Cellulose Dissolution in Ethylene Diamine/Salt Solvent Systems

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Abstract

Ethylene diamine (EDA)/salt solvent systems can dissolve cellulose without any pretreatment. A comparison of the electrical conductivity of different salts in EDA was made at 25°C, and conductivity decreased in the order of KSCN>KI>NaSCN at the same molar concentration. Among the salts tested, potassium thiocyanate (KSCN) was capable of dissolving both high molecular weight (DP>1000) and low molecular weight (DP=210) cellulose, and this was confirmed by polarized light microscopy. 39K and 14N NMR experiments were conducted at 70°C with different cellobiose concentrations in EDA/KSCN. The results showed that K+ interacts with cellobiose more than SCN–. Wide angle X-ray diffraction studies revealed that cellulose, recovered by precipitating cellulose solutions with water, underwent a polymorphic transformation from cellulose I to cellulose II. Changes in the FTIR absorption bands at 1430 and 1317 cm-1 were associated with a change in the conformation of the C-6 CH2OH group. The changes in positions and/or intensities of absorption bands at 2900, 1163, and 897cm-1 were related to the breaking of hydrogen bonds in cellulose and were consistent with cellulose II.

Keywords: Cellulose; Dissolution; Ethylene diamine; Potassium thiocyanate; NMR spectroscopy; Polymorph

Introduction

Cellulose consists of a long chain of glucose units joined by . (1,4)-glucosidic linkages. Cellulose is biodegradable, renewable and abundant in nature, but very difficult to dissolve in common solvents due to considerable inter- and/or intra-molecular hydrogen bonding. Among the non-derivatizing solvents for cellulose are N-methyl morpholine-N-oxide/water (NMMO/H_2O) [1], lithium chloride/dimethyl acetamide (LiCl/DMAc) [2], SO_2-amine-dimethylsulfoxide [3], phosphoric acid/water [4], calcium thiocyanate/water ($Ca(SCN)_2/H_2O$) [5], NaOH/thiourea aqueous system [6], inorganic molten salts [7, 8], an ionic liquid solvent containing 1-butyl-3-methylimidazolium chloride [9, 10], ammonia/ammonium thiocyanate (NH_3/NH_4SCN) [11-13], and ethylene diamine (EDA)/salt [14, 15].

Many cellulose solvents include salt. For instance, LiCl/DMAc, $Ca(SCN)_2/H_2O$, inorganic molten salts, and NH_3/NH_4SCN all require significant concentrations of the salt component to dissolve cellulose. However, the role of salt in the system is not always the same. In the $Ca(SCN)_2/H_2O$ system [5], cellulose is dissolved when the concentration of $Ca(SCN)_2$ is higher than 48.5 wt%. The dissolution arises from the cationic calcium which binds oxygen atoms of cellulose at O5 and O6 to form a five-membered ring, leading to breakage of cellulose hydrogen bonds. Meanwhile, two water molecules and two -NCS groups associate with Ca to achieve its 6-valence coordination. In the LiCl/DMAc system [2, 16], cellulose dissolution occurs when the chloride anion hydrogen bonds to the hydroxyl protons of cellulose and along with a Li^+(DMAc) macrocation. In the inorganic molten salts system, Fischer et al. [7] observed direct interactions between the lithium cation and the cellulose hydroxyl groups by means of 2D ^{7}Li-^{1}H heteronuclear Overhauser effect spectroscopy (HOESY). In these cases cations and/or anions from the salt interact with hydroxyl groups of cellulose to break hydrogen bonds.

Analogs of the NH_3/NH_4SCN solvent system, the NH_2NH_2/thiocyanate salt system [17] and the EDA/salt system [14, 18] have been found to dissolve cellulose. But NH_2NH_2 is toxic and carcinogenic [15], which makes it a poor alternative. EDA is less volatile than NH_3 and can swell cellulose and facilitate the diffusion of the solvent into the tightly packed crystalline regions. However, complete dissolution of cellulose is not achieved until a salt is added. Measurements of the solubility of some salts in EDA [19] show that NaSCN, KSCN, NH_4SCN, LiSCN, NaI, KI, LiI and NaBr are soluble in EDA. Among those salts, NaSCN, KSCN or KI can work with EDA to dissolve cellulose. The goal of this article is to investigate the role of salt (KSCN) in the EDA/salt solvent system in cellulose dissolution and in the polymorphic transformation of cellulose recovered by precipitating cellulose solutions with water.

Experimental

Materials

Microgranular cellulose powder CC41 (DP=210 by intrinsic viscosity) was supplied by Whatman Chemical Ltd.. Dissolving pulp TYEE from Weyerhaeuser, Inc. (DP>1000 by product specifications) was ground to 60 mesh in a Wiley mill. D(+)–cellobiose was obtained from Acros Organics. Reagent grade ethylene diamine (EDA) and potassium thiocyanate (KSCN) were obtained from J.T.Baker and used without further purification. Sodium thiocyanate (NaSCN), sodium iodide (NaI) and potassium iodide (KI) were purchased from Fisher Scientific, Mallinckrodt, Inc., and EM Science, respectively, and used as received. Cellulose and salts were dried in a vacuum oven at 60 °C prior to use.

Dissolution of cellulose in EDA/salt solvent systems

A solution of salt in EDA was chilled in a freezer at ca. –20°C [14]. A known weight of cellulose was then mixed with the solvent and kneaded in a sealed ziplock bag at ambient temperature. The resulting cellulose samples were categorized visually as solutions, gels or no solution. Complete dissolution was confirmed using a polarized light microscope Olympus BX51 equipped with a PAXcam camera.

The cellulose dissolution rate was measured by using a rheometer (TA Instruments AR-2000) in steady shear mode. A mixture of cellulose/EDA/KSCN was loaded onto the rheometer without mixing or kneading and then sheared at 15ºC at a steady shear rate of 10 s^{-1}. Variation in viscosity with time was followed as a function of salt concentration and cellulose concentration.

Electrical conductivity measurement of salt solutions in EDA

A series of solutions with varying salt concentration were prepared and the electrical conductivity of those solutions was measured at 25°C using the VWR traceable® conductivity meter. The salts tested included potassium thiocyanate (KSCN), sodium thiocyanate (NaSCN) and potassium iodide (KI).

^{39}K and ^{14}N NMR measurements of cellobiose solutions in EDA/KSCN system

Cellobiose (DP=2) was dissolved in 92.3/7.7 (w/w) EDA/KSCN solvent system. The chemical shifts for ^{39}K and ^{14}N were determined on a Bruker ARX-300 spectrometer at 70 °C as a function of cellobiose concentration.

Preparation of recovered cellulose

5 wt% of cellulose (CC41) was swollen in EDA and dissolved in 77/23 (w/w) EDA/KSCN, respectively, followed by precipitation from solution with distilled/deionized water. The resulting cellulose was then washed thoroughly with distilled/deionized water until the pH of the residual water was constant, which indicated no residual EDA. The absence of salt (KSCN) in the recovered cellulose was confirmed by the absence of the strong peak (2047 cm^{-1}) associated with SCN in FTIR spectra. All the recovered cellulose samples were dried in a vacuum oven at 60°C before characterization.

FTIR spectroscopy and wide angle X-ray diffraction studies

FTIR spectra of the recovered cellulose samples were collected in absorbance mode on a Perkin Elmer Magna-IR 560 spectrometer. All spectra were recorded with 64 scans and a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1}. Cellulose powder was mixed with KBr to make a pellet before measurement.

Wide angle X-ray diffraction (WXAD) studies were run on a SCINTAG theta-theta diffractometer using a standard target Cu at 45 KV and 40 mA. The diffraction angle (2θ) ranged from 2-40° with a scan rate of 0.075º/min.

Results and Discussion

Dissolution of cellulose in EDA/salt solvent systems

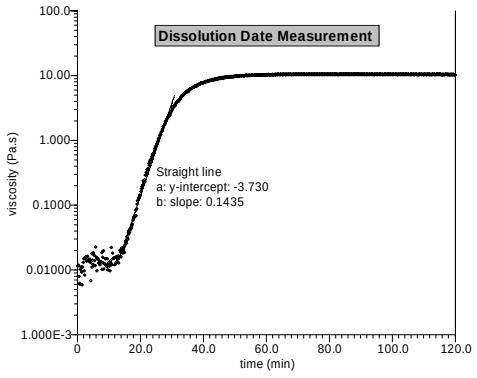

Figure 1: Change in viscosity during dissolution at steady shear for 1.5 wt% of TYEE in 74/26 w/w EDA/KSCN

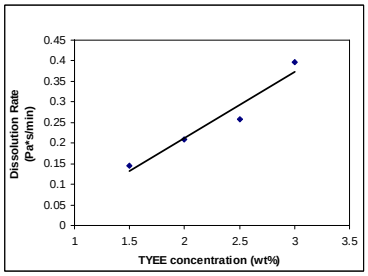

Figure 2: Variation in dissolution rate with cellulose (TYEE) concentration in 74/26 w/w EDA/KSCN

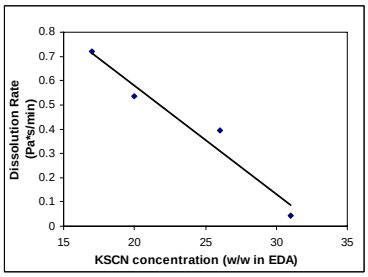

Figure 3: Variation in dissolution rate with salt concentration for 1.5 wt% of TYEE

Salt concentration, salt type, cellulose concentration and cellulose molecular weight all played important roles in cellulose dissolution. Cellulose exhibited different behavior in the different EDA/salt solvent systems. Among the salts tested (KSCN, NaSCN, KI and NaI), KSCN had the best dissolving ability, and was capable of dissolving cellulose over a broad range of solvent compositions. Phase diagrams for EDA/NaSCN and EDA/KSCN solvent systems can be found in cellulose electrospinning studies conducted by Frey et al [20].

Figure 1 shows the change in viscosity with time at a steady shear rate of 10 s^{-1}. The slope of the straight line in figure 1 is used as a measure of the dissolution rate for the system and has units of Pa·s/min. As seen in figure 2, the increase in cellulose concentration gives rise to an increase in the dissolution rate, whereas increasing salt concentration leads to a decrease in the dissolution rate (figure 3).

Electrical conductivity studies of various salts in EDA

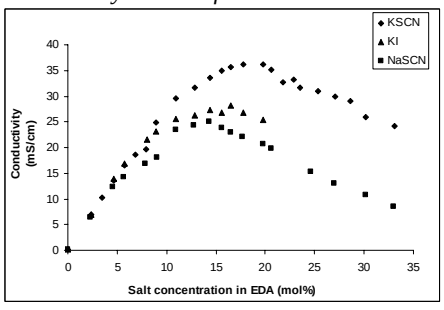

Figure 4. Electrical conductivity of different salts in EDA at 25°C as a function of salt concentration.

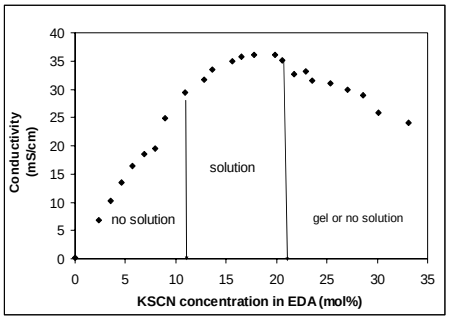

Figure 5. Dependence of 5 wt% of CC41 solubility on the electrical conductivity of EDA/KSCN.

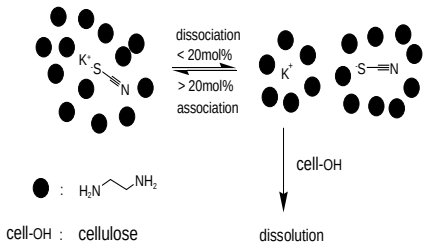

Figure 6. Schematic dissociation and association process for KSCN in EDA

Considering the similarities between aqueous salt solutions and solutions of salt in hydrazine, Hattori et al. [17] applied Williams's theory to the hydrazine/thiocyanate salt system and proposed an equilibrium existing in the salt dissociation process, that is, the formation of a salt-solvent complex and the dissociation of salt into cations and anions, followed by solvation of ions through ion-dipole interaction. Similar behavior is observed in EDA/salt solvent systems. KSCN is taken as an example to illustrate the salt dissociation process (Figure 6).

At low salt concentrations, the conductivity of a solution of salt in EDA increases with increasing salt content (Figure 4), which indicates that the equilibrium proceeds in the forward direction (Figure 6), and the number of solvated ions is larger than KSCN-EDA complexes. Beyond a critical point, ca. 20 mol% for KSCN, 15 mol% for KI, and 17 mol% for NaSCN, the increase in salt concentration leads to a decrease in conductivity. Cations and anions tend to pair up at higher concentrations (Figure 6). The same is true of the EDA/NaSCN and EDA/KI systems. The size of the ions also has an effect on the dissociation behavior of salts in EDA as well as the solubility of cellulose in the solvent. The smaller Na^+ ion bonds more strongly to SCN^- than the larger K^+ ion. The lower ion mobility of NaSCN than of KSCN in EDA is confirmed by the lower conductivity of NaSCN/EDA solutions. Furthermore, small ions are likely to be tightly surrounded by EDA molecules and may not access the OH groups of cellulose as easily as large ions. To effect cellulose dissolution, breaking hydrogen bonding in cellulose chains is vital, which is achieved by the accessibility of solvent to the hydroxyl groups in cellulose [12].

In the aqueous $Ca(SCN)_2/H_2O$ and NH_2NH_2/thiocyanate salt solvent systems, cellulose dissolution requires high salt concentrations where salt and solvent tend to form a solvent-salt complex. The EDA/KSCN solvent system, however, dissolves cellulose when the solvent concentration is in the range of 83/17-71.5/28.5 (w/w) EDA/KSCN. Within this range, salt dissociation is more favorable than formation of a KSCN-EDA cluster, as demonstrated in Figure 5. Evidence of whether the SCN^- anion or K^+ cation participates in cellulose dissolution is provided by ^{39}K and ^{14}N NMR spectroscopy.

^{39}K and ^{14}N NMR spectroscopy studies of cellobiose solutions in EDA/KSCN solvent system

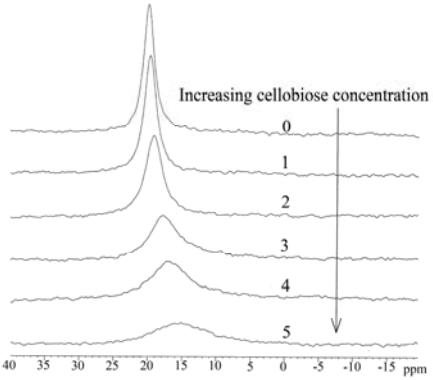

Figure 7. ^{39}K NMR spectra of cellobiose solutions in 92.3/7.7 (w/w) EDA/KSCN as a function of cellobiose concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of 1-5.

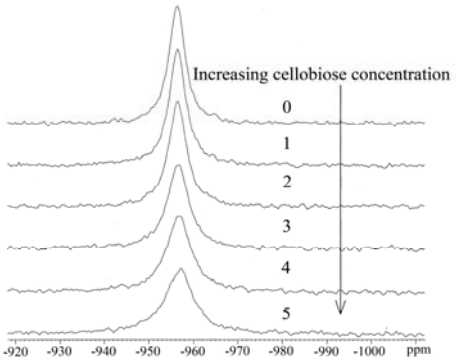

Figure 8. ^{14}N from KSCN NMR spectra of cellobiose solutions in 92.3/7.7 (w/w) EDA/KSCN as a function of cellobiose concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of 1-5.

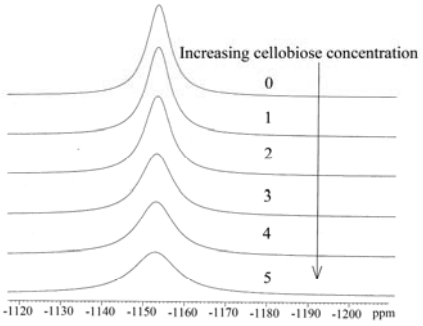

Figure 9. ^{14}N from EDA NMR spectra of cellobiose solutions in 92.3/7.7 (w/w) EDA/KSCN as a function of cellobiose

concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of 1-5.

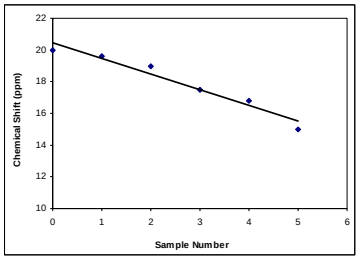

Figure 10. Dependence of the chemical shift of ^{39}K on cellobiose concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of sample number from 1-5.

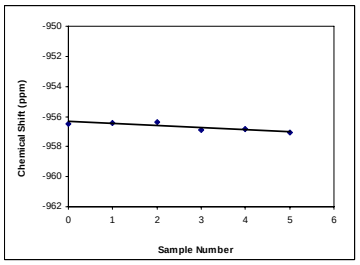

Figure 11. Dependence of the chemical shift of ^{14}N from KSCN on cellobiose concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of sample number from 1-5.

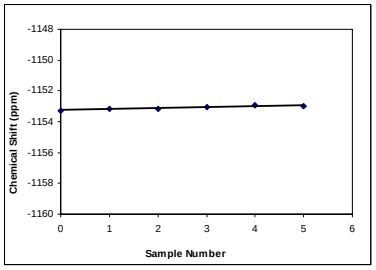

Figure 12. Dependence of the chemical shift of ^{14}N from EDA on cellobiose concentration. 0 denotes no cellobiose in the solvent. Cellobiose concentration increases in the order of sample number from 1-5.

High-resolution NMR spectroscopy has been used extensively in the study of cellulose and cellulose derivatives. For liquid-state NMR [21], the rapid tumbling of molecules in solution averages out the molecular conformations, giving rise to an average chemical shift. This explains why only a single peak shows up in the ^{39}K NMR spectrum, despite the fact that the K^+ ions exist in at least two chemically different environments (free and bound by cellobiose). Additionally, increasing solution viscosity reduces molecular tumbling, thereby broadening the NMR signals and causing lower resolution [22, 23], as seen in Figure 7-9. To lessen the effect of high viscosity on the resolution of NMR spectra, cellobiose (DP=2) was used as a model compound, and NMR spectroscopy studies were conducted at 70°C. Figure 10 shows that the increase in cellobiose concentration gives rise to an appreciable change in the ^{39}K chemical shift. This shift is attributed to the increasing dominance of the peak associated with bound K^+ as more K^+ ions are moving towards cellobiose with increasing cellobiose concentration. No significant shifts, however, are found for ^{14}N nuclei in SCN^- in figure 11 and ^{14}N nuclei in EDA in figure 12. Peaks corresponding to interaction between cellobiose reducing end groups and EDA were not detectable in these experiments because EDA was present in excess and exchange between free EDA and EDA associated with reducing end groups was very rapid at the elevated experimental temperature. The ^{39}K and ^{14}N NMR studies indicate that the K^+ ion interacts with cellobiose more than the SCN^- ion does.

FTIR studies of recovered cellulose

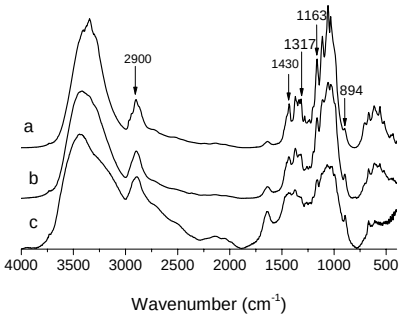

Figure 13. FTIR spectra of cellulose: (a) pure CC41; (b) CC41 recovered from cellulose swollen in EDA; (c) CC41 recovered from a 5 wt% of cellulose solution with a solvent concentration of 77/23 (w/w) EDA/KSCN.

FTIR analysis was used to detect changes in the conformation of cellulose chains and the crystal structure of cellulose swollen in EDA and recovered from solution in EDA/KSCN. Figure 13 shows the FTIR spectra for pure CC41 without any chemical and mechanical treatment, CC41 recovered by precipitating cellulose swollen in EDA with water, and CC41 recovered by precipitating a 5 wt% of CC41 solution with water. The absence of a peak at 2047 cm^{-1} characteristic of the SCN group of KSCN in FTIR spectrum c (Figure 13) indicates that there is no residual salt in the recovered cellulose. The infrared studies also suggest that the recovered cellulose is not derivativitized form since no new absorption peaks appear in the spectra.

The absorption peak at 2900 cm^{-1} is assigned to a CH stretching vibration. As cellulose dissolution progresses from swelling in EDA to solvation in EDA/KSCN, as is seen in the spectra from a through b to c, the CH stretching frequency decreases from 2900 cm^{-1} to 2898 cm^{-1} to 2891 cm^{-1}. This indicates the cellulose chains have undergone changes in intra- and/or inter- hydrogen bonding.

The absorption bands at 1430 cm^{-1} and 1317 cm^{-1} are assigned to CH_2 symmetric bending and CH_2 wagging, respectively. Changes in the intensities and/or positions of these two bands reveal variations in the environment/conformation of the C-6 CH_2OH group [24]. The addition of EDA shifts the band at 1430 cm^{-1} to a higher wavenumber (1436 cm^{-1}) and decreases the intensity of the band at 1317 cm^{-1} considerably. Further addition of salt (KSCN) makes these two bands too weak to be detected.

The intensity of the antisymmetric bridge oxygen stretching band at 1163 cm^{-1} is reduced after recovering CC41 from solution, indicating a change in the hydrogen-bonding of the bridge oxygen after the addition of salt in the system. The band at 894 cm^{-1} is characteristic of β-anomers or β-linked glucose polymers. This band is very weak in spectrum a (Figure 13). In spectra b and c

this band becomes sharp and strong. The change in intensity of this band results from participation of the oxygen atom attached to C1 in this vibration and changes in the hydrogen bonding in cellulose [25].

The breaking of hydrogen bonds in cellulose brought about by the EDA/KSCN solvent system is also confirmed by wide angle X-ray diffraction studies of recovered cellulose.

Wide angle X-ray diffraction studies of recovered cellulose

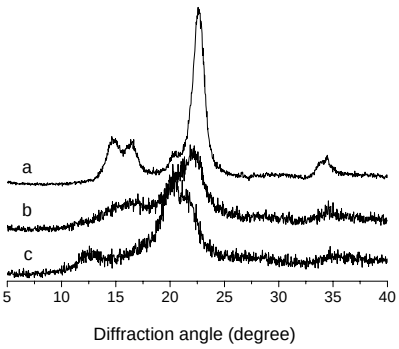

Figure 14. X-ray diffractograms for cellulose: (a) pure CC41; (b) CC41 recovered from cellulose swollen in EDA; (c) CC41 recovered from a 5 wt% of cellulose solution with a solvent concentration of 77/23 (w/w) EDA/KSCN.

Figure 14a displays three diffraction angles for pure CC41 at 2θ=14.7, 16.4 and 22.6°, which correspond to $(1\bar{1}0)$, (110) and (020) planes of cellulose I, respectively [6, 26]. After swelling in EDA and subsequent precipitation in water, the recovered cellulose is a different polymorph with two broad diffraction peaks at 2θ=16.2 and 22.0° in Figure 14b. After being dissolved in 77/23 (w/w) EDA/KSCN, the recovered cellulose exhibits diffraction angles 2θ at 13.7, 20.1 and 21.7°, typical of cellulose II, shown in Figure 14c. The peak at 13.7° is very broad, and centered at a slightly different point from the published spectrum 2θ=12.1° [26].

Studies [27] show that intramolecular hydrogen bonds O3-H···O-5', O2-H···O-6' and intermolecular hydrogen bond O6-H···O3' are found in native crystalline cellulose (cellulose I). (Index' denotes atom of the different anhydroglucose unit). When swollen in EDA, cellulose I and EDA form a complex having a different polymorph from cellulose I. After thorough washing with water, the cellulose I-EDA complex is transformed back into cellulose I [28, 29]. In our studies, however, recovered cellulose swollen in EDA by washing with water assumes a polymorph similar to a mixture of cellulose I and II. The subsequent addition of salt (KSCN) causes recovered cellulose to convert from polymorph I to II, which means the CH_2OH group of crystalline cellulose undergoes conversion from a t-g conformation for cellulose I to a g-t conformation for cellulose II (g-t means that the C6-O6 bond is gauche to the C5-O5 bond and trans to the C4-C5 bond) [30]. A new crystal structure has developed in the recovered cellulose with an intramolecular bond O3-H···O-5' and an intermolecular bond O6···HO-2'.

Conclusions

In EDA/salt solvent systems, salt concentration, salt type, cellulose concentration and cellulose molecular weight were important factors in the cellulose dissolution. EDA/KSCN had a broader range of solvent concentrations for cellulose than the EDA/NaSCN solvent system. The electrical conductivity data indicated that the dissociation of salt (KSCN) into free ions and subsequent solvation of those ions corresponded with concentrations where cellulose dissolution occurred. Furthermore, the ion size affected the dissociation behavior of salts in EDA. Na^+ ions had lower mobility in EDA than K^+ ions at the same molar concentration. The ^{39}K and ^{14}N NMR spectroscopy studies, using cellobiose as a model system, showed a detectable change in the chemical shift of the ^{39}K nuclei with increasing cellobiose concentration, but no significant shifts for ^{14}N nuclei from KSCN and EDA. A stronger interaction occurred between the K^+ ion and cellobiose than the SCN^- ion. ^{13}C-^{1}H 2D NMR experiments are underway to probe the specific interactions between salt and hydroxyl groups of cellulose.

FTIR studies of recovered cellulose indicated a conformational change for the CH_2OH group at C-6 of the anhydroglucose repeating unit and the breaking of hydrogen bonds in cellulose. Wide angle X-ray diffraction studies revealed that cellulose underwent a polymorphic transformation from I to II when recovered by precipitating cellulose solutions with water, while cellulose recovered after swelling in EDA assumed a polymorph similar to a mixture of cellulose I and II.

Acknowledgements

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