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Role of sodium zincate on cellulose dissolution in NaOH/urea aqueous solution at low temperature

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ABSTRACT

ZnO was added to the NaOH/urea aqueous solution to increase the solubility of cellulose at low temperature. The cellulose solution was characterized with ^{13}C NMR, wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM) and dynamic light scattering (DLS) to evaluate the interaction between solvent and cellulose and the dissolution mechanism. The results indicated that the solubility of cellulose in NaOH/urea solution was improved significantly by the introduction of a small amount of ZnO (0.5 wt%), which existed as $Zn(OH)_4{}^{2-}$ in the alkali system. It has been demonstrated that $Zn(OH)_4{}^{2-}$ could form stronger hydrogen bonds with cellulose than hydrated NaOH, leading to the enhancement of the dissolution power. The cellulose concentration could be achieved to 8 wt% with molecular weight of 5.7×10^4, and the solvent could dissolve cellulose with molecular weight of 1.7×10^5.

1. Introduction

The utilization of renewable resources to produce environment-friendly materials, which avoids using or producing harmful substances, has become an international frontier (Tilman et al., 2009). A great number of natural polymers, such as polysaccharides, chitins, proteins and various composite materials based on renewable resources have been developed as potential biomaterials and biodegradable packaging materials due to their various special structures and excellent properties that cover multiple applications (Chen, Liu, Chang, Cao, & Anderson, 2009; Ng et al., 2009; Zhang, Li, Yu, & Hsieh, 2010). Cellulose, a polysaccharide consisting of a linear chain of several hundred to over 10,000 β (1→4) linked D-glucose units, is the most abundant natural polymer (Nishiyama, Langan, & Chanzy, 2002). It can be used to yield various products with renewable, biodegradable, biocompatible, and derivable properties (Ragauskas et al., 2006; Regalbuto, 2009; Tomita & Kondo, 2009. However, cellulose is very difficult to dissolve in common solvents due to the presence of strong inter- and intra-molecular hydrogen bonds. Therefore, it has been a long-standing goal to find a good solvent to dissolve cellulose (Heinze & Liebert, 2001). Some new solvents for cellulose such as N-methylmorpholine-N-oxide (NMMO) (Fink, Weigel, Purz, & Ganster, 2001), lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) (Klemm, Heublein, Fink, & Bohn, 2005), 1-butyl-3-methylimidazolium chloride (Swatloski, Spear, Holbrey, & Rogers, 2002) and NaOH solution have appeared in recent decades (Isogai & Atalla, 1998; Yamane, Mori, Saito, & Okajima, 1996).

In our laboratory, we have developed a novel solvent of cellulose, namely, 7 wt% NaOH/12 wt% urea aqueous solution pre-cooled to −12 °C (Cai & Zhang, 2005; Cai et al., 2008). Cellulose with viscosity-average molecular weight (M_η) smaller than 1.2×10^5 can be dissolved in the NaOH/urea aqueous solution within 2 min on a typical laboratory scale and within 5 min even in a dissolution tank of 1000 L capacity (Jiangsu Long-Ma Green Fibers Co. Ltd.). Moreover, from the cellulose dope in NaOH/urea system, we have successful prepared high-quality cellulose multi-filament fibers, films, hydrogels and cellulose based magnetic materials (Cai, Zhang, Zhou, et al., 2007; Liu et al., 2008; Chang, Peng, Zhang, & Pang, 2009). We believe that the reason why the solvent can dissolve only the cellulose with M_η less than 1.2×10^5 and the maximum solubility can only reach about 4–5 wt% is related to the structure and characteristic of NaOH that interactes directly with cellulose. Our previous work has demonstrated that NaOH "hydrates" can be easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperatures, while the urea hydrates cannot associate directly with cellulose, but can self-assemble at the surface of the NaOH hydrogen-bonded cellulose to form a worm-like inclusion complex (IC), leading to good dispersion of cellulose. The cellulose dissolution at low temperature arises as a result of a fast dynamic self-assembly process among solvent small molecules (NaOH,

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urea and water) and the cellulose macromolecules (Cai et al., 2008).

It has been reported that adding a relatively small mounts of ZnO to the concentrated sodium hydroxide solution can improve the solubility of cellulose in the sodium hydroxide solution (Borgin & Stamm, 1950; Davidson, 1937; Lang & Laskowski, 1991; Vehviläinen et al., 2008). ZnO can be reacted to form zincate sodium in the sodium hydroxide solution. Therefore, studying on the role of sodium zincate in alkali hydrate system is helpful for us to further find the structure factor to improve the solubility of cellulose. In our previous work, ZnO was added to the NaOH/urea aqueous solution, leading to the improvement of the solubility of cellulose (Zhang, Qi, & Yang, 2007). In the present paper, we attempt to understand the role of sodium zincate in the NaOH/urea aqueous solution on the improvement of the solubility of cellulose. The solubility test, ^{13}C NMR, wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), dynamic light scattering (DLS) were carried out to evaluate the dissolution mechanism and solution behaviors of cellulose in the solvent containing zincate. We hope to formulate the theory of dissolving cellulose at low temperature and provide valuable data for improving the solubility of cellulose.

2. Experimental

2.1. Materials

Cellulose (cotton linter pulps) with α-cellulose content of more than 95% was provided by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). Its viscosity-average molecular weight (M_η) was determined by using an Ubbelohde viscometer in LiOH/urea aqueous solution at 25 ± 0.05 °C. The cellulose was dried in vacuo for 24 h at 60 °C before use. All other reagents were of analytical grade and were provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Solubility test

7 wt% NaOH/12 wt% urea/n wt% ZnO (n to be varied from 0 to 2.5) aqueous solutions were prepared by mixing NaOH, urea, ZnO and distilled water (7:12: n:81 − n by weight). After 188 g solvent was cooled to −13 °C, an appropriate amount of cellulose sample was added immediately into it with vigorous stirring for 2 min. The resultant solution was then centrifuged at 8,000 rpm at 5 °C for 10 min to obtain a transparent cellulose solution. The remaining undissolved fractions were washed using water and acetone, respectively, and then dried at 60 °C for 24 h in a vacuum oven. Thus, the solubility of cellulose ($C_{\max}$) in NaOH/urea/ZnO aqueous solution was calculated by

$$C_{\max} = \frac{(W_0 - W_1)}{(188 + W_0 - W_1)} \qquad (1)$$

where W_0 is weight of original cellulose, and W_1 is weight of the undissolved fractions.

2.3. Characterizations

Relative viscosities (η_r) of the cellulose in 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO aqueous solution were measured at 25 ± 0.1 °C using an Ubbelohde capillary viscometer. The M_η values of the cellulose samples with different molecular weight were measured by using an Ubbelohde viscometer in 4.5 wt% LiOH/15 wt% urea aqueous solution at 25 °C, and were calculated from the equation (Cai, Liu, & Zhang, 2006).

^{13}C NMR measurements of the cellulose solution in 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO/D_2O were carried out on a Mercury 600 MHz NMR spectrometer (Varian, USA) at ambient temperature. The cellulose concentration was adjusted to be 4 wt%. Sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonic acid was used as an internal reference to determine the chemical shifts.

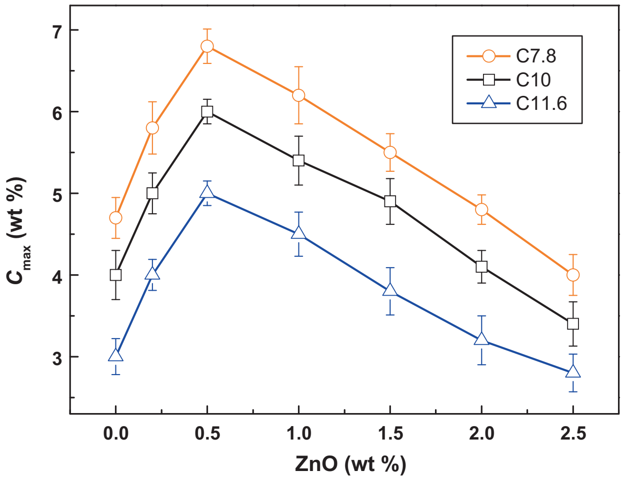

Fig. 1. The dependence of the solubility values ($C_{\max}$) of cellulose with M_η of 7.8×10^4 (C7.8), 1.0×10^5 (C10) and 1.16×10^5 (C11.6) on the content of ZnO.

Wide-angle X-ray diffraction measurement was carried out on a WAXD diffractometer (D8-Advance, Bruker, USA). The patterns with Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 30 mA were recorded in the region of 2θ from 4° to 60°. The freeze–dried sample of cellulose in NaOH/urea/ZnO solution was obtained by freeze-drying cellulose (ca. 4 wt%) in the aqueous NaOH/urea/ZnO solution. The samples were ground into powders and dried in vacuum oven at 60 °C for 48 h before testing.

TEM observation of cellulose in aqueous NaOH/urea/zincate solution was carried out on a JEM-2010 (HT) transmission electron microscope (JEOL TEM, Japan). A thin layer of the dilute cellulose solution at a concentration of 1×10^{-4} g/ml was suspended on a holey carbon film, which was supported on a copper grid. The specimen was dried in air at ambient temperature and pressure for 20 min and was then imaged at an accelerating voltage of 200 kV.

Dynamic light scattering was used to characterize the chain conformation of cellulose in the dilute solution. 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO aqueous solution was used as the solvent for the cellulose sample. A modified commercial light-scattering spectrometer (ALV/SP-125, ALV, Germany) equipped with an ALV-5000/E multi-τ digital time correlator and a He–Ne laser (at λ = 632.8 nm) was used at a scattering angle θ of 30°. The cellulose dilute solutions were made optically clean by filtration through 0.45 μm Millipore filters. The CONTIN program was used for the analysis of the dynamic light-scattering data (Chu, 1991). The hydrodynamic radius, R_h, was calculated by using the Stokes–Einstein relation as

$$R_h = \frac{k_B T}{6\pi \eta_0 D} \qquad (2)$$

where k_B is the Boltzmann constant, T is the temperature in units of K, η_0 is the solvent viscosity, and D is the translational diffusion coefficient.

3. Results and discussion

3.1. Solubility of cellulose in NaOH/urea/zincate aqueous solution

The dependence of the maximum solubility ($C_{\max}$) of cellulose with M_η of 7.8×10^4, 1.0×10^5 and 1.16×10^5 on the ZnO content is shown in Fig. 1. The $C_{\max}$ values increased in the beginning to reach a maximum at 0.5 wt% ZnO, and then decreased with

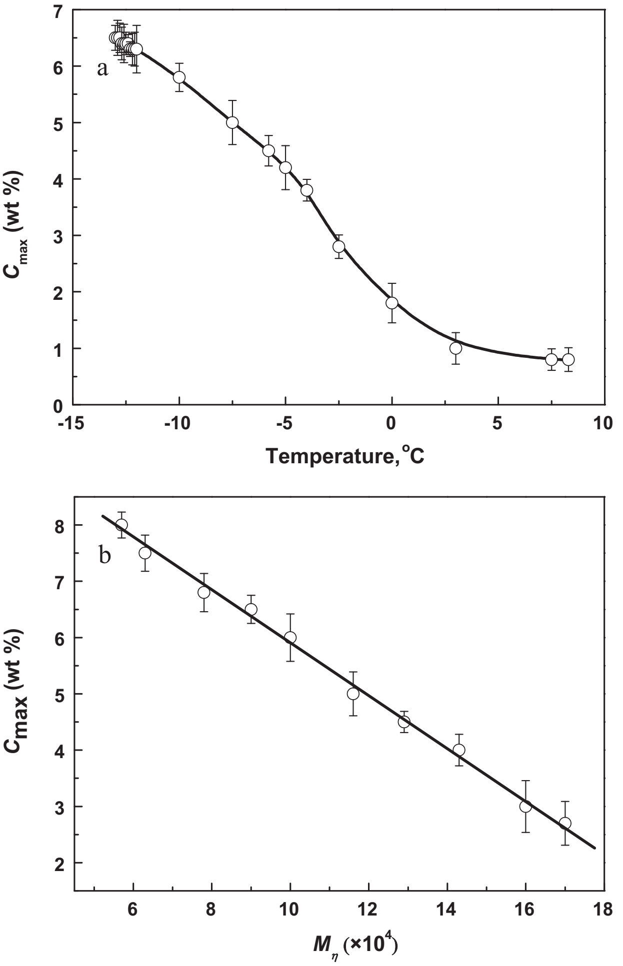

Fig. 2. The dependence of the C_{max} values of cellulose on temperature (a) and M_η (b) for the cellulose dissolution in NaOH/urea/zincate solution.

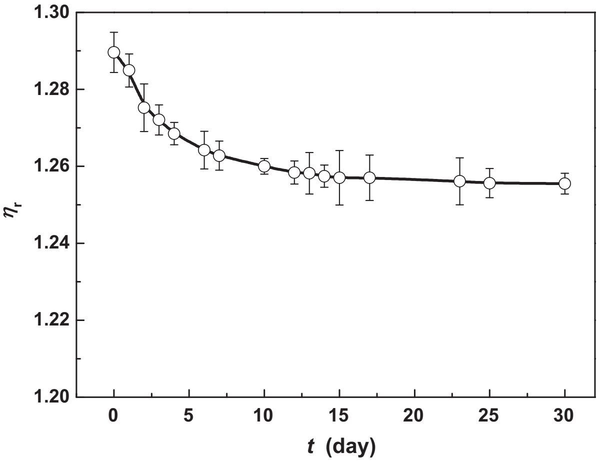

Fig. 3. The dependence of relative viscosity on storage time of the cellulose solution with M_η of 6.8×10^4 in NaOH/urea/zincate aqueous system at 25 °C.

increasing amounts of ZnO because the overfull ZnO led to the decrease of NaOH contribution which was useful for cellulose dissolution. The C_{max} value of 6 wt% of cellulose with M_η of 1.0×10^5 in this solution was much higher than the C_{max} value of 4 wt% in 7 wt% NaOH/12 wt% urea solution without ZnO. When the ZnO content was higher than 2 wt%, ZnO could not be completely dissolved in 7 wt% NaOH/12 wt% urea aqueous solution. The result indicated that the solubility of cellulose in NaOH/urea solution can be improved significantly by the addition of a small amount of ZnO (0.5 wt%) to the solvent. The solubility of the cellulose in 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO aqueous solution was better than 7 wt% NaOH/12 wt% urea aqueous solution with other content of ZnO, it was, therefore, used for the following investigations.

The dependence of the C_{max} values of cellulose with M_η of 9×10^4 on temperature is shown in Fig. 2a. In the temperature range from 8 to 3 °C, C_{max} maintained a low and constant value (about 1 wt%), indicating that only a small fraction of cellulose with low molecular weight could be dissolved. However, as the temperature decreased from 3 to −13 °C, the C_{max} value of cellulose increased rapidly, and cellulose could be dissolved in the range from −7.5 to −13 °C. Interestingly, in the range from −12 to −13 °C, cellulose could be dissolved completely to reach the concentration of 6.3–6.5 wt%, indicating a considerable enhancement in the cellulose solubility in the NaOH/urea/zincate system at low temperature. Ice would form in this solvent below −13 °C (freezing point), which is a critical temperature (T_c) of this mixture solution. A liquid–solid two-phase occurred below T_c, but in which cellulose could also be dissolved completely at −13.5 °C. The results indicated that the low temperature played an important role in the improvement of the cellulose dissolution in the NaOH/urea/zincate system. Fig. 2b shows the dependence of the C_{max} values on M_η of the cellulose sample during dissolution in the solvent pre-cooled to −13 °C. It was revealed that the polymer concentration increased with a decrease of M_η to achieve about 8 wt% for M_η of 5.7×10^4. Moreover, cellulose with M_η of 1.7×10^5 could be dissolved in the NaOH/urea aqueous solution, indicating that the addition of ZnO could improve significantly the solubility of cellulose in NaOH/urea system.

The dependence of relative viscosity on storage time of the cellulose solution with M_η of 6.8×10^4 in the NaOH/urea/zincate aqueous system at 25 °C is shown in Fig. 3. About 2.6% loss in the viscosity value of the cellulose solution was observed after 30 days, as a result of the tiny degradation of the cellulose dilute solution during storage, suggesting a good stability. Therefore, the cellulose dilute solution in the NaOH/urea/zincate system was relatively stable, and its stability is significantly higher than that of cuprammonium (Zhou & Zhang, 2000) and the NaOH/urea without zincate (Cai & Zhang, 2005).

Why the addition of zincate could improve the cellulose dissolution at low temperature? The zincate is primary presented as $Zn(OH)_4{}^{2-}$ in strongly alkaline solutions (Dirkse, Postmus, Vandenbosch, & Vandenbosch, 1954; Reichle, Mccurdy, & Hepler, 1975; Xu & Chen, 1999). Hydrogen bonds between cellulose and $Zn(OH)_4{}^{2-}$ in NaOH/urea/zincate system are stronger than that between cellulose and NaOH hydrate in NaOH/urea system. This could be explained that there are more chance to form new hydrogen bonds between $Zn(OH)_4{}^{2-}$ and cellulose, as a result of the relatively slow motion compared with NaOH, making it easier to attract to the cellulose chains. Therefore, the solubility of cellulose in the NaOH/urea/zincate solution was higher than that in the solvent without zincate.

3.2. Structure of cellulose in NaOH/urea/zincate solution

The ^{13}C NMR spectra of cellulose in 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO/D_2O solution at different temperature and in 7 wt% NaOH/12 wt% urea/D_2O solution at 18 °C are shown in Fig. 4. Six major peaks for cellulose in the solution were readily identified and exhibited sharpness, when compared with original cellulose I (Cai et al., 2006). The chemical shifts of C1 (103.7 ppm), C4 (79.1 ppm), C2 (73.9 ppm), and C6 (60.6 ppm) for cellulose in NaOH/urea/zincate/D_2O were almost the same as

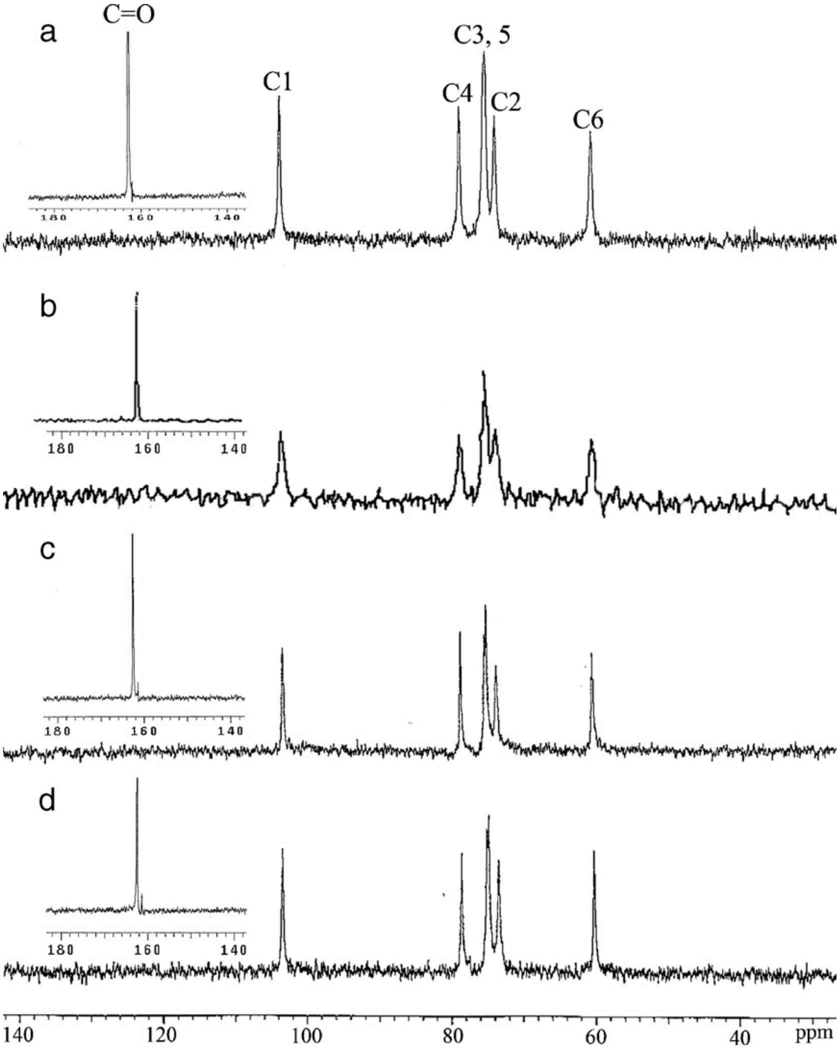

Fig. 4. The ^{13}C NMR spectrum of cellulose in NaOH/urea/zincate/D_2O solution at 18 °C (a), 25 °C (b), 35 °C (c) and in NaOH/urea/D_2O solution at 18 °C (d).

those for cellulose in cadoxen (Nehls, Wagenknecht, Philipp, & Stscherbina, 1994), DMAc/LiCl (Hattori, Koga, Shimaya, & Saito, 1998), NMMO/DMSO (Gagnaire, Mancier, & Vincendon, 1980), and NaSCN/D_2O (McCormick, Callais, & Hutchinson, 1985), which are good solvents of cellulose, indicating the NaOH/urea/zincate aqueous solution was also a good solvent. The peak at 162.6 ppm was assigned to the chemical shift of the carbonyl carbon for urea, similar to that (162.5 ppm) in 7 wt% NaOH/12 wt% urea/D_2O solution. There were no new peaks for cellulose derivates in the ^{13}C NMR spectra of the cellulose solution, indicating the absence of derivatization. Namely, there was no chemical reaction in this system, and this solvent was a direct solvent.

^{13}C NMR chemical shifts of the cellulose solutions are summarized in Table 1. In the previous work from our laboratory, we have demonstrated that urea hydrate could surround the cellulose chains bonded with NaOH or LiOH to form a channel inclusion complex (IC). Clearly, the chemical shifts of cellulose in NaOH/urea/zincate system were approximate to those in NaOH/urea system, indicating the similar structure of cellulose in the two solvent systems, namely, cellulose existed as a channel inclusion complex. It was noted that the chemical shifts of cellulose in the NaOH/urea/zincate system at 18 °C were higher than those at 25 and 35 °C and in the NaOH/urea system by about 0.2–0.4 ppm. This clear change should be related to the formation process of hydrogen bonds between NaOH or zincate and cellulose. The previous work has proved that the NaOH hydrates cleaved the chain packing of cellulose through the direct formation of new hydrogen bonds in NaOH/urea system (Cai et al., 2008). The electron density of C2, C4 and C6 decreased when the hydrogen bonds between cellulose and NaOH or zincate strengthened, resulting in the chemical shifts moving to lower field. When the temperature of the cellulose in the NaOH/urea/zincate/D_2O system increased to 35 °C, the hydrogen bonds between cellulose and NaOH or zincate could weaken, leading to a chemical shift lower than those at 18 °C (Isogai, 1997; Kamide, Okajima, Matsui, & Kowsaka, 1984; Östlund, Lundberg, Nordstierna, Holmberg, & Nyden, 2009). Similarly, compared with the case in the NaOH/urea aquesous system (Table 1), the results also indicated that the hydrogen bonds between cellulose and NaOH in NaOH/urea system without zincate were weaker than those between cellulose and zincate. In this NaOH/urea/zincate system, ZnO existed as $Zn(OH)_4^{2-}$ in the alkali system, which could form stronger hydrogen bonds with cellulose than hydrated NaOH, as a result of the slower exchange enables the coordinated ion to keep its structure and amphoteric compound nature, leading to the improvement of the cellulose dissolution. $Zn(OH)_4^{2-}$ with more hydroxyl groups could easily form new hydrogen bonds with cellulose to break intermolecular hydrogen bonds of cellulose, and its larger steric hindrance kept the cellulose chains farther apart from each other. Therefore, the enhancement of cellulose solubility in the solvent system with

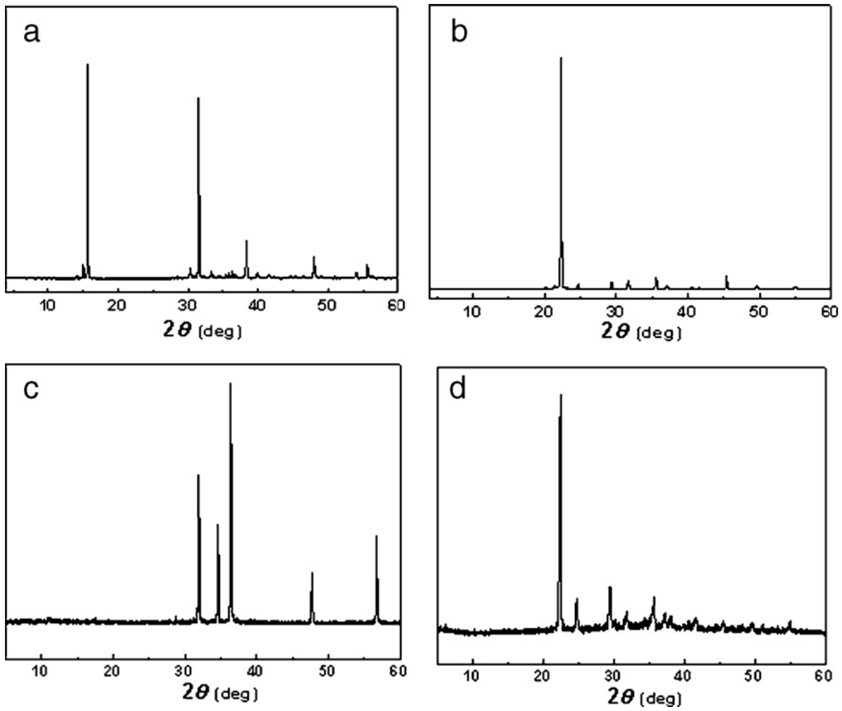

Fig. 5. The WAXD pattern of NaOH (a), urea (b), ZnO (c), and the cellulose/NaOH/urea/zincate inclusion compound (d).

Table 1
^{13}C NMR chemical shifts of cellulose solution in different solvents at different temperature.

	C=O	C1	C2	C3	C4	C5	C6
NaOH–Urea 18 °C	162.4	103.6	73.7	75.1	78.8	75.1	60.4
NaOH–Urea–ZnO 18 °C	162.8	103.9	74.2	75.6	79.1	75.6	60.8
NaOH–Urea–ZnO 25 °C	162.6	103.7	73.9	75.5	79.1	75.5	60.6
NaOH–Urea–ZnO 35 °C	162.5	103.5	73.8	75.4	78.7	75.2	60.5

zincate owed to the stronger interaction between $Zn(OH)_4{}^{2-}$ and cellulose.

Fig. 5 shows the WAXD pattern of NaOH (a), urea (b), ZnO (c), and cellulose/NaOH/urea/zincate inclusion compound (d). The crystal peaks of the freeze–dried sample of cellulose in NaOH/urea/zincate solution were similar to that of pure urea (powder). NaOH, zincate and cellulose peaks disappeared in the WAXD pattern of cellulose in NaOH/urea/zincate solution. There were only peaks of urea while all other signals including those from cellulose, NaOH and zincate were shielded. The results strongly indicated that urea hydrates as host existed in the cellulose inclusion complexes (ICs), whereas the complex associated with cellulose, NaOH and zincate was encaged in the IC, leading to a shield for cellulose, NaOH and zincate (Nehls et al., 1994).

To provide direct evidence of the cellulose IC, the diluted cellulose solution was examined by TEM. Fig. 6 shows the TEM images of NaOH/urea/zincate solution (a) and cellulose dilute solution in the NaOH/urea/zincate system which were dried at room temperature at 25 °C (b). The image from NaOH/urea/zincate aqueous solution (Fig. 6a) showed some irregular crystals of urea, NaOH and sodium zincate, which were partly destroyed in the solution. The TEM image of the dried cellulose dilute solution (Fig. 6b) exhibited some

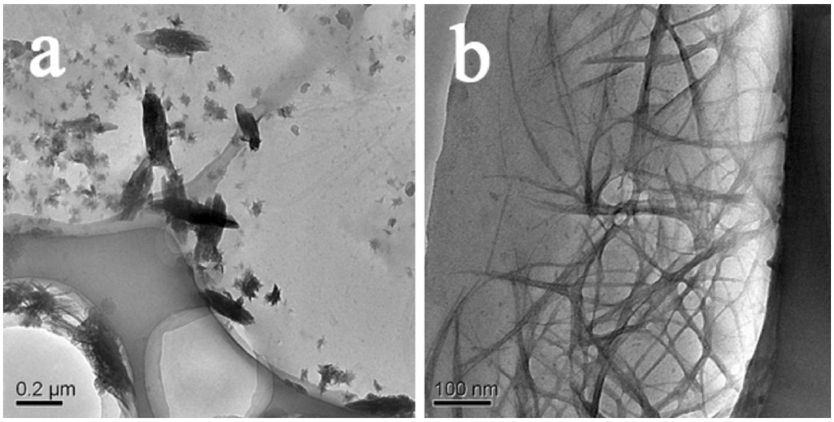

Fig. 6. TEM images of NaOH/urea/zincate solution (a) and cellulose/NaOH/urea/zincate solution at 1×10^{-4} g/ml (b) at 25 °C.

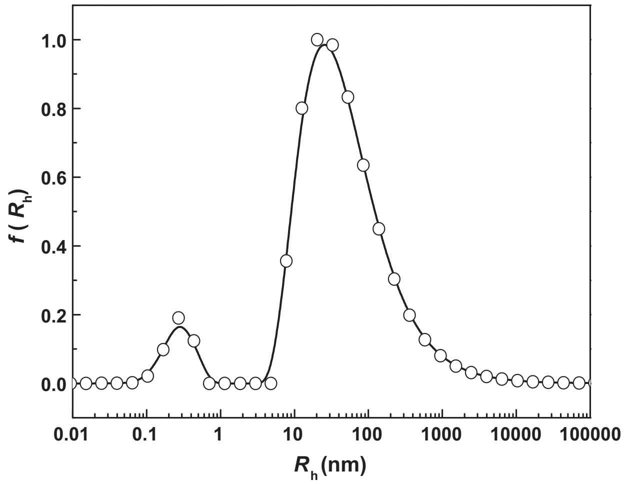

Fig. 7. The dependence of hydrodynamic radius distributions f (R_h) on R_h of the cellulose solution in NaOH/urea/zincate system at the scattering angle of 30°.

tubules, which are similar to the TEM images of cellulose solution from the NaOH/urea and LiOH/urea solvent system (Cai et al., 2008; Cai, Zhang, Chang, Cheng, Chen, & Chu, 2007). The average diameter of the single worm-like tubule was calculated to be 13 nm, which is comparable with that calculated from the IC structure. In this system urea hydrate could surround the cellulose chains, NaOH and zincate to form a channel inclusion complex. These data suggested that the individual cellulose molecules could be linked with each other through the hydrogen-bonding interaction between hydroxyl end groups, forming longer channel IC in the dried state. The channel IC hosted by the urea hydrates prevented the self-association of cellulose chains in solution, leading to good dispersion of cellulose. The structure of IC associated with NaOH, zincate, water clusters, and cellulose chains through stronger hydrogen bonding interaction was more stable than that without zincate, leading to the improvement of the dissolution ability of the system at low temperature.

In order to further investigate the chain conformation of the ICs in this system, the hydrodynamic radius (R_h) and its distributions f (R_h) of the cellulose solution (4.9×10^{-4} g/ml) in NaOH/urea/zincate system at the scattering angle of 30° were measured by DLS. The dependence of f (R_h) on R_h is shown in Fig. 7. The CONTIN analysis of DLS measurement on the cellulose solution was performed. The apparent average value of $\langle R_h \rangle_{app}$ for the cellulose single chains obtained from the cumulative analyses was 20 nm, supported by the result of TEM.

The molar ratio of glucose in cellulose, $Zn(OH)_4{}^{2-}$, NaOH, urea, and H_2O in the 7 wt% NaOH/12 wt% urea/0.5 wt% ZnO system was 1:0.25:6.1:8.1:181. Namely, $Zn(OH)_4{}^{2-}$ could bound a part of cellulose, whereas hydrated NaOH attached on most of the cellulose chains. However, $Zn(OH)_4{}^{2-}$ played an important role in breaking the intermolecular hydrogen bonds of cellulose and keeping the cellulose chains farther apart from each other.

4. Conclusions

The solubility of cellulose in NaOH/urea solution was improved significantly by adding a small amount of ZnO (0.5 wt%) to the solvent. The results from WAXD, TEM and DLS revealed that urea hydrate surrounded the cellulose chains bonded with NaOH and zincate to form a channel inclusion complex. The increased solubility of cellulose in the NaOH/urea aqueous solution containing ZnO was a result of the stronger interaction between $Zn(OH)_4{}^{2-}$ and cellulose than that between NaOH and cellulose. $Zn(OH)_4{}^{2-}$ played an important role in breaking the intermolecular hydrogen bonds of cellulose and keeping the cellulose chains farther apart from each other, as a result of the slower exchange and amphoteric compound nature, leading to the enhancement of the dissolution power.

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