

Variables Affecting the Methylation Reactions of Cellulose

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SYNOPSIS

Solubility of methyl cellulose (MC) depends on the degree of substitution (DS), the average degree of polymerization (DP), and the distribution of methoxyl groups. Of these, the DS appears to be the most important. The DS of the MC depends on the conditions of preparation. The conditions studied in this work revealed that the DS of the MC increased as the concentration of sodium hydroxide increased from 10 to 50%. This result is attributed to the increase in the extent of formation of alkali cellulose II as a result of the increase in the alkali concentration and hence the increase of the DS of the MC. Decreasing both the ratio of dimethyl sulfate : cellulose and the liquor ratio increased the DS. High DS was achieved within a period of 2 and 3 h. However, the DS increased as the time increased. The decrease of the DS as the liquor ratio increased may be attributed to the sol-gel transition due to the interaction of the hydrophobic methoxyl groups within the polymer chains. To reveal the effect of the thermal sol-gel transition, the reaction was carried out in nonaqueous medium and the results obtained showed an increase of the DS with the increase of the solvent ratio until a maximum. This result may be contributed to the breakdown of the hydrogen bonding in the presence of solvents that transfer the reaction medium to the sol-form and hence more methylating reaction takes place. The degree of the solvation of the methyl groups into the solvents also plays a role. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The insolubility of cellulose is caused by numerous intra- and intermolecular hydrogen bonds. The aim of etherification of cellulose is the cleavage of these bonds. Thereby, the hydrophilic character of the hydroxyl groups develops and hence the solubility in aqueous systems. Cellulose ethers are classified according to the kind of substituents, the degree of etherification, the solubility in water at different temperatures, and the property with regard to application.¹ The nonuniformity of the distribution along the chain is related to the presence of crystalline and amorphous regions in cellulose and caused by heterogeneous reactions.^{2,3} Moreover, it is known that the solubility of methyl cellulose (MC) depends on the degree of substitution (DS), the average degree of polymerization (DP), and the methoxyl group distribution. Of these, the DS is the most

important.⁴ The DS values of water-soluble *O*-MC depends strongly on the conditions of preparation.^{5,6}

Generally, commercially available MC is prepared by heterogeneous reaction and shows a thermally reversible sol-gel transformation in aqueous solution. There is a possibility that trimethyl glucose units may be found in the chain that are responsible for the cross-linking loci formation on warming.⁶ Alternatively, MC samples prepared by homogeneous reaction showed no sol-gel transformation⁵ and in such cases, no relationship was obtained between the distribution of substituents in MC and its solubility in water.

On the other hand, Abe et al.⁶ reported that all the MC samples prepared from cotton linters with dimethyl sulfate (DMS) and alkali in toluene were insoluble in water despite their DS values, which ranged from 0.8 to 2.0. Such a difference is obviously due to the difference in the distribution of substituents along the cellulose chain.

In this work, the conditions of preparation of MC in heterogeneous reactions were considered to reveal the variables that influenced the DS and the degree of the solubility of MC in aqueous medium.

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EXPERIMENTAL

Bleached cotton linter was used as a source of the cellulosic material. For DS up to 0.3, cotton linter, 1 g, was mercerized using 10–50% sodium hydroxide solution, at 5% consistency, for 1 h at 20°C. Different ratios of DMS to cellulose were used, 2–6 mL. The reagent was added dropwise and the reaction mixtures were allowed to proceed at 50°C for different periods of time.

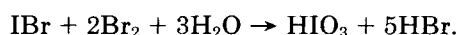
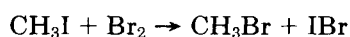
For higher DS products, up to 0.7, the excess sodium hydroxide, used for mercerization, was first removed by pressing, before adding the DMS. Also, for DS up to 1.0, solvents were used as a diluent instead of water in some reactions.

At the end of the reaction, the material was neutralized with 10% acetic acid, filtered in a G₂ sintered glass crucible, and washed with acetone. The MC obtained was dried in a vacuum oven at 50°C.

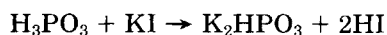
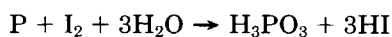
Methoxyl Content Determination

Methoxyl content of the samples was determined according to Zesel⁷ and as modified by Viebock and Schwappach⁸ or Viebock and Brecher,⁹ which has proved to be safe and reliable.

When substances containing methoxyl groups are boiled with hydroiodic acid, the methoxyl groups are quantitatively split off as methyl iodide. The methyl iodide is distilled off in a stream of carbon dioxide or nitrogen and bubbled into a solution of bromine in glacial acetic acid. The excess bromine is decomposed by reduction with formic acid, and the iodate formed is titrated against thiosulfate.



In a 50-mL flask, about 5–10 mg sample was accurately weighed, to which about 0.2 g phenol, 0.2 g red phosphorus, and 0.2 g potassium iodide were added. The red phosphorus is used to remove iodine from solution, while the produced phosphorus acid yields hydroiodic acid,



that is, both phosphorus and potassium iodide will give hydroiodic acid and thus increase the strength of the hydroiodic acid. Distilled hydroiodic acid (3 mL) was added to the mixture in the reaction flask.

Bromine solution, 10 mL (20 g potassium acetate in 200 mL acetic acid + 5 mL bromine), were added in the bubbling tube. Nitrogen gas was allowed to bubble into the mixture with a rate of 30–60 bubbles/min. The mixture was heated gradually until boiling and continued to bubble for 10 min. The tap was then opened and the contents of the bromine-containing tube were washed into a 250-mL conical flask that contained 10 mL of saturated sodium acetate solution. Formic acid was added dropwise to reduce the excess of bromine. The presence of any remaining bromine was tested with the aid of methyl red; if the color of methyl red disappeared more drops of formic acid were added until the red color of the indicator persisted. Ten percent potassium iodide solution (10 mL) and 10% sulfuric acid (10 mL) were then added, and the liberated iodine was titrated against the sodium thiosulfate solution.

The weight percent of methoxyl groups was calculated according to the following equation:

$$\text{wt \% of methoxyl groups} = \frac{n \times v \times 31}{w \times 60}$$

where n = normality of thiosulfate solution, v = volume of thiosulfate required, w = weight of the dry sample used, and the DS is given by:

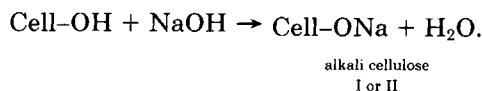
$$\text{DS} = \frac{1.62 \times \% \text{OCH}_3}{31 - (0.14 \times \% \text{OCH}_3)}$$

RESULTS AND DISCUSSION

Methylation reaction of cellulose may be carried out according to the following scheme.

Formation of Alkali Cellulose

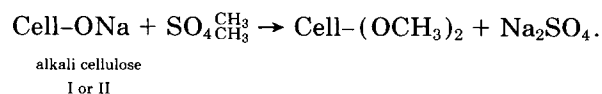
The first step for the methylation reaction is the formation of alkali cellulose I or II depending on the concentration of the alkali used. In this work sodium hydroxide of concentrations 10–50% were used. The formation of alkali cellulose was carried out according to the following equation:



Formation of Methyl Cellulose

MC was formed when alkali cellulose was subjected to an alkylating agent such as methyl iodide or DMS.

In this work DMS was used in different ratios with respect to cellulose to obtain different DS. The reaction may be carried out according to the following equation:



Effect of Sodium Hydroxide Concentration

A series of experiments were carried out to reach the DS, which lead to the dissolution of the MC. Thus, different concentrations of sodium hydroxide, (10, 20, 30, 40, and 50%, w/v), were used to treat cotton linter in a ratio of cellulose : NaOH, 1 : 20 for 1 h, thereafter DMS in a ratio to cellulose of 3 : 1, was added and the reaction was carried out at 50°C for 2 h. The results obtained in Figure 1, showed that the DS increased as the concentration of sodium hydroxide increased until DS was 0.315, when 50% sodium hydroxide concentration was used. The results revealed that the increase of sodium hydroxide concentration more than 25%

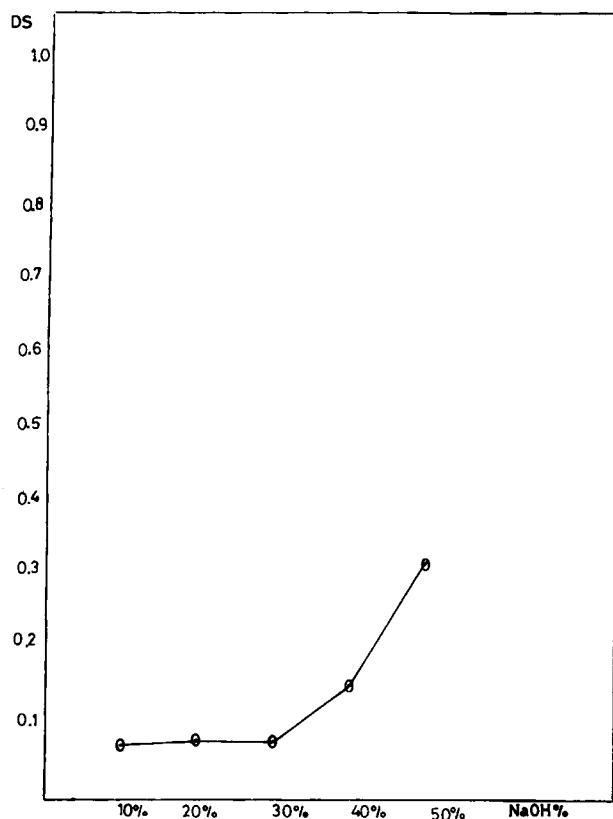


Figure 1 Cellulose : NaOH and cellulose : DMS 1 : 20 and 1 : 3, respectively, at 50°C for 2 h.

Table I Effect of DMS : Cellulose Ratio on DS of Products

Cellulose : DMS	% OCH ₃	DS
1 : 2	8.6474	0.4700
1 : 3	5.8812	0.3150
1 : 4	5.1345	0.2700
1 : 5	2.8096	0.1480
1 : 6	3.0114	1.1590

Alkali liquor ratio 1 : 20, NaOH concentration 50%.

means an increase in the formation of alkali cellulose II. As the alkali cellulose II increased, the DS of the MC increased. So, methylation reaction is more successful on alkali cellulose II than on alkali cellulose I (Fig. 1).

Effect of Ratio of Methylating Agent

From Table I, different ratios of cellulose : DMS were used, namely, 1 : 2, 1 : 3, 1 : 4, 1 : 5, and 1 : 6, on using 50% sodium hydroxide concentration at liquor ratio of 20 : 1 (liquor : cellulose) at 50°C for 2 h. The results obtained are shown in Table I, that shows that the DS decreased as the ratio of DMS increased. On increasing the time of methylation reaction under the same conditions of reaction, namely, 50% sodium hydroxide solution at ratio 20 and at cellulose to DMS ratio 3, the results obtained (Fig. 2) showed that there are maxima of DS, 0.315 and 0.322, obtained within a period of 2 and 3 h, respectively. Before and after this period of time the DSs were low. Obviously, the increase of the ratio of DMS means an increase in the methylating agent, hence the increase of the DS but up to a limit.

Effect of Liquor Ratio

It is clear that the ratio of the cellulose to sodium hydroxide solution plays a role. Thus cellulose was impregnated in a concentrated solution of 50% sodium hydroxide for 1 h at 20°C. Then it was pressed until different cellulose to alkali ratios, namely, 1 : 15, 1 : 10, and 1 : 5 were obtained. The methylating agent was used at a ratio of 3 at 50°C for different periods of 1–4 h. This reaction was carried out in a heterogeneous medium. The results illustrated in Figure 3 showed that there is an increase in the DS with increased time and decreased liquor ratio. The higher DS was obtained at a liquor ratio 5. It is clear also from Figure 3 that for the relations between the DS and time at liquor ratios more than 5, there

are maxima and minima DSs, but for liquor ratio 5 the DS increased as the time increased. This result may be attributed to the sol-gel transition, at a liquor ratio more than 5, because the increased liquor permitted the formation of gels that prevent the reacting methylating agent to reach the active sites of alkali cellulose. It has been found by Abe et al.⁶ that commercial MC prepared by heterogeneous reaction showed a thermally reversible sol-gel transition in aqueous solution. Fowler¹⁰ also found that the aqueous solution of many cellulose ethers exhibit an unusual phenomena of reversible thermal precipitation. For such polymers of which the major substituent is methoxyl, this phenomenon is modified to one of the reversible thermal gelation. Accordingly, the precipitation/gelation temperature and gel strength of these polymer solutions has been shown to be a function of the polymer molecular weight concentration, molecular structure, and the presence of additives. The overall mechanism is widely recognized as the result of hydrophobic interaction between the methoxyl groups within the polymer chains, which in this case is the cellulose backbone. It is obvious also from the results that

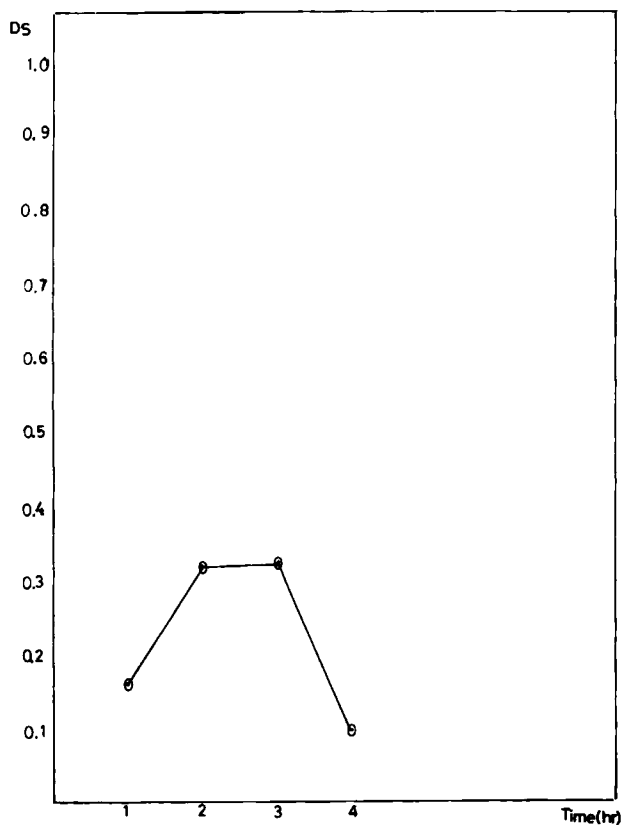


Figure 2 Cellulose : NaOH and cellulose : DMS 1 : 20 and 1 : 3, respectively, using 50% NaOH at 50°C.

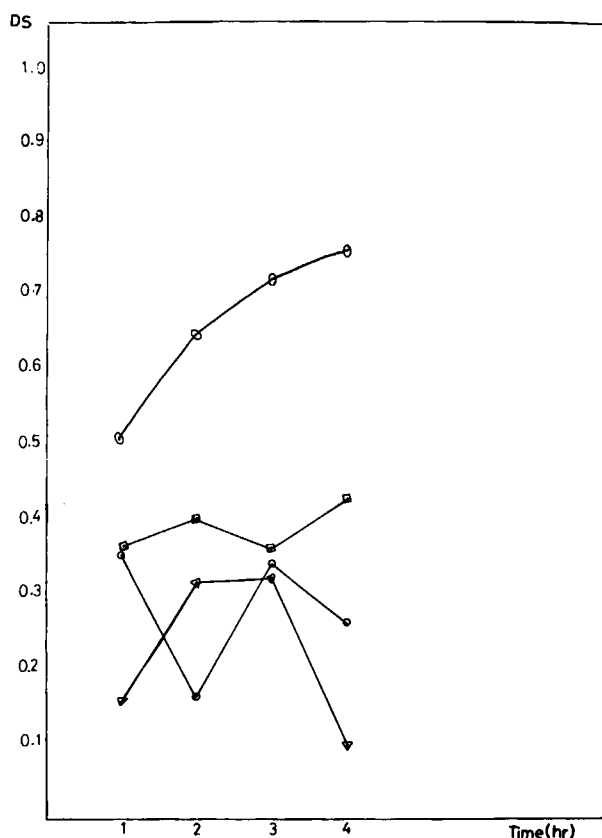


Figure 3 Cellulose : DMS, 1 : 3, and cellulose : NaOH, (∇) 1 : 20, (∇) 1 : 15, (O) 1 : 10, (\square) 1 : 5, (O) using 50% NaOH at 50°C.

such a phenomenon is also a function of the ratios of methylating agent and the liquor to cellulose ratio.

Effect of Using Solvents

To reveal the effect of the aqueous medium on the reversible sol-gel transition, the reaction was carried out in nonaqueous media using different organic solvents as diluents; namely, acetone, dioxane, toluene, isobutanol and tertiary-butanol, with different ratios of cellulose : solvent as 1 : 3, 1 : 6, 1 : 9, and 1 : 12. The reaction conditions were 50% sodium hydroxide, liquor to cellulose ratio was 5 : 1, and cellulose to DMS ratio was 1 : 3 at 50°C for 2 h. The results obtained are presented in Table II.

It is worthy of mention that on mixing organic solvent with water a gradual breakdown of a quasi-crystalline tetrahedral structure of water occurs in which the protons were supposed to be accommodated in the interstices of the tetrahedral lattice and bonded equally to the surrounding oxygen atom. This breakdown is supposed to be due to the interposition of organic solvent molecules, so that hydrogen bonding between neighboring water mole-

Table II Effect of Using Solvent on DS of Products

Cellulose : Solvent Ratio	Type of Solvent									
	<i>t</i> -Butanol		Dioxane		Toluene		Isobutanol		Acetone	
	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS
1 : 3	5.3726	0.2877	9.7315	0.5319	13.2795	0.7382	5.9207	0.3179	9.5288	0.5203
1 : 6	15.9738	0.8996	7.6906	0.4164	12.8521	0.7130	14.6448	0.8195	13.4715	0.7496
1 : 9	13.6080	0.7576	13.1924	0.7331	14.9109	0.8355	10.0791	0.5518	15.6691	0.8812
1 : 12	15.5222	0.8723	11.7645	0.6493	14.4243	0.8065	13.7055	0.7634	12.4295	0.6882

Using 50% NaOH, Liquor Ratio of 1 : 5 and cellulose : DMS of 1 : 3.

cules will be partially replaced by much weaker hydrogen bonds with the foreign molecules. The importance of the water-organic solvent mixtures lies in the fact that many physicochemical properties can be varied by varying their composition. This variation of physicochemical properties has an important role in controlling the chemical reaction.^{11,12}

Regarding the physicochemical properties when the alcohols mixed with the aqueous solution, the density slightly decreased and the viscosity increased. The same happened when acetone was mixed with water; the reverse was obtained when dioxane was mixed with water. With respect to toluene, it is immiscible with water.^{11,12}

On the other hand, alcohols, water, and carboxylic acid are strong hydrogen bond donors,^{11,12} and are protic solvents compounds. These solvents formed hydrogen bonds that produce associated molecules. Such associations exhibit large dielectric constants with strong solvation ability.

The presence of alcohols weakens the hydrogen bonding. Thus, the addition of 1 : 3 cellulose to alcohols or acetone decreased the extent of the methylation reactions (Table II). The decrease may be attributed to the increased liquor ratio, from 5 to 8. In this case the effect of the increase of the liquor ratio is more effective than the effect of the breakdown of the hydrogen bonding as a consequence of mixing organic solvents other than toluene, that is, protic solvents. As the solvent to cellulose ratio was increased, the breakdown of the hydrogen bonding increased the availability of the hydroxyl groups of the cellulose chains to be methylated (Table II). Hence, the methoxyl percent and the DS increased for all alcohols and acetone. For dioxane, the increase in the density contributed to the mixing with water^{11,12} with some effect on the DS of the MC obtained (Table II). In conclusion, the breakdown of the hydrogen bonding means the transfer of the

reaction medium to the sol-form, thus the easier transfer of the reacting agents that enhances the methylation reaction rate.

Additionally, increasing the solvents meant the increased chance of the solubility of the formed methyl groups in the organic solvents, more power of the organic solvent on the solvation of the formed methyl groups, less formation of the gel-structure, and hence the increased ability of the hydroxyl groups of the cellulose chains to undergo further methylation reaction. This was clear when toluene was used as diluent at all ratios. The methoxyl group showed relatively increased values because toluene is immiscible with the hydroxyl groups and thus the ability of forming hydrogen bonds was minimum and the gel-effect was nearly absent. Therefore, the methylation reaction was enhanced to take place at the available hydroxyl groups of the cellulose chains. Moreover, mixing aromatic hydrocarbons such as toluene and water leads to the formation of the Van der Waals forces responsible for the solvation in nonpolar aprotic solvents. Moreover, in our opinion, this type of solvation decreased the gel-form and enhanced the reaction rate. This is clear from the increased methoxyl percent and DS on increasing the toluene ratio (Table II). On the other hand, *t*-butanol at liquor ratios 6 and 12 and acetone at liquor ratio 9 showed increased methoxyl groups. This may be explained by the view that these two solvents at these ratios affect the proper solvation of the formed methyl groups over the remaining free hydroxyl groups leading to more methylating reactions.

From another point of view, the gel-structure can be caused by the formation of an MC-water complex that is unstable in hot water.¹³ The increased solvation power on this MC-water complex minimized the gel-structure formation leading to more methylation reactions. Thus, a series of experiments using a liquor to cellulose ratio of 3 : 1 and different acetone

Table III Effect of Cellulose : Acetone Liquor Ratio and NaOH Concentration on DS of Products

Concentration of NaOH (%)	Cellulose : Acetone									
	1 : 0		1 : 3		1 : 6		1 : 9		1 : 12	
	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS	% OCH ₃	DS
10	3.9952	0.2126	6.2364	0.3353	1.0719	0.0563	2.6796	0.1418	4.9696	0.2627
20	10.0854	0.5522	8.1365	0.4414	10.5726	0.5802	13.7395	0.7655	5.2619	0.2817
30	10.7188	0.5886	13.9831	0.7799	14.3242	0.8003	13.0574	0.7251	11.1085	0.6112
40	13.9831	0.7799	16.1756	0.9119	14.4216	0.8062	18.0757	1.0286	16.1756	0.9119
50	13.5933	0.7568	14.8114	0.8295	15.9320	0.8971	17.9783	1.0225	14.9088	0.8354

Using liquor ratio of 1 : 3 and cellulose : DMS of 1 : 3.

to cellulose ratios, namely, 3 : 1, 6 : 1, 9 : 1, and 12 : 1 were used at 50°C for 2 h. The sodium hydroxide concentration used ranged between 10 and 50%. Increasing the concentration of the sodium hydroxide means the decrease of the percent of water used in the alkaline solution. The results are shown in Table III. It is clear that there is a relationship between the increase of the sodium hydroxide concentration and the methoxyl content; that is, the methoxyl percent increased as the concentration of the alkali increased or, in other words, as the water percent of the solution decreased. With an increased ratio of acetone, generally observed from Table III, there was a gradual increase in the DS for ratios of 1 : 3, 1 : 6, and 1 : 9, with a slight decrease on using a ratio of 1 : 12. The increase of the acetone ratio to 1 : 12 and the formation of the weak hydrogen bonds between the acetone and the water in mixture depends mainly on the keto-enol tautomerism of the acetone. When acetone is in its keto-form, the hydrophobicity of this structure increased the strength of the hydrophobic interaction and hence the slight decrease in the DS was achieved. On the reverse, when the acetone is in its enol-form, the weak hydrogen bonds formed enhanced the reaction rate; accordingly the DS increased (Table III). Thus, one may say that there is a threshold for the increase of

the hydrophobicity that leads to the appearance of the sol-gel transition phenomenon.

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