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# Stability of inclusion complex formed by cellulose in NaOH/urea aqueous solution at low temperature

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ABSTRACT

Cellulose has been demonstrated to be dissolved in 7 wt% NaOH/12 wt% urea aqueous solution pre-cooled to −12 °C, as a result of the formation of inclusion complexes (ICs) associated with cellulose, urea and NaOH. However, this cellulose solution is meta-stable, and IC aggregate could form. In this work, the influences of solvent composition and temperature on the stability of the cellulose ICs in NaOH/urea aqueous solvent system were investigated by dynamic and static light scattering. The stability of cellulose ICs in NaOH/urea aqueous solvent system was firstly enhanced and then lessened with NaOH concentration increasing. The addition of urea slightly enhanced the stability of ICs. Furthermore, the solvent composition had been optimized to reduce the aggregation phenomenon of ICs. The proportion of single cellulose ICs in 9 wt% NaOH/13 wt% urea system increased to 0.96, indicating a stable and better dispersion system of the cellulose ICs. Moreover, temperature exhibited great effect on the IC stability. The molecular weight of cellulose in 9 wt% NaOH/13 wt% urea system at 10 °C reached a low value about $7.6 \times 10^4$ g/mol and the single cellulose ICs were predominant species in this case. This work provided a better pathway to characterize the dilute cellulose in NaOH/urea aqueous solution, in which the single cellulose ICs were predominant species.

## 1. Introduction

In recent years, the preparation of regenerated cellulose materials has attracted much attention because of the increasing demand for environmentally friendly and biocompatible products (Eichhorn, Baillie, Zafeiropoulos, et al., 2001; Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; Klemm, Heublein, Fink, & Bohn, 2005; Kocherbitov, Ulvenlund, Kober, Jarring, & Arnebrant, 2008; Wu & Kuga, 2006; Zhang, Yuan, Yuan, Shen, & Lin, 2003). However, the inter- and intra-molecular hydrogen bonds have made the dissolution of cellulose a difficult process in common solvents (Bochek, Petropavlovsky, & Kallistov, 1993). Therefore, several solvents such as N-methylmorpholine-N-oxide, lithium chloride in N-dimethylacetamide, aqueous NaOH solutions, as well as ionic liquid have been developed to dissolve cellulose (Budtova et al., 2010, chap. 10; Eckelt & Wolf, 2005; Fink, Weigel, & Bohn, 1999; Isogai & Atalla, 1998; Swatloski, Spear, Holbrey, & Rogers, 2002; Zhang, Wu, Zhang, & He, 2005). In our laboratory, novel solvents for the fast dissolution of cellulose such as NaOH/thiourea, NaOH/urea and LiOH/urea aqueous solution precooled to low temperatures (−12 to −5 °C) have been developed. Moreover, functional cellulose materials were successfully prepared from the cellulose dopes (Cai et al., 2008; Chang, He, Zhou, & Zhang, 2011). In the pre-cooled 7 wt% NaOH/12 wt% urea aqueous solution, NaOH “hydrates” could be more easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperatures, and the urea hydrates could possibly be self-assembled at the surface of the NaOH hydrogen-bonded cellulose to form an inclusion complex (IC), leading to the dissolution of cellulose (Cai et al., 2007). However, this system was meta-stable, single ICs easily associated with each other to form IC aggregates. Therefore, the single ICs co-existed with IC aggregates in NaOH/urea system.

It is well-known that cellulose molecules were difficult to truly disperse in most “known” solvents at the molecular level, and the aggregation of cellulose in various solutions had been reported (Chen et al., 2007). Moreover, in NaOH/urea aqueous solvent system, cellulose ICs were unstable and can be destroyed probably, leading to the cellulose IC aggregates. Therefore, a further understanding of small solvent molecule and temperature influences on the existence of individual cellulose chains and aggregates is helpful to improve the dissolution of cellulose. The aim of this work was to investigate the effect of NaOH and urea composition and storage temperature on the stability of cellulose ICs in NaOH/urea aqueous solution without adding extra component. Dynamic and static light scattering (DLS and SLS) were used to characterize the effect of NaOH and urea composition and storage temperature in

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the aqueous system on the aggregation behaviors of cellulose ICs. The IC structure would be destroyed spontaneously, making defects in the shell, and then exposed hydroxyls on cellulose dominated the self-association trend, leading to the further association of partly destroyed ICs (Cai et al., 2008). Therefore, the cellulose ICs with relatively perfect shell was stable and the large proportion of cellulose ICs could be found in the solution. On the contrary, the cellulose solution was relatively unstable, while larger proportion of IC aggregates could be obtained. Our work was expected to reveal a precise method to characterize the dissolution and dispersion of cellulose, and to seek a new approach for the improvement of the dissolution of cellulose in NaOH/urea aqueous solution.

## 2. Experimental

### 2.1. Materials

Cellulose (the cotton linter pulp) was supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China), and its $M_\eta$ value in 4.6 wt% LiOH/15.0 wt% urea aqueous solution pre-cooled to −12 °C was determined using viscometer and calculated from the equation $[\eta] = 3.72 \times 10^{-2} M_\eta{}^{0.77}$ to be $7.3 \times 10^4$ at 25 °C (Cai, Liu, & Zhang, 2006). Commercially available LiOH, NaOH and urea were of guaranteed reagent levels (Shanghai Chemical Reagent Co. Ltd., China).

### 2.2. Preparation of cellulose solution

Cellulose was dispersed in NaOH/urea aqueous solution pre-cooled to −12 °C, and then stirred for 5 min to obtain a homogeneous cellulose solution. In order to clarify the effect of NaOH and urea composition on the stability of cellulose and aggregation behavior, by changing NaOH concentration in 12 wt% urea aqueous solution, such as 7 wt%, 8 wt%, 9 wt%, 10 wt% and 12 wt% were coded as $Na_7Ur_{12}$, $Na_8Ur_{12}$, $Na_9Ur_{12}$, $Na_{10}Ur_{12}$ and $Na_{12}Ur_{12}$, respectively. By changing urea concentration in 7 wt% NaOH aqueous solution, such as 13 wt%, 14 wt% and 15 wt% were coded as $Na_7Ur_{13}$, $Na_7Ur_{14}$ and $Na_7Ur_{15}$, respectively. Concentration of NaOH and urea of 8 wt% and 13 wt%, 9 wt% and 13 wt%, 9 wt% and 14 wt%, 10 wt% and 15 wt% were coded as $Na_8Ur_{13}$, $Na_9Ur_{13}$, $Na_9Ur_{14}$ and $Na_{10}Ur_{15}$, respectively. The cellulose solution was filtered though a 0.45 μm Millipore filter to purify before measurements.

### 2.3. Characterization

SLS and DLS were used to characterize the weight-average molecular weight ($M_{w,app}$) and the hydrodynamic radius ($R_h$) of cellulose in the dilute solution (NaOH/urea aqueous system). 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 scattering angle $\theta$ of 30°. All of the cellulose solutions were prepared at the concentration of $6.0 \times 10^{-4}$ g/mL and made optically clean by filtration through 0.45 μm Millipore filters. A Zimm plot was used to calculate the $M_{w,app}$ and the radius of gyration ($R_g$). In static LS, the excess of scattered intensity $I(q)$ with respect to the solvent was measured, and the magnitude of the scattering wave vector $q$ is given by

$$q = |\vec{q}| = \frac{4\pi n_0}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \tag{1}$$

where $n$ is the refractive index of the solvent, $\lambda_0$ is the wavelength of light in the vacuum, and $\theta$ is the scattering angle. In our experiments, the scattering angle $\theta$ has been varied between 30 and 150°. Corrections to the absolute time-averaged scattering intensities $R_{vv}(q)$ (excess Rayleigh ratio) were made using a toluene sample reference, for which the excess Rayleigh ratio is well-known as follows

$$R_{vv}(q) = \frac{\langle I_{solution}(q)\rangle - \langle I_{solvent}(q)\rangle}{\langle I_{ref}(q)\rangle} R_{ref} \left(\frac{n_{solvent}}{n_{ref}}\right)^2 \tag{2}$$

$R_{vv}(q)$ of a dilute polymer solution at concentration $c$ (g/mL) is related to the $M_w$. The $R_g$ and the scattering wave vector ($q$) are expressed as (Luo et al., 2006)

$$\frac{Kc}{R_{vv}} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g\rangle_z q^2\right) + 2A_2 c \tag{3}$$

The scattering constant is $K = 4\pi^2 n^2 (dn/dc)^2 / N_A \lambda_0{}^4$, where $dn/dc$ is the refractive index increment, $N_A$ is Avogadro's number, and $A_2$ is the second virial coefficient. The plots of $[Kc/R_{vv}(q)]_{c\to 0}$ versus $q^2$ and $[Kc/R_{vv}(q)]_{q\to 0}$ versus $c$ lead to $\langle R_g\rangle$ and $A_2$, respectively.

The CONTIN program was used for the analysis of dynamic light-scattering data. The hydrodynamic radius, $R_h$, was calculated by using the Stokes–Einstein relation as

$$R_h = \frac{k_B T}{6\pi \eta_0 D} \tag{4}$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature in units of K, $\eta_0$ is the solvent viscosity, and $D$ is the translational diffusion coefficient.

## 3. Results and discussion

### 3.1. Effect of NaOH concentration

The SLS and DLS are very sensitive to formation of aggregates in the dilute solutions. It should be noted that the laser light scattering (LLS) technique mainly detects information about aggregates because molecularly dissolved chains contribute little to the scattering intensities (Wu, Siddiq, & Woo, 1995). Thus, the LLS technique can be applied to study the stability and IC aggregation behavior of the cellulose dilute solution in NaOH/urea aqueous system.

In our previous work, it had been proved that molecular dispersion of cellulose in 4.6 wt% LiOH/15.0 wt% urea aqueous solution pre-cooled to −12 °C could be achieved at low temperature (Lue, Liu, Zhang, & Potthas, 2011). In the monomolecularly dispersed cellulose solution, the $M_{w,app}$ value measured could be used approximately as the weight-average molecular weight of individual cellulose chains ($M_{single}$). In this case, the $M_{w,app}$ value evaluated from the Zimm plot of cellulose solution in LiOH/urea aqueous solution at 10 °C to be $7.4 \times 10^4$ g/mol was treated as the $M_{single}$ value approximately for the following calculation.

The influence of NaOH concentration on $f(R_h)$ of cellulose with a concentration of $6 \times 10^{-4}$ g/mL at 25 °C is shown in Fig. 1. The CONTIN analysis of DLS measurements on the cellulose solution was performed. Each peak area ($A$) is proportional to the weight fraction of corresponding molecular size. When only individuals and aggregates co-exist in solutions at a given temperature, $M_{w,app}$, $N_{agg}$ may be expressed by (Burchard, 1999)

$$M_{w,app} = \omega_{single} M_{single} + \omega_{agg} M_{agg} \tag{5}$$

$$A_{single} : A_{agg} = \omega_{single} M_{single} + \omega_{agg} M_{agg} \tag{6}$$

$$N_{agg} = \frac{M_{agg}}{M_{single}} \tag{7}$$

where subscripts single, and agg represent two kinds of the components (individuals and aggregates), and $\omega_{single} + \omega_{agg} = 1$. The $N_{agg}$ is apparent mean aggregation number, and $M_{agg}$ is the

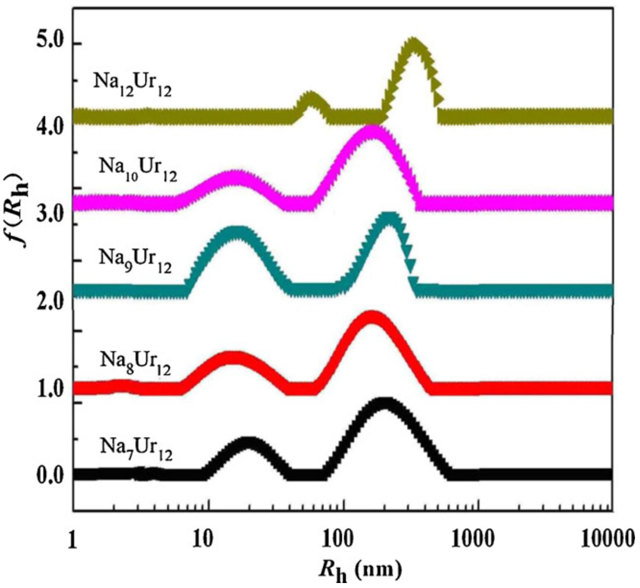

**Fig. 1.** Hydrodynamic radius distributions of cellulose solution in different NaOH concentration in 12 wt% urea aqueous solution with concentration of $6 \times 10^{-4}$ g/mL at 25 °C and scattering angle $\theta = 30°$.

weight–average molecular weight of their aggregates. The experiment results of $A_{single}/A_{agg}$, $M_{w,app}$, $\omega_{single}$ and $N_{agg}$ are summarized in Table 1. As a result of imperfect shell of ICs, the single ICs would associate with each other to form aggregates. Similar results had also reported for some other cellulose solvent systems (Fischer, 1994; Morgenstern & Röder, 1998; Schulz, Seger, & Buchard, 2000). As shown in Fig. 1, the $R_h$ value obtained from the cumulative analyses was ~20 nm for the single ICs in the cellulose solution, whereas the peaks at higher $R_h$ value were attributed to the cellulose IC aggregates. IC aggregates in $Na_7Ur_{12}$ exhibited the $R_h$ value of about 200 nm. With increasing NaOH, the solution showed a narrower distribution, the proportion of single chains increased, indicating the aggregation phenomenon had been reduced with a small amount addition of NaOH. In $Na_{12}Ur_{12}$ system, the area of the single ICs decreased and the peak positions of both components significantly moved to higher value, suggesting lager IC aggregates, it was noted that the solution of $Na_{12}Ur_{12}$ possessed a narrow hydrodynamic radius distribution. The peak position for aggregates appeared at both 40–70 nm and 200–500 nm, indicating the peak of single ICs disappeared and two kinds of aggregates with different $R_h$. The results suggested that NaOH concentration higher than 10 wt% led to significant aggregations. This could be explained that as NaOH increased, excessive NaOH could attract to urea easily, leading to the breakdown of the ICs structure (the shell of cellulose ICs), and the exposed cellulose would interact with each other through hydrogen bonding into larger clusters (Cai et al., 2008).

**Table 1**
Experimental results of cellulose solution in different composition of NaOH and urea aqueous solvent system at 25 °C.

| Sample | $A_{single}/A_{agg}$ | $M_{w,app}$ ($\times 10^4$ g/mol) | $\omega_{single}$ | $N_{agg}$ |
|---|---|---|---|---|
| $Na_7Ur_{12}$ | 0.32 | 19.6 | 0.63 | 5.5 |
| $Na_8Ur_{12}$ | 0.43 | 16.3 | 0.67 | 4.6 |
| $Na_9Ur_{12}$ | 0.84 | 10.6 | 0.86 | 4.1 |
| $Na_{12}Ur_{12}$ | – | 139 | – | – |
| $Na_7Ur_{13}$ | 0.34 | 18.9 | 0.65 | 5.4 |
| $Na_7Ur_{15}$ | 0.33 | 18.8 | 0.65 | 5.4 |
| $Na_9Ur_{13}$ | 1.40 | 8.1 | 0.96 | 3.6 |

Fig. 2 shows the Zimm plot of cellulose solution in NaOH/urea systems at 25 °C with different NaOH concentrations, and the relative $M_{w,app}$ are summarized in Table 1. Compared with the results of $Na_7Ur_{12}$, the $M_{w,app}$ value from a typical Zimm plot of $Na_9Ur_{12}$ exhibited a remarkable decrease from $1.96 \times 10^5$ to $10.6 \times 10^4$ g/mol. It indicated that a favorable amount of NaOH could promote the formation and stability of cellulose ICs in the NaOH/urea aqueous system. As shown in Fig. 2, the Zimm plot of $Na_{12}Ur_{12}$ exhibited a deformation at small angles, indicating an existence of intensive large aggregates (Li, He, Ng, Wu, & Ng, 2000). With the content of additive NaOH exceeding 9 wt%, the $M_{w,app}$

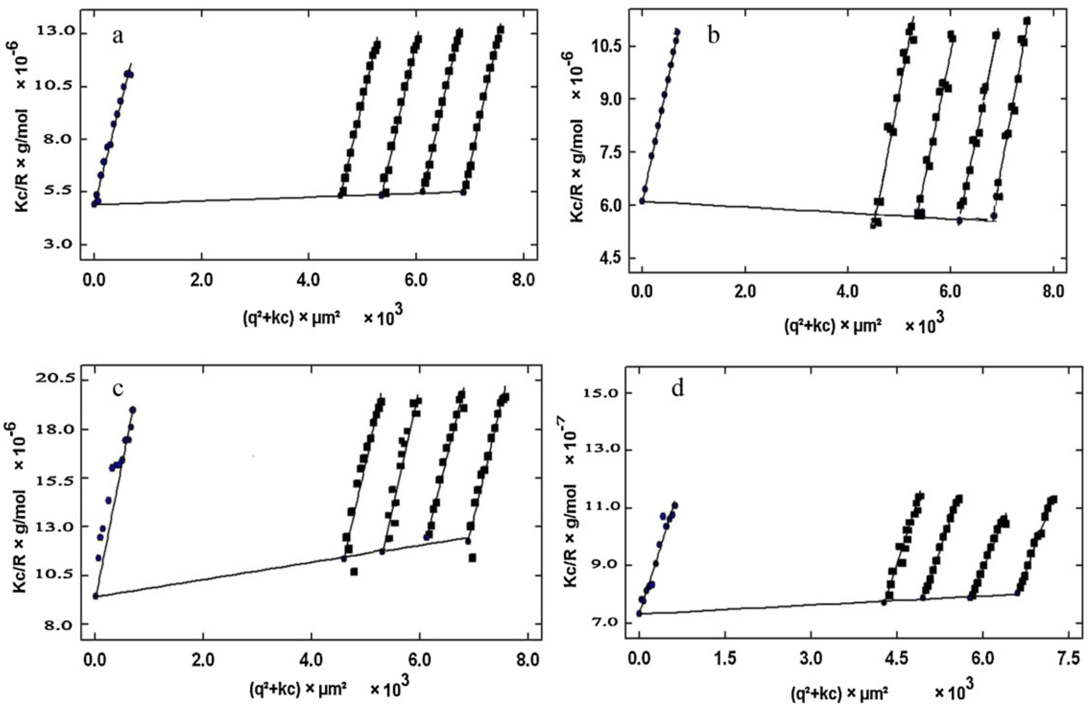

**Fig. 2.** Zimm plot of cellulose solution in different NaOH concentration in 12 wt% urea aqueous solution at 25 °C (a) $Na_7Ur_{12}$, (b) $Na_8Ur_{12}$, (c) $Na_9Ur_{12}$, and (d) $Na_{12}Ur_{12}$.

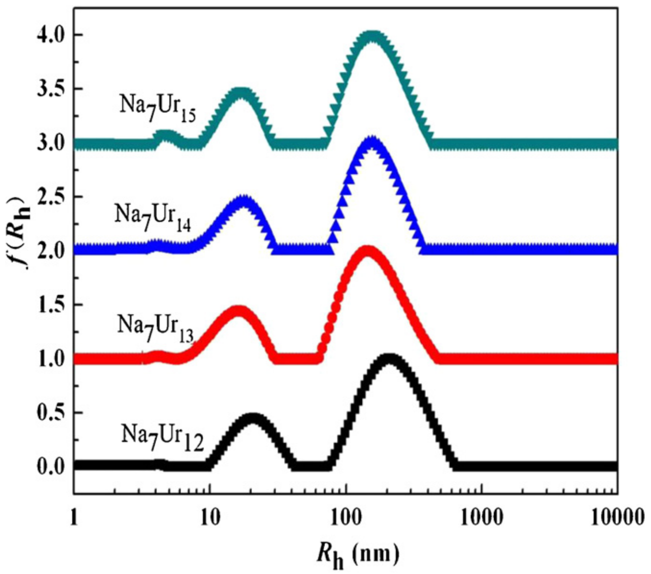

**Fig. 3.** DLS profiles of cellulose solution in different urea concentration in 7 wt% NaOH aqueous solution with concentration of $6 \times 10^{-4}$ g/mL at 25 °C and scattering angle $\theta = 30°$.

value increased, indicating an increase of the ICs aggregate proportion. It further validated the conclusion that the right amount of NaOH in cellulose solution could promote the dispersion of cellulose, but too high NaOH concentration would induce much severe aggregation phenomenon. Namely, the stability of cellulose ICs in NaOH/urea aqueous solvent system was firstly enhanced and then lessened with NaOH concentration increasing.

In view of the results in Table 1, the aggregation behavior was dominated by the NaOH concentration. The results revealed that the cellulose IC aggregates could be affected by increasing NaOH concentration. In our previous work, it had been proved that the NaOH "hydrates" penetrated the cellulose and destroyed the intra- and inter-molecular hydrogen bonding of the cellulose through the formation of new more stable hydrogen-bonded networks, resulting in solvation of the cellulose chains (Cai et al., 2008; Lue, Zhang, & Ruan, 2007). In $Na_7Ur_{12}$, an imperfect shell consisted of NaOH and urea hydrate occurred in the ICs structure, leading to cellulose dispersion and also to fore aggregation as a result of exposed hydroxyls of cellulose. With increasing NaOH, a fuller combination between NaOH and cellulose chain took place, and individuals increased. However, in $Na_{10}Ur_{12}$ and $Na_{12}Ur_{12}$ with high NaOH concentration, single ICs were easily to associate with each other to form aggregates. Therefore, in NaOH/urea aqueous solvent system, 9 wt% NaOH was favorable to the formation and stability of cellulose ICs.

### 3.2. Effect of urea concentration

The influences of urea concentration on $f(R_h)$ of cellulose in NaOH/urea aqueous solution with concentration of $6 \times 10^{-4}$ g/mL at 25 °C are shown in Fig. 3. The corresponding hydrodynamic radius distributions were calculated from the CONTIN analysis. The relative $A_{single}/A_{agg}$ ratios are summarized in Table 1. Interestingly, there was no visible shift of the main peaks, and with the increase of urea, and there were single ICs and IC aggregates in the cellulose solution. However, with an increase of urea content, the slight increase of $A_{single}/A_{agg}$ value illustrated that the proportion of IC aggregates slightly decreased. It indicated that increasing amount of urea was able to reinforce the shell of cellulose ICs and disrupt the cellulose aggregates in the NaOH/urea aqueous solution. Therefore, the dissolution of cellulose was slightly improved by the addition of urea.

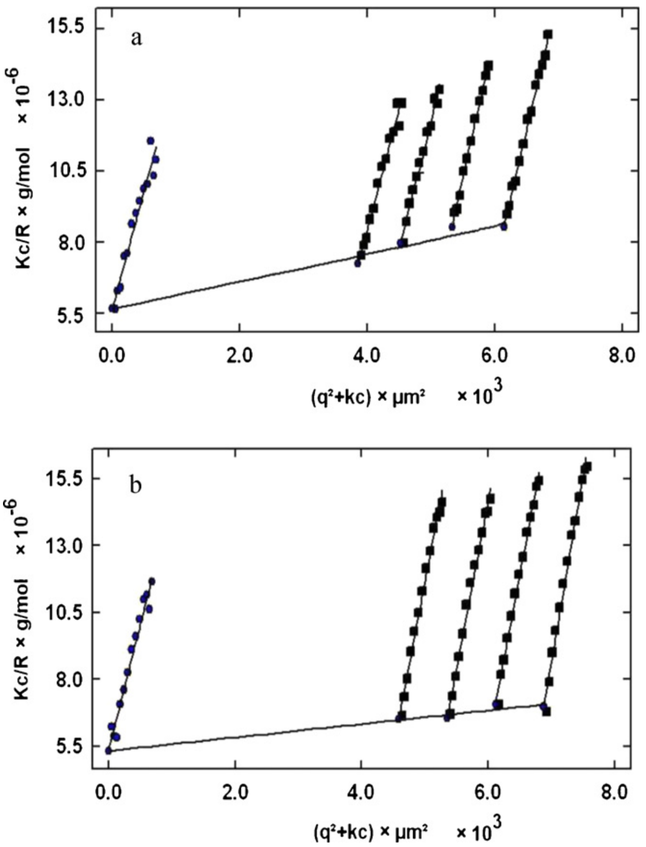

**Fig. 4.** Zimm plot of cellulose solution in different urea concentration in 7 wt% NaOH aqueous solution at 25 °C (a) $Na_7Ur_{13}$ and (b) $Na_7Ur_{15}$.

Fig. 4 shows the Zimm plots of cellulose solution in NaOH/urea aqueous systems with different urea concentration at 25 °C. The relative $M_{w,app}$, $\omega_{single}$ and $N_{agg}$ values are also summarized in Table 1. All the Zimm plots exhibited ordinary polymer solution properties. From Table 1, the $M_{w,app}$ decreased with the increase of urea and the $N_{agg}$ dropped to a little lower value. The results were supported by the conclusion above that urea addition could slightly prevent the aggregation phenomenon of cellulose ICs in NaOH/urea aqueous solution. The hydrogen bonds around amino groups of urea were similar to those of the bulk water (Vanzi, Madan, & Sharp, 1998), and it could bind to both polar and non-polar groups of peptides driven by enthalpy and entropy (Zou, Habermann, & Murphy, 1998). Thus, as hydrogen bonding donor and receptor, urea with a lone pair electron on oxygen atom could locate at the surface of the new hydrogen-bonded networks and associate with cellulose and NaOH in the process of cellulose dissolved in NaOH/urea aqueous solution (Cai & Zhang, 2005). With increase of urea, the urea assembled on the surface of imperfect shell to form a relative intact overcoat on the ICs. Therefore, the single cellulose chains became stable, and the aggregation behaviors were reduced. Compared with NaOH, urea was unable to associate directly with cellulose, leading to weak interactions between urea and cellulose. Therefore, the proportion of single ICs increased slightly with urea addition. Based on the conclusion above, it suggested that the addition of urea slightly enhanced the stability of ICs.

### 3.3. Effect of NaOH and urea composition

Fig. 5 shows the $f(R_h)$ of cellulose solution in different composition of NaOH and urea, where the corresponding hydrodynamic radius distributions were calculated from the CONTIN analysis. Fig. 6 shows the Zimm plot of cellulose solution in $Na_7Ur_{12}$ and

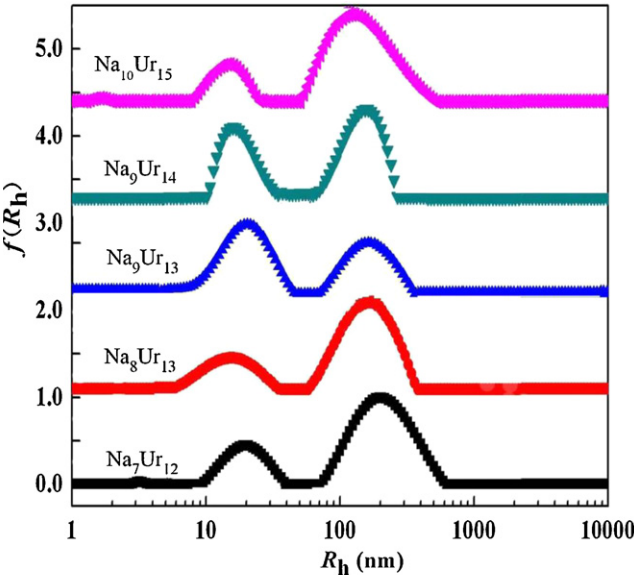

**Fig. 5.** Hydrodynamic radius distributions of cellulose solution in different ratio of NaOH and urea with concentration of $6 \times 10^{-4}$ g/mL at 25 °C and scattering angle $\theta = 30°$.

$\mathrm{Na_9Ur_{13}}$ at 25 °C. The $A_{\text{single}}/A_{\text{agg}}$, $M_{\text{w, app}}$, $\omega_{\text{single}}$ and $N_{\text{agg}}$ values are shown in Table 1. It was noted that the proportion of the single ICs peaks values increased in the beginning to reach a maximum when NaOH and urea concentrations were increased to 9 wt% and 13 wt%, and then decreased with further increasing NaOH and urea, indicating IC aggregation phenomenon. From Fig. 6 and Table 1, a reduction of $M_{\text{w,app}}$ value dropped from $19.6 \times 10^4$ g/mol in $\mathrm{Na_7Ur_{12}}$ to $8.1 \times 10^4$ g/mol in $\mathrm{Na_9Ur_{13}}$. The $\omega_{\text{single}}$ value increased significantly. The $N_{\text{agg}}$ reached a low value of 3.6 in $\mathrm{Na_9Ur_{13}}$, indicating the aggregation of cellulose ICs was inhibited effectively. The 9 wt% NaOH/13 wt% urea was more advantageous than the 7 wt% NaOH/12 wt% urea aqueous solution in accordance with our previous results (Cai et al., 2008). The predominant species of the single ICs existed in the 9 wt% NaOH/13 wt% urea aqueous solution. In view of the results, it could be concluded that cellulose single ICs was much stable in he 9 wt% NaOH/13 wt% urea aqueous solvent.

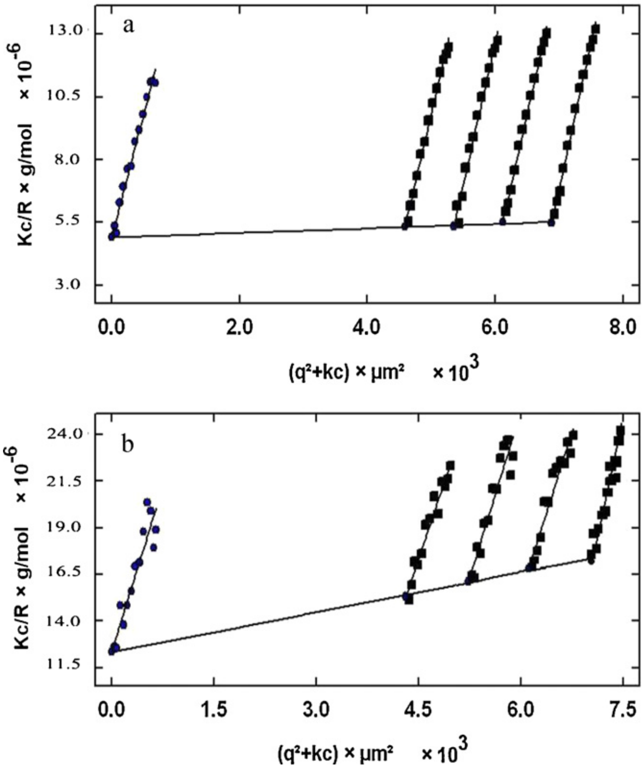

**Fig. 6.** Zimm plot of cellulose solution in (a) $\mathrm{Na_7Ur_{12}}$ and (b) $\mathrm{Na_9Ur_{13}}$ at 25 °C.

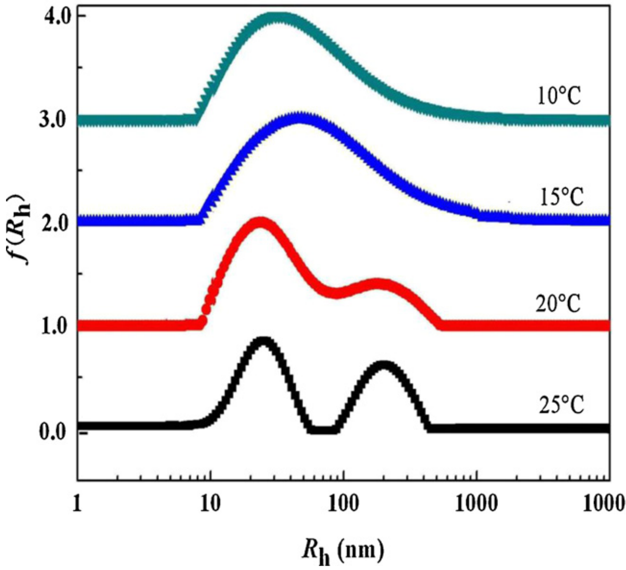

**Fig. 7.** Hydrodynamic radius distributions of cellulose solution in $\mathrm{Na_9Ur_{13}}$ with concentration of $6 \times 10^{-4}$ g/mL at different temperature and scattering angle $\theta = 30°$.

### 3.4. Effect of temperature

It is noting that the cellulose solution was meta-stable in the NaOH/urea solvent system. The ICs structure could be destroyed by the system fluctuations, leading to the cellulose IC aggregates. The temperature played an important role on the stability of the IC aggregation behaviors in NaOH/urea aqueous system. Cellulose inclusion complexes should be stable at relatively low temperature. Fig. 7 shows the $f(R_h)$ of cellulose solution in $\mathrm{Na_9Ur_{13}}$ with concentration of $6 \times 10^{-4}$ g/mL at different temperature and scattering angle $\theta = 30°$. The cellulose solution exhibited two peaks at 25 °C, corresponding to single ICs and IC aggregates, respectively. However, with decrease of temperature, only one peak was observed in the cellulose solution assigned to single ICs and the peak shifted to small dimension, indicating the aggregation behavior has been weakened and the ICs structure was stable relatively

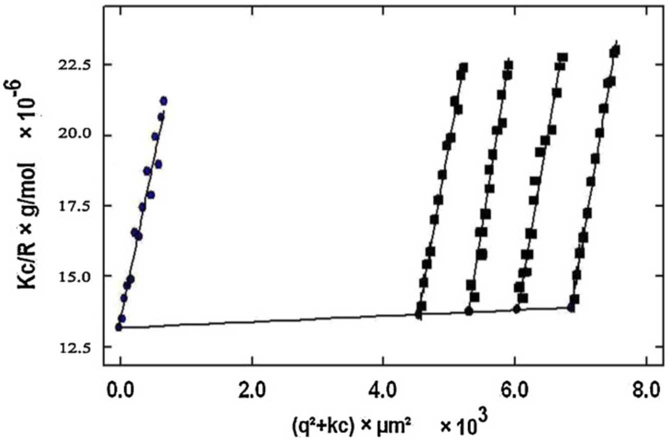

**Fig. 8.** Zimm plot of cellulose solution $\mathrm{Na_9Ur_{13}}$ at 10 °C.

at low temperature. At high temperatures, the IC structure would be entirely destroyed, and the exposed cellulose would interact with each other through hydrogen bonding into larger clusters. As shown in Fig. 8, a low $M_{w,app}$ about $7.6 \times 10^4$ g/mol which was similar with the one in LiOH/urea system was obtained in $Na_9Ur_{13}$ at 10 °C. In view of the results, it suggested that a low level aggregation occurred and almost as single ICs existed in the $Na_9Ur_{13}$ system at 10 °C, whereas it formed more and relatively larger sized aggregates at high temperature. In this case, the single cellulose inclusion complexes were predominant species. Therefore, 9 wt% NaOH/13 wt% urea aqueous solvent system could be used to investigate the molecular weight and the chain conformation of cellulose at 10 °C.

## 4. Conclusion

Stable cellulose solution, in which the single cellulose inclusion complexes were the predominant species, could be obtained in 9 wt% NaOH/13 wt% urea aqueous system at 10 °C. A little increasing amount of NaOH could improve the dissociation and reconstruction of hydrogen bond among the cellulose, leading to a better dispersion of cellulose. The IC aggregates were reduced slightly with urea increasing. However, favorable increase of urea could repair the imperfect shell of the ICs, resulted in a more stable cellulose solution. Temperature also exhibited great influence on the aggregation phenomenon. The exposed cellulose could associate with each other via hydrogen bonding, and form large dimension clusters under the high temperature. Therefore, the cellulose solution was relatively stable at low temperature such as 10 °C.

## Acknowledgments

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