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.

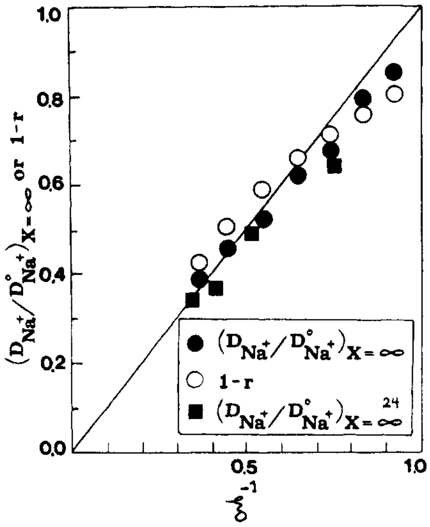

Figure 4. Experimental values of $(1 - r)$ and $D_{Na^+}/D_{Na^+}{}^\circ$ dependence in ξ^{-1}. The line is from the Manning theory.

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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Received June 22, 1984

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-

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fusion coefficients are evaluated. While tracer diffusion coefficients are unambiguously interpretable, single ion activity coefficients are not. Also, they do not always reveal the same findings. For instance, sodium ion tracer diffusion coefficients in aqueous sodium acrylate/acrylic acid copolymers exhibited a discontinuity at a critical charge density when the charge densities were varied,[1] whereas sodium ion activity coefficients for aqueous sodium methacrylate/methacrylic acid copolymers did not.[2]

Here we compare the results of sodium ion tracer diffusion measurements with four vinylic polyelectrolytes of fairly constant charge density in salt-free and NaCl-containing aqueous solutions: sodium polyacrylate (NaPA), sodium poly(styrenecarboxylate) (NaPSC), sodium poly(vinylsulfonate) (NaPVS), and sodium poly(styrenesulfonate) (NaPSS). It was desirable to examine the effect of the pendant ionic group on the counterion–polyion long range interaction, including the ionic strength effect, the additivity rule, and the charge fraction of the polyelectrolyte in terms of the Manning theory.[3-9]

Experimental Section

Sodium poly(styrenecarboxylate) (NaPSC) was prepared by polymerizing *p*-vinylbenzoic acid using benzoyl peroxide as the initiator, followed by titration with NaOH. The polymerization was performed at 60 °C for 3 days with continuous stirring and THF as the solvent. The monomer was prepared by the reaction of *p*-chlorostyrene, purchased from Aldrich Chemical Co., with a Grignard reagent.[10] The resulting polymer was found to have a molecular weight of 5.5×10^5, which was evaluated from the Flory–Mandelkern equation[11] with the experimentally determined polyelectrolyte diffusion coefficient at infinite dilution $D_p°$ and the intrinsic viscosity. A value of 5.7×10^{-7} cm^2/s was determined for $D_p°$ by extrapolating the linear plots of D_p against the polyelectrolyte normality in aqueous 0.010 N NaCl solution. A capillary diffusion technique using tracer amounts of $^{45}Ca^{2+}$ was employed, where the Ca^{2+} ions are known to be condensed onto the polyelectrolyte. The intrinsic viscosity of 17.0 dL/g for NaPSC in 0.010 N NaCl was determined with an Ubbelohde viscometer. Sodium poly(vinylsulfonate) (NaPVS) was polymerized in similar manner using 2,2′-azobis(isobutyronitrile), Du Pont Vaso 64, as the initiator and water as the solvent. The monomer, sodium vinylsulfonate, was supplied by Polysciences. The resulting polymer was then precipitated with a methanol–acetone mixture and purified by repeated aqueous dissolution followed by reprecipitation.

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.

Sodium poly(styrenesulfonate) (NaPSS) was supplied by the Dow Chemical Co.

Passage of NaPSS, NaPVS, NaPSC, and NaPA through a cation-exchange resin in the hydrogen form and titration of the resulting acids with standardized NaOH to a phenolphthalein end point gave values for the charge density parameter ξ of 2.64, 2.52, 2.57, and 2.73 for NaPSS, NaPVS, NaPSC, and NaPA, respectively. The charge density parameter is defined as

$$\xi = e^2/\epsilon kTb$$

where e, k, and T are standard constants and b is the average axial distance between stoichiometric charges along the polyelectrolyte chain. All prepared samples were dried in a vacuum oven at 50 °C for at least 48 h and handled with minimum exposure to air.

NaPSS, NaPVS, and NaPA samples were found to have molecular weights of 5.21×10^5, 3.61×10^5, and 4.11×10^5, respectively, as determined from the measured intrinsic viscosities of the polymers, NaPSS in 0.010 N NaCl, HPVS in 0.349 N KCl, and NaPA in 0.010 N NaBr, which were found to be 3.43, 4.11, and 16.95 dL/g, respectively, and known Mark–Houwink parameters.[12-14]

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

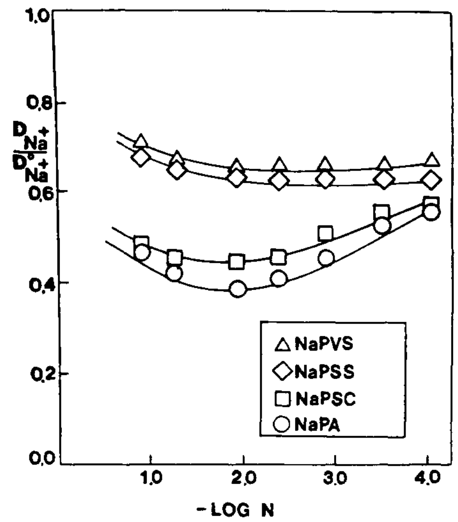

Figure 1. $D_{Na^+}/D_{Na^+}°$ dependence on the equivalent concentration and nature of polyelectrolyte in aqueous salt-free solutions.

To determine the self-diffusion coefficients of ions, the open-end capillary method originally introduced by Anderson and Saddington was employed without stirring.[15,16] The tracer diffusion coefficient of Na^+ ions in aqueous salt-free and NaCl-containing solutions of NaPSS, NaPVS, NaPSC, and NaPA were determined at 25 °C 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

$$X = N_p/N_s$$

Salt concentrations ranged from 5.0×10^{-4} to 1.0×10^{-2} N, with the polymer concentration ranging from 5.00×10^{-5} to 1.00×10^{-1} N.

The self-diffusion coefficient of polyelectrolytes 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 $^{45}Ca^{2+}$.[17] The measured Ca^{2+} diffusion coefficient $D_{Ca^{2+}}$ is thus the diffusion coefficient of the polyelectrolyte D_p. All self-diffusion coefficients were calculated with the exact solution of Fick's law.

Results and Discussion

To note if the nature of the pendant ionic groups on the polyelectrolyte chain affects the long-range counterion–polyion interactions, values of D_{Na^+} were determined for the sodium salts of four vinylic polyelectrolytes. Measurements were made in aqueous solutions of NaPA (ξ = 2.7), NaPSC (ξ = 2.6), NaPVS (ξ = 2.5), and NaPSS (ξ = 2.6) without and with NaCl present.

The results for aqueous salt-free solutions of the polyelectrolytes for the concentration range 1.0×10^{-4} to 5.0×10^{-1} N are shown in Figure 1. Two observations are evident from Figure 1. The lower $D_{Na^+}/D_{Na^+}°$ curves for the two carboxylate polyelectrolytes lie close together, as do the two upper curves for the two sulfonate polyelectrolytes. Also, the curves show relatively flat minima at approximately 5.0×10^{-3}–1.0×10^{-2} N. The minimum $D_{Na^+}/D_{Na^+}°$ values are 0.38 for NaPA, 0.45 for NaPSC, 0.63 for NaPVS, and 0.62 for NaPSS. Similar diffusion curves with shallow minima in the range 1.0×10^{-3} to 1.0×10^{-2} N have been reported for other polyelectrolytes in aqueous salt-free solutions.[18] It is supportive that others reported minimum $D_{Na^+}/D_{Na^+}°$ values of 0.38 and 0.36 for NaPA[19,20] with ξ = 2.85 and 0.62 for NaPSS[19] with ξ = 2.65. The $D_{Na^+}/D_{Na^+}°$ values in NaCl-containing solutions extrapolated for $X \rightarrow \infty$ are also in accord with the above values,

Table I
Values of $D_{Na^+}/D_{Na^+}^\circ$ for Aqueous NaCl Solutions Containing Sodium Polyacrylate

X	0.0005 N	0.0010 N	0.0050 N	0.0100 N	av
0.1	0.938 ± 0.007	0.944 ± 0.014	0.936 ± 0.011	0.947 ± 0.003	0.941 ± 0.009
0.5	0.862 ± 0.016	0.843 ± 0.011	0.853 ± 0.005	0.862 ± 0.011	0.855 ± 0.011
1.0	0.813 ± 0.016	0.825 ± 0.017	0.829 ± 0.014	0.812 ± 0.011	0.819 ± 0.014
2.0	0.667 ± 0.011	0.695 ± 0.005	0.668 ± 0.005	0.705 ± 0.005	0.684 ± 0.007
3.0	0.616 ± 0.009	0.574 ± 0.021	0.605 ± 0.005	0.591 ± 0.013	0.598 ± 0.013
5.0	0.563 ± 0.019	0.538 ± 0.007	0.605 ± 0.004	0.572 ± 0.005	0.569 ± 0.011
6.0	0.503 ± 0.009	0.468 ± 0.019	0.583 ± 0.003	0.585 ± 0.004	0.486 ± 0.014
8.0	0.449 ± 0.011	0.460 ± 0.019	0.562 ± 0.017	0.571 ± 0.009	0.455 ± 0.015
10.0	0.444 ± 0.005	0.450 ± 0.017	0.575 ± 0.016	0.576 ± 0.009	0.447 ± 0.012

Table II
Values of $D_{Na^+}/D_{Na^+}^\circ$ for Aqueous NaCl Solutions Containing Sodium Poly(styrenecarboxylate)

X	0.0005 N	0.0010 N	0.0050 N	0.0100 N	av
0.1	0.944 ± 0.002	0.949 ± 0.005	0.946 ± 0.004	0.943 ± 0.007	0.945 ± 0.004
0.5	0.851 ± 0.015	0.857 ± 0.001	0.848 ± 0.011	0.854 ± 0.002	0.853 ± 0.009
1.0	0.742 ± 0.024	0.742 ± 0.011	0.749 ± 0.031	0.750 ± 0.019	0.746 ± 0.022
2.0	0.725 ± 0.018	0.726 ± 0.025	0.732 ± 0.005	0.731 ± 0.009	0.729 ± 0.016
3.0	0.644 ± 0.008	0.649 ± 0.024	0.643 ± 0.002	0.653 ± 0.026	0.647 ± 0.018
5.0	0.601 ± 0.002	0.601 ± 0.002	0.613 ± 0.013	0.598 ± 0.017	0.603 ± 0.011
6.0	0.524 ± 0.031	0.528 ± 0.001	0.597 ± 0.002	0.596 ± 0.012	0.526 ± 0.021
8.0	0.491 ± 0.006	0.519 ± 0.029	0.538 ± 0.002	0.569 ± 0.002	0.505 ± 0.020
10.0	0.469 ± 0.003	0.485 ± 0.002	0.513 ± 0.023	0.512 ± 0.011	0.477 ± 0.002

as will be discussed below. Also, counterion activity coefficient and osmotic coefficient curves in salt-free polyelectrolyte solutions show the same trend with the shallow minima in approximately the same concentration range.[21] The maximum counterion–polyion interaction occurs, of course, at the minimum value of the diffusion ratio. The observed increase in $D_{Na^+}/D_{Na^+}^\circ$ as the concentration is increased from the minimum diffusion value has been attributed[18,22] to the polyion attracting more water molecules with increasing concentration and therefore attracting fewer counterions, making the counterions more mobile. This observation could also be due to the overlapping of ionic atmospheres of different polyions as their concentration increases. The increase in $D_{Na^+}/D_{Na^+}^\circ$ as the solution is diluted from the minimum is found principally for the carboxylate polyelectrolytes, polyanions in which two adjacent groups might bind at Na^+ ion.[23] With chain expansion occurring on extreme dilution, 10^{-4} N, perhaps this binding is loosened slightly to increase the Na^+ ion mobility, and/or perhaps an increase in the size of Debye–Hückel atmosphere causes the increase in Na^+ ion mobility.

According to the Manning theory, $D_{Na^+}/D_{Na^+}^\circ$ in salt-free polyelectrolyte solutions depends on the nature of the polyelectrolyte only through its charge density and for $\xi > 1$

$$D_{Na^+}/D_{Na^+}^\circ = 0.866\xi^{-1} \tag{1}$$

While the Manning theory assumes zero mobility for condensed ions, the Yoshida theory[24] assumes that the condensed ions are able to move parallel to the axis of the polyion, taking into account the mobility of these condensed ions to be equal to one-third that of the free ions in solutions. For $\xi > 1$ the Yoshida equation in salt-free polyelectrolyte solutions is

$$D_{Na^+}/D_{Na^+}^\circ = (1/3)(1 + 1.300\xi^{-1}) \tag{2}$$

From eq 1 and 2, for a polyelectrolyte with $\xi = 2.6$, the average value for the four polyelectrolytes used, in salt-free solutions, the Manning theory gives $D_{Na^+}/D_{Na^+}^\circ = 0.33$ and the Yoshida theory gives $D_{Na^+}/D_{Na^+}^\circ = 0.50$. Both theoretical values are independent of concentration. The experimental findings show $D_{Na^+}/D_{Na^+}^\circ$ to be fairly independent of concentration in the range $5 \times 10^{-3} < N_p < 5 \times 10^{-2}$. This is the same concentration range previously reported for constant Na^+ ion diffusion ratios in salt-free solutions of NaPA of varying charge density.[1]

It is known that the sodium ion binds primarily by ionic atmosphere interactions to sulfonate polyelectrolytes[25–27] and thus the Na^+ ion would have freer mobility to move parallel to the axes of the polyion. The ions having smaller crystallographic radii like sodium, on the other hand, are known to bind more tightly to carboxylate polyelectrolytes[27–29] and should have negligible mobility along the axis of the polyion. Therefore, the minimum D_{Na^+} value for sulfonate polyion solutions should be expected to agree better with the Yoshida predicted value and the carboxylate polyions would be expected to give better agreement with the Manning value. It has been suggested that the theories might best be compared to the experimental minimum values.[18] Compared to the minimum $D_{Na}{}^+/D_{Na^+}^\circ$ values in Figure 1, the Manning value of 0.33 underestimates the mobility of Na^+ ions in the presence of both sulfonate and carboxylate polyions but does so to a much lesser extent for the carboxylate polyions. The Yoshida value of 0.50 overestimates the mobility of Na^+ ions in the presence of carboxylate polyions but still underestimates the value for sulfonate polyions.

Here, it is worthwhile to indicate that the diffusion results show that the long-range interactions depend on the nature of the pendant group in salt-free polyelectrolyte solutions. The minimum $D_{Na^+}/D_{Na^+}^\circ$ values are in the order NaPA < NaPSC < NaPVS ≈ NaPSS, indicating that the Na^+ ions interact with the carboxyl group to a much greater extent than with the sulfonate group, a fact that is well established. The phenyl group of NaPSC slightly decreases the effectiveness of its carboxyl group to bind Na^+ ion, when compared to NaPA. One can introduce a hydrophobic interaction argument here. More will be said of salt-free solutions later in this paper.

The experimental values of $D_{Na^+}/D_{Na^+}^\circ$ for aqueous NaCl solutions of NaPA ($\xi = 2.7$), NaPSC ($\xi = 2.6$), NaPVS ($\xi = 2.5$), and NaPSS ($\xi = 2.6$) are listed in Tables I–IV, respectively. These diffusion ratios were determined with the NaCl normality N_s held constant while varying the polyelectrolyte normality N_p, such that $X = N_p/N_s$ was $0.1 < X < 10$.

To determine whether condensed Na^+ ions contributed to the measured values of D_{Na^+}, tracer amounts of radio-

Table III
Values of $D_{Na^+}/D_{Na^+}{}^\circ$ for Aqueous NaCl Solutions Containing Sodium Poly(vinylsulfonate)

X	0.0005 N	0.0010 N	0.0050 N	0.0100 N	av
0.1	0.963 ± 0.029	0.962 ± 0.002	0.965 ± 0.018	0.973 ± 0.005	0.966 ± 0.017
0.5	0.909 ± 0.023	0.899 ± 0.004	0.904 ± 0.006	0.904 ± 0.003	0.904 ± 0.012
1.0	0.872 ± 0.004	0.858 ± 0.002	0.869 ± 0.005	0.867 ± 0.006	0.867 ± 0.004
2.0	0.808 ± 0.016	0.807 ± 0.028	0.837 ± 0.003	0.829 ± 0.010	0.808 ± 0.022
3.0	0.725 ± 0.021	0.727 ± 0.008	0.829 ± 0.006	0.811 ± 0.001	0.726 ± 0.015
5.0	0.689 ± 0.006	0.706 ± 0.012	0.793 ± 0.012	0.801 ± 0.004	0.698 ± 0.009
6.0	0.676 ± 0.017	0.684 ± 0.005	0.711 ± 0.011	0.717 ± 0.002	0.680 ± 0.012
8.0	0.659 ± 0.016	0.683 ± 0.002	0.718 ± 0.004	0.702 ± 0.001	0.671 ± 0.011
10.0	0.662 ± 0.008	0.668 ± 0.017	0.703 ± 0.015	0.708 ± 0.014	0.665 ± 0.013

Table IV
Values of $D_{Na^+}/D_{Na^+}{}^\circ$ for Aqueous NaCl Solutions Containing Sodium Poly(styrenesulfonate)

X	0.0005 N	0.0010 N	0.0025 N	0.0050 N	0.0100 N	av
0.1	0.948 ± 0.008	0.950 ± 0.011	0.957 ± 0.005	0.967 ± 0.006	0.965 ± 0.009	0.957 ± 0.008
0.5	0.925 ± 0.014	0.919 ± 0.003	0.926 ± 0.005	0.918 ± 0.003	0.919 ± 0.007	0.921 ± 0.008
1.0	0.846 ± 0.006	0.840 ± 0.003	0.859 ± 0.005	0.879 ± 0.004	0.887 ± 0.005	0.862 ± 0.005
2.0	0.767 ± 0.004	0.763 ± 0.007	0.762 ± 0.011	0.875 ± 0.003	0.865 ± 0.000	0.765 ± 0.006
3.0	0.709 ± 0.005	0.705 ± 0.001	0.742 ± 0.011	0.819 ± 0.003	0.829 ± 0.003	0.707 ± 0.004
5.0	0.689 ± 0.004	0.698 ± 0.004	0.718 ± 0.005	0.782 ± 0.001	0.771 ± 0.002	0.694 ± 0.004
6.0	0.649 ± 0.005	0.685 ± 0.007	0.695 ± 0.011	0.696 ± 0.001	0.761 ± 0.001	0.667 ± 0.006
8.0	0.676 ± 0.003	0.673 ± 0.001	0.714 ± 0.011	0.706 ± 0.016	0.739 ± 0.001	0.674 ± 0.002
10.0	0.649 ± 0.004	0.655 ± 0.001	0.665 ± 0.005	0.697 ± 0.008	0.715 ± 0.001	0.652 ± 0.003

active $^{45}Ca^{2+}$ were added to NaCl solutions of each polyelectrolyte under study. From the tracer amounts used, it was known that all the $^{45}Ca^{2+}$ ions were condensed and hence $D_{Ca^{2+}} = D_p$, the polyelectrolyte diffusion coefficient. For each polyelectrolyte, fairly constant values of D_p were obtained at $N_p = 5.0 \times 10^{-3}$ N for X = 1.0, 5.0, and 10.0, $D_p = (0.051 \pm 0.003) \times 10^{-5}$ for NaPA, $D_p = (0.057 \pm 0.003) \times 10^{-5}$ for NaPSC, $D_p = (0.088 \pm 0.003) \times 10^{-5}$ for NaPVS, and $D_p = (0.086 \pm 0.004) \times 10^{-5}$ for NaPSS, all in the units of cm^2/s. Using these values and assuming that the fraction of condensed Na$^+$ ions is $(1 - \xi^{-1})$, the observed diffusion coefficient D_{Na^+} is

$$D_{Na^+}{}^{obsd} = D_p(1 - \xi^{-1})N_p/(N_p + N_s) + D_{Na^+}{}^{u} = D_p(1 - \xi^{-1})/(1 + X^{-1}) + D_{Na^+}{}^{u} \quad (3)$$

where the first term represents the contribution to $D_{Na^+}{}^{obsd}$ of the condensed Na$^+$ ions and $D_{Na^+}{}^{u}$ is the uncondensed Na$^+$ ion contribution. At low X values, D_p is much less than D_{Na^+} and there is hardly any correction required, but at high X values, where the polyelectrolyte is in excess, up to a 4% correction was noted. The results presented in Tables I–IV are the values of $D_{Na^+}/D_{Na^+}{}^\circ$ corrected for the contribution of polyelectrolyte diffusion to $D_{Na^+}{}^{u}$.

The Manning theory for polyelectrolytes having $\xi > 1$ with Na$^+$ counterions gives[4]

$$D_{Na^+}/D_{Na^+}{}^\circ = f_{Na^+}(1 - A/3) \quad (4)$$

where the condensation term f_{Na^+} is given by $(\xi^{-1}X + 1)/(X + 1)$ and the interaction term A can be written

$$A = \sum_{\substack{m=-\infty \\ (m,n)\neq(0,0)}}^{\infty} \sum_{n=-\infty}^{\infty} [\pi(m^2 + n^2) + 1 + 2\xi X^{-1}]^{-2} \quad (5)$$

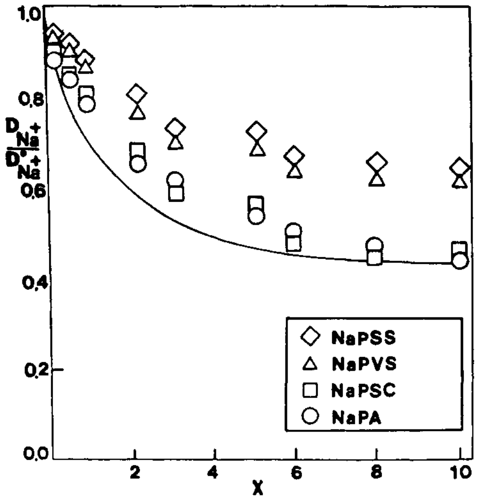

Figure 2. $D_{Na^+}/D_{Na^+}{}^\circ$ dependence on the X in aqueous NaCl solutions.

Note that for a given ξ value, $D_{Na^+}/D_{Na^+}{}^\circ$ ratios depend only on X and are independent of salt concentration. From the results in Tables I–IV, it can be seen that for lower salt concentrations, i.e., 5.0×10^{-4} and 1.0×10^{-3} N NaCl, at a given X value, the $D_{Na^+}/D_{Na^+}{}^\circ$ ratios are fairly independent of salt concentration, just as is predicted by the Manning theory. At slightly higher salt concentrations, i.e., 5.0×10^{-3} and 1.0×10^{-2} N NaCl, however, very slightly higher diffusion ratio values were found when $X > 5$ for the carboxylate polyelectrolytes, NaPA and NaPSC, and when $X > 3$ for sulfonate polyelectrolytes, NaPVS and NaPSS. The increase of $D_{Na^+}/D_{Na^+}{}^\circ$ with increasing simple salt concentration at high X values is probably due to increased polyion–polyion interactions, which may cause slight weakening of the counterion–polyion interactions. The average of $D_{Na^+}/D_{Na^+}{}^\circ$ values, over the concentration range of NaCl where the Na$^+$ ion diffusion is independent of simple salt concentration, which perhaps is the range where the Manning model is best approximated, is presented in the last columns in Tables I–IV and in Figure 2. For comparison the theoretical line for ξ = 2.6, the average charge density parameter for the four polyelectrolytes used, is also displayed. The dominant feature in Figure 2 is the dependence of Na$^+$ ion diffusion on the nature of the pendant group of polyelectrolyte in salt solutions, just as was observed for salt-free polyelectrolyte solutions. The lower curves for two carboxylate polyelectrolyes are close together, as are the upper two curves for the sulfonate polyelectrolytes. From these results, it is apparent that in NaCl solutions the Na$^+$ ions interact with polyelectrolytes via long-range electrostatic forces in the order NaPA ≈ NaPSC > NaPVS ≈ NaPSS. The difference between carboxylates and sulfonate polyelectrolytes is pronounced at high X values, where polyelectrolyte is in excess. It appears that the introduction of a phenyl group to the

Table V
Slope and Intercept Obtained from Plots of Eq 6

	intercept	slope	$(D_{Na^+}/D_{Na^+}^{\circ})_{min}$
NaPA	1.15 ± 0.03	0.38 ± 0.02	0.38
NaPSC	1.14 ± 0.04	0.43 ± 0.02	0.45
NaPVS	1.06 ± 0.02	0.62 ± 0.03	0.63
NaPSS	1.04 ± 0.02	0.62 ± 0.03	0.62

chain in salt-containing solutions does not affect the counterion–polyion long-range interactions.

It is of interest to compare the value of $D_{Na^+}/D_{Na^+}^{\circ}$ extrapolated to infinite dilution of NaCl for each polyelectrolyte, i.e., in the limit of X going to infinity, with the values obtained for the minimum $D_{Na^+}/D_{Na^+}^{\circ}$ values in salt-free solutions, which are given in Table V. Extrapolated least-squares plots of $D_{Na^+}/D_{Na^+}^{\circ}$ vs. X^{-1} to $X^{-1} = 0$ using the points at $X = 6.0$, 8.0, and 10.0 for each polyelectrolyte give 0.38 for NaPA, 0.41 for NaPSC, 0.64 for NaPVS, and 0.64 for NaPSS. It is gratifying that these extrapolated values agree excellently with the respective minimum $D_{Na^+}/D_{Na^+}^{\circ}$ values in salt-free solutions. Similar behavior has been reported for counterion diffusion coefficients[30,31] and activity coefficients[32] as a function of X for salt-containing solutions of polyelectrolytes.

From Figure 2 it can be seen that the experimental $D_{Na^+}/D_{Na^+}^{\circ}$ values for both carboxylate and sulfonate polyelectrolytes are higher than predicted by the Manning theory, indicating that the theory overestimates the counterion–polyion interactions. The theory ignores any effect due to the nature of the polyion charge groups, which experimentally are shown to influence the long-range interactions.

An empirical additivity rule based on counterion activities determined in salt-free polyelectrolyte solutions and in polyelectrolyte-free salt solutions has been established for polyelectrolytes having a large range of charge densities.[2,33] Recently we showed[1] that for NaPA/HPA copolymers having $\xi > \xi_c$, the additivity law for Na^+ ion diffusion is valid. It is worthwhile to test whether this additivity rule is valid here. The additivity rule for Na^+ ion diffusion could be written as

$$(D_{Na^+}/D_{Na^+}^{\circ})_X = X(X+1)^{-1}(D_{Na^+}/D_{Na^+}^{\circ})_p + (X+1)^{-1}(D_{Na^+}^{\circ}/D_{Na^+}^{\circ})_X \tag{6}$$

where the first term on the right-hand side is the salt-free contribution and the second term is the simple salt contribution for any given X value, denoted by the subscripts. Equation 6 plots linearly for $(X + 1)(D_{Na^+}/D_{Na^+}^{\circ})_X$ vs. X with intercept of unity and slope of $(D_{Na^+}/D_{Na^+}^{\circ})_p$, if the additivity law is valid for Na^+ ion diffusion in polyelectrolyte solutions. Using the average $(D_{Na^+}/D_{Na^+}^{\circ})_X$ from Tables I–IV and using eq 6, $(X + 1)(D_{Na^+}/D_{Na^+}^{\circ})$ was plotted against X in Figure 3 for each polyelectrolyte. The ordinate intercepts of resulting lines, listed in Table V, are close to unity within the experimental error, demonstrating the validity of the additivity rule. It was of interest to compare the slopes of these lines, $(D_{Na^+}/D_{Na^+}^{\circ})_p$, with the minimum values of $D_{Na^+}/D_{Na^+}^{\circ}$ obtained in salt-free polyelectrolyte solutions from Figure 1. The excellent agreement between these two sets of results, listed in Table V, further substantiates the additivity rule, and suggests that properties based on long-range Coulombic interactions can be determined for polyelectrolyte in salt-containing solutions, by appropriate measurements in salt-free solutions.

In aqueous solutions of polyelectrolytes with Na^+ as the counterions, rN_p equivalents of the total $(N_p + N_s)$ equivalents of Na^+ ions are condensed on the polyion and the fraction of condensed Na^+ ions $f_{Na^+}{}^c$ ions in solution is[30,34]

$$f_{Na^+}{}^c = rN_p/(N_p + N_s) = rX/(1 + X) \tag{7}$$

where r is the fraction of condensed or bound Na^+ ions originally on the polyelectrolyte and $(1 - r)$ is the charge fraction of the polyelectrolyte. In a NaCl-containing polyelectrolyte solution, the Manning theory gives

$$f_{Na^+}{}^c = 1 - (D_{Na^+}/D_{Na^+}^{\circ})/(D_{Cl^-}/D_{Cl^-}^{\circ}) \tag{8}$$

Assuming that all co-ion–polyion interactions, if at all present, are negligible, i.e., $D_{Cl^-}/D_{Cl}^{\circ} = 1$, in eq 8, then combining eq 7 and 8 and using the experimental values of $D_{Na^+}/D_{Na^+}^{\circ}$ result in a simple linear relation between $f_{Na^+}{}^c(1 + X)$ and X, as shown in Figure 4. Thus r is constant over the whole X range and therefore, the polyelectrolyte charge fraction $(1 - r)$ can be calculated from the Na^+ ion diffusion measurements. Furthermore, the linearity is consistent with the result of the condensation model that the polyelectrolyte charge fraction is a constant value and independent of the salt concentration. Similar results have been obtained for other polyelectrolytes[34] and from ^{23}Na NMR measurements in salt-containing DNA solutions.[35] In accord with eq 7, the intercepts in Figure

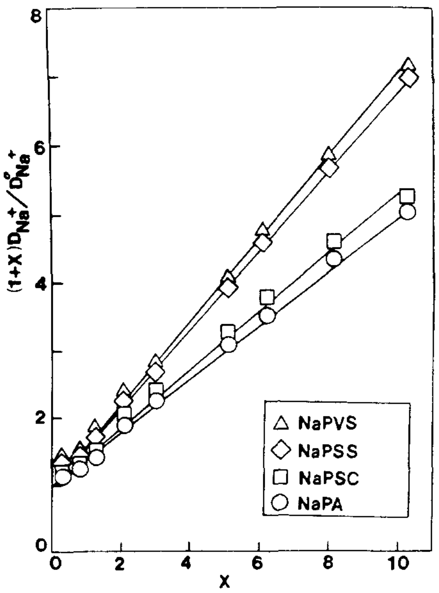

Figure 3. $(D_{Na^+}/D_{Na^+}^{\circ})(X + 1)$ vs. X.

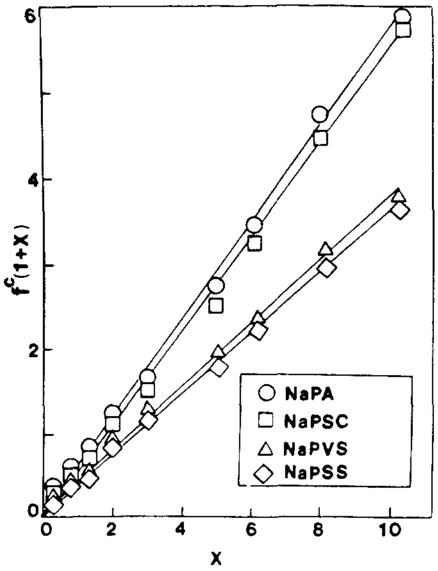

Figure 4. $f^c(1 + X)$ vs. X.

Table VI
Slope and Intercept Obtained from Plots of Eq 7

	intercept	slope	(1 − r)	$(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_{\min}$
NaPA	−0.15 ± 0.09	0.62 ± 0.03	0.38 ± 0.02	0.38
NaPSC	−0.14 ± 0.09	0.58 ± 0.03	0.42 ± 0.02	0.45
NaPVS	−0.05 ± 0.04	0.38 ± 0.03	0.62 ± 0.05	0.63
NaPSS	−0.03 ± 0.03	0.39 ± 0.02	0.61 ± 0.03	0.62

4, listed in Table VI, are close to the origin within experimental error and the slopes are 0.62 ± 0.03 for NaPA, 0.58 ± 0.03 for NaPSC, 0.38 ± 0.03 for NaPVS, and 0.39 ± 0.02 for NaPSS. For carboxylate polyelectrolytes, the resulting charge fractions $(1 - r)$ of 0.38 and 0.42 for NaPA and NaPSC, respectively, compare excellently with the theoretical values of ξ^{-1} for these polyelectrolytes. This gives some validity to calculate a charge fraction from eq 7, which states that condensation is the dominant interaction. For the sulfonate polyelectrolytes, however, the calculated charge fractions of 0.62 and 0.61, for NaPVS and NaPSS, respectively, deviate from the predicted theoretical value of ξ^{-1}. It appears that the fraction of condensed or bound $\mathrm{Na^+}$ ions originally on the polyelectrolyte, and therefore the polyelectrolyte charge fraction, depends on the nature of the charge groups on the polyion.

It is interesting that the additivity rule (eq 6) and the charge fraction equation (eq 7) are of the same form, with $(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_{\mathrm{p}}$ identified with $(1 - r)$. When plotted as $(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_X(1 + X)$ vs. X, both eq 6 and 7 gave straight lines for $\xi > 1$, with the phenomenological parameters $(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_{\mathrm{p}}$ and $(1 - r)$ independent of N_{s}. Both phenomenological parameters are close in value for each polyelectrolyte studied here. Equations 6 and 7 stem from the same concept that $\mathrm{Na^+}$ ions are either condensed onto the polyion and do not contribute to the measured $D_{\mathrm{Na^+}}$ or that the $\mathrm{Na^+}$ ions are free so as to *not* interact with the polyion and contribute to the measured $D_{\mathrm{Na^+}}$. The interpretation of Wall[20] for $(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_{\mathrm{p}}$ as the degree of dissociation of the polyelectrolyte is consistent with the values obtained for $(1 - r)$ from eq 7. The theoretical equation of Manning, eq 4, can be cast in the same form as eq 6 and 7 if the Debye–Hückel interaction term vanishes. Then, the theoretical value for the fraction of $\mathrm{Na^+}$ ions dissociated from the polyion ξ^{-1} is identified with $(D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ})_{\mathrm{p}}$ of eq 6 and $(1 - r)$ of eq 7. It becomes clearer then as to why eq 6 and 7 should appear to be valid. For high charge density polyelectrolytes, i.e., those used in the present study, the contribution of the condensation term to $D_{\mathrm{Na^+}}/D_{\mathrm{Na^+}}{}^{\circ}$ in eq 4 is much greater than that of the interaction term A.

Registry No. $\mathrm{Na^+}$, 17341-25-2; sodium polyacrylate (homopolymer), 9003-04-7; sodium poly(*p*-styrenecarboxylate) (homopolymer), 92078-72-3; poly(sodiumvinylsulfonate) (homopolymer), 9002-97-5; sodium poly(styrenesulfonate) homopolymer, 9080-79-9.

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Notes

Monte Carlo Calculation of the Friction Coefficient and Viscosity Number of Wormlike Star Molecules. 2

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Received January 18, 1984

In a recent article[1] we reported preliminary results from Monte Carlo calculations of the effects of star branching on the sedimentation and viscosity of dilute solutions of polymers. Here we extend these calculations to larger model molecules and larger ensembles with smaller statistical errors. We have also included an ensemble with excluded volume, corresponding to solutions in good solvents. In general, the new results confirm the trends seen in the earlier ones; most notably, the viscosity ratio, g', is consistently less than the ratio of root-mean-square radii, $g^{1/2}$.

The calculations were carried out on ensembles of rigid-body chain models, both with and without preaveraging of the hydrodynamic interactions. The calculations on models without excluded volume were carried out as before, except that 100 chains each of 49 beads were generated in each case instead of 50 chains of 25 beads. Each such run consumed about 40 min of processor time on the VAX 11-780. In addition, we generated models in which all approaches of beads closer than twice the hydrodynamic

0024-9297/84/2217-2441$01.50/0