

New Solvents for Cellulose. II. Ethylenediamine/Thiocyanate Salt System[†]

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ABSTRACT: The ethylenediamine/thiocyanate salt system was found to be a new solvent for cellulose. The solubility, dissolution behavior, solution properties, and cellulose recovered from the solutions were investigated. The dissolution took place at room temperature, and the maximum solubility achieved was 16 % (w/w) for cellulose of DP210 in the ethylenediamine/sodium thiocyanate 54/46 (w/w). The dependence of cellulose solubility on DP is also described. Tracing the dissolution behavior of the cellulose by CP/MAS ¹³C NMR measurements revealed the polymorphic conversion of cellulose I to III to amorphous structure during the dissolution process. The cellulose dissolved was stable for 30 days storage at room temperature. Microscopic observations and steady-shear viscosity measurements of the solutions indicated mesophase formation of cellulose in the ethylenediamine/sodium thiocyanate system. This anisotropic phase appeared from *ca.* 10 % (w/w) cellulose with DP210 and greatly depended on the cellulose concentrations. Coagulation studies disclosed that cellulose II and amorphous cellulose were recovered from the cellulose/ethylenediamine/thiocyanate salt solutions when water and alcohol were used as a coagulant, respectively. It was suggested that this solvent system has high potential for cellulosic fiber and film formations.

KEY WORDS Cellulose / Cellulose Solvent / Cellulose Solution / Amine / Thiocyanate / Dissolution Mechanism / Regenerated Cellulose /

Cellulose is a linear and high molecular weight polymer as well as a natural, renewable, and biodegradable material. However, due to its considerable inter- and intramolecular hydrogen bonds, cellulose neither melts nor dissolves readily in common solvents. The complicated crystalline and amorphous morphology has also been preventing cellulose from being exploited to its fullest potential. Any process which simplifies or hastens the dissolution of cellulose represents a significant step forward in the development of cellulose as a viable, ecologically favorable polymer source. Furthermore, the ability of cellulose and cellulose derivatives to form mesophase in certain solvents has resulted in attempts to develop high-performance cellulosic fibers and membrane.²

At present, there are a few solvents that can directly dissolve cellulose without heavy metal complexation and any chemical derivatization, which are lithium chloride/dimethyl acetamide (LiCl/DMAc),³ *N*-methylmorpholine-*N*-oxide/water (NMMO/H₂O),⁴ calcium thiocyanate/water (Ca(SCN)₂/H₂O),⁵ etc. Quite recently, ionic liquids containing 1-butyl-3-methylimidazolium cations were discovered to dissolve high *M_w* pulp (DP ≈ 1000) with 10 % (w/w) at elevated temperatures.⁶ However, almost known solvents still have some undesirable points, for example, chemical

safety, environmental concern, degradation of cellulose, requirements of high temperatures and/or pretreatment of cellulose, poor mechanical properties of the cellulose recovered, and high cost for commercial use.

We have been studied new solvent for cellulose and found amine/salt systems to be a good solvent. The first one in this series is liquid ammonia/ammonium thiocyanate (NH₃/NH₄SCN) system.⁷ This solvent is prepared⁸ by dissolving NH₄SCN into liquid NH₃ so that a condensation process of the NH₃ is required and care must be exercised to minimize its volatilization to avoid the subsequent crystallization of NH₄SCN. To overcome this problem, the use of other amines which possesses high boiling point was attempted instead of NH₃, resulting that the hydrazine/sodium thiocyanate (NH₂NH₂/NaSCN) of composition of 52/48 w/w had high dissolution power for cellulose.¹ However, hydrazine is, unfortunately, toxic and carcinogenic though much lower volatile than NH₃, so the utilization is limited.

Besides the ability of dissolving cellulose, another interest of the cellulose solutions on the amine/salt solvent is mesophase formation. Due to the semi-rigidity of cellulose molecule, both cellulose solutions in the NH₃/NH₄SCN⁹⁻¹³ and NH₂NH₂/NaSCN¹ sys-

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tems form liquid crystals dependent on cellulose concentration, cellulose DP, and temperature. Generally, an anisotropic cellulose solution such as liquid crystals gives high-performance cellulosic fibers and films with high strength and modulus after proper drawing and subsequent coagulation process.¹⁴

Thus, it is important to investigate not only the solubilization of cellulose but also the solution properties in a certain solvent. Here we report on the third solvent for cellulose in the series of amine/salt system, ethylenediamine/thiocyanate salt to realize a simple and convenient cellulose solvent. The physical and chemical properties of the cellulose solutions prepared by this solvent system are also discussed.

EXPERIMENTAL

Solubility Measurements of Thiocyanate Salt in Ethylenediamine

Prior to use, all thiocyanate salts except for $\text{Ca}(\text{SCN})_2$ were treated with the same procedure as described in the previous paper.¹ $\text{Ca}(\text{SCN})_2$ was obtained only as a tetrahydrate form through Wako Pure Chemical Industries, Ltd. It was converted into the anhydrous form by heating overnight at 110 °C *in vacuo*. Anhydrous ethylenediamine was used without further purification.

Solubility measurements of the thiocyanate salts were carried out in a dry box filled with nitrogen to avoid moisture. A known amount of dried salt (0.100 mol) was placed in a 100 mL necked flask equipped with a magnetic stirrer tip and thermometer. The flask was attained to 25 °C in a constant-temperature bath, then ethylenediamine was added dropwise onto the salt with stirring until the salt was completely dissolved, as observed visually. The solubility of the salt was determined from the weight ratio of the salt to the added ethylenediamine.

Solubility Measurements of Cellulose in the Ethylenediamine/Salt System

Several cellulose samples were used for the solubility measurements. Cellunier P, which underwent a sulfite pulping process, was obtained from ITT Rayonier, Inc. From Cellunier P, two cellulose samples with different molecular weight were prepared according to the previous article.¹ The average degree of polymerization (*DP*) was calculated from Eq 1 using the intrinsic viscosity $[\eta]$ of the cellulose solution in 0.500 M cuene (cupriethylenediamine hydroxide solution) applying the ASTM D1795 and D4243 methods.^{15,16}

$$DP^\alpha = [\eta]/K \quad (1)$$

where $\alpha = 1$ and $K = 0.750 \text{ cm}^3 \text{ g}^{-1}$. The average

molecular weight (M_w) is readily able to be converted from the DP. The DPs of the cellulose prepared from Cellunier P (DP716) were 536 and 376. Microcrystalline Cellulose Powder CC41 (DP210) and bacterial cellulose (DP2250) were also obtained from Whatman Bio Systems and Biopolymer Engineering, Inc., respectively.

A known weight of cellulose was placed in a thick polyethylene bag (13.5 cm × 10 cm). In a dry box filled with nitrogen, 10 g of the ethylenediamine solution saturated thiocyanate salt was added to the bag. After the removal of gas from the bag, the mixture was cooled to -20 °C for 1 h and then warmed to 50 °C for 30 min together with intermittent shearing using a wooden roller. The mixture was subjected several times to this temperature cycling technique.¹⁷ By increasing the cellulose concentration by 1.0 % (w/w) increments, the solubility of the cellulose was determined. The maximum cellulose solubility was considered to be the concentration observed just before the one exhibiting undissolved cellulose after 5 days. Judgment of the dissolution was performed by visual observation through a polarizing microscope with a Nikon ECLIPSE E400 POL under crossed polars.

Solution Viscosity

Relative viscosity of the cellulose solutions in the ethylenediamine/NaSCN 54/46 (w/w) was determined at the concentration of 1.00 % (w/v) of Cellulose Powder CC41 using an Ubbelohde type capillary viscometer at 25 ± 0.1 °C.

Steady shear viscosity was measured by a Rheometrics DSR II cone and plate rheometer for non-dilute region ranged from 7 to 12 % (w/w) of the cellulose at 40 ± 0.1 °C. The cone angle and diameter were 0.04 rad and 25 mm, respectively. The gap between the cone and plate was set to 1 mm. The shear rate was conducted to $1.0 \times 10^{-3} \text{ s}^{-1}$.

CP/MAS ¹³C NMR Measurements

Dissolving process of cellulose in the ethylenediamine/NaSCN was monitored by means of ¹³C NMR spectroscopy with cross polarization and magic angle spinning (CP/MAS) technique on a Bruker AM300 spectrometer operating at 75 MHz. For the rapid dissolution of cellulose, the temperature cycling method¹⁷ was applied as follows:

1. Whatman CC41 cellulose powder was taken to the CP/MAS ¹³C NMR measurement before dissolving.
2. In a polyethylene bag, Whatman CC41 cellulose (5 g) was dispersed in the ethylenediamine/NaSCN 54/46 (w/w) (100 g), then mixed with intermittent shearing by a wooden roller at room temperature (sample 1).

3. After 3 h, a part of sample 1 was taken from the bag and filtered by forced filtration to remove the ethylenediamine/NaSCN solvent and the cellulose dissolved. The residue was fully washed with water and recorded on the CP/MAS ^{13}C NMR.
4. After 3 h storage of sample 1 at room temperature, it was cooled to -20°C for 3 h (sample 2). A part of sample 2 was taken from the bag, warmed to room temperature quickly, and filtered by forced filtration. The residue was fully washed with water and then recorded on the CP/MAS ^{13}C NMR.
5. Another temperature cycling between room temperature and -20°C was subjected to sample 2 (sample 3). A part of sample 3 was taken from the bag, received the same procedure, and was recorded on the CP/MAS ^{13}C NMR.
6. The same temperature cycling was imposed three times (sample 4), then, it was filtered, washed, and recorded on the CP/MAS ^{13}C NMR.

All CP/MAS ^{13}C NMR spectra were measured at room temperature using a double air-bearing probe and a zirconium oxide sample rotor. The MAS rate was 4000 Hz. The data acquisition was performed with a standard CP pulse sequence using a $3.5\ \mu\text{s}$ ^1H 90° pulse, 1 ms contact pulse, and 4 s delay time for 5000 scans. The chemical shift was referenced to 29.5 and 38.6 ppm from tetramethylsilane by adamantane as an external standard.

Infrared and Wide Angle X-Ray Diffraction Measurements

Infrared (IR) spectra were obtained with a Shimadzu FT IR-8300 spectrometer using a KBr pellet method. Wide angle X-Ray diffraction (WAXD) measurements were performed on a Rigaku RINT1200 RAD diffractometer using $\text{CuK}\alpha$ radiation with 40 kV of acceleration voltage and 30 mA tube current. The diffraction angles (2θ) observed ranged from 10 to 30° by 0.1° intervals.

Crossed Polars Microscopic Observations

Mesophase formation of the cellulose solutions in

the ethylenediamine/NaSCN was observed by using a Nikon ELIPSE E400 POL crossed-polars microscopy under cross nicol. It was equipped with an electrical hot stage and digital camera.

RESULTS AND DISCUSSION

Solubility of Cellulose in the Ethylenediamine/Salt System

In the early work,^{1,18,19} it was revealed that several inorganic salts such as NH_4SCN , LiSCN , NaSCN , KSCN , NaNO_3 , NaI , and NH_4I were dissolved in liquid NH_3 and NH_2NH_2 and that some of the solutions had high dissolving power for cellulose. However, in the NH_3 system, only the solution of NH_4SCN was kept liquid state under ambient conditions of temperature and pressure. In the solutions of NaSCN , KSCN , NaNO_3 , and NaI in NH_3 , the NH_3 was rapidly evaporated at ordinary temperatures and pressures due to high volatility of NH_3 even though they dissolved cellulose at -10°C . This suggests that the strong interactions exist between NH_3 and NH_4SCN molecules through hydrogen bonds and ion-dipole forces. On the other hand, in the NH_2NH_2 system, LiSCN , NaSCN , KSCN , and NaI were effective but NH_4SCN was ineffective for dissolving cellulose. Thus, in the amine/salt system, there is a close relationship between physical properties of salt, particularly ionic radius and strength of the interactions with amine, and dissolving power for cellulose. In the present work, the solubility of these thiocyanate salts in ethylenediamine and the dissolving power for cellulose were examined. The results are summarized in Table I.

Of the salts tested, LiSCN and $\text{Ca}(\text{SCN})_2$ were commercially obtained as a hydrate form. Both solubilities of the hydrate and anhydrous forms were measured. Multihydrate of LiSCN and $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ showed high solubility of 174 g and 152 g, respectively, in 100 g of ethylenediamine, however, these solutions did not dissolve cellulose at all. It is known that a concentrated $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ aqueous solution dissolves cellulose above 100°C .⁵ Hattori *et al.*²⁰ also showed that cellulose interacts with $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ in water at the concentration of

Table I. Solubility of salt in ethylenediamine at 25°C and dissolution power for cellulose

Salt	Solubility of salt (g/100 g of ethylenediamine)	Dissolution power for cellulose ^a (g/100 g of the solvent)
LiSCN	101	0
$\text{LiSCN} \cdot n\text{H}_2\text{O}$	174	0
NaSCN	86	16
KSCN	81	15
$\text{Ca}(\text{SCN})_2$	0	0
$\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$	152	0

^aWhatman CC41 Cellulose Powder (DP210) was used.

$\text{Ca}(\text{SCN})_2$ more than 48.5% (w/v). They speculated the mechanism of the interaction that the hydration number of $\text{Ca}(\text{SCN})_2$ changed from 4 to 2 to form a cellulose- $\text{Ca}(\text{SCN})_2-(\text{H}_2\text{O})_2$ complex. In water, the coordinated water molecules in $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ could be released and replaced to the hydroxyl groups of cellulose at elevated temperatures, while may be little released in ethylenediamine at room temperature. Therefore, the dissolution of cellulose would not be accomplished in the ethylenediamine/ $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ system. Anhydrous $\text{Ca}(\text{SCN})_2$ was not dissolved in ethylenediamine at 25 °C, so that no dissolution of cellulose occurred in the system.

Saturated solutions of NaSCN and KSCN in ethylenediamine, *i.e.*, the systems of ethylenediamine/NaSCN 54/46 (w/w) and ethylenediamine/KSCN 55/45 (w/w) dissolved cellulose (DP210) with high concentrations of 16 and 15% (w/w), respectively. According to the dissolution mechanism of cellulose in the amine/salt system we hypothesized,¹ it is important to form a salt-amine complex, which is constructed through dipole interaction and/or hydrogen bonding and exists only in the region of high salt concentrations. Further important thing is that at least one amine molecule must be released from the salt-amine cluster and replaced to the hydroxyl group of cellulose. The strength of the salt-amine interaction would greatly depend on the ion size of the salt. The size of Na^+ and K^+ may be suitable for the formation of the complex with reasonable intensity between salt and amine. This moderate binding of NaSCN and KSCN with ethylenediamine permits the substitution of ethylenediamine molecule to hydroxyl group of cellulose leading ultimately to the cellulose dissolution.

Generally, solubility of cellulose depends on its molecular weight, crystallinity, polymorph, and crystal size. The molecular weight is an important factor for the physical and mechanical properties of cellulose regenerated from the solutions. Higher molecular weights are advantageous to obtain higher mechanical properties of cellulosic materials. However, there are

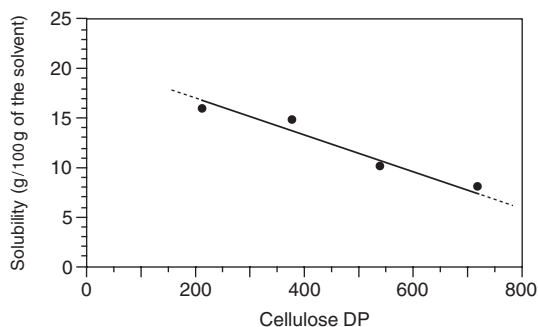


Figure 1. Solubility of cellulose dependent on DP in the ethylenediamine/NaSCN.

few reports on the solubility difference between different molecular weights of cellulose. Figure 1 shows the solubility of cellulose dependent on DP in the ethylenediamine/NaSCN 54/46 (w/w). Four celluloses with different DP were used for the measurements. Among them, two were prepared from Cellunier P (DP716) by acid hydrolysis to give DP536 and 376. The DP210 was from a different source, Whatman CC41. Interestingly, the solubility decreased almost linearly from 16 to 8% (w/w) with increasing DP from 210 to 716 even though the solubility of cellulose with different molecular weight can not be compared precisely each other because of their different molecular weight distributions. Matsumoto *et al.*²¹ investigated the differences in the solubility and solution properties of celluloses from different biological origins such as plants, bacteria, and marine animals in LiCl/DMAc solvent. In the ethylenediamine/NaSCN 54/46 (w/w) system, bacterial cellulose (DP2250) was also dissolved up to 5% (w/w) maximum. However, it took 5 d to attain the complete dissolution. This is presumably due to the high crystallinity and molecular weight.

Chemical Stability of Cellulose in the Ethylenediamine/NaSCN System

The chemical stability of cellulose in the solution is an important criterion for the utilization of any particular cellulose solvent. In regard to this, experiments were conducted to ascertain the stability of cellulose in the ethylenediamine/NaSCN 54/46 (w/w) for a long period of storage. Relative viscosity (η_{rel}) change was traced in a solution of 1.00% (w/v) Cellulose Powder CC41 at 25 °C as shown in Figure 2. The viscosity loss was only 2.2% for 30 d storage. These diminutive decreases could be caused by, not degradation, but conformational changes of the main chain

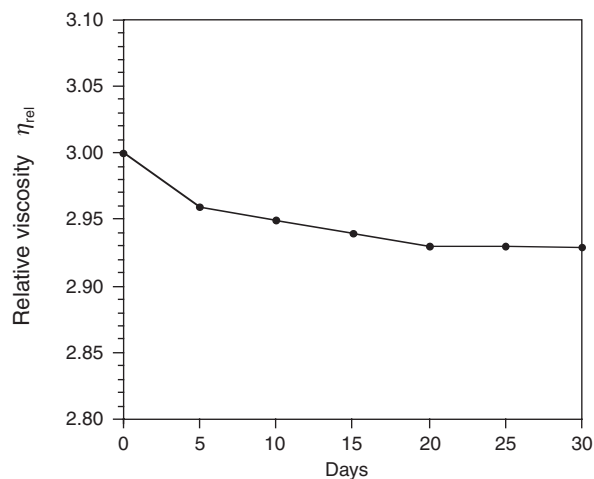


Figure 2. Relative viscosity change of a 1.00% cellulose solution in the ethylenediamine/NaSCN.

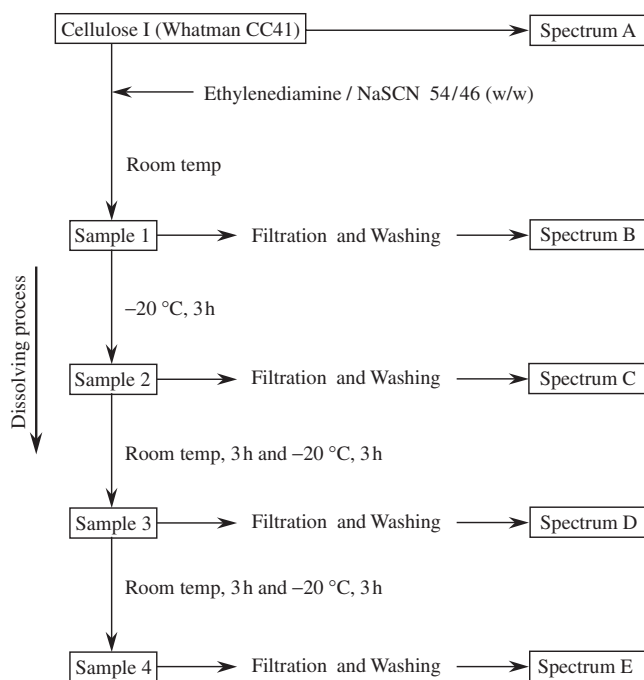


Figure 3. Dissolution process of cellulose in the ethylenediamine/NaSCN subjecting the system to the temperature cycling processes.

due to breaking hydrogen bondings. Slight color change of the solution was observed for 30 d storage. This yellow tint is a likely result of thiocyanogen arisen from the solvent. It disappeared on additions of small amounts of water. As described later, no thiocyanogen peak appeared in the IR spectrum of the cellulose recovered from the solutions. It is concluded that no significant degradation of cellulose occurred in the ethylenediamine/NaSCN solvent for 30 d storage.

Dissolution Behavior of Cellulose in the Ethylenediamine/NaSCN System

To achieve the dissolution of cellulose, scission of its inter- and intramolecular hydrogen bonds is required. Using the rapid dissolution method for cellulose we have developed,¹⁷ it could be continuously monitored in a short time by ¹³C NMR technique to break the hydrogen bondings as well as change the conformations of cellulose during the dissolution process. Figure 3 shows the dissolving process of cellulose involving the temperature cycling between room temperature and -20°C . Each temperature was subjected to the system by 3 h. The results of the CP/MAS ¹³C NMR measurements are presented in Figure 4.

Figure 4A shows a CP/MAS ¹³C NMR spectrum of Whatman CC41 cellulose powder prior to dissolving in the ethylenediamine/NaSCN 54/46 (w/w) solvent. It is a typical pattern of cellulose I as the C1, C4, and C6 resonances appeared at 106, 90, and 65 ppm, re-

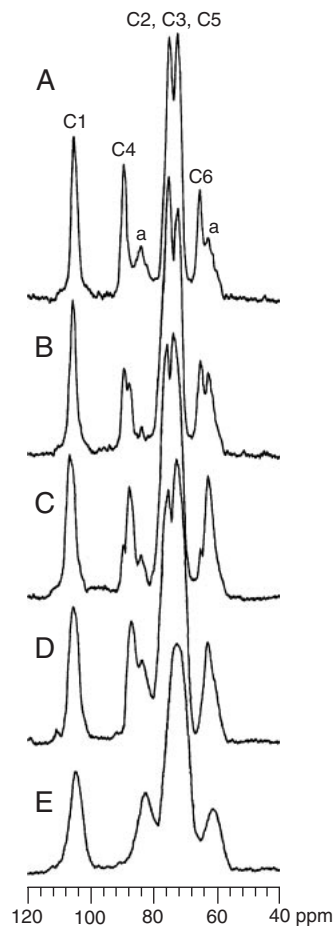


Figure 4. 75 MHz CP/MAS ¹³C NMR spectra of the cellulose during dissolving process in the ethylenediamine/NaSCN.

spectively. Additionally, two broad peaks appear at *ca.* 84 and 63 ppm (Marked with a). According to Atalla *et al.*,²² these two peaks are derived from the C4 and C6 absorptions in the amorphous cellulose, respectively.

After the cellulose I was mixed with the solvent for 3 h at room temperature, the spectrum of the sample apparently changed as shown in Figure 4B. The intensity of the C4 peak at 90 ppm decreased and a new peak appeared at 88 ppm. It is probable that this new peak resulted from shifting of the C4 peak at 90 ppm owing to changing the high-order structure of the cellulose I and/or breaking intramolecular hydrogen bond between oxygen of the glycosidic linkage (C1–O–C'4) and hydrogen of the hydroxyl group at C2 position (C2–OH) of the cellulose I. Very recently, the occurrence of this type of hydrogen bond was found in cellulose I_β by using neutron fiber diffraction.²³

For the following 3 h storage at -20°C , the intensities of each C4 peak were reversed (Figure 4C), then, after the second temperature cycling process, the C4 peak at 90 ppm disappeared entirely (Figure 4D). Similar reversal was observed between C6 peaks.

As the dissolution process proceeds, the C6 peak at 65 ppm disappeared and the intensity of another C6 at 63 ppm increased. This is probably due to change of the hydrogen-bonding system and/or the chain conformation of the cellulose **I**. Taking the spectrum pattern and chemical shift of each peak into consideration, it seems that Figure 4D shows a mixture of cellulose **III** polymorph and amorphous cellulose.²⁴ On the other hand, Figure 4E shows exemplary amorphous cellulose as the C1, C4, and C6 absorptions appeared with relatively broad resonance. From these interpretations in Figure 4, it is concluded that polymorphic transformations from cellulose **I** to **III** to amorphous structure and ultimate dissolution occurred as the dissolution process proceeds when cellulose **I** was mixed with the ethylenediamine/NaSCN solvent. It is known that ethylenediamine is a strong swelling reagent for cellulose and converts cellulose **I** to **III** polymorph. Therefore, these transformations in Figure 4 seem to be reasonable as the dissolution of cellulose proceeds in the ethylenediamine/NaSCN solvent.

Mesophase Formation

It is of interest that some cellulose solutions form anisotropic phase in a certain solvent, however, others are isotropic even though the same cellulose is used. For instance, cellulose solutions in LiCl/DMAc²⁵ and NMMO/H₂O²⁶ solvents exhibit anisotropy under appropriate conditions, whereas there are no reports on the anisotropic solutions of cellulose in Ca(SCN)₂/H₂O. We have also reported liquid-crystalline properties of the cellulose/NH₃/NH₄SCN^{9–13} and cellulose/NH₂NH₂/thiocyanate salt¹ systems. Thus, the formation of anisotropic phase in the cellulose solutions depends on the solvent component. In the present work, the mesophase formation of the cellulose/ethylenediamine/NaSCN system was investigated by crossed polars microscopic observations and steady-shear viscosity measurements.

Figure 5 exhibits photomicrographs of a 12% (w/w) cellulose (DP210) solution in the ethylenediamine/NaSCN 54/46 under non-crossed polars (A) and crossed polars (B) at 40 °C. Nothing was observed except for bubbles under non-crossed polars, affording a proof of the complete dissolution of cellulose in the solvent. On the other hand, a pattern of dark and bright textures was observed under crossed polars as shown in Figure 5B. Since a polarizer and analyzer of the microscopy were set to cross nicols, the dark and bright areas demonstrate isotropic and anisotropic regions, respectively. The bright domains appeared initially at *ca.* 10% (w/w) of cellulose concentration and increased with increasing the concentration. This critical concentration suggests that the orienting behavior of cellulose in the ethylenediamine/NaSCN is slightly lower than that in the NH₃/NH₄SCN¹¹ and NH₂NH₂/thiocyanate salt¹ systems. Presently, it is not clear the relationship, if any, between the difference of amine and the critical concentration.

Viscosity behavior of the cellulose (DP210)/ethyl-

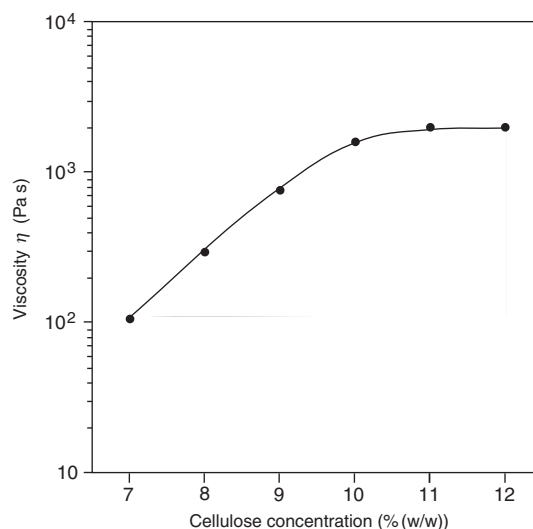


Figure 6. Viscosity of the cellulose solutions in the ethylenediamine/NaSCN 54/46 at 40 °C.

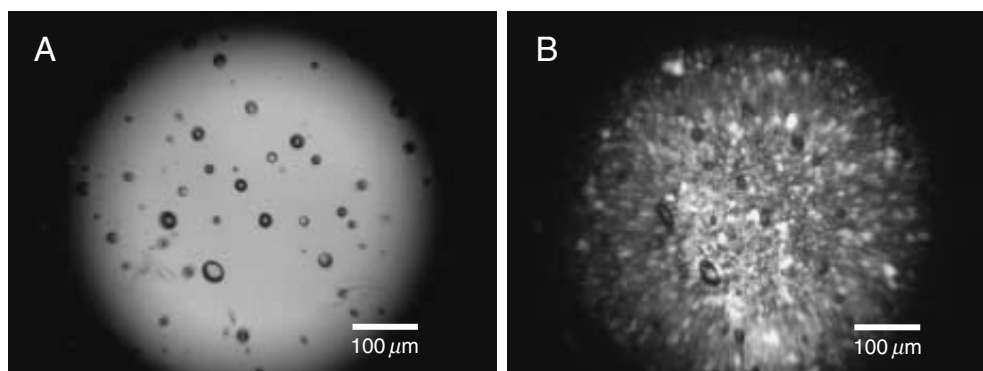


Figure 5. Photomicrographs ($\times 200$) of a 12% (w/w) cellulose (DP210) solution in the ethylenediamine/NaSCN under non-crossed polars (A) and crossed polars (B).

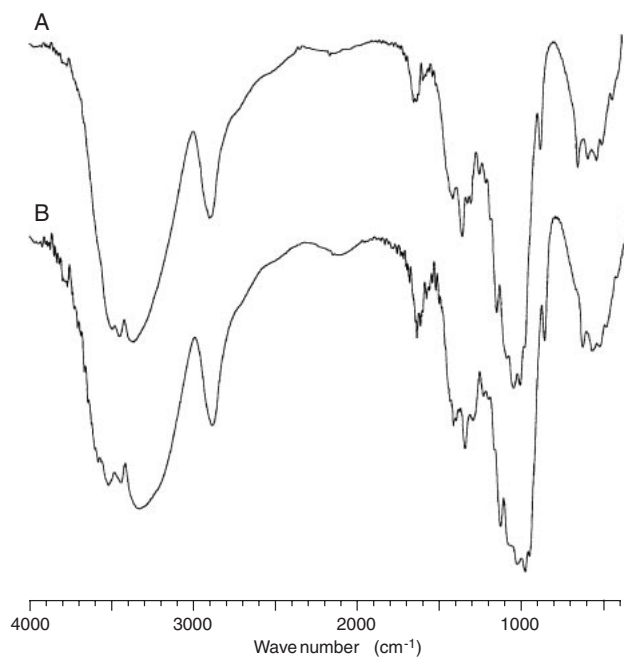


Figure 7. IR spectra of cellulose; (A) Whatmann CC41 and (B) recovered by coagulating the cellulose/ethylenediamine/NaSCN solution in water.

enediamine/NaSCN solutions is shown in Figure 6 as a function of cellulose concentration. The viscosity was measured at low shear rate of $1.0 \times 10^{-3} \text{ s}^{-1}$ using a cone and plate rheometer. An exponentially rapid increase in viscosity was observed from 7 to 10% (w/w) of the cellulose concentrations. However, from 10 to 12% (w/w), the viscosity was nearly constant despite an increment of cellulose concentration, suggesting that the molecular orientation of cellulose was initiated from 10% (w/w). This critical concentration is in agreement with that in the initial appearance of a birefringent region in the crossed-polars microscopic observations.

Recovered Cellulose

Coagulation and recovery of cellulose from the cellulose solutions are important process for the production of cellulosic fiber and films. Physical and chemical structures of the cellulose recovered from the cellulose/ethylenediamine/NaSCN solution were studied by IR and X-Ray analyses. Figures 7 and 8 represent, respectively, IR spectra and X-Ray diffractograms of the cellulose (A) before dissolving in the solvent and (B) recovered by coagulating the cellulose/ethylenediamine/NaSCN solution in water.

In Figure 7, the two spectra are quite similar and no thiocyanate absorption appears around 2200 cm^{-1} in spectrum B, which indicates that no chemical reaction with the solvent occurred during the dissolution and coagulation processes of the cellulose. The cellulose recovered was white flocculent. The solvent was

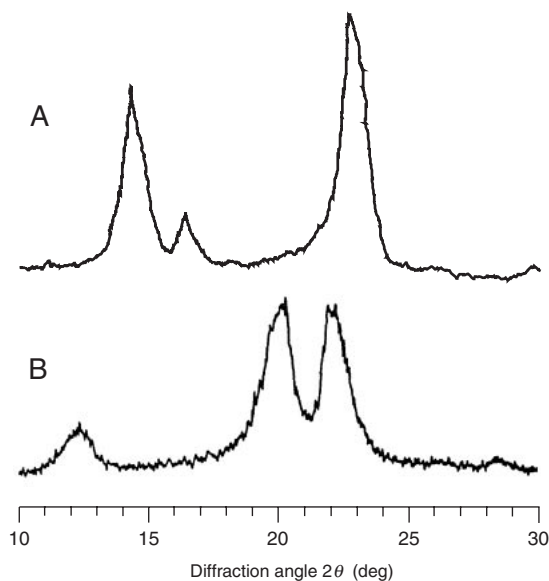


Figure 8. X-Ray diffractograms of cellulose; (A) Whatmann CC41 and (B) recovered by coagulating the cellulose/ethylenediamine/NaSCN solution in water.

found to be completely eliminated by coagulating and the following enough washing with water.

X-Ray diffractograms in Figure 8 display the polymorphic difference between the celluloses before dissolving and after coagulating with water. The original cellulose, Whatman CC41, was cellulose **I** as indicated by the diffraction angles 2θ values²⁷ of 14.2° , 16.4° , and 22.6° in Figure 8A. After dissolution and subsequent coagulation with water, the cellulose recovered was **II** polymorph with the diffraction angles of 12.3° , 20.2° , and 22.1° ²⁷ shown in Figure 8B. This polymorphic conversion is ordinary phenomena in the production of typical regenerated cellulosic fibers such as viscose rayon, cupra, and Tencel[®]. Interestingly, there are some differences as to the polymorph of cellulose recovered from the cellulose/amine/thiocyanate salt solutions: when ammonia was used as a component of the solvent system, cellulose **III** was recovered in water,²⁸ while the use of hydrazine and ethylenediamine afforded cellulose **II** after coagulating the solution with water. Furthermore, in the cellulose/ethylenediamine/NaSCN solution, other coagulants such as methanol, 2-propanol, and acetone brought about the amorphous cellulose. From these results, water seems to be preferred as a coagulant for the formation of high-performance cellulosic materials recovered from the cellulose/ethylenediamine/NaSCN solutions.

CONCLUSION

The ethylenediamine/thiocyanate salt system was discovered to be a good solvent for cellulose. The salts, NaSCN and KSCN were effective, while LiSCN

and $\text{Ca}(\text{SCN})_2$ were ineffective in both hydrate and anhydrous forms. The ionic radius of the salt as well as the size of amine are apparently the most important factor for the solubilization of cellulose in the amine/salt system. The maximum solubility reached 16 % (w/w) for the cellulose of DP210 in the ethylenediamine/NaSCN 54/46 (w/w), and decreased linearly with increasing cellulose DP. Bacterial cellulose was also dissolved, but, it took 5 d to obtain complete dissolution. All cellulose dissolutions took place at room temperature, and the cellulose dissolved was chemically stable for 30 d storage at room temperature.

The CP/MAS ^{13}C NMR measurements disclosed the polymorphic conversion of cellulose in the dissolving process. When cellulose **I** was dissolved in the ethylenediamine/NaSCN system, the polymorph was transformed from **I** to **III** to amorphous structure as the dissolution process proceeds. This behavior was different from that in the $\text{NH}_3/\text{NH}_4\text{SCN}$ system.

Microscopic observations and steady-shear viscosity measurements showed mesophase formation of the cellulose/ethylenediamine/NaSCN system. The anisotropic phase appeared from *ca.* 10 % (w/w) of cellulose with DP210 and greatly depended on the cellulose concentrations. This critical concentration was slightly lower than those in the $\text{NH}_3/\text{NH}_4\text{SCN}$ and $\text{NH}_2\text{NH}_2/\text{NaSCN}$ systems. Coagulation studies disclosed that cellulose **II** and amorphous cellulose were recovered from the cellulose/ethylenediamine/thiocyanate salt solutions when water and alcohol were used as a coagulant, respectively. This system is a promising solvent for cellulose which is environmentally favorable, low cost, low toxicity, needs neither heating nor pretreatment of cellulose, and provides liquid-crystal formation.

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