

Alkalization Mechanism of Cellulose in Hydroxypropylcellulose Preparation Process

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Synopsis

The role of alkali treatment of cellulose in hydroxypropylcellulose (HPC) preparation has been studied from the viewpoint of the selective distribution of sodium hydroxide between HPC and cellulose phases. Generally it is considered to be important to prepare uniform alkali cellulose, whose calculated value of composition is $C_6H_{10}O_5 \cdot NaOH \cdot x H_2O$, prior to etherification of cellulose. Therefore, enough alkali to obtain alkali cellulose is used by major manufacturers of cellulose ethers. However, HPC having good solution qualities and performance properties can be prepared even from partially alkalized cellulose by using 0.2–0.4 molar sodium hydroxide per anhydroglucose unit. The results obtained from a series of experiments indicate the following mechanism for the formation of HPC. Hydroxypropylation is initiated in the alkalized portion of cellulose if such portion and propylene oxide are present together. As the hydroxypropylation proceeds, the liberated sodium hydroxide in HPC phase migrates into the cellulose phase due to the shift of distribution equilibrium of sodium hydroxide; the above tendency is enhanced by byproducts such as propyleneglycol. Some newly alkalized portions are present and hydroxypropylation follows. These processes are repeated, and then all portions of cellulose are alkalized and hydroxypropylated.

INTRODUCTION

Cellulose ethers are prepared by reaction of etherizing reagents with alkali cellulose; alkali cellulose is formed by reacting cellulose with sodium hydroxide. The presence of fine structures in the cellulose fiber requires precise control of the alkali cellulose formation. Nonuniformity can cause major problems in solution quality and performance properties of the products.

A concentrated aqueous solution of sodium hydroxide or a solution system consisting of organic solvent, water, and sodium hydroxide is used for the preparation of alkali cellulose whose calculated value of composition is $C_6H_{10}O_5 \cdot NaOH \cdot xH_2O$. These solution systems contain enough sodium hydroxide to produce the alkali cellulose.

There are several basic patents¹⁻⁵ concerning the preparation of hydroxypropylcellulose (HPC). From the standpoint of the alkalization of cellulose, a very interesting HPC preparation method⁴ is reported in a patent; Cellulose is treated with only 0.2–0.4 molar sodium hydroxide per anhydroglucose unit (AHGU), the amount of which is far less than required to prepare the alkali cellulose. HPC with good solution and performance properties can be prepared by this method. The use of such a small quantity of sodium hydroxide results in control of side reaction, and therefore the yield of hydroxypropylcellulose is increased.

In our tracing experiments to the patent,⁴ it was found that the changes

occurred in the X-ray diffraction pattern as the hydroxypropylation proceeds from that of the original cellulosic material (cellulose I crystal form), to HPC.⁶ It was observed microscopically that the hydroxypropylation proceeds with noticeable interfibrous heterogeneity.⁶ Furthermore the HPC with MS=3 obtained by this method dissolved in water, methyl alcohol, ethyl alcohol, and neither micro gels nor free fibers were observed. (MS is defined as the total number of molecules of propylene oxide that have combined with the original cellulose per AHGU.)

Cellulose ethers such as carboxymethylcellulose (CMC) or hydroxyethylcellulose (HEC), being soluble in water or alkali solution can be obtained only when cellulose alkalization is carried out with the use of enough sodium hydroxide to form uniform alkali cellulose. Needless to say, HPC can also be prepared by using sodium hydroxide as in the case of CMC or HEC.

The hydroxypropylation of cellulose by using a little sodium hydroxide is very unique and draws our interest to the following points.

1. Is it possible that alkali cellulose is formed even partially in this case?
2. If alkali cellulose is formed partially, what is the mechanism of hydroxypropylation of nonalkalized portion of cellulose?
3. If alkali cellulose is not formed at all, it can be said that hydroxypropylation of cellulose proceeds without alkalization of cellulose prior to etherification; is the function of alkali only as a catalyst for etherification of cellulose?

Even though these questions are very important to explain the mechanism of cellulose etherification, no answers were given in preceding articles. The purpose of the present work is to elucidate the behavior and the role of alkali on the course of the hydroxypropylation of cellulose.

EXPERIMENTAL

Materials

Ether-grade cotton linters 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%. HPC used was the commercial product, grade H, of Nihon Soda Co., Ltd. All other chemicals used were standard reagent grade. Deionized water was used throughout this study.

Distribution of Sodium Hydroxide in Solution System for HPC Preparation

Each component of the solution system employed for this study, the composition of which is shown in Tables I and II, was weighed out in a Erlenmeyer flask and stood overnight at room temperature to attain distribution equilibrium after being shaken occasionally for 1 h. The concentration of sodium hydroxide in both upper and lower layer solutions was determined by acidimetry.

TABLE I
 Solution System for Alkali Treatment in HPC Preparation and the Concentration of Sodium Hydroxide in Upper and Lower Layer Solutions

Run no.	1	2 ^b	3	4	5
NaOH in solution system ^a (mol/AHGU)	0.2	0.4	0.6	1.0	1.4
NaOH in upper layer solution (wt%)	0	0	0	0	0
NaOH in lower layer solution (wt%)	15.2	22.3	26.2	35.9	41.6

^a *tert*-Butylalcohol 50; toluene 190; water 9; sodium hydroxide 1, 2, 3, 5, 7; (cellulose 20); (parts by wt.).

^b Standard composition in this study.

TABLE II
Change of the Sodium Hydroxide Distribution in Upper and Lower Layer Solutions by
Addition of Propyleneglycol

Run no.	2	6	7	8
Propyleneglycol (wt%) ^a	0	2	4	6
NaOH in upper layer solution (wt%)	0	0.02	0.02	0.03
NaOH in lower layer solution (wt%)	22.3	17.6	14.2	10.1

^a Weight percent to the solution system [*tert*-butylalcohol 50, toluene 190, water 9, sodium hydroxide 2 (parts by weight)].

Alkali Treatment of Cellulose in Solution System for HPC Preparation

A 20-g portion of cotton linters was treated with the solution systems (Table I), for 1 h at 20°C with stirring in a three-neck flask. The slurry was filtered through a glass filter and the residue was subjected to X-ray diffraction measurement to determine if alkali cellulose was formed. Some portions of the residue were washed several times by agitation first in methyl alcohol and later in deionized water until the filtrate had the same pH as the deionized water. The residue was oven dried and subjected to X-ray diffraction measurement to determine if cellulose II was formed.

Acetylation of Cellulose Regenerated After Alkali Treatment and of Partially Hydroxypropylated Cellulose

Acetylation procedure was applied to the samples in which alkali cellulose formation was not confirmed by X-ray diffraction. This was to re-examine if alkali cellulose was not truly formed even with a little portion, because dried mercerized cellulose is relatively inert to acetylation.

A 10-g portion of the regenerated cellulose or partially hydroxypropylated cellulose was soaked in 50 g of acetic acid at room temperature for 1 h, centrifuged off to about three times by weight, and then 200 g of mixed acid (acetic anhydride 40, acetic acid 60 parts by volume; sulfuric acid 0.54 N in acetic anhydride) was added. The esterification was carried out at 30°C for 2.5 h.

Distribution of Sodium Hydroxide in HPC and Cellulose Phases in Solution System for HPC Preparation

In Case of HPC or Cellulose Individually in Solution System. Various quantities of HPC or cellulose were placed in a three-neck flask containing 150 g of the solution (Table II, Run numbers 2 and 8). The slurry was stirred for 6 h at 65°C (mean temperature of the hydroxypropylation of cellulose) to attain the distribution equilibrium, and was filtered through a glass filter to separate solid from solvent. The quantity of sodium hydroxide distributed in both solid and solvent phases was determined by acidimetry.

In Case of HPC and Cellulose Together in Solution System. Specially designed equipment (Fig. 1) was used for the tests. The components of the solution can migrate from one chamber to another through the sintered glass partition wall, but the solids cannot.

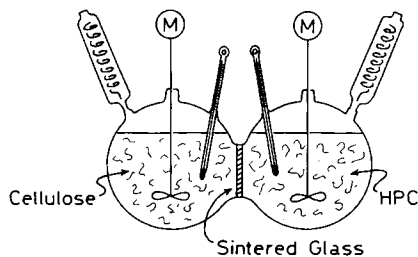


Fig. 1. Apparatus for experiment on sodium hydroxide distribution in HPC and cellulose phases. Two three-neck flasks are connected with sintered glass wall through which solution can but solids cannot pass from one chamber to another.

A 150 g measure of the solution (Table II, Run numbers 2 for one test and 8 for another separate test), was placed in each chamber, then designated quantities of HPC and cellulose were added separately in each solution; the quantity of HPC and cellulose was set to be equal in reduction to that of cellulose. The slurries in the two chambers were stirred for 6 h at 65°C; it had been confirmed that the distribution equilibrium was attained in 4–5 h. Each slurry was filtered through a glass filter. The quantity of sodium hydroxide present in HPC, cellulose, and solvent phases was determined by acidimetry.

X-Ray Diffraction

X-ray diffraction patterns of the alkali-treated cellulose, the regenerated cellulose after alkali treatment, and the residual cellulose after acetylation were obtained by using a Rigaku Denki diffractometer with a nickel-filtered copper target X-ray tube.

RESULTS AND DISCUSSION

Solution for Alkali Treatment and X-ray Diffraction Patterns of Alkali-Treated Cellulose

At first the experimental confirmation has been made concerning the cellulose alkalization ability of the solution system (Table I). The solution system consisted of toluene, *tert*-butylalcohol, water, and sodium hydroxide. It spontaneously separates into two layers: upper layer solution (ULS) consisting of organic solvents with a little water and lower layer solution (LLS) consisting of concentrated aqueous solution of sodium hydroxide with a trace of organic solvents. Table I shows the concentration of sodium hydroxide in both the upper and the lower layers of the solution system when the amount of sodium hydroxide added was changed.

One requirement for alkalization of cellulose in the solution system consisting of organic solvent, water, and sodium hydroxide is that the concentration of sodium hydroxide in the LLS is as high as that of aqueous solution of sodium hydroxide in which cellulose can be converted to alkali cellulose.⁷ For the formation of uniform alkali cellulose, the ULS must be able to

dissolve a little amount of sodium hydroxide. The ULS has a function to distribute sodium hydroxide with water in cellulose uniformly according to the distribution equilibrium between ULS and cellulose. The ULS recovers sodium hydroxide with water from the LLS as the distribution equilibrium shifts in the alkalization of cellulose.⁷

Judging from the value of the concentration of sodium hydroxide in the LLS (Table I), each solution has the ability to convert cellulose to alkali cellulose. The amount of sodium hydroxide is less than 1 mol/AHGU in the solution system; partially alkalized cellulose is formed. However, it seems that uniform alkali cellulose cannot be formed even if one molar or more sodium hydroxide per AHGU is applied (run numbers 4 and 5 in Table I); none of the ULS (Table I) contains sodium hydroxide, therefore it cannot fulfil its function mentioned before.

Figure 2 shows the X-ray diffractograms of cellulose treated in each solution (Table I). The celluloses treated in the solutions containing 0.6, 1.0, and 1.4 molar sodium hydroxide per AHGU gave diffraction patterns with reflections of alkali cellulose and cellulose I, while those treated in the solutions containing 0.2 and 0.4 mol/AHGU showed only cellulose I; neither were reflections of cellulose II found in X-ray diffractograms of the cellulose regenerated after the treatment [Fig. 3 (a)].

The alkalization ability of the solution systems was confirmed in the former three lots but not in the latter two lots. All the said solution systems were insufficient to form uniform alkali cellulose.

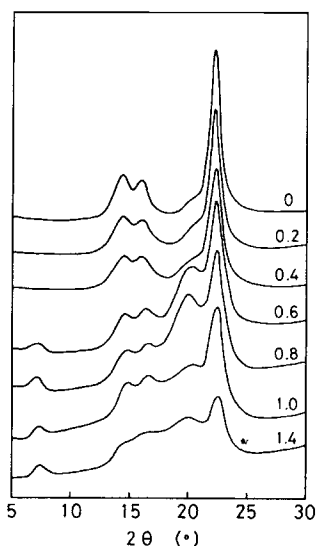


Fig. 2. X-ray diffractograms of alkali-treated celluloses. The values of molar ratio of sodium hydroxide to cellulose are shown on the curves.

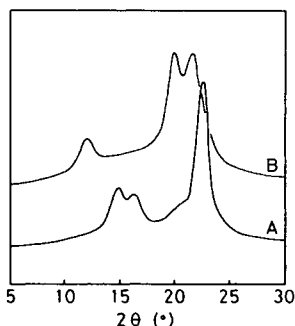


Fig. 3. X-ray diffractograms of the regenerated cellulose after the alkali treatment in the solution containing 0.4 molar sodium hydroxide per anhydroglucose units (a) and of the acetylation residue of the regenerated cellulose mentioned above (b).

Confirmation of Alkali Cellulose Formation

Concerning the solution system containing 0.4 molar sodium hydroxide another series of experiments were carried out to clarify whether the amount of alkali cellulose formed was too small to be detected by X-ray diffraction measurement or alkali cellulose was not formed at all.

It is known that dried mercerized cellulose is relatively inert to acetylation as a consequence of structural collapse in the interfibrillar spaces upon drying.⁸ Cellulose sample, which was treated in the said solution (Table I, Run number 2), washed with methyl alcohol and water, and then dried, was subjected to a conventional acetylation process and gave acetate gums with a small amount of fibrous residues. The acetate gums were diluted with methylene chloride so as to separate the fibrous residues by filtration. The recovered fibrous residues were washed with methylene chloride, dried, and subjected to X-ray measurement. The X-ray diffractogram shows the perfect pattern with reflections of cellulose II [Fig. 3 (b)]. The quantity of recovered cellulose was about 8%. The result means that alkali cellulose was formed partially in cellulose which was treated in the solution system containing only 0.4 molar sodium hydroxide per AHGU.

Subsequently a series of experiments were carried out to confirm that hydroxypropylation was initiated in the partially alkalized parts mentioned above. At first, two kinds of samples were taken in the very initial stage of hydroxypropylation; they were purified by washing with boiling water after neutralization of sodium hydroxide with acetic acid and oven dried. The MS of each sample was 0.03 and 0.16. Secondly, the above two samples were subjected to the acetylation process. The one sample (MS=0.03) gave acetate gums with a very little amount of unreacted fibers, and the other (MS=0.16) yielded acetates with good clarity and complete absence of unreacted fibers; the unreacted fibers were confirmed to have cellulose II crystal structure by X-ray diffraction measurement.

The hydroxypropyl substituents appear to act as "wedges" which prevent structural collapse in the interfibrillar spaces of mercerized parts and also overcome the inactivation of mercerized cellulose to acetylation which nor-

mally occurs upon drying. However, the lower level of substitution ($MS=0.03$) is inadequate for "wedges," so a very little amount of undissolved fibers was left in the acetate gums. This result means that hydroxypropylation is initiated in the alkalized portion of cellulose when such portion and propylene oxide are present together.

Role of Byproducts, Propyleneglycol (PG), Di-PG and Tri-PG

The author presumed that the changes occurred in the distribution equilibrium of sodium hydroxide in the reaction system as the hydroxypropylation proceeded in the partially alkalized portion of cellulose, and that newly alkalized portions occurred due to the migration of sodium hydroxide.

The hydroxypropylation of cellulose PG, di-PG, and tri-PG are produced as byproducts in about 10 wt% in the solution system. They are similar in characteristics; each of them intermingle with water, alcohols, and aqueous sodium hydroxide, and has a certain degree of mutual solubility with toluene.

The effects of PG, the main byproduct, on the distribution equilibrium of sodium hydroxide in the solution systems were examined (Table II). Sodium hydroxide was found to be distributed in the ULS by the presence of PG. When hydroxypropylation of cellulose was carried out in the solution systems (Table I), sodium hydroxide was not found in the solvent phase in the initial stage, but was present as the etherification (and the side reaction) proceeded. The byproducts make it possible for sodium hydroxide to dissolve in the ULS (or solvent phase), and then the solvent phase can recover sodium hydroxide from some portion for cellulose and redistribute it to another portion if the distribution equilibrium shifts in the hydroxypropylation of cellulose.

Distribution of Sodium Hydroxide in HPC and Cellulose Phases

HPC is a polar-solvent-soluble cellulose ether as well as a water-soluble one. It is thought that HPC has a hydrophobic property to some extent, and therefore that sodium hydroxide has relatively weaker affinity for HPC than for cellulose. The distribution of sodium hydroxide in HPC phase was examined in comparison with that in cellulose phase in the solution systems (Table II, Run numbers 2 and 8).

Experiments were carried out for the system of HPC or cellulose present individually in the solution. Figure 4 illustrates the change in the quantity of sodium hydroxide in each phase of HPC and cellulose, expressed by the molar quantity of sodium hydroxide per AHGU, as a function of that of sodium hydroxide presenting in the slurry, expressed by the same terms. Almost all of the sodium hydroxide is distributed in the HPC phase when PG is not present. As the quantity of sodium hydroxide to HPC in the slurry is increased, some portions of sodium hydroxide remain in the aqueous droplets in the solvent phase without distribution in the HPC phase. When PG is present, the quantity of sodium hydroxide distributed in the HPC phase becomes less than that in the case of no PG being present. In the cellulose phase all of the sodium hydroxide is distributed independently of

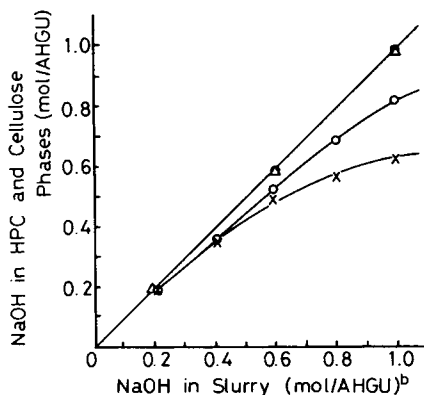


Fig. 4. Sodium hydroxide in HPC (\circ - PG=0, \times - PG=6%)^a and cellulose (\bullet - PG=0, \triangle - PG=6%)^a phases at distribution equilibrium state. HPC or cellulose is present individually in the solution. ^aThe value of PG means the weight percent of PG to the solution (see Table II). ^bThe ratio of sodium hydroxide to cellulose (HPC) was regulated by the quantity ratio of the solution to cellulose (HPC).

the quantity of sodium hydroxide to cellulose in the slurry when PG is not present, and the distribution is almost the same even when PG is present.

It has been recognized that sodium hydroxide has relatively weaker affinity for HPC than for cellulose and that PG decreases the affinity of sodium hydroxide for HPC.

Experiments were also carried out for the system of both HPC and cellulose being present together in the solution. The results are shown in Figure 5. When PG is not present, all of the sodium hydroxide present in

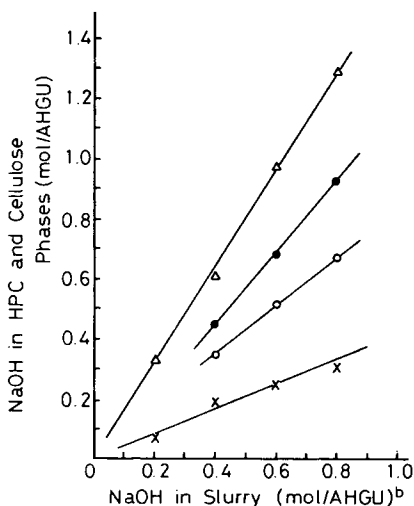


Fig. 5. Sodium hydroxide in HPC (\circ - PG=0, \times - PG=6%)^a and cellulose (\bullet - PG=0, \triangle - PG=6%)^a phases at distribution equilibrium state. HPC and cellulose are present together in the solution. ^aThe value of PG means the weight percent of PG to the solution (see Table II). ^bThe ratio of sodium hydroxide to cellulose (HPC) was regulated by the quantity ratio of the solution to cellulose (HPC).

the slurry is distributed in both HPC and cellulose phases. When PG is present, the distribution equilibrium of sodium hydroxide is attained in that almost all of the sodium hydroxide in the slurry is distributed in both HPC and cellulose phases and that the distribution in the solid phases shifts largely to the cellulose. The quantity of sodium hydroxide is considerably increased in the cellulose phase and decreased in HPC in comparison with when no PG is present.

It is considered that the above-said increment of sodium hydroxide in cellulose phase (and the decrement in HPC phase) is due to the migration of sodium hydroxide through the solvent phase from the HPC phase (or from the chamber containing HPC) to the cellulose phase. The affinity of sodium hydroxide is stronger for cellulose than for HPC, which is amplified by the presence of PG. HPC with MS of 3.0 was used in all experiments described above.

Separate experiments were carried out for HPC with MS of 1.5 in the same manner. It was found that the distribution of sodium hydroxide in the solid phases shifts a little to the cellulose. This result is reasonable, because the lower the MS, the closer to cellulose is the characteristic affinity for sodium hydroxide.

CONCLUSIONS

The purpose of this investigation was to elucidate the meaning of alkali treatment of cellulose in HPC preparation with a small quantity of alkali, such as 0.2–0.4 molar sodium hydroxide per AHGU.

It has been confirmed that the role of sodium hydroxide is that of alkalization of cellulose as well as the catalyst for etherification. The mechanism of cellulose alkalization with such a small quantity of alkali is explained as follows:

1. Cellulose is converted to alkali cellulose locally.
2. Hydroxypropylation is initiated in the alkalized portion of cellulose and proceeds in it.
3. The sodium hydroxide in the hydroxypropylated portion is redistributed in the unreacted portion of cellulose phase through the solvent phase as the byproducts such as PG are produced. The redistribution of sodium hydroxide is enhanced by the presence of the byproducts. Thus, newly alkalized portion is formed in the unreacted cellulose phase.
4. This alkalized portion is followed by hydroxypropylation.

The steps said above are repeated. And as a result all portions of cellulose are alkalized and hydroxypropylated.

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