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Sodium Ion Diffusion Coefficients in Aqueous Salt-Free Polyelectrolyte Solutions

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ABSTRACT: Counterion tracer diffusion coefficients of the sodium ion in aqueous salt-free solutions of sodium alginate, sodium ι-carrageenan, and sodium dextran sulfate are found to be dependent on polyion concentration over the range (3×10^{-5})–(8×10^{-2}) equiv/L. The diffusion coefficients obtained are fairly constant over a limited range varying in polyion concentration from (1×10^{-2})–(1×10^{-3}) equiv/L. In this flat region a minimum value for the diffusion coefficient is observed, which is used to correlate with the Manning and Yoshida theoretical predictions.

Studies pertaining to the diffusion of counterions in aqueous salt-free polyelectrolyte solutions are important in the understanding of small ion–polyion and polyion–polyion interactions in aqueous solutions. However, few such studies have been done with polyelectrolytes other than poly(styrene sulfonate) (PSS) and polyacrylate (PA).[1-4] The purpose of this counterion tracer diffusion study was to investigate how well modern polyelectrolyte theories predict the behavior of other polyelectrolytes, namely the sodium salts of dextran sulfate, ι-carrageenan, and alginate in aqueous salt-free solutions, and to determine the dependence of the sodium ion diffusion coefficient on the polyion concentration of these ionic polysaccharides.

The Manning theory[5-7] has proven most useful in describing the transport and equilibrium properties of polyelectrolyte solutions. Comparison of the theoretical diffusion coefficients of counterions in polyelectrolyte solutions containing simple salt, for example, has shown good agreement with experiment at low concentrations.[8-12] This is expected since the Manning theory is a limiting law and strictly can only be applied at the limit of infinite dilution.

In the salt-free limit for monovalent counterions, the Manning theory states that the ratio of the diffusion coefficient of the counterion i in the presence of the polyion D_i to the diffusion coefficient of the counterion in water D_i^0 is a constant and is given by

$$D_i/D_i^0 = 0.866/\xi \qquad \text{for } \xi > 1 \tag{1}$$

$$D_i/D_i^0 = 1 - (0.55\xi^2)/(\xi + \pi) \qquad \text{for } \xi < 1 \tag{2}$$

where ξ is a linear charge density parameter

$$\xi = e^2/\epsilon kTb \tag{3}$$

where e is the protonic charge, ϵ is the dielectric constant of the solvent, T is the temperature, b is the average distance between charge groups on the polyelectrolyte, and k is the Boltzman constant. The theory predicts that condensation occurs in solution if ξ_c is less then ξ, where ξ_c is the critical charge density parameter

$$\xi_c = |z_i z_p|^{-1} \tag{4}$$

where z_i is the valence of the counterion and z_p is the valence of the polyion. Condensation continues until the effective value of ξ is reduced to an effective ξ_c; at this point the uncondensed mobile ions in solution interact with polyion via Debye–Hückel forces. The theory thus predicts that when $\xi > 1$ for a system containing only monovalent counterions the fraction of undissociated ions is $(1 - \xi^{-1})$ and the fraction ξ^{-1} makes up the diffuse ion atmosphere. The fraction of condensed ions in the theory is assumed to have negligible mobility along the polyion chain. The site bound ions are those which lose their hydration shells and bind close to the polyion bringing about a strong decrease in the electrostatic field in the space surrounding the charged site and the ion. These ions have negligible mobility for the most part because of the strong electrostatic interactions. Ionic atmosphere bound ions, on the other hand, retain most of their hydration shell and bind at larger distances from the polyion. These ions are less tightly held than the site binding ions and are free to move parallel to the axis of the polyion.

A phenomenological approach to diffusion in salt-free polyelectrolyte solutions has been developed,[13] and Yoshida has developed a molecular theory.[14] Yoshida uses many of the assumptions of the Manning model.[14] Like the Manning theory, Yoshida predicts that the diffusion coefficients of the counterion in the presence of a polyion in salt-free aqueous solutions should be constant and a function of the linear charge density parameter only. The Yoshida equation is

$$D_i/D_i^0 = (1 + 1.300/\xi)/3 \qquad \text{for } \xi > 1 \tag{5}$$

However, Yoshida's theory differs from Manning's theory in that he assumes the condensed ions are able to move parallel to the axis of the polyion, taking into account the mobility of these condensed ions by assuming that it is equal to one-third that of the free ions in solution. Such an assumption seems more reasonable than Manning's assumption of negligible condensed ion mobility especially in light of recent evidence from NMR studies performed by Leyte et al.[15,16] Since both of these theories predict that there is no concentration dependence on the polyion in the salt-free case, it is difficult to compare literature values,[1,2]

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which show a definite concentration dependence, to the theoretical values, which are independent of polyelectrolyte concentration. It has been suggested, however, that the theories might best be compared to a flat region, where the diffusion coefficients of the counterions show the least variation with the concentration of the polyelectrolyte.[17] At the center of these flat regions, minima have been observed for the diffusion coefficients of the sodium ion in NaPSS, where $D_{Na^+}/D_{Na^+}{}^0 = 0.49$ and 0.39, and the silver ion in AgPSS, where $D_{Ag^+}/D_{Ag^+}{}^0 = 0.35$.[1,2] Since the minimum appears at the center of the flat region, it is believed that this is the value which should be compared to the theoretical values. According to Manning, $D_{Na^+}/D_{Na^+}{}^0 = 0.30$ for PSS ($\xi = 2.85$), while according to Yoshida $D_{Na^+}/D_{Na^+}{}^0 = 0.49$; both values are constant. Recalling that the Yoshida value accounts for the mobility of the condensed ions while Manning's value does not, these experimental values obtained are in good agreement with what might be predicted. The sodium ion is known to bind primarily by ionic atmosphere binding to PSS,[18-21] and thus would have freer mobility to move parallel to the axis of the polyion; so the value for the sodium ion should show better agreement with the Yoshida predicted value. Large ions like silver are known to bind more closely to PSS[21] and should show negligible mobility along the axis of the polyion; so the silver ion would be expected to give better agreement with the Manning value. This could be explained by site bonding or by the partial formation of real covalent complexes as previously suggested.[1] Since the observed value for the silver ion is somewhat higher than that predicted by Manning, the theory underestimates the contribution of the ionic atmosphere binding to the counterion diffusion. Counterion binding in the polyelectrolyte theory has recently been reviewed by Manning[22] in which different degrees of binding are discussed.

Here we report counterion tracer diffusion coefficients of the sodium ion in aqueous salt-free solutions of sodium alginate, sodium ι-carrageenan, and sodium dextran sulfate at 25 °C. The results are compared to those of the Manning and the Yoshida theories, where the counterion diffusion coefficient in water at 25 °C is dependent only in the linear charge density parameter.

Experimental Section

The sodium ι-carrageenan used in this study was supplied by Marine Colloids Inc. The sodium dextran sulfate used in this study was supplied by Pharmacia Fine Chemicals Inc. The sodium alginate used in this study was supplied by the Kelco Co. These ionic polysaccharides were described previously.[8-10] Radioactive ^{22}NaCl was supplied by the New England Nuclear Company.

The open-end capillary method originally introduced by Anderson and Saddington[23] was employed without stirring to determine the diffusion coefficients. This method has been described previously.[10] The following expression was used to determine the diffusion coefficients[23]

$$C/C^0 = (8/\pi^2)\sum_{n=0}^{\infty}[\exp(-(2n+1)^2\pi^2Dt/4L^2)]/(2n+1)^2 \qquad (6)$$

where $D = D_{Na^+}$, the sodium ion self-diffusion coefficient for the labeled species, t is the time allowed for diffusion, L is the capillary length, 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 taking place. Previous studies used an approximate solution of eq 6[24]

$$D_{Na^+} = (\pi/4)(1 - C/C^0)^2(L^2/t) \qquad (7)$$

However, because of the approximation used in deriving eq 7, the lower the ratio of C/C^0 used the higher is the error in D_{Na^+}. Values of C/C^0 lower than 0.5 could not be used to determine D because the error would have been significant. However, such low values of C/C^0 would help eliminate error due to experimental manipulation. For this reason the experimental values were determined using eq 6, which was solved by successive approximations with the aid of a computer. This allowed for more accurate determinations of D_{Na^+} and minimized the error due to experimental manipulation.

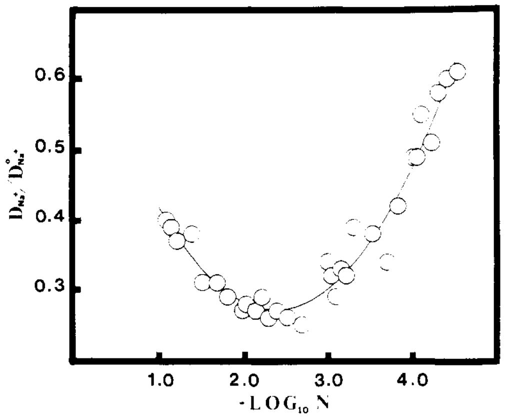

Figure 1. The dependence of the sodium ion self-diffusion coefficient ratios on the equivalent concentration of sodium dextan sulfate in water at 25 °C.

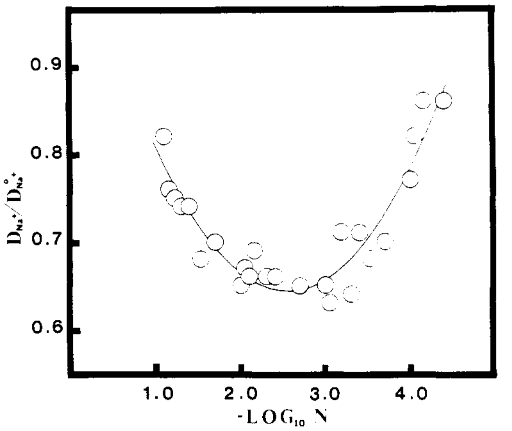

Figure 2. The dependence of the sodium ion self-diffusion coefficient ratios on the equivalent concentration of sodium ι-carrageenan in water at 25 °C.

Results and Discussion

In this study the ionic polysaccharides ι-carrageenan ($\xi = 1.66$) and dextran sulfate ($\xi = 2.85$), which contain sulfate groups, and alginate ($\xi = 1.43$), which contains carboxyl groups, were used. These polymers were used since they are stiffer than the synthetic polyelectrolytes used in previous studies; therefore, they are thought to better represent the rodlike model used by Manning and Yoshida.

The polyelectrolyte concentration N studied ranged from 0.08–(3×10^{-5}) equiv/L. Concentrations above 0.05 equiv/L were difficult to work with because the solutions were generally very viscous. No values were obtained for concentrations below 3×10^{-5} equiv/L because at such low concentrations the error associated with preparing the solutions becomes substantial. The results obtained are shown in Figures 1, 2, and 3 for dextran sulfate, ι-carrageenan, and alginate, respectively, and are listed in Table I. The ratio of the diffusion coefficient in the presence of polymer to that of the diffusion coefficient in water alone, $D_{Na^+}/D_{Na^+}{}^0$, is plotted against the common log to the base ten of the polyelectrolyte concentration. The curves drawn in the figures are the best fit second degree lines through all of the points. For the sodium ion in water at 25 °C, $D_{Na^+}{}^0 = 1.33 \times 10^{-5}$ cm^2 s^{-1}. The values on these

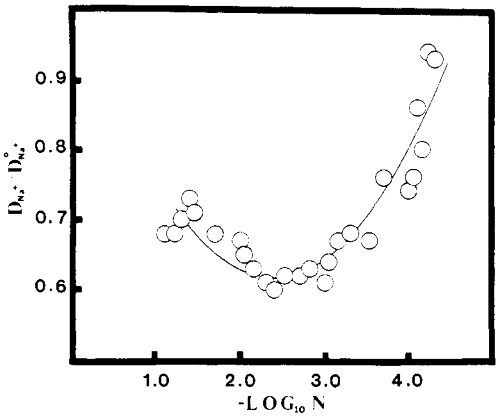

Figure 3. The dependence of the sodium ion self-diffusion coefficient ratios on the equivalent concentration of sodium alginate in water at 25 °C.

Table I
Sodium Ion Self-Diffusion Coefficients in Aqueous Solutions at 25 °C

$N \times 10^3$, equiv/L	$D_{Na^+} \times 10^5$, cm^2 s^{-1}	$N \times 10^3$, equiv/L	$D_{Na^+} \times 10^5$, cm^2 s^{-1}
Sodium Dextran Sulfate			
0.030	0.81 ± 0.09	2.00	0.33 ± 0.08
0.040	0.80 ± 0.09	3.00	0.35 ± 0.06
0.050	0.77 ± 0.09	4.00	0.36 ± 0.05
0.060	0.68 ± 0.07	5.00	0.35 ± 0.03
0.080	0.73 ± 0.06	6.00	0.39 ± 0.07
0.090	0.65 ± 0.07	7.00	0.36 ± 0.06
0.100	0.65 ± 0.08	9.00	0.37 ± 0.06
0.150	0.56 ± 0.03	10.0	0.36 ± 0.05
0.200	0.45 ± 0.08	15.0	0.39 ± 0.03
0.300	0.51 ± 0.05	20.0	0.41 ± 0.03
0.500	0.52 ± 0.09	30.0	0.41 ± 0.08
0.600	0.43 ± 0.08	40.0	0.51 ± 0.03
0.700	0.44 ± 0.05	60.0	0.49 ± 0.02
0.800	0.39 ± 0.08	70.0	0.52 ± 0.06
0.900	0.43 ± 0.05	80.0	0.53 ± 0.05
1.00	0.45 ± 0.06		
Sodium ι-Carrageenan			
0.040	1.14 ± 0.08	5.00	0.88 ± 0.06
0.070	1.14 ± 0.08	7.00	0.92 ± 0.06
0.090	1.09 ± 0.08	8.00	0.88 ± 0.04
0.100	1.02 ± 0.07	9.00	0.89 ± 0.06
0.200	0.93 ± 0.07	10.0	0.86 ± 0.09
0.300	0.90 ± 0.08	20.0	0.93 ± 0.08
0.400	0.94 ± 0.07	30.0	0.90 ± 0.08
0.500	0.85 ± 0.06	40.0	0.98 ± 0.08
0.650	0.94 ± 0.07	50.0	0.98 ± 0.06
0.900	0.84 ± 0.08	60.0	1.00 ± 0.07
1.00	0.86 ± 0.06	70.0	1.01 ± 0.07
2.00	0.86 ± 0.08	80.0	1.09 ± 0.06
4.00	0.88 ± 0.04		
Sodium Alginate			
0.050	1.24 ± 0.06	2.00	0.82 ± 0.06
0.060	1.06 ± 0.05	3.00	0.82 ± 0.06
0.070	1.06 ± 0.05	4.00	0.80 ± 0.05
0.080	1.14 ± 0.08	5.00	0.81 ± 0.07
0.090	1.01 ± 0.04	7.00	0.84 ± 0.05
0.100	0.98 ± 0.06	9.00	0.86 ± 0.04
0.200	1.01 ± 0.08	10.0	0.89 ± 0.04
0.300	0.89 ± 0.06	20.0	0.90 ± 0.08
0.500	0.90 ± 0.05	35.0	0.94 ± 0.07
0.700	0.89 ± 0.05	40.0	0.97 ± 0.03
0.900	0.85 ± 0.06	50.0	0.93 ± 0.06
1.00	0.81 ± 0.05	60.0	0.90 ± 0.08
1.50	0.84 ± 0.08	80.0	0.90 ± 0.03

[a] Each value is an average of at least six determinations.

curves are compared with the theoretical values.

All of the figures show a minimum similar to those reported for the sodium ion diffusion in aqueous salt-free solutions of NaPSS and for the silver ion in AgPSS.[1,2] However, the minima observed here were found to occur at somewhat lower concentrations than previously reported. For ι-carageenan and dextran sulfate, the polyelectrolytes containing sulfate groups, the minima occur at 2.8×10^{-3} and 4.2×10^{-3} equiv/L, respectively; for alginate, the polyelectrolyte containing carboxyl group, the minimum occurs at 4.1×10^{-3} equiv/L. These results show that the minima occur at about the same concentration of polyion, independent of the nature of the ionic species on the polyelectrolyte and of its linear charge density.

Previous studies, however, have shown that a dependence of the ionic species on the polyion exists in determining the type of binding which occurs upon condensation. Polysulfonates have been reported to bind preferentially through ionic atmosphere binding, while polycarboxylates have shown a greater affinity for site binding.[18,19,25] If such observations are to hold for the ionic polysaccharides used in this study, then both the dextran sulfate and ι-carrageenan would be expected to bind preferentially via the ionic atmosphere, while the alginate would show a higher degree of site binding.

As discussed in the introduction, the correlation between the values predicted from theory will be made using the values at the minima in the curves since the Manning and the Yoshida theories predict that the diffusion constant should be independent of polyelectrolyte concentration. For ι-carrageenan, the agreement is fairly good with the experimental value of $D_{Na^+}/D_{Na^+}^{0} = 0.65$ correlating better with Yoshida's value of 0.59 than with Manning's value of 0.52. That the experimental value is somewhat higher could be taken to mean that, in this case, Yoshida underestimates the mobility of the condensed counterions. The experimental value for the minimum for alginate occurs at $D_{Na^+}/D_{Na^+}^{0} = 0.62$, which is slightly closer to Manning's value of $D_{Na^+}/D_{Na^+}^{0} = 0.61$ than to Yoshida's value of $D_{Na^+}/D_{Na^+}^{0} = 0.64$. The two theoretical values are very close together and are in excellent agreement with the experimental value. For dextran sulfate, however, there appears to be a definite disagreement between the experimental value of $D_{Na^+}/D_{na^+}^{0} = 0.27$ and Yoshida's value of 0.49, and agreement is very good with Manning's value of 0.30. The quasi-salt-free values in NaCl solutions in the limit of zero simple salt concentration should be compared with the experimental salt-free values obtained at the minima of the curves. At the lowest NaCl molarities employed, $D_{Na^+}/D_{Na^+}^{0}$ level off at the values of 0.57, 0.38, 0.53, and 0.58 for NaPSS,[9] sodium dextran sulfate,[10] sodium alginate,[8] and sodium heparin,[10] respectively. It is interesting that the sodium alginate results obtained using salt-free and salt-containing solutions are in closest agreement with both the Manning and Yoshida predictions. This, of course, is not surprising since Na alginate has a low charge density where both theories are in the best accord, as is shown in Figure 4. This is also noted with the salt-free value of $D_{Na^+}/D_{Na^+}^{0} = 0.65$ for sodium carrageenan ($\xi = 1.66$) compared to the predicted values of 0.52 and 0.59 of Manning and Yoshida, respectively. However, the theoretical predicted values begin to diverge as the charge density of the polyelectrolytes increases, with the Manning theory having the lower $D_{Na^+}/D_{na^+}^{0}$ value because condensed ions are assumed *not* to move along the axis of the polyelectrolyte. For sodium dextran sulfate ($\xi = 2.85$), the minimum $D_{Na^+}/D_{Na^+}^{0}$ value in the salt-free solution of 0.27 is closer to the Manning value of 0.30 as compared to the Yoshida value of 0.49, indicating, perhaps, little, if any, motion along the polyion. This is somewhat borne out by the lower value of 0.38 for sodium dextran sulfate[10] when $D_{Na^+}/D_{Na^+}^{0}$ is extrapolated to zero salt

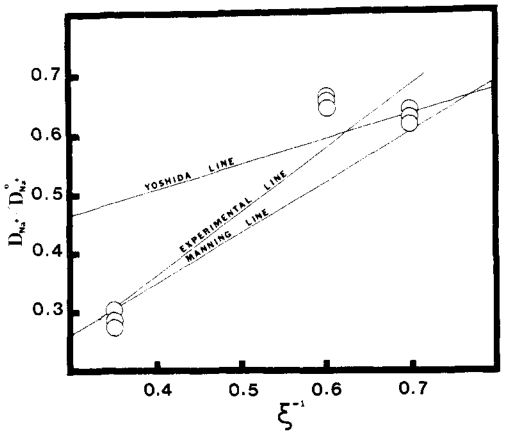

Figure 4. The dependence of $D_{Na^+}/D_{Na^+}{}^{0}$ on the linear charge density parameter of the polyelectrolyte. The experimental points correspond to $D_{Na^+}/D_{Na^+}{}^{0}$ obtained at concentrations of $-\log N$ equal to 2.0, 2.5, and 3.0 for the sodium salts of dextran sulfate, ι-carrageenan, and alginate.

concentration in NaCl solutions, as compared to values of 0.58 for sodium heparin ($\xi = 3.0$)[10] and 0.57 for sodium poly(styrene sulfonate) ($\xi = 2.65$).[9]

Figures 1, 2, and 3 show steep rises in the curves at concentrations lower than 10^{-3} equiv/L. It would be expected that Manning's values should have given better agreement in this region since the theory is a limiting law and holds strictly only in the limit of infinite dilution. However, the correlation is poor in this region. Apparently what is happening in this region is that as the solution becomes more dilute the counterions find themselves further apart from the polyions and so the interaction is decreased. Experimental studies have shown that the half-times for exchange between free and bound ions in polyelectrolyte solutions must be less than 2 s and greater then 0.03 s, while theoretical considerations place such values in the microseconds range.[26] So it is expected that the diffusion coefficient of the sodium ion should increase at lower polyion concentrations since its mobility will be less hindered by the polyion. This is further substantiated by quasithermodynamic studies, which show a similar rise in the single ion activities of Na^+, Ag^+, Zn^{2+}, Cd^{2+}, and Pb^{2+} at concentrations below 10^{-3} equiv/L of polymer for PSS solutions.[27]

Within the concentration range of $-\log N$ from 1.5–3.5, the values for the diffusion coefficients remain fairly constant. This region corresponds to the range of polymer concentrations from (3×10^{-2})–(3×10^{-4}) equiv/L. Apparently in this region the interactions between the polyion and the counterion are maximized.

At concentrations higher than 0.03 equiv/L, the curve for alginate levels off and seems to show a maximum similar to one reported for NaPSS at 0.5 equiv/L of polymer.[1,28] However, the curves for dextran sulfate and ι-carrageenan do not show definite maxima, at least not at the concentrations measured. It is possible that maxima do occur at higher concentrations, but it is difficult to verify this by the open-end capillary method because of the large experimental error associated with using this method for such viscous solutions.

Since both Manning and Yoshida predict that there should be a linear relationship between $D_{Na^+}/D_{Na^+}{}^{0}$ and ξ^{-1}, such a plot is shown in Figure 4. The experimental points shown were for the concentration range between $-\log N = 2.0$ and $-\log N = 3.0$, since in this region the experimental values are the most constant and give the best agreement with theoretical values. This region corresponds to polymer concentrations in the range of 10^{-2}–10^{-3} equiv/L. For each polyelectrolyte studied here, the points at three different concentrations in this region were plotted and the best least-squares line through the points was determined. These concentrations correspond to $-\log N$ equal to 2.0, 2.5, and 3.0

Figure 4 shows that throughout this concentration and ξ range the experimental values seem to agree better with the Yoshida line at lower ξ values ($\xi = 1.66$ and 1.43), while at higher ξ values ($\xi = 2.85$) better agreement is obtained with the Manning line. More intermediate ξ values are needed to verify this and to determine if $D_{Na^+}/D_{Na^+}{}^{0}$ is linear with respect to ξ^{-1} as predicted or whether the dependence is that of a higher order polynomial. These experimental results, therefore, suggest that the ability of counterions to bind to the polyion depends on the linear charge density of the polyion and, perhaps, on specific effects. Observed minimum values might be used to differentiate specific effects.

Assuming linearity, the best fit least-squares line through these experimental points in Figure 4 gives a slope of 1.08 and a y intercept of -0.07. The slope of the experimental line is larger than the slope of 0.866 predicted by Manning or 0.433 predicted by Yoshida. The ordinate intercept, however, is close to the origin and in good agreement with Manning's prediction.

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