acid) contains a significant contribution from interactions with charges which are not carried by neighboring monomer residues, it is reasonable to assume that the three parameters k_0, k_1, and k_2 are also functions of the overall polymer charge. If this is so in 0.2 N NaOH, it would of course be even more pronounced at lower ionic strength. Beyond this, it is also possible that k_0, k_1, and k_2 are dependent on the stereoisomerism of the chain. If this effect is important, it might be revealed by comparing the course of amide hydrolysis of polyacrylamides prepared at different temperatures, since a lowering of the polymerization temperature generally favors syndiotacticity.

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Interactions of Sodium Ions with Polyelectrolytes of Varying Charge Density

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ABSTRACT: Sodium ion interactions with polyelectrolytes of varying charge densities have been determined from tracer diffusion measurements. Sodium acrylate/acrylic acid, sodium acrylate/acrylamide, and sodium acrylate/*N,N*-dimethylacrylamide copolymers, each of varying linear charge density parameter ξ between 0.2 and 2.7, were used. The first copolymer was studied in aqueous salt-free and NaCl-containing solutions and the latter two copolymers only in salt-free solutions. It was found that the sodium ion diffusion coefficients were linear with ξ^{-1} above $\xi = 1$ for both salt-free and NaCl-containing solutions, as predicted from the Manning theory. Evidence for a critical ξ value is discussed. Also, constant values for the sodium ion diffusion coefficients were observed below the critical ξ value. An empirical additivity rule is discussed. The charge fractions for the sodium acrylate/acrylic acid copolymers were evaluated.

The theories that describe the dilute solution properties of polyelectrolytes have not been widely accepted. The failure of the establishment of accepted limiting laws for polyelectrolyte solutions is in part due to the lack of systematic experimental investigations, making it difficult to judge the dominant theories adequately to note where their modifications would be appropriate. The line charge model of Manning[1-7] has, of course, received the most attention because of its simplicity, because it represents high charge density polyelectrolytes fairly well, and because limiting laws are derived for thermodynamic, mass, and electric transport properties of polyelectrolyte solutions.

Briefly, when the stoichiometric charge density parameter ξ, where $\xi = e^2/kTb$, with e, k, and T the standard constants and b the average axial distance between stoichiometric charges along the polyelectrolyte chain, is greater than ξ_c, where $\xi_c = |Z_1|^{-1}$, with Z_1 the counterion valence, counterions condense onto the polyion until ξ_c is reached and the remaining counterions are in the Debye–Hückel atmosphere. Recently, Zimm and LeBret gave further theoretical justification of the Manning "two state" condensation theory.[8] Experimental evidence exists for this type of counterion binding, and the operational definition of counterion condensation, where the charge fraction of the polyelectrolyte equals a constant value of $(\xi|Z_1|)^{-1}$ over a broad concentration range, was found to hold for several polyelectrolytes.[9-12] The nature of the counterion condensed state may vary from a localized, dehydrated counterion which is site bound to a delocalized, hydrated counterion which can translate along the polyion. When $\xi < \xi_c$, the polyelectrolyte is thought by Manning to be completely dissociated with all counterions interacting with the polyion by Debye–Hückel forces. Co-ion–polyion interactions have been discussed elsewhere.[13-15]

Here we report the results of investigations of the interactions of Na$^+$ ions with polyelectrolytes determined by Na$^+$ ion tracer diffusion coefficients, which, of course, monitor the long-range counterion–polyion interactions. Recently, it was reported by Kowblansky and Zema[16,17] that the sodium ion activity coefficients in salt-free aqueous solutions of sodium acrylate/acrylamide copolymers and of sodium methacrylate/methacrylic acid copolymers are linearly dependent on $\xi^{1/2}$ over the range $0.2 < \xi < 2.7$. This is not in accord with the Manning

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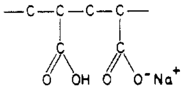
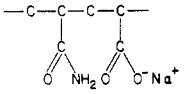
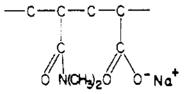
Table I
Copolymers Used in This Study, Their Symbols, and Range of the Charge Density Parameter

	NaPA/HPA	$0.2 < \xi < 2.7$
	NaPA/PAM	$0.2 < \xi < 2.6$
	NaPA/PDAM	$0.2 < \xi < 2.7$

theory, except that agreement between theory and experiment was attained only for $\xi = 2.7$. It was important to note if another measurement that monitors long-range interactions, namely Na^+ ion tracer diffusion coefficients, gave similar results. Thus, Na^+ ion tracer diffusion coefficients were determined in aqueous salt-free and NaCl-containing solutions of copolymers of sodium acrylate and acrylic acid (NaPA/HPA) and in aqueous salt-free solutions of copolymers of sodium acrylate and acrylamide (NaPA/PAM) and copolymers of sodium acrylate and *N,N*-dimethylacrylamide (NaPA/PDAM) over a large charge density range, $0.2 < \xi < 2.7$. These copolymers are shown in Table I. The three copolymers were used to note any possible effect caused by hydrogen bonding, which might form in NaPA/HPA and might form to a much lesser extent in NaPA/PAM and to zero extent in NaPA/PDAM. It was to be noted if an empirical relationship exists between $D_{Na^+}/D_{Na^+}{}^{\circ}$ and ξ in salt-free and salt-containing solutions. Also, how do the sodium diffusion ratios depend on the polyelectrolyte concentration and in salt solution on the NaCl concentration? Could additivity rules for diffusion be extracted from the data as well as a polyelectrolyte charge fraction? The Manning theory was a useful guide.

Experimental Section

Sodium polyacrylate (NaPA) was prepared by titration of poly(acrylic acid) (HPA), provided by Rohm and Haas Co., with NaOH to an approximate pH of 10, followed by precipitation with a methanol–acetone mixture. Aqueous dissolution followed by precipitation was repeated three times. Passage of the NaPA through a cation-exchange resin in the hydrogen form and titration of resulting acids with standardized NaOH to a phenolphthalein end point gave a charge density parameter of 2.73.

All prepared samples were dried in a vacuum oven at 50 °C for at least 48 h and handled with minimum exposure to air. The NaPA had a molecular weight of 4.11×10^5, determined from the measured intrinsic viscosity of 17.0 dL/g in 0.010 N NaBr and the known Mark–Houwink parameters.[18]

Aqueous solutions of sodium polyacrylate with different charge densities, but identical degree of polymerization, were prepared by titration of poly(acrylic acid) with NaOH. A stoichiometric quantity of each polymer was transferred to volumetric flasks and the required quantity of standardized sodium hydroxide solution was then added to each polymer solution. Upon dissolution of the polymer, water was added to the mark and the solution was dialyzed against distilled water for 24 h. This procedure was followed for each polyelectrolyte. The concentration of each resulting NaPA solution was determined by potentiometric titration with standardized NaOH solutions.

Poly(*N,N*-dimethylacrylamide) (PDAM) was prepared from *N,N*-dimethylacrylamide using 2,2′-azobis(isobutyronitrile), Du Pont Vazo 64, as the initiator and water as the solvent. The monomer *N,N*-dimethylacrylamide was supplied by Polysciences. The resulting polymers were then precipitated with a methanol–acetone mixture and purified by repeated aqueous dissolution followed by reprecipitation. The PDAM sample had a molecular weight of 1.66×10^5, determined from the measured intrinsic viscosity of 3.92 dL/g in water at 25 °C.[19] The polyacrylamide (PAM) sample, obtained from Cyanamid, had a molecular weight of 7.39×10^5 and an intrinsic viscosity of 2.42 dL/g in water at 25 °C.[20]

Aqueous solutions of sodium acrylate/acrylamide copolymers (NaPA/PAM) with charge densities varying from $0.2 < \xi < 2.6$ and sodium acrylate/*N,N*-dimethylacrylamide copolymers (NaPA/PDAM) with charge densities varying from $0.2 < \xi < 2.7$ were prepared in similar manner by alkaline hydrolysis of polyacrylamide and poly(*N,N*-dimethylacrylamide), respectively. The hydrolysis was performed in the presence of NaOH at 60 °C.[21] After dialyzing, the concentration of the resulting polyelectrolytes in solution was determined by potentiometric titration with standardized NaOH.

The radioactive species used were $^{22}Na^+$ in the form of sodium chloride and $^{45}Ca^{2+}$ in the form of calcium chloride, supplied by the New England Nuclear Co.

To determine the self-diffusion coefficients of ions, the open-end capillary method originally introduced by Anderson and Saddington[22,23] was employed without stirring. The tracer diffusion coefficient of Na^+ ions in aqueous NaPA solutions containing NaCl was determined varying X from 0.10 to 10, where X is the ratio of normality of the polyelectrolyte N_p to the normality of the simple salt N_s

$$X = N_p/N_s \qquad (1)$$

Salt concentrations were varied from 5.00×10^{-4} to 1.00×10^{-2} N, with the polymer concentration ranging from 5.00×10^{-5} to 1.00×10^{-1} N.

The self-diffusion coefficient of polyelectrolytes D_p in NaCl solutions was determined by introducing a tracer amount of $^{45}Ca^{2+}$ ion in the solution. The addition of a small quantity of $^{45}Ca^{2+}$ ion results in its complete condensation onto the polyelectrolyte and yields a polyelectrolyte tagged with $^{45}Ca^{2+}$. For NaPA the values of D_p were 2 orders of magnitude less than for D_{Na^+}; hence, the contribution of the diffusion of condensed Na^+ ions to the observed D_{Na^+} was assumed to be negligible. This was also assumed for the PAM and PDAM derivatives because of their high molecular weights.

Tracer diffusion coefficients of Na^+ ion in aqueous salt-free NaPA/HPA, NaPA/PAM, and NaPA/PDAM solutions were determined at 25 °C. All self-diffusion coefficients were calculated with the complete solution of Fick's second law.

Results and Discussion

Salt-Free Solutions of Polyelectrolytes of Varying Charge Density. Tracer D_{Na^+} values were determined in salt-free polyelectrolyte solutions at four concentrations of 5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, and 1.0×10^{-2} N for NaPA/HPA, NaPA/PAM, and NaPA/PDAM whose charge densities were in the range $0.2 < \xi < 2.7$. The results are in Tables II–IV. A glance at these tables shows that for each ξ value for all three polyelectrolytes, the $D_{Na^+}/D_{Na^+}{}^{\circ}$ ratios are fairly independent of N_p in the concentration range studied. Very slightly higher diffusion ratio values are found at the lowest concentration, but nevertheless each average $D_{Na^+}/D_{Na^+}{}^{\circ}$ value indicates fairly constant ratios at each charge density, independent of the polyelectrolyte concentration. Most striking is the discontinuity found at $\xi_c = 1$ for NaPA/HPA when the averages of $D_{Na^+}/D_{Na^+}{}^{\circ}$ for the four concentrations are plotted against ξ^{-1}, as is illustrated in Figure 1. Here, for NaPA/HPA, the plot is linear in the range $2.7 > \xi > 0.95$ with a slope of 0.79 ± 0.04 and an intercept of 0.11 ± 0.03. The diffusion ratio falls precipitously (about 22%) at $\xi \approx 1$ to a constant diffusion ratio of 0.631 ± 0.017 for $\xi < 1$. The few Na^+ ion diffusion coefficients in NaPA/HPA solutions obtained by Wall et al.,[24] shown in Figure 1, agree with those presented here for $\xi > 1$. For NaPA/PAM and NaPA/PDAM, Figure 1 shows that $D_{Na^+}/D_{Na^+}{}^{\circ}$ is linear in ξ^{-1} for $2.7 > \xi > 0.95$ with respective slopes of 0.68 ± 0.04 and 0.77 ± 0.05 and respective intercepts of 0.18 ± 0.03 and 0.11 ± 0.04, and $D_{Na^+}/D_{Na^+}{}^{\circ}$ remains constant at

Table II
$D_{Na^+}/D_{Na^+}{}^\circ$ Values for Aqueous Salt-Free Solutions of NaPA/HPA at Several Normalities at 25 °C

ξ	5.0 × 10^{-4} N	1.0 × 10^{-3} N	5.0 × 10^{-3} N	1.0 × 10^{-2} N	av
2.73	0.432 ± 0.017	0.396 ± 0.005	0.411 ± 0.011	0.381 ± 0.006	0.405 ± 0.010
2.22	0.541 ± 0.009	0.453 ± 0.004	0.440 ± 0.021	0.399 ± 0.006	0.458 ± 0.011
1.82	0.609 ± 0.003	0.459 ± 0.026	0.509 ± 0.004	0.549 ± 0.010	0.532 ± 0.014
1.54	0.728 ± 0.026	0.648 ± 0.010	0.610 ± 0.007	0.558 ± 0.017	0.636 ± 0.017
1.33	0.804 ± 0.016	0.688 ± 0.005	0.643 ± 0.017	0.648 ± 0.016	0.696 ± 0.014
1.18	0.932 ± 0.012	0.748 ± 0.010	0.710 ± 0.029	0.778 ± 0.030	0.792 ± 0.022
1.05	0.926 ± 0.026	0.818 ± 0.006	0.805 ± 0.024	0.848 ± 0.020	0.849 ± 0.021
0.80	0.699 ± 0.003	0.628 ± 0.004	0.559 ± 0.012	0.708 ± 0.004	0.649 ± 0.007
0.67	0.657 ± 0.003	0.578 ± 0.006	0.612 ± 0.026	0.648 ± 0.018	0.624 ± 0.016
0.40	0.670 ± 0.008	0.608 ± 0.036	0.570 ± 0.011	0.608 ± 0.020	0.614 ± 0.021
0.20	0.691 ± 0.027	0.596 ± 0.004	0.628 ± 0.026	0.638 ± 0.019	

Table III
$D_{Na^+}/D_{Na^+}{}^\circ$ Values for Aqueous Salt-Free Solutions of NaPA/PAM at 25 °C

ξ	5.0 × 10^{-4} N	1.0 × 10^{-3} N	5.0 × 10^{-3} N	1.0 × 10^{-2} N	av
2.61	0.442 ± 0.010	0.421 ± 0.011	0.428 ± 0.016	0.426 ± 0.008	0.429 ± 0.012
2.22	0.468 ± 0.021	0.431 ± 0.021	0.439 ± 0.014	0.441 ± 0.023	0.445 ± 0.020
1.82	0.573 ± 0.026	0.561 ± 0.004	0.571 ± 0.012	0.569 ± 0.002	0.569 ± 0.015
1.54	0.685 ± 0.017	0.671 ± 0.021	0.657 ± 0.004	0.662 ± 0.003	0.669 ± 0.013
1.33	0.722 ± 0.003	0.703 ± 0.006	0.726 ± 0.006	0.711 ± 0.010	0.716 ± 0.007
1.18	0.769 ± 0.017	0.767 ± 0.013	0.743 ± 0.021	0.754 ± 0.017	0.758 ± 0.017
1.05	0.824 ± 0.021	0.769 ± 0.021	0.798 ± 0.003	0.781 ± 0.022	0.793 ± 0.019
0.80	0.811 ± 0.013	0.791 ± 0.001	0.812 ± 0.008	0.793 ± 0.010	0.802 ± 0.009
0.67	0.805 ± 0.004	0.795 ± 0.032	0.774 ± 0.022	0.816 ± 0.008	0.798 ± 0.019
0.40	0.812 ± 0.011	0.815 ± 0.016	0.769 ± 0.017	0.785 ± 0.004	0.795 ± 0.013
0.20	0.792 ± 0.007	0.771 ± 0.004	0.808 ± 0.005	0.781 ± 0.011	0.788 ± 0.007

Table IV
$D_{Na^+}/D_{Na^+}{}^\circ$ Values for Aqueous Salt-Free Solutions of NaPA/PDAM at Several Normalities at 25 °C

ξ	5.0 × 10^{-4} N	1.0 × 10^{-3} N	5.0 × 10^{-3} N	1.0 × 10^{-2} N	av
2.67	0.425 ± 0.003	0.406 ± 0.003	0.401 ± 0.019	0.411 ± 0.008	0.411 ± 0.011
2.22	0.451 ± 0.006	0.422 ± 0.011	0.418 ± 0.006	0.431 ± 0.022	0.431 ± 0.013
1.82	0.558 ± 0.021	0.547 ± 0.009	0.539 ± 0.017	0.542 ± 0.006	0.547 ± 0.015
1.54	0.648 ± 0.007	0.632 ± 0.011	0.626 ± 0.021	0.629 ± 0.016	0.634 ± 0.014
1.33	0.712 ± 0.021	0.703 ± 0.018	0.688 ± 0.005	0.691 ± 0.013	0.699 ± 0.015
1.18	0.801 ± 0.011	0.792 ± 0.001	0.786 ± 0.017	0.785 ± 0.009	0.791 ± 0.011
1.05	0.826 ± 0.001	0.811 ± 0.007	0.816 ± 0.015	0.813 ± 0.011	0.817 ± 0.009
0.80	0.821 ± 0.022	0.814 ± 0.022	0.797 ± 0.013	0.807 ± 0.003	0.809 ± 0.016
0.67	0.815 ± 0.009	0.809 ± 0.006	0.815 ± 0.004	0.811 ± 0.010	0.813 ± 0.007
0.40	0.817 ± 0.016	0.795 ± 0.016	0.812 ± 0.007	0.816 ± 0.021	0.810 ± 0.015
0.20	0.823 ± 0.010	0.816 ± 0.0014	0.818 ± 0.003	0.820 ± 0.017	0.819 ± 0.011

0.796 ± 0.013 and 0.813 ± 0.013 respectively, in the range $0.95 > \xi > 0.20$.

The dominant feature in Figure 1 is the abrupt change in slope at $\xi = 1$ for each of the three polyelectrolytes, with a discontinuity occurring for NaPA/HPA. This appears to be strong evidence for counterion condensation since the breaks in the slopes occur just where the Manning theory predicts that it should occur, at $\xi = \xi_c$. That condensation occurs close to $\xi = 1$ for monovalent counterions has been reported by Zana et al.,[25] Leyte et al.,[26] and Gustavsson et al.[27] from magnetic resonance experiments, by Ikagami[28] from refractive index experiments and by Ware et al.[29] from electrophoretic mobility experiments. It should be pointed out these experiments are sensitive to measurements close to the polyelectrolyte chain, while the tracer Na^+ ion diffusion coefficients determined in the present study monitor the long-range, Debye–Hückel interactions.

The Manning theory also predicts that $D_{Na^+}/D_{Na^+}{}^\circ$ in salt-free polyelectrolyte solutions depends only on the nature of the polyelectrolyte through its charge density

$$D_{Na^+}/D_{Na^+}{}^\circ = 0.866\xi^{-1} \qquad \text{for } \xi > 1 \qquad (2)$$

and

$$D_{Na^+}/D_{Na^+}{}^\circ = 1 - (0.55\xi^2)/(\xi + \pi) \qquad \text{for } \xi < 1 \quad (3)$$

It should be noted from Figure 1 that the functional dependency predicted by eq 2, given by the solid line, is obeyed. The $D_{Na^+}/D_{Na^+}{}^\circ$ ratios at each ξ value for all three polyelectrolytes have close values within experimental error and the line resulting from their average values, which are shown in Figure 1, has an average experimental slope of

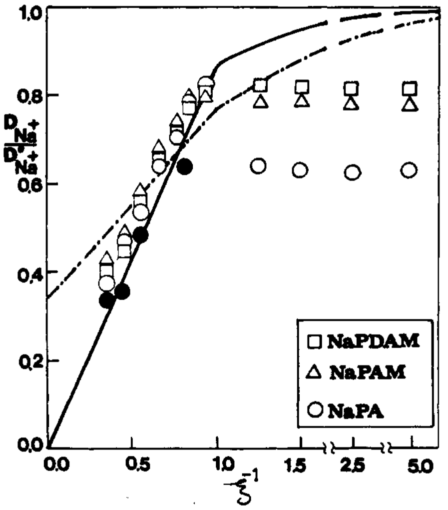


Figure 1. $D_{Na^+}/D_{Na^+}{}^\circ$ dependence on ξ^{-1} for (○) NaPA/HPA, (△) NaPA/PAM, (□) NaPA/PDAM, and (●) NaPA/HPA.[24] The solid line is the Manning theory prediction and the broken line the Yoshida theory prediction.

0.74 ± 0.04 and an average experimental intercept of 0.13 ± 0.03. Thus good agreement with eq 2 is achieved. It is interesting that if the zero point ($D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ} = 0$; $\xi^{-1} = 0$) is used along with the experimental points for $\xi > 1$, then almost exact accord with the theoretical slope of eq 2 is achieved, i.e., 0.88, 0.87, and 0.87 for NaPA/HPA, NaPA/PAM, and NaPA/PDAM, respectively. The similar results obtained for the three polyelectrolytes indicate that the polyelectrolytes have their carboxyl groups distributed along the chain in the same manner, most probably random. Other facts support this.

The discontinuity at $\xi = \xi_c$ for NaPA/HPA and the change in slope at $\xi = \xi_c$ for NaPA/PAM and NaPA/PDAM are evident from Figure 1. With counterion condensation occurring at ξ_c, the reduction of charge along the chain causes it to coil, thereby facilitating intramolecular hydrogen bond formation at lower charge densities, i.e., $\xi < 1$, for NaPA/HPA. Cooperative hydrogen bonding by two adjacent carboxylate groups in polycarboxylates has been discussed by Begala and Strauss.[30] This would increase the charge density of the coil and result in lower D_{Na^+} values, as is observed. Such an amount of coiling is not as pronounced for the other two polyelectrolytes at $\xi_c = 1$ because intramolecular hydrogen bond formation is not probable and hence, only a change in slope occurs at ξ_c. The constant $D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ}$ values for $\xi < \xi_c$ which were obtained for all three polyelectrolytes indicate that the effective charge density of the coils is fairly constant in this charge density range and that rod-like behavior does not occur since eq 3 is not obeyed. It is interesting that the electrophoretic mobilities of 6–6 ionene bromide in 4.0 mM KBr remained fairly constant for $\xi > 1$, followed by a precipitous drop at $\xi = 1$ to a constant value for $\xi \leq 1$.[29] Ware explains these results by noting that near $\xi = 1$, the spacing of the condensed ions predicted by condensation theory is greater than the Debye screening length, resulting in further counterion condensation. Perhaps ξ_c is the effective value for $\xi < \xi_c$ as well as for $\xi > \xi_c$ to give stability to the solution. For $\xi > \xi_c$ this stability is achieved by condensation reducing the charge on the chain. For $\xi < \xi_c$ this stability is achieved by a slight conformation change to increase the charge density of the chain. It would be interesting to examine this idea by noting the change in the radius of gyration of the chain as ξ decreases below ξ_c.

Since D_{Na^+} and the sodium activity coefficient γ_{Na^+} are measures of the long-range counterion–polyion interaction, it would be of interest to note how the diffusion results in Figure 1 compare with the reported Na^+ ion activity coefficient results for salt-free solution of NaPA/PAM in the range $0.02 < \xi < 2.85$.[16] The plot of γ_{Na^+} vs. $\xi^{1/2}$ was found to be continuous and linear over the whole range studied, with no change in slope occurring at ξ_c. These results differ qualitatively from the diffusion results in Figure 1. However, the positive deviations from the Manning lines for the higher ξ values and the negative deviations from the Manning lines for $\xi < \xi_c$ are evident for both activity and diffusion coefficients results.

Yoshida used the cell model with cylindrical symmetry and the potential obtained from the solution of the Poisson–Boltzmann equation to derive expressions for tracer diffusion coefficients of the counterions and co-ions in salt-free polyelectrolyte solution in the limit of infinite dilution.[31,32] More realistic co-ion diffusion coefficients are predicted by the Yoshida theory than by the Manning theory because the latter theory overestimates the interaction of multicharged co-ions with the polyion. However, it is gratifying that similar results are obtained for the counterion–polyion interaction, no matter whether the fuller Poisson–Boltzmann potential is used or the Debye–Hückel approximation. Both theories predict that the fraction of condensed monovalent counterions is $(1 - \xi^{-1})$ for $\xi > 1$. The Yoshida interpretation has the condensed counterions moving undisturbed parallel to the axis of the polyion, while the condensed counterions have the mobility of the polyion according to Manning. The Yoshida equation

$$D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ} = (1/3)(1 + 1.300\xi^{-1}) \qquad \text{for } \xi > 1 \quad (4)$$

and eq 2 show that the same linear functionality in ξ^{-1} is predicted from both theories for $\xi > 1$, only with different slopes and intercepts. Equation 4 predicts the broken line shown in Figure 1 and gives the respective slope and intercept of 0.43 and 0.33, compared to the average experimental slope of 0.74 ± 0.04 and intercept of 0.13 ± 0.03. The experimental values appear to be closer to the Manning values given by eq 2. The discrepancy between the two theories is that Manning has a negligible contribution of the diffusion coefficient of the condensed counterions to the observed diffusion coefficient, while Yoshida has a finite contribution. In the limit of $\xi \rightarrow \infty$ where all counterions are condensed and for $\xi = 1.1$ where 0.09 is the fraction of counterions condensed, the contribution of the condensed counterions to the predicted diffusion coefficient is $D^{\circ}/3$ and $0.09(D^{\circ}/3)$, respectively, according to Yoshida, and zero assumed by Manning. Note that as ξ decreases toward unity, the values predicted from both theories get closer because there is a decreasing contribution to D_{Na^+} from the condensed counterions.

For $\xi < 1$, Yoshida obtained

$$D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ} = 1/3 + (2/3)(2 - \xi)(1 - \xi)G \qquad (5)$$

where G is a function which depends on ξ, so $D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ}$ depends only on ξ. From Figure 1 it is clear that eq 5 predicts stronger counterion–polyion interactions than Manning's eq 3 predicts. However, since both theories underestimate the constant counterion–polyion interactions for $\xi < 1$, it appears that the rod-like model does not adequately represent low charge density polyelectrolyte chains.

Salt-Containing Solutions of Polyelectrolytes of Varying Charge Density. D_{Na^+} values were obtained in aqueous NaCl solutions containing NaPA/HPA polyelectrolytes of the same range of charge densities as those used for the salt-free solutions, i.e., in the range $0.20 < \xi < 2.7$. Since maximum counterion–polyion interaction in salt-free solutions was noted to be at approximately $N_p = 5.0 \times 10^{-3}$ N, this polyelectrolyte concentration was used to prepare aqueous solutions with X values of 0.10, 0.50, 1.00, 5.0, and 10.0 by adding the desired amount of NaCl. The data are illustrated in Figure 2, where the points are experimental and the lines are drawn in accord with the Manning theory.[1,2] It should first be noted that in NaCl solutions for each constant X value, $D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ}$ appears to be linear in ξ^{-1} in the range $0 < \xi^{-1} < 1.0$, just as was obtained for the salt-free solutions. The linearity of $D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ}$ vs. ξ^{-1} can be deduced from the Manning theory for $\xi > \xi_c$ for monovalent counterions. The theoretical equation can be written as

$$D_{\mathrm{Na}^+}/D_{\mathrm{Na}^+}{}^{\circ} = \xi^{-1}(1 - A/3)/(1 + X^{-1}) + (1 - A/3)/(1 + X) \qquad (6)$$

where A, the interaction parameter for monovalent ions, is

$$A = \sum_{m=-\infty}^{\infty} \sum_{\substack{n=-\infty \\ (m,n) \neq (0,0)}}^{\infty} [\pi(m^2 + n^2) + 1 + 2\xi X^{-1}]^{-2} \qquad (7)$$

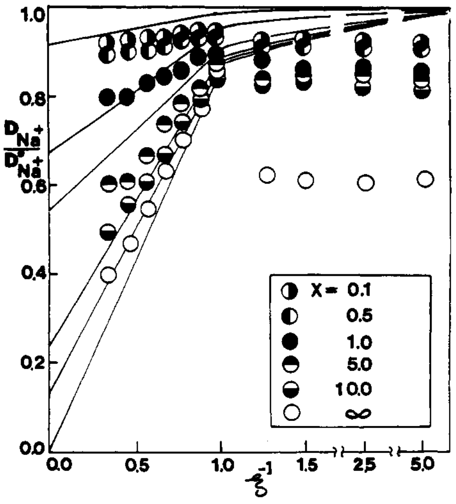


Figure 2. $D_{Na^+}/D_{Na^+}{}^\circ$ dependence on ξ^{-1} for NaPA/HPA in aqueous NaCl solutions at several constant X values. The lines are predicted by the Manning theory.

Table V
Comparison of the Experimental Slopes and Intercepts Obtained from Figure 2 with Those Predicted from Eq 6

X	slope	$(X^{-1} + 1)^{-1}$	intercept	$(X + 1)^{-1}$
0.1	0.04 ± 0.03	0.091	0.91 ± 0.09	0.91
0.5	0.09 ± 0.02	0.33	0.85 ± 0.07	0.67
1.0	0.23 ± 0.09	0.50	0.71 ± 0.12	0.50
5.0	0.52 ± 0.08	0.83	0.40 ± 0.15	0.17
10.0	0.63 ± 0.08	0.91	0.26 ± 0.10	0.09

In the limit of $\xi^{-1} = 0$, eq 7 indicates that $A = 0$ and the intercept of eq 6 reduces to $(1 + X)^{-1}$ for constant X values. In this limit, $\xi = \infty$ and, hence, all counterions would be condensed. A glance at Table V shows that the experimentally determined intercept values are in best agreement with the theoretical values $(1 + X)^{-1}$ for the case of excess NaCl over the polyelectrolyte concentration, i.e., for X values less than unity. The agreement between the theoretical and experimental intercept values for X greater than unity is fairly good, especially when the indicated experimental error is considered.

At constant X values, the slopes of the lines for $D_{Na^+}/D_{Na^+}{}^\circ$ vs. ξ^{-1} could be closely approximated by $(1 + X^{-1})$ in eq 6. This is because while A, given by eq 7, depends on ξ, it does so weakly. Between $\xi = 1.1$ and 2.7, the $(1 - A/3)$ values differ by at most 2% for each X value. Thus, the Manning theory shows that $D_{Na^+}/D_{Na^+}{}^\circ$ could be linear in ξ^{-1} for $\xi > 1$ at constant X. As is illustrated in Figure 2 and noted in Table V, the theoretical slopes overestimate the counterion–polyion interaction.

For $\xi < 1$, Figure 2 shows that the $D_{Na^+}/D_{Na^+}{}^\circ$ values remain constant in the range $0.20 < \xi < 1.0$ for each X value. There appears to be only a change in slope at $X = 1$ for each curve and no discontinuity as is evidenced for the salt-free case. Also, at each constant ξ for $\xi > 1$, there is a slight increase in the $D_{Na^+}/D_{Na^+}{}^\circ$ values as the salt concentration increases. It appears that the hydrogen bonding proposed for salt-free NaPA/HPA solutions for $\xi < 1$ does not take place when NaCl is present, and hence a discontinuity is not noted in salt solutions. Similar results were discussed previously for salt-free solutions of NaPA/PAM and NaPA/PDAM, where hydrogen bond formation was not favored. Also, it should be pointed out that Figure 2 shows the Manning theory is not a good representation of the polyelectrolyte for $\xi < \xi_c$.

Additivity of the counterion activity of a salt-free polyelectrolyte solution and a polyelectrolyte-free salt solution has resulted in useful additivity rules for a polyelectrolyte solution containing simple salt. Recently, additivity rules were shown to be valid for the activities of monovalent and divalent counterions.[16,17] For Na$^+$ ion diffusion the additivity rule could be written as

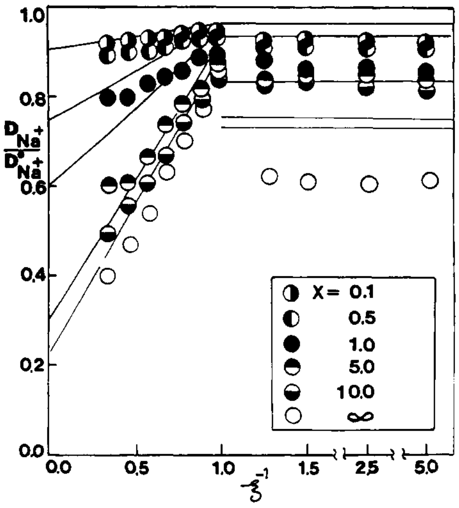


Figure 3. Test of the Na$^+$ ion diffusion additivity rule. The lines in the figure are given by eq 8 and the points are experimental.

$$(D_{Na^+}/D_{Na^+}{}^\circ)_X = (X^{-1} + 1)^{-1}(D_{Na^+}/D_{Na^+}{}^\circ)_{X=\infty} + (X + 1)^{-1}(D_{Na^+}{}^\circ/D_{Na^+}{}^\circ)_X \quad (8)$$

where the first term on the right-hand side is the salt-free contribution and the second term on the right-hand side is the simple salt contribution. The lines in Figure 3 are based on eq 8 and the points are experimental. Best accord is achieved at $X = 0.1$, 5.0, and 10.0, where one component is in large excess. A most stringent test would be for $X = 1$, i.e., where both components contribute equally. Here good accord is achieved for the charge densities in the range $1.05 < \xi < 1.82$, and poor accord is obtained for $\xi > 2$. It seems from Figure 3 that below $\xi = 1$ an additivity rule for diffusion coefficients does not exist.

For a solution containing a total $(N_p + N_s)$ equivalents of Na$^+$ ions with rN_p equivalents of Na$^+$ ions bound, the fraction of Na$^+$ ions bound $f_{Na^+}{}^c$ is

$$f_{Na^+}{}^c = rN_p/(N_p + N_s) = rX/(1 + X) \quad (9)$$

where $f_{Na^+}{}^f = ((1 - r)N_p + N_s)/(N_p + N_s)$ is the fraction of Na$^+$ ions in the solution that are "free". Counterion condensation onto polyelectrolytes has been operationally defined as association such that the total fraction of polyion sites compensated for with counterion remains invariant over a wide range of X values.[5] If the interaction of Na$^+$ ions with polyelectrolytes is properly described as "counterion condensation", then a plot of $f_{Na^+}{}^c(X + 1)$ vs. X should be linear with slope r. Note that this would indicate that the fraction of sodium ions dissociated from the polyelectrolyte is constant and independent of the concentrations of polyelectrolyte and of simple salt. It is clear that r is the fraction of the condensed or bound Na$^+$ ions which are originally on the polyelectrolyte and $(1 - r)$ is the charge fraction of the polyelectrolyte.

To evaluate r from the diffusion measurements presented here, an assumption must be made. It is plausible to assume that $f_{Na^+}{}^f$ is given by $D_{Na^+}/D_{Na^+}{}^\circ$ and that any small co-ion–polyion interaction, if at all present, does not affect the assumption. So, $f_{Na^+}{}^c$ is given by $[1 - (D_{Na^+}/D_{Na^+}{}^\circ)]$ and plots were made of $f_{Na^+}{}^c(1 + X)$ vs. X for each NAPA/HPA polyelectrolyte with $\xi < 1$. The results from such plots indicate linearity was obtained for $0.1 < X < 10$, as shown in Table VI. The charge fraction $(1 - r)$ is plotted against ξ^{-1} in Figure 4. It should first be noted

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Table VI
Parameters of Eq 9 Obtained for NaPA/HPA Copolymers

ξ^{-1}	slope[a]	intercept[a]	$(1 - r)$	$(D_{Na^+}/D_{Na^+}{}^{\circ})_{X=\infty}$
0.37	0.57 ± 0.08	−0.13 ± 0.10	0.43 ± 0.06	0.41 ± 0.01
0.45	0.50 ± 0.06	−0.08 ± 0.05	0.50 ± 0.06	0.46 ± 0.01
0.55	0.43 ± 0.06	−0.08 ± 0.06	0.58 ± 0.08	0.53 ± 0.01
0.65	0.34 ± 0.04	−0.06 ± 0.06	0.66 ± 0.08	0.64 ± 0.02
0.75	0.28 ± 0.05	0.08 ± 0.04	0.72 ± 0.13	0.70 ± 0.01
0.85	0.24 ± 0.03	0.06 ± 0.04	0.76 ± 0.10	0.79 ± 0.02
0.95	0.19 ± 0.03	0.00 ± 0.00	0.81 ± 0.13	0.85 ± 0.02

[a] $f_{Na^+}{}^{c}(X + 1)$ vs. X.

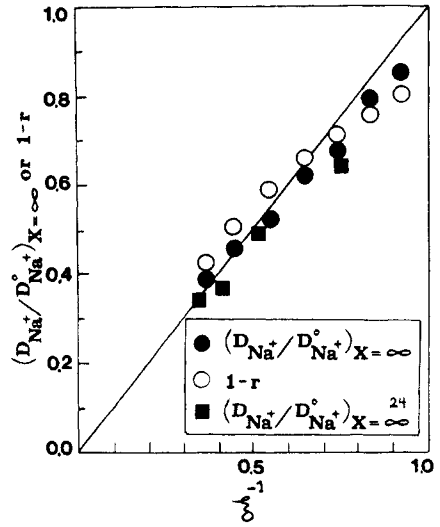

Figure 4. Experimental values of $(1 - r)$ and $D_{Na^+}/D_{Na^+}{}^{\circ}$ dependence in ξ^{-1}. The line is from the Manning theory.

from Table VI and Figure 4 that within the indicated experimental error, the calculated charge fractions $(1 - r)$ have values close to the theoretical values ξ^{-1}, especially for the range $1.3 < \xi < 2.7$. This gives some validity to calculating a charge fraction from eq 9, which states that condensation (and not electrostatic) is the dominant interaction. In fact, eq 9 can be obtained from eq 6 by letting the interaction term vanish. Also, for the higher charge density parameter values, the contribution of condensation term to $D_{Na^+}/D_{Na^+}{}^{\circ}$ in eq 6 is much greater than the contribution of the interaction term, while for lower charge densities both terms contribute about equally. This explains why the lower charge density points in Figure 4 show the greatest deviation from the theoretical line. Because of the agreement Wall obtained in calculating $(1 - r)$ from electrical transference and diffusion experiments for salt-free NaPA/HPA solutions,[24] his values for salt-free $(D_{Na^+}/D_{Na^+}{}^{\circ})_{X=\infty}$ are included in Figure 4. The agreement between these and the $(1 - r)$ values for each value of ξ gives further creditability to the evaluation of a charge fraction for each polyelectrolyte. Also, it seems that Manning is correct in stating that the charge fraction depends only on ξ.

Registry No. NaPA/HPA (copolymer), 9033-79-8; NaPA/PAM (copolymer), 25085-02-3; NaPA/PDAM (copolymer), 92078-73-4; Na^+, 17341-25-2.

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Interactions of Sodium Ions with Polyelectrolytes of Constant Charge Density

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ABSTRACT: Sodium ion interactions with polyelectrolytes of constant charge density have been determined from sodium ion tracer diffusion measurements. The sodium salts of polyacrylate, poly(styrenecarboxylate), poly(vinylsulfonate), and poly(styrenesulfonate) were studied in salt-free and NaCl-containing aqueous solutions over large concentration ranges of polyelectrolyte and of NaCl. Sulfonate polyelectrolytes interacted with the sodium ions to a smaller extent than the carboxylate ones. The sodium ion tracer diffusion coefficients were found to be fairly independent of NaCl concentration for each polyelectrolyte. The additivity rule and the polyelectrolyte charge fraction are discussed in terms of the Manning theory.

Measurements in polyelectrolyte solutions that are sensitive to long-range interactions are not always in accord. To monitor counterion–polyion interactions, usually single ion activity coefficients and radioactive tracer dif-