Carboxymethylcellulose Synthesis in Organic Media Containing Ethanol and/or Acetone

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ABSTRACT: A study of the carboxymethylation of wood pulp cellulose and cotton linters cellulose in different organic media, namely, ethanol, acetone, and ethanol−acetone mixtures, is performed. Previously, the ethanol−acetone 1 : 1 (w/w) mixture used as reaction medium was found to give a higher degree of substitution (DS) than the pure solvents separately. In the present work, the kinetic investigation of cellulose carboxymethylation was carried out in ethanol-acetone 3 : 7 (w/w) mixture, as well as in acetone as reaction media, and the same synergistic effect of the solvents mixture was observed. The data suggested a pseudo-first-order kinetic behavior satisfactorily described by the following equation: $\ln(1.11 - DS) = -kt$. The two reaction steps observed are related to the transformations of less ordered regions with higher reaction rate and more ordered regions with smaller reaction rates, respectively. A possible explanation for this behaviour is given, taking into account the different structural changes of cellulose crystallinity and accessibility produced by ethanol-acetone 3 : 7 (w/w) mixture, ethanol, and acetone, as revealed by X-ray diffraction and calorimetry determinations. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 481–486, 1998

Key words: carboxymethylcellulose; x-ray diffraction; kinetics; cellulose crystallinity; calorimetry

INTRODUCTION

Carboxymethylcellulose (CMC) is the most important water-soluble cellulose derivative, with many applications in the food industry and in cosmetics, pharmaceuticals, drilling muds, detergents, etc. CMC with a degree of substitution (DS) of about 1.0 is generally obtained by the slurry procedure, with high efficiency when using isopropyl alcohol as organic solvent; but other organic media like acetone or ethanol may be more advantageous from an economical point of view.

In recent years, several works have been performed on the effect of the organic diluent on carboxymethylation step, as well as on the structural transformations of cellulose during alkalization in organic solvents.[1–3] A kinetic study of cellulose carboxymethylation in the isopropyl alcohol system has also been related by Lin Xiquan et al.[4]

In a previous article, we discussed the kinetics of cellulose carboxymethylation in three organic media: ethanol, acetone, and ethanol-acetone mixture 1 : 1 (w/w), in connection with cellulose crystallinity and the concentration of sodium hydroxide in the alkalization step [5]. At the molar ratio of NaOH to cellulose of 3.44, the reaction rate of cellulose carboxymethylation in the ethanol-acetone mixture 1 : 1 (w/w) was found to be greater than in both ethanol and acetone and dependent neither on the crystallinity nor on the particle size of the starting cellulose.

In the present article, cellulose carboxymethylation is carried out comparatively in ethanol-acetone mixtures of various proportions, as well as in pure solvents. The kinetic behavior of the pro-

cesses performed in ethanol-acetone mixture at optimum composition (3 : 7 w/w) and in acetone for a lower molar ratio of NaOH to cellulose (2.11) is correlated with the structural transformations of cellulose during alkalization in these solvent systems, as revealed by X-ray diffraction (XRD) and calorimetry data.

Although this heterogeneous process is rather complex, we adopted a pseudo-first-order kinetics to describe it, assuming that sodium hydroxide is uniformly distributed in the system and the etherifying agent is consumed, especially for cellulose carboxymethylation, at least at the beginning of the process.

EXPERIMENTAL

Materials

Wood pulp cellulose and cotton linters of about 20 mesh were chosen as starting materials. Sodium hydroxide, sodium monochloroacetate (MCA), ethanol, and acetone were of reagent grade.

Alkalization

The experiments were carried out in ethanol-acetone mixtures of various compositions, ethanol, and acetone, at molar ratios of NaOH to cellulose of 2.11, water to cellulose of 22.5, and MCA to cellulose between 0.7 and 1.9. The ratio of organic solvent to cellulose was 20 : 1 (w/w). The time and temperature were 60 min and 20°C, respectively, and the reaction mixture was vigorously stirred during the process.

Cellulose Regeneration

After alkalization, portions of alkalicelluloses obtained from both wood pulp and cotton linters celluloses in ethanol, acetone, and the ethanol-acetone 3 : 7 (w/w) mixture at a molar ratio of MCA to cellulose of 1.1 were washed to regenerate cellulose and air-dried in order to determine the wetting heats and to record the X-ray diffractograms.

Carboxymethylation

The temperature of the reaction bath containing alkalicellulose was raised to 45°C, then the corresponding amount of MCA was added under vigorous stirring; the reaction was performed at this temperature for various times. After the desired
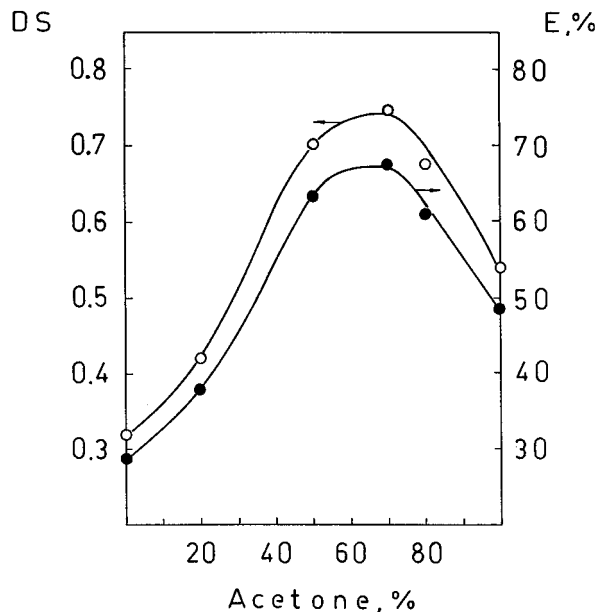

Figure 1 DS and E versus the composition of the reaction system ethanol-acetone at molar ratios of NaOH to cellulose of 2.11 and MCA to cellulose of 1.1 for the carboxymethylation of wood pulp cellulose.

time of carboxymethylation, the reaction system was rapidly cooled and neutralized with hydrochloric acid, and the product purified by several washings with ethanol 70% and air-dried.

Characterization

The X-ray diffractograms of original and regenerated celluloses were recorded on a diffractometer Rontgen-Universal HZG 4/A with CuKα radiation. The wetting heats were measured with a conduction Calvet-type calorimeter, at room temperature. The degree of substitution of all CMC samples was determined by the ash sulphate method.[6]

RESULTS AND DISCUSSION

Our preliminary results concerning the heterogeneous carboxymethylation of cellulose in ethanol-acetone mixtures of various proportions as reaction media demonstrated that the degree of substitution and carboxymethylation efficiency are both dependent on the composition of the reaction medium employed (Fig. 1). The data suggested that a solvent system containing about 30% ethanol can be the most convenient from this point of view.

On the other hand, for this reaction medium, the curve efficiency (E) against the molar ratio of MCA to cellulose showed a maximum at about 1.1 (Fig. 2).

Figure 1 shows that at the molar ratio of NaOH to cellulose of 2.1 and of MCA to cellulose of 1.1, maximum values were obtained indeed in a reaction medium containing 30% ethanol for both carboxymethylation efficiency and the degree of substitution of the product. Furthermore, DS was as high as that realized in comparable conditions in pure isopropanol, which is the most efficient reaction medium for cellulose carboxymethylation.[4]

The kinetic curves obtained for the carboxymethylation of either wood pulp or cotton linters cellulose in acetone and the ethanol-acetone 3 : 7 (w/w) mixture, as well as in ethanol for wood pulp cellulose, are depicted in Figure 3. As expected, the etherification proceeds much slower in ethanol than in acetone medium. An interesting behavior is observed for the mixture of these two organic solvents, i.e., a higher reaction rate than for each pure solvent separately. The same behavior was reported previously[5] for a higher molar ratio of NaOH to cellulose and a 1 : 1 (w/w) ethanol-acetone proportion.

As in the case of the isopropyl alcohol system[4] and in that reported earlier by us,[5] two steps of reaction with first-order rate constants with respect to the etherifying agent were observed; the
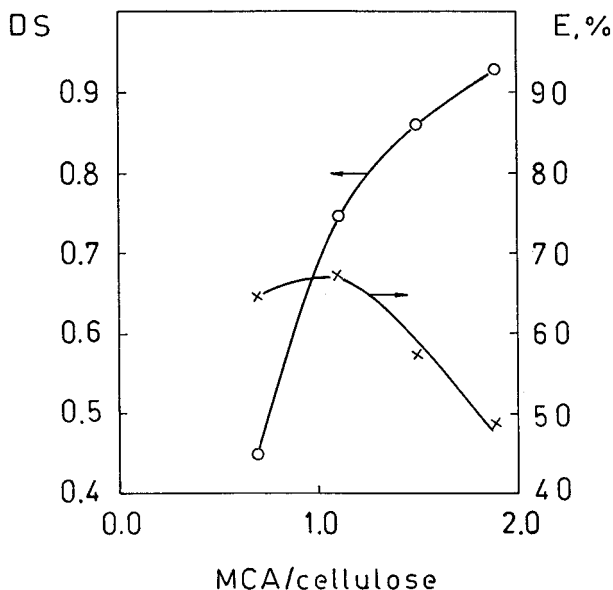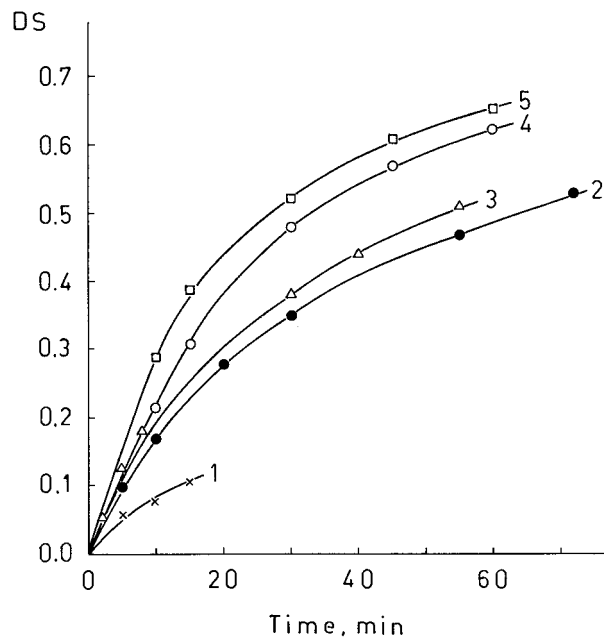

Figure 3 Kinetic curves for the carboxymethylation of cellulose in different organic media at the molar ratio of NaOH to cellulose of 2.11: (1) wood pulp in ethanol; (2) cotton linters in acetone; (3) wood pulp in acetone; (4) cotton linters in ethanol-acetone 3 : 7 (w/w); and (5) wood pulp in ethanol-acetone 3 : 7 (w/w).

first one was found to be faster than the second one. The process can be described by the following kinetic equation:

$$d(\text{DS})/dt = k(1.11 - \text{DS})$$

or

$$\ln(1.11 - \text{DS}) = -kt + c,$$

where 1.11 is the molar ratio of MCA to cellulose at $t = 0$.

Kinetic plots $\ln(1.11 - \text{DS})$ versus t for the carboxymethylation of wood pulp and cotton linters in organic media are depicted in Figures 4 and 5, respectively. A possible explanation for this behavior can be related to the dualistic nature (crystalline–amorphous) of the cellulose. Thus, while the first step may describe the reaction in the less ordered regions, the second one reffers to the transformation of more ordered regions and is characterized by a lower rate constant (Table I). The latter stage may be mainly controlled by the diffusion of the reagent molecules to the reactive centres of cellulose.

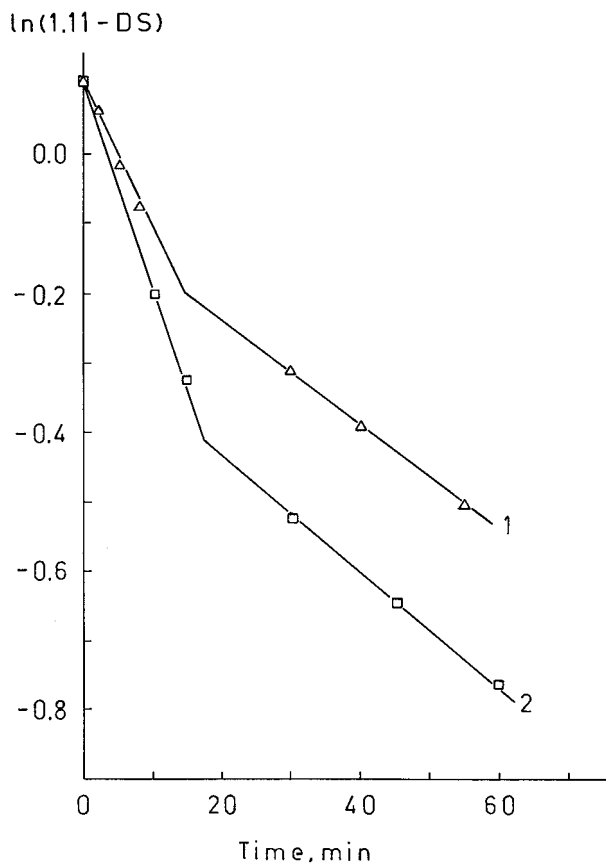Also, the synergistic effect of ethanol-acetone

Figure 2 DS and E versus the molar ratio of MCA to cellulose for the carboxymethylation of wood pulp cellulose.

Figure 4 Kinetic plots for the carboxymethylation of wood pulp in (1) acetone and (2) ethanol-acetone 3 : 7 (w/w).

plane and specific to cellulose II is visible at 12.6° on both diffractometer tracings. Also, a little shoulder at about 19–20° corresponds to the $10\bar{1}$ plane of cellulose II and is partially overlapped with the peak of the 002 plane. These transformations are consistent with a partial conversion of the crystalline structure of cellulose I to that of cellulose II. These effects are more pronounced in the case of acetone medium (curve 4), which suggests that cellulose alkalization in acetone produced a higher proportion of cellulose II in comparison with the mixture ethanol-acetone 3 : 7 (w/w). On the other hand, the X-ray diffractograms also show a considerable broadening of the peaks, which indicates a partial decrystallization of cellulose during alkalization in acetone and ethanol-acetone mixture.

Similar effects can be observed in Figure 7 for cotton linters cellulose. However, in this case, ethanol did not produce any significant change of crystallinity during alkalization. A higher proportion of cellulose II after alkalization in acetone can also be detectable (curve 4).
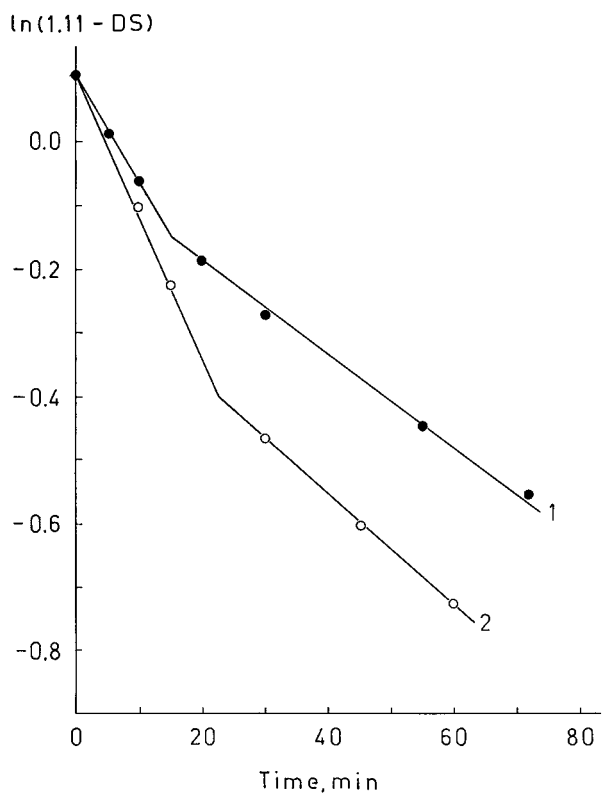
The partial decrystallization of cellulose during

mixtures may be explained in terms of a better accessibility of the reagent molecules to the cellulose fibers. The presence of ethanol besides acetone in the alkalization medium produces structural changes significantly different from those observed after alkalization in pure solvents. The X-ray diffractograms of celluloses regenerated from alkalicelluloses (Figs. 6 and 7) and the calorimetry data (Table II) illustrate the crystallinity and accessibility changes produced in different alkalization media.

As can be seen in Figure 6, the alkalization of wood pulp cellulose in ethanol medium (curve 2) produced only a slight decrystallization proved by the overlaping of the peaks corresponding to the 101 and $10\bar{1}$ planes, without any change of polymorphism. In turn, the X-ray diffractometer tracings of celluloses regenerated after alkalization in ethanol-acetone mixture and acetone (curves 3 and 4, respectively) reveal significant transformations of crystallinity as compared with the initial sample. A new peak corresponding to the 101

Figure 5 Kinetic plots for the carboxymethylation of cotton linters in (1) acetone and (2) ethanol-acetone 3 : 7 (w/w).

Table I   Rate Constants for the Carboxymethylation of Wood Pulp and Cotton Linters Celluloses in Acetone and Ethanol–Acetone 3 : 7 (w/w)

Cellulose Sample	Molar Ratio of NaOH to Cell	Rate Constant k (min^{-1})			
		Acetone		Ethanol–Acetone 3 : 7 (w/w)	
		k_I	k_{II}	k_I	k_{II}
Wood pulp	2.11	0.021	0.0075	0.029	0.0082
Cotton linters	2.11	0.017	0.0075	0.022	0.0082

alkalization in acetone and the ethanol–acetone mixture is confirmed by the calorimetry data (Table II). The values of the wetting heat prove that the ethanol-acetone 3 : 7 (w/w) mixture (having the higher wetting heat) is the most efficient among the three reaction media from the point of view of cellulose decrystallization. This fact is in
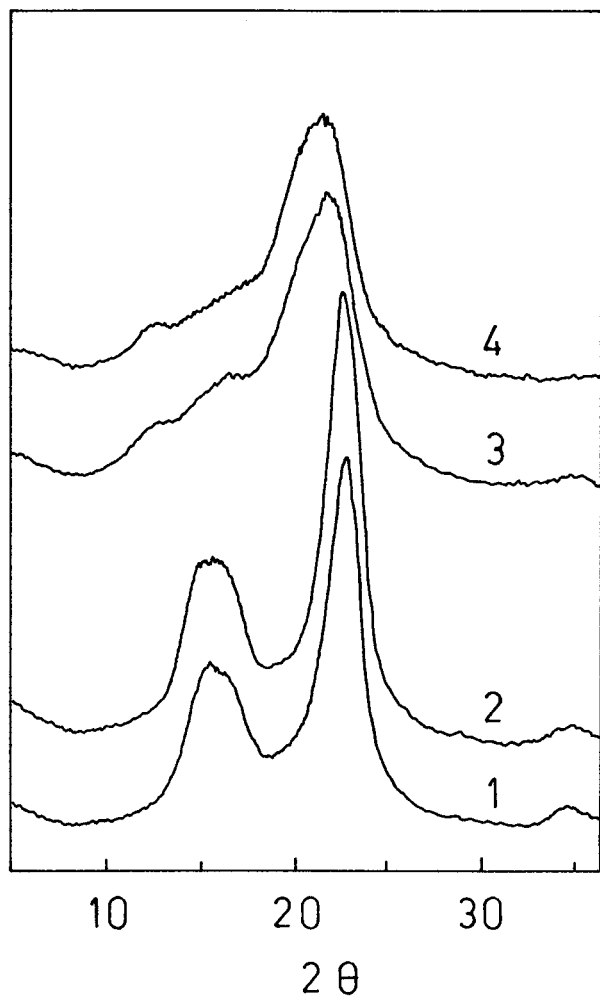

Figure 6   The X-ray diffractograms of (1) wood pulp and wood pulp regenerated after alkalization in (2) ethanol, (3) ethanol-acetone 3 : 7 (w/w), and (4) acetone.
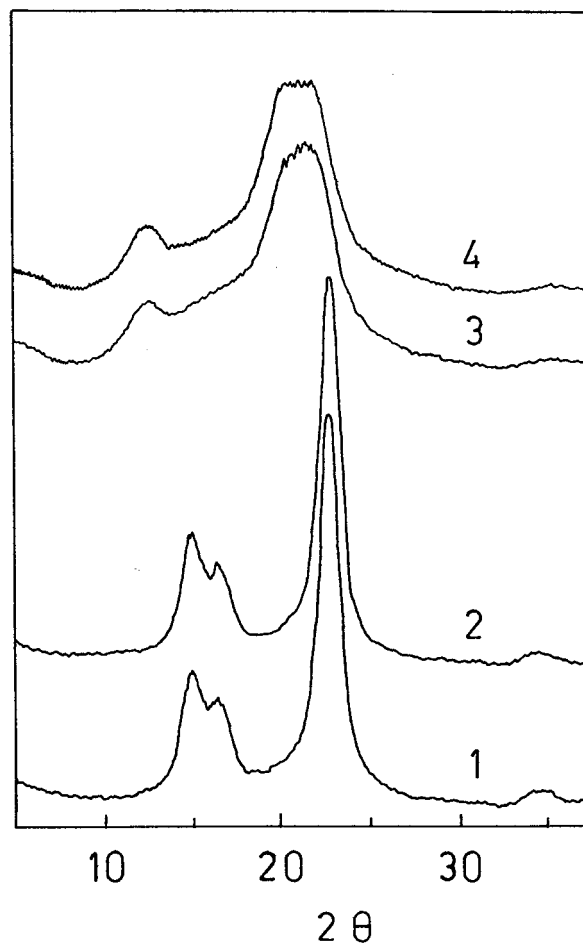

Figure 7   The X-ray diffractograms of (1) cotton linters and cotton linters regenerated after alkalization in (2) ethanol, (3) ethanol-acetone 3 : 7 (w/w), and (4) acetone.

Table II The Wetting Heats of Untreated Cellulose and Cellulose Regenerated After Alkalization in Different Organic Media

Cellulose Sample	Alkalization Medium	Wetting Heat (J/g)
Cotton linters	No alkalization	40.8
Cotton linters	Ethanol	44.0
Cotton linters	Ethanol–acetone 3 : 7 (w/w)	68.3
Cotton linters	Acetone	64.4
Wood pulp	No alkalization	47.5
Wood pulp	Ethanol	57.7
Wood pulp	Ethanol–acetone 3 : 7 (w/w)	86.0
	Acetone	81.0

good agreement with the behavior of each alkali-cellulose towards carboxymethylation in the first stage of reaction. Furthermore, the ethanol-acetone mixture facilitates the diffusion of the etherifying agent in the more ordered regions as the carboxymethylation proceeds. Thus, the higher rate constant values observed in the second stage of carboxymethylation are probably in connection with a higher rate of diffusion in the new structural matrix of the polymer, consisting of a mixture of crystalline forms of cellulose I and cellulose II.

These observations are valid for both kinds of cellulose used in this article; but, as can be seen in Table I and in Figures 4 and 5, the rate constants in the first stage of reaction are higher for wood pulp cellulose in both acetone and the ethanol-acetone mixture. Therefore, the rate of carboxymethylation is dependent not only on the structural transformations produced in different reaction media but also on the crystallinity of the starting cellulose.

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