

Preparation of Cellulose Derivatives in Alkaline Urea Aqueous Solvents

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The petroleum resources are supposed to run out in 50 years. Thus, 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 β -(1,4) glycoside bond and a system of well-organized hydrogen 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, 4-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°C ¹⁰⁾. 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. Further, in our recent work, wood pulp and cotton cellulose can also be dissolved in these alkaline/urea aqueous solution at low temperature and under high speed mixing¹²⁾.

The aim of present work is to investigate the preparation of some cellulose derivatives in alkaline urea aqueous solution whose dissolution procedure is almost same as these indicated in previous literature¹²⁾. Reactions of cellulose with sodium vinyl sulfonate and chloroacetic acid were investigated in these alkaline/urea aqueous solution mentioned above, that is to say, preparation of sulfoethyl cellulose and carboxymethyl cellulose was examined in the present study, as shown in Fig. 1.

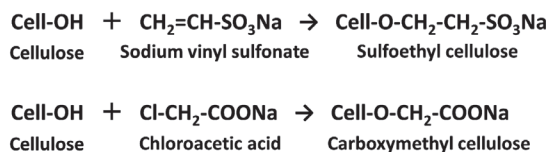


Fig. 1 Preparation scheme of sulfoethyl cellulose carboxymethyl cellulose

Experimental

Materials

Microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich Co., USA) and cotton cellulose (Daisan Co. Ltd, Japan) were commercially obtained and used without further purification. Instead, cotton cellulose was pulverized into small pieces by Wiley rotary cutter (Yoshida Seisakusho Co. Ltd, Japan) just before use. Sodium hydroxide, lithium

hydroxide, and urea were purchased and used as received.

Preparation of solution

Preparation method of cellulose solution is listed in Fig. 2 with the reference of the previous study¹²⁾.

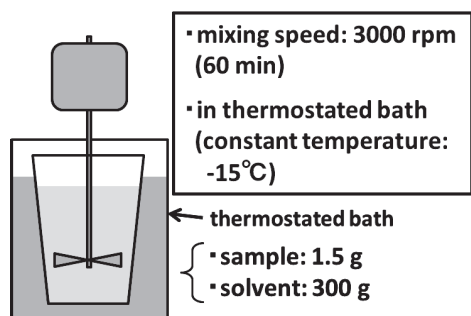


Fig. 2 Preparation method of cellulose solution in alkaline urea aqueous solvents

The alkaline urea aqueous solution with cellulose sample was cooled in thermostated bath at -15°C. Then, it was mixed for 60 min with special high-speed motor whose mixing speed is 3000 rpm. The solution temperature was kept constant; consequently, reproducibility was good.

Preparation of cellulose derivatives

In the case of preparation of sulfoethyl cellulose, sodium vinyl sulfonate was added to the solution of cellulose prepared as mentioned above, and treated at 75°C for 3 h under stirring. Then the reaction mixture was poured into large amount of methanol to precipitate the reaction product. The precipitate was separated by filtration, and dried under vacuum.

For the preparation of carboxymethyl cellulose, chloroacetic acid was added to the solution of cellulose prepared as mentioned above, and treated at 55°C for 5 h, under stirring. Then the reaction mixture was poured into large amount of methanol to precipitate the reaction product. The precipitate was separated by filtration, and dried under vacuum.

Structural analysis of cellulose derivatives

IR spectra of cellulose, sulfoethyl cellulose, carboxymethyl cellulose, and the reaction products in the present study were recorded on a HORIBA FT-710 spectrophotometer (KBr disk).

Results and Discussion

Preparation of sulfoethyl cellulose

Usually, preparation of sulfoethyl cellulose is carried out in alcoholic solvents such as isopropyl alcohol obtained from petroleum, which is one of representative exhaustive resources. Sulfoethyl cellulose thus obtained is soluble in water, so this cellulose derivative should be useful for many applications such as thickener, superabsorbent hydrogels, and medical use. In the present study, we have investigated the preparation of sulfoethyl cellulose in some alkaline urea aqueous solvents. The experimental results are shown in Table 1. Addition reaction of sodium vinyl sulfonate to hydroxyl group of cellulose proceeded judging from the weight of the reaction products. But the solubility of the reaction products in water was quite low, irrespective of the kind of alkaline (Table 1).

To investigate the reason for low solubility of the reaction products, we conducted FT-IR measurements for some samples. As shown in Fig. 3, IR spectra of the reaction products were quite different from those of cellulose and sulfoethyl cellulose prepared by the conventional method. The reason for this difference is not clear at present. More detailed investigation on the reaction condition is necessary to obtain water soluble reaction products.

Preparation of carboxymethyl cellulose

As is well known, carboxymethyl cellulose is one of representative water-soluble cellulose derivatives. Application field of carboxymethyl cellulose is quite wide; it is used as a viscosity modifier or thickener, and to stabilize emulsions in various food products. It is also used in non-food products such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, reusable heat packs, various paper

Table 1 Reaction of cellulose and sodium vinyl sulfonate in alkaline urea aqueous solvents

Alkaline in solvent	Reagents	Kind of Cellulose	Solvent (g)	Cellulose (g)	Product (g)	Water solubility
NaOH	CH ₂ =CH-SO ₃ Na	Pulverized cotton	80	0.4	1.08	×
LiOH			80	0.4	0.94	×

Composition of solvents : alkaline/urea/H₂O = 8/12/80wt%

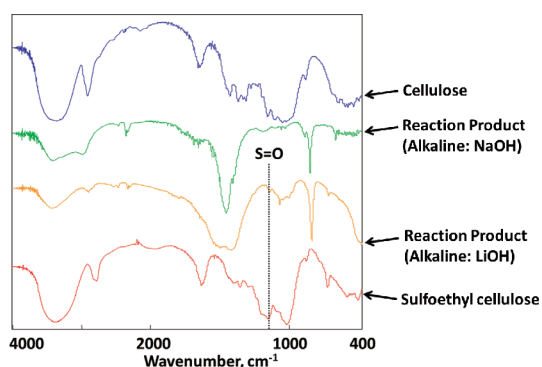


Fig. 3 FT-IR spectra of cellulose, reaction products, and sulfoethyl cellulose obtained by the conventional procedure

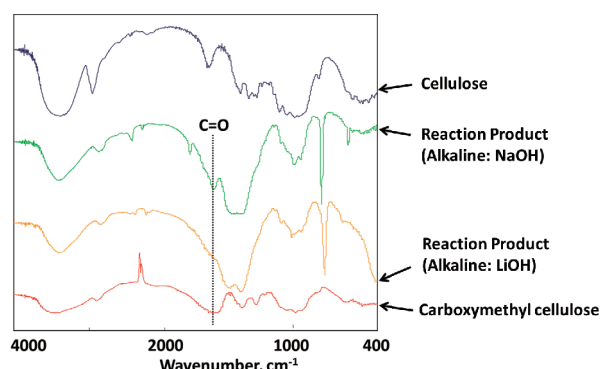


Fig. 4 FT-IR spectra of cellulose, reaction products, and carboxymethyl cellulose obtained by the conventional procedure

products, and so on.

Just like the case of sulfoethyl cellulose, preparation of carboxymethyl cellulose is usually performed in alcoholic solvents such as isopropyl alcohol. Here, the preparation of carboxymethyl cellulose in some alkaline urea aqueous solvents was examined. And the results are shown in Table 2. Two kinds of cellulose, pulverized cotton and microcrystalline cellulose were employed for starting materials. Reaction of chloroacetic acid to hydroxyl group of cellulose proceeded according to the weight of the reaction products. But the solubility of the reaction products in water was quite low, irrespective of the kind of cellulose and/or alkaline (Table 2).

To investigate the reason for low solubility of the reaction products, we conducted FT-IR measurements for some samples. As shown in Fig. 4, IR spectra of the reaction products were different from those of cellulose and carboxymethyl cellulose prepared by the conventional method. The reason for this difference is not clear at present also in this case. More detailed investigation on the reaction condition is necessary to obtain water soluble reaction products.

Summary

Preparation of some cellulose derivatives, that is to say, sulfoethyl cellulose and carboxymethyl cellulose was investigated in alkaline urea aqueous solvent. Reaction proceeded to some extent according to the weight of reaction products but solubility of them in water was quite low. IR spectra of reaction products were different from those obtained by conventional method, indicating chemical structure of the reaction products in the present study is not same as sulfoethyl cellulose and carboxymethyl cellulose. More extensive research on the reaction condition for preparation should be continue to achieve water-soluble reaction products in alkaline urea aqueous solvents, and that is on going.

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Table 2 Reaction of cellulose and chloroacetic acid in alkaline urea aqueous solvents

Alkaline in solvent	Reagents	Kind of Cellulose	Solvent (g)	Cellulose (g)	Product (g)	Water solubility
NaOH	Cl-CH ₂ -COOH	Pulverized cotton	300	3.0	4.21	×
LiOH			300	3.0	3.52	×
NaOH		Microcrystalline cellulose	300	3.0	5.15	×
LiOH			300	3.0	4.36	×

Composition of solvents : alkaline/urea/H₂O = 8/12/80wt%

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