7.6NaOH/0.05AP/water (▲)
The nature of solvent is indicated close to the curve, intrinsic viscosity is the corresponding value in the rectangle.

In addition to the intrinsic viscosity, another important parameter which characterises cellulose solutions is its gelation temperature. Oscillatory rheological measurements were performed in the same way as for cellulose solutions described in the previous parts: G' and G" were recorded as a function of temperature, gelation point was determined and the results are summarised in the Tab.IV.5-1.

5 B342 cellulose /	T_{gel} (°C)	G'=G" (Pa)
7.6NaOH/water	31.5	2.5
7.6NaOH/0.05AP/water	30	2.4
7.6NaOH/0.05Zonyl FS/water	32	2.7
7.6NaOH/0.05Zonyl FSN/water	28	2.2

Tab.IV.5-1: Gelation temperature and gel strength for 5 B342 cellulose/7.6NaOH/water solutions with and without surfactant.

Whatever the cellulose solution studied here, with and without surfactant, the gelation temperature and the gel strength are the same, within the experimental error, about 30°C and 2.5Pa, respectively. Thus the addition of surfactant does not improve the stability of solutions.

To conclude, we can say that the addition of non-ionic surfactants, at least the ones studied here, improves neither the cellulose dissolution nor the stability of solutions. These surfactants are thus acting during another step of the industrial process. For example, during the rapid mixing stage, the presence of surfactant induces a lot of tiny air bubbles. This increases the total volume of pores and thus could improve the absorption properties of sponges.

IV.5.3- Other additives: salts and oxides

We saw that the addition of ZnO improves cellulose dissolution and delays gelation of solutions. However, because ZnO is not soluble in water and thus cannot be removed during regeneration, its presence may not be acceptable for certain applications. The aim of this part is thus to test if other additives improve stability of cellulose solutions, in particular other oxides and salts. In order to compare the results with the ones of cellulose/NaOH/ZnO aqueous solutions, the preparation of solutions remain the same but ZnO is replaced by $ZnSO_4$, $MgCl_2$ or $CaSO_4$.

The optical micrographs of 5 B342 cellulose/7.6NaOH/water solutions in the presence of $ZnSO_4$ and $MgCl_2$ are shown in Fig.IV.5-4 'b' and 'c' respectively. These compounds do not improve cellulose dissolution; more fibres than in pure 7.6NaOH/water remain non-dissolved (Fig.IV.5-4 'a'). These additives are not efficient to increase the quality of the dissolution.
$CaSO_4$ seems to improve cellulose dissolution but it is difficult to dissolve in sodium hydroxide and a lot of crystals stay in suspension (Fig.IV.5-4d). This way would be interesting to investigate if knowing the limit of $CaSO_4$ dissolution in a strong basic solution as 7.6NaOH/water and in pure water also (important for the removal of the chemicals present in the solution during the regeneration in the form of sponges).

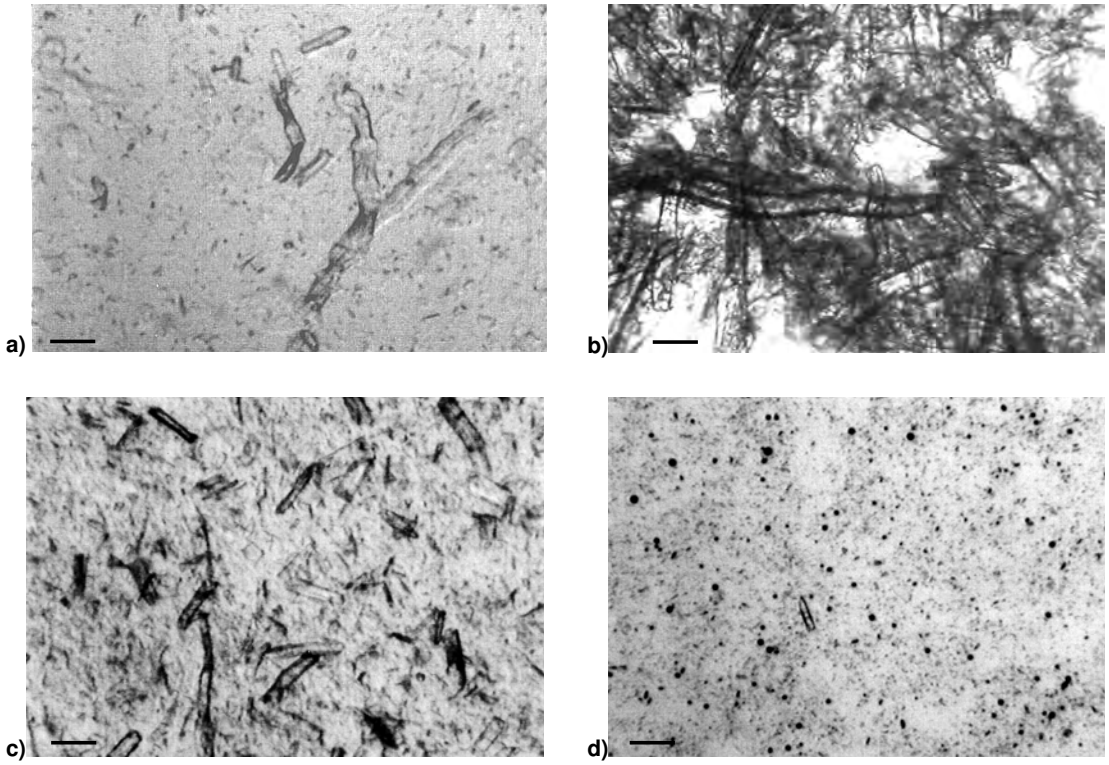


Fig.IV.5-4: Observation with optical microscope of
a) 5 B342 cellulose/7.6NaOH/water, b) 5 B342 cellulose/7.6NaOH/0.7$ZnSO_4$/water,
c) 5 B342 cellulose/7.6NaOH/0.7$MgCl_2$/water and d) 5 B342 cellulose/7.6NaOH/0.7$CaSO_4$/water
Scale bar represents 100µm.

IV.5.4- Conclusions

The goal of this section was to explore other conditions to dissolve cellulose: other alkali media, other additives.
First of all, we tested potassium hydroxide as solvent of cellulose: using KOH instead of NaOH is not efficient; this result is in agreement with literature.
We thus explored the way of additives to improve the cellulose solubility in sodium hydroxide. We studied metallic salts and oxide as well as surfactants but none of them are efficient to improve cellulose dissolution.

IV.6- CONCLUSIONS

The detailed investigation of rheological properties, in steady-state and dynamic modes as well as the study of solutions in dilute state, enables us to better understand the behaviour of cellulose in sodium hydroxide aqueous solutions:

- From viscosity versus shear rate measurements, we concluded that the steam exploded cellulose solutions in NaOH/water are not molecularly dispersed solutions and show a behaviour close to the one of a suspension. This behaviour was observed for all cellulose contents and DP studied here as well as with the presence of ZnO and urea.
- Although some cellulose fibres still remain non-dissolved, the addition of ZnO and urea improves cellulose dissolution (microscopic observations). Intrinsic viscosity measurements revealed that this improvement is due to an increase of the solvent quality in the following order 7.6NaOH/0.7ZnO/water > 7.6NaOH/6urea/water > 7.6NaOH/water.
- The intrinsic viscosity is decreasing when increasing temperature showing that the cellulose chains are collapsing. The quality of the solvent decreases. This effect favours cellulose-cellulose interactions and leads to gelation. The fact that the shift factor of intrinsic viscosity and gelation time is the same is in full agreement with this explanation.
- The addition of zinc oxide in 7.6NaOH/water is more and more efficient up to 1.5ZnO, which corresponds to its limit of solubility. Beyond this concentration, properties remain constant. ZnO is acting on cellulose dissolution and stability of solution only if it was dissolved in NaOH before being added to the cellulose pulp. These results show that complexes between ZnO and NaOH, like the zinc hydroxyl ions $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$, have to be formed to improve cellulose dissolution and to delay gelation.
- The gelation mechanisms and physical reasons are the same with and without the presence of ZnO. The only difference is that the ZnO-NaOH complexes which are formed during mixing ZnO, NaOH and water are preventing the cellulose-cellulose interactions to start at temperature higher than without the presence of ZnO.
- The addition of urea also delays gelation but the behaviour of solutions is very different depending on cellulose origin and urea content. If the urea content is too high, the cellulose solutions are gelling during the preparation at -6°C, but this content depends on cellulose origin: with the Borregaard cellulose pulps, the limit of urea content is 12g whereas with the Lenzing cellulose pulps it reaches 20g in 100g of solution. The reasons of such differences stay an open question. These results explain why we found results different from the ones reported in the literature, since the dissolution and gelation depend on the cellulose treatment.

We made the hypothesis in Chapter III that the addition of urea improves the quality of the solvent by trapping the free water. The same was also thought to be true for the addition of ZnO. The results of this chapter does not allow to confirm or infirm this hypothesis.

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RESUME DU CHAPITRE V

PROPRIETES MECANIQUES D'OBJETS REGENERES PREPARES A PARTIR DE SOLUTIONS AQUEUSES DE CELLULOSE/NAOH

L'objectif de ce chapitre est d'étudier les propriétés mécaniques d'objets régénérés préparés à partir de solutions aqueuses de cellulose/NaOH, avec ou sans additifs, mais également d'étudier l'influence de la congélation sur les propriétés finales des éponges.

Pour ce faire, nous avons procédé étape par étape.

Nous avons d'abord préparé des solutions de cellulose/NaOH/eau, sans fibres de renfort, ni porophores, c'est la matrice de cellulose régénérée que nous trouvons ensuite dans les éponges. Après gélification, nous les avons régénérées. Les échantillons ainsi obtenus ont été testés mécaniquement dans leur état humide afin de déterminer leur contrainte à la rupture. Nous avons fait varier de nombreux paramètres, à savoir la présence ou non d'additifs (urée et ZnO), les conditions de gélification (2 heures à +70°C, 20 heures à +25°C ou 20 heures à -20°C), les bains de régénération (eau à +5°C, +25°C ou +70°C, ou encore acide acétique à 10%, +25°C).
Il apparaît que la régénération à haute température (+70°C) est très défavorable à la résistance à la rupture et qu'un séjour prolongé à -20°C n'améliore pas les propriétés mécaniques de la matrice de cellulose régénérée. Les échantillons, préparés au Cemef, ayant la plus haute contrainte à la rupture ont été gélifiés et régénérés à température ambiante.
Bien que les deux additifs utilisés dans cette étude améliorent la dissolution de la cellulose et retardent la gélification, leur effet sur les propriétés mécaniques est différent. La présence d'urée améliore nettement la résistance à la rupture ce qui n'est pas le cas pour ZnO. Des observations microscopiques révèlent la présence de particule d'oxyde de zinc dans les échantillons régénérés créant probablement des points de rupture.

L'ajout de fibres de renfort dans la matrice de cellulose régénérée entraîne une augmentation de la contrainte à la rupture. Mais cette amélioration des propriétés mécaniques n'est pas considérable, nous avons donc testé différentes méthodes pour améliorer l'adhésion entre les fibres et la matrice.
La congélation étant une étape nécessaire à l'obtention de bonnes éponges, nous avons pensé qu'un séjour à basse température agissait sur l'adhésion fibres/matrice. Avant d'introduire les fibres de renfort dans la solution de cellulose/NaOH/eau, nous les avons d'abord imprégnées de soude (8%) à différentes températures (+25°C, -6°C et -20°C). Leur observation microscopique

montre un gonflement à basse température uniquement. Mais les tests mécaniques ne révèlent aucune influence des conditions de pré-imprégnation sur la contrainte à rupture. La congélation n'agit pas sur l'adhésion fibres/matrice et il n'est donc pas nécessaire d'imprégner les fibres de renfort à basse température.
L'ajout de promoteur d'adhésion n'a pas été probant non plus.

Pour finir, nous avons ajouté des porophores au système matrice de cellulose régénérée/fibres de renfort et effectué des tests de traction sur les échantillons obtenus, toujours dans leur état humide. Les conditions de préparation des éponges au Cemef n'étant pas optimales, les propriétés mécaniques sont très faibles. Nous constatons néanmoins que pour des systèmes complets matrice de cellulose régénérée + fibres de renfort + porophores, l'étape de congélation augmente la contrainte à la rupture.
De plus, si nous considérons les propriétés d'absorption et de retrait, l'étape de congélation est également primordiale, bien que les propriétés restent largement inférieures à celles obtenues pour des éponges viscose. Les observations au MEB des différents échantillons montrent une grande disparité au niveau de leur porosité. En effet, pour des éponges viscose, la microporosité est très importante alors qu'elle est totalement absente d'une éponge soude non congelée. Quant à l'éponge soude congelée, la microporosité, bien que faible, est présente. Ces résultats concordent tout à fait avec les valeurs obtenues pour l'absorption. En ce qui concerne le retrait, on constate, en effet, que la microporosité des éponges soude congelées se ferme après séchage à l'air ambiant.

Ces résultats ne nous permettent pas encore de comprendre et d'expliquer le rôle de la congélation mais ils nous ont permis d'améliorer nos connaissances sur l'influence d'un séjour prolongé à -20°C sur les propriétés mécaniques et physiques d'objets régénérés.

CHAPTER V

MECHANICAL PROPERTIES OF REGENERATED OBJECTS PREPARED FROM CELLULOSE/NAOH AQUEOUS SOLUTIONS

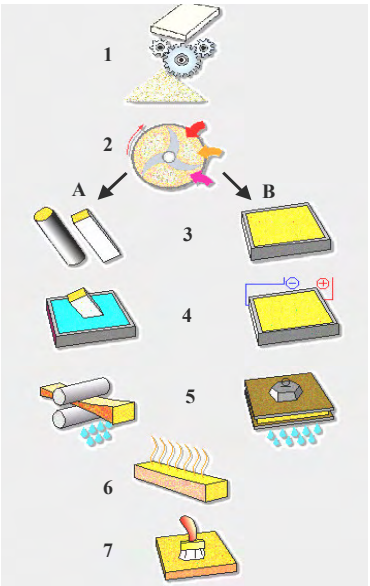
This chapter concerns the preparation and some mechanical properties of sponges using direct cellulose dissolution in aqueous NaOH solutions. Being much less polluting than the viscose process, it is not yet industrialised because of an intermediate energy consuming step: freezing of cellulose/NaOH/water solution at -20°C for several hours. This step is supposed to be necessary for obtaining mechanical properties of sponges comparable with the ones from viscose process. Spontex is making sponges from cellulose/NaOH/water solutions (with the freezing step) on laboratory scale keeping most of the other processing parameters the same as in viscose process. The goal of this chapter is to determine the mechanical properties of sponges prepared by the NaOH process in order to study the influence of different processing parameters (treatment of reinforcing fibres, freezing step, regeneration bath temperature, etc) on the final properties.

The chapter is divided into two parts. The first gives a brief overview of existing sponge preparation through viscose and NaOH processes. The second part describes the results obtained on the mechanical properties of sponges made via NaOH process with the accent on the different processing parameters.

V.1- SUMMARY ON SPONGE PREPARATION: VISCOSE AND NAOH PROCESSES

V.1.1- Viscose process

One of the ways for manufacturing sponges from cellulose is the viscose process. It consists in the cellulose derivation and then the dissolution. First, cellulose fibres are swollen in a concentrated aqueous 18-20%NaOH solution in order to improve their accessibility for other chemicals, as carbon disulfide in the next step of the process: the xanthation. The sodium xanthate of cellulose can be dissolved in a dilute 2.7%NaOH solution. As a result, a viscous paste is obtained; it is called viscose. Then, the reinforcing fibres, porophores (salt crystals) and dyers are added to the viscose in order to obtain the appropriate mechanical and absorption properties of sponges. The mass is homogenised, aged, regenerated, shaped, and dried.
The following Fig.V.1-1 schematises sponge manufacturing via viscose process.



1- Cellulose pulp and viscose formation

2- Addition of reinforcing fibres, porophores and dryers

3- Shaping

4- Coagulation/Regeneration

5- Washing

6- Drying

Fig.V.1-1: The different steps to manufacture cellulose sponges from viscose process.

- Viscose formation: The step of forming cellulose xanthate and then viscose is shown in Fig.V.1-2 and described in part I.2.1.

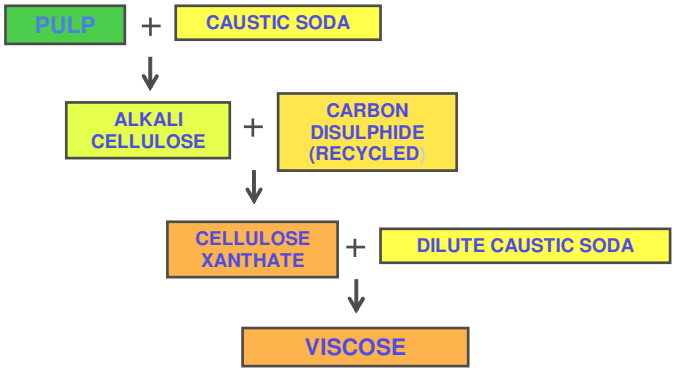


Fig.V.1-2: Scheme of the xanthation step in the viscose process. The chemical reactions are described in the Chapter I.

- Addition of reinforcing fibres and porophores (step 2 on the Fig.V.1-1): In order to improve the final properties of sponges, reinforcing fibres are added to the viscose. They consist of long fibres such as cotton or flax fibres, or wood pulp with high DP. The reinforcing fibres are wetted with water or dilute sodium hydroxide solutions; they are then mixed with viscose (in the wet state). The viscose/reinforcing fibres system is aged to improve adhesion and homogenisation.
  After the ageing step, a large amount of sodium sulphate Na_2SO_4, $10H_2O$ crystals is added (3-4 times of the total weight of viscose/reinforcing fibres). The addition of these salt crystals enables to form the porous structure of sponges after cellulose regeneration and crystals removal (melting).
  Finally, dyers giving the colour of the sponge are added (regenerated cellulose swollen in water is white).

- Shaping (step 3 on the Fig.V.1-1): the viscose/reinforcing fibres/salt crystals system is shaped, at room temperature.

- Coagulation/regeneration (step 4 on the Fig.V.1-1): After the shaping step, the mixture is coagulated to give the final cellulose product; two different 'A' and 'B' methods are used and briefly described below. During this step, cellulose is precipitating around the Na_2SO_4,$10H_2O$ crystals. CS_2 and other sulphured compounds are released. Almost simultaneously, the Na_2SO_4,$10H_2O$ crystals are melting (at a temperature superior to 40°C) forming a porosity which is directly dependent on the crystals size (between 100µm and 3mm)

  The method of *vapour coagulation* (A) consists in immersing the moulds in a sodium sulphate aqueous solution progressively heated to 100°C. By this way, the coagulation/ regeneration step lasts approximately 8 hours.
  For the *electrical coagulation* method (B), a voltage from 20V to 120V is applied between the two opposite walls of the mould. The heating of the mixture is due to the joule effects until boiling. The duration of the electrical coagulation is around 3 hours.

  At the end of the coagulation step, the physical and chemical reactions which enable the manufacture of cellulose sponges are completed.

- Washing, bleaching (step 5 on the Fig.V.1-1): The washing and bleaching stages allow recovering the sodium sulphate present in sponges (due to the melting of Na_2SO_4,$10H_2O$ crystals) and to destroy the sulphured compounds causing a blackish colouring of the sponge blocks. Finally, the blocks are de-moulded and spin-dried.

- Drying (step 6 on the Fig.V.1-1): The blocks of sponges are dried at 80°C, for 24 hours. Finally, they are cut to obtain the final product and undergo a fungicidal and plastification treatment with magnesium chloride $MgCl_2$. Sponges can then be packaged.

The viscose process of sponge preparation is very efficient but its major problem is the use of carbon disulfide. This chemical is very polluting as well as the by-products obtained during the series of chemical reactions of cellulose transformation into viscose.

The viscose process has already been improved to reduce:

The pollution in aqueous phase: The sulphured compounds formed during the process induce a decrease of the oxygen amount in water. Nowadays, these compounds are completely recycled and are not discharged in nature.
The atmospheric pollution: It is due to the release of CS_2 and H_2S. The latter has an extremely bad smell even at low concentration. In order to decrease pollution, these gases are absorbed on active coal which enables to recycle 70% of the carbon disulfide used during the whole process. Nowadays, the gaseous discharge is limited at 10% of the CS_2 used in the process.

However, treatments of pollution are very expensive and thus the viscose process is less and less economically interesting. That is why less polluting alternative routes are searched. One of the possible ways is to dissolve cellulose fibres in sodium hydroxide.

V.1.2- NaOH process

This process is only using the sodium hydroxide as chemical. The dissolution, even partial, is direct and does not generate polluting by-products. The schematic presentation of the steps of sponge manufacturing via NaOH process is shown on Fig.V.1-3.

- Dissolution (step 1 on the Fig.V.1-3): Dissolution is performed according to the procedure described in part II.2.2: swelling of cellulose in water, mixing with NaOH/water at -5°C reaching resulting concentrations of 5% cellulose in 7-9%NaOH/water. Depending on cellulose DP, not all fibres may be dissolved.

- Addition of reinforcing fibres (step 2 on the Fig.V.1-3): The quantity of reinforcing fibres is 40% of cellulose weight. For example, if 5% cellulose solution was prepared, 2% of fibres have to be added. Before being added to the cellulose solution, the reinforcing fibres that are cellulose fibres with high DP – superior to 1000 – are pre-impregnated for some minutes with 8% NaOH, at room temperature. Then these fibres are progressively introduced into the cellulose solution kept at -5°C under mixing. The mixing still lasts 1.5 hour. The system obtained is called the "cellulose fibrous solution".

- Ageing (step 3 on the Fig.V.1-3): The cellulose mixture undergoes a step of ageing, as in the viscose process, at 0°C, for about 4 hours. During this ageing, gelation probably starts to occur.

- Addition of porophores ($Na_2SO_4,10H_2O$ crystals) (step 4 on the Fig.V.1-3): The cellulose fibrous solution/crystals weight ratio is 1/3 or 1/4. There are several sizes of crystals and their proportions define the macro- and micro-porosity of the final product. Because cellulose/NaOH solution has to be kept at rather low temperatures in order to avoid gelation and because the amount of crystals is large, they have to be cooled down before being added to the cellulose system. The whole system is still maintained at -5°C and mixed for 30min. The cellulose mixture is then put into the moulds.

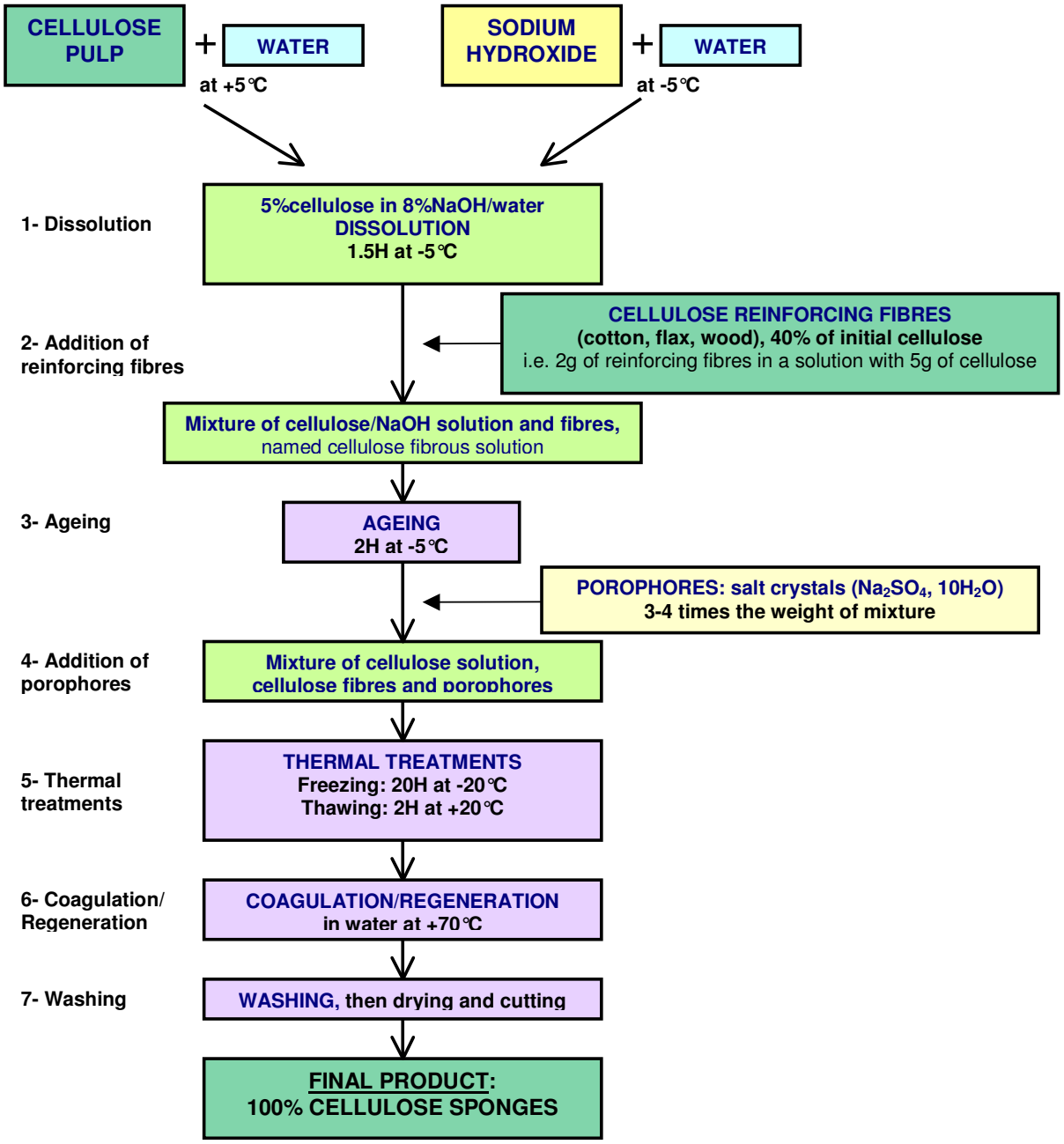


Fig.V.1-3: The different steps to manufacture cellulose sponges from the NaOH process.

- Thermal treatments (step 5 on the Fig.V.1-3): The cellulose solution containing reinforcing fibres and porophores are frozen for 8 hours at -20°C. It appears that freezing is an essential step to obtain sponges with relatively good mechanical properties. After freezing, the system is thawed at room temperature.

- Coagulation/regeneration (step 6 on the Fig.V.1-3): This is the last stage of the process and is similar to the one described in the viscose process. The moulds are either immersed in a bath

of warm water (70-90°C) or connected to a voltage inducing the precipitation of cellulose around the crystals of $Na_2SO_4,10H_2O$.

- Washing (step 7 on the Fig.V.1-3): The blocks of sponges are washed with cold water (20°C) for about 8 hours. The aim of this step is to remove the soda.

The final product contains only cellulose.

Industrial problem of NaOH process

The sponges obtained with NaOH process have final properties almost similar to the one obtained with the traditional viscose process. Moreover, because sodium hydroxide can be recovered, there is practically no pollution. This is the main advantage of this process. However, the temperatures used during cellulose dissolution and especially during the freezing step at -20°C makes this process industrially not viable. In the next section the properties of sponges prepared with and without freezing will be described.

V.2- PROPERTIES OF SPONGES PREPARED WITH THE NAOH PROCESS

This section is devoted to the properties of the wet sponges prepared in Cemef following the NaOH procedure. Wet samples, just after regeneration, were tested supposing that the trends obtained can be translated to dry sponges. First, the influence of sponge preparation on wet sponge mechanical properties is studied. Second, the adhesion between reinforcing fibres and cellulose matrix is investigated for different fibre treatments, keeping in mind that the adhesion is one of the important factors controlling the mechanical properties of a composite material. A special attention is paid to the role of the freezing step. In all cases cellulose and NaOH contents were kept constant: 5g of cellulose and 7.6g of NaOH in 100g of solution.

The measurements of the mechanical properties were performed on sponges using a "step by step" approach, i.e. by studying the properties of sponges on different stages of their preparation:

- first step: sponges were made only from cellulose/NaOH solution followed by regeneration;
- second step: sponges were made from cellulose/NaOH solution + reinforcing fibres; followed by regeneration;
- third step: sponges were made from cellulose/NaOH solution + reinforcing fibres + $Na_2SO_4,10H_2O$ crystals (porophores), followed by regeneration.

In each step, different thermal treatments of cellulose/NaOH solutions were performed: solutions were either gelled or frozen at -20°C. When reinforcing fibres were added, their different treatments were performed in order to vary their adhesion to cellulose matrix.

Regeneration was performed in water baths of different temperatures, an aqueous acid solution being also tested. Finally, the influence of additives on the mechanical properties of sponges was investigated.

V.2.1- Wet samples made from regenerated 5cellulose/7.6NaOH/water solutions, without reinforcing fibres and porophores

V.2.1.1. Tensile stress results

Cellulose was dissolved in NaOH, with or without additives (urea or ZnO), as described in part II.2.2. The cellulose solution was poured in a Petri box in order to obtain a film with a 1-1.5mm thickness. Then, after various thermal treatments (gelation at 25°C for 20 hours, gelation at 70°C for 2 hours and freezing at -20°C for 20 hours), cellulose solutions were regenerated in different regeneration baths (in water at 5°C, 25°C and 70°C and in 10% acetic acid at 25°C). Finally, tensile tests were performed on wet regenerated cellulose, until the rupture of the sample (see the description of tensile measurements in part II.3.5). An example of a typical stress-strain curve is given on Fig.V.2-1. The rupture stress is directly obtained from the graph as the y-axis is in daN/cm². The values of rupture stress for all samples studied are shown on Fig.V.2-2 and correspond to the average of three measurements performed on a same solution.

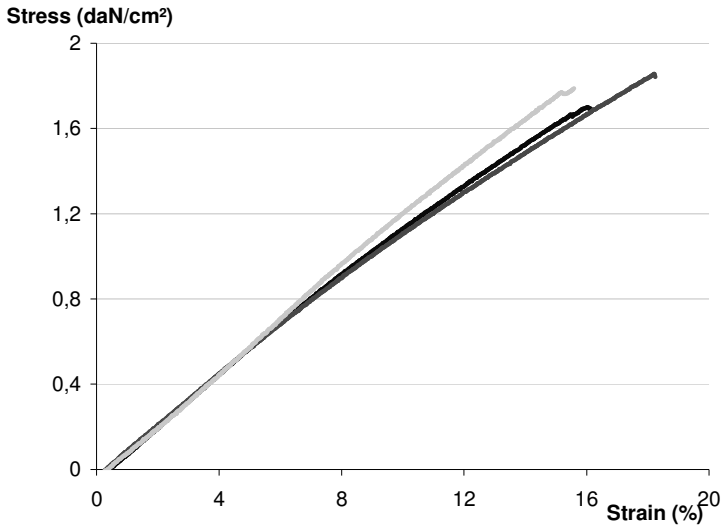


Fig.2-1: Example of a tensile test on a regenerated cellulose solution initially containing 5B407 cellulose/7.6NaOH/water; solution was frozen for 20 hours at -20°C and regeneration in water at +70°C.
The three curves represent three different experiments.
v=5mm/min.

V.2.1.2. Influence of regeneration bath parameters

Whatever is the nature of the solvent – NaOH/water, NaOH/urea/water or NaOH/ZnO/water – regeneration in water at 70°C considerably decreases the value of the rupture stress (Fig.V.2-2 a, b and c). Regeneration in water at 70°C was studied because in the industrial process,

Na_2SO_4,$10H_2O$ crystals that are playing the role of porophores must be melted at this temperature in order to be removed from regenerated cellulose

Regeneration in 10% acetic acid is relatively efficient to obtain good mechanical properties, especially for cellulose dissolved in 7.6NaOH/6urea/water (Fig.V.2-2b). But according to our industrial partners, the kinetics of regeneration in acid baths is very fast and a skin is thus formed around the blocks of sponges. Consequently, the non-solvent cannot easily penetrate in the block of sponge and precipitation of cellulose cannot occur anymore. In the manufacturing of cellulose films, acid non-solvent can be used since the thickness of cellulose is very small.

Regeneration in a water bath at room temperature seems to be the most efficient in terms of the mechanical properties and energy consumption.

V.2.1.3. Influence of solution thermal treatment

Four different thermal treatments were tested: 2 hours at +70°C, 20 hours at +25°C, 20 hours at -20°C and 20 hours at -20°C followed by 20 hours at +25°C. Fig.V.2-2 shows the different values of rupture stress obtained with these four treatments, with various regeneration bath conditions.
For the solution without additives and whatever is the regeneration method, the best properties are obtained when the cellulose solution is kept 20 hours at +25°C. In this condition, the cellulose solution is gelling.

The results show that gelation for 20 hours at 25°C after a freezing step at -20°C does not increase the rupture stress up to the level of the sample than was gelled in these conditions without freezing. The state of solution after freezing/thawing is not the same as the one of a freshly prepared solution (see part IV-4), and thus gelation of frozen sample did not give the same result as gelation of a non-frozen solution.

Fig.V.2-2a reveals that gelation at room temperature is the most efficient thermal treatment to resist to the rupture as compared with gelation at +70°C and freezing at -20°C.

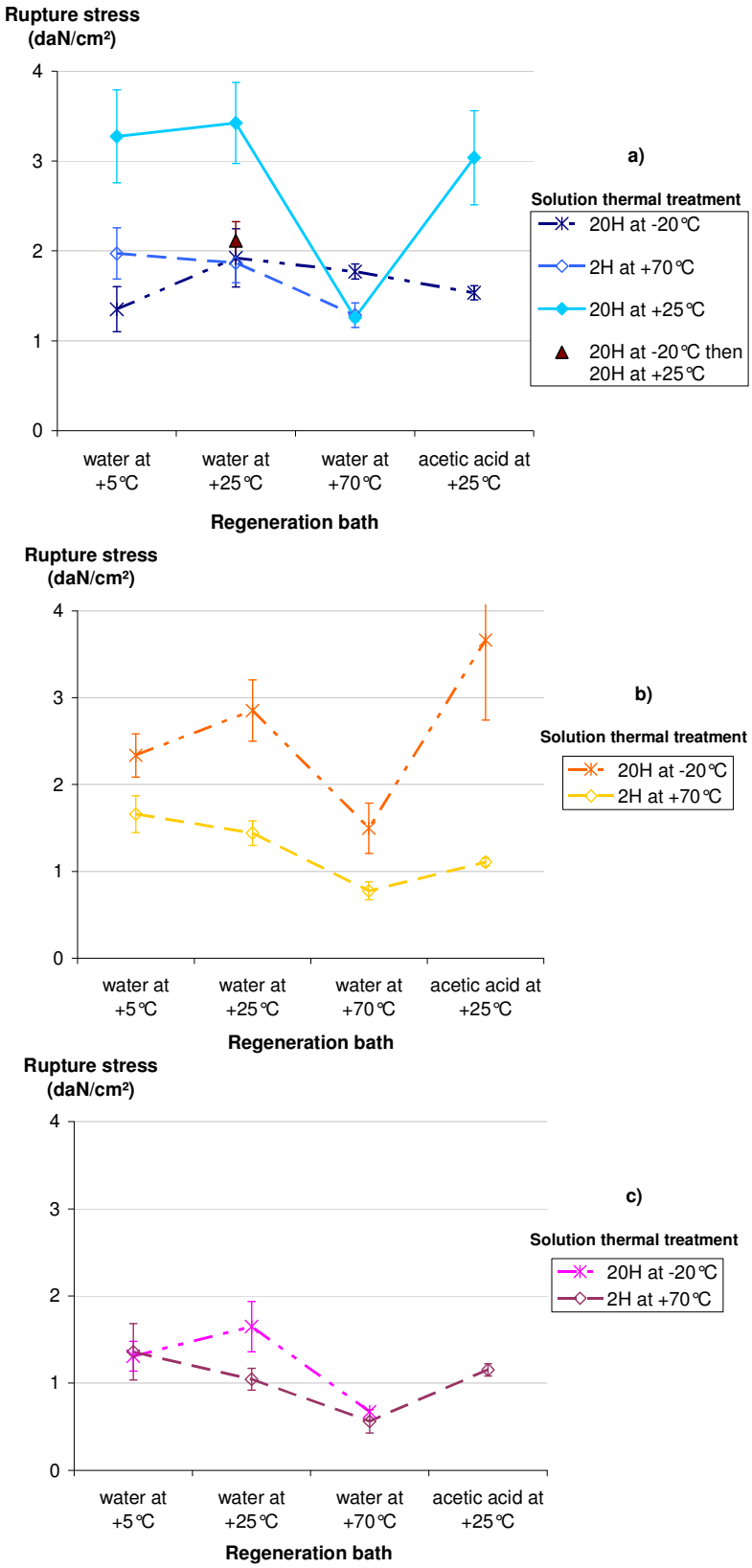


Fig.V.2-2: Rupture stress of wet regenerated B407 cellulose for different solutions, treatments, regenerating baths
Initial solutions: a) 5cellulose/7.6NaOH/water; b) 5cellulose/7.6NaOH/6urea/water; c) 5cellulose/7.6NaOH/0.7ZnO/water;
Thermal treatment: 20 hours at -20°C; 20 hours at +25°C and 2 hours at +70°C;
Regeneration bath: water at +5°C, +25°C, +70°C and 10%acetic acid at +25°C

V.2.1.4. Influence of additives

Although the addition of zinc oxide improves cellulose dissolution and stability of solutions, it does not increase the mechanical properties of regenerated cellulose samples (see Fig.V.2-2 a and c). This can be explained by the presence of zinc oxide crystals that cannot be either dissolved in water during regeneration or washed out from the regenerated cellulose. The presence of ZnO crystals is seen in SEM images (Fig.V.2-3b). These crystals may generate rupture points in the sample.

As far as ZnO can be dissolved either in acids or in strong basis (see Chapter III, Fig. III.2.12), it could be possible to regenerate cellulose from cellulose/NaOH/ZnO/water solution in relatively strong acids. As mentioned previously, this could be for a way for the film manufacture but not for the sponges.

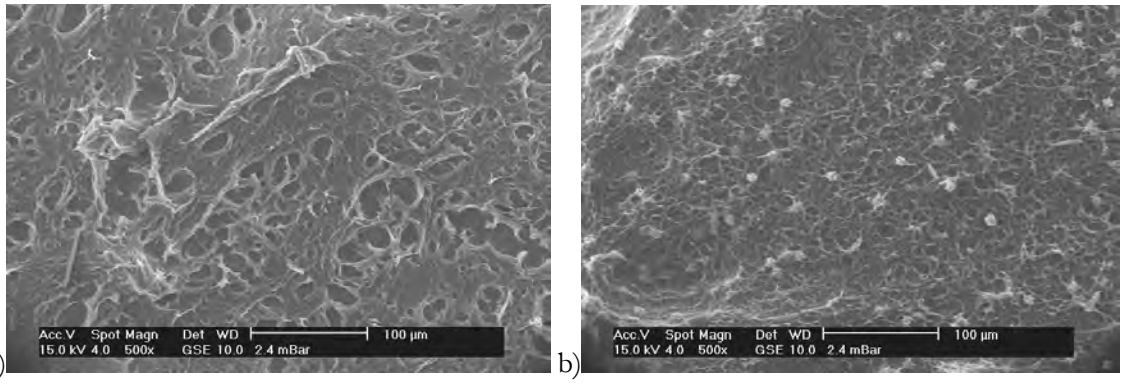


Fig.V.2-3: SEM observations of regenerated B407 cellulose from a) 5cellulose/7.6NaOH/water and b) 5cellulose/7.6NaOH/0.7ZnO/water, after 2H gelation at 70°C and regeneration in water at 70°C

From the results on cellulose dissolved in the presence of urea, we can see that gelation at 70°C is not interesting to produce sponges: the rupture stress is low and even inferior to the one obtained in NaOH without additives. Cellulose/NaOH/urea/water solutions are better than without urea whatever the regeneration bath is.

V.2.1.5. Conclusions

The tensile tests performed for cellulose/7.6NaOH/water solutions with or without additives and without reinforcing fibres and porophores showed that, first, regeneration in a hot bath decreases the mechanical properties of wet regenerated cellulose whatever are solution treatments and additives, and second, that gelation at room temperature gives the highest rupture stress of the material.

As far as the presence of Na_2SO_4,$10H_2O$ crystals requires a high temperature to melt to be washed from regenerated cellulose, one of the ways to reach higher rupture stress is to perform solution gelation at room temperature, to regenerate cellulose in water also at room temperature and finally to heat the regenerated cellulose blocks for the Na_2SO_4,$10H_2O$ crystals to melt.

The presence of ZnO does not increase mechanical properties and will not be studied anymore in the following. The presence of urea seems to increase the rupture resistance of samples and thus can be a promising way to be tested for the preparation of sponges.
The best conditions at this stage are solutions with urea, gelled at +25°C and regenerated in water at +25°C.

V.2.2- Wet samples made from regenerated 5cellulose/7.6NaOH/water solutions with reinforcing fibres without porophores

V.2.2.1. Influence of added reinforcing fibres

The addition of fibres into a matrix usually leads to the increase in the mechanical properties of the obtained composite material. In the viscose process, cellulose fibres are added to cellulose solution in order to improve the mechanical properties of sponges.

Two types of reinforcing fibres were used: cotton and fluff with DP1100 (more details are given in part II.1.2). Due to their high DP, these cellulose fibres cannot be dissolved in 7.6NaOH/water, even at -6°C (see Chapter II, Fig.II.1.1).
Before being added to the cellulose solution, the reinforcing fibres were pre-impregnated by 2.7%NaOH/water solution for some minutes. Then they were added into cellulose solution and mixed for 1.5hour. To mix impregnated fibres with cellulose/NaOH solutions, a blade mixer was used (see part II.3.5). Long cotton fibres coiled around the blades and the mixture was not homogeneous. We mainly used fluff fibres which was not having this difficulty.
The samples for tensile measurements were prepared in the same way as in the previous section. The comparison of the stress at rupture for wet regenerated cellulose with and without the reinforcing fibres is shown in Fig.V.2-4. Samples were gelled at +25°C for 20 hours and regenerated in water at +25°C and +70°C.

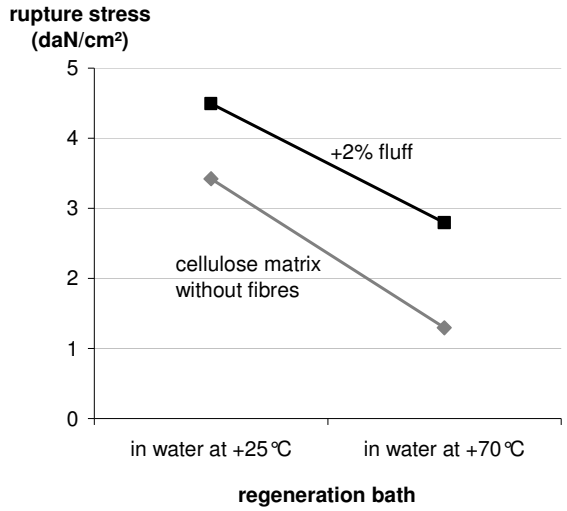


Fig.V.2-4: Comparison of the rupture stress of wet regenerated cellulose with and without reinforcing fibres.
Matrix: 5B389 cellulose/7.6NaOH/water
All-cellulose composite: Matrix + 2g of fluff fibres pre-impregnated in 2.7%NaOH
Treatment: gelation at +25°C for 20 hours; regeneration in water at +25°C and +70°C

Two observations can be made:

- As expected, the addition of reinforcing cellulose fibres increases the value of the rupture stress (Fig.V.2-4).
- The regeneration bath of water at +25°C shows better results, regarding the resistance to rupture, as compared with regeneration at +70°C, as already shown.

V.2.2.2. Influence of fibres treatment of the rupture stress

As far as the addition of fluff fibres improves the mechanical properties of regenerated cellulose, a special attention was paid to the adhesion between the fibres and the matrix. The goal is to increase the adhesion that should lead to the increase of the mechanical properties.

Fluff fibres were treated with different adhesion promoters (see their chemical formulations in part II.1.3). Instead of being pre-impregnated by 2.7%NaOH/water, the 2.3g of fibres were pre-impregnated by a solution containing 2.7%NaOH/water+the adhesion agent. A reference was prepared without adhesion agent. Wet treated fibres were added to cellulose solution in the same way as described above. The results of tensile tests are shown on Fig.V.2-5.

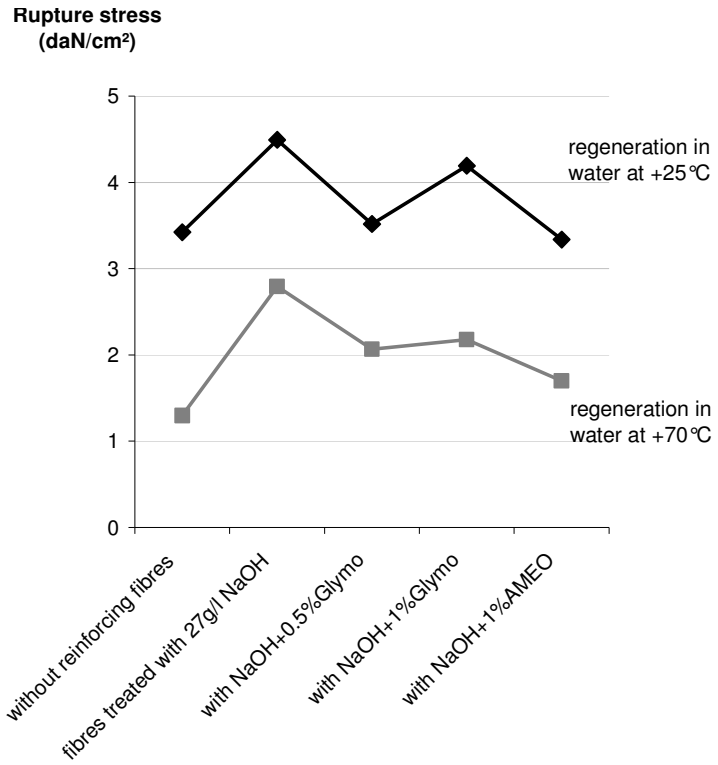


Fig.V.2-5: Rupture stress as a function of fibres treatment for 5B389 cellulose/7.6NaOH/water + 2.3 treated fibres solutions gelled for 20hours at +25°C and regenerated in water at +25°C or +70°C.
Data for regenerated cellulose without reinforcing fibres are also shown.
Treatments of fibres are directly indicated on the graph.

First of all, whatever is the treatment of fibres, regeneration in water at room temperature showed better mechanical results as compared with regeneration at 70°C.

Secondly, a comparison of results obtained for regenerated cellulose, without reinforcing fibres (on the left side of the graph Fig.V.2-5), with the ones obtained for fibres pre-impregnated with NaOH without adhesion agent, shows that the rupture stress is considerably increased.
Finally, the treatment of fibres by the adhesion agents (GLYMO, AMEO, CPTMO) does not improve the rupture stress.

V.2.2.3. Influence of freezing on rupture stress and adhesion between fibres and matrix

When making real sponges, porophores (Na_2SO_4,$10H_2O$ crystals) are added to create large pores. Because it is not possible to form thin films with porophores, thick samples have to be made in order to obtain reproducible rupture stress measurements. To anticipate the forthcoming experiments with crystals, parallelepiped blocks of regenerated cellulose with reinforcing fibres and without porophores were prepared and studied. The goal is to investigate the influence of freezing on the mechanical properties of wet samples and on the adhesion between the reinforcing fibres (cotton or fluff) and cellulose matrix.

The cellulose/NaOH/water + reinforcing fibres solutions were prepared as in the section V.2.2.1:

- 2g of fibres were pre-impregnated in 8%NaOH/water for some minutes, at room temperature
- the mixing of fibres with cellulose solution was performed at -6°C, for 1.5 hour
- a thermal treatment was applied
- only the shape of specimens for tensile tests was changed (parallelepiped blocks versus film)

It should be noted that when studying parallelepiped blocks, the value of the rupture stress is up to ten times smaller than the ones obtained for films. This dramatic decrease can be explained by the fact that there is no skin since the specimens were cut in a block. Moreover, as the cutting of samples was performed by hand, specimens are more irregular. Even by change of the razor blade each time, cellulose fibres are difficult to cut and we probably induced cracks in the sample.

In order to be as close as possible to the Spontex conditions of sponge preparation, the regeneration of samples was performed in water at +70°C. The rupture stress of wet parallelepiped samples is shown in Tab.V.2-1.

Reinforcing fibres	Cellulose solution thermal treatment	Rupture stress, daN/cm²
Cotton	Gelation at 25°C for 20 hours	0.13
	Freezing at -20°C for 20 hours	0.26
Fluff	Gelation at 25°C for 20 hours	0.47
	Freezing at -20°C for 20 hours	0.43

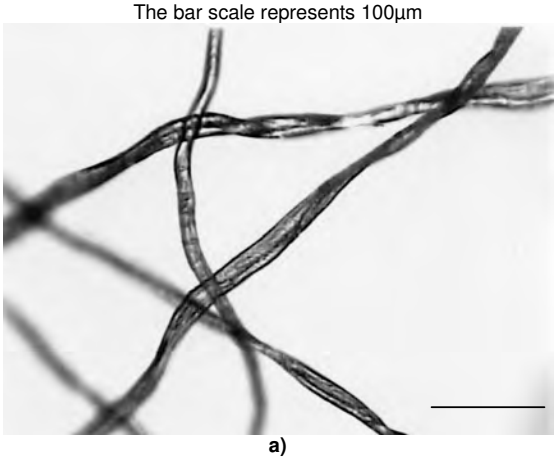
Tab. V.2-1: Rupture stress of wet regenerated parallelepiped cellulose samples from 5B389 cellulose/7.6NaOH/water reinforced by 2g of cotton or fluff fibres pre-impregnated with 8%NaOH/water at room temperature, regeneration in water bath at 70°C.

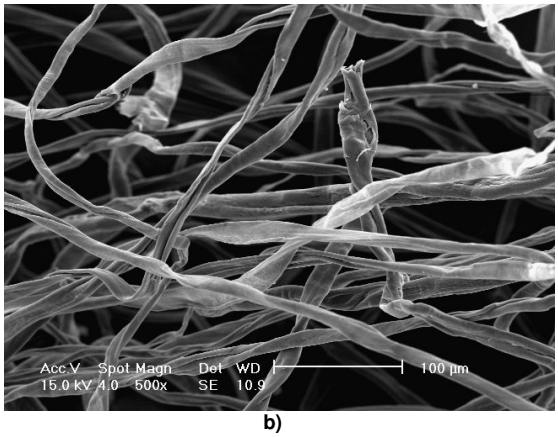
First of all, Tab.V.2-1 shows that the cotton fibres give very low rupture stresses in comparison with fluff fibres. This is explained by the fact that the cotton fibres enrolled around the blades of the mixer and thus that the solutions were not homogeneous.
Freezing either improves or does not change mechanical properties depending on the nature of the reinforcing fibres, cotton or fluff respectively. In order to better understand what happened during freezing, we observed by optical and electron microscopy the samples containing cotton fibres, since there is a difference between the two thermal treatments. The pictures obtained with optical microscope and SEM are shown on Fig.V.2-6.

If we compare the observations with optical microscope 'a' and 'c' of the Fig.V.2-6, it seems that cotton fibres are almost unchanged before and after their introduction into the cellulose solution after a gelation at +25°C for 20 hours. The photo of sponges prepared with the freezing step (Fig.V.2-6e) reveals that the fibres are cylindrical whereas natural cotton (Fig.V.2-6a) has a flat ribbon shape: cotton fibres have been modified during the step at -20°C.
On the other hand, after freezing and after gelation (Fig.V.2-6 pictures 'd' and 'f' in comparison with picture 'b'), we can see the matrix is attached to the cotton fibres, as seen by SEM. This is compatible with the fact that both cases (freezing and gelation) give similar results in term of rupture stress. The variation seen in Tab.V.2-1 for cotton is most probably due to the inhomogeneous structure of the mixture (bad mixing). In both cases, some matrix material is attaching to the cellulose reinforcing fibres. It is known that the external layer of cotton fibres is not easily dissolved by NaOH/water [CUI2006]. Nevertheless, a treatment in NaOH/water in dissolving conditions (-6°C or -20°C) seems to help the cellulose from the matrix to interact with the surface of the fibre, so that it will stick to it after regeneration.

OBSERVATION WITH AN OPTICAL MICROSCOPE **OBSERVATION WITH A SEM**

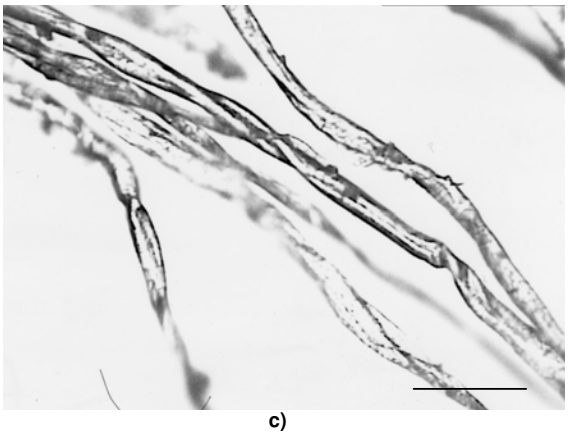
The bar scale represents 100µm

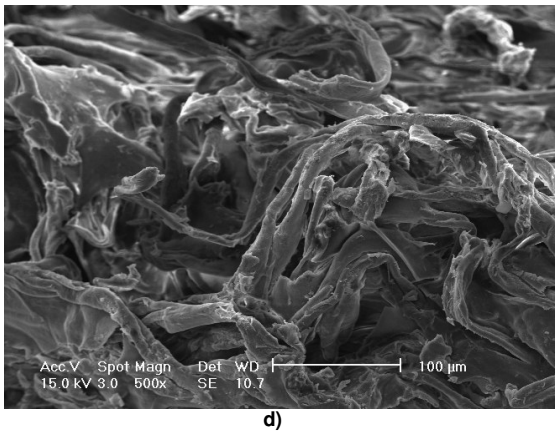




a) **b)**

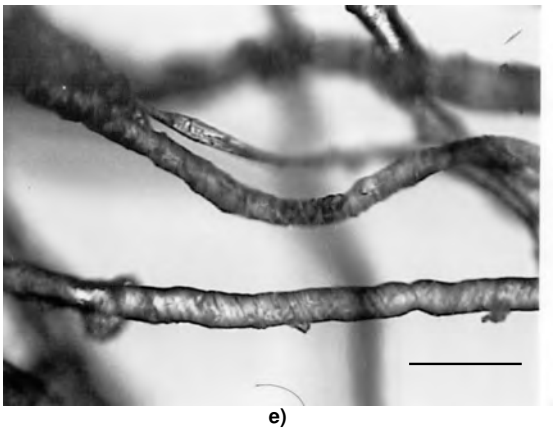
Initial dried cotton fibres

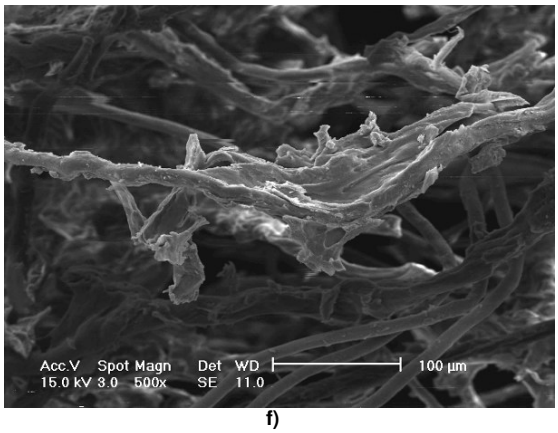




c) **d)**

Cotton fibres inside a regenerated cellulose matrix
Thermal treatment: gelation for 20 hours at +25°C





e) **f)**

Cotton fibres inside a regenerated cellulose matrix
Thermal treatment: freezing for 20 hours at -20°C

Fig.V.2-6: Observation of cotton fibres in the initial dry state (a, b) and after different thermal treatment and regenerated in water at +70°C: c) and d): gelation for 20 hours at +25°C; e) and f): freezing for 20 hours at -20°C.

V.2.2.4. Influence of the thermal history of fibres treatment with 8%NaOH aqueous solution on the mechanical properties of wet regenerated samples

The goal of this section is to investigate if the mechanical properties of wet regenerated samples (regeneration bath: water at 70°C) are influenced by the following:

a) Temperature of fibre treatment before they are mixed with cellulose/NaOH solution and
b) Thermal history (gelation, freezing) of the mixture composed of cellulose/NaOH/water solution and pre-impregnated fibres.

a) We know that at least two conditions have to be fulfilled to dissolve cellulose in sodium hydroxide: (i) NaOH concentrations should be in the interval of 7-10% at -6°C – 0°C temperatures according to the phase diagram [SOB1939] and (ii) to have cellulose with a DP inferior to about 400-600 [YAM1990]
The DP of the reinforcing fibres is at least 1100. These fibres cannot be fully dissolved in sodium hydroxide, even in 8%NaOH aqueous solution, at -6°C. But in these conditions of low temperature, the fibres are swelling.

The fibres were placed in a large amount of 8%NaOH aqueous solution for 20 hours at different temperatures: +25°C, -5°C and -20°C. At the end of this impregnation, they are removed from the alkaline solution, spin-dried and observed with an optical microscope (Fig.V.2-7).

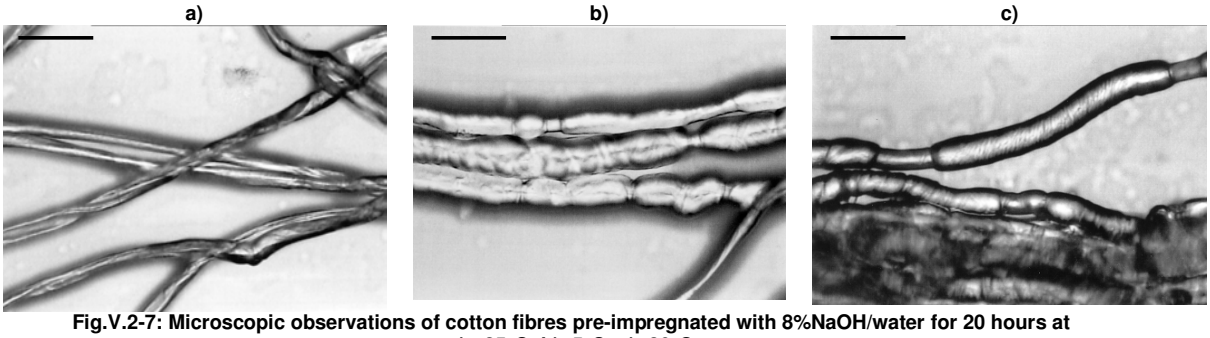


Fig.V.2-7: Microscopic observations of cotton fibres pre-impregnated with 8%NaOH/water for 20 hours at a) +25°C; b) -5°C; c) -20°C
Scale bars represent 100µm

It is clear that after 20 hours in 8%NaOH/water, at +25°C (Fig.V.2-7a), the aspect of the fibres did not change much (Fig.V.2-6a). Keeping fibres at -6°C or freezing them at -20°C in 8%NaOH/water solutions clearly changes the aspect of fibres (pictures 'b' and 'c' respectively): fibres are swelling. After freezing at -20°C, the swollen part of the fibre is rather homogeneous and smooth, while after being kept at -6°C the diameter of swollen zones varies from place to place. Are these treatments influencing the mechanical properties of wet regenerated samples?

b) Two types of fibres treatment were chosen: 20 hours at 25°C and 20 hours at -6°C, with 8%NaOH aqueous solution. After one of these two treatments, fibres were spin-dried and then mixed with cellulose/7.6NaOH aqueous solution following the procedure described in part II.3.5. The mixture was then either:

- aged for 2 hours at +5°C and then gelled at +25°C for 20 hours or
- aged for 2 hours at +5°C and then frozen at -20°C for 20 hours or
- not aged at all and gelled at +25°C for 20 hours or
- not aged at all and frozen at -20°C for 20 hours.

The results of rupture stress for these cases are presented in Fig.V.2-8.

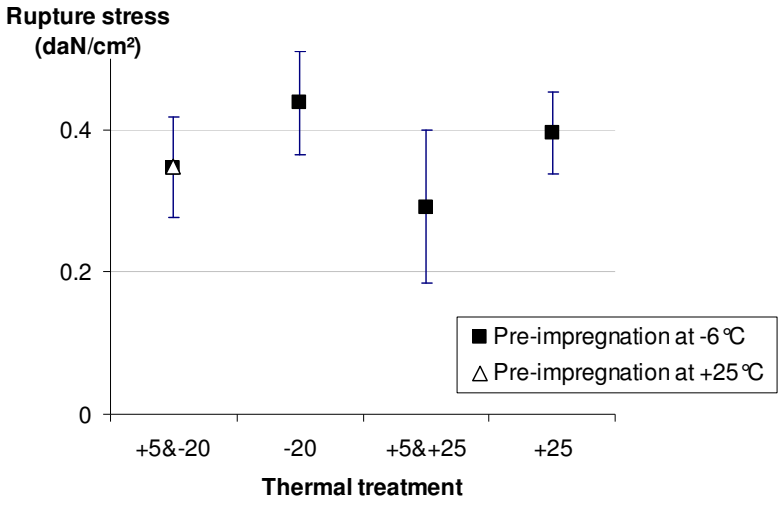


Fig.V.2-8: Rupture stress for wet regenerated samples (in water at +70°C) as a function of thermal treatment for 5B389 cellulose/7.6NaOH/water+2 fluff pre-impregnated in 8%NaOH at +25°C (△, one value at '+5&-20') and at -6°C (■)
'+5&-20': 2 hours of ageing at +5°C then 20 hours of freezing at -20°C;
'-20': 20 hours of freezing at -20°C (without ageing);
'+5&+25': 2 hours of ageing at +5°C then 20 hours of gelation at +25°C;
'+25': 20 hours of gelation at +25°C (without ageing).

The following conclusions can be made from this graph.

- Regarding the results two by two, freezing at -20°C and gelation at +25°C, with or without ageing (2 hours at +5°C), it is clear that the ageing step does not increase mechanical properties.
- Secondly, pre-impregnating the fibres at -6°C does not improve the resistance to the rupture compared with a pre-impregnation at room temperature.
- Freezing (with or without aging) does not lead to a considerable increase of the rupture stress.

Thus it is not necessary to decrease the temperature of pre-impregnation and to apply an ageing step.

V.2.2.5. Conclusions

The addition of the reinforcing fibres (fluff) leads to the increase in the rupture stress of wet regenerated samples. But the effect is rather small and we tried to find a method to increase the mechanical properties by improving the adhesion matrix/fibres. It appears that the addition of an adhesion promoter (GLYMO, AMEO or CPTMO) is not efficient.

The treatment of the reinforcing fibres at -20°C does not improve the mechanical properties of the samples.
Finally, as previously in the case of wet regenerated cellulose, without reinforcing fibres, regeneration in water at +25°C gives better mechanical properties than regeneration in water at +70°C.

V.2.3- Wet samples made from regenerated 5cellulose/7.6NaOH/water solutions with reinforcing fibres and porophores

In the last step of our investigation, we added $Na_2SO_4,10H_2O$ crystals to create a porosity and thus to obtain a sponge from NaOH process. Fig.V.2-9 shows a wet regenerated sample, seen by optical microscopy.

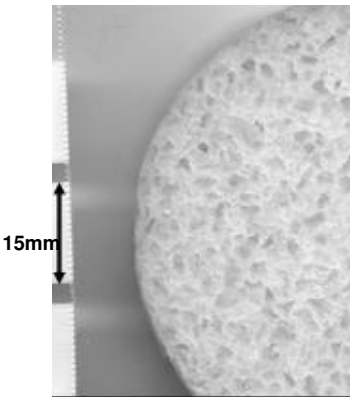


Fig.V.2-9: Wet sponge made in Cemef from the NaOH process.

Tensile tests were performed on wet sponge sample after two different thermal treatments of cellulose solution + reinforcing fibres + porophores: 20 hours of freezing at -20°C or 20 hours of gelation at +25°C. No ageing step was applied as we saw that it does not improve the results. The fibres of fluff were pre-impregnated with 8%NaOH/water at -6°C. Samples were regenerated at 70°C. The values of the rupture stress and other characteristics of sponges are reported in Tab.V.2-2 and their calculation is given below (details are given in part II.3.6).

Property	Calculation	Meaning
Rupture stress *'F_R'*	$F_R = \frac{F}{S}$ In our case F_R is directly determined from the graph	*F* is the tensile force when rupture appears (daN) *S* is the initial specimen section (cm^2) F_R is the rupture stress (daN/cm^2)
Density *'d'*	$d = \frac{m_d}{V_w}$	d represents the density of the sponge (g/dm^3) m_d is the weight of the dry sample (g) V_w is the volume of the wet sample (dm^3)
Water absorption *'Abs.'*	$Abs. = \frac{(m_w - m_d)}{m_d}$	*Abs.* is the absorption capacity m_w represents the weight of wet sample (g) m_d is the weight of dry sample (g)
Shrinkage *'Shr.'*	$Shr. = \frac{A_w - A_{dw}}{A_w}$	*Shr.* is the shrinkage of the sponge sample A_w is the surface of a never-dried-wet sample (cm^2) A_{dw} is the surface of a dried-and-swollen again sample (cm^2)

All the properties described above depend on the conditions of preparation of sponges. But they are also closely connected to the density. In other words, when two samples have very different densities, the comparison of other characteristics does not mean much. In our case (Tab.V.2-2), the density values are similar, around 25g/dm^3. It is thus possible to compare the mechanical and physical properties as a function of the thermal treatment applied to the mixtures before regeneration, i.e. if the mixture was frozen or not.

With $Na_2SO_4,10H_2O$ crystals						Without crystals
Impregnation	Treatment	F_R	d	Abs.	Shr.	F_R
+20°C	-20°C	0.17	24.9	19.6	37	0.31
-6°C	-20°C	0.20	25.8	20.6	27	0.40
-6°C	+25°C	0.09	24.6	9.7	58	0.35
+20°C	+25°C	0.05				

	Sponges from Viscose process			
	F_R	d	Abs.	Shr
CV	1.6-1.7	35	24-25	6
CE	1.5	30	29	1.5

Tab.V.2-2: Properties of sponges prepared from NaOH and viscose processes,
For the viscose process, the properties are given by Spontex
CV: Vapour coagulation; CE: Electrical coagulation part V.1.1-

From the results reported in Tab.V.2-2, it is clear that the properties of sponges prepared in Cemef with the NaOH process are very low in comparison with the ones of standard sponges, prepared industrially with the viscose process.

Now, let us compare the frozen and gelled sponges, prepared from the NaOH process.

V.2.3.1. Rupture stress

As seen in Tab.V.2-2, the presence of crystals forming the pores dramatically decreases the resistance of sponges. This is an expected result since the amount of solid materials is decreased. But the difference between Cemef and Spontex sponges is extremely high. Sponges made with the NaOH process have very poor resistance to rupture.

From the results of the rupture stress (F_R) obtained for sponges containing regenerated cellulose + reinforcing fibres + porophores (Tab.V.2-2 column 3), we can see that the freezing step allows to double the resistance to rupture. A pre-impregnation of reinforcing fibres with 8%NaOH/water at -6°C instead of +20°C slightly improves the rupture stress, but this increase is within the experimental error.

These tensile tests on 'final sponges' (system containing regenerated cellulose + reinforcing fibres + porophores) reveal that the freezing step enables to improve the mechanical resistance of sponges. This result is in complete contradiction with the values of the rupture stress obtained

when the mixture does not contain the porophores, see Tab.V.2-1. Without porophore, the freezing step (-20°C) has no effect on the tensile stress of the wet regenerated material.
Pre-impregnation of the reinforcing fibres at -6°C does not seem to be, in our experiments, a necessary step for improving the rupture stress.
The most important finding of this measurement is the absence of suitable mechanical property of the NaOH processed sponges, made in Cemef.

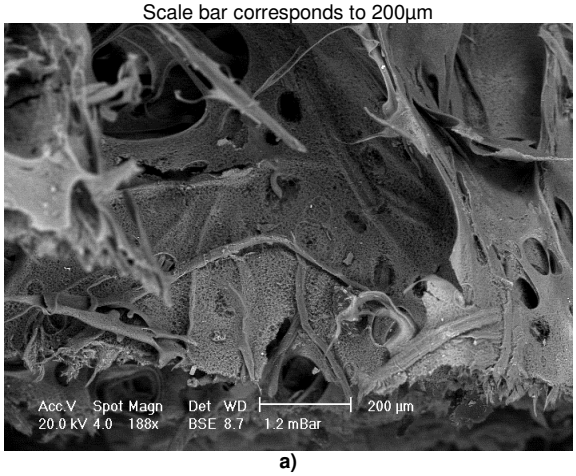
V.2.3.2. Absorption

The comparison of the absorption values (*Abs.*) between NaOH and viscose sponges shows that the viscose ones have better properties, but that the NaOH ones are not very far from the viscose sponges. Absorption is linked primarily to the amount of porosity and to the way pores are structured. Porosity of viscose and NaOH processed sponges is compared using SEM and shown on Fig.V.2-10.

NaOH sponges contained a cellulose matrix from 5B389 cellulose/7.6NaOH/water solution, reinforcing fibres (fluff) and a macroscopic porosity due to the presence of $Na_2SO_4,10H_2O$ crystals. Regeneration in water at +70°C, in several baths, was performed to obtain the final wet product. Viscose sponges contained a Raywhite DP1044 cellulose matrix, reinforcing fibres (cotton, flax and fluff) and a macroscopic porosity due to the presence of $Na_2SO_4,10H_2O$ crystals. The coagulation/regeneration step was performed by electrical coagulation and the blocks were washed in water at +70°C.
In both cases, the sponges were left uncovered to dry naturally and then they were observed with the SEM. Without drying, sponges have to be observed with the SEM in Environmental mode (ESEM), and it is not possible to obtain high enough magnification. This is why we dried them, to be able to use classical SEM.

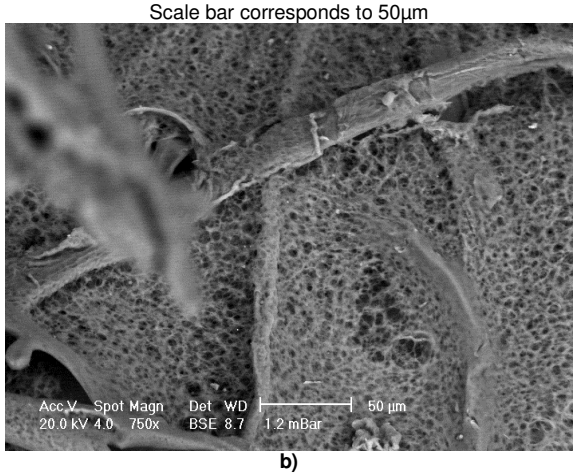
Fig.V.2-10 'a' and 'b' reveal an important and fine porosity in viscose sponges (on the top) which explains the high water absorption value (25-30%). Small pores have diameter inferior to 5µm. As the $Na_2SO_4,10H_2O$ crystals have diameter between 100µm and 3mm, it is obvious that the small pores observed on this picture do not come from the melting of crystals. In the "viscose" process, they are due to the gases (CS_2, H_2S…) that are released during the coagulation/regeneration step, when the structure of cellulose is recovered. In sponges prepared from cellulose/NaOH solutions with a freezing step (Fig.V.2-10 c and d), the quantity of micron-size pores is low and they are not regularly distributed. Indeed, in the NaOH process, no chemical reaction occurs and thus no gas leaves the sample that could lead to the formation of the micro pores. This explains the low absorption value. Finally, sponges prepared from cellulose/NaOH solutions with gelation at +25°C (Fig.V.2-10 e and f) contain no micron-size pores in the regenerated cellulose. Freezing step also plays a role in the formation of some small pores at all, thus decreasing water absorption (see Tab.V.2-2).

Scale bar corresponds to 200µm



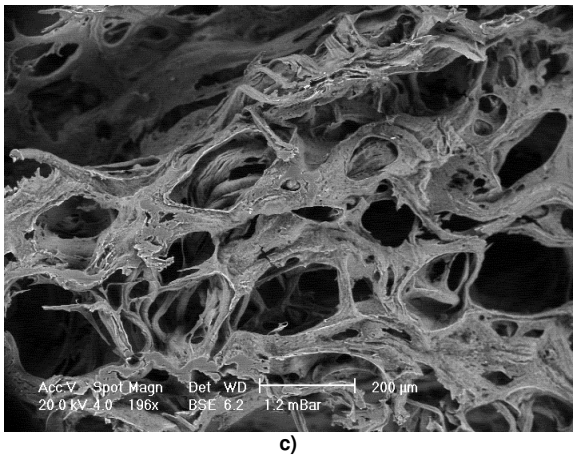
a)

Scale bar corresponds to 50µm

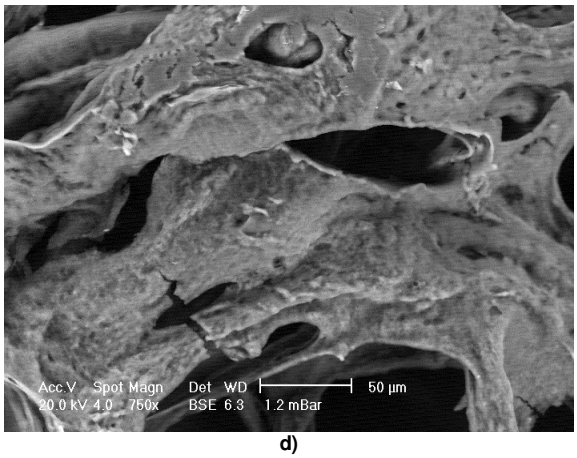


b)

Sponges made from the viscose process: cellulose Rayonier DP1044 with a mixture of cotton, flax and fluff regeneration in water at +70°C

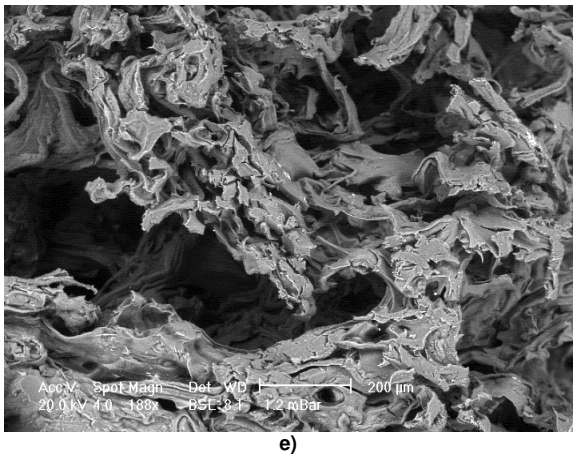


c)

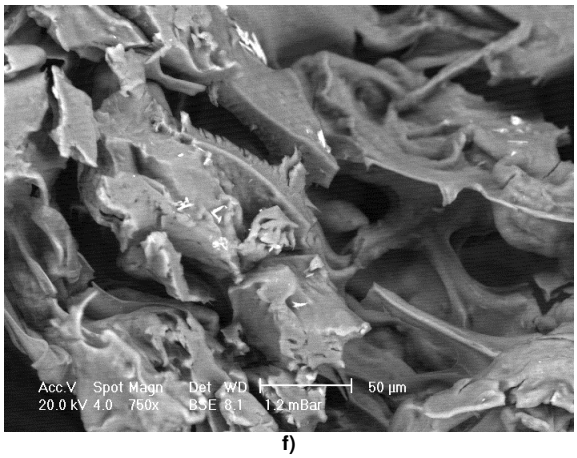


d)

Sponges made from the NaOH process: 5B389 cellulose/7.6NaOH/water with 2 reinforcing fluff fibres pre-impregnated with 8%NaOH/water at -6°C, porophores added, 20 hours of freezing at -20°C, regeneration in water at +70°C



e)



f)

Sponges made from the NaOH process: 5B389 cellulose/7.6NaOH/water with 2 reinforcing fluff fibres pre-impregnated with 8%NaOH/water at -6°C, porophores added, 20 hours of gelation at +25°C, regeneration in water at +70°C.

Fig.V.2-10: SEM observation of dried sponges.

As it could be anticipated, knowing the gaseous origin of the good water absorbance properties of the viscose sponges, NaOH sponges cannot be as good as viscose ones. The absence of chemical reaction is not bringing any micron-size holes. To form them can only occur through the phase separation process that is occurring during regeneration. It seems that there is a large difference in the production of holes between samples that went or not at -20°C. The freezing is changing something in the structuration of the solution that is leading to a phase separation during regeneration that is producing tiny holes.

V.2.3.3. Shrinkage

The shrinkage (*Shr.*) corresponds to the decrease of surface area of a wet sponge as compared with a wet/dried/re-wet sponge. In high performance sponges the shrinkage should be as low as possible, like in viscose sponges where it reaches 1.5% and 6% for sponges prepared from electrical and vapour coagulation methods respectively. A high value means that a large quantity of pores has been closed.

The shrinkage of the NaOH sponges is very high, up to 58%, as compared with less than 10% for viscose sponges. This is a rather puzzling result since it should be in coherence with the absorption properties. We showed that the absorption is low in NaOH sponges because of the absence or the low quantity of micron-scale holes. These should be the first candidates for closing after drying.

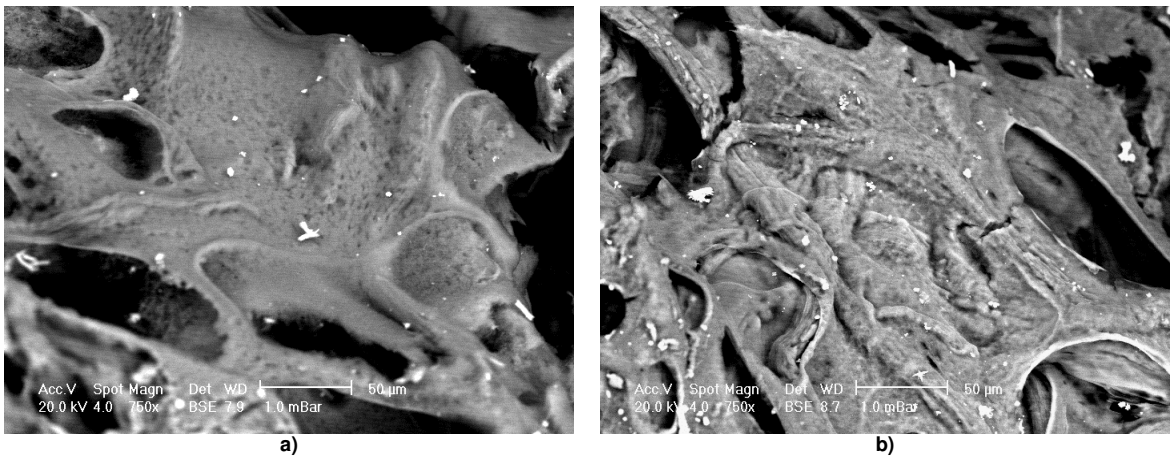
In order to understand what happens during the natural drying of sponges, we dried them with supercritical CO_2 technique.
This specific drying is used in order to replace solvent by air. This technique allows avoiding the pores collapse due to the liquid surface tension and keeping intact the initial micro- or nanostructure of 3D-objects. The supercritical fluid used in our study to dry samples is supercritical CO_2 (sc CO_2) mainly because its critical point is easily obtainable (P=73.8bar and 31.1°C). As water was not compatible with supercritical CO_2, the swollen cellulose was washed five times with acetone, solvent miscible with this supercritical fluid. Following this exchange of solvents the cellulose was in a swollen state in acetone and the supercritical CO_2 drying can be applied.
CO_2 supercritical extraction was performed at laboratory scale in CEP, at Sophia-Antipolis, France.

First of all, the regenerated cellulose + reinforcing fibres + porophores system was prepared as described in Chapter II: with the freezing step and the regeneration in water at +70°C. It results a wet regenerated sponge. From this sponge, two samples were observed:

- The wet regenerated sponge is directly placed in an acetone bath. There, an exchange between water, present in the cellulose sample, and acetone, present in the bath, is occurring. When the equilibrium is reached, the sample is dried in supercritical CO_2.

- The wet regenerated sponge is first dried at ambient air, and then re-wet in water to obtain a wet/dried/re-wet sample. This latter is then placed in an acetone bath where both solvents – water and acetone – are exchanged. The super-critical CO_2 drying is applied.

Fig.V.2-11 'a' and 'b' show the microscopic observations of the wet and wet-dried-rewet samples, respectively, seen by SEM.



a) b)

Fig.V.2-11: SEM observation of a wet (a) and a wet/dried/re-wet (b) NaOH sponge prepared from 5B389 cellulose/7.6NaOH/water solution, reinforcing fibres pre-impregnated with 8%NaOH/water at -6°C, porophores added. 20 hours of freezing at -20°C, regeneration in water at +70°C, dried using super-critical CO_2 technique

From these pictures we can note that the micro porosity of a wet/naturally dried/re-wet NaOH sponge (Fig.V.2-11b) has dramatically decreased as compared with the micro porosity of a wet NaOH sponge (Fig.V.2-11a). These observations can explain the high value (>30%) obtained for the shrinkage (Tab.V.2-2). This means that drying the frozen sponges prepared with NaOH process at ambient air is closing must of the micro-pores of the sponges.

For non-frozen NaOH sponges, it is clearly not the case because of the absence of micro porosity (Fig.V.2-10f). What are closing in the NaOH sponges are the large pore made from the traces of crystal blocks of porophore. And these some large pores are not closing in the case of viscose. One reason that should be investigated is the way OH- groups are organised at the extreme surface of the solid cellulose parts, and why they are prevented to form a strong hydrogen network with neighbouring cellulose surfaces in the case of viscose while they are doing it for NaOH sponges.

Moreover, if we look at the Fig.V.2-11a, we can see that the porosity is lower than the one observed for viscose sponge (Fig.V.2-10b) but not very far. This can explain a not too bad absorption value (20%) for a frozen NaOH sponge.

V.2.4- Conclusion on the role of the freezing step

The results concerning the frozen NaOH sponges (system with regenerated cellulose + reinforcing fibres + porosity left after the melting of $Na_2SO_4,10H_2O$ crystals) are:

- The freezing step leads to a swelling of reinforcing fibres but does not improve the adhesion between the regenerated cellulose matrix and the reinforcing cellulose fibres.
- During the freezing step, certain porosity is created which is not the case when sample are gelled at room temperature before regeneration.
- During the freezing step, the free water present in cellulose solution crystallised and formed needle crystals (Fig.V.2-12). Tensile tests on such a sample should give a break along the imprint of ice crystals. But it is not the case (unfortunately, we do not have photos), the breaking occurs across these imprints and does not take into account them. Moreover, we saw in the section V.2.2.3 that thin specimens are ten times more resistant than thick one, probably because of the skin effect. Thus we can think that a skin is formed around the ice crystals improving the mechanical properties of frozen sponges.

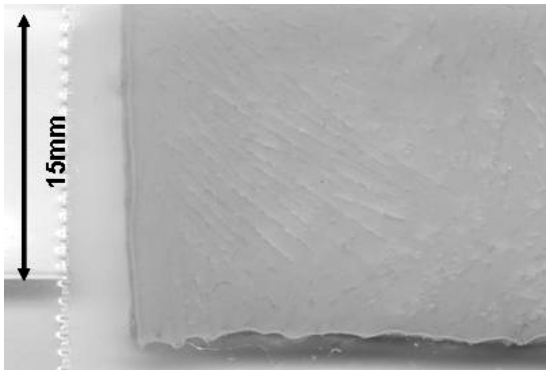


Fig.V.2-12: Imprints of ice crystals in a regenerated cellulose prepared from 5B389 cellulose/7.6NaOH/water, frozen for 20 hours at -20°C and regenerated in water at +70°C.

The influence of freezing step on the rupture stress is very pronounced when the samples contain $Na_2SO_4,10H_2O$ crystals and not important without.

The results of Cemef sponges confirm the findings of Spontex, i.e. that a freezing step at -20°C is needed to obtain a material that will not shrink and will have better mechanical properties. Nevertheless, at least with the Cemef preparation, the mechanical properties of the NaOH sponges are very poor. An interesting question lies in the difference of results between the wet material obtained by the NaOH process with and without porophores, aside the large difference in mechanical properties between these two cases. Without porophore, a freezing step has no effect. With porophores, it dramatically increases the mechanical properties. Two hypotheses can be made taking into account that the effect of freezing on the structure of the solution is not very clear (DSC results seem to show that a small amount of water is crystallised):

- With porophores, freezing allows a long time in the best dissolution range, leading to a better solution in the small thin walls that are between porophore crystals. Upon regeneration, they

give thin cellulose wall with good properties. Without freezing, these walls are not continuous and are breaking easily.

- There is a specific interfacial interaction between the porophore crystals and the cellulose solution that is wetting the crystal better at low temperature, leading to the formation of continuous walls upon regeneration.

A change in the porophore system should bring some clues whether it is due to the chemical nature of the porophores.

V.3- CONCLUSIONS

Mechanical properties of the regenerated cellulose matrix

- Testing only the cellulose matrix reveals not only that the freezing step does not improve the rupture stress but also that the water regeneration bath at +70°C is not favourable to obtain good mechanical properties. Gelation and regeneration in water at room temperature give the highest rupture stress for a cellulose/NaOH/water solution
- We saw that the presence of urea or ZnO in NaOH/water improves the cellulose dissolution and delays the gelation of solutions. But concerning the mechanical tests, the two additives behave differently: urea increases the rupture stress whereas ZnO decreases it, probably because of the presence of ZnO particles in the regenerated cellulose sample.

Mechanical properties of the regenerated cellulose matrix + reinforcing fibres

The addition of reinforcing fibres improves the mechanical properties but the improvement is relatively low. So we tested two ways to improve it.

- The addition of adhesion agent (GLYMO, AMEO and CPTMO) does not increase the rupture stress of samples.
- The pre-impregnation of reinforcing fibres with 8%NaOH/water, at -6°C, induces the swelling of fibres but does not improve the rupture stress.

Mechanical properties of the regenerated cellulose matrix + reinforcing fibres + porophores

First of all, we can note that the NaOH sponges have lower properties (rupture stress, absorption and shrinkage) in comparison with the viscose sponges. Moreover, the influence and the necessity of freezing in NaOH sponges clearly appear.

- Despite the low values of the rupture stress of these final sponges, prepared in Cemef, we can see that the freezing step improves the mechanical properties of samples.
- The very bad absorption value of a non-frozen NaOH sponge can be explained by an absence of micro-porosity. In a frozen NaOH sponge, we can observe (SEM) some micro-pores but their amount is low in comparison with a viscose sponge, this result is in agreement with the absorption.
- The drying at the ambient air of NaOH sponges is closing micro-pores leading to a high value of shrinkage.

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CONCLUSIONS

The work performed in the present thesis tackles both scientific questions and industrial problems. This study is focused on the structure of solvents, 7.6NaOH/water, 7.6NaOH/6urea/water and 7.6NaOH/0.7ZnO/water, and on the properties of solutions of cellulose dissolved in these solvents, in particular, the rheology, the conditions of gelation (temperature and kinetics) and the influence of freezing the solutions on their structures. These results were used to evaluate the possibility of making films and sponges.

Structure of solvents: NaOH/water, NaOH/ZnO/water and NaOH/urea/water

The phase diagrams of cellulose solvents, NaOH/water, NaOH/urea/water and NaOH/ZnO/water, were studied using the DSC technique.

The NaOH/water binary phase diagram was studied in details for 0-30%NaOH/water solutions. The results are in agreement with the NaOH/water phase diagram reported in literature [PIC1893] [ROL1964]. The possibility to calculate at all compositions and temperatures the composition of the mixture and the existence of a eutectic peak ($NaOH,5H_2O+4H_2O$ at -33.4°C) allowed studying the influence of the incorporation of cellulose.

The urea/water binary system forms a eutectic mixture, at -11.4°C, composed of urea+$8H_2O$. In the ternary NaOH/urea/water system, both NaOH and urea eutectic mixtures are formed independently when enough water is present in solution. When water is missing, NaOH is attracting water at the expense of urea. NaOH and urea do not interact.

Mixing ZnO with NaOH/water leads to the formation of ZnO-NaOH-water complexes which change the NaOH/water phase diagram by decreasing the melting temperature and enthalpy of NaOH eutectic. ZnO reacts with 3NaOH molecules and can be surrounded by up to 25 water molecules.

Structure and properties of cellulose/NaOH/water solutions

Cellulose was dissolved in NaOH/water with NaOH concentrations from 7 to 9%. The addition of cellulose in NaOH/water does not change the melting temperatures of the NaOH eutectic and of free ice. This means that the presence of cellulose does not disrupt the phase diagram of the solvent.

The melting enthalpy of the NaOH eutectic peak significantly decreases when cellulose content increases. This allows to calculate the amount of NaOH linked to each anhydroglucose unit (AGU) and thus to determine the maximal amount of cellulose that can be dissolved in a given NaOH/water solution. The dissolution of Avicel cellulose in NaOH/water is occurring if at least four NaOH are bound to one AGU which corresponds to a weight ratio $m_{cell}/m_{NaOH} \leq 1$.
The constant enthalpy of free ice (no dependence on cellulose content) means that water molecules linked to cellulose are the only ones that are involved in the eutectic through NaOH. (i.e. 9 water molecules per NaOH).
As the upper limit of NaOH concentration that can dissolve cellulose is 10% [SOB1939], the maximal Avicel cellulose concentration that can be dissolved in a sodium hydroxide aqueous solution is 10%, which is a relatively low value for an industrial process.

Other than Avicel cellulose samples were studied: steam-exploded Borregaard (DP = 389) and Solucell (DP = 198 and 307). The enthalpy of the eutectic peak is also decreasing in the presence of cellulose as in the case of Avicel, but the amount of the decrease depends not only on cellulose concentration but also on its origin. This is due to the fact that the cellulose solutions other than pure cellulose materials are difficult to dissolve properly and completely.
The viscosity versus shear rate measurements showed that the steam-exploded cellulose/NaOH/water solutions are not molecularly dispersed and behave as a suspension. This is compatible with the fact that cellulose chains are coated with several NaOH and water molecules.

The intrinsic viscosity of cellulose/NaOH/water solutions is decreasing with temperature increase. The quality of the solvent thus decreases and the cellulose-cellulose interactions are favoured leading either to compactisation of macromolecules in the case of dilute solutions and to gelation in the case of semi-dilute solutions.

Structure and properties of cellulose/NaOH/urea/water and cellulose/NaOH/ZnO/water solutions

Although some parts of cellulose fibres remain non-dissolved, the presence of urea or zinc oxide in cellulose/NaOH/water solutions improves the cellulose dissolution (microscopic observation). The intrinsic viscosity of cellulose/NaOH/water solutions in the presence of both additives is slightly higher than without them demonstrating better solvent (NaOH/water + additives) quality, but it decreases with temperature increase.

The limit of cellulose dissolution in NaOH/urea/water determined with DSC is the same as in NaOH/water. All these solutions have the same structure: cellulose chains coated with NaOH and water molecules. As previously, this explains the flow behaviour under shear being close to the one of a suspension.

It seems that the role of urea is to "trap" a part of water which is not favourable for the cellulose dissolution. Higher is the urea content up to a certain value, higher is the gelation temperature, which means that solvent quality increases. Gelation occurs at low temperatures if there is too much urea in the solution probably because the proportions between NaOH and water are such that the NaOH hydrates are not able to dissolve cellulose anymore. The maximal urea content to delay gelation depends on the cellulose origin, but the reasons of this difference stay an open question.

The addition of zinc oxide in NaOH/water is also efficient to better dissolve cellulose and delay gelation up to the limit of ZnO solubility, which is reached at the molar ratio NaOH:ZnO=10. Further increase of ZnO content does not lead to the improvement in dissolution or gelation. We concluded that the improvement of solvent quality is due to the formation of ZnO-NaOH-water complexes. These complexes are preventing the cellulose-cellulose interactions but do not modify the gelation mechanism of cellulose/NaOH/water solutions.

Influence of freezing step on thermal properties of cellulose/NaOH/water solutions

To keep cellulose/NaOH/water solutions at -20°C for several hours seems to improve the mechanical properties of regenerated cellulose products. That is why the influence of the freezing step on the thermal properties of cellulose solutions was investigated. Using DSC, we studied the melting behaviour of cellulose/NaOH/water and cellulose/NaOH/ZnO/water solutions frozen to -28°C and kept at this temperature for several hours. Cellulose does not change the phase diagram of the NaOH/water binary system, so keeping the solution at -28°C leads to the crystallisation of a part of free water. This free water melts at a certain temperature that depends on NaOH concentration. During the isothermal step at -28°C of several hours, some water is "detached" from cellulose, about $1H_2O$ per AGU, and is released. This "detached" water crystallises as it was alone, giving the melting peak at 0°C. Several hours of freezing are needed for "detached" water to appear. The same occurs for cellulose/NaOH/ZnO/water solutions.

Mechanical properties of regenerated objects prepared from cellulose/NaOH/water solutions. Influence of freezing.

Tensile tests on regenerated cellulose with and without reinforcing fibres and porophores were performed.

Without reinforcing fibres and without porophores, the best properties are obtained when the cellulose/NaOH/water solution is gelled at room temperature for about 20 hours and regenerated in water at room temperature. Regeneration in water at temperatures around 70-80°C leads to a strong decrease in the mechanical properties of regenerated samples as compared with regeneration at room temperature. The freezing step (keeping solution at -20°C for 20 hours) does not improve the mechanical properties of regenerated cellulose.

All-cellulose composite, consisting of a matrix of regenerated cellulose and reinforcing fibres of cotton or fluff (wood pulp with high DP), was then prepared. Although the addition of fibres improves the rupture stress, this improvement is not high enough because of a bad matrix/fibre adhesion.
During the freezing step, the reinforcing fibres are swelling but this does not induce better adhesion matrix/fibres and thus does not explain better properties of frozen sponges as compared with non-frozen ones.

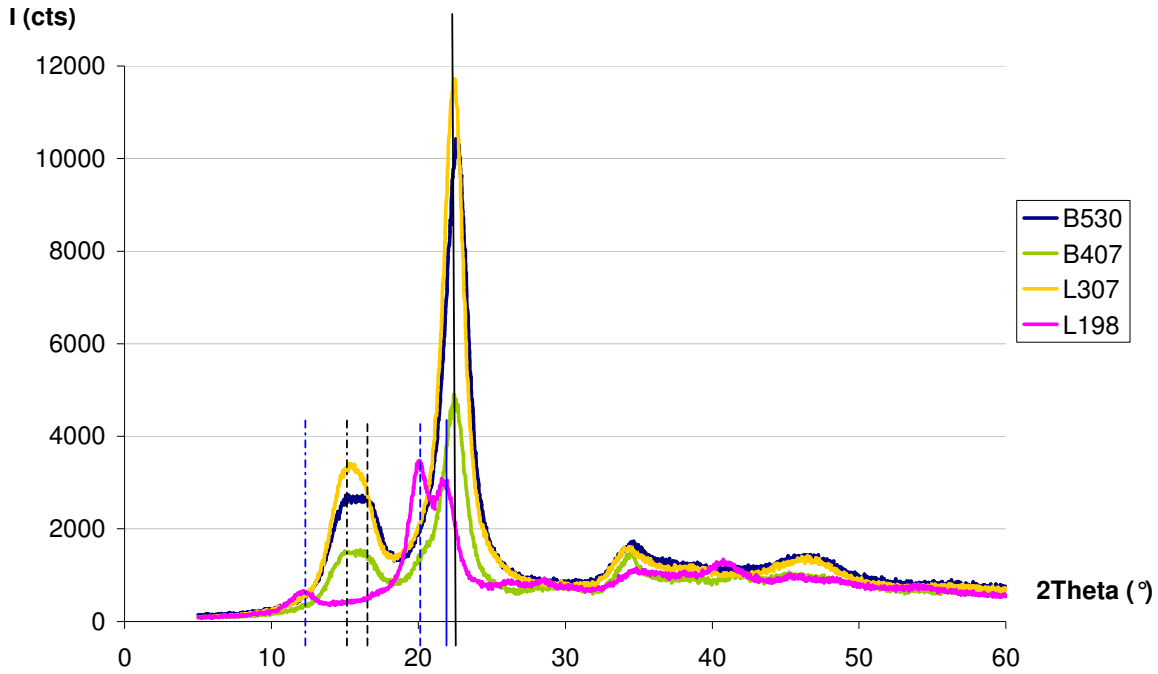
The Na_2SO_4,$10H_2O$ crystals used as porophores were then added to the cellulose/NaOH/water + reinforcing fibres system to obtain the final product. Tensile properties of frozen and non-frozen NaOH sponges are lower as compared with the ones of viscose sponges. Nevertheless, the freezing step improves properties of NaOH sponges like the rupture stress, the shrinkage and the absorption. Indeed, a SEM observation of the final product reveals that frozen sponges have a relatively good micro-porosity but the pores are closing after drying. On the contrary, non-frozen sponges have low micro-porosity leading to weaker properties.

PERSPECTIVES

The proper knowledge of the phase diagrams and the physical properties of cellulose dissolved in NaOH-water-additive mixtures is opening the way to a deeper study of the structure of the cellulose mixtures by techniques able to probe the organisation of the molecules, like NMR, high resolution X-ray scattering and dynamic light scattering. Such results, combined to our work, could bring more information about the way hydrogen bond networks are organised and on which compounds are formed. This should open the way to find either new additives better dissolving cellulose at the molecular level (decreasing the amount and size of micro-gels) or either treatments (activation) of cellulose.

APPENDIXES

APPENDIX 1



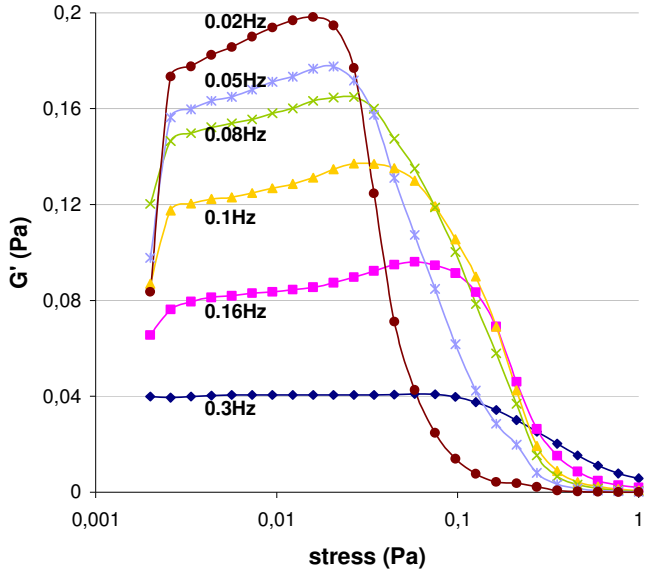
X-Ray diffraction patterns for initial dry cellulose samples (described in the part II.1.1.3)
B530: non-steam exploded Borregaard cellulose (DP530)
B407: steam-exploded Borregaard cellulose (DP407)
L307: electron-beam irradiated Lenzing cellulose (DP307)
L198: regenerated Lenzing cellulose (DP198)

The ref [CIO2005] reports that the characteristic peaks for:

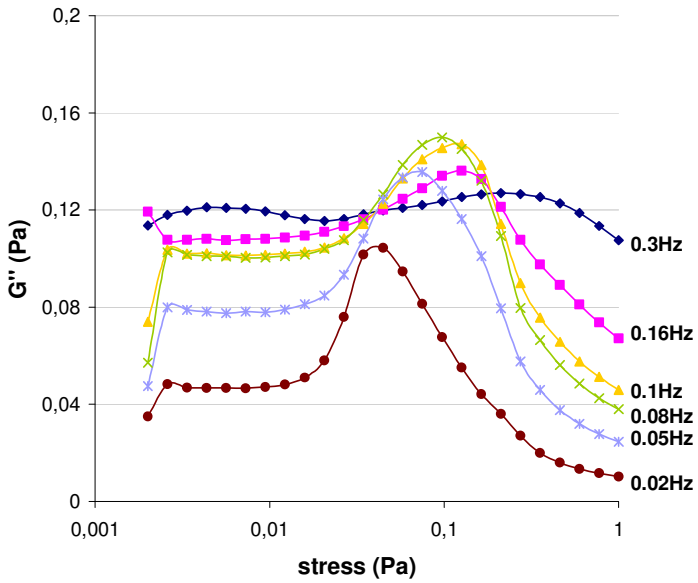
- **Cellulose I** appear at
  - 14.8° for (101)
  - 16.6° for (10-1)
  - 22.6° for (002)
- **Cellulose II** appear at
  - 12.1° for (101)
  - 19.8° for (10-1)
  - 22.0° for (002)

[CIO2005] CIOLACU D., POPA V.I.; *Cellulose chemistry and technology* (2005), **39** (3-4), 179-188

APPENDIX 2

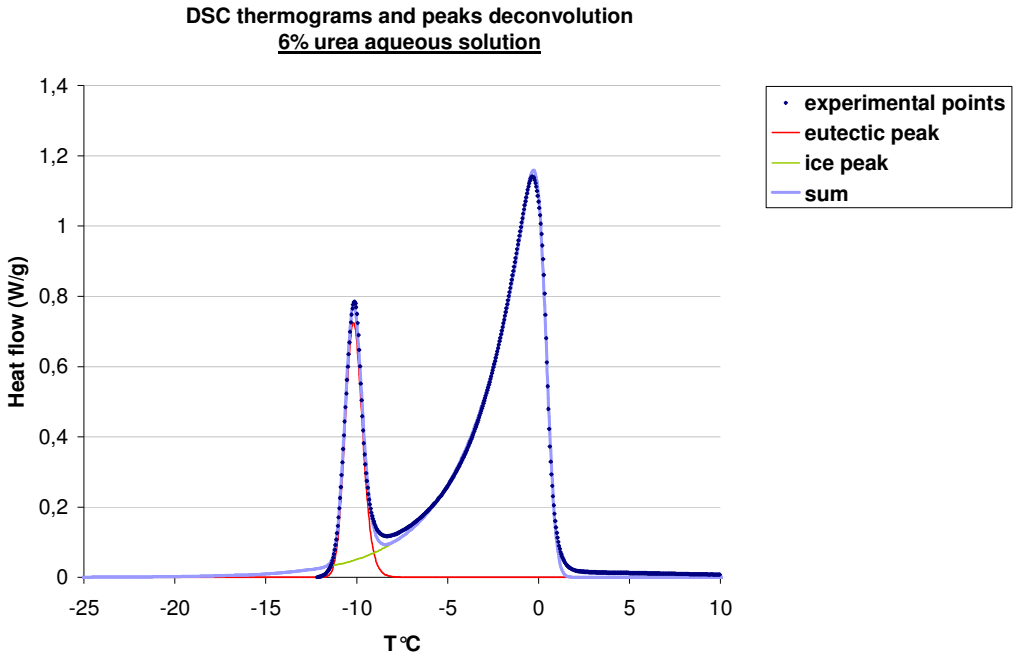


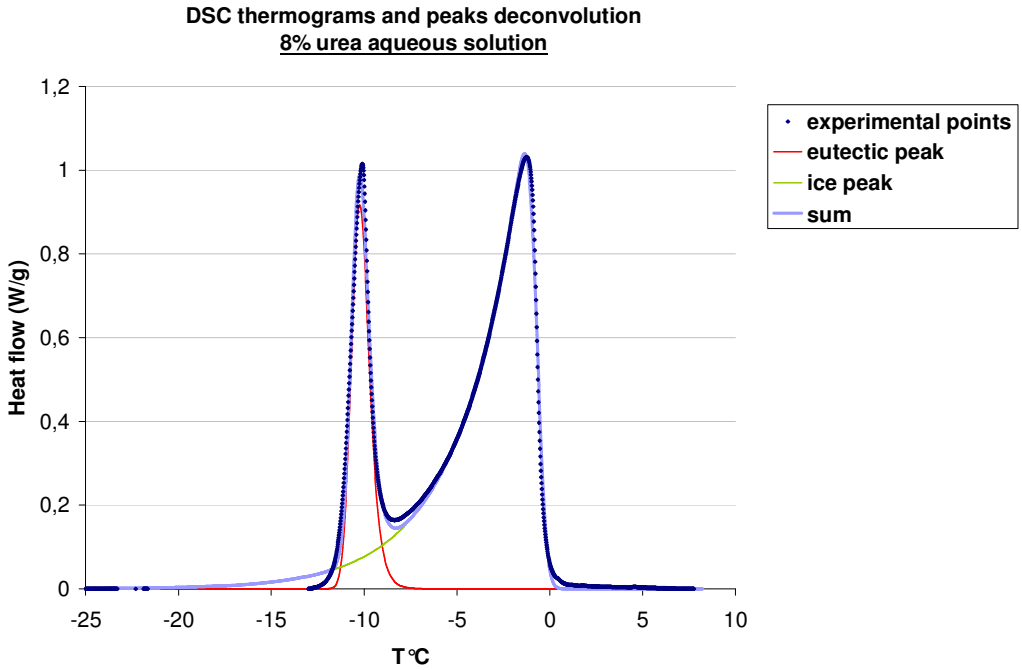
Storage modulus G' as a function of the applied stress for various frequencies, at 20°C for 2.3% B500 cellulose/7.6%NaOH aqueous solutions
Measurements on the StressTech rheometer



Loss modulus G'' as a function of the applied stress for various frequencies, at 20°C for 2.3% B500 cellulose/7.6%NaOH aqueous solutions
Measurements on the StressTech rheometer

APPENDIX 3


DSC thermograms and peaks deconvolution
6% urea aqueous solution
Heat flow (W/g)
1,4
1,2
1
0,8
0,6
0,4
0,2
0
-25
-20
-15
-10
-5
0
5
10
T°C
experimental points
eutectic peak
ice peak
sum


DSC thermograms and peaks deconvolution
8% urea aqueous solution
Heat flow (W/g)
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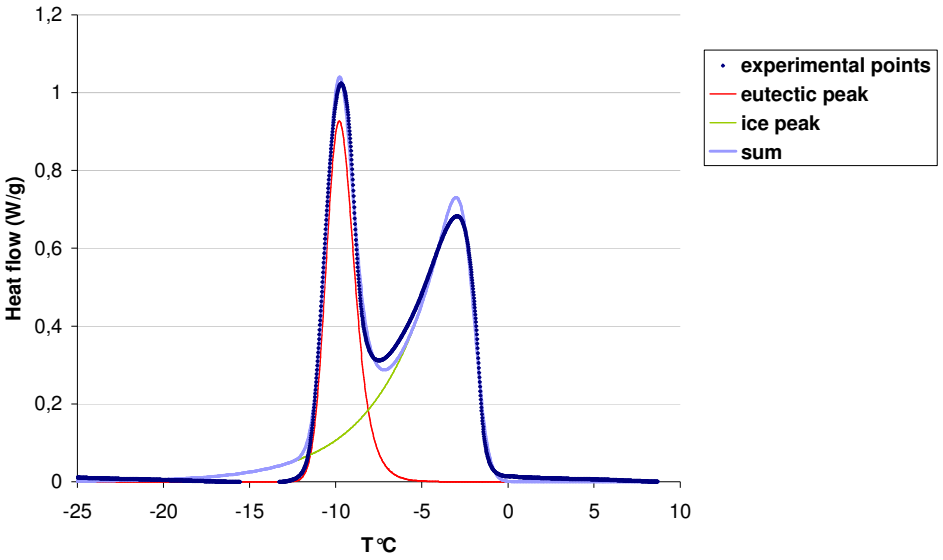
1
0,8
0,6
0,4
0,2
0
-25
-20
-15
-10
-5
0
5
10
T°C
experimental points
eutectic peak
ice peak
sum

DSC thermograms and peaks deconvolution
12% urea aqueous solution



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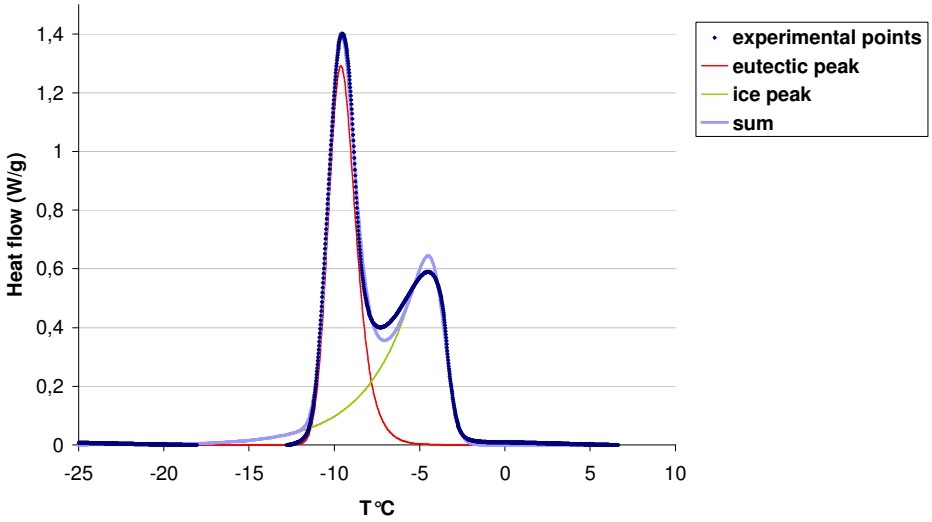
16% urea aqueous solution



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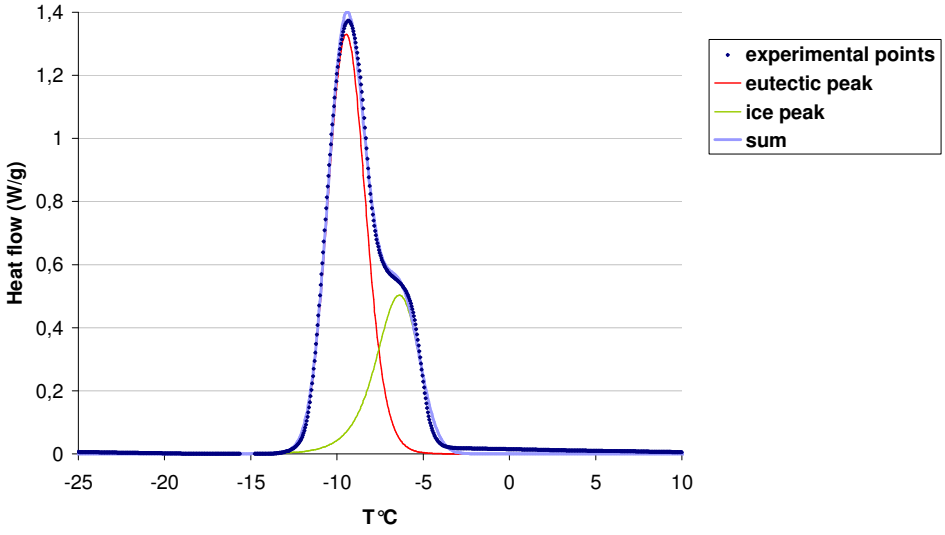
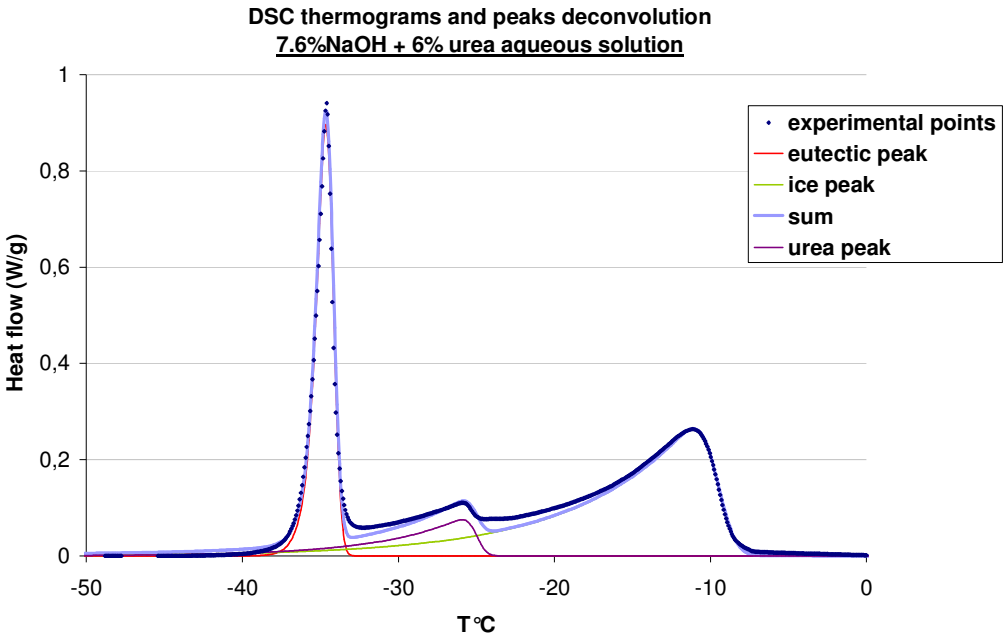
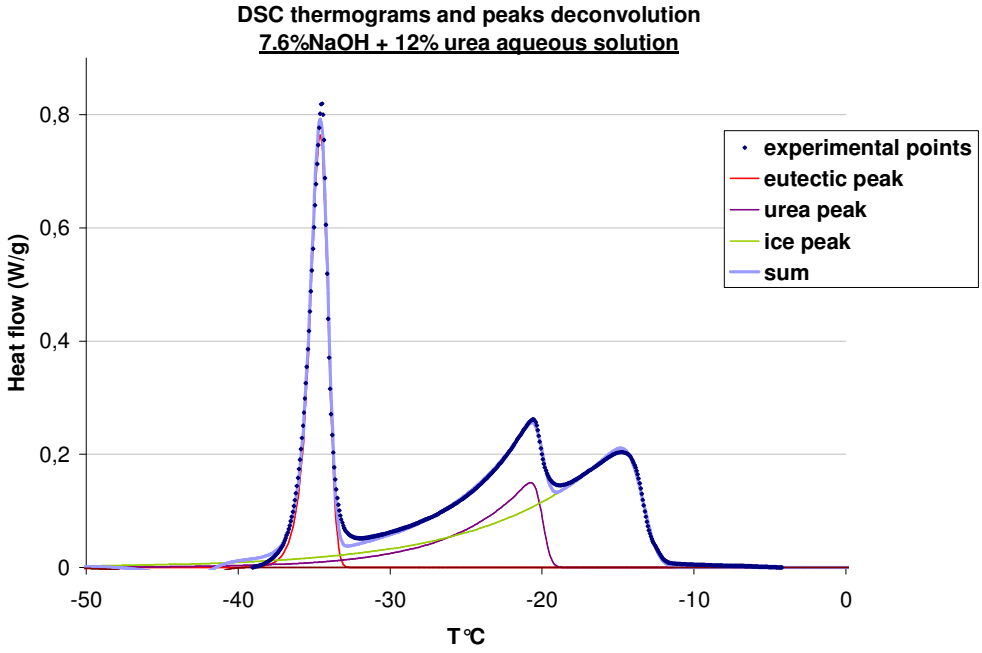
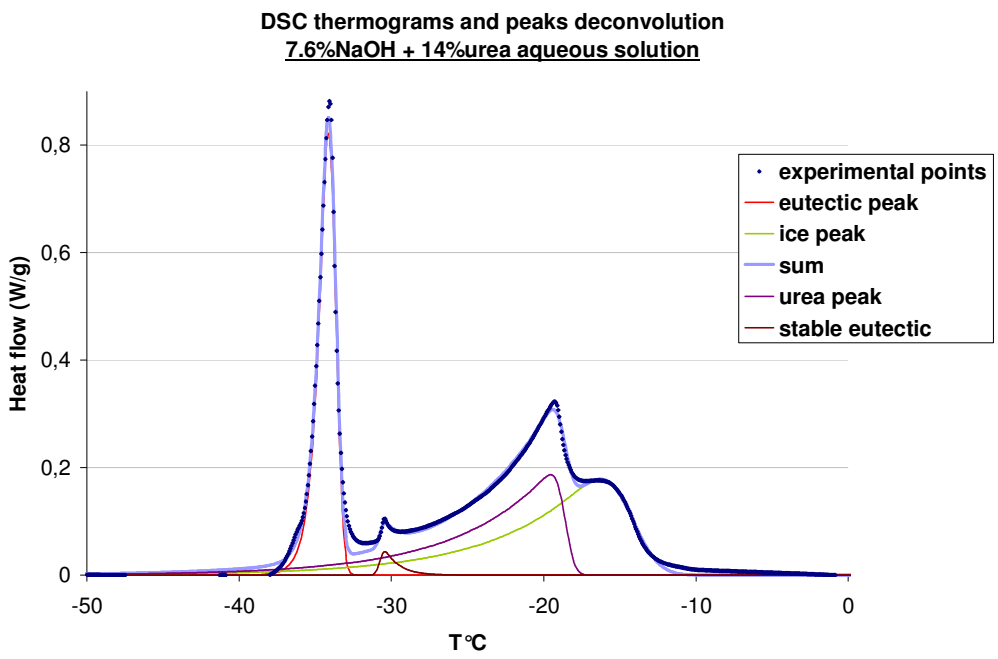
20% urea aqueous solution



APPENDIX 4


DSC thermograms and peaks deconvolution
7.6%NaOH + 6% urea aqueous solution
Heat flow (W/g)
T°C
experimental points
eutectic peak
ice peak
sum
urea peak
1
0,8
0,6
0,4
0,2
0
-50
-40
-30
-20
-10
0


DSC thermograms and peaks deconvolution
7.6%NaOH + 12% urea aqueous solution
Heat flow (W/g)
T°C
experimental points
eutectic peak
urea peak
ice peak
sum
0,8
0,6
0,4
0,2
0
-50
-40
-30
-20
-10
0


DSC thermograms and peaks deconvolution
7.6%NaOH + 14%urea aqueous solution
Heat flow (W/g)
0,8
0,6
0,4
0,2
0
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-20
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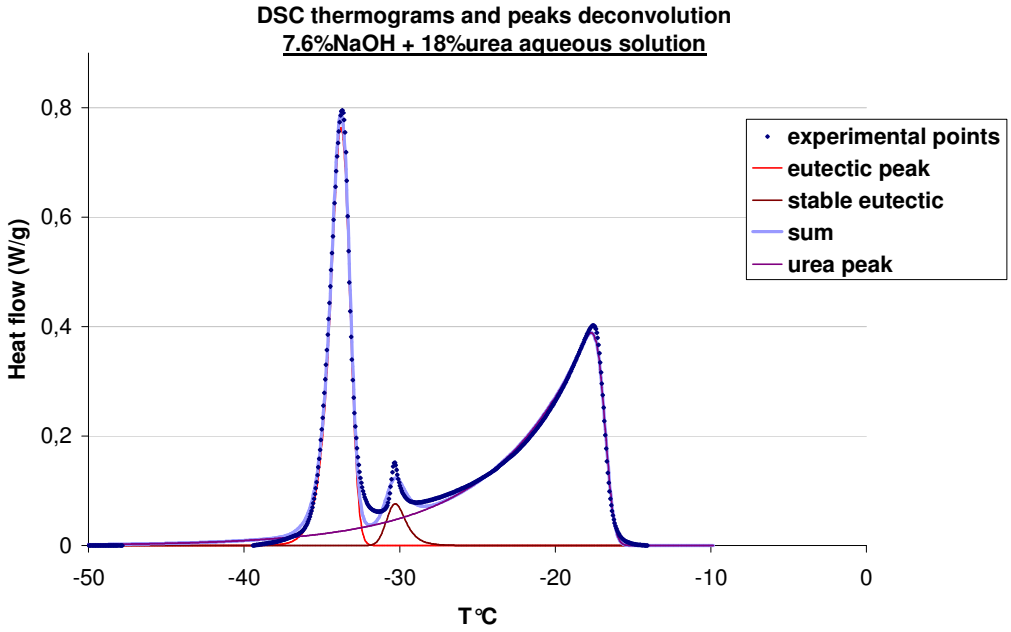
0
T°C
experimental points
eutectic peak
ice peak
sum
urea peak
stable eutectic


DSC thermograms and peaks deconvolution
7.6%NaOH + 18%urea aqueous solution
Heat flow (W/g)
0,8
0,6
0,4
0,2
0
-50
-40
-30
-20
-10
0
T°C
experimental points
eutectic peak
stable eutectic
sum
urea peak

APPENDIX 5

NMR investigations of NaOH-water-samples

I- OBJECTIVE

The current report contains the results of NMR spectroscopic experiments with NaOH water and NaOH water ZnO solutions. By means of the nuclei ^{1}H and ^{23}Na is to be examined whether in the concentration interval of 6% to 10% NaOH discrete NaOH hydrates (NaOH water complexes) are detectable. In addition the temperature influence is to be examined within the range of 20°C to – 20°C.

Table 1 Composition of the samples and measuring temperatures

sample	1	2	3	4	5	6	7	8	9
% NaOH	6	7	8	8	8	8	8	9	10
% ZnO	0	0	0	0,2	0,5	1	1,5	0	0
-20°C	X	X	X	X	X	X	X	X	X
-10°C	X	X	X	X	X	X	X	X	X
0°C	X	X	X	X	X	X	X	X	X
10°C	X	X	X	X	X	X	X	X	X
20°C	X	X	X	X	X	X	X	X	X

II- EXPERIMENTAL

II.1- Sodium lyes

From water-free sodium hydroxide and/or zinc oxide and water without ions the caustic soda solutions and/or zinc containing caustic soda solutions were made by weighing the components in polyethylene containers, which were sealed.

II.2- NMR measurements

The NMR investigations has been carried out with a spectrometer INOVA 500 (Varian Inc.) at measuring frequencies of 499.84 MHz for the ^{1}H nuclei and 132.22 MHz for the ^{23}Na nuclei. The samples were measured in 2 mm OD capillaries in a 5 mm OD sample tube. The gap was filled with deuterated chloroform. That served as stabilizer (NMR lock) and also as reference substance for the determination of the chemical shifts of the ^{1}H spectra. The chemical shifts of the ^{23}Na spectra were referred to the sample with the smallest NaOH concentration at the highest temperature (6%, 20 °C), so that all shift values are positive.

The spin-lattice relaxation times T_1 were measured with the inversion recovery method. Control measurements of the transversal relaxation times T_2 with the CPMG-method resulted in an agreement with T_1 at all concentrations and temperatures in the limits of the measuring errors, so that the evaluation and discussion without T_2 could be done.

III- RESULTS AND DISCUSSION

III.1- ^{23}Na measurements

In liquids and in diluted solutions, which were measured here, the Na nuclei have a large mobility. An extreme movement-conditioned line narrowing arises. Therefore the chemical shift for ^{23}Na can be measured exactly. It reacts very sensitively to the environment of the Na nucleus and is suitable therefore very well for the indication of ion water interactions, which are the subject of the investigations here. [1] By the movement-conditioned line narrowing specified above the spin-lattice and spin-spin relaxation times (T_1 and T_2) are about alike.

The measured relaxation time is determined by the mobility of the Na nuclei and by the electrical field gradients at the position of the nucleus. The environment of the nucleus yields a contribution to gradients of the electrical field at the position of the nucleus. In the here investigated

system this contribution comes from field gradients by the water molecules located near the Na nucleus. Highly symmetrical arrangements of the water molecules (e.g. tetrahedral or octahedronal) do not yield a contribution to the field gradients.

In accordance with these considerations, changing or preferred hydratations of the Na ions should identifiable by a nonlinear behaviour of the relaxation times or the chemical shifts as a function of the NaOH concentration.

In the concentration range between 10% and 40% NaOH expected minima and maxima could be observed. [2]

As the Figures 1 to 4 show, only linear relations exist in the interval from 6% to 10% NaOH and also with additive ZnO from 0% to 1.5% for all examined temperatures.

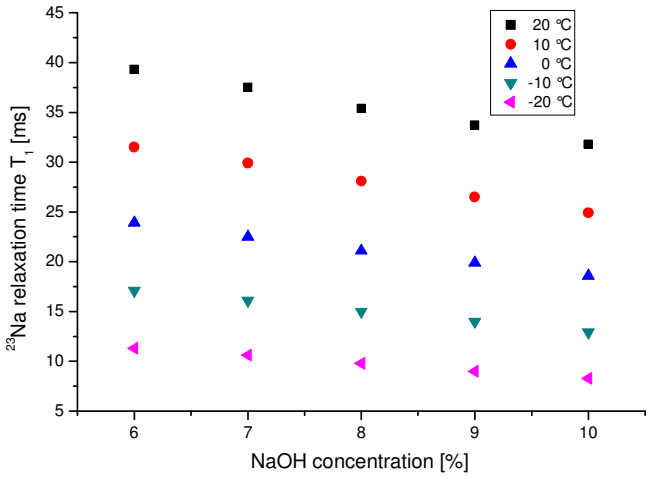


Figure 1 Results of ^{23}Na relaxation times for the lyes

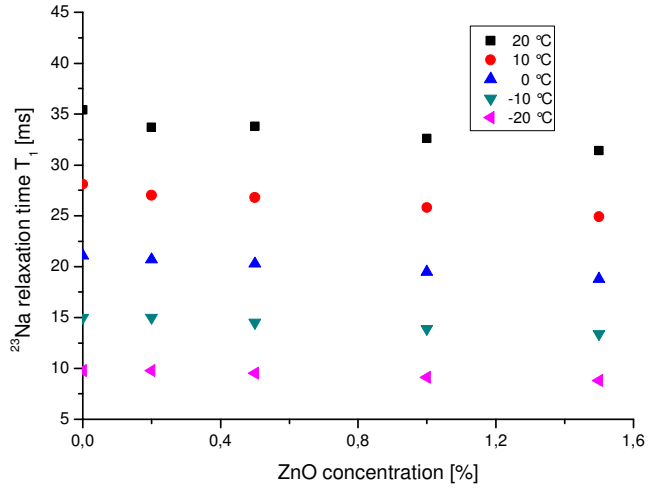


Figure 2 Results of ^{23}Na relaxation times for the lyes with ZnO

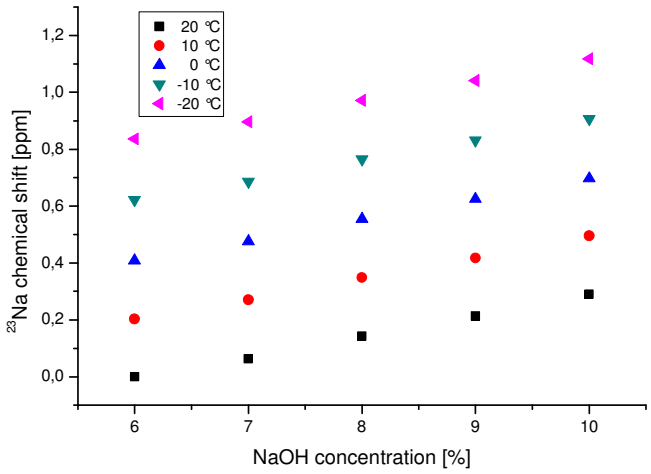


Figure 3 Results of the ^{23}Na chemical shifts for the lyes

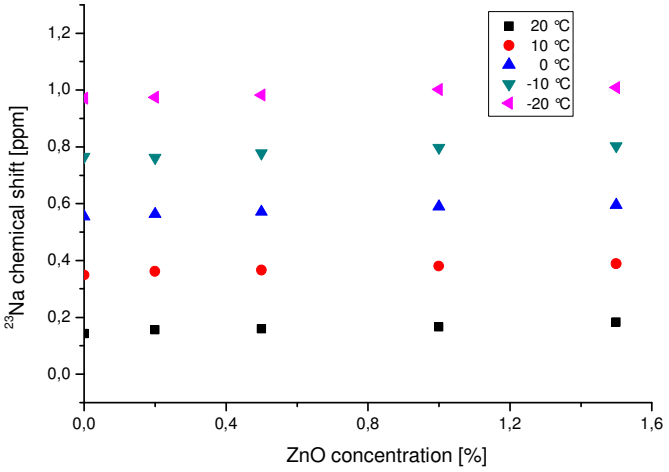


Figure 4 Results of the ^{23}Na chemical shifts for the lyes with ZnO

III.2- ^{1}H measurements

The relaxation behaviour of the protons in the water molecule is determined predominantly by the direct dipolar interaction of the two protons. That is a difference to the quadrupole relaxation of the ^{23}Na-nuclei. In the case of extreme narrowing ($\omega\tau_c \ll 1$) the relaxation time is indirectly proportional to the middle thermal correlation time τ_c.
The relaxation behaviour of the water protons in the caustic solutions is a single-component exponential one at all examined concentrations and temperatures. This means that either all protons have the same interaction and mobility or (compared to the aquisition time and the relaxation time) a very fast exchange between possible different states is present. This results in a

middle relaxation time, weighted whit the relative fractions of the water molecules into the corresponding states.
The measured relaxation times T_1 are represented in Figure 5 as a function of NaOH concentration and temperature. An extrapolation of the T_1 values (at 10 and 20 °C) to the NaOH concentration 0% results nearly exactly in the relaxation times of pure water. The reduction of the relaxation times with increasing NaOH concentration can be explained qualitatively by an increase of the correlation times (dicrease of the mobility, viscosity increase) and/or a shift of the fractions of the water in different states (free, bound). We could not be observe a dependency on the ZnO concentration (Figure 6).
The chemical shifts of the protons (Figures 7 and 8) show likewise only very small changes as a function of the concentrations. That permits no reference to any changing of water structures within the examined concentration range.

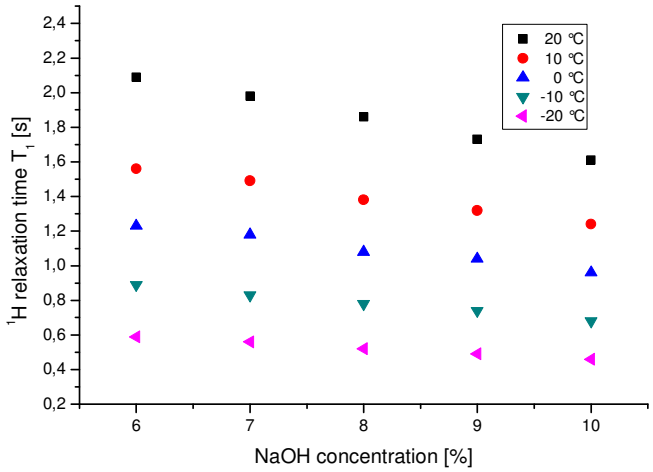


Figure 5 Results of ^{1}H relaxation times for the lyes

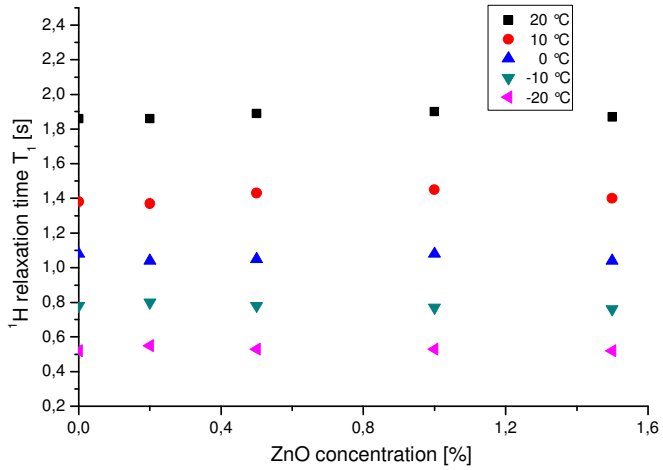


Figure 6 Results of ^{1}H relaxation times for the lyes with ZnO

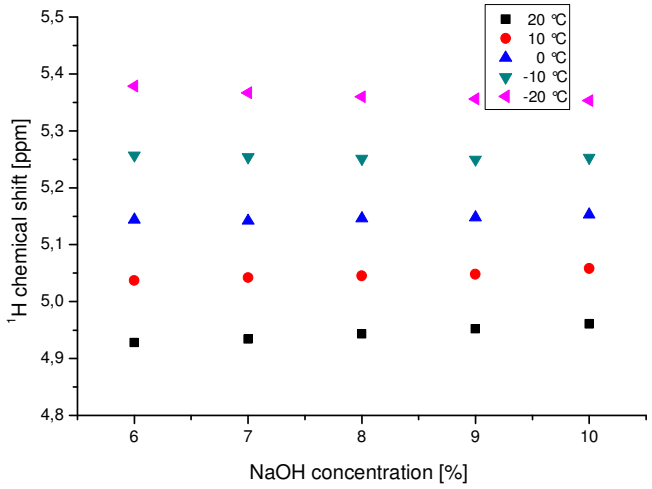


Figure 7 Results of the ^{1}H chemical shifts for the lyes

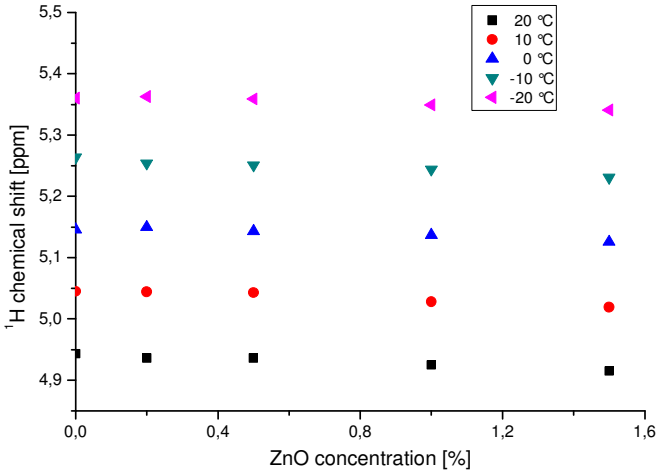


Figure 8 Results of the ^{1}H chemical shifts for the lyes with ZnO

IV- SUMMARY

Changing or preferred hydratations of the Na ions should to be identifiable by a nonlinear characteristic of the relaxation times or the chemical shifts as a function of the NaOH concentration.

As the Figures 1 to 4 show, only linear relations exist in the interval from 6% to 10% NaOH and also with the additive ZnO for all examined temperatures.

In the concentration range between 10% and 40% NaOH expected minima and maxima could be observed for ^{23}Na earlier.

The relaxation behaviour of the water protons in the caustic solutions is a single-component one at all examined concentrations and temperatures (Figures 5 and 6).

The chemical shifts of the protons (Figures 7 and 8) show likewise only very small changes, which do not permit a reference to any changing of water structures within the examined concentration range.

V- LITERATURE

[1] G. J. Templeman et al.: J. Amer. Chem. Soc. **94**, 5578 (1972)

[2] J. Kunze, A. Ebert et al.: Z. phys. Chemie, Leipzig **266**, 49 (1985)

Appendix

Tables: Values of the relaxation times and chemical shifts

^{1}H-measurements of leys

	^{1}H - T_1 [s]				
concentraton; NaOH [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
6	2,09	1,56	1,23	0,89	0,59
7	1,98	1,49	1,18	0,83	0,56
8	1,86	1,38	1,08	0,78	0,52
9	1,73	1,32	1,04	0,74	0,49
10	1,61	1,24	0,96	0,68	0,46

	^{1}H – chemical shift [ppm]				
concentraton; NaOH [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
6	4,928	5,037	5,144	5,257	5,379
7	4,934	5,042	5,142	5,254	5,367
8	4,943	5,045	5,146	5,251	5,360
9	4,952	5,048	5,148	5,250	5,356
10	4,961	5,058	5,153	5,253	5,353

^{1}H-measurements of leys with ZnO (8% NaOH)

	^{1}H - T_1 [s]				
concentraton; ZnO [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
0	1,86	1,38	1,08	0,78	0,52
0,2	1,86	1,37	1,04	0,8	0,55
0,5	1,89	1,43	1,05	0,78	0,53
1	1,9	1,45	1,08	0,77	0,53
1,5	1,87	1,4	1,04	0,76	0,52

	^{1}H – chemical shift [ppm]				
concentraton; ZnO [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
0	4,943	5,045	5,146	5,264	5,36
0,2	4,936	5,044	5,15	5,254	5,363
0,5	4,936	5,043	5,143	5,251	5,359
1	4,925	5,028	5,137	5,244	5,349
1,5	4,915	5,019	5,126	5,231	5,341

^{23}Na- measurements of leys

	^{23}Na - T_1 [ms]				
concentraton; NaOH [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
6	39,3	31,5	23,9	17,1	11,3
7	37,5	29,9	22,5	16,1	10,6
8	35,4	28,1	21,1	15	9,8
9	33,7	26,5	19,9	14	9
10	31,8	24,9	18,6	12,9	8,3

	^{23}Na – chemical shift [ppm]				
concentraton; NaOH [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
6	0	0,203	0,409	0,622	0,836
7	0,063	0,271	0,476	0,686	0,896
8	0,143	0,349	0,555	0,765	0,972
9	0,213	0,417	0,625	0,831	1,042
10	0,29	0,496	0,697	0,906	1,118

^{23}Na- measurements of leys with ZnO (8% NaOH)

	^{23}Na - T_1 [ms]				
concentraton; ZnO [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
0	35,4	28,1	21,1	15	9,8
0,2	33,7	27	20,7	15	9,77
0,5	33,8	26,8	20,3	14,5	9,55
1	32,6	25,8	19,5	13,9	9,12
1,5	31,4	24,9	18,8	13,4	8,81

	^{23}Na – chemical shift [ppm]				
concentraton; ZnO [%]	20 °C	10 °C	0 °C	-10 °C	-20 °C
0	0,143	0,349	0,555	0,765	0,972
0,2	0,156	0,361	0,564	0,762	0,974
0,5	0,16	0,366	0,571	0,778	0,983
1	0,166	0,38	0,59	0,797	1,002
1,5	0,183	0,388	0,596	0,803	1,009

Dr. H.-P. Fink
Division Director

Dr. A. Ebert
Project Manager

RESUME

Il est connu que la cellulose peut-être dissoute dans des solutions aqueuses d'hydroxyde de sodium dans un petit domaine de concentrations (6-10%NaOH) et de températures (-10°C/-4°C). Les solutions de cellulose ainsi obtenues ne sont pas stables et gélifient en fonction du temps et de la température. Il a également été montré que la présence d'additifs – tels qu'oxyde de zinc et urée – améliore la dissolution des fibres de cellulose et la stabilité des solutions.

Afin de comprendre la structure des solutions de cellulose dans NaOH/eau avec et sans additifs, nous avons étudié les diagrammes de phase des solvants d'une part et l'influence de la cellulose sur les thermogrammes de DSC d'autre part. Nous avons ainsi pu déterminer (i) la limite de dissolution de la cellulose dans des solutions de NaOH/eau et NaOH/urée/eau et (ii) la nature des interactions entre les différentes espèces en solution : chaînes de cellulose, NaOH, urée, ZnO et eau.

Nous avons également étudié les propriétés rhéologiques des solutions de cellulose dans NaOH/eau, NaOH/urée/eau et NaOH/ZnO/eau. La gélification des solutions de cellulose est d'une part retardée par la présence d'additifs et correspond à une diminution de la qualité du solvant quand la température augmente. Cependant le mécanisme de gélification reste le même pour les trois solvants étudiés.

Pour finir, l'étude des propriétés mécaniques, et notamment la résistance à rupture, sur des objets de cellulose régénérée a montré l'importance des paramètres de gélification et de régénération.

ABSTRACT

It has been reported that cellulose can be dissolved in aqueous sodium hydroxide solutions in a narrow range of NaOH concentrations (6-10%) and temperatures (-10°C/-4°C). Cellulose solutions obtained are not stable and gelation occurs with time and temperature increase. It has been also showed that the presence of additives, such as urea or zinc oxide, in solvent system improves the dissolution of cellulose fibres and the solution stability.

In order to understand the structure of cellulose solutions in NaOH/water without or with additives, we first studied phase diagrams of solvents and then the influence of the addition of cellulose in these solvents on the DSC thermograms. We determined (i) the limit of cellulose dissolution in NaOH/water and in NaOH/urea/water and (ii) the nature of interactions occurring between cellulose chains, NaOH, urea, ZnO and water molecules.

We also studied rheological properties of cellulose solutions in NaOH/water, NaOH/urea/water and NaOH/ZnO/water. The presence of additives delays gelation (in time and in temperature) but does not change its mechanism. Gelation of cellulose solutions is due to a decrease of solvent quality which favours the cellulose-cellulose interactions with the temperature increase.

Finally, the study of mechanical properties, and especially the measurements of the stress at rupture of regenerated cellulose objects showed the great influence of gelation and regeneration parameters on the properties of the final products.