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Interactions and chain mobilities of *O*-carboxymethyl-*O*-2-(diethylamino)ethylcellulose in aqueous solutions

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The hydrophobic interactions between the 2-(diethylamino)ethyl substituents of *O*-carboxymethyl-*O*-2-(diethylamino)ethylcellulose in aqueous solutions were studied by gel permeation chromatography (g.p.c.). Intermolecular associations caused by the hydrophobic interactions between the 2-(diethylamino)ethyl substituents occur in 0.10 M NaOH, and such intermolecular hydrophobic interactions are restrained when the extension of chains is depressed as a result of the addition of NaCl. The mobilities of the carboxylmethyl and 2-(diethylamino)ethyl substituents (protonated or non-protonated) were evaluated from their ^{13}C nuclear magnetic resonance (n.m.r.) spin-lattice relaxation times, and were found to be affected by the interaction between the substituents, distance from the cellulose chains, and degree of solvation. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polyampholytes have unique physico-chemical characteristics due to the presence of both cationic and anionic groups. Previously, we have reported the inter- and intramolecular ionic interactions of two amphoteric cellulose derivatives[1,2]. It was expected, and ^{1}H n.m.r. spectra later confirmed[1], that *O*-carboxymethyl-*O*-2-(diethylamino)ethylcellulose (CM-DEAEC) is converted from a hydrophilic polyampholyte into an amphiphilic polyanion with a change in pH from 6–7 to 12.0. The hydrophobic 2-(diethylamino)ethyl (DEAE) substituents may interact intermolecularly or intramolecularly, leading to association and contraction of the cellulose chains, respectively. Thus, one purpose of this present paper is to evaluate such hydrophobic interactions by measuring the distribution of apparent molecular sizes and viscosities.

The structures of cellulose derivatives are more complicated than those of conventional synthetic polymers. For the motions of cellulose chains, we proposed that the six-membered rings of the anhydroglucose units, particularly those substituted by large groups, can maintain a stable chair-form conformation, and the rotational motions around the glucosidic bonds are the elementary motions dominating the behaviour of a cellulose chain in solution[3]. The interactions between the anhydroglucose units is one of the factors affecting the potential barrier of such rotational motions. On the other hand, the motions of the substituents depend on the position of substitution and on the interactions with neighbouring groups. Another purpose of this study is to examine the ionic attraction between the anionic carboxymethyl (CM) and the protonated DEAE substituents, as well as the hydrophobic interactions between the non-protonated DEAE substituents, from their respective mobilities.

^{13}C n.m.r. spectroscopy has been extensively employed to investigate the chain motions of numerous polymers in solution or as amorphous solids. A large amount of information concerning these chain motions can be obtained from spin-lattice, spin-spin relaxation times and the nuclear Overhauser enhancement effect. Among these, the ^{13}C n.m.r. spin-lattice relaxation times of protonated carbons are the most useful for evaluating the motions of polymer chains in solution[4–8]. In this present study, we used these spin-lattice relaxation times to examine the mobilities of the anhydroglucose units, and the CM, and DEAE substituents.

EXPERIMENTAL

Samples for g.p.c. measurements

In a 50-ml flask, 2.0 g of carboxymethyl cellulose (CMC) (F30LC, Nippon Paper Industries Co. Ltd) were mixed with 3.6 g of 16.6% aqueous NaOH, and then a specific amount of 2-(diethylamino)ethyl chloride was added. During the subsequent reaction, stirring was not carried out because of the occurrence of gelation. After

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reaction at 60°C under nitrogen for 30 min, the contents were dissolved in 200 ml of deionized water, and 18% hydrochloric acid was then added until the pH of the solution fell below 2. This solution was dialysed against 1 l of aqueous HCl (pH 1–2), which was replaced with a fresh volume every 4–10 h, over a period of 4 days, and then against deionized water until no chloride ion was detected in the dialysis solution with aqueous $AgNO_3$. This CM-DEAEC solution was adjusted to pH 12 with 10% aqueous NaOH, dialysed against deionized water to remove the excess NaOH, and finally freeze-dried. Two water-soluble CM-DEAEC samples, designated as CM-DEAEC-A and CM-DEAEC-B, were prepared using 0.75 and 2.0 g of 2-(diethylamino)ethyl chloride, respectively.

The original CMC (2.0 g) was mixed with 3.6 g of 16.6% aqueous NaOH, and the mixture was then kept at 60°C under nitrogen for 30 min. The CMC thus treated was purified by the dialysis procedure described above, and is designated as CMC-A. The *DS*-values (degree of substitution, number of substituents per anhydroglucose unit) of CMC-A, CM-DEAEC-A and CM-DEAEC-B are listed in *Table 1*.

Samples for ^{13}C n.m.r. spectroscopic measurements

At 80°C, 8.5 g of CMC (FPP-84, Nippon Paper Industries Co. Ltd) were dissolved in 60 ml of deionized water, and then 50 g of 50% NaOH and 22.0 g of 2-(diethylamino)ethyl chloride were added successively at room temperature. The mixture was stirred under nitrogen at 60°C for 70 min, and was then adjusted to pH 1–2 with 18% aqueous HCl. After dialysis against deionized water for 2 days, the CM-DEAEC solution (~200 g) was adjusted to pH 2.9 and the gel-like component was removed by centrifugation. The clear CM-DEAEC solution was then fractionated by the use of a Sepharose CL-6B column (530 ml, 60 × 35 cm^2), calibrated with sodium polystyrene sulfonate standards, using 0.1 M aqueous NaCl of pH 2.9 as the eluent. The concentrated fraction was dialysed against aqueous HCl of pH 1 for 4 days, then against dilute aqueous NaOH for 1 day, and finally against pure water for 4 days. The original CMC was also fractionated by the same column using 0.10 M NaCl as the eluent. The two samples thus obtained are designated as CM-DEAEC-1 and CMC-1, respectively. Their *DS*-values calculated from ^1H n.m.r. spectra[1,9] and the average molecular weights are shown in *Table 1*.

G.p.c. and viscosity measurements

The distribution of apparent molecular sizes and viscosities were measured according to the methods described elsewhere[1].

Measurement of ^{13}C n.m.r. spin-lattice relaxation times (T_1s)

In a 10 mm flat-bottomed n.m.r. tube, an appropriate vacuum-dried sample was dissolved in D_2O, and its concentration and pH were then adjusted with 10% NaOD, 6% DCl and D_2O. The solution was sealed under an atmosphere of highly pure nitrogen after deoxygenation on a vacuum line, and a vortex plug was used to keep the sample solution within the receiver coil of a probe. ^{13}C n.m.r. spectroscopic measurements were performed on a Bruker AC 300 spectrometer operating at 75.47 MHz, using proton broad-band decoupling, with the inversion-recovery $180°-\tau-90°$ pulse sequence being used for the T_1 measurements. Depending on the sample used and the measurement temperature employed, 240–1200 scans were carried out for each value of τ. The estimated accuracy of the spin-lattice relaxation times is better than 5% depending on the intensities of the peaks.

Table 1 Molecular weights and *DS*-values of CMC and CM-DEAEC samples[a]

Sample	Molecular weight ($\times 10^4$)	DEAE substituent	Position of CM substituent		
			C(6)	C(3)	C(2)
CMC-A	–	–	0.250	0.127	0.268
CM-DEAEC-A	–	0.191	0.264	0.128	0.254
CM-DEAEC-B	–	0.420	0.273	0.127	0.263
CMC-1	2.1	–	0.285	0.143	0.318
CM-DEAEC-1	0.75	0.870	0.280	0.152	0.312

[a] Molecular weights were calculated using sodium polystyrene sulfonate standards; *DS*-values were determined from proton n.m.r.spectra

RESULTS AND DISCUSSION

Intermolecular hydrophobic interactions

The g.p.c. curves of CMC-A and CM-DEAEC-B in alkaline solutions are shown in *Figure 1*. Sepharose CL-2B, a non-ionic crosslinked agarose gel, has a very large exclusion volume, but some parts of the CMC-A and CM-HTMAPC-B samples studied here are obviously excluded near the void volume (~30 ml). In 0.1 M NaOH, non-protonated DEAE substituents can be regarded as hydrophobic groups, with the larger apparent molecular size of CM-DEAEC-B compared with that of the original CMC-A (curves A and B in *Figure 1*) indicating that intermolecular interactions between the non-protonated DEAE substituents occur.

Hydrophobic interactions were found to have a great effect on the conformation of amphiphilic polyampholytes[10,11]. By light scattering measurements, Salamone *et al.*[10] studied the solution behaviour of an amphoteric amphiphilic polymer prepared from 2-methacryloyloxy-*N*,*N*-dimethyl-*N*-n-dodecyl-ammonium, 2-methacryloyloxyethanesulfonate and acrylamide, and pointed out that the addition of salt weakens the intramolecular ionic attraction, and without the constraint of ionic attractive forces the intermolecular bridges form via hydrophobic interactions between the dodecyl groups. However, in the case of CM-DEAEC-B, the apparent molecular size decreases to close to that of CMC-A (g.p.c. curves C and D) when NaCl is added.

CM-DEAECs can behave as polycations, hydrophilic polyampholytes, amphiphilic polyampholytes, or amphiphilic polyanions, depending on the dissociation of the carboxylic acids of the CM substituents and the protonation of the DEAE substituents. In 0.10 M NaOH, CM-DEAEC-B exists as amphiphilic polyanions, and intermolecular hydrophobic bridges form between the non-protonated DEAE substituents. When NaCl is added, it can be expected that the extension of the CM-DEAEC chains is depressed as a consequence of suppressed intramolecular repulsion. However, the changes in the g.p.c. curves of CMC corresponding

to the addition of NaCl is not so great as that of CM-DEAEC, and therefore an apparent drop near the void volume in the g.p.c. curve of CM-DEAEC can be realistically attributed to the breakup of the intermolecular hydrophobic bridges. Apparently, the amount of 'external' non-protonated DEAE substituents, which can make contact with the DEAE substituents of other chains, will decrease when the extension of the CM-DEAEC chains is depressed as a consequence of the suppressed intramolecular repulsion between the dissociated CM substituents at higher ionic strengths. Although the effect of ionic strength on the formation of intermolecular hydrophobic bridges varies with the chemical structures of the polyelectrolytes, both our results and those from Salamone *et al.*[10] show that intermolecular hydrophobic interactions occur readily so long as the chains are extended.

The reduced viscosities of the various collected fractions are listed in *Table 2*. The reduced viscosities of the same g.p.c. fraction vary depending on the sample, NaCl concentration and pH condition. First, we shall discuss why the viscosities of the same fraction can be quite different. The reduced viscosities of fractions 1, 3 and 4 are not discussed here, because fraction 1 includes

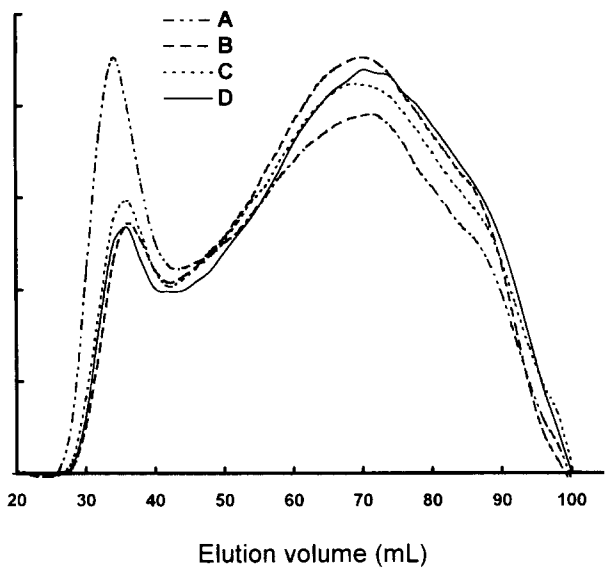

Figure 1 G.p.c. curves of CMC-A and CM-DEAEC-B in alkaline solutions: (A) CM-DEAEC-B in 0.10 M NaOH; (B) CMC-A in 0.10 M NaOH; (C) CM-DEAEC-B in 0.10 M NaOH and 0.10 M NaCl; (D) CMC-A in 0.10 M NaOH and 0.10 M NaCl

polymers excluded near the void volume, while the low viscosity values of fractions 3 and 4 result in poor accuracy. When intermolecular association occurs, the polymers shift towards the side of the larger apparent molecular sizes, and consequently the viscosity of the fraction decreases. For example, in 0.10 M NaCl of pH 6–7, the higher reduced viscosity (fraction 2) of CMC-A compared to that of CM-DEAEC-A is the result of intermolecular ionic attraction; the lower viscosity of CM-DEAEC-A in 0.10 M NaCl of pH 12.0, compared with that of CMC-A at pH 6–7 can be attributed to intermolecular hydrophobic bridges. The result that the reduced viscosity of CMC-A in fraction 2 decreases with a change in pH from 6–7 to 2.5 implies that intermolecular hydrogen bonds may be formed from the hydroxyl groups of the cellulose and the carboxylic acids of the CM substituents.

Let us now examine the reduced viscosities of the different fractions. When intermolecular association occurs strongly, polymers cannot be fractionated by their real molecular sizes, and the differences in the viscosities of the fractions become small accordingly. The difference between the reduced viscosities of fractions 1 and 2 is smallest at pH 2.5, implying that under these pH conditions, strong association occurs. The strong association at pH 2.5 may be partially attributed to the hydrogen bonds formed between the hydroxyl groups of the cellulose chain and the carboxylic acids of the CM substituents.

^{13}C n.m.r. spectra of CM-DEAEC in D_2O

The spectra of CM-DEAEC-1 between 102 and 52 ppm under three different pH conditions are shown in *Figure 2*, with the very strong peaks between 52 and 5 ppm plotted in *Figure 3*. By comparison with the ^{13}C n.m.r. spectra of CMC (not shown here), the peaks corresponding to the anhydroglucose units and the methylene carbons of the CM substituents can be distinguished, and these are labelled as G and CM, respectively (in spectrum A of *Figure 2*). Recently we assigned the ^{13}C n.m.r. spectra of CMC by the use of selectively substituted CMC samples (partly substituted *O*-carboxymethylcellulose at C(2) and C(3))[3]. When the anhydroglucose units of CMC are further substituted by DEAE groups, the peaks corresponding to these units are found to broaden (*Figure 2*).

We turn now to the assignment of the peaks corresponding to the DEAE substituents. If we consider the structure A for the DEAE substituents shown in *Figure 4* in addition to the peaks of CMC, four

Table 2 Reduced viscosities of fractionated CMC-A and CM-DEAEC-A

Sample	pH of eluent[a]	Reduced viscosity ($dl\,g^{-1}$)			
		Fraction 1 (31–42 ml)	Fraction 2 (43–56 ml)	Fraction 3 (57–70 ml)	Fraction 4 (71–84 ml)
CMC-A	6–7	18.8	11.1	6.7	3.5
CM-DEAEC-A	6–7	11.4	8.7	5.3	3.0
CM-DEAEC-A	12.0	15.6	8.9	5.5	2.9
CMC-A	2.5	9.0	7.1	5.0	2.8
CM-DEAEC-A	2.5	8.8	6.2	4.3	2.3

[a] Concentration of NaCl = 0.10 M in all experiments

additional peaks should appear in the spectra of CM-DEAEC. The four additional peaks of the protonated DEAE substituents are identified from the spectra of *O*-2-(diethylamino)ethylcellulose (not shown here). In spectra A and B of *Figure 3*, the two strong peaks at 10.8 and 50.4 ppm can be assigned to the methyl (C(δ)) and methylene (C(γ)) carbons of the ethyl groups. Regarding the other two methylene carbons (C(α) and C(β)) of the ethylene groups, the signal for C(α) should appear at a lower field, i.e. as a pair of peaks at 68.7 and 67.4 ppm (spectra A and B of *Figure 2*). The spectrum of an *O*-2-(diethylamino)ethylcellulose, selectively substituted at C(2) and C(3), clearly shows that more than two peaks correspond to the C(α) of the protonated DEAE substituents, at C(2) or C(3), and at C(6), respectively. When the DEAE substituents change from the protonated to the non-protonated state, the signals for C(α) shift downfield and partly overlap with the peaks of the methylene carbons of the CM substituents (spectrum C).

However, five of the peaks, labelled as a, b, c, d and e, in spectra A of *Figures 2* and *3*, cannot be assigned from the spectra of CMC and DEAEC. Probably another type of amino substituent, whose structure is shown in *Figure 4* (structure B), is formed by the nucleophilic displacement reaction of 2-(diethylamino)ethyl chloride with the DEAE substituents. Among the eight types of carbon in structure B (*Figure 4*), the resonance of C(δ'') is expected to overlap with that of C(δ) of the DEAE substituents; a small peak at 9.8 ppm, which does not shift with the change in pH from 0.65 to 13.4 and is confirmed to be a methylene carbon from its DEPT spectrum, can be attributed to C(δ'). The chemical shifts of the main peaks are summarized in *Table 3*.

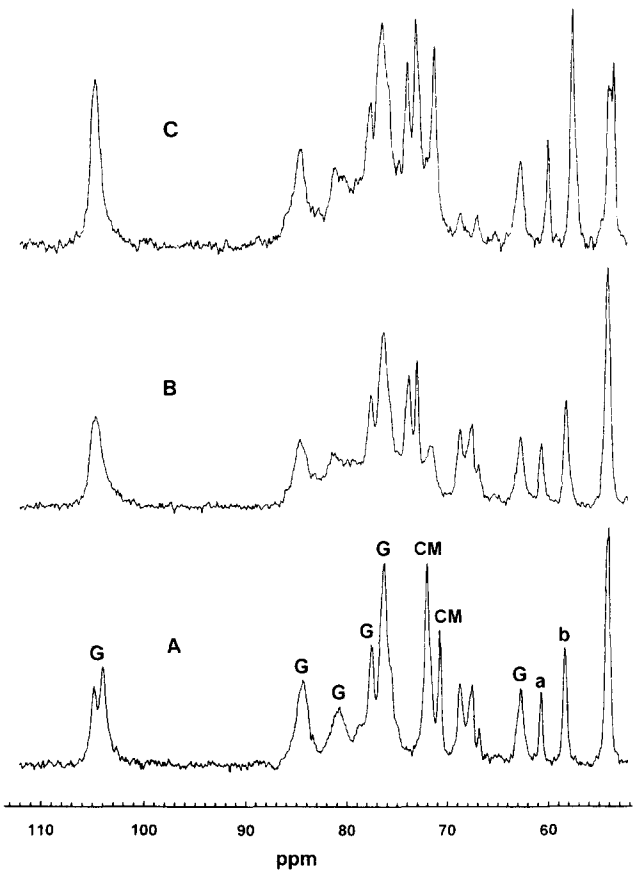

Figure 2 ^{13}C n.m.r. spectra of 10% CM-DEAEC-1 between 102 and 52 ppm at 60°C: (A) at pH 0.65; (B) at pH 6.7; (C) at pH 13.4 In spectrum A, the peaks corresponding to the anhydroglucose units and the methylene carbons of the CM substituents are labelled as G and CM respectively; peaks a and b represent the resonances of another type of amino substituent

Ionic interactions and mobilities of ionic substituents

Recently we reported the chain motions of CMC in

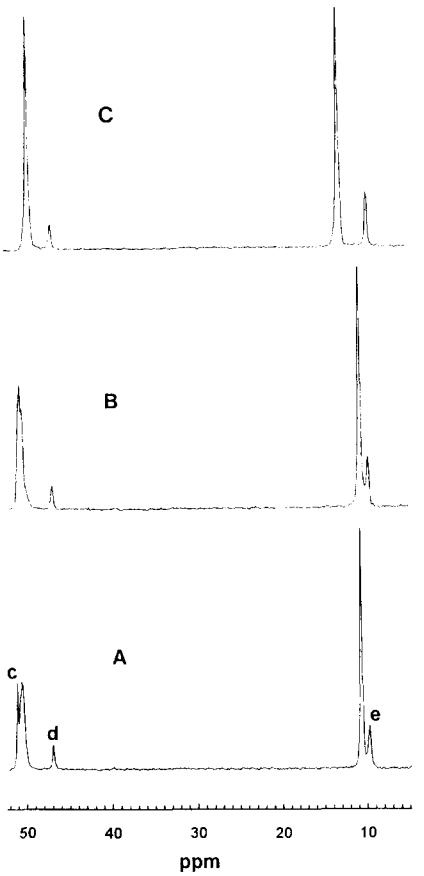

Figure 3 ^{13}C n.m.r. spectra of CM-DEAEC-1 between 52 and 5 ppm observed for 10% solutions in D_2O at 60°C: (A) at pH 0.65; (B) at pH 6.7; (C) at pH 13.4. In spectrum A, peaks c, d and e represent the resonances of another type of amino substituent

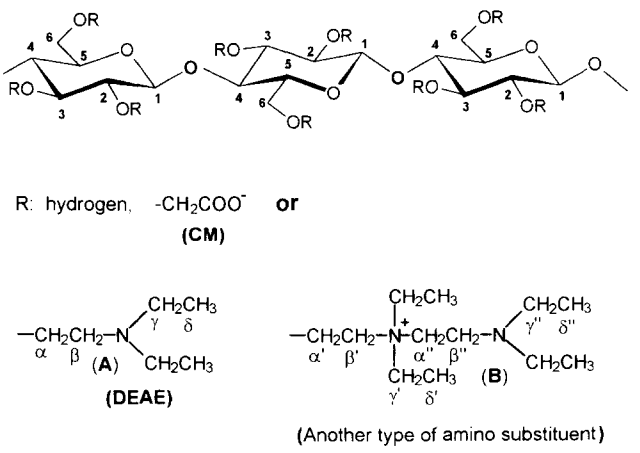

Figure 4 Structures for the anhydroglucose units, CM substituents and two types of amino substituents

aqueous solution, and found that the rotational motions of the anhydroglucose units are impeded by the substituents[3]. This conclusion can also be drawn from the data (*Table 4*) obtained from this present study. From the result that T_1 becomes longer at higher temperatures (*Tables 4* and *5*), we can conclude that in the temperature range studied here (30–80°C), the longer T_1 value for a considered carbon implies a more rapid motion. At 30°C there is almost no difference between the T_1 data of the anhydroglucose units of CMC and DEAEC, while at higher temperatures (60–80°C), the T_1 data of CMC are apparently longer than those of CM-DEAEC. Besides the conclusion mentioned above, this result implies that at 30°C the rotational motions of the anhydroglucose units are not rapid enough to be detected by T_1 measurements due to the high potential barrier for rotational motion.

Table 3 ^{13}C n.m.r. chemical shifts of CM-DEAEC-1 in D_2O solution[a]

	pH		
Carbon[b]	0.65	6.7	13.4
C(1)	104.7, 104.0	104.7	104.6
C(2,3)	76.2	76.3	76.3
C(2,3)(sub)[c]	84.3	84.7	84.6
C(4)	80.7	81.0	81.0
C(5)	77.4	77.5	77.5
C(6)	62.5	62.5	62.5
C(δ)	10.8	10.8	13.0
C(γ)	50.4	50.5	49.3
C(β)	53.9	53.9	53.8, 53.3
C(α(2,3))[d]	68.6	68.8	–
C(α(6))[e]	67.4	67.4	–
C(δ')	9.7	9.8	9.8
CM(2,3)[d]	71.9	73.7	73.7
CM(6)[e]	70.6	72.9	72.9

[a] Chemical shift in ppm relative to 3-(trimethylsilyl)propanesulfonic acid
[b] The symbols for the carbons are given in *Figure 4*
[c] The hydroxyl group of this carbon is substituted
[d] Substituent at C(2) or C(3)
[e] Substituent at C(6)

Ionic attraction between the cationic and anionic substituents is considered to be an important factor dominating the behaviour of CM-DEAEC in aqueous solution[1]. Here, we used the mobilities of the substituents, which are evaluated from the ^{13}C n.m.r. spin-lattice times (*Table 5*), as a probe to detect such ionic attraction. Under the three pH conditions studied here, the DEAE substituents are protonated and some CM substituents exist as anions at pH 4.9, while at pH 1.0 and 13.4 one type of substituent (CM or DEAE substituent) is in the non-ionic state. In other words, ionic attraction between the CM and DEAE substituents occurs only at pH 4.9. The T_1 data of C(γ) and C(δ) apparently indicate that the mobility of the DEAE substituents at pH 4.9 is the lowest for the three pH conditions studied here. The T_1 data for the methylene carbons of the CM substituents also clearly show the apparent effect of ionic attraction on the mobilities of the substituents.

A calculation based on the two peaks corresponding to C(δ) and C(δ') shows that about 18% of the amino substituents exist in structure B (*Figure 4*). This type of substituent exists as cations even in an alkaline solution, and ionic attraction with the anionic CM substituents occurs, as indicated by the T_1 value of C(δ'). Because of the fact that at pH 4.9 some of the CM substituents are in the non-ionic state and some are engaged in ionic interactions with the protonated DEAE substituents, the T_1 value of C(δ') is the shortest at pH 13.4, rather than at pH 4.9 as shown by the T_1 data for the DEAE substituents.

From the distribution of apparent molecular sizes (*Figure 2*), we found that the association between the hydrophobic non-protonated DEAE substituents occurs in 0.1 M NaOH, but the T_1 values of C(β), C(γ) and C(δ) of the DEAE substituents at pH 13.4 are slightly higher than those at pH 1.0. The reason why, following a change in pH from 13.4 to 1.0, the T_1 values of the DEAE substituents do not decrease as expected may be that at pH 1.0 the hydrophilic protonated DEAE substituents are solvated by water molecules and their motions are consequently restricted.

The T_1 values of the methylene carbons of the CM substituents make it clear that the substituents bonded at

Table 4 ^{13}C n.m.r. spin-lattice relaxation times of the anhydroglucose units of CMC-1 and CM-DEAEC-1[a]

				Relaxation time T_1 (s)				
No.	Sample	T (°C)	pH[b]	C(1)	C(2,3)	C(2,3(sub))[c]	C(5)	C(6)
1	CMC-1	30	6.7	0.25	0.25	0.24	0.26	0.14
2	CM-DEAEC-1	30	0.65	0.23	0.24	0.22	0.22	0.12
3	CM-DEAEC-1	30	13.4	0.24	0.23	0.23	0.22	0.11
4	CMC-1	60	6.7	0.31	0.31	0.31	0.30	0.15
5	CM-DEAEC-1	60	0.65	0.25	0.24	0.22	0.25	0.14
6	CM-DEAEC-1	60	13.4	0.25	0.27	0.24	0.28	0.15
7	CMC-1	70	6.7	0.32	0.34	0.31	0.34	0.17
8	CM-DEAEC-1	70	0.65	0.28	0.26	0.23	0.25	0.15
9	CM-DEAEC-1	70	13.4	0.26	0.27	0.27	0.27	0.16
10	CMC-1	80	6.7	0.35	0.39	0.33	0.36	0.19
11	CM-DEAEC-1	80	6.7	0.27	0.26	0.28	0.27	0.15

[a] Measured at 75.47 MHz; 10% solutions in D_2O; symbols for the carbons are given in *Table 3*
[b] Measured with glass electrode
[c] The hydroxyl group of this carbon is substituted

Table 5 ^{13}C n.m.r. spin-lattice relaxation times of CM and the DEAE substituents of CM-DEAEC-1[a]

No.	T (°C)	pH[b]	Relaxation time nT_1[c] (s)							
			CM(2,3)	CM(6)	C(α(2,3))	C(α(6))	C(β)	C(γ)	C(δ)	C(δ′)
1	30	4.9	0.42	0.53	0.35	0.36	0.30	0.50	3.25	2.26
2	30	1.0	0.48	0.61	0.36	0.42	0.30	0.61	3.50	2.39
3	30	13.4	–	–	–	–	0.46	0.64	3.57	2.09
4	40	4.9	0.44	0.67	0.35	0.45	0.36	0.64	3.77	2.54
5	40	1.0	0.57	0.74	0.37	0.48	0.36	0.76	4.50	2.68
6	40	13.4	–	–	–	–	0.55	0.83	4.80	2.41
7	60	4.9	0.56	0.82	0.46	0.59	0.51	0.95	–	–
8	60	1.0	0.65	1.10	0.46	0.73	0.68	1.12	–	–
9	60	13.4	–	–	–	–	0.76	1.17	–	–
10	70	4.9	0.57	0.91	0.51	0.68	0.57	1.11	–	–
11	70	1.0	0.74	1.22	0.56	0.88	0.80	1.42	–	–
12	70	13.4	–	–	–	–	1.00	1.44	–	–

[a] Measured at 75.47 Hz; 10% solution in D_2O; symbols for the carbons are given in *Table 3*
[b] Measured with glass electrode
[c] n = number of attached protons

C(6) of the anhydroglucose units are more mobile than those at C(2) or C(3) due to their relatively longer distances from the cellulose chains. The T_1 values of C(α) of the DEAE substituents also reflect the effect of steric hindrance of the cellulose chains on the motions of the DEAE substituents. The nT_1 values of the DEAE substituents decrease in the sequence C(δ) > C(γ) > C(β), implying that the internal rotations of those segments which are closer to the cellulose chains are more readily impeded.

CONCLUSIONS

Intermolecular hydrophobic interactions between non-protonated DEAE substituents occur readily, and the formation of such intermolecular bridges becomes difficult when the extension of the chains is depressed as a result of an increase in the ionic strength of the aqueous solution. On the other hand, the viscosity of the same g.p.c. fraction varies with the pH conditions because of intermolecular association.

The rotational motions of the anhydroglucose units are readily impeded by the substituents due to the increasing interactions between the substituents of the neighbouring anhydroglucose units. In addition to ionic attraction the cellulose chains as well as solvation restrain the motions of the CM and DEAE substituents.

REFERENCES

1 Zheng, G. Z., Meshitsuka, G. and Ishizu, A. *Polym. Int.* 1994, **34**, 241
2 Zheng, G. Z., Meshitsuka, G. and Ishizu, A. *J. Polym. Sci. Polym. Phys. Edn.* 1995, **33**, 867
3 Zheng, G. Z., Meshitsuka, G. and Ishizu, A. *J. Polym. Sci. Polym. Phys. Edn.* in press
4 Cais, R. E. and Bovey, F. A. *Macromolecules* 1977, **10**, 757
5 Jones, A. A. and Stockmayer, W. H. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 1347
6 Schaefer, J. and Natusch, D. F. S. *Macromolecules* 1972, **5**, 416
7 Dejean de la Batie, R., Laupretre, F. and Monnerie, L. *Macromolecules* 1988, **21**, 2045
8 Dais, P. and Marchessault, R. H. *Macromolecules* 1991, **24**, 4611
9 Ho, F. F.-L. and Klosiewicz, D. W. *Anal. Chem.* 1880, **52**, 913
10 Salamone, J. C., Thompson, A. M., Su, C. H. and Watterson, A. C. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1989, **30**, 326
11 Strauss, A. U. P. and Chiao, Y. C. *Macromolecules* 1986, **19**, 355