Solubility of Cellulose in NaOH / Urea Aqueous Solution

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ABSTRACT: NaOH/urea aqueous solution as solvent of cellulose including cotton linter, bagasse, alkali-soluble cellulose and Bemliese[®] was studied by solubility analysis, viscometry and light scattering. The addition of 2—4 wt% urea significantly improved the solubility of cellulose in 6—8 wt% NaOH aqueous solutions, and moderate urea plays a role in improving solubility and avoiding the formation of cellulose gel. Celluloses I with viscosity-average molecular weight (M_η) of 6.7×10^4 were completely dissolved in 6 wt% NaOH/4 wt% urea aqueous solution. Cellulose dissolved in 6 wt% NaOH/4 wt% urea aqueous solution degraded slowly with storage time, and M_η of cellulose in the solution decreased 20% after storage for 100 days. The stability of cellulose solution was higher than cellulose cuoxam. A regenerated cellulose membrane having the tensile strength of 88.7 MPa and breaking elongation of 11% was successfully prepared by coagulating 4 wt% Bemliese[®] solution in 6 wt% NaOH/4 wt% urea with 5 wt% $CaCl_2$ then 1.3 wt% HCl aqueous solution as coagulate at 20°C.
    KEY WORDS   NaOH / Urea Aqueous Solution / Solubility / Viscosity / Stability of Cellulose / Regenerated Cellulose Membrane /

Polymers from renewable resources attract much attention due to biodegradability and potential as substitute for petrochemicals in some fields. Plant cellulose is the richest natural polymer on the earth. Making use of cellulose to produce various products cannot only protect the environment from pollution, but save limited petroleum resources.[1] However, the molecular structure of cellulose, β-(1→4)-D-glucan, allows chain-packing by strong inter- and intramolecular hydrogen-bonding, which interferes with efforts to process or modify the material.[2] Therefore, cellulose still has not reached its potential in many areas for all its availability. The most general solvents for dissolving cellulose are unsuitable. It is worth noting that in the viscose industry, pollution control places ever increasing restraint on the process.[3] The development of non-polluting process based on organic and inorganic solvents of cellulose is of great scientific or practical interest, and much attention should be given to such solvents as ammonia/ammonium thiocyanate,[4,5] calcium- and sodium thiocyanate,[6,7] zinc chloride,[8–10] lithium chloride/dimethylacetamide,[2,11,12] N-methylmorpholine-N-oxide[13–15] and aqueous solution of sodium hydroxide.[16,17] N-methylmorpholine-N-oxide has been recognized as a direct cellulose solvent, but commercial facility producing cellosic fibers *via* this solvent has developed very slowly due to high cost and high spinning temperature.[18] 7—9 wt% NaOH aqueous solution is one of the cheapest cellulose solvents, in which cellulose can be dissolved near 4°C, since intermolecular hydrogen bonds are destroyed.[16,19] However, only from cellulose of relatively low molecular weight is impossible to obtain fibers, and cellulose with polymerization of over 250 is unstable.[18] Kamide, Okajima, and coworkers[16,17,20–22] report that an alkali-soluble cellulose can be dissolved in NaOH aqueous solution at low temperature, and prepared a solution from wood pulps and method of regeneration process. However, only cellulose with lower molecular weight could be dissolved in this

solvent, limiting the process and mechanical properties of products. The development of a new solvent of cellulose, to effectively destroy the intermolecular hydrogen banding, is essential for successful applications of cellulose. Intermolecular hydrogen bondings of polysaccharides can be broken by using urea.[23,24] Interestingly, NaOH and especially urea broke intermolecular hydrogen bondings of polysaccharides, loading to enhance water-solubility.[24] The addition of organic compounds such as urea, thiourea to NaOH solution could have substantial impact on cellulose solubility, though no satisfactory explanation of this has been given.[18,25,26] Thus it is of interest for further study of NaOH/urea aqueous solution system.

This work clarifies the solvent composition of urea and NaOH, and elucidates the solubility of cellulose based on viscosity of the cellulose solution. The stability of cellulose in the NaOH/urea aqueous solution was studied by light scattering and viscometry, and compared with cuoxam solution.

EXPERIMENTAL

Materials

Two cotton linters were purchased from Hubei Chemical Fiber Group Ltd. and coded as linter-1 and linter-2, the viscosity-average molecular weight (M_η) were measured to be 10×10^4 and 15.9×10^4 using a viscometer, respectively. Bagasse-1 $(M_\eta = 8.32 \times 10^4)$ and bagasse-2 $(M_\eta = 7.26 \times 10^4)$ were supplied by Liuzhou Papermaking factory of Guangxi. The cellulose from bagasse was treated by hot water (100°C) for one hour, mashed by a triturator, washed by water and acetone for five times, and finally vacuum-dried. Alkali-soluble cellulose powder (steam exploded spruce pulp) and Bemcot non-woven cloth made from cotton linters (Bemliese[®]) were a gift of Asahi Chemical Industry Co., Ltd. in Japan, and M_η were 4.75×10^4 and 11.2×10^4, respectively.

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Table I. Solubility (S_a) of celluloses in NaOH / urea aqueous solution

Cellulose	S_a/%									
	S6-0	S6-2	S6-4	S6-6	S6-8	S8-0	S8-2	S8-4	S8-6	S8-8
Linter-1	44.7	50.5	48.4	43.3	36.1	40.6	48.5	40.5	28.3	23.7
Linter-2	21.0	26.8	30.2	30.8	17.6	24.2	27.8	25.9	18.9	12.2
Bagasse-1	53.4	58.0	69.3	63.3	49.5	51.4	54.0	53.4	52.8	46.2
Bagasse-2	56.0	61.7	74.3	68.6	54.0	62.8	64.0	62.7	58.1	56.1
Alkali-soluble cellulose	Gel	100	100	100	100	100	100	100	100	100
Bemliese®	Gel	100	100	100	100	100	100	100	100	99

Solvents

NaOH and urea were of analytical grade and purchased from the Chemical reagent store in China. By changing the weight rate of NaOH to urea such as 8:0, 8:2, 8:4, 8:6, 8:8, 6:0, 6:2, 6:4, 6:6, and 6:8, the NaOH /urea aqueous solutions were prepared, and coded as S8-0, S8-2, S8-4, S8-6, S8-8, S6-0, S6-2, S6-4, S6-6, and S6-8, respectively.

X-Ray Diffractometry

X-Ray diffraction was measured with an X-Ray diffractometer (D/MAX-1200, Rigaku Denki, Japan). X-Ray diffraction patterns with Cu-K_α radiation ($\lambda = 1.5405 \times 10^{-10}$ m) at 40 kV and 30 mA were recorded at $2\theta = 6-40°$. The degree of crystallinity (χ_c) was calculated according to the usual method.[27]

Viscosity Measurement

Cellulose was dispersed in NaOH/urea aqueous solutions, stirred for 5 min and stored in a refrigerator (0℃) for 12 h to prepare cellulose dilute solution at ca. 4.0×10^{-3} g mL^{-1}. The viscosity of the cellulose dilute solution was measured at 25 ± 0.1℃ using an Ubbelodhe viscometer. Huggins and Kraemer plots were used to estimate intrinsic viscosity $[\eta]$.[28,29] Viscosity was measured three times and $[\eta]$ was taken as the average.

Viscosity-average molecular weights (M_η) of the samples and original cellulose materials were determined in cadoxen at 25℃ by viscometry and calculated from following equation[30]

$$[\eta] = 3.85 \times 10^{-2} M_w^{0.76} \text{ (mL g}^{-1}) \qquad (1)$$

Solubility Test of Concentration Solution

A 5 g sample of cellulose was dispersed in 95 g NaOH/urea aqueous solution, stirred for 10 min, and stored in a refrigerator (0℃) for 12 h. Dissolved and insoluble parts of cellulose were isolated by centrifuging at 9000 rpm for 45 min. The insoluble cellulose was washed with water and by acetone, and vacuum-dried. NaOH/urea solution containing the dissolved cellulose fraction was neutralized with 2 mol L^{-1} H$_2$SO$_4$, and the cellulose precipitate was isolated using a sand filter, washed with water for twenty times and with acetone three times respectively, and vacuum-dried. Solubility S_a of cellulose was calculated by

$$S_a = [w_1/(w_1 + w_2)] \times 100\% \qquad (2)$$

where w_1 is weight of the dissolved cellulose, and w_2,

weight of the insoluble cellulose. The solubility experiments were repeated three times, and average value considered S_a.

Light Scattering

Static light scattering experiments were performed using a multi-angle laser photometer equipped with a He–Ne laser ($\lambda = 633$ nm) (DAWN-DSP, Wyatt Technology Co.), operated at 18 angles. Astra software was to obtain data. Refractive index increment (dn/dc) of cellulose in 6 wt% NaOH/4 wt% urea aqueous solution (S6-4) was measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co.) at 633 nm and 25℃ to be 0.178. The cellulose solution ($c = 4.5609 \times 10^{-3}$ g mL^{-1}) was filtered by a sand filter and 0.45 μm filter (Whattman, England) directly into a scintillation vial for light scattering measurement. Weight-average molecular weight (M_w) was determined with Debye plots processed with Astra Software.

Stability Test

To study the degradation of cellulose molecules with storage time, cellulose was taken out from the solution at a given time and measured for viscosity-average molecular weight (M_η) using a viscometer. 5 g cellulose were dissolved in 95 g 6 wt% NaOH/4 wt% urea aqueous solution (S6-4), and stored in refrigerator at 4℃ for desired time. Cellulose solution was taken out and neutralized with 2 mol L^{-1} H$_2$SO$_4$ to precipitate cellulose. Isolated cellulose was washed with water and acetone, and vacuum-dried for 24 h. M_η of the cellulose was determined from intrinsic viscosity $[\eta]$ in cadoxen at 25℃.
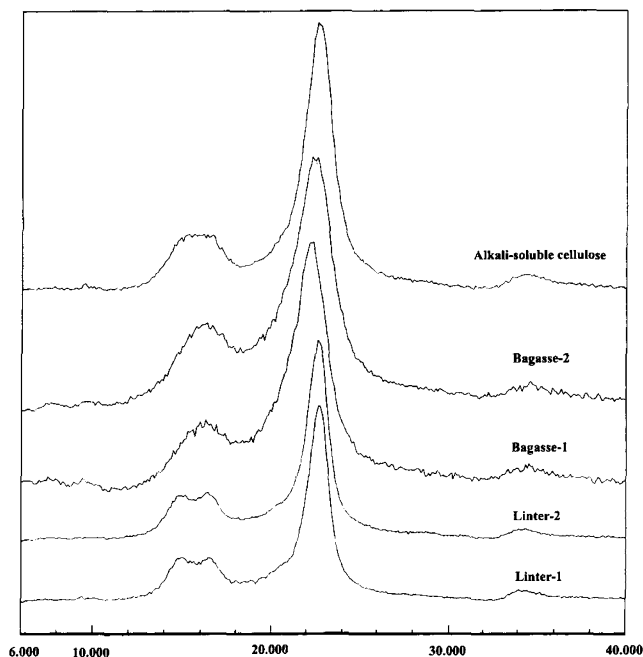
The stability of cellulose dilutes solution in aqueous solution S 6-4 was measured by a viscometer and light scattering at 25℃. For comparison, inherent viscosity $\ln \eta_r/c$ of cellulose in cuoxam solution for desired time was measured.

RESULTS AND DISCUSSION

Solubility (S_a) characteristics of cotton linters, bagasses, alkali-soluble cellulose and Bemliese® are given in Table I. The addition of moderate urea to the NaOH solution significantly improved the solubility of cellulose. The solubility of cotton linters and bagasses at 0—4℃ increased with urea concentration and reached maximum in S6-4 and S8-2 aqueous solutions. With continued addition of urea, S_a of cellulose decreased. Alkali-soluble cellulose and Bemliese® exhibited excellent solubility in all NaOH/urea solution. Solutions of alkali-soluble cellulose and Bemliese® were stable at least for

Table II. Crystallinity χ_c, solubility (S_a) and viscosity-average molecular weight (M_η) of dissoluble and indissoluble parts of cellulose in the solvent of S6-4
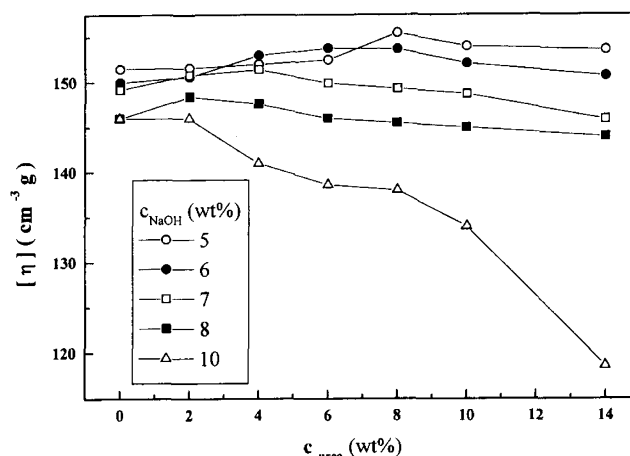
Cellulose	χ_c	$M_\eta \times 10^{-4}$			$S_a/\%$
		Initial cellulose	Indissoluble cellulose	Dissoluble cellulose	
Linter-1	0.73	10.0	12.8	5.57	48
Linter-2	0.74	15.9	17.4	6.70	30
Bagasse-1	0.64	8.32	15.4	2.97	69
Bagasse-2	0.61	7.26	16.2	2.25	74
Alkali-soluble cellulose	0.76	4.75	—	4.54	100

Figure 1. X-Ray diffraction patterns of original celluloses.

Figure 2. Dependence in intrinsic viscosity $[\eta]$ of alkali-soluble cellulose in NaOH/urea aqueous solution on urea concentration c_{urea} at 25°C.

three months at 4°C, and did not form gels. Cellulose can be dissolved in 6 wt% NaOH aqueous solution at the lower temperature (0°C), but soon turns into a gel with increasing temperature. This did not occur with the addition of urea. According to the Table I, the optimum solvents for cellulose are S6-4 and S8-2, a 6 wt% NaOH/4 wt% urea and 8 wt% NaOH/2 wt% urea aqueous solution. S_a of cellulose is thus improved significantly with the addition of 2—4 wt% urea to 6—8 wt% NaOH aqueous solution.

Figure 1 shows the X-Ray diffraction patterns of the cellulose. The crystalline form of cellulose I has typical diffraction peaks $(2\theta$ angles at ca. 14.8°, 16.3°, and 22.6°).[31] The crystallinity of linter-1, linter-2, bagasse-1, bagasse-2, and alkali-soluble cellulose was 0.73, 0.74, 0.64, 0.61, and 0.76, respectively, as shown in Table II. All these are the form of cellulose I, difficult to dissolve in NaOH aqueous solution. Bemliese[®] is cellulose II form, because it is regenerated cellulose made from cellulose cuoxam solution. Celluloses I and II may thus dissolved in 6—8 wt% NaOH aqueous solution containing 2—4 wt% urea.

The viscosity-average molecular weight of dissolved cellulose and indissoluble fractions of five materials in aqueous solution S6-4 are listed in Table II. Celluloses of cotton linters or bagasses dissolve in 6 wt% NaOH/4 wt% urea, when molecular weights are lower than 5.57×10^4 for linter-1 and 6.70×10^4 for linter-2. 6 wt% NaOH/4 wt% urea solution can thus dissolve cellulose directly, that has not been subjected to structural modification.[22] The dissolved mass of bagasses was much larger than that of cotton linters as shown in Table I. However, the molecular weight of dissolved and indissoluble bagasses were much lower and higher, respectively, than that of linters, indicating that bagasses have large polydispersity. The molecular weight distribution of cellulose could hardly be determined by size exclusion chromatography (SEC), but maximum M_η for the dissolved bagasses was deduced as ca. 9×10^4.

Viscometry is a simple, quick and sensitive analytical technique and reflects the extent of macromolecular chains as extent of solvation. $[\eta]$ of polymer with same M_η is more high, indicates the solvent is better. Figure 2 shows the dependences of $[\eta]$ of alkali-soluble cellulose on the concentration of NaOH and urea in aqueous solution. $[\eta]$ hardly changed with increasing urea in 6—8 wt% NaOH aqueous solution. When NaOH exceeded 10 wt%, $[\eta]$ of alkali-soluble cellulose decreased sharply with the addition of urea. The solution was unstable and cellulose precipitated at room temperature. 6 wt% NaOH/2—8 wt% urea aqueous solution is thus a good solvent for alkali-soluble cellulose. Considering saving urea, aqueous solution S6-4 was the most suitable solvent for cellulose.
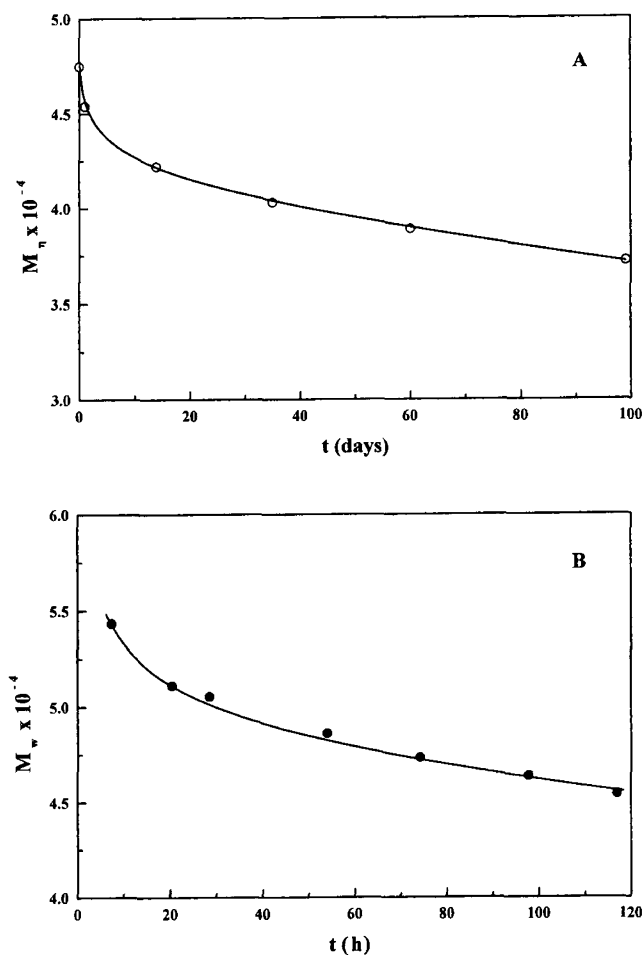
Figure 4. $\ln \eta_r/c - t$ curves of alkali-soluble cellulose in 6 wt% NaOH/4 wt% urea aqueous solution (●) and cuoxam solution (○) at 25°C.

Figure 3. Dependence of molecular weights of alkali-soluble cellulose on storage time measured by viscometry (A) and light scattering (B).

A stable system of polymer solution is essential for produce and the characterization of viscosity and molecular weight. The dependence of M_η and M_w of the cellulose in aqueous solution S6-4 on the storage time is shown in Figure 3. 5 wt% alkali-soluble cellulose solution in S6-4 stored for 100 days at 4°C remained clear. M_η of alkali-soluble cellulose determined in dilute solution by viscometry decreased fast in the first ten days to be 90% of the original, and then slowly. Change of M_η was only 20% of the original. M_w of cellulose dilute solution in S6-4 decreased from 5.4×10^4 to 4.5×10^4, with increase of storage time from 8 h to 120 h. Thus the degradation of the celluloses in aqueous solution S6-4 is relatively small.

The dependence of inherent $\ln \eta_r/c$ of alkali-soluble cellulose solution in S6-4 and cuoxam, respectively, on storage time (t) at 25°C is shown in Figure 4. $\ln \eta_r/c$ of alkali-soluble cellulose in cuoxam solution more readily decreased than in aqueous solution S6-4 with increase of storage time. Cellulose in aqueous solution S6-4 is thus more stable than in cuoxam solution.

Alkali-soluble cellulose and Bemliese® dissolved in 6 wt% NaOH to easily form a gel not useful for making a membrane or fibers. However, the addition of urea to NaOH aqueous solution avoided the formation of a cellulose gel. The regenerated cellulose membrane was satis-
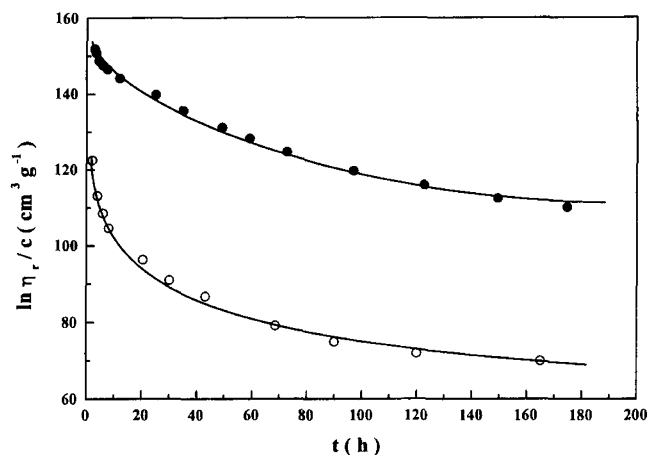
factorily prepared by coagulating 4 wt% Bemliese® solution in S6-4 with 5 wt% CaCl$_2$ then 1.3 wt% HCl aqueous solution as coagulate.[32] The tensile strength (σ_b), breaking elongation (ε_b) and optical transmission of the dry membrane were measured using a universal testing machine (CMT-6503, Shenzhen SANS Co., Ltd. China) at 5 mm min^{-1} and a UV spectroscopy (UV-160A, Shimadzu), and found to be 88.7 MPa, 11% and 90% (at 400—800 nm). This suggests that the 6 wt% NaOH/4 wt% urea aqueous solution as a new and cheap solvent of cellulose has potential application.

CONCLUSIONS

The solubility of cellulose in 6—8 wt% NaOH aqueous solutions was significantly improved by 2—4 wt% urea. 10 wt% urea or 10 wt% NaOH resulted in decreased solubility of the cellulose. 6 wt% NaOH/4 wt% urea aqueous solution was a good solvent for cellulose I and II, and dissolved completely cellulose I with the viscosity-average molecular weight $ca.$ 6.7×10^4. M_η of cellulose stored in aqueous solution S6-4 decreased only 20% after storage for 100 days, suggesting relatively low degradability of the cellulose in solution. The degradation rate of the cellulose in aqueous solution S6-4 was obviously slower than in cuoxam solution. 2—4 wt% urea avoided the formation of cellulose gel in 6—8 wt% NaOH aqueous solutions and cellulose solution was used to prepare regenerated cellulose membrane.

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