

Effect of the Distribution of Substitution of the Sodium Salt of Carboxymethylcellulose on Its Absorbency toward Aqueous Liquid

Kenji KAMIDE, Kunihiro OKAJIMA, Keisuke KOWSAKA,
Toshihiko MATSUI, Sigeru NOMURA, and Kunio HIKICHI*

*Textile Research Laboratory, Asahi Chemical Industry Co., Ltd.,
11-7 Hacchonawate, Takatsuki, Osaka 569, Japan*
**Department of Polymer Science, Faculty of Science,
Hokkaido University, Kita-ku, Sapporo 060, Japan*

(Received November 9, 1984)

ABSTRACT: An attempt was made to correlate the capacity of the aqueous liquid absorption of sodium salt of carboxymethylcellulose with its chemical structure, in particular with the total degree of substitution $\langle F \rangle$ and distribution of substitution $\langle f_k \rangle$. Here, $\langle f_k \rangle$ is the average degree of substitution of hydroxyl group attached to C_k carbon ($k=2, 3, \text{ and } 6$) in an anhydroglucopyranose unit. For this purpose, 26 samples of NaCMC having $\langle F \rangle$ less than 0.64 were synthesized by reacting cellulose having crystal form of cellulose I or II with a mixture of sodium hydroxide, monochloroacetic acid and 2-propanol. Their absorbency was determined at 37°C toward water, 0.9 wt% aq. sodium chloride, calcium chloride and aluminium chloride solutions. $\langle f_2 \rangle + \langle f_3 \rangle$, $\langle f_6 \rangle$, and $\langle F \rangle$ were determined for these polymers by ^{13}C NMR in 10 wt% sodium hydroxide–90 wt% D_2O mixture. On using the cellulose with the crystal form cellulose II, carboxymethylation occurred almost preferentially at the hydroxyl group attached to the C_6 carbon. This was not observed for the cellulose having the crystal form of cellulose I. Absorbency was found to be definitely governed by $\langle f_6 \rangle$, which can be explained in consideration of the solid structure of cellulose and NaCMC.

KEY WORDS Sodium Salt of Carboxymethylcellulose / Distribution of Degree of Substitution / Absorbency / Cellulose I / Cellulose II /

Jansen¹ synthesized carboxymethylcellulose (CMC) as early as in 1918 using the reaction of alkali cellulose with sodium monochloroacetate. Since then, CMC with a total degree of substitution $\langle F \rangle$ of 0.5—1.0 has been commercialized world-wide and found numerous applications as stabilizing, thickening and absorbing agents in printing, detergent, foodstuffs, medicine, toilet, sanitary and petroleum industries. At the present, the industrial manufacturing of CMC is carried out either in aqueous or organic media.^{2,3} Natural cellulose with the crystal form of cellulose I (hereafter simply referred to as cellulose I) is exclusively used in the present commercial process, but no regenerated cellulose with the

crystal form of cellulose II (hereafter referred to as cellulose II) is used.

Characteristic features, including solubility in water and aqueous salt solutions and interaction with cationic compounds, have been discussed so far only in a non-systematic manner.^{4,5} Recently, Kamide and his coworkers⁶ found the anticoagulant activity and acute toxicity of the sodium salt of cellulose sulfate to be quite closely related to its molecular properties, and in particularly to the probability of the substitution of hydroxyl groups attached to the C_2 , C_3 , and C_6 carbons in the glucopyranose unit, $\langle f_2 \rangle$, $\langle f_3 \rangle$, and $\langle f_6 \rangle$. The anticoagulant activity increased strongly with an increase in $\langle f_2 \rangle + \langle f_3 \rangle$. The chemical and

physical properties of cellulose derivatives, including CMC, should thus be governed primarily by $\langle\langle f_k \rangle\rangle$ and $\langle\langle F \rangle\rangle$.

In this article we report in particular the high degree of the absorbency of the sodium salt of CMC (NaCMC), prepared from regenerated cellulose having the crystal form of cellulose II, toward various liquids and explain the absorbency on the basis of $\langle\langle f_k \rangle\rangle$ and $\langle\langle F \rangle\rangle$.

EXPERIMENTAL

Synthesis of Carboxymethylcellulose

As starting materials, four kinds of cellulose were used. Cellulose II (viscosity-average molecular weight $M_v = 7.3 \times 10^4$ and degree of crystallinity by the X-ray diffraction method $\chi_c = 46\%$), regenerated from a cuprammonium cotton linter cellulose solution was used and is referred to as sample BLC. Natural wood pulp (cellulose I, $M_v = 21 \times 10^4$ and $\chi_c = 76\%$) and two acid-hydrolyzed wood pulps, prepared in 6*N* sulfuric acid at 60°C for 15 and 65 min ($M_v = 9.4 \times 10^4$ and 7.4×10^4 , $\chi_c = 77\%$) were used and are referred to as NC-1, NC-2, and NC-3, respectively.

Twenty six samples of NaCMC having $\langle\langle F \rangle\rangle_{\text{chem}} = 0.01\text{--}0.64$, chemically determined, were synthesized in following manner: 20 g of cellulose were dipped in a 80 ml of a system containing 3.3 g of sodium hydroxide and a mixture of 2-propanol–methanol–water (56:28:16, v/v/v) at 25°C and allowed to stand for 30 min. At 60°C, 2-propanol solution saturated with monochloroacetic acid was added to the system. The reaction appeared heterogeneous and was processed at 60°C for 120 min without mechanical agitation. In this case, 0.07–7.15 g of monochloroacetic acid per 10 g of cellulose were added so as to obtain CMC with the desired $\langle\langle F \rangle\rangle$. Immediately on termination of the reaction, the resultant system was neutralized with a mixture of methanol–30 wt% hydrochloric acid (9:1, w/w). The CMC in acid form was separated by filtration and washed with excess aq. me-

thanol, immersed in a mixture of methanol–2 wt% aq. sodium chloride (9:1, w/w) for 24 h for conversion into the salt form, washed again with aq. methanol, dried in air and then *in vacuo* at 70°C for 8 h. By this method, 9 NaCMC samples, coded the BL series, were synthesized from BLC, 9 samples from NC-1 (N-1 series), 5 samples from NC-2 (N-2 series), and 3 samples from NC-3 (N-3 series).

Viscosity-Average Molecular Weight

The number-average and weight-average molecular weights of the NaCMC samples were not determined owing to experimental difficulty. We determined only M_v of starting cellulose from the limiting viscosity number $[\eta]$ in cadoxen (cadmium oxide–sodium hydroxide–ethylenediamine–water (4:1:12:83, w/w/w/w) using the Brown–Wikström relation⁷:

$$[\eta] = 3.85 \times 10^{-2} M_w^{0.76} \quad (\text{at } 25^\circ\text{C}) \quad (1)$$

X-Ray Diffraction

X-Ray diffraction patterns of the original cellulose(s) and NaCMC were recorded with a RU-200PL type X-ray diffractometer (Rigaku Denki Co., Japan). χ_c of cellulose was calculated by the Segal's method,⁸ using the relation

$$\chi_c = \frac{I_c - I_a}{I_c} \quad (2)$$

Here, I_a and I_c are the relative intensities of the amorphous and crystalline peaks from the base line drawn by connecting the relative intensities at $2\theta = 4$ and 32° (see Figure 1). For NaCMC, I_c was defined as the highest intensity at the diffraction angle $2\theta = 19\text{--}30^\circ$ and I_a , the lowest intensity at $2\theta = 15\text{--}20^\circ$.

¹³C NMR Measurement

Each of the four samples of the BL and N-1 series in a mixture of sodium hydroxide–deuterium oxide (1:9, w/w) was measured for the ¹³C NMR spectrum on a JEOL FX-400 and FX-500 pulse-Fourier Transform NMR

Table I. Shielding and deshielding effects of the *O*-carboxymethyl group in 2-, 3-, and 6-substituted carboxymethyl glucose

Type of substitution	Chemical shift from unsubstituted group					
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
2-Substituted	-0.4	8.1	-1.2	-0.4	-0.3	-0.5—1.1
3-Substituted	-0.4	-0.9	9.1	-0.8	-0.7	-0.9—1.0
6-Substituted	-0.3	-0.7	-0.8	-1.1	-1.8	8.1

spectrometer (100.7 and 125.9 MHz for ¹³C nuclei, respectively). The proton decoupled ¹³C NMR method in the NNE mode was applied using dioxane (67.8 ppm) as the internal standard. For detection of CH₂ carbon peaks, the insensitive nuclei enhanced by the polarization transfer/complete decoupling (INEPT/COM) method⁹ (delay time, Δ = 3(4*J*)⁻¹, *J* being the scalar coupling constant between ¹³C and ¹H), was carried out.

NMR Peak Assignment

Using the reported results^{10,11} for β-glucose and its C₂-, C₃-, and C₆-monocarboxymethylated β-glucoses, the shielding or deshielding effect on ring carbons, induced by monosubstitution, was estimated (see Table I). By this results along with the ring carbon peaks of unsubstituted cellulose (*i.e.*, C₁, 104.7; C₂, 75.0; C₃, 76.4; C₄, 80.0; C₅, 76.4, and C₆, 61.9 ppm), the ring carbon peaks for all possible substituted forms of cellulose was calculated. For example, the peak position of the C₁ carbon of NaCMC with ⟨f₆⟩ = 1.00, ⟨f₂⟩ = 1.00, and ⟨f₃⟩ = 0.00, is 104.7 - 0.4 - 0.3 = 104.0 ppm. The results are shown in Table II. The calculated peaks were compared with those observed.

Determination of the Distribution of Substitution by the NMR Method

Total degree of substitution ⟨F⟩_{NMR}, ⟨f₆⟩, ⟨f₂⟩ + ⟨f₃⟩ were calculated from ¹³C NMR spectra using the following relations:

$$\langle F \rangle_{\text{Chem}} = \frac{I_{\text{CO}}}{I_{\text{C}_1}} \quad (3)$$

$$\langle f_6 \rangle = \frac{I_{\text{SC}_6}}{I_{\text{C}_6} + I_{\text{SC}_6}} \quad (4)$$

$$\langle f_2 \rangle + \langle f_3 \rangle = \frac{I_{\text{SC}_2} + I_{\text{SC}_3}}{I_{\text{C}_1}} \quad (5)$$

where *I*_{C₁}, *I*_{CO}, *I*_{C₆}, *I*_{SC₆}, *I*_{SC₂}, and *I*_{SC₃} are the integrated peak intensities of C₁ carbon (103—105 ppm), CO carbon (180 ppm), unsubstituted C₆ carbon (61 ppm), substituted C₆ carbon (72.3 ppm) and substituted C₂ and C₃ carbons (81—86 ppm), respectively. Note that ⟨f₆⟩ is independently determined from ⟨F⟩_{NMR} or ⟨f₂⟩ + ⟨f₃⟩ since the Overhauser effect in the C₆ carbon was found somewhat smaller than in other carbons.

Total Degree of Substitution Determined by Chemical Analysis

Before determining ⟨F⟩_{Chem} by chemical analysis, NaCMC was converted to the acid form and immersed in a 3 wt% aq. sodium chloride solution. The hydrochloric acid thus produced was diluted with alkali and the excess of which was back-titrated with hydrochloric acid.

Absorbency

*W*₀ gram (about 0.5 g) was placed in a non-woven fabric bag having a weight of *a* gram. The bag was immersed for 10 min at 37°C in pure water, 0.9 wt% of NaCl, CaCl₂, and AlCl₃ aq. solutions, respectively. It was then suspended for 20 min in air to remove water adhering to the bag and sample and weighed ((*W*₁ + *a*) gram). The bag containing the

NaCMC sample was dried and weighed ($(W_2 + a)$ gram). Absorbency A and solubility S were then defined by the following relations:

For water,

$$A = \frac{W_1}{W_2} \times 100 (\%) \quad (6)$$

$$S = \frac{W_0 - W_2}{W_0} \times 100 (\%) \quad (7)$$

and for aq. salt solutions

$$A = \frac{W_1}{W_2 - 0.009(W_0 - W_1)} \times 100 (\%) \quad (8)$$

$$S = \frac{W_0 - W_2 + 0.009(W_0 - W_1)}{W_0} \times 100 (\%) \quad (9)$$

Here, W_0 , W_2 , and a were determined for sample which was conditioned at 20°C at 65% relative humidity for 24 h.

RESULTS AND DISCUSSION

Figure 1 shows the change in X-ray diffraction patterns of cellulose I(A) and II(B) by alkali treatment and carboxymethylation. The characteristic diffraction peaks for both cellulose I ($2\theta = 9.0, 14.7, 16.4, \text{ and } 22.6^\circ$) and II ($2\theta = 9.5, 12.0, 20.0, \text{ and } 21.5^\circ$) remain distinct despite any treatment, although the X-ray diffraction pattern of NaCMC with relatively high $\langle F \rangle$ (0.5–0.6) shows only the main peaks of the original celluloses. The original celluloses are thus not converted to alkali celluloses and the reaction is principally heterogeneous. Carboxymethylation first occurs in the amorphous region and proceeds to the crystalline part. Thus, the reaction from start to finish is influenced by the structure of the original celluloses.

Figure 2 shows χ_c plotted against $\langle F \rangle_{\text{Chem}}$. χ_c of the NaCMC sample prepared from cellulose I decreases gradually as $\langle F \rangle$ increases and abruptly drops to 10% at $\langle F \rangle \approx 0.4\text{--}0.5$. The hydroxyl group present in the crystalline region does not react with

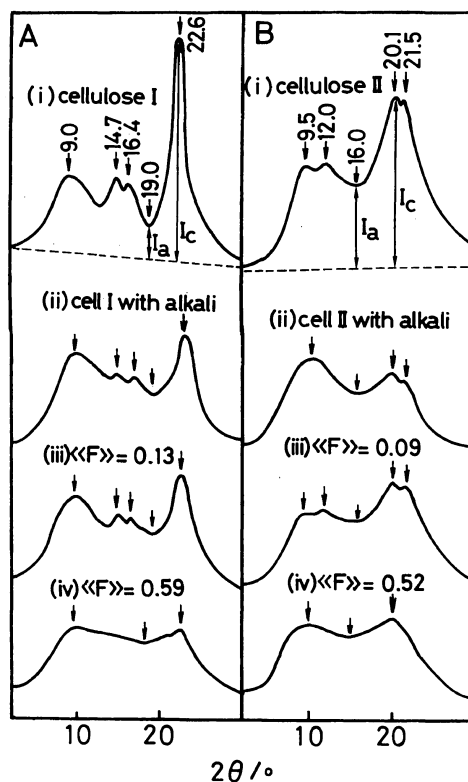


Figure 1. Change in X-ray diffraction curves of cellulose I (A) and II (B) alkali treatment and carboxymethylation: (A) (i), cellulose I; (ii), cellulose I with alkali; (iii), CMC ($\langle F \rangle_{\text{Chem}} = 0.13$) from cellulose I; (iv), CMC ($\langle F \rangle_{\text{Chem}} = 0.59$) from cellulose I; (B) (i), cellulose II; (ii), cellulose II with alkali; (iii), CMC ($\langle F \rangle_{\text{Chem}} = 0.09$) from cellulose II; (iv), CMC ($\langle F \rangle_{\text{Chem}} = 0.52$) from cellulose II, I_a and I_c denote the relative intensity from amorphous and crystalline regions.

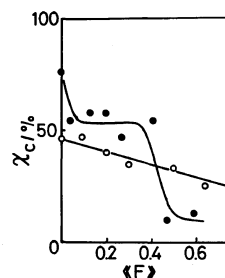


Figure 2. Relationships between crystallinity χ_c and total degree of substitution $\langle F \rangle_{\text{Chem}}$: ○, CMC from cellulose II (BL series); ●, CMC from cellulose I (N-1 series).

Table II. Calculated chemical shift of CMC

Type of CMC	Chemical shift δ /ppm					
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
Unsubstituted	104.7	75.0	76.4	80.0	76.4	61.9
2-Substituted	104.3	85.9	75.2	79.6	76.1	61.4
3-Substituted	104.3	74.1	84.3	79.2	75.7	61.1
6-Substituted	104.4	74.3	75.6	78.9	74.6	70.0
2,3-Substituted	103.9	83.0	85.3	78.8	75.5	60.6
2,6-Substituted	104.0	83.1	74.4	78.5	74.3	69.5
3,6-Substituted	104.0	73.4	84.7	78.1	73.9	69.2
2,3,6-Substituted	103.6	82.3	83.5	77.7	73.6	68.7

^a CH₂ for substituent group is expected to be around 71.2 ppm.
COONa for substituent group was seen at 178.4 and 178.8 ppm.

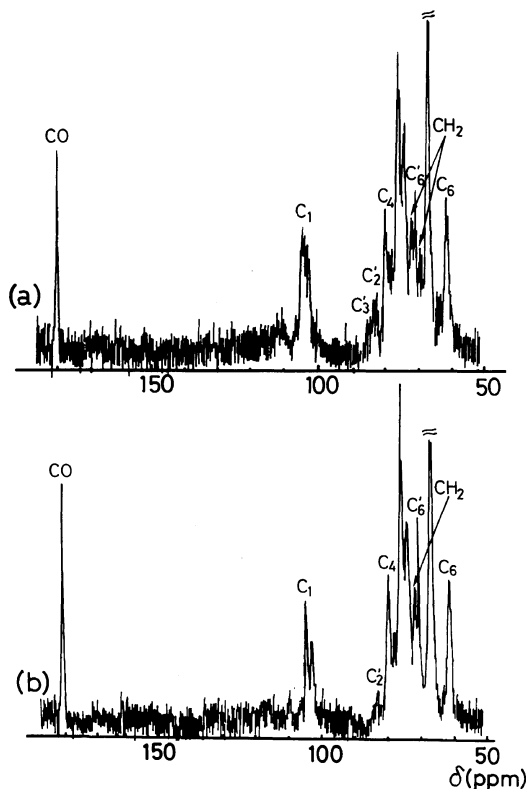


Figure 3. Typical ¹³C NMR spectra of CMC (N-1-8) from cellulose I (a) and CMC (BL-9) from cellulose II (b).

monochloroacetic acid in a very random manner. χ_c of sample, prepared from cellulose II decreases linearly with increasing $\langle F \rangle$. The cellulose II sample is a regenerated cellulose

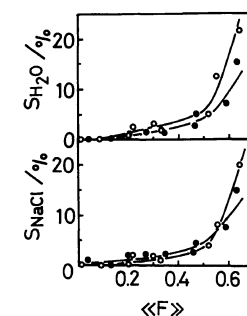


Figure 4. Solubility of NaCMC in H₂O and 0.9 wt% aq. NaCl as a function of total degree of substitution $\langle F \rangle_{\text{Chem}}$: ○, CMC from cellulose II (BL series), ●, CMC from cellulose I (N-1 series).

having low χ_c and is very reactive with chemical reagents.

Figure 3 shows the ¹³C NMR spectra of sample N-1-8 ($\langle F \rangle_{\text{Chem}} = 0.59$) and BL-9 ($\langle F \rangle_{\text{Chem}} = 0.64$) at 125.7 MHz. The observed peak positions (CO; 178.4–178.8 ppm, C₁; 103–104 ppm, substituted C₂ and C₃; 82–85 ppm, substituted C₆; 72.3 ppm, unsubstituted C₆; 61.9 ppm) were in good agreement with those calculated in Table II and those reported by Parfondry *et al.*¹² using commercial CMC decomposed enzymatically or by hydrolysis. Methylene carbons for carboxymethyl groups substituted at C₂ and C₆ are reported to be positioned at 67.6 and 72.6 ppm, respectively. But, in this study, the former peak was overlapped by a peak for the dioxane standard.

Table III. Characterization and properties of CMC samples

Sample	M_v	Total $\langle F \rangle$		Distribution		$S/\%$		χ_c	$A/100\%$			
	10^4	Chem. anal.	NMR	$\langle f_2 \rangle + \langle f_3 \rangle$	$\langle f_6 \rangle$	H ₂ O	NaCl	%	H ₂ O	NaCl	CaCl ₂	Al ₂ Cl ₃
BL-1	7.3	0.01	—	—	—	0.0	0.0	—	16.2	18.0	—	—
BL-2	7.3	0.09	0.03	0.00	0.03	0.0	0.0	46.9	17.5	17.5	13.5	15.2
BL-3	7.3	0.20	0.14	0.02	0.11	0.5	0.0	40.2	49.6	22.3	13.0	40.2
BL-4	7.3	0.22	—	—	—	2.5	2.0	—	51.9	25.0	—	—
BL-5	7.3	0.30	0.27	0.01	0.27	3.0	1.5	34.7	52.0	32.0	18.0	13.0
BL-6	7.3	0.33	—	—	—	2.0	1.0	—	60.0	38.5	—	—
BL-7	7.3	0.52	—	—	—	5.0	4.0	32.8	22.5	48.5	—	—
BL-8	7.3	0.55	—	—	—	12.5	8.0	—	20.0	45.0	—	—
BL-9	7.3	0.64	0.65	0.09	0.54	21.5	20.0	25.0	15.4	29.1	24.0	12.0
N-1-1	21.0	0.04	—	—	—	0.0	1.0	54.3	14.5	16.0	—	—
N-1-2	21.0	0.13	—	—	—	0.0	0.0	57.8	19.3	20.0	—	—
N-1-3	21.0	0.20	0.24	0.16	0.08	1.0	2.0	57.8	29.1	22.0	13.5	13.7
N-1-4	21.0	0.27	—	—	—	1.5	2.5	47.0	42.6	21.0	—	—
N-1-5	21.0	0.35	0.41	0.20	0.21	1.5	2.5	54.3	44.0	19.6	17.0	17.8
N-1-6	21.0	0.46	—	—	—	3.0	2.5	—	61.8	29.3	—	—
N-1-7	21.0	0.47	—	—	—	5.0	4.5	9.1	61.0	27.4	—	—
N-1-8	21.0	0.59	0.60	0.39	0.20	7.0	7.5	12.8	49.0	28.6	16.5	11.0
N-1-9	21.0	0.63	0.71	0.34	0.37	15.0	15.0	—	30.7	26.5	21.0	11.8
N-2-1	9.4	0.14	—	—	—	—	—	—	19.4	16.0	—	—
N-2-2	9.4	0.24	—	—	—	—	—	—	29.0	15.5	—	—
N-2-3	9.4	0.31	—	—	—	—	—	—	37.2	18.0	—	—
N-2-4	9.4	0.38	—	—	—	—	—	—	23.0	16.6	—	—
N-2-5	9.4	0.51	—	—	—	—	—	—	22.6	13.0	—	—
N-3-1	7.4	0.16	—	—	—	—	—	—	12.5	7.5	—	—
N-3-2	7.4	0.23	—	—	—	—	—	—	22.5	12.6	—	—
N-3-3	7.4	0.39	—	—	—	—	—	—	23.5	12.5	—	—

Figure 4 indicates the peaks in region lower and higher than the substituted C₆ carbon peak (72.3 ppm) to be complicated in shape owing to incomplete proton decoupling, increasing their intensity in proportion to that of the substituted C₂ and C₃ carbon peaks (82–85 ppm). Their intensity for N-1-8 is much stronger than those for BL-9, despite the same order of $\langle F \rangle$.

Table III shows the M_v , $\langle F \rangle_{\text{Chem}}$, $\langle F \rangle_{\text{NMR}}$, $\langle f_k \rangle$, solubility S , χ_c , and absorbency A for the NaCMC samples. It should be noted that $\langle F \rangle_{\text{NMR}}$ coincided well with $\langle F \rangle_{\text{Chem}}$ with an experimental uncertainty less than 0.04 and $\langle F \rangle_{\text{NMR}}$, $\langle f_2 \rangle + \langle f_3 \rangle$, and $\langle f_6 \rangle$ evaluated independently satisfied the conditions $\langle F \rangle_{\text{NMR}} = \langle f_2 \rangle + \langle f_3 \rangle + \langle f_6 \rangle$. This shows the equations used for evaluating the degree of substitution to be valid.

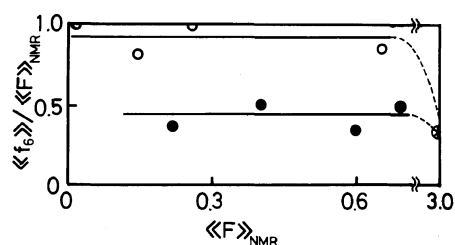


Figure 5. Plot of $\langle f_6 \rangle / \langle F \rangle_{\text{NMR}}$ versus $\langle F \rangle_{\text{NMR}}$. Symbols are the same as in Figure 4.

The solubility S in water and aq. NaCl is plotted as a function of $\langle F \rangle_{\text{Chem}}$ in Figure 4. NaCMC did not dissolve significantly in either aq. CaCl₂ or aq. AlCl₃. S in water and in aq. NaCl was always less than 5% for $\langle F \rangle_{\text{Chem}} < 0.55$ and increased remarkably when $\langle F \rangle_{\text{Chem}}$ exceeded 0.55.

Figure 5 shows a plot of the ratio $\langle f_6 \rangle /$

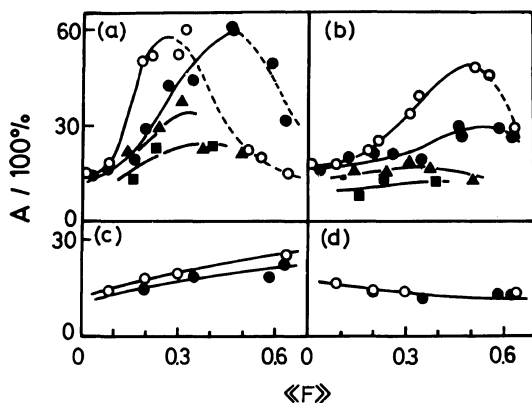


Figure 6. Absorbency A of NaCMC toward various liquids as a function of total degree of substitution $\langle F \rangle_{\text{Chem}}$: a, H_2O ; b, 0.9 wt% aq. NaCl; c, 0.9 wt% aq. CaCl_2 ; d, 0.9 wt% aq. AlCl_3 ; \circ , CMC from cellulose II (BL series, $M_v = 7.3 \times 10^4$); \bullet , CMC from cellulose I (N-1 series, $M_v = 21.0 \times 10^4$); \blacktriangle , CMC from cellulose I (N-2 series, $M_v = 9.4 \times 10^4$); \blacksquare , CMC from cellulose I (N-3 series, $M_v = 7.4 \times 10^4$).

$\langle F \rangle_{\text{NMR}}$ versus $\langle F \rangle_{\text{NMR}}$ for the BL (open mark) and the N-1 (closed mark) series CMC. $\langle f_6 \rangle / \langle F \rangle_{\text{NMR}}$ for the BL series CMC was 0.9 ± 0.1 , when $\langle F \rangle_{\text{NMR}} < 0.7$, indicating carboxymethylation to occur almost preferentially at the hydroxyl group attached to the C_6 carbon on using cellulose II. $\langle f_6 \rangle / \langle F \rangle_{\text{NMR}}$ for N-1 series was 0.43 ± 0.1 within $\langle F \rangle_{\text{NMR}} < 0.7$. The reactivity of the hydroxyl groups is thus seen to depend very significantly on the cellulose sample, particularly its crystalline form.

Factors Influencing Absorbency of NaCMC

Figure 6 shows the relations between absorbency A against pure water (a), aq. NaCl (b), aq. CaCl_2 (c), and aq. AlCl_3 (d) and $\langle F \rangle_{\text{Chem}}$ for N-1 ($M_v = 21 \times 10^4$, closed circle) and BL ($M_v = 7.3 \times 10^4$, open circle) series. Figure 6a and b include the data for N-2 ($M_v = 9.4 \times 10^4$, closed triangle) and N-3 ($M_v = 7.4 \times 10^4$, closed rectangle) series in order to elucidate the molecular weight dependence of A . For the N series, A increases somewhat with an increase in M_v at a given $\langle F \rangle_{\text{Chem}}$. Compared with BL series at the same M_v level, the absolute A value for the N-3 series in water and aq. NaCl

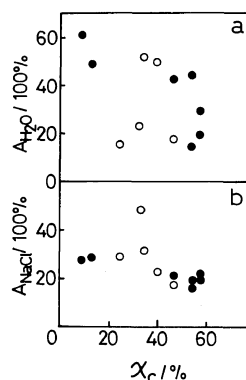


Figure 7. Absorbency A of NaCMC towards H_2O (a) and 0.9 wt% aq. NaCl (b) as a function of the degree of crystallinity χ_c . Symbols are the same as those in Figure 4.

is much lower than that of the BL series, indicating molecular weight not to be the main factor controlling A . On comparing the BL series with the N-1 series, maximum A in aq. NaCl of the former is 1.5 times that of the latter, so that NaCMC synthesized from cellulose II is particularly suitable as an absorbing agent, especially for aq. NaCl and similar solutions.

Neither $\langle F \rangle_{\text{Chem}}$ is the main factor since its value giving maximum A against water and aq. NaCl differ according to the sample. A in aq. CaCl_2 increased gradually with an increase in $\langle F \rangle_{\text{Chem}}$ for both samples. The BL series samples had a somewhat larger A than that of the N-1 series. But, A in aq. AlCl_3 decreased slightly with an increase in $\langle F \rangle_{\text{Chem}}$, due of course to cross-linking between carboxyl groups and Al^{3+} cations.

Figure 7 shows the effects of the crystallinity χ_c on A in pure water (a) and in aq. NaCl (b). As χ_c increased A tended slightly to decrease, and the correlation coefficients γ for A and χ_c were as follows: $A_{\text{H}_2\text{O}} - \chi_c$, -0.34 ; $A_{\text{NaCl}} - \chi_c$, -0.88 for the BL series and $A_{\text{H}_2\text{O}} - \chi_c$, -0.79 and $A_{\text{NaCl}} - \chi_c$, -0.82 for the N-1 series. Thus, there is no significant correlation between A and χ_c and χ_c is concluded not to be an additional factor controlling A .

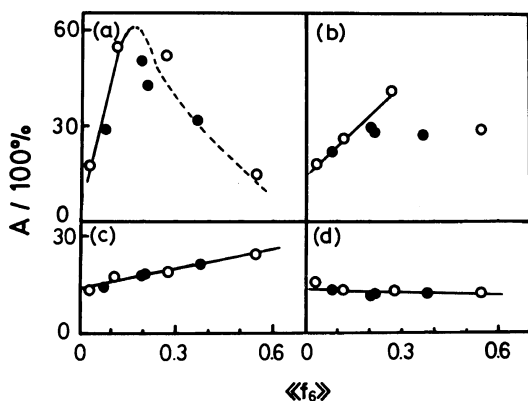


Figure 8. Absorbency A of NaCMC towards various liquids as a function of $\langle\langle f_6 \rangle\rangle$: a, H_2O ; b, 0.9 wt% aq. NaCl; c, 0.9 wt% aq. CaCl_2 ; d, 0.9 wt% aq. AlCl_3 . Symbols are the same as those in Figure 4.

Figure 8 shows a plot of the absorbency A against $\langle\langle f_6 \rangle\rangle$, giving a single master curve for each liquid, irrespective of the sample series. As long as NaCMC does not dissolve in the liquid being used, the absorbency can be accurately determined by $\langle\langle f_6 \rangle\rangle$. The following relations were obtained using the least-squares method:

$$A = 400\langle\langle f_6 \rangle\rangle + 7.0 \quad \text{in pure water,}$$

$$\langle\langle f_6 \rangle\rangle < 0.17$$

$$A = 79\langle\langle f_6 \rangle\rangle + 14.2 \quad \text{in 0.9 wt\% aq. NaCl,}$$

$$\langle\langle f_6 \rangle\rangle < 0.30$$

$$A = 19.5\langle\langle f_6 \rangle\rangle + 14.2 \quad \text{in 0.9 wt\% aq. CaCl}_2,$$

$$\langle\langle f_6 \rangle\rangle < 0.57$$

$$A = -3.25\langle\langle f_6 \rangle\rangle + 13.7 \quad \text{in 0.9 wt\% aq. AlCl}_3,$$

$$\langle\langle f_6 \rangle\rangle < 0.57$$

Mechanisms of Carboxymethylation and Water Absorption by NaCMC

Figure 9 schematically illustrates the mechanism of carboxymethylation of cellulose (a—c) and that of water absorption by NaCMC (a→a', b→b', c→c'). In this figure, the full line is the cellulose chain and the

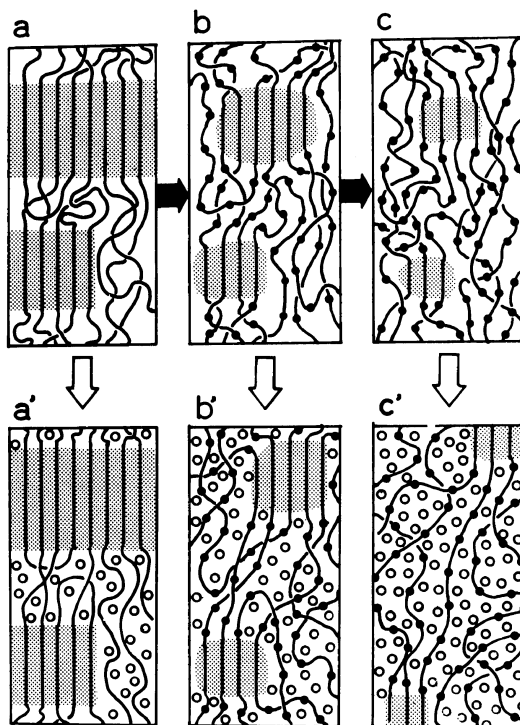


Figure 9. Schematic representation of carboxymethylation and swelling by water: —, cellulose chain; ●, carboxymethylated glucose unit; ○, H_2O molecule; shadowed area denotes crystalline part.

shadowed area, the crystalline region. The filled circle is carboxymethylated glucose and open circle, water molecules. On immersing cellulose (a) in water, only a part of the amorphous region absorbs water (a'). Carboxymethylation of the cellulose occurs first in the amorphous region, the crystalline region collapses from the surface with further carboxymethylation (b and c). CMC with relatively low $\langle\langle F \rangle\rangle$ (b) dissociates, resulting in strong solvation with the surrounding water molecules and the consequent swelling (b'). CMC with relatively high $\langle\langle F \rangle\rangle$ (c) remains its smaller crystalline region and becomes hydrogel with its crystalline region as a kind of cross-linking point when immersed in water (c'). This mechanism is considered to be applicable to both BL and N series samples.

However, the reason for preferential car-

boxymethylation at the C_6 position of cellulose having the crystalline form of cellulose II and the paramount role of $\langle f_6 \rangle$ in the absorbency A should be clarified in great detail. In considering the present carboxymethylation, it should be noted that 1) cellulose is not converted to alkali cellulose, 2) monochloroacetic acid reacts as an electrophilic reagent,¹² and 3) carboxymethylation proceeds from an amorphous to crystalline region. A hydroxyl group having strong acidity in cellulose molecules thus reacts much more easily with monochloroacetic acid. This acidity is proportional for the most part to the electron density on its adjacent carbon atom. This density in turn governs the ^{13}C NMR resonance position, resonating at a higher magnetic field when the carbon has a higher electron density. A recent NMR analysis on cellulose showed the C_6 carbon NMR peak to appear at about 65–62 ppm, while both C_2 and C_3 carbons resonate at 77–72 ppm, regardless of the crystalline form. The hydroxyl group attached to the C_6 carbon thus reacts more easily with monochloroacetic acid than those at the C_2 and C_3 carbons. This agrees with the experimental facts that $\langle f_6 \rangle / \langle F \rangle_{\text{NMR}}$ for celluloses I and II were found to be 0.43 ± 0.1 and 0.9 ± 0.1 , respectively.

A more detailed investigation of the NMR spectrum of the C_6 carbon region, carried out in our previous work¹³ indicated that 1) hydroxyl groups at the C_6 position for cellulose II participate in two types of intramolecular hydrogen bonds ($\text{O}_2\text{-H} \cdots \text{O}'_6$ and $\text{O}_6\text{-H} \cdots \text{O}'_2$, the latter being much more acidic), 2) hydroxyl groups of cellulose I does not form the $\text{O}_6\text{-H} \cdots \text{O}'_2$ type intramolecular hydrogen bond, and 3) the electron density on C_6 carbon for cellulose II in both ordered (crystalline) and amorphous regions is higher than that for cellulose I and the reverse is true for the electron density on the C_2 carbon. Thus, the reactivity of the hydroxyl group at the C_6 position of cellulose II may possibly be relatively higher than that of cellulose I. The reverse situation applies at the C_2 position.

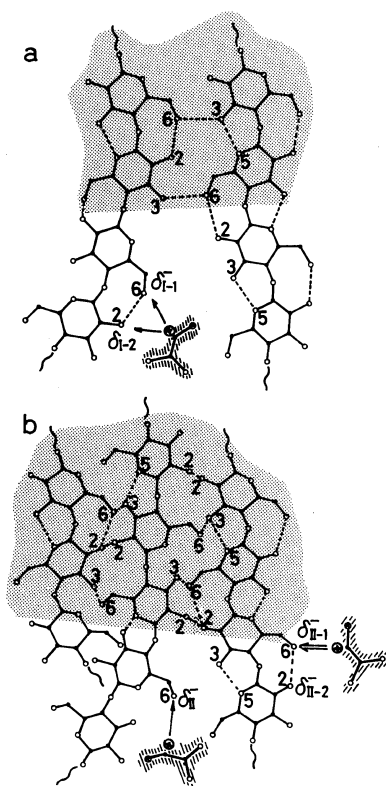


Figure 10. Schematic representation of carboxymethylation toward $\text{O}_2\text{-H} \cdots \text{O}'_6$ type intramolecular hydrogen bonds in cellulose I (a) and cellulose II (b). Shaded area denotes the cationized monochloroacetic acid. δ_{I-1} and δ_{I-2} mean the electronegativity (EN) for cellulose I and δ_{II} , δ_{II-1} , and δ_{II-2} , EN for hydroxyl groups at the C_6 and C_2 positions of cellulose II. EN has the following order: $\delta_{II-1} > \delta_{II} > \delta_{I-1} > \delta_{I-2} > \delta_{II-2}$. The $\text{O}_6\text{-H} \cdots \text{O}'_2$ type intramolecular hydrogen bonds for cellulose II are not shown. NE on the hydroxyl group at the C_6 position is much stronger than δ_{I-1} .

The exclusively preferential substitution of the hydroxyl group at the C_6 position does not occur in the case of cellulose I under the same conditions of carboxymethylation, as evident from Figure 10. The introduction of a bulky substituent at the C_6 position destroys the intermolecular hydrogen bonds and widens the distance between molecular chains, creating a wider space to readily receive the absorbed liquids. This is because the hydroxyl groups at the C_6 position in the original cellulose mainly govern the intermolecular hydrogen bonds.

REFERENCES

1. E. Jansen, Ger. Patent, 332203 (1918).
2. see, for example, W. F. Waldeck and F. W. Smith, *Ind. Eng. Chem.*, **44**, 2803 (1952).
3. see, for example, R. H. Charles, US Patent 2607772 (1952).
4. C. D. Callihan, "Cellulose Technology Research," A. F. Turbak Ed., ACS Series 10, 1975, p 33.
5. E. Otto and H. M. Spurlin, "Cellulose and Cellulose Derivatives," Vol. II, John Wiley & Sons Inc., New York, N. Y., 1954, p 944.
6. K. Kamide, K. Okajima, T. Matsui, M. Ohnishi, and H. Kobayashi, *Polym. J.*, **13**, 116 (1983).
7. W. Brown and R. Wikstrom, *Eur. Polym. J.*, **1**, 1 (1965).
8. L. Segal, *Text. Res. J.*, **29**, 786 (1959).
9. D. M. Doddrell and D. T. Pegg, *J. Am. Chem. Soc.*, **102**, 6388 (1980).
10. A. S. Perlin, B. Casu, and H. J. Koch, *Can. J. Chem.*, **48**, 2596 (1970).
11. A. Parfondry and A. S. Perlin, *Carbohydr. Res.*, **57**, 39 (1977).
12. see, for example, L. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961.
13. K. Kamide, K. Okajima, K. Kowsaka, and T. Matsui, *Polym. J.*, **17**, 701 (1985).