The Mechanism of Cellulose Alkalization in the Isopropyl Alcohol–Water–Sodium Hydroxide–Cellulose System

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Synopsis

The mechanism of cellulose alkalization in isopropyl alcohol (IPA)–water–sodium hydroxide system was studied from the viewpoint of the selective distribution of sodium hydroxide between cellulose and the medium, and of the lattice transition of cellulose. A mixture of IPA, water, and sodium hydroxide spontaneously separates into two layers, i.e., the upper layer solution (ULS) consists of IPA, water, and a small amount of sodium hydroxide and the lower one (LLS) consists of sodium hydroxide, water, and a very small quantity of IPA. The role of the ULS and the LLS was distinctive. The ULS has a function to distribute sodium hydroxide with water in cellulose uniformly according to the distribution equilibrium between ULS and cellulose, and the ULS recovers sodium hydroxide with water from the LLS as the distribution equilibrium shifts in the alkalization of cellulose. The concentration of sodium hydroxide in the LLS and that of IPA in the ULS exerts an influence on the lattice structure of alkali cellulose. During the transformation from cellulose I to alkali cellulose, decrystallization does not occur. Some portion of alkali cellulose reverted to cellulose I by regeneration.

INTRODUCTION

Commercial production of cellulose ethers such as carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) are generally accomplished in nonaqueous media. Isopropyl alcohol (IPA) is the most popular solvent for the above medium. The effects of solvent on etherification were investigated by a number of authors.[1] However, only a few articles discussed alkalization in the medium containing organic diluent. Legrand et al.[2] and Jeffries et al.[3] studied the effect of alcohols on the formation of alkali cellulose, and Kuroiwa et al.[4] investigated the distribution of alkali to cellulose in organic solvents; but none of them referred to the mechanism of distribution of reagents in cellulose or of alkalization of cellulose in the presence of organic diluents.

When IPA is used as the organic diluent, alkalization of cellulose is carried out in IPA–water–sodium hydroxide medium. After mixing the medium and on standing, it separates into two layers of a volume ratio according to their solubility curve (Fig. 1). The upper layer solution (ULS) consists of IPA, water, and a very small amount of sodium hydroxide, while the lower layer solution (LLS) consists of sodium hydroxide, water, and a
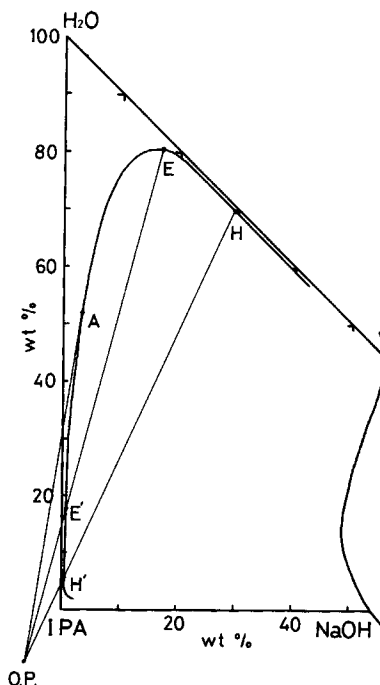
Fig. 1. Solubility curve of the three components of IPA, water, and sodium hydroxide (at 15°C). (A) plait point; (EE', HH', etc.) tie line; (O.P.) operating point; the codes of A, ---, H, — and H' correspond to those of Table I.

very small quantity of IPA. Although LLS of the mixture is in the form of droplets dispersed in a large volume of ULS under stirring during commercial production, we can discuss the contribution to the alkalization of cellulose by each layer solution separately.

The LLS is a concentrated solution of sodium hydroxide, and, therefore, it may have the ability to convert cellulose to alkali cellulose without participation of the ULS. A question arose from the fact that, in CMC or HEC production conditions, the quantity of the LLS is too small to immerse all of the cellulose fibers in it, i.e., the weight ratio of the LLS to cellulose is

TABLE I

Tie-Line Data of Liquid–Liquid Equilibrium of IPA–H_2O–NaOH System (at 15°C, wt %)

	Upper layer solution				Lower layer solution		
	IPA	H_2O	NaOH		IPA	H_2O	NaOH
A'[a]	45.5	52.0	2.5	A[a]	45.5	52.0	2.5
B'	58.8	39.9	1.3	B	27.6	66.6	5.8
C'	68.80	30.55	0.65	C	11.3	79.5	9.3
D'	74.50	25.05	0.45	D	8.7	80.3	11.0
E'	81.77	18.00	0.23	E	2.8	80.5	16.7
F'	86.00	13.84	0.16	F	1.2	79.4	19.4
G'	89.43	10.45	0.12	G	1.0	76.5	22.5
H'	94.70	5.20	0.10	H	0.9	70.1	29.0

[a] Plait point.

only about 2 or 3. If alkalization takes place only between cellulose and LLS, formation of uniform alkalized cellulose under such conditions cannot be explained.

The purpose of the present work is to elucidate the role of each layer, i.e., the ULS is not only a diluent medium but also an alkalization reagent to cellulose, and the LLS is the alkali supplier to the ULS. Another consideration of this work is to discuss the conversion mechanism from cellulose I (Cell I) to alkali cellulose (Na–Cell) and to cellulose II (Cell II) by regeneration. The x-ray diffraction data are extensively used for the study of the mechanism.

EXPERIMENTAL

Materials

Ether-grade cotton linters (Hercules, Inc., ES-4,000) cut through 0.5 mm ϕ screen of cutting mill were used for cellulose material. The moisture content of the cut cotton linters was about 5%. All other chemicals used were standard reagent grade. Deionized water was used throughout this study.

Solubility Curve

The solubility curve of the three component system of IPA, water, and sodium hydroxide was obtained by the following method. Eighteen kinds of three-component systems having different composition were shaken in separatory funnels and stood overnight at 15°C. The compositions of ULS and LLS formed in each system were analyzed by gas chromatography for IPA, by Karl–Fisher titration method for water, and by acidimetry for sodium hydroxide. The solubility curve and some tie line data are shown in Figure 1 and Table I.

Tests of Alkalization of Cellulose

Cotton linters were treated in various kinds of solutions containing sodium hydroxide for alkalization, where the temperature of alkalization was 15–20°C. X-ray diffraction analysis on alkalized cellulose was studied throughout this experiment.

Alkalization with ULS Composition. Alkalization reaction in a very dilute solution of sodium hydroxide corresponding to a ULS composition was carried out for 24 h in a separable flask with agitator. In the first test, cotton linters were treated in a homogeneous solution such as E′ and H′ in Table I with various ratios of solution to cellulose, from 300 to 3000 by weight, in order to demonstrate that the reaction proceeds even with a small concentration of sodium hydroxide (Figs. 3–5). In the second test, cotton linters were alkalized with a solution corresponding to the ULS composition (Table I as A′, B′, . . ., H′) with the weight ratio of solution to cellulose being 4000. The x-ray structure was compared for the obtained alkalized cellulose with that in a solution of LLS composition and in an aqueous solution of sodium hydroxide (Fig. 6).
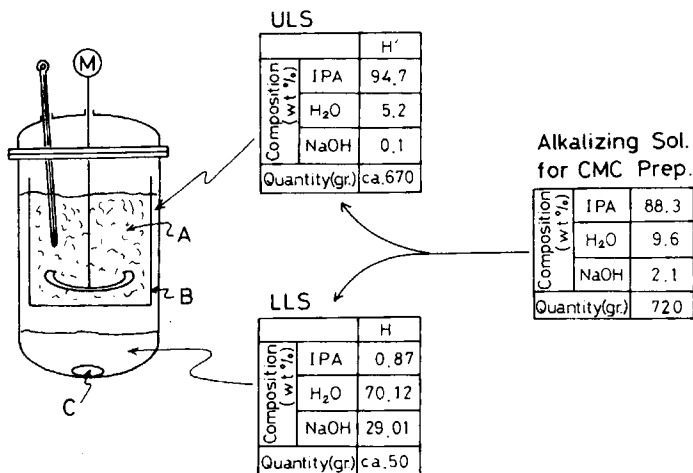
Fig. 2. Equipment for alkalization of cellulose in ULS coexisting with LLS underneath and the compositions of the solutions. The codes H and H' correspond to those of Table I. (A) cotton linters; (B) basket made of 200-mesh wire gauze (stainless steel); (C) stirrer chip.

Alkalization with LLS Composition and in Aqueous Solution of Sodium Hydroxide.

Homogeneous solutions corresponding to the LLS composition (Table I as A, B, . . ., H) were prepared. Alkalization of cellulose in a solution of LLS composition and in a 10–27 wt % concd aqueous solution of sodium hydroxide was also carried out in the same manner mentioned before except that the liquid ratio to cellulose was 500 by weight since all solutions contain plenty of sodium hydroxide (Figs. 7 and 8).

Alkalization in ULS Coexisting with LLS. The time-course alkalization study up to 100 h was carried out in the ULS coexisting with the LLS underneath while the cotton linters were retained in the ULS by using specially designed equipment (Fig. 2). Separate batch treatment was carried out for every designated time. The composition and the quantity of the solution employed are also shown in Figure 2 (Figs. 9–11).
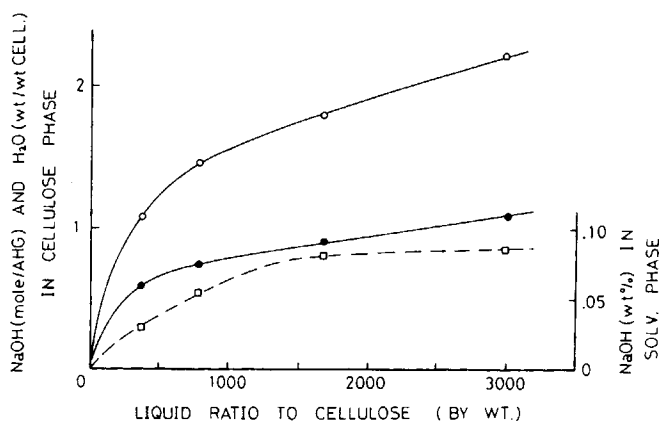

Fig. 3. Effect of the ratio of a solution of ULS composition to cellulose on the quantities of sodium hydroxide (○) and water (●) in cellulose phase, and on the concentration of sodium hydroxide (□) in solvent phase (ULS composition: H' in Table I).
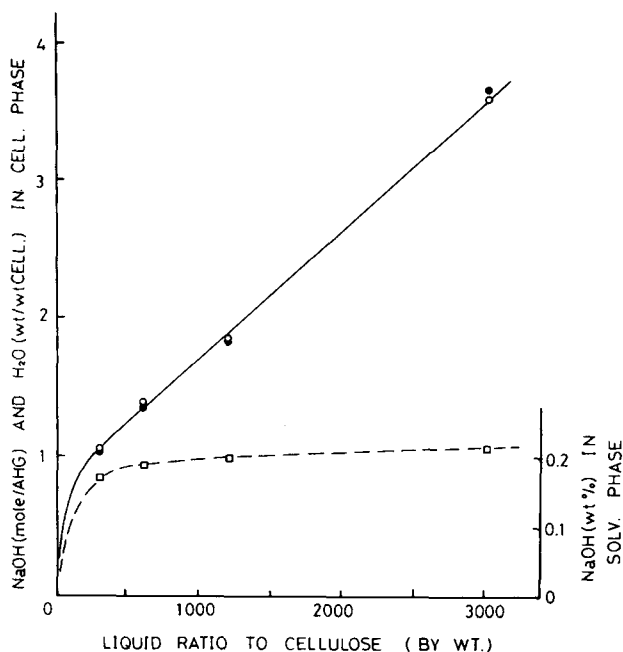
Fig. 4. Effect of the ratio of a solution of ULS composition to cellulose on the quantities of sodium hydroxide (○) and water (●) in cellulose phase, and on the concentration of sodium hydroxide (□) in solvent phase (ULS composition: E′ in Table I).

Alkalization under a Condition of CMC Preparation in Slurry Method.
Mixture of four components of IPA, water, sodium hydroxide, and cellulose were vigorously agitated in a separable flask at room temperature for 1 h under the condition described in the note in Figure 2 corresponding to that of CMC preparation. The ratio of medium to cellulose is about 35.

Preparation of CMC. After the alkalization was carried out, a designated amount of monochloroacetic acid was added and heated for 1 h at 70°C. The
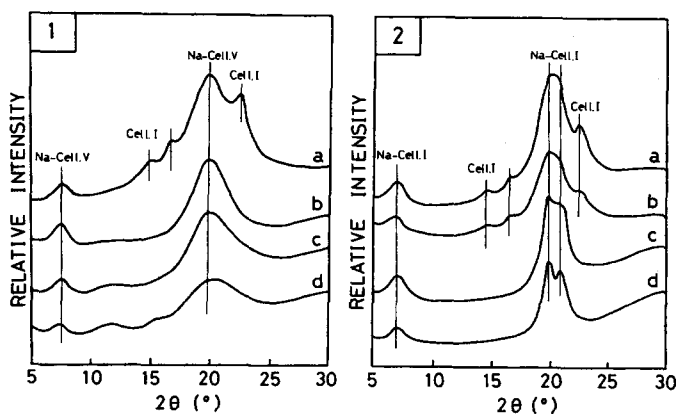

Fig. 5. X-ray diffractograms of alkalized cellulose prepared in various amounts of solution of ULS composition. □ ULS composition: H′ in Table I; liquid ratio to cellulose: (a) 380; (b) 780; (c) 1680; (d) 3000. ☑ ULS composition: E′ in Table I; liquid ratio to cellulose: (a) 300; (b) 600; (c) 1200; (d) 3000.
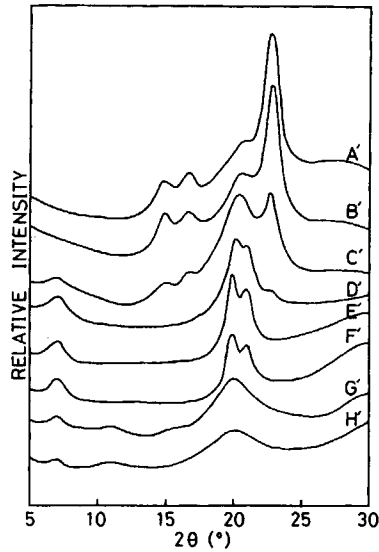
Fig. 6. X-ray diffractograms of alkalized cellulose prepared in various solutions of ULS composition. Compositions of the solutions are shown in Table I with the same codes as are used here.

excess quantity of sodium hydroxide was neutralized with acetic acid and the product was purified by washing in a 75 wt % aqueous methanol solution. After centrifugation, the CMC was dried overnight at 60°C.

Analysis

After alkalization for a designated period, quantities of sodium hydroxide and water, present in the cellulose phase, were analyzed as follows. The
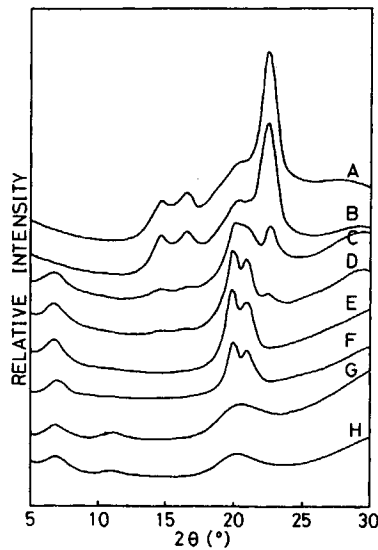

Fig. 7. X-ray diffractograms of alkalized cellulose prepared in various solutions of LLS composition. Compositions of the solutions are shown in Table I with the same codes as are used here.
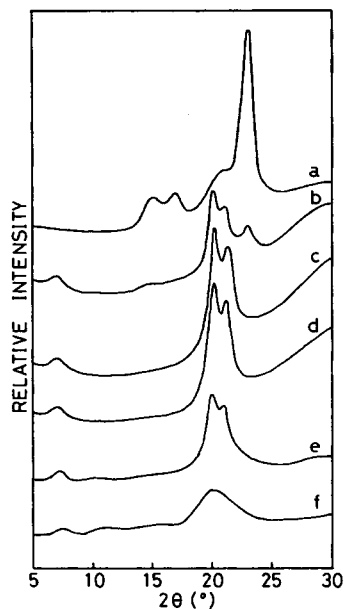
Fig. 8. X-ray diffractograms of alkalized cellulose prepared in various concentration of aqueous solutions of sodium hydroxide. Concentration of sodium hydroxide (wt %): (a) 10; (b) 12; (c) 14; (d) 16; (e) 21; (f) 27.

alkalized cellulose slurry was filtered through a glass filter. A portion of the drained-off sample was suspended in water and analyzed for sodium hydroxide by acidmetry. Another portion of the sample was suspended in dehydrated IPA and analyzed for water content by Karl–Fisher titration. The quantity of cellulose was determined in the form of regenerated cel-
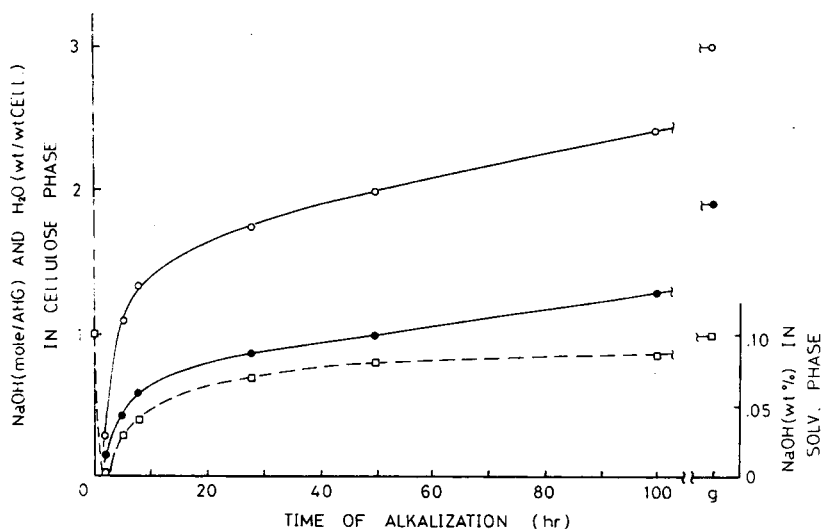

Fig. 9. Relationship between the time of alkalization and the quantities of sodium hydroxide (○) and water (●) in cellulose phase and the concentration of sodium hydroxide (□) in solvent phase under the alkalization of cellulose with ULS coexistence of LLS in equilibrium state. Point g on the horizontal line refers to alkalization reaction under vigorous agitation for 1 h.
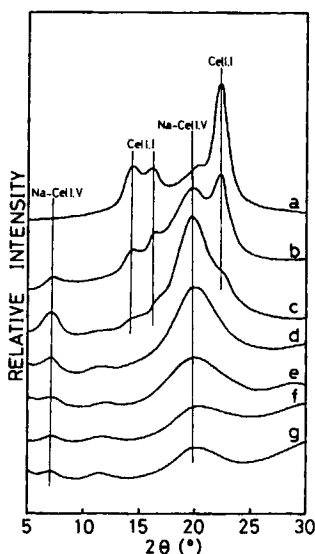
Fig. 10. X-ray diffractograms of alkalized cellulose prepared in ULS coexistence of LLS underneath for various times. Compositions of the ULS and the LLS are shown as H' and H in Table I. Time of alkalization (h): (a) 2; (b) 5.5; (c) 8; (d) 28; (e) 50; (f) 100; (g) vigorous agitation for 1 h.

lulose. Alkalized sample was washed in water, poured into a dilute solution of acetic acid, washed in water again and then in a very dilute solution of ammonium hydroxide, and finally washed in water and oven-dried at 105°C for 5 h. Concentration of sodium hydroxide and water in the filtrate was also analyzed.

X-Ray Examinations

Nickel-filtered CuK_α radiation from a Rigaku Denki KOT-130B Unit operated at 40 kV and 30 mA was used. Diffractometer technique was employed with a goniometer having geometry as follows: divergence slit, 0.5; receiving slit, 0.15; scatter slit, 0.5.

The wet specimen of alkali cellulose inserted in two pieces of cellulose nitrate thin film was used for measurement. Regenerated cellulose sample obtained from alkalized cellulose by the same method described in the Analytical Section was cut through 60-mesh sieve and subjected to x-ray measurement in powder form. The contents of Cell I and II in the regenerated cellulose were calculated according to Rånby's method[5] from x-ray diffractogram.

RESULTS AND DISCUSSION

Alkalization of Cellulose with ULS Composition

Sodium hydroxide content in the ULS of production CMC or HEC is only 0.1–0.2 wt %. The quantity of the ULS is 15–35 times that of cellulose by weight. Therefore, even if all of the sodium hydroxide were distributed to cellulose under treatment with ULS without coexistence of LLS, the molar
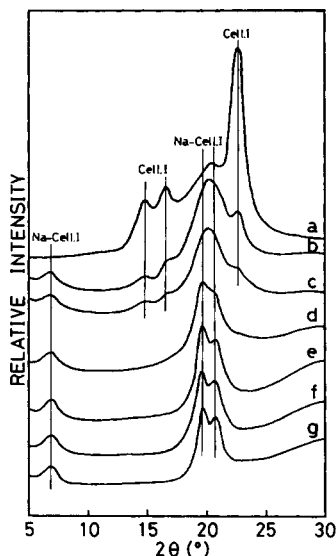
Fig. 11. X-ray diffractograms of alkalized cellulose prepared in ULS coexistence of LLS underneath for various times. Compositions of the ULS and the LLS are shown as E' and E in Table I. Time of alkalization (h): (a) 2; (b) 7; (c) 10; (d) 20; (e) 40; (f) 80; (g) vigorous agitation for 1h.

ratio of sodium hydroxide to cellulose would be a maximum of 0.28. This value is far below the calculated value of composition of alkali cellulose such as $C_6H_{10}O_5 \cdot NaOH \cdot 3H_2O$ of Na–Cell I, $C_6H_{10}O_5 \cdot NaOH \cdot H_2O$ of Na–Cell II. On the other hand, if cellulose is alkalized with larger amounts of the ULS solution so as to involve enough sodium hydroxide, the quantity of sodium hydroxide in cellulose phase would be sufficient for the formation of alkali cellulose.

The experiment was carried out to confirm the assumption mentioned above. The compositions of the ULSs which were employed for treatment
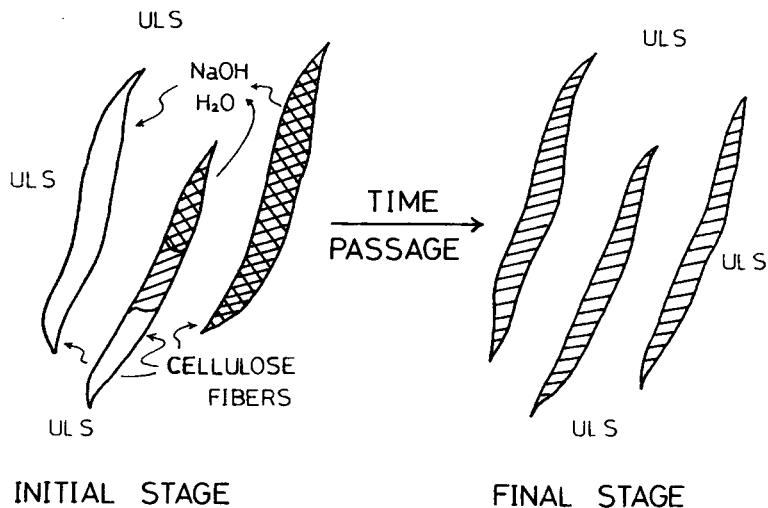

Fig. 12. Schematic diagram showing the redistribution of NaOH into cellulose phase via ULS during non- (□), less (▨), and excessively (▧) distributed regions.
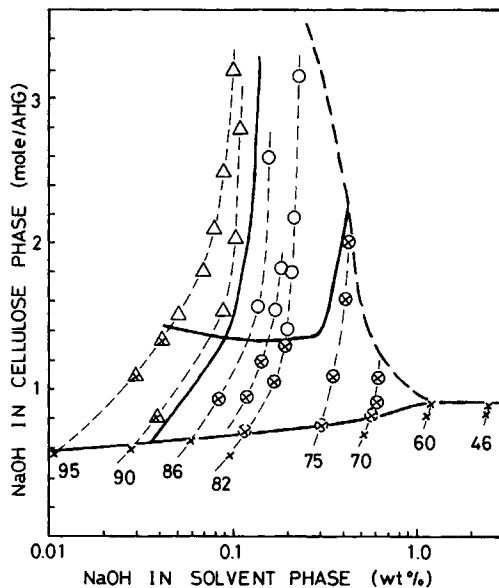
Fig. 13.   Distribution equilibrium curve of NaOH and phase diagram of alkali cellulose in
IPA–H$_2$O–NaOH–cellulose system: (–) distrib. eq. curve; (——) boundary of phase diag.; (○)
Na-Cell I; (△) Na-Cell V; (⊗) Na–Cell I + Cell I, (△) Na-Cell V + Cell I; (×) Cell I. Parameter:
conc of IPA in solvent phase (wt %).

of cellulose are shown in rows H', and E' of Table I. The compositions of
H' and E' correspond to those of the ULSs of production CMC and HEC,
respectively. Figure 3 illustrates the effect of the ratio of the solution of
ULS composition (H') to cellulose on the quantities of sodium hydroxide (○)
and water (●) distributed in the cellulose phase. The concentration of sodium
hydroxide in the solvent phase (□), i.e., in the filtrate is also plotted.

The larger the liquid ratio to cellulose, the more sodium hydroxide and
water are distributed in cellulose. The quantity of sodium hydroxide in
cellulose phase is a little over 1 mol/AHG (anhydroglucose) residue in case
of the liquid ratio to cellulose being 500 and over 2 mol/AHG residue in
the case of 3000. The concentration of sodium hydroxide in solvent phase
decreased after distribution of initial ULS composition, 0.1 wt %. This
results from the fact that sodium hydroxide in the solution of ULS com-
position has been selectively distributed to cellulose. As the ratio of ULS
composition to cellulose becomes higher, the phenomenon of selective dis-
tribution has a small influence on the concentration of sodium hydroxide.

A pair of values on the two curves of the quantity of sodium hydroxide
in cellulose phase (○) and the concentration of sodium hydroxide in solvent
phase (□) at the same distance from the vertical axis represents the values
of the distribution equilibrium of sodium hydroxide in the IPA–water–so-
dium hydroxide–cellulose system. A similar result was achieved in the ex-
periment on the solution of ULS composition E' (Fig. 4).

X-ray diffractograms (Fig. 5) show that partially alkalized cellulose is
formed when sodium hydroxide is distributed to cellulose from the medium
of relatively lower liquid ratio, and that alkali cellulose in high conversion
is formed as the liquid ratio to cellulose becomes higher.

The solution of ULS composition, in which sodium hydroxide contained only 0.1 or 0.2 wt %, had the ability to convert cellulose to alkali cellulose provided that the liquid ratio was high. The reason why alkali cellulose can be formed in such a dilute solution of sodium hydroxide as ULS composition is that the concentrated (aqueous) solution of sodium hydroxide is formed in the cellulose phase by selective distribution of sodium hydroxide with water to cellulose. Another interesting observation is that the different composition of ULS (E' and H') influences the structure of alkali cellulose. Different types of alkali cellulose are obtained and were identified as Na–Cell V (Fig. 5 ①) and Na-Cell I (Fig. 5 ②).

Comparison of Alkali Cellulose Structure between Samples Prepared with ULS and LLS Compositions

Although ULS plays a dominant role in alkalization of cellulose, we would like to know how LLS acts if the amount of LLS is sufficient to immerse cellulose fiber. The x-ray structure of alkali cellulose prepared in both ULS and LLS solutions (Table I) was compared.

Figures 6 and 7 show the x-ray diffractograms of the alkali celluloses. Alkali cellulose is not formed in the solution of plait point composition (A' of Fig. 6 and A of Fig. 7). Concerning the solutions of ULS and LLS com- position, whether cellulose is converted to partially alkalized cellulose or to total alkali cellulose depends on how high the concentration of sodium hydroxide is in LLS composition (Fig. 7), and how high the concentration of IPA is in ULS composition (Fig. 6). The same structural alkali cellulose (or partially alkalized cellulose) is formed, though the alkali cellulose is obtained in ULS or in LLS independently, in a set of solutions of ULS and LLS composition which are in liquid–liquid equilibrium. (The codes in Fig. 6 and 7 correspond to those of Table I, e.g., the x-ray diffractogram E' in Fig. 6 means the diffractogram of alkali cellulose formed in the solution of ULS composition E' in Table I.)

The reason why the same structural alkali cellulose is formed is due to the same composition of concentrated (aqueous) solution of sodium hydroxide in the cellulose phase. For comparison, x-ray diffractograms of alkali cellulose prepared in various concentrations of aqueous solutions of sodium hydroxide were taken (Fig. 8). The relation between the concentration of sodium hydroxide and the x-ray structure of alkali cellulose in case of the solution of LLS compositon shows fairly good agreement to that in case of aqueous solution of sodium hydroxide in the range of 11–12 wt % of sodium hydroxide (Figs. 7 and 8). Below 11–12 wt %, partially alkalized cellulose is formed. There is a tendency for the degree of conversion to alkali cellulose in the solution of LLS composition to be higher than that in aqueous sodium hydroxide at the same level of concentration.

The polymorphic structure of alkali cellulose was studied[6] extensively in terms of the alkalization of cellulose in aqueous sodium hydroxide. There- fore, the identification of the polymorphic structure of alkali cellulose formed in the solution of ULS and LLS can be discussed with reference to the literature.[6] Na-Cell I is formed in the solution of LLS below about 20 wt % of sodium hydroxide and in the solution of ULS below about 86 wt

% of IPA. Na–Cell V is formed in the solution of LLS over 20–21 wt % of sodium hydroxide and in the solution of ULS over 89 wt % of IPA.

Treatment of Cellulose with ULS Coexisting with LLS in Equilibrium State

The experimental results under the condition described (Fig. 2), which is for CMC production, are shown in Figures 9 and 10. The quantities of sodium hydroxide and water distributed in the cellulose phase increase (Fig. 9) and the formation of Na–Cell V proceeds (Fig. 10) with an increase in time. The concentration of sodium hydroxide in ULS, i.e., in solvent phase decreases in the initial stage of treatment and subsequently increases (Fig. 9). The behavior of sodium hydroxide in ULS will be discussed later. Beyond 100 h, the quantity of sodium hydroxide and water in cellulose phase and the concentration of sodium hydroxide in ULS reach the values attained by vigorous agitation of the system, i.e., in the case of alkalization of cellulose under a condition of CMC preparation by the slurry method (Fig. 9).

The distribution of sodium hydroxide to cellulose and the process of alkalization of cellulose in such a system (Fig. 2) are possibly explained as follows:

Step 1: When cellulose is added to ULS, sodium hydroxide is selectively absorbed by cellulose which causes a decrease in the concentration of sodium hydroxide in the ULS. A distribution equilibrium is reached for the four component system, i.e., IPA–water–sodium hydroxide–cellulose system. Alkalization occurs after equilibrium is obtained. As the ratio of ULS to cellulose is small, the quantity of sodium hydroxide distributed in the cellulose phase is not enough to convert cellulose to alkali cellulose at the initial stage.

Step 2: The liquid–liquid equilibrium state between ULS and LLS is broken because sodium hydroxide and water in the former decrease in concentration due to absorption by cellulose. LLS supplies both components to ULS to form a new equilibrium state.

Step 3: With the recovery of the equilibrium state, more sodium hydroxide and water are distributed in the cellulose phase to attain a newer distribution equilibrium in the four-component system. The cellulose is gradually converted to alkali cellulose. Until all of the LLS moves into the cellulose phase via the ULS, steps 2 and 3 follow on repeatedly, and then alkalization is completed.

The ULS has a function to distribute the alkalizing agents to cellulose uniformly according to the distribution equilibrium between ULS and cellulose; and the LLS is the source of sodium hydroxide and water to cellulose via the ULS.

The x-ray diffractograms (Fig. 11) are the result of the same type of experiment in another set of ULS and LLS, i.e., solutions of E' and E (Table I). The very similar result was achieved in terms of the distribution behavior of sodium hydroxide and the conversion process to alkali cellulose. In the case of solutions of E' and E, Na–Cell I is formed in the same manner as shown in former sections.

During the transformation from Cell I to either Na–Cell I or Na–Cell V, the conversion proceeds without decrystallization, i.e., the transformation is occurred from Cell I crystalline phase to Na–Cell without passage through an intermediate decrystallized amorphous stage. The crystal structure of both Cell I and Na–Cell are simultaneously present during the intermediate stage of conversion. One probable explanation of alkalization mechanism is as follows: Sodium hydroxide and water are distributed to the regions of amorphous, poorly ordered and/ or the smaller crystallites of Cell I and convert them to crystalline Na–Cell. And later well-formed crystallites are converted to Na–Cell, probably by some type of surface reaction.

Alkalization Mechanism in the IPA–Water–Sodium Hydroxide–Cellulose System

During the alkalization treatment in commercial cellulose ethers, the IPA–water–sodium hydroxide–cellulose system is stirred vigorously, and, therefore, the alkalization mechanism proceeds as follows:

Step 1: Under the vigorous agitation, the fine droplets of the LLS are suspended in the ULS.

Step 2: When cellulose is added to the above-mentioned solution, droplets of LLS which have a high affinity to cellulose are instantaneously distributed in the cellulose phase (Fig. 12, left).

Step 3: Sodium hydroxide and water move from the excessively distributed regions to the less or nondistributed regions of the cellulose phase by mediation of ULS, in which cellulose is suspended, according to the distribution equilibrium between ULS and cellulose. And finally uniform alkali cellulose is formed (Fig. 12, right).

It is very difficult to confirm the mechanism mentioned above by direct experiments, because it is impossible to carry out the time-course analysis of individual fibers in terms of the distribution quantities of sodium hydroxide and water and in terms of the structural change of cellulose. Considering the above, CMC was prepared by a modified method in order to offer an indirect proof of the mechanism. At first, a half of the regular quantity of cellulose was alkalized with a regular quantity of sodium hydroxide for one hour. (It was confirmed by analysis that at this time almost all the soldium hydroxide in the system was distributed in the cellulose phase.) And then the other half of cellulose was added and the system was stirred for more than 1 h. Carboxymethylation was then carried out as described in the Experimental section. The solution quality and performance properties of the product were uniform. Consequently, it is reasonable to think that uniform alkali cellulose is formed by the redistribution mechanism mentioned above and shown schematically (Fig. 12).

Distribution Equilibrium Curve of Sodium Hydroxide in IPA–Water–Sodium Hydroxide–Cellulose System and Phase Diagram of Alkali Cellulose

Figure 13 summarizes the results obtained in terms of the distribution of sodium hydroxide and the lattice transition of cellulose in IPA-water-sodium hydroxide-cellulose system. The quantity of sodium hydroxide dis-

tributed in the cellulose phase is plotted logarithmically against the concentration of sodium hydroxide in the solvent phase. The marks of circle, triangle, and so forth show the experimentally measured data of above-mentioned quantities according to the type of alkali cellulose. Thus the fine break lines are the distribution equilibrium curves of sodium hydroxide in IPA–water–sodium hydroxide–cellulose system. The numerals near the lines mean the concentration of IPA in solvent phase. The solid lines show the boundary of two kinds of alkali cellulose, cellulose, and their mixtures. The heavy break line means the maximum quantities of sodium hydroxide which could be distributed in the cellulose phase.

There is a boundary at a little less than 90 wt % of IPA in terms of the type of Na–Cell, i.e., Ca–Cell I and Na–Cell V. In the range of 60–75 wt % of IPA cellulose is not fully alkalized, because the concentration of (aqueous) solution of sodium hydroxide formed in the cellulose phase is relatively low. In 46–60 wt % of IPA, no alkalization occurred. Even if the concentration of IPA is over 75 wt % in the lower concentration range of sodium hydroxide in each IPA aqueous solution, the quantity of sodium hydroxide distributed in the cellulose phase is not enough to form Na–Cell completely; so there occurred partial or no alkalization.

Regeneration of Cellulose from Alkalized Cellulose

Some portions of Na–Cell revert to Cell I after neutralization. The calculated data of Cell II content of regenerated cellulose from alkalized cellulose shown (Figs. 10 and 11) are listed in Table II. X-ray diffractogram b (Fig. 10) shows the well-defined existence of Na–Cell, but Cell II is scarcely formed by regeneration (b of Table IIA). Alkalized cellulose containing a small amount of residual Cell I (e.g., c in Fig. 10, b and c in Fig. 11) regenerates a large amount of Cell I (c in Table IIA, b and c in Table IIB). Alkali cellulose (g in Fig. 10), containing no trace of Cell I, cannot convert to Cell II completely (g in Table IIA).

Hayashi et al.[7] explain the formation of Cell I from Na–Cell I by two types of Na–Cell I existing, i.e., Na-Cell I_I (Cell I type conformation, retransformation to Cell I) and Na-Cell I_{II} (Cell II type conformation, transformation to Cell II). Na–Cell I_I has a tendency to form without passing the

TABLE IIA
Cell II Content of Regenerated Cellulose from Alkalized Cellulose in Figure 10 (%)

Sample code[a]	a	b	c	d	e	f	g
Cell II content of regenerated cellulose	0	3	20	50	61	68	85

[a] The sample codes correspond to those in Figure 10.

TABLE IIB
Cell II Content of Regenerated Cellulose from Alkalized Cellulose in Figure 11 (%)

Sample code[b]	a	b	c	d	e	f	g
Cell II content of regenerated cellulose	0	35	44	75	89	100	100

[b] The sample codes correspond to those in Figure 11.

stage of full hydration of the cellulose chain, i.e., decreased swelling as in fixed length alkalization of high crystalline cellulose. When Na–Cell I_I is regenerated under lower swelling condition, crystallite of cellulose is formed without passing the stage of hydration of the cellulose chain and the chain conformation maintains the Cell I type: then Cell I is regenerated.

In the case of hereto mentioned alkalization in the IPA system, IPA acts as a kind of swelling restrictive agent to cellulose. Therefore, alkalization and regeneration are carried out under the lower swelling condition especially in higher concentration of IPA and as a result there occurs a tendency of Cell I to be formed; here it is assumed that there exists Na–Cell V_I, which has the Cell I type conformation as well as Na–Cell I_I.

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