Comparison of Sodium Ion Interactions with Sodium Salts of (Carboxymethyl)cellulose and Vinylic Polyelectrolytes of Varying Charge Density by Diffusion

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ABSTRACT: Sodium ion tracer diffusion coefficients were determined in aqueous salt-free and NaCl-containing solutions of sodium (carboxymethyl)cellulose (NaCMC) with the degree of carboxyl substitution varying from 0.38 to 1.47. The concentration range for the NaCMC was 5×10^{-2} to 1×10^{-4} N in aqueous solution. For the salt-containing solutions, the sodium (carboxymethyl)cellulose range was 5×10^{-5} to 1×10^{-1} N and 5×10^{-4} to 1×10^{-2} N was the range for NaCl. The results presented here were compared to the sodium ion tracer diffusion coefficients obtained for the sodium salts of poly(acrylate), poly(acrylamide), and poly(dimethylacrylamide) of varying charge density. Charge fractions for the NaCMC were evaluated from the data. The experimental findings were discussed in terms of the Manning and Yoshida theories. Generally, it was found that the sodium ion diffusion coefficients were linear with ξ^{-1} above the critical ξ value of unity for both salt-free and NaCl-containing solutions with the stiffer NaCMC polymer following the Yoshida line while the more flexible vinylic polyelectrolytes followed the Manning line. Constant values of the sodium ion diffusion coefficients and the polyion charge fractions for $\xi < 1$ for both types of polymers were cited as evidence for a critical polyelectrolyte configuration. It was shown how the theoretical charge fraction ξ^{-1} and the experimental charge fraction could be incorporated into equations of the form of the empirical counterion additivity rule to indicate that the sodium ion diffusion ratio in salt-free solutions can be equated with the charge fraction of the polyion.

With too few studies reported of counterion–polyion interactions with the same polyelectrolyte of varying charge density, the tracer diffusion of sodium ion in aqueous sodium (carboxymethyl)cellulose (NaCMC) solutions with and without NaCl present was investigated. The results obtained for this relatively stiff ionic polysaccharide, whose degree of carboxyl substitution ranged from 0.38 to 1.47 (see Figure 1), will then be compared to similar results obtained with the more flexible vinylic polyelectrolytes, sodium poly(acrylate)/poly(acrylic acid) (NaPA/HPA), sodium poly(acrylate)/poly(acrylamide) (NaPA/PAM), and sodium poly(acrylate)/poly(dimethacrylamide) (NaPA/PDPAM) copolymers.[1] Also, the results will be correlated with the Manning[2-8] and Yoshida[9,10] theoretical predictions. Of importance is the charge density parameter ξ

$$\xi = e^2/\epsilon kTb \tag{1}$$

where b is the average axial stoichiometric charge-to-charge distance along the polyelectrolyte and the other symbols are the standard electrochemical constants. According to the Manning theory, the counterions are completely dissociated from the infinite line charge polyelectrolyte when $\xi < \xi_c$, where $\xi_c = |Z_c|^{-1}$ and Z_c is the valence of the counterion. When $\xi > \xi_c$, counterion condensation takes place until the effective ξ value is ξ_c and the remaining dissociated counterions interact with the infinite line charge via Debye–Hückel forces. Counterion condensation has been experimentally verified, and several investigators indicate that it occurs in the region of ξ_c.[1,11-16] This also appears to be in accord with the NMR studies by Leyte et al.[17] and the transport studies of Turq et al.,[18] which suggest that the bound ions retain some degree of mobility.

While both models adequately describe polyelectrolytes with monovalent counterions for $\xi > 1$, they predict weaker counterion–polyion interactions for $\xi < 1$ than is observed experimentally.[1,13,19,20] Counterion diffusion coefficients in solutions of carboxyl copolymers[1] and electrophoretic mobilities[11] of ionene bromides have been shown to be essentially constant for $\xi < 1$, indicating that the charge density of the polyion is also constant in this region. It has been suggested that an instability exists below ξ_c because of the increased distance between charged groups, such that the polyelectrolyte may attain a more stable configuration by coiling to increase the effective charge density to ξ_c.[1]

In this investigation we note if a polyelectrolyte that is less flexible than those previously studied shows similar effects, including a constant effective charge density over the region $\xi < 1$. Here we report Na^+ ion diffusion results obtained in aqueous salt-free and NaCl-containing solutions of NaCMC at 25 °C.

Experimental Section

The purified sodium (carboxymethyl)cellulose (NaCMC) used in this study was kindly provided in powder form by Hercules, Inc. Prior to use of the samples, they were dried in a vacuum oven at 50 °C for at least 24 h and handled with minimum exposure to air. The equivalent weight of each sample was determined by passing an aliquot of the aqueous solution through a cation-exchange resin in the hydrogen form and titrating the resulting acids with standardized NaOH to a phenolphthalein end point. The equivalent weights were found to be 191 ± 1, 252 ± 1, 300 ± 1, 306 ± 1, 334 ± 1, 418 ± 1, and 507 ± 1 g, which corresponded to degrees of substitution of 1.47, 0.95, 0.74, 0.72, 0.64, 0.48, and 0.38 carboxyl groups per monomer unit (and charge densities of 2.04, 1.32, 1.03, 1.00, 0.89, 0.67, and 0.53), respectively. Aqueous salt-free polymer solutions were prepared with a concentration range of 1×10^{-4} to 5×10^{-2} N. Aqueous NaCl-containing polymer solutions were prepared with salt concentrations of 1×10^{-2}, 5×10^{-3}, 1×10^{-3}, and 5×10^{-4} N, and polymer concentrations varying from 5×10^{-5} to 1×10^{-1} N. Thus X, which is defined as the ratio of the normality of the polyelectrolyte N_p to the normality of the simple salt N_s

$$X = N_p/N_s \tag{2}$$

varied from 0.10 to 10.

The radioactive species used, $^{22}Na^+$, in the form of sodium chloride was supplied by New England Nuclear Co. A stock solution of $^{22}NaCl$ was prepared by diluting 0.1 mCi to 100 mL. Radioactively tagged polymer solutions of the same concentration as the nonradioactive solution were prepared by placing 1 or 2 mL of the radioactive stock solution in 10-mL volumetric flasks, evaporating these solutions in a vacuum oven, and adding a radioactively inert solution to the tagged salts in the 10-mL flasks.

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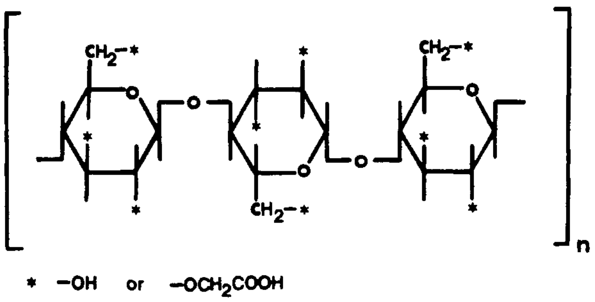

Figure 1. (Carboxymethyl)cellulose polyion.

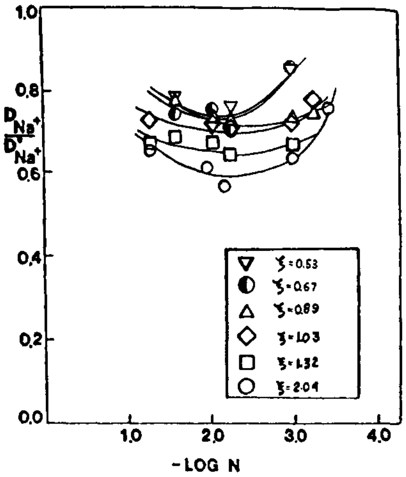

Figure 2. $D_{Na^+}/D^0_{Na^+}$ dependence on the normality of polyelectrolyte in aqueous salt-free solutions.

The self-diffusion coefficients of the sodium D_{Na^+} were determined at 25.00 ± 0.01 °C by the open-end capillary method originally introduced by Anderson and Saddington without stirring. Precision-bore capillaries of 1.00 ± 0.005-mm diameter and 2.76 ± 0.005-cm length were filled with the polymer solution containing the radioactively labeled sodium. Each capillary was placed into a test tube that was subsequently filled with the inert polymer solution of identical concentrations. The rate of the diffusion of the $^{22}Na^+$ ion out of the capillary was thus a measure of the polyion–counterion interaction.

The self-diffusion coefficients were calculated from the solution of Fick's second law, which yields the expression

$$C/C^0 = (8/\pi^2)\sum_{n=0}^{\infty}[\exp[(-(2n + 1)^2\pi^2Dt/4L^2)]]/(2n + 1)^2 \quad (3)$$

where $D = D_{Na^+}$, the sodium ion self-diffusion coefficient, t is the time allowed for diffusion in seconds, L is the length of the capillary in centimeters, C is the radioactive content of the capillary after diffusion has taken place, and C^0 is the radioactive content of the capillary prior to diffusion. This equation was solved for the diffusion coefficient D by successive approximations with the aid of a computer. Each reported D_{Na^+} value is the average of at least six determinations. The contribution of the diffusion of condensed Na^+ ions to the observed D_{Na^+} was assumed to be negligible because of the high molecular weight of NaCMC. The Na^+ ion diffusion coefficient $D^0_{Na^+}$ at 25 °C is 1.33×10^{-5} cm²/s in polyelectrolyte-free salt solutions.

Results and Discussion

Salt-Free Polyelectrolyte Solutions. The results for aqueous salt-free solutions of NaCMC are presented in Figure 2, with the D_{Na^+} values determined over the polyelectrolyte normality range 10^{-4} to 10^{-1} for ξ values of 0.53, 0.67, 0.89, 1.00, 1.03, 1.32, and 2.04. The curves in Figure 2 have shapes similar to those reported for the sodium salts of heparin,[21] algin[22] ι-carrageenan,[22] dextran sulfate,[22] NaPA/HPA,[1] NaPA/PAM,[1] NaPA/PDAM,[1] poly(styrenesulfonate) and poly(styrenecarboxylate).[1] Farily constant minimum $D_{Na^+}/D^0_{Na^+}$ values were obtained for the approximate concentration range $10^{-3} < N_p < 10^{-2}$, where, of course, maximum sodium ion–polyion interaction occurs. Such behavior has been observed with NMR techniques on aqueous solutions of fully neutralized tetramethylammonium poly(acrylate), where the TMA^+ diffusion coefficient rose sharply below 10^{-3} N.[23] At lower N_p values, D_{Na^+} increases with a decrease in N_p because of an expanding ionic atmosphere with its concomittant increased screening of polyion charges and increased dissociation. At higher N_p values, D_{Na^+} increases with an increase in N_p due to increased screening because of overlapping ionic atmospheres between polyions. In addition, the increasing number of polyions attracts water molecules to a greater extent, thereby screening the charges and leaving a larger number of mobile counterions to contribute to the value of D_{Na^+}. The broad, fairly constant minima values of $D_{Na^+}/D^0_{Na^+}$ will be used for the discussion inasmuch as both theories that are used to compare the experimental data, predict that $D_{Na^+}/D^0_{Na^+}$should be independent of N_p for salt-free polyelectrolyte solutions. Also, as will be seen later, the values of $D_{Na^+}/D^0_{Na^+}$ at high X values for the lowest NaCl concentrations $(D_{Na^+}/D^0_{Na^+})_{X=10}$ agree quite well with the minimum $D_{Na^+}/D^0_{Na^+}$ salt-free values, as is shown in Table I.

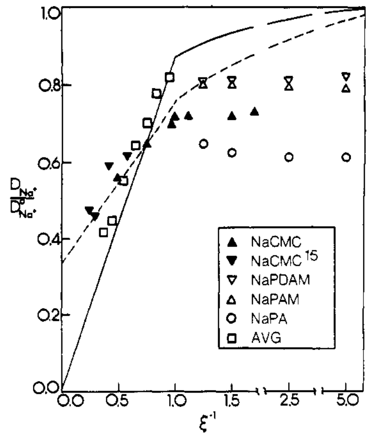

Figure 3. Minimum values of $D_{Na^+}/D^0_{Na^+}$ vs. ξ^{-1} for NaCMC and average values (AVG) for NaPA, NaPAM, and NaPDAM.[1]

From Manning's infinite line charge model

$$D_{Na^+}/D^0_{Na^+} = 0.87\xi^{-1} \quad \text{for } \xi > 1 \quad (4)$$

$$D_{Na^+}/D^0_{Na^+} = 1 - (0.55\xi^2)/(\xi + \pi) \quad \text{for } \xi < 1 \quad (5)$$

where for $\xi < 1$ the polyelectrolyte is fully dissociated and for $\xi > 1$ for the concentration of dissociated monovalent ions is $\xi^{-1}N_p$, with the condensed counterions having the mobility of the polyions, which is usually much less than the mobility of the uncondensed counterions.

From Yoshida's cell model

$$D_{Na^+}/D^0_{Na^+} = 0.33 + 0.43\xi^{-1} \quad \text{for } \xi > 1 \quad (6)$$

$$D_{Na^+}/D^0_{Na^+} = 0.33 + 0.67(2 - 3\xi + \xi^2)G \quad \text{for } \xi < 1 \quad (7)$$

where G is a function that depends only on ξ. While eq 6 relates the total contribution to the Na^+ ion diffusion, condensed counterions are considered free to move along the length of the chain and contribute $(1/3)(1 - \xi^{-1})$ to $D_{Na^+}/D^0_{Na^+}$. The contribution of the uncondensed ions to $D_{Na^+}/D^0_{Na^+}$ is $0.76\xi^{-1}$.

The minimum values for $D_{Na^+}/D^0_{Na^+}$ in Figure 2 for NaCMC of ξ values 0.53, 0.67, 0.89, 1.00, 1.03, 1.32, and 2.04 shown in Table I are compared with the predictions of eq 4–7 and plotted in Figure 3 according to the predicted

Table I
Sodium Ion Diffusion Ratios Obtained from Minimum Values in Salt-Free Solutions and from Constant Values in Solutions of High Polyelectrolyte to NaCl Normalities

DS	ξ	ξ^{-1}	$(D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})_{\mathrm{min}}$	$(D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})_{x=10}$	$(D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})_{x=\infty}$[a]	r
			NaCMC			
0.38	0.53	1.89	0.73	0.74	0.72	0.28
0.48	0.67	1.49	0.72			
0.64	0.89	1.12	0.72	0.72	0.71	0.29
0.72	1.00	1.00	0.72	0.69	0.68	0.32
0.74	1.03	0.97	0.70			
0.95	1.32	0.76	0.65	0.64	0.63	0.37
1.47	2.04	0.49	0.56	0.57	0.53	0.47
			NaPA/HPA			
0.07	0.20	5.00	0.64	0.84	0.83	0.17
0.14	0.40	2.50	0.61	0.82	0.81	0.19
0.24	0.67	1.49	0.62	0.85	0.84	0.16
0.28	0.80	1.25	0.65	0.84	0.82	0.18
0.37	1.05	0.95	0.85	0.83	0.81	0.19
0.41	1.18	0.85	0.79	0.78	0.76	0.24
0.47	1.33	0.75	0.70	0.74	0.71	0.28
0.54	1.54	0.65	0.64	0.69	0.66	0.34
0.64	1.82	0.55	0.53	0.62	0.58	0.43
0.78	2.22	0.45	0.46	0.52	0.50	0.50
0.96	2.73	0.37	0.40	0.48	0.43	0.57

[a] Obtained from the slope of eq 16.

dependence of $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ vs. ξ^{-1}. For comparison, similar results are included from ref 1 for the more flexible vinylic polyelectrolytes NaPA/HPA, NaPA/PAM, and NaPA/PDAM, whose charge density parameter range is $0.2 < \xi < 2.7$.

First it should be noted that for the high charge density range, $\xi > \xi_c$, the linear dependence of $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ on ξ^{-1} is obeyed for each polyelectrolyte studied. The experimental values for the slopes are 0.79 ± 0.02, 0.69 ± 0.07, and 0.77 ± 0.05 and the experimental values for the intercepts are 0.11 ± 0.02, 0.18 ± 0.05, and 0.12 ± 0.03 for NaPA, NaPAM, and NaPDAM, respectively.[1] If one considers an average of these points for each ξ value (recalling that each point is the average $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ value for the range $5.0 \times 10^{-4} < N_p < 1.0 \times 10^{-2}$), the slope and intercept for these vinylic polyelectrolytes are 0.75 ± 0.03 and 0.13 ± 0.02, respectively. These values are more in accord with the Manning predictions from eq 4 for a slope of 0.87 and an intercept of zero than the Yoshida predictions from eq 6 for a slope of 0.43 and an intercept of 0.33. It is fair to conclude that for these vinylic polyelectrolytes for $\xi > \xi_c$ the condensed Na^+ ions move *with* the polyion, which moves about 2 orders of magnitude slower than the counterions. From Figure 3, the slope and intercept for the NaCMC points are 0.32 ± 0.04 and 0.41 ± 0.03, respectively. The experimental value for the slope of the line for NaCMC for $\xi > \xi_c$ is significantly smaller than the Manning prediction and closer to the Yoshida prediction and also smaller than the slope obtained for the vinylic polyelectrolytes. This might be due to both the hydrophilic nature of the NaCMC surface and the rigid backbone of this polymer as compared to the hydrophobic surface and flexible backbone of the vinylic polymers. In the region of $\xi > 1.32$, for which the NaCMC polymers have more than one carbonyl group per glucose ring (DS > 1), the charge density is most likely high enough to make the NaCMC and vinylic polymers seem equally rigid. The hydrophilic nature of the NaCMC polymers, due to the hydroxyl groups, becomes more significant in this region. The attraction of water molecules to the NaCMC backbone screens the charges, thereby weakening the long-range polyion–counterion interactions and leads to the observed higher diffusion coefficients for the NaCMC polymers as compared to the vinylic polymers in Figure 3. For intermediate ξ values, $1.32 > \xi > 1$, the weaker electrostatic repulsive forces between the charged groups on the chains permit the polyions to coil to a greater extent and the diffusion coefficient rises. Consequently the sodium ions that interact with the more flexible vinylic polymers, which can coil more easily than the polysaccharides, have greater diffusion coefficients in this region. This results in the smaller slope in the region of $\xi > 1$ for the NaCMC polymers as compared to the vinylic polymers.

The rodlike models of Manning and Yoshida both predict that condensation does *not* occur for $\xi < 1$ for sodium polyelectrolytes. Since NaCMC was used in this study because ionic polysaccharides are relatively stiffer than vinylic polyelectrolytes for $\xi < \xi_c$, one would expect the experimental diffusion curve to approach unity as ξ approaches zero. It is obvious from Figure 3 that for NaCMC for $\xi < 1$, a constant value of $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+} = 0.72$ has been reached. When this line of zero slope for $\xi < 1$ is extrapolated to the experimental NaCMC line for $\xi > 1$, they intersect close to $\xi = 1$, the ξ_c value. This again, as for NaPA/PAM and NaPA/PDAM, indicates that the critical charge density parameter is correctly predicted from theory. (The discontinuity observed for NaPA/HPA at $\xi = \xi_c$ also shows this!)

Figure 3 also shows for $\xi < \xi_c$ that the $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ points for each polymer are *all* below those predicted by the rodlike theories, indicating that these models are inappropriate in this range. Similar results were obtained for sodium ion activity coefficients for aqueous solutions of sodium pectinate,[19] NaCMC,[24] and NaPA/HPA.[20] The zero slope line for NaCMC for $\xi < \xi_c$ lies close to the zero slope lines for NaPA/PAM and NaPA/PDAM. Also, for $\xi < \xi_c$, the $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ values for NaPA/HPA are constant. For each of these polyelectrolytes below ξ_c, the Na^+ interacts with a polyion of constant effective charge density no matter what the value of the stoichiometric charge density. The only way this can happen is that the rodlike polyelectrolyte folds when $\xi < \xi_c$ to a constant effective ξ value. It is tempting to speculate that this constant effective ξ is ξ_c; i.e., at ξ_c the free energy of the solution is minimized. From electrophoretic mobility measurements, Ware[11] found that for the 6-6 ionene bromide in solvents of different dielectric constants (and different ξ values according to eq 1) the electrophoretic mobility of

Table II
$D_{Na^+}/D^0_{Na^+}$ Values for NaCMC in Aqueous Salt Solutions at 25 °C[a]

ξ	N_s	0.10	0.50	1.0	2.0	2.5	5.0	7.5	10.0
0.53	0.00050	0.87	0.78	0.82		0.76	0.73	0.76	0.74
	0.0010	0.85	0.82	0.86		0.79	0.73	0.71	0.74
0.89	0.0005	0.89	0.88	0.83		0.78	0.76	0.74	0.72
	0.0010	0.85	0.79	0.76		0.77	0.72	0.72	0.75
1.32	0.0005	0.87	0.82	0.79	0.70	0.72	0.66	0.65	0.64
	0.0010	0.87	0.82	0.78	0.72	0.70	0.68	0.67	0.66
	0.0050	0.94	0.82	0.78	0.75	0.73	0.73	0.72	0.72
	0.0100	0.93	0.81	0.80	0.76	0.76	0.73	0.76	0.75
2.04	0.0005	0.89	0.81	0.77		0.66	0.60	0.57	0.57
	0.0010	0.89	0.82	0.77		0.66	0.59	0.58	0.58

ξ	N_s	0.08	0.40	0.80	2.0	4.0	6.0	8.0
1.00	0.0005	0.84	0.82	0.80	0.77	0.72	0.71	0.69
	0.0010	0.91	0.89	0.82	0.78	0.76	0.72	0.71

[a] The reproducibility of these values is up to 3%.

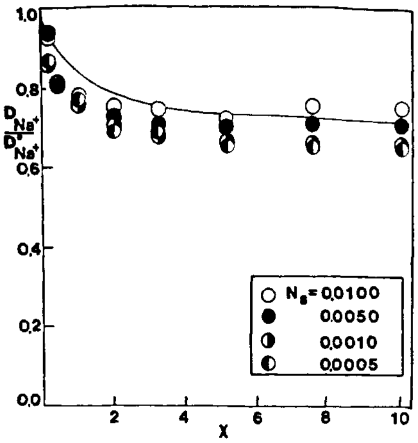

Figure 4. $D_{Na^+}/D^0_{Na^+}$ dependence on X at several NaCl concentrations for NaCMC of $\xi = 1.32$ in aqueous solutions at 25 °C. The solid line is predicted from the Manning theory.

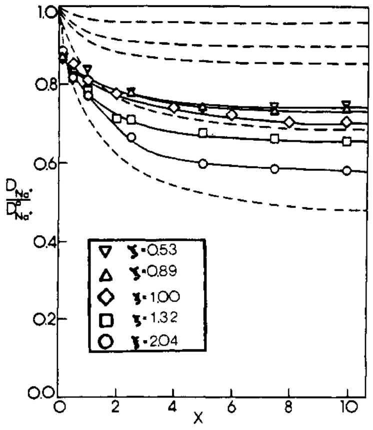

Figure 5. $D_{Na^+}/D^0_{Na^+}$ vs. X for different ξ values. The dotted lines are those predicted from the Manning theory, with corresponding decreasing ξ values from top to bottom.

the polyelectrolyte was constant for $0 < \xi < \xi_c$ and dropped precipitously at $\xi = \xi_c$. This could mean that the electrostatic potential of the polyion remains constant below the ξ_c value. It would be of interest to examine the dimensions and the electrostatic potential of the polyelectrolyte as a function of its stoichiometric charge density to help estimate the effective charge density.

Salt-Containing Solutions. To monitor the long-range counterion–polyion interactions in the presence of added salt, values of D_{Na^+} were obtained in aqueous NaCl solutions containing NaCMC of the same ξ values (2.04, 1.32, 1.00, 0.89, and 0.53) as those used for the salt-free experiments. Solutions with X values of 0.1, 0.5, 1.0, 2.5, 5.0, 7.5, and 10.0 were prepared by adding the desired amount of NaCMC to 0.0005 and 0.001 N NaCl solutions. For the $\xi = 1.32$ NaCMC, additional experiments were run in 0.005 and 0.01 N NaCl for $0.1 < X < 10$. The results are illustrated in Figure 4. The values for $D_{Na^+}/D^0_{Na^+}$ are fairly independent of the NaCl concentration for $X < 5$, a prediction of the Manning theory. Because of this and since Manning's equations are limiting laws, the experiments using NaCMC with the other charge densities were conducted only in 0.0005 and 0.001 N NaCl. These results are reported in Table II.

The Manning theory for polyelectrolytes with monovalent counterions in salt solutions predicts that the diffusion ratio should follow the equation

$$D_{Na^+}/D^0_{Na^+} = f^u_{Na^+}(1 - A/3) \qquad (8)$$

where $f^u_{Na^+}$ is the fraction of *all* Na$^+$ ions in the solution that are uncondensed and A is an interaction term. For the two cases of $\xi > 1$ and $\xi < 1$ eq 8 becomes

$$D_{Na^+}/D^0_{Na^+} = [(\xi^{-1}X + 1)/(X + 1)](1 - A/3) \qquad \xi > 1 \qquad (9)$$

where

$$A = \sum_{\substack{m=-\infty \\ (m,n)\neq(0,0)}}^{\infty} \sum_{n=-\infty}^{\infty} [\pi(m^2 + n^2) + 1 + 2\xi X^{-1}]^{-2} \qquad (10)$$

and

$$D_{Na^+}/D^0_{Na^+} = (1 - A/3) \qquad \xi < 1 \qquad (11)$$

where

$$A = \sum_{\substack{m=-\infty \\ (m,n)\neq(0,0)}}^{\infty} \sum_{n=-\infty}^{\infty} [\pi\xi^{-1}(m^2 + n^2) + 1 + 2X^{-1}]^{-2} \qquad (12)$$

These equations were used to plot the theoretical curves in Figures 4 and 5. They predict that for a given ξ value the $D_{Na^+}/D^0_{Na^+}$ ratio depends only on X and is independent of simple salt concentration.

From Figure 4 one can see that for the lowest NaCl concentrations (0.0005 and 0.0010 N) at a given X value the $D_{Na^+}/D^0_{Na^+}$ ratios are fairly independent of salt concentration, just as predicted by the Manning theory. However, an ionic strength effect is observed in solutions of higher salt concentrations (0.005 and 0.01 N), where the diffusion ratios are slightly higher than in the more dilute salt solutions for $X > 5$. The increase of the diffusion coefficient with increasing simple salt concentration at high X values for the higher simple salt concentrations is probably due to the overlapping ionic atmospheres of the polyions, which slightly weakens the counterion–polyion interactions and becomes more significant as the salt concentration increases. For small X values at which the salt concentration exceeds that of the polymer, the charges on the polymer are screened to a greater extent by the counterions, thereby weakening the long-range polyion–counterion interactions. Consequently, the diffusion ratio approaches unity.

In Figure 5, the diffusion ratios of the two lowest salt concentrations (0.0010 and 0.0005 N) were averaged and plotted against X for the ξ values studied. By comparing the experimental points with the Manning theoretical lines in Figure 5, one can see that the Manning theory predicts stronger interactions than observed for the NaCMC polymer with the largest ξ value (2.04). The weaker experimental interactions may be due to the stiffness of the NaCMC molecules which restricts coiling and the attraction for water by ionic polysaccharides which allows for translation of the counterions along the length of the polyion, thereby reducing the effect of the charges in the polyelectrolyte. For $\xi = 1.32$ and 1.00 the experimental points lie below the theoretical line indicating stronger interactions than predicted. For $\xi < 1$ ($\xi = 0.89$ and $\xi = 0.53$) the interactions are significantly underestimated by the theory. These observations may be explained by the coiling of the polyion to attain a critical effective ξ value, which may characterize the stability of its state.

When the diffusion ratios at $X = 10$ (low salt concentration relative to the polymer concentration) are compared to the minimum values obtained in the salt-free solutions, excellent agreement is obtained for each ξ value as shown in Table I. These results are reassuring in that they indicate the consistency between the salt-free data and the data for the low concentration salt-containing solutions. The results also show that for $\xi > 1$, $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ is linear in ξ^{-1}, as was found for the salt-free solutions. The linearity of $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ vs. ξ^{-1} for $\xi > 1$ with monovalent counterions can be deduced from the Manning theory if $A/3 \ll 1$ in eq 9

$$D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+} = \xi^{-1}X(1 + X)^{-1} + (1 + X)^{-1} \qquad (13)$$

i.e., the contribution of the counterion–polyion interaction term is small compared to the condensation term. In the range of $0.10 < X < 10$, for $\xi = 1.03$, $0.01 < A/3 < 0.15$, and for $\xi = 2.04$, $0.01 < A/3 < 0.13$. Thus, the assumption that $A/3 \ll 1$ is somewhat justified. Also, from eq 13 as X increases, ξ^{-1} is identified with $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$, which becomes a measure of the charge fraction of the polyelectrolyte. From Table I it is noted that ξ^{-1} gets closer to $(D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})_{X=\infty}$ as the charge density of the polyelectrolyte increases.

It is also possible to determine the charge fraction of polyelectrolyte using the Manning theory and the experimentally determined counterion tracer diffusion coefficients in salt-containing aqueous solutions. If a solution containing a total of $(N_p + N_s)$ equivalents of Na^+ ions has rN_p equivalents of Na^+ ions condensed on the polyion, then the fraction of all Na^+ ions condensed $f^c_{\mathrm{Na}^+}$ is

$$f^c_{\mathrm{Na}^+} = rN_p/(N_p + N_s) = rX/(1 + X) \qquad (14)$$

where r is the fraction of condensed or bound Na^+ ions of those originally on the polyelectrolyte and $(1 - r)$ is the charge fraction of the polyelectrolyte. If the interactions of Na^+ ions with the carboxyl groups are properly described as "counterion condensation", i.e., an association such that the fraction of polyion sites compensated for with counterions remains constant for all X values, then a plot of $f^c_{\mathrm{Na}^+}(X + 1)$ vs. X would be linear with a slope for r. This would indicate that the charge fraction of the polyion is constant, independent of the concentration of the polyelectrolyte and of simple salt.

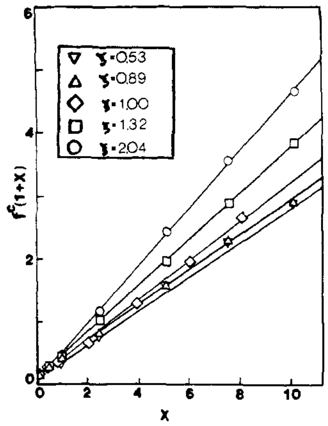

Figure 6. Averaged diffusion ratios of 0.00050 and 0.0010 N NaCl plotted against X for five ξ values of NaCMC.

To determine the value of $f^c_{\mathrm{Na}^+}$ from the experimental data, it is necessary to assume that the value of $(1 - A/3)$ in eq 9 is close to unity. A calculation of A values from eq 10 will show that this assumption is valid for the charge densities and X values studied here. For $0.1 < X < 10$, the A values vary from 0.04 to 0.38 for $\xi = 1.03$ and from 0.02 to 0.35 for $\xi = 2.04$. Even as ξ approaches unity, where the electrostatic term A and the condensation terms contribute about equally to eq 9, the maximum error in neglecting A will be approximately 8% for $\xi = 1.00$, $X = 10$. With this assumption, the diffusion ratio $D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+}$ can be equated with the fraction of all uncondensed Na^+ ions, $f^u_{\mathrm{Na}^+}$. Thus, the fraction of Na^+ ions condensed is given by $(1 - D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})$ and a plot of $(1 - D_{\mathrm{Na}^+}/D^0_{\mathrm{Na}^+})(X + 1)$ vs. X should give a slope of r. The linearity in the plots of $f^c_{\mathrm{Na}^+}(1 + X)$ vs. X in Figure 6 for all ξ values is in agreement with the operational definition of condensation, where the charge fraction is constant and independent of X. The calculated charge fractions $(1 - r)$ and the theoretical charge fractions ξ^{-1} are reported in Table I. Good accord between $(1 - r) = 0.53$ and $\xi^{-1} = 0.49$ is found for $\xi = 2.04$. The assumption that the uncondensed counterions are much freer to move than condensed ones is empirically justified because of the good agreement between r and ξ^{-1} for high ξ values. For $\xi = 1.32$, the difference between $(1 - r)$ and ξ^{-1} is much larger at 17%, and for $\xi = 1.00$, a 28% difference exists. The deviations for $\xi < 1.3$ are too large to be solely attributed to the increase in the Debye–Hückel interaction term, so that condensation must be occurring to a greater extent than is predicted for $\xi < 1.3$, leading to a smaller charge fraction than expected ($(1 - r) = 0.68$ while $\xi^{-1} = 1.00$ for $\xi = 1.00$).

When the charge fractions of NaCMC are compared to those of the flexible NaPA/HPA polymers, it is noted that for high charge densities the fraction of "free" charges are about equal. For NaCMC, $\xi = 2.04$, $(1 - r) = 0.53$, while for NaPA/HPA, $\xi = 1.82$, $(1 - r) = 0.57$. As the ξ values decrease to unity, the charge fractions for both polymers increase, indicting that fewer charges are being neutralized; however, the charge fractions for the NaPA/HPA polymers rise more rapidly. For NaCMC, $\xi = 1.00$, the charge fraction is 0.68, whereas that for NaPA/HPA, $\xi = 1.05$, is 0.81. For $\xi < 1$ the charge fractions for both types of polymers seem to level off, the NaCMC polyions attaining a value of 0.72, and the NaPA/HPA polymers attaining a value of 0.83. The smaller charge fraction for the NaCMC polymers as compared to the NaPA/HPA polymers may be due to the more rodlike structure of the

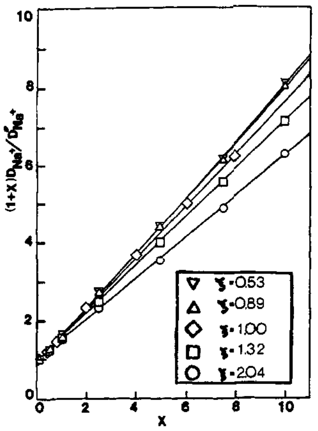

Figure 7. Plot of eq 16.

polysaccharide and its hydrophilic nature, which would tend to attract more counterions to neutralize the polyion's charges and lead to a smaller fraction of unbound charges. More significantly, however, the relatively constant charge fractions for both the NaCMC and NaPA/HPA polymers for $\xi < 1$ is further evidence that through coiling and condensation the polyions may maintain a critical configuration, such that the effective charge fraction is that of the polyelectrolyte at $\xi = 1$, i.e., at $\xi = \xi_c$.

It is appropriate to note the relationships between the charge fraction of the polyelectrolyte, the theoretical charge fraction for monovalent counterions, and the empirical addivity rule. According to the Manning theory, for $\xi < \xi_c$ condensation will occur until the effective ξ value is equal to the critical value of $\xi_c = 1$ for monovalent counterions. Thus the charge fraction is given by $\xi_c/\xi = \xi^{-1}$. An empirical charge fraction is was obtained from eq 9. As stated previously, $A/3 \ll 1$ for the ξ and X values studied here; therefore, eq 9 can be approximated to have the form of eq 13. For a solution containing a total of $(N_p + N_s)$ equivalents of Na^+ ions with rN_p equivalents of Na^+ bound, the fraction of "free" Na^+ ions is $((1 - r)N_p/(N_p + N_s)$. When eq 14 is rewritten as

$$D_{Na^+}/D^0_{Na^+} = (1 - r)(X^{-1} + 1)^{-1} + (X + 1)^{-1} \quad (15)$$

where $(1 - r)$ is the charge fraction of the polyelectrolyte, the connection between the theoretical charge fraction ξ^{-1} and the experimental charge fraction $(1 - r)$ becomes obvious. Furthermore, eq 13 and 15 are in the form of the additivity rule, where the diffusion of Na^+ ions in a salt-containing polyelectrolyte solution can be viewed as having contributions from Na^+ ions in a salt-free polyelectrolyte solution and from Na^+ ions in a polyelectrolyte-free salt solution

$$(N_p + N_s)(D_{Na^+}/D^0_{Na^+})_X = N_p(D_{Na^+}/D^0_{Na^+})_{X=\infty} + N_s(D^0_{Na^+}/D^0_{Na^+})_X$$

When $(D_{Na}{}^+/D^0_{Na^+})(X + 1)$ is plotted against X as was done in Figure 7, the slope corresponds to the diffusion ratio in salt-free solutions, $(D_{Na^+}/D^0_{Na^+})_{X=\infty}$

$$(D_{Na^+}/D^0_{Na^+})_X = (D_{Na^+}/D^0_{Na^+})_{X=\infty}(X^{-1} + 1)^{-1} + (X + 1)^{-1} \quad (16)$$

The first term on the right-hand side in eq 13, 15, and 16 is the polyelectrolyte contribution, due to the Na^+ ions that have dissociated from the polyion. As X increases this term increases, making it more important when $N_p > N_s$. The second term in these equations is the simple salt contribution, due to Na^+ ions from NaCl. As X increases this term decreases, making it more important when $N_s > N_p$. The identical form of eq 15 and 16 indicates why the charge fractions $(1 - r)$ and the $(D_{Na^+}/D^0_{Na^+})_{X=\infty}$ values, which were obtained with different equations, were found to be equal for each ξ value (see Table I). The diffusion ratio in salt-free solution is therefore a measure of the charge fraction of the polyelectrolyte. It is interesting that Wall et al.[25] had a similar view years ago.

Registry No. NaPA, 25549-84-2; NaCMC, 9004-32-4; Na^+, 17341-25-2.

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