

Solubility of Some Cellulose in Alkaline Urea Aqueous Solvent Systems

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The petroleum resources are supposed to run out in 50 years. Polymers from renewable resources have attracted much attention because of their biodegradability and potential to substitute for petrochemicals in some fields. Cellulose remains as the main chemical resource of the future that will be available¹⁾. However, cellulose cannot be melted to fabricate or be dissolved in common solvent; the solvents of cellulose have long been limited in metal complex, strong acid, and alkali solution because of its stretched chain conformation caused by the -(1,4) glycoside bond and a system of well-organized H bonds²⁾. Moreover, cellulose in solution exhibits a high tendency to aggregate or self-associate; therefore, the characterization of its solution behavior gives serious problems³⁻⁵⁾. A basic understanding of conformation and solution properties of cellulose is essential for the successful investigation and application of cellulose. The solution of cellulose in water containing metal complexes, such as cuoxam⁶⁾, cuen⁶⁾, and cadoxen⁷⁾, as well as in lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc)⁸⁾, have been investigated. Among them, cadoxen seems to be a most convenient solvent, because of its colorless property and the suitability for light scattering (LS) measurement. However, cadoxen is highly toxic. Recently, *N*-methylmorpholine-N-oxide (NMMO)⁹⁾ process has become a desirable method for producing cellulose fibers. However, using NMMO as solvent in the laboratory is limited because of high cost and the harsh condition required for the dissolution of cellulose. Therefore, the aforementioned solvents could not be commonly used for molecular characterization of cellulose.

In the extensive work by Zhang *et al.*, it has been studied that the dissolution and rheological behaviors of cellulose in LiOH/urea and NaOH/urea aqueous solution precooled to -10°C¹⁰⁾. Cellulose could be rapidly dissolved in these solvents precooled to low temperature, and the dissolution

power of LiOH/urea is much higher than that of NaOH/urea aqueous solution¹¹⁾. Cellulose employed in the previous studies were mainly microcrystalline cellulose, which is easily soluble because of its low molecular weight.

The aim of present work is to investigate the solubility of some cellulose in alkaline urea aqueous solution. Cotton is one of the common cellulosic material but is much less soluble due to its high molecular weight and crystallinity. Therefore, some important data will be obtained in the present study.

Experimental

Materials

Microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich Co., USA), wood pulp, cotton cellulose (Daisan Co. Ltd, Japan) were commercially obtained and used without further purification. Sodium hydroxide, lithium hydroxide, and urea were purchased and used as received.

Preparation of solution

Two kind of preparation methods of cellulose solution were investigated in the present study, whose brief condition is shown in Fig. 1.

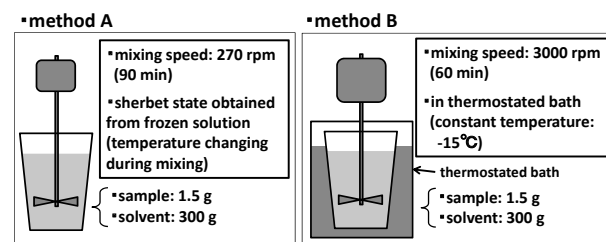


Fig. 1 Mixing method in the present study

a. Method A

The alkaline urea aqueous solution with cellulose sample was frozen in freezer of household refrigerator. The frozen solution was kept at ambient temperature until it became sherbet state. Then, it was mixed with normal type motor whose mixing speed was 270 rpm. In this case, the solution temperature was changing during mixing and solution changed from frozen state to liquid state, so reproducibility was not good.

b. Method B

The alkaline urea aqueous solution with cellulose sample was cooled in thermostated bath at -15°C . Then, it was mixed with special high speed motor whose mixing speed is 3000 rpm. In this case, the solution temperature was kept constant, so reproducibility was good.

Measurement

SEM observation of the cellulose sample was conducted with JSM-IT300 (JEOL, Japan).

Intrinsic viscosity of cellulose sample in LiCl/DMAc solvent was measured at 30°C with Ubbelohde type viscometer.

In the case of method A, solubility of cellulose sample was evaluated by the procedure shown below. The prepared solution mentioned above was centrifuged at 4000 rpm for 10 min to separate soluble part and insoluble part. The transparent supernatant solution was poured into large amount of methanol to isolate the soluble part of cellulose. The isolated cellulose was separated, dried and weighed. The precipitated part after centrifugation was washed with large amount of methanol, separated, dried and weighed.

In the case of method B, solubility of cellulose sample was estimated by the transparency of the solution after mixing (wavelength: 420nm, light path: 1 cm). It is much easier and more convenient than those employed for method A.

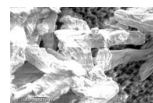

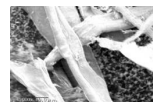

Results and Discussion

Cellulose samples

Cellulose samples employed in the present study were listed in Table 1. Intrinsic viscosity and fiber length of microcrystalline cellulose was quite small. Those of wood pulp was slightly larger than those of microcrystalline cellulose. Those of pulverized cotton was much higher than those of microcrystalline cellulose and wood pulp. And those of unprocessed cotton was the highest among those in

the present study. SEM photograph of cellulose samples was also listed in Table 1.

Table 1 Cellulose samples employed in the present study

	Intrinsic viscosity (dL/g)	Fiber length (mm)	SEM photograph
Microcrystalline cellulose (Avicel PH-101)	1.2	0.1	
Wood pulp	2.8	0.2	
Pulverized cotton	7.5	0.4	
Unprocessed cotton	9.5	20	

Preparation of solution by method A

Solubility of some cellulose samples in NaOH/urea/ H_2O (6/4/90 wt%) was exhibited in Table 2. Microcrystalline cellulose was completely soluble in this solvent system, which indicates its high solubility. Contrary to the case of microcrystalline cellulose, the solubility of other cellulose samples was much lower in this solvent system. These experimental results indicate that molecular weight of cellulose is quite important for their solubility in the solvent system in the present study.

Table 2 Solubility of some cellulose in NaOH/Urea/ H_2O (6/4/90 wt%)

Sample	Soluble part (%)	Insoluble part (%)
Microcrystalline cellulose	100	0
Wood pulp	35	65
Pulverized cotton	21	79
Unprocessed cotton	3	97

(Concentration of cellulose: 2.0%)

Table 3 shows the solubility of some cellulose samples in NaOH/urea/ H_2O (7/12/81 wt%). The solubility of cellulose samples in this solvent system was totally lower than that of NaOH/urea/ H_2O (6/4/90 wt%) (Table 1). Therefore, composition of NaOH and urea is of importance for high solubility.

Table 3 Solubility of some cellulose in NaOH/Urea/H₂O (7/12/81 wt%)

Sample	Soluble part (%)	Insoluble part (%)
Microcrystalline cellulose	92	8
Wood pulp	15	85
Pulverized cotton	6	94
Unprocessed cotton	1	99

(Concentration of cellulose: 2.0%)

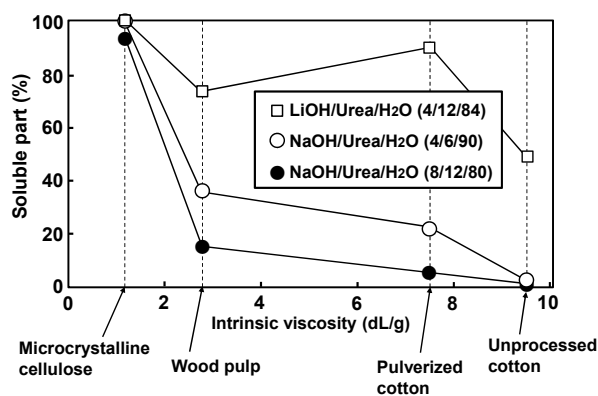
Solubility of some cellulose samples in LiOH/urea/H₂O (4/12/84 wt%) was shown in Table 4. This solvent system exhibited considerably higher solubility for various cellulose samples than NaOH-based solvent systems (Table 2, 3). This tendency is consonant with the previous study¹¹⁾.

Table 4 Solubility of some cellulose in LiOH/Urea/H₂O (4/12/84 wt%)

Sample	Soluble part (%)	Insoluble part (%)
Microcrystalline cellulose	100	0
Wood pulp	74	26
Pulverized cotton	93	7
Unprocessed cotton	46	54

(Concentration of cellulose: 0.5%)

Relationship between intrinsic viscosity and solubility of some cellulose samples by method A was exhibited in Fig.2. Higher intrinsic viscosity, higher molecular weight of cellulose induces lower solubility. And LiOH-based solvent system dissolves various cellulose regardless of their molecular weight.

**Fig. 2 Relationship between intrinsic viscosity and solubility of some celluloses**

Preparation of solution by method B

Table 5 lists solubility of some cellulose samples in four

kinds of alkaline urea aqueous solution. Solution of microcrystalline cellulose was almost transparent, which indicates high solubility of microcrystalline cellulose regardless of solvent system. In the case of wood pulp, transparency of the solution was totally high, probably because of superior mixing condition of method B. The solubility of pulverized cotton was also much higher than those by method A; it was almost soluble in these solvents examined except in the case of LiOH/urea/H₂O (4/6/90 wt%). On the other hand, unprocessed cotton showed the limited solubility; it was soluble only in LiOH/urea/H₂O (8/12/80 wt%).

Table 5 Solubility of some cellulose in LiOH/Urea/H₂O and NaOH/Urea/H₂O

Microcrystalline cellulose	Wood pulp

A: LiOH/Urea/H₂O (4/6/90 wt%)B: LiOH/Urea/H₂O (8/12/80 wt%)C: NaOH/Urea/H₂O (4/6/90 wt%)D: NaOH/Urea/H₂O (8/12/80 wt%)

Figures in the table indicate transparency of the solution.

Fig. 3 exhibits relationship between intrinsic viscosity and solution transparency of some cellulose by method B. Among those examined, LiOH/urea/H₂O (8/12/80 wt%) showed the highest solubility; it dissolved all of four cellulose samples almost completely. In the case of NaOH-based solvent system, concentration of NaOH and urea hardly affected the solubility of cellulose. On the other hand, in the case of LiOH-based solvent system, concentration of LiOH and urea was quite important for the solubility of cellulose. Consequently, method B is better than method A to attain high solubility of various kinds of cellulose.

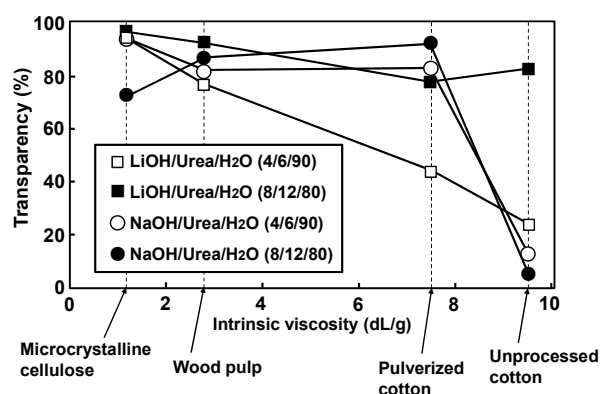


Fig. 3 Relationship between intrinsic viscosity and solution transparency of some celluloses

Summary

Solubility of four kinds of cellulose (microcrystalline cellulose, wood pulp, pulverized cotton, and unprocessed cotton) in some alkaline urea aqueous solution was investigated. Among those examined, LiOH/urea/H₂O (8/12/80 wt%) exhibited the best solubility of cellulose; it dissolved all four cellulose almost completely. In

general, the higher the intrinsic viscosity of cellulose was, the lower the solubility of cellulose was. Vigorous mixing and keeping low temperature during mixing are important to attain high solubility.

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