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Dissolution behaviour and solubility of cellulose in NaOH complex solution

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ABSTRACT

Aqueous mixture of NaOH/urea/thiourea at a 8/8/6.5 composition and pre-cooled at −10 °C readily dissolved cellulose to produce stable solutions at relatively high concentrations. The exothermic dissolution process was favored at −2 to 0 °C. Aqueous NaOH/urea/thiourea solution as non-derivatizing solvent broke the intra- and inter-molecular hydrogen bonding of cellulose and prevented the approach toward each other of the cellulose molecules, leading to the good dispersion of cellulose to form solution. The strength of the solvent network structure as well as the interaction between cellulose and solvent decreased as a function of increasing solution temperature. In the semi-dilute entangled solutions (>3.5% concentration), the entropy-driven gelation occurred, and the gel temperature dropped with increasing cellulose contents in the solution. The NaOH/urea/thiourea/H_2O was demonstrated to be the most powerful solvent among all aqueous NaOH solutions and this novel solvent does not degrade cellulose even after storage times of up to 1 month.

1. Introduction

Cellulose is the most important skeletal component in plants and the most abundant renewable material in nature (Dogan & Hilmioglu, 2009; Klemm, Heublein, Fink, & Bohn, 2005). The non-thermal plastic nature and insolubility in most common solvents remain to be the challenges in processing cellulose for effective utilization. In fact, dissolution of cellulose without chemical modification or derivatization is difficult to achieve because of the rigid long-chain and strongly inter-molecular and intra-molecular hydrogen-bonded structure in cellulose (Fink, Weigel, Purz, & Ganster, 2001; Zhang, Yang, & Liu, 1999). More common than not, cellulose needs to be “activated” or made “accessible” to be dissolved, even though these notions are not clearly defined. Traditional production of regenerated cellulose fibers and films has been largely based on the viscose or the cuprammonium technologies, that generate hazardous environmental pollution (Kamide & Saito, 1986). Thus, identifying new solvent systems for cellulose processing would help to reduce these environmental problems.

Some solvents for cellulose, such as cuoxam, cuen, and cadoxen as well as lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) contain metal complexes (McCormick, Callais, & Hutchinson Jr, 1985). Others including N_2O_4/N,N-dimethylformamide (DMF) (Philipp, Nehls, Wagenknecht, & Schnabelrauch, 1987), NH_3/NH_4SCN (Cuculo, Smith, Sangwatanaroj, Stejskal, & Sankar, 1994), N-methylmorpholine-N-oxide monohydrate (NMMO) (Loubinoux & Chaunis, 1987) and ionic liquid (Swatloski, Spear, Holbrey, & Rogers, 2002) are limited to laboratory scale applications due to volatility, toxicity and high cost. Among the solvents developed, the NMMO/H_2O system is the most powerful in attaining exceedingly high concentration solutions and has been commercialized to produce Tencel or Lyocell fibers. However, the NMMO/H_2O system also has disadvantages of requiring high temperature for dissolution and antioxidants to avoid side reactions of solvents, causing degradation of cellulose, and high costs. Thus, it is not suitable for complete replacement of the viscose technology.

Kamide, Okajima, Matsui, and Kowsaka (1984) and Isogai and Atalla (1998) have systematically studied the solubility of microcrystalline cellulose and steam-exploded cellulose in aqueous NaOH systems in which native cellulose pulps have very limited solubility. Recently, Zhang’s group (Cai & Zhang, 2006; Weng, Zhang, Ruan, Shi, & Xu, 2004; Zhang, Ruan, & Gao, 2002; Zhang, Ruan, & Zhou, 2001; Zhou, Zhang, & Cai, 2004) successfully developed aqueous NaOH solution systems with either urea or thiourea for cotton linter dissolution. The optimal solubility was found with either 7/12/81 NaOH/urea/H_2O or 9.5/4.5/86 NaOH/thiourea/H_2O in compositions. Both solvent systems were inexpensive and less toxic, but the precise structure of the solvent complex involved is still not clearly understood.

Recently, we developed a new complex aqueous solvent that consisted of NaOH, urea and thiourea and was capable of dissolving cellulose quickly when pre-cooled to temperatures between −8

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and −12 °C (Jin, Zha & Gu, 2007; Zhang, Li, Yu, & Gu, 2009; Zhang, Li, Yu, Fu, & Gu, 2009). With the aim to gain basic understanding of the rapid dissolution of cellulose in this solvent, the present work was to further clarify the dissolution behaviour and solubility of cellulose based on this novel aqueous NaOH/urea/thiourea platform. The behaviour of cellulose solutions among the three aqueous NaOH/urea/thiourea, NaOH/thiourea and NaOH/urea solvent systems was also compared.

2. Materials and methods

2.1. Materials

Cellulose used in this study was cotton linter, with a degree of polymerization of 520 and denoted as C520, supplied by Xinxiang Bailu Chemical Fibers Co. Ltd. (Henan, China). All cellulose samples were shredded into powder to pass 40 mesh and dried under vacuum at 70 °C for 24 h. All chemicals were of analytical grade and used as received. All concentrations of cellulose and solvent mixtures were expressed in weight percent unless specified. For dual or tri-component solutions, the concentration of each component was expressed in number, such as *x*/*y*/*z* NaOH/urea/thiourea representing *x* wt% of NaOH, *y* wt% of urea and *z* wt% of thiourea.

2.2. Preparation of cellulose solutions

Three aqueous mixtures with the optimal mass ratios of urea, thiourea and NaOH reported in the literature were used as solvent systems in this study. They were 7/12 NaOH/urea (Cai & Zhang, 2006), 9.5/4.5 NaOH/thiourea (Zhou et al., 2004) and 8/8/6.5 NaOH/urea/thiourea (Jin et al., 2007). Two dissolution procedures were employed. For aqueous NaOH/urea and NaOH/thiourea systems, the solvents were pre-cooled to −12 to −10 °C for 10 min before cellulose was added (referred to as *method I*). In aqueous 8/8/6.5 NaOH/urea/thiourea, cellulose was dispersed after the solvent was pre-cooled to −10 °C, followed by vigorously stirring for 3 min. The solution temperature was then maintained between −2 to 0 °C using a salt–ice bath and the mixture was vigorously stirred for 7 min to obtain transparent cellulose dope (referred to as *method II*).

All prepared cellulose dopes were subjected to centrifugation at 5000 rpm for 10 min at 5–10 °C in order to exclude the minute amount of undissolved cellulose and to help degasify. The apparent viscosity of each prepared solution was determined at 20 °C with a rotational viscometer (NDJ-1, Cany Precision Instruments Co., China).

2.3. Experimental design

Solubility of cellulose in aqueous NaOH/thiourea, NaOH/urea and NaOH/urea/thiourea systems was studied at 1–7.3% (w/w) cellulose concentrations. Dissolution of cellulose was observed by the disappearance of the highly crystalline cotton linter using a polarized light microscope (PLM, Olympus RX51-P, Japan). In the aqueous NaOH/urea/thiourea system, the effects of NaOH on the dissolution of cellulose were observed at −10 °C using 1–10% NaOH at a constant 8% urea and 6.5% thiourea composition. The effects of solvent temperatures from 15 to −15 °C on the appearance of the solutions was recorded by photography. The solubility (S_a) characterized by the quantity of cellulose dissolved was expressed as $S_a = [W_1/(W_1 + W_2)]$, where W_1 was the weight of the dissolved cellulose and W_2 was the combined weight of the gel and insoluble cellulose isolated by centrifugation.

The solvent for ^{13}C NMR measurements, i.e., 8/8/6.5 NaOH/urea/thiourea in D_2O, was prepared in a 5-mL tube. A 7 wt% cellulose solution was prepared by dispersing cellulose at −10 °C with vigorous stirring for 10 min. The solvent and solution were injected into NMR tubes using syringes and solid-state ^{13}C NMR measurements were carried out using a CP/MAS unit (Bruker AV 400, Switzerland, magnetic field 9.4 T) at room temperature.

The refractive index of the cellulose solutions was measured by an Abbe refractometer at 20 °C. The zero-shear viscosity of the solutions was obtained by measuring the shear viscosity value using a rheometer (ARES-RFS, TA Instruments, USA) at varying shear rates from 0.01 to 100 s^{-1} and extrapolating to zero-shear rate. The gelation temperature was also measured on the rheometer from 10 to 100 °C.

The dependence of the viscosity on the storage time in aqueous NaOH/urea/thiourea solvent was carried out immediately upon dissolution of cellulose and when the solution became transparent. The storage time was calculated from when cellulose was placed in the solvent. The viscosities of the cellulose solutions were measured with a Ubbelohde capillary viscometer at 25 ± 0.1 °C. Relative viscosity (η_r), the ratio of the dynamic viscosity of the solution (η) to that of the pure solvent (η_s), was used. To avoid aggregation of cellulose in the solution, a relatively low cellulose concentration of 3×10^{-3} g/ml was examined. In addition, the viscosity of the cellulose in cadoxen at 25 ± 0.1 °C was measured. After sealed and storage at 25 °C for 30 days, cellulose solution was taken out and neutralized with 1 mol/l H_2SO_4 to precipitate cellulose. Isolated cellulose was washed with water and acetone, and vacuum-dried for 24 h. Its viscosity-average molecular weight ($\bar{M}_\eta$) can be calculated with equation (Brown & Wiskston, 1965):

$$[\eta] = 3.85 \times 10^{-2} \times \bar{M}_\eta^{0.76} \quad (1)$$

3. Results and discussion

3.1. Effect of NaOH concentration on solubility

The effects of NaOH concentration on cellulose dissolution kinetics was evaluated from 1 to 10% NaOH in 8/6.5 urea/thiourea aqueous solutions. The solubility of 7% cellulose improved significantly with increasing NaOH concentrations and peaked at 8% NaOH with 91% solubility (Fig. 1).

This is probably due to the concentration-dependent size of NaOH-water hydrates (Yamashiki et al., 1988). Crystalline cellulose chains are very densely packed, with an inter-sheet distance of about 10 Å and a crystallite diameter of only 10 nm. At low alkali concentrations, the hydrodynamic diameters of NaOH-water hydrates may be too large to penetrate into the crystalline region

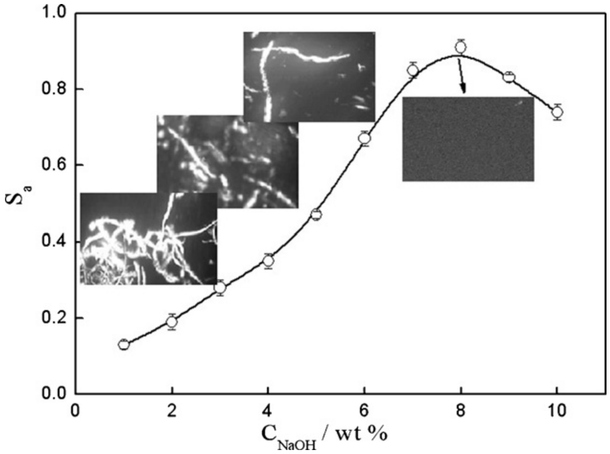

Fig. 1. Dependence of cellulose solubility values on NaOH in aqueous 8%/6.5% urea/thiourea. The insets are the PLM images of cellulose solutions with specific NaOH contents.

of cellulose. It is also possible that there is not enough NaOH to dissolve cellulose at very low NaOH concentrations. At NaOH concentrations higher than 18–20%, on the other hand, NaOH prefers to stay close to the cellulose chains, forming Na/cellulose crystals as in the mercerization process. In that case, cellulose will not be dissolved either.

It has been well recognized that NaOH play a leading role during the dissolution of cellulose in NaOH/urea/thiourea aqueous solution, that is, NaOH can penetrate not only between crystallites but also into the crystallites to destroy inter- and intra-hydrogen bonds between cellulose molecules. Urea and thiourea, however, function as hydrogen bond donor and receptor to prevent the re-association of cellulose molecular chains (Zhou & Zhang, 2000). Since none of the individual component of this solvent system can dissolve native cellulose, a synergic interaction of NaOH, urea and thiourea was thought to exist during the dissolving of cellulose (Jin et al., 2007). At 8/6.5 urea/thiourea composition, the synergic effect was optimal at 8% NaOH at −10 °C. At the optimal 8/8/6.5 NaOH urea/thiourea ratio, NaOH-water hydrates can penetrate the amorphous area to solvate cellulose then destruct the neighboring crystalline regions.

3.2. *Effect of pre-cool temperature on cellulose solubility*

The dissolving ability of solvent systems has been shown to improve with decreasing temperatures (Cai & Zhang, 2006; Kamide et al., 1984; Zhang et al., 2002; Zhang et al., 1999; Zhou et al., 2004). Cellulose has shown to be highly swollen and even soluble in solvents with 6–10% NaOH at temperatures from −15 to 4 °C. Kunze and Fink (2005) also stated NaOH to be similarly active at decreased temperatures as at increased concentrations at room temperature.

As seen in Fig. 2, the solubility of cellulose in aqueous NaOH/urea/thiourea solution was enhanced with decreasing solvent temperatures, reaching the highest solubility at −10 °C.

The more favorable dissolution at lower temperatures has been analyzed by the total enthalpy of cellulose dissolution as given by (Marson & El Seoud, 1999; Wang & Deng, 2009):

$$\Delta H_{\text{Dissolution}} = \Delta H_{\text{fusion}} + \Delta H_{\text{transition}} + \Delta H_{\text{interaction}} + \Delta H_{\text{mixing}} \tag{2}$$

In that, the dissolution of crystalline cellulose into molecular dispersion is divided into several stages: firstly, the transition of the solid polymer to a hypothetical, highly elastic liquid state which corresponds to disintegration of the crystalline regions (ΔH_{fusion}) and transition of the amorphous regions from a vitreous to a highly elastic state ($\Delta H_{\text{transition}}$); secondly, the solvation of the polymer molecules ($\Delta H_{\text{interaction}}$); and thirdly, the mixing of the solvation of the polymer molecules to give an infinitely diluted solution (ΔH_{mixing}). The only endothermic term in the equation is ΔH_{fusion} associated with breaking the hydrogen bonds in the crystalline regions. All other terms relate to interactions between cellulose hydroxyl groups and the solvent system and are exothermic. The overall process of cellulose dissolution is exothermic and is favored by lower temperature.

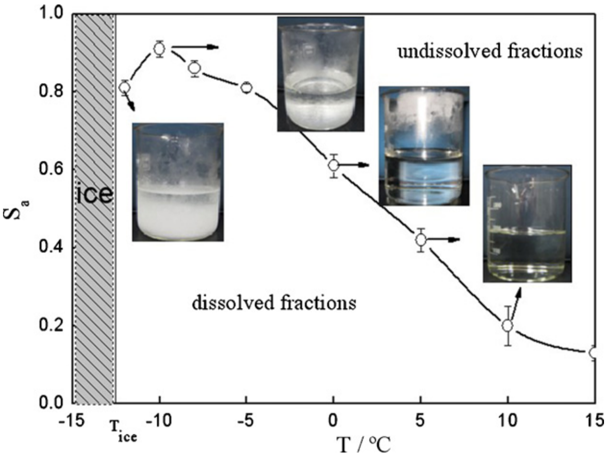

Fig. 2. Dependence of cellulose dissolution on solvent temperature. The insets present the state of the solvent under different temperature.

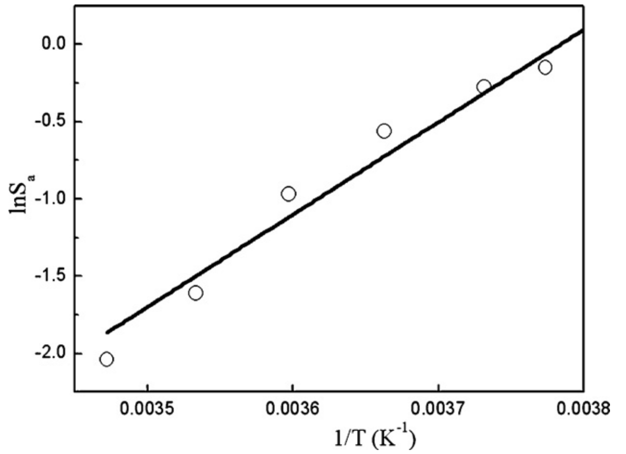

Fig. 3. Arrhenius plots of temperature dependence of S_a value for 6% cellulose solution in the range from 10 to −10 °C.

The change in energy of cellulose from solid to solution can be illustrated quantitatively by the apparent activation energy $E_{a,s}$. The relationship between S_a and temperature can be described by the Arrhenius equation (Su & Puls, 1999):

$$\ln S_a = \ln A - \frac{E_{a,s}}{RT} \tag{3}$$

where $E_{a,s}$ is the apparent activation energy of dissolution (kJ/mol), R is the molar gas constant (0.008314 kJ mol^{-1} K^{-1}), T is the absolute temperature (K), and A is a pre-exponential factor. The $E_{a,s}$ could be obtained from the slope of $\ln S_a$ vs. $1/T$ plot using linear least-squares analysis (Fig. 3). Interestingly, the calculated E_a value was −49.77 kJ/mol in the 10 to −10 °C range, as a result of the dissolution at low temperature. The negative apparent activation energy in our system suggests that the soluble form of cellulose has a lower enthalpy than the solid cellulose, and the dissolution of cellulose in aqueous NaOH/urea/thiourea solution pre-cooled to low temperature may be described as an entropy-driven process as previously proposed (Cai et al., 2007).

In addition, temperature appeared to play an important role in affecting the solvent properties. As the temperature lowered, the network of the solvent hydrates became stronger, probably due to the increasing hydrogen bonding strength. Take NaOH hydrates for example, the Na^+ and OH^- ions are surrounded by a "cage" of water molecules because of ionization equilibrium and hydration. That is, the Na^+ ion exists as $[Na(H_2O)_m]^+$, and the OH^- ion as $[OH(H_2O)_n]^-$ at sub-zero temperatures (Cédric, Tatiana, Patrick, & Olivier, 2001). At room temperature, the fast exchange between bulk and coordinated water molecules cannot sustain such $[Na(H_2O)_m]^+$ and $[OH(H_2O)_n]^-$ structures. When cellulose is dissolved at low temperatures, this strong network of solvent hydrates cleave mainly the closely chain packed cellulose chains through the formation of new hydrogen bonds between cellulose and NaOH hydrates. Meanwhile, urea and thiourea associate with the cellulose hydroxyl groups and prevent the aggregation of cellulose chains through the inter- and intra-molecular hydrogen bonds association. This behaviour is similar to the cuprammonium solvation of cellulose, in which ammonia molecules coordinated to copper are hydrogen-bonded to cellulose

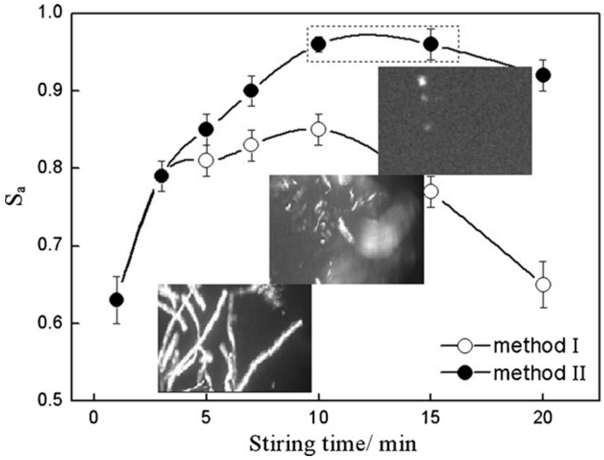

Fig. 4. Dependence of cellulose solubility values on dissolving methods. The insets present the PLM pictures of cellulose solution under different dissolving method.

as blockers. When the temperature is raised, the hydrogen bonds are weaker, and the network of hydrates is gradually destroyed (Egal, Budtova, & Navard, 2007).

It also could be seen from inset images in Fig. 2 that crystal precipitation appeared during pre-cooling. It was interesting that the long, needle-like crystal precipitated out of the solvent at the optimal pre-cool temperature (−10 °C) was tested to be thiourea, not urea, NaOH or their mixtures. The amount of thiourea precipitation and the ice formation increase with the further decreases in temperature. Consequently, the solubility of cellulose also decreases, because the concentration and the composition ratio of thiourea in the solvent is changed significantly the concentration and the composition ratio of thiourea in the solvent is changed significantly. In fact, the entire solvent would become solid ice-block at −15 °C and could not be used to dissolve cellulose. The temperature at which thiourea precipitated out was also found to be higher in any other NaOH/urea/thiourea solvent composition. It can be concluded that crystal separating out is not only caused by decreased solubility of thiourea but also influenced by interaction between compositions of solvent. This “interaction” is being studied in detail to be reported later.

3.3. Effect of stirring rate on cellulose solubility

The stirring rate has also been found to be of great importance to prepare solutions of higher cellulose concentrations. Cellulose solubility increased with increasing stirring rates. It was found that certain amount of cellulose could be dissolved in the pre-cool solvent even without any stirring.

It indicated a rapid dissolution of cellulose in aqueous NaOH/urea/thiourea solution. However, the remained cellulose cannot be dissolved completely without stirring or under low rate stirring. The increasing shear stress from high stirring rates is thought to help to improve solvent diffusion and break off partially dissolved chains from the solid surfaces to accelerate dissolution.

3.4. Effect of dissolution method on cellulose solubility

The solubility of cellulose under the two dissolution methods was studied over time. In dissolution method I, cellulose was dispersed in pre-cool solvent and stirred at room temperature. Nearly 80% of the cellulose dissolved in 3 min and the solubility increased slightly to 85% after 10 min (Fig. 4). However, dissolution drastically reduced to 77% and 65% after 15 and 20 min, respectively. The undissolved cellulose solids appeared to be surrounded by more viscous solution. With vigorous stirring without further cooling aids, the solvent appeared to lose its dissolution ability with the elevation in temperature and the cellulose solution would easily suffer gelation with prolonged stirring.

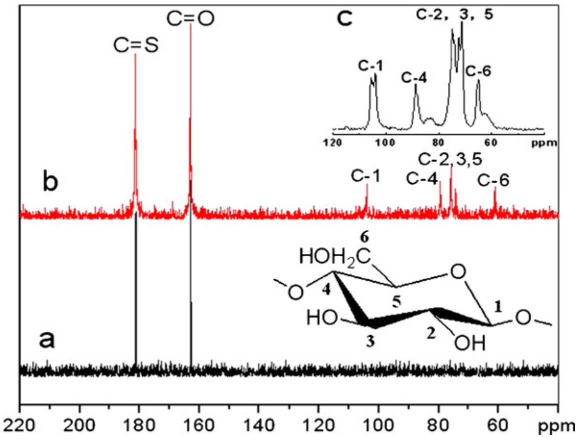

Fig. 5. ^{13}C NMR spectra of (a) aqueous NaOH/urea/thiourea solvent and (b) 6% cellulose solution. (c) The solid-state CP/MAS ^{13}C NMR spectrum of raw cellulose.

To improve dissolution of cellulose in aqueous NaOH/urea/thiourea, the optimal dissolution temperature of −10 °C observed previously was combined with the most stable solution at 0 °C reported by others (Jin et al., 2007) as method II. 6% cellulose was dispersed in solvent pre-cooled to −10 °C, followed by vigorous stirring for 3 min. After 3 min, most of the cellulose was dissolved while the temperature of the solution increased to approximately 0 °C. Further dissolution at −2 to 0 °C for another 7 min reached a high 96% dissolution or $S_a = 0.96$. The solution was more transparent and rather easy to filter compared with solution prepared at room temperature or by method I. At a higher cellulose concentration of 7%, continuing dissolution at −2 to 0 °C also increased the solubility to 0.91 from 0.72 by method I. Therefore, method II was proven to be the more efficient and time-saving approach to dissolve cellulose and is very suitable for preparing more concentrated cellulose solutions.

3.5. Structure of the cellulose solution

Fig. 5 shows the ^{13}C NMR spectrum of cellulose in deuterated 8/8/6.5 NaOH/urea/thiourea. Five major peaks were sharp and readily identified in the spectra as cellulose I. The chemical shifts at 104.1 ppm, 79.5 ppm, 75.8 ppm, 74.3 ppm, and 61.4 ppm for C1, C4, C3/C5, C2 and C6, respectively. This indicates that the NaOH/urea/thiourea aqueous solution is indeed a good solvent for cellulose (Cai, Liu, & Zhang, 2006). The C-4 chemical shift for raw cellulose (Fig. 5c) is located at 88.9 ppm, which is assigned to intra-molecular hydrogen bonds (C-3–H···O-5′) (Zhang et al., 2002). It is obvious that the chemical shift of the C-4 peak shifts upfield compared with that for raw cellulose, which indicates that the intra-molecular hydrogen bonds of cellulose have been destroyed. The chemical shifts of these peaks are very similar to those for some good solvents of cellulose, such as cadoxen (Nehls, Wagenknech, Philipp, & Stscherbina, 1994), DMAc/LiCl (Hattori, Koga, Shimaya, & Saito, 1998), NMMO/DMSO (Gagnaire, Mancier, & Vincendon, 1980), NaSCN/D_2O (McCormick et al., 1985) and BMIMCl (Moulthrop, Swatloski, Moyna, & Rogers, 2005). Moreover, no new peaks appeared in the ^{13}C NMR spectrum, indicating the absence of derivatization of cellulose. Therefore, the aqueous 8/8/6.5 NaOH/urea/thiourea dissolve cellulose directly rather than through a cellulose derivative.

One of the earliest techniques used to study polymer dissolution was refractometry (Ueberreiter, 1968). This technique is based

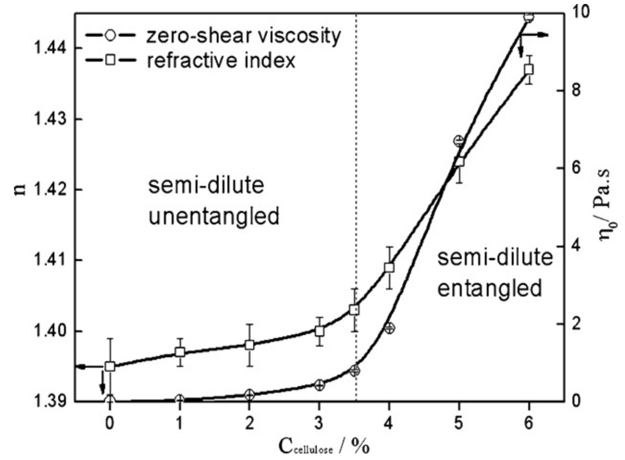

Fig. 6. The dependence of refractive index (n) and zero-shear viscosity (η_0) on cellulose concentration (C) at 20 °C.

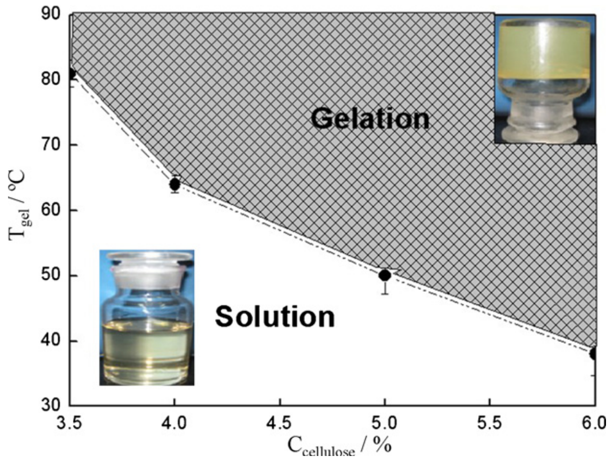

Fig. 7. Phase diagram of gel formation in the cellulose solution. The insets present the sol and gel states of cellulose solutions.

on polymer concentration dependence of refractive index during dissolution. The zero-shear viscosity (η_0) is also always used to investigate the structure properties of polymer solution. Fig. 6 shows the relations between n and η_0 of solution and cellulose concentration (C). It is interesting to find that the transitions of refractive index and zero-shear viscosity curves occurred at almost the same cellulose content of 3.5%.

This 3.5% concentration was therefore used to divide the semi-dilute unentangled regime below from the semi-dilute entangled regime above. The n and η_0 values rise in different rates with increasing concentrations in both regions. In the $C < 3.5\%$ semi-dilute unentangled regime, n and η_0 increase linearly with increasing concentrations. The thermodynamics of cellulose chains in this region are different from that of linear flexible polymers as can be described by the Rouse model (Heo & Larson, 2005). In the semi-dilute entangled regime ($C > 3.5\%$), n and η_0 increase more sharply which indicates some aggregation of cellulose chains caused by increasing chance of collision among cellulose molecules. This concentration dependence is consistent with that observed for cellulose solutions in ionic liquids and the MCC solutions in LiCl/DMAc (Kuang, Zhao, Niu, Zhang, & Wang, 2008; Tamai, Aono, Tatsumi, & Matsumoto, 2003).

3.6. Gelation behaviour of cellulose solution

Cellulose dissolved in NaOH gels easily and is not practical for processing into membranes or fibers. Moreover, thermal gelation of cellulose in aqueous NaOH/thiourea and NaOH/urea solutions has also been reported. Such gelation was believed to be due to self-aggregation of the cellulose chains in the solution at elevated temperatures (Cai & Zhang, 2006; Weng et al., 2004).

The thermally induced gelation of cellulose solution in aqueous NaOH/urea/thiourea solvent was investigated by rheometry. Fig. 7 displays the phase diagram of gel formation in the prepared cellulose solutions. Gelation of solutions was observed with increasing temperatures from 38 to 81 °C. Below 3.5% cellulose concentration, thermally induced gelation behaviour was not observed from 20 to 90 °C. This suggests that the extent of cellulose chains aggregation is very limited in relatively dilute or semi-dilute unentangled solutions. The dropping temperatures of gelation (T_{gel}) with increasing cellulose concentrations above 3.5% can be explained by the progressively increased number of junction zones between the cellulose chains in the semi-dilute entangled solution. However, the gel formed could not be re-dissolved even when the temperature was cooled to −10 °C, the optimal solvent temperature to dissolve cellulose. Thus, the irreversible gelation from heating may be a result of altered solvent components caused by chemical reactions among NaOH, urea and thiourea at elevated temperatures (Cai & Zhang, 2006), losing the ability to prevent self-association of cellulose macromolecules. The random self-association of cellulose chains having exposed hydroxyl in the aqueous solution promotes the entanglement networks at elevated temperatures.

Thermodynamically, gelation occurs only when the free energy change (ΔG) is negative at a given constant temperature T, or $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the changes of enthalpy and entropy, respectively. Gelation is a thermodynamic process as it involves energy exchanges between the gel system and the surroundings, resulting in the sol–gel transition of the system. It should be taken into consideration both the process of the cellulose molecular chains self-associated in the aqueous solution and the action of small molecules including water, thiourea, urea and some ions. When cellulose is dissolved in an aqueous solution, the small solvent molecules interact with cellulose molecules to give some degree of order in the solution. When the cellulose solution is heated to gel, the heat provides the activation energy to destroy the interaction between the solvent molecules and cellulose. The exposed hydroxyls form random junctions between cellulose molecules from self-association, forming gel network. Meanwhile, the solvent molecules were released and move randomly. The changes in entropy and enthalpy for the system are defined as:

$$\Delta H = \Delta H_{\text{self-association}} + \Delta H_{\text{demixing}} \tag{4}$$

$$\Delta S = \Delta S_{\text{entanglement}} + \Delta S_{\text{demixing}} \tag{5}$$

where $\Delta H_{\text{self-association}}$ is from self-association of the hydroxyl groups in gelation and is exothermic ($\Delta H_{\text{self-association}} < 0$); $\Delta H_{\text{demixing}}$ stands for destroying the interaction between the small molecules and cellulose and is endothermic ($\Delta H_{\text{demixing}} > 0$); $\Delta H_{\text{entanglement}}$ refers to the aggregation of cellulose molecule chains and should be negative ($\Delta S_{\text{entanglement}} < 0$); while the release of small molecules from the chain gives an increase in the entropy of the system ($\Delta S_{\text{demixing}} > 0$).

The gelation occurred at a high temperature with the endothermic heat $\Delta H > 0$ (the absolute value of $\Delta H_{\text{demixing}}$ is greater than that of $\Delta H_{\text{self-association}}$), as confirmed by the preliminary results of differential scanning calorimetric analysis, which revealed a relatively broad endothermic peak. If the gelation process can take place, the entropy (ΔS) should be more positive to meet the $\Delta G < 0$ requirement. As we noticed that, compared with the energy needed in the destruction of the cellulose–solvent interaction structure, the energy for the formation of self-association (its intrinsic ten-

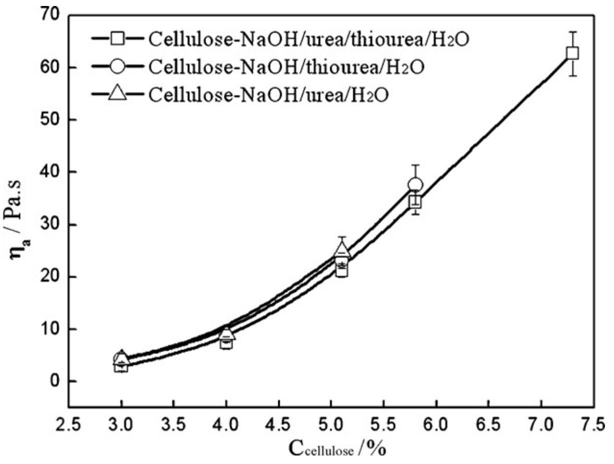

Fig. 8. Comparison of the solubility values and apparent viscosity (η_a) of cellulose in different NaOH complex solvent systems.

dency) is much lower (Weng et al., 2004), so the gelation process is an endothermic process ($\Delta H > 0$) on the whole. For the same reason, $\Delta S_{\text{demixing}}$ should be more significant than $\Delta S_{\text{entanglement}}$ and it should exhibit as a positive value. It can be concluded that the gelation of cellulose in the aqueous solution upon heating is an entropy-driven process.

3.7. Comparison of the dissolution power of varied NaOH aqueous systems and the stability of the prepared solution

In comparing solubility of cellulose in the different aqueous NaOH solutions (Fig. 8), the aqueous NaOH/urea/thiourea system was obviously most powerful. The apparent viscosity values among the three prepared cellulose solutions appeared to be more distinctively different at higher cellulose concentrations. Moreover, the aqueous NaOH/urea/thiourea solution is capable of dissolving cellulose with higher molecule weights ($\bar{M}_\eta$ as high as 2.3×10^5, Jin et al., 2007) than any other aqueous NaOH systems (Cai & Zhang, 2005; Zhou et al., 2004). This is another evidence to support the better dissolving capacity of the aqueous NaOH/urea/thiourea solution.

The stability of cellulose solutions is essential for wet-spinning and thus industrial applications. The relative viscosity (η_r) of cellulose solutions exhibited a 15% reduction after being stored under a sealed condition at 25 °C for 30 days with most reduction occurring within the first 10 days. The cellulose precipitated from the 30-day stored solution showed the $\overline{M}_\eta$ decreased from 10.2×10^4 to 8.83×10^4, indicating slight degradation of cellulose occur during dissolution and storage periods. Therefore, the cellulose solution in NaOH/urea/thiourea aqueous system is considered stable at room temperature for practical processing purposes.

4. Conclusions

The rapid dissolution behaviour and solubility of cellulose in aqueous NaOH/urea/thiourea solution at a 8/8/6.5 mass ratio composition and pre-cooled to −10 °C was aided by vigorous stirring for 3 min and further dissolution at −2 to 0 °C for 7–10 min evaluated by ^{13}C NMR, optical microscopy, solubility as well as viscometry. The low temperature, thought to be driven by entropy hydrate formation kinetics, played an important role in creating the stable hydrogen-bonded networks between cellulose, NaOH hydrate, urea, thiourea and water clusters, leading to the dissolution of cellulose. The low temperature condition for dissolution of cellulose avoids the evaporation of the chemical agents and qualifies this aqueous 8/8/6.5 NaOH/urea/thiourea system as a green solvent. The cellulose solutions exhibit a transition from semi-dilute unentangled to entangled regions at 3.5% concentration. Whereas gelation was absent in the semi-dilute unentangled concentration range from 20 to 90 °C, thermally induced gelation was observed at lower temperatures at cellulose concentrations above 3.5%. This unique gelation process was thought to be an entropy-driven process. Moreover, this aqueous NaOH/urea/thiourea system exhibits higher solubility capacity for cellulose when compared with either aqueous NaOH/thiourea or NaOH/urea systems and the as-prepared cellulose solution is rather stable. These findings confirm a direct and efficient process for preparing stable cellulose solutions for film and fiber processing, a promising substitution for the viscose technology that involves hazardous by-products. This dissolution approach offers a convenient, environmentally friendly process platform and potential new strategies for expanding applications or chemical modification of cellulose, the nature's most abundant polymer.

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