Interactions of Multivalent Coions with Sodium Iota Carrageenan and Sodium Alginate by Self-Diffusion Measurements

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Received July 19, 1976

ABSTRACT: The coion self-diffusion coefficients were determined for Cl^-, SO_4^{2-}, and $Fe(CN)_6^{4-}$ as their Na^+ salts at 0.000 500, 0.001 00, 0.005 00, and 0.010 0 N in aqueous solutions containing sodium alginate or sodium iota carrageenan at concentrations ranging from 5.00×10^{-5} to 1.00×10^{-1} N. Sodium ion self-diffusion coefficients are reported for aqueous sodium alginate solutions containing NaCl and Na_2SO_4. A comparison of these results with those obtained with sodium poly(sytrenesulfonate) and sodium polyacrylate showed similarity in the trends of the self-diffusion coefficients with varying polyelectrolyte and simple salt concentrations. Correlation of the experimental findings with the line charge model for the polyion of Manning is discussed.

Ionic polysaccharides should receive more attention from chemists because of their inherent importance in biological systems and because of their use in medicine and in various industries. From the viewpoint of a chemist they are exciting entities due to their interesting conformation in the solid state, the gel state, and in aqueous solutions[1-16] and due to their interactions with positively and negatively charged small ions.[17-27]

With our interest in the interaction of small ions with synthetic polyelectrolytes and ionic polysaccharides, we have recently undertaken a systematic investigation of the interaction of coions, i.e., small ions of the same charge as that of the polyion, with polyions. While it is obvious that the counterions should interact strongly with polyions, coions were considered to interact to a negligible extent with the polyion; yet experimental results indicate that the coion has a noticeable effect on the solution properties of polyelectrolytes. Also, the interesting approach to the theory of polyelectrolyte solutions by Manning states that the coions should interact appreciably with the polyion by Debye–Hückel forces.[28-31] A good correlation between the theoretically predicted and experimental self-diffusion coefficients for Cl^- ion in aqueous NaCl solutions containing sodium polyacrylate was reported.[32] Recently, Kowblansky and Ander[33] have shown from the results for capillary self-diffusion measurements that monovalent, divalent, and tetravalent coions interact with sodium poly(styrenesulfonate) and divalent coions interact with sodium polyacrylate to different extents at finite concentrations but interact to the same extent at infinite dilution. Upon comparing these results for coion self-diffusion with the theoretically predicted values from Manning's line charge model for the polyion, it was found that the theory agreed quite well with the experimental findings for the monovalent and multivalent coions at very low *ratios* of polyelectrolyte to simple salt concentration. However, at higher concentration *ratios* good accord between theory and experiment was obtained only for the monovalent chloride ion and poor agreement resulted for the divalent sulfate and tetravalent ferrocyanide anions. It is of interest that monovalent and divalent *counterions* do obey Manning's theoretical diffusion equations for synthetic[33,34] and natural[19] polyelectrolytes. Kwak and Johnston[17] showed from electrical conductivity studies that much better agreement with the theory was obtained for the alkali-metal ion salts of carboxymethylcellulose than for the alkali-metal ion salts of polystyrenesulfonate. More recently Magdelenat et al.[27] showed that electrophoretic mobilities of bivalent cations in aqueous solutions containing chondroitin sulfate were in accord with the Manning theory. Because ionic polysaccharides are stiffer than synthetic polyelectrolytes, they should be better models to test Manning's comprehensive theory of dilute polyelectrolyte solutions.

Here we report the results of self-diffusion studies of Cl^-, SO_4^{2-}, and $Fe(CN)_6^{4-}$ in aqueous solutions of sodium alginate (NaAlg) and sodium iota carrageenan (NaCarr) and Na^+ ions in NaCl and Na_2SO_4 solutions containing NaAlg at 25 °C. Alginic acids are linear copolymers of D-mannuronic acid and L-guluronic acid; their x-ray patterns indicate that the distance between carboxyl groups on the backbone is 5.0 Å.[1-11] Iota carrageenan is a linear copolymer of β-D-galactose 4-sulfate and 3,6-anhydro-α-D-galactose 2-sulfate; the x-ray diffraction patterns indicate that the average distance between sulfate groups on the backbone is 4.3 Å.[1-3,12] The results will be compared with the experimental findings for coion self-diffusion coefficients in aqueous solutions of sodium poly(styrenesulfonate) and sodium polyacrylate and with the results predicted from Manning's line charge model.

Experimental Section

A sample of highly purified iota carrageenan was kindly supplied by Marine Colloids, Inc. The sample was prepared by a sodium hydroxide extraction of Eucheuma spinosum and after isolation by alcohol precipitation, washing, drying, and grinding the sample was further purified by washing with NaCl in 50% isopropyl alcohol four times, followed by four alcohol washes to remove salts. Its weight average molecular weight was found to be 290 000. Chemical analysis of the purified iota carrageenan gave 23.52% 3,6-anhydro-α-D-galactose and a sulfate–hexose ratio of 0.99; hence, we will assume one sulfate group per sugar unit.

The sample of sodium alginate was kindly supplied by the Kelco Co. The sample was dissolved in water and precipitated three times from water with ethyl alcohol and dried in vacuo at 50 °C. A portion of the purified sample was converted to the acid and titrated with standard NaOH to determine its equivalent weight which was found to be 208 ± 1 g. This indicates one carboxyl group per sugar unit. The sodium alginate sample has a reported molecular weight of 50 000.

$^{22}NaCl$, $Na^{36}Cl$, and $Na_4Fe(^{14}CN)_6$ were obtained from ICN Pharmaceutical Inc., and $Na_2{}^{35}SO_4$ was obtained from the New England Nuclear Co.

The preparation of the radioactive solutions and the open-end capillary method employed were described previously.[33] After allowing diffusion to proceed for an appropriate amount of time, the outer solution was removed using an aspirator, the outside walls of the capillaries were washed and dried, and the radioactivity of the capillary was determined using liquid scintillation counting. Self-diffusion coefficients of ion i were then calculated using[33]

$$D_i = \frac{\pi}{4}\left(1 - \frac{C}{C_0}\right)^2 \frac{L^2}{t} \qquad (1)$$

where C_0 and C are the respective radioactive activities before and after diffusion, L is the length of the capillary (2.82 ± 0.005 cm), and t is the time allowed for diffusion.

After removal of the capillaries from the test tubes, the outsides

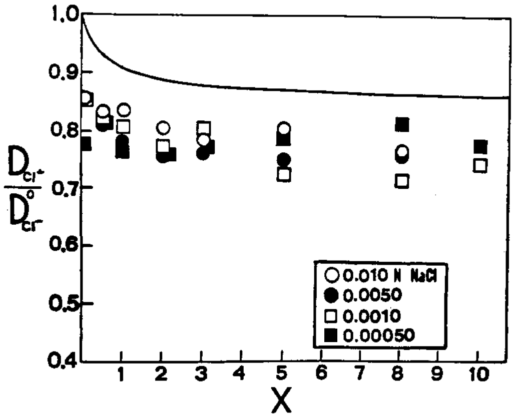

Figure 1. The dependence of the self-diffusion ratio of chloride ion in sodium alginate solutions containing NaCl on X. The solid line is predicted from Manning's theory for $\xi = 1.43$.

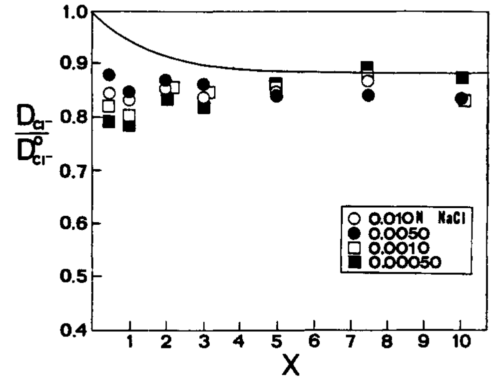

Figure 2. The dependence of the self-diffusion ratio of chloride ion in sodium carrageenan solutions containing NaCl on X. The solid line is predicted from Manning's theory for $\xi = 1.66$.

of the capillaries were washed in a small beaker of circulating distilled water and dried, and the test tubes were placed upside down in a scintillation vial containing 5 ml of scintillation fluid. The vials were centrifuged, shaken in a vortex mixer, and then analyzed using a Packard Tri-Carb liquid scintillation spectrometer Model 3385. The validity of this method was checked by determining the values of the self-diffusion coefficient of simple ions in water and comparing them with the literature values. To eliminate the need of analyzing the radioactive content both before and after diffusion, matched capillaries (precision-bore to within ±0.005 cm length and ±0.005 mm i.d.) were used to determine the radioactive count before self-diffusion was allowed. A minimum of five capillaries were employed to determine each value of C and C_0. The average standard errors of the reported values of the self-diffusion coefficients were approximately 3%.

Results and Discussion

The coion self-diffusion coefficients were determined for Cl^-, SO_4^{2-}, and $Fe(CN)_6^{4-}$ as their Na^+ salts at 0.000 500, 0.001 00, 0.005 00, and 0.010 0 N in aqueous solutions containing sodium alginate or sodium iota carrageenan at concentrations ranging from 5.00×10^{-5} to 1.00×10^{-1} N. Thus the concentration ratio parameter X, defined as the equivalent concentration of polyelectrolyte n_e to the equivalent concentration of simple salt n_s, ranged from 0.1 to 10. The results are expressed as the dependence of the self-diffusion ratio of ion i D_i/D_i^0 on X, where D_i is the self-diffusion coefficient of ion i in a simple salt solution containing polyelectrolyte and D_i^0 is the self-diffusion coefficient of ion i at infinite dilution of simple salt containing *no* polyelectrolyte. As calculated from the Nernst equation,[35] the values of D_i^0 for Cl^-, SO_4^{2-}, and $Fe(CN)_6^{4-}$ are 2.03×10^{-5}, 1.06×10^{-5}, and 0.738×10^{-5} cm²/s, respectively. The experimental results for D_i/D_i^0 as a function of X are presented respectively for NaAlg and NaCarr in Figures 1 and 2 for the Cl^- ion, Figures 3 and 4 for the SO_4^{2-}, ion and Figures 5 and 6 for the $Fe(CN)_6^{4-}$ ion. These results are listed in Tables I and II, where the experimental error of each self-diffusion coefficient is denoted as the deviation of the mean of four to six determinations. For each ion the diffusion ratio D_i/D_i^0 is less than unity indicating that the ionic polysaccharide lowers the coion diffusion coefficient as compared to the polyelectrolyte-free simple salt solution at infinite dilution. At 25 °C for 0.010 N aqueous simple salt solution Turq reported[36] $D_{Cl^-} = 1.32 \times 10^{-5}$ cm²/s for NaCl and we determined $D_{SO_4^{2-}} = 1.00 \times 10^{-5}$ cm²/s for

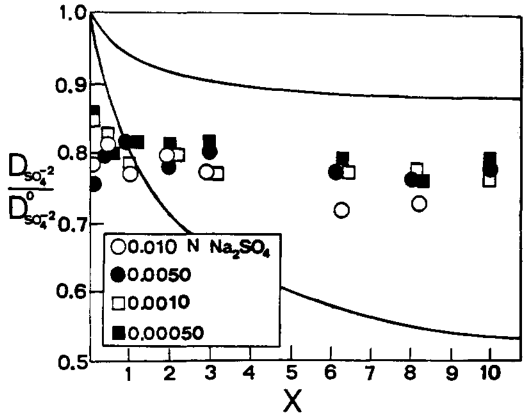

Figure 3. The dependence of the self-diffusion ratio of sulfate ion in sodium alginate solutions containing Na_2SO_4 on X. The solid lines are predicted from Manning's theory for monovalent (top) and divalent coions for $\xi = 1.43$.

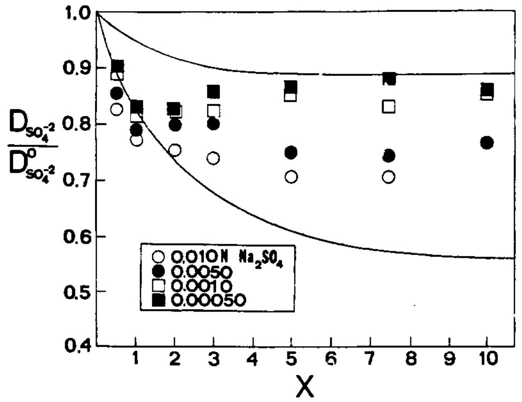

Figure 4. The dependence of the self-diffusion ratio of sulfate ion in sodium carrageenan solutions containing Na_2SO_4 on X. The solid lines are predicted from Manning's theory for monovalent (top) and divalent coions for $\xi = 1.66$.

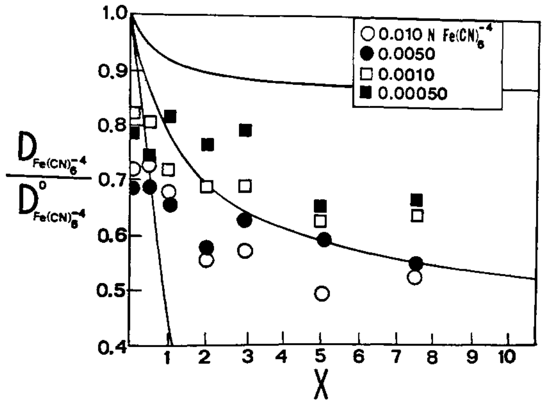

Figure 5. The dependence of the self-diffusion ratio of ferrocyanide ion in sodium alginate solutions containing $Na_4Fe(CN)_6$ on X. The solid lines are predicted from Manning's theory for monovalent, divalent, and tetravalent coions for $\xi = 1.43$.

Table I
Self-Diffusion Coefficients of Coions in Aqueous Sodium Alginate Solutions Containing Simple Salts at 25 °C

Salt	X	$D_2 \times 10^5$, cm^2/s		
		NaCl	Na_2SO_4	$Na_4Fe(CN)_6$
0.000 500 N	0.10	1.59 ± 0.01	0.92 ± 0.01	0.58 ± 0.03
	0.50	1.63 ± 0.04	0.86 ± 0.03	0.56 ± 0.03
	1.00	1.56 ± 0.12	0.88 ± 0.02	0.60 ± 0.01
	2.00	0.55 ± 0.04	0.87 ± 0.00	0.57 ± 0.02
	3.00	1.55 ± 0.06	0.87 ± 0.01	0.58 ± 0.01
	5.00	1.59 ± 0.09		0.40 ± 0.01
	6.30		0.85 ± 0.01	
	7.50			0.49 ± 0.02
	8.00	1.66 ± 0.05		
	8.20		0.81 ± 0.03	
	10.00	1.59 ± 0.13	0.84 ± 0.03	
0.001 00 N	0.10	1.73 ± 0.04	0.92 ± 0.02	0.61 ± 0.01
	0.50	1.67 ± 0.08	0.90 ± 0.01	0.60 ± 0.02
	1.00	1.64 ± 0.05	0.85 ± 0.02	0.53 ± 0.01
	2.00	1.57 ± 0.02	0.86 ± 0.02	0.51 ± 0.01
	3.00	1.53 ± 0.06	0.82 ± 0.06	0.51 ± 0.02
	5.00	1.48 ± 0.03		0.46 ± 0.01
	6.30		0.82 ± 0.02	
	7.00			0.47 ± 0.03
	8.00	1.45 ± 0.06		
	8.20		0.81 ± 0.03	
	10.00	1.51 ± 0.05	0.82 ± 0.02	
0.005 00 N	0.10		0.80 ± 0.02	0.51 ± 0.02
	0.50	1.63 ± 0.08	0.86 ± 0.01	0.52 ± 0.03
	1.00	1.58 ± 0.02	0.88 ± 0.02	0.48 ± 0.01
	2.00	1.53 ± 0.03	0.84 ± 0.02	0.42 ± 0.01
	3.00	1.54 ± 0.03	0.86 ± 0.02	0.47 ± 0.01
	5.00	1.51 ± 0.01		0.44 ± 0.04
	6.30		0.82 ± 0.02	
	7.50			0.40 ± 0.01
	8.00	1.54 ± 0.04		
	8.20		0.81 ± 0.03	
	10.00		0.82 ± 0.02	
0.010 0 N	0.10	1.73 ± 0.06	0.85 ± 0.02	0.53 ± 0.01
	0.50	1.69 ± 0.02	0.88 ± 0.02	0.54 ± 0.04
	1.00	1.70 ± 0.02	0.82 ± 0.02	0.51 ± 0.02
	2.00	1.63 ± 0.04	0.86 ± 0.03	0.41 ± 0.02
	3.00	1.59 ± 0.06	0.82 ± 0.02	0.42 ± 0.01
	5.00	1.64 ± 0.04		0.37 ± 0.01
	6.30		0.75 ± 0.02	
	7.50			0.38 ± 0.01
	8.00	1.55 ± 0.07		
	8.20		0.77 ± 0.04	

Na_2SO_4 and $D_{Fe(CN)_6{}^{4-}} = 0.72 \times 10^{-5}$ cm^2/s for $Na_4Fe(CN)_6$. Since for simple salt solutions D_i increases as the concentration decreases, these self-diffusion coefficients would be the lowest ones applicable to the concentrations used in this study. Then from these polyelectrolyte-free simple salt values and the values of salt-containing polyelectrolyte solutions shown in Figures 1 to 6, it is evident that the presence of the polyelectrolyte depresses the coion self-diffusion coefficient from its value in simple salt solution, indicating that the coion does interact with the polyion. Similar findings were noted for the interaction of monovalent and multivalent coions with sodium poly(styrenesulfonate) and sodium polyacrylate.[32,33]

From Figure 1 it should be noted that $D_{Cl^-}/D_{Cl^-}{}^0$ for NaAlg is fairly independent of simple salt concentration and that the average values of $D_{Cl^-}/D_{Cl^-}{}^0$ for a given X value initially decrease slightly with increasing X values, leveling off at X greater than 2 to a value of 0.76. As is shown in Figure 2, the values of $D_{Cl^-}/D_{Cl^-}{}^0$ for NaCarr are independent of simple salt concentration over the whole range of X values with an average value of 0.85. The $D_{Cl^-}/D_{Cl^-}{}^0$ ratios for sodium poly(styrenesulfonate) decreased with increasing X values until approximating $X = 3$ where the diffusion ratio values for each simple salt concentration leveled off at slightly different values, for 0.0100 N NaCl at 0.80 and 0.000 500 N NaCl at 0.90. Thus, the Cl^- diffusion ratios in NaCarr solutions do approximate the values obtained for this synthetic polyelectrolyte.

The presence of both the NaAlg and NaCarr decreased the value of $D_{SO_4{}^{2-}}$ from its value in polyelectrolyte-free Na_2SO_4 solution at infinite dilution as is shown in Figures 3 and 4, respectively, and from the values in polyelectrolyte-free Na_2SO_4 solutions at finite concentrations. From Figure 4, the values of $D_{SO_4{}^{2-}}$ for NaCarr solutions initially decrease with increasing X values; at the higher X values where the concentration ratio of polyelectrolyte to salt becomes more appreciable, the diffusion ratio becomes fairly independent of X. For the most dilute simple salt concentration, the curve levels off at approximately $D_{SO_4{}^{2-}}/D_{SO_4{}^{2-}}{}^0 = 0.86$. For the same simple salt concentration, i.e., 0.000 500 N Na_2SO_4, it is shown in Figure 3 that the leveling off $D_{SO_4{}^{2-}}/D_{SO_4{}^{2-}}{}^0$ value for NaAlg is 0.83, while it was found that these values for sodium poly(styrenesulfonate) and sodium polyacrylate are both 0.86. This indicates that the interaction of $SO_4{}^{2-}$ ion with the polyion is independent of the nature of the pendant charges

Table II
Self-Diffusion Coefficients of Coions in Aqueous Sodium Iota Carrageenan Solutions Containing Simple Salts at 25 °C

		$D_2 \times 10^5$, cm^2/s		
Salt	X	NaCl	Na_2SO_4	$Na_4Fe(CN)_6$
0.000 500 N	0.50	1.62 ± 0.04	0.96 ± 0.01	0.51 ± 0.03
	1.00	1.60 ± 0.01	0.88 ± 0.02	
	1.50			0.56 ± 0.03
	2.00	1.69 ± 0.04	0.88 ± 0.01	0.44 ± 0.01
	3.00	1.67 ± 0.02	0.91 ± 0.01	0.49 ± 0.02
	5.00	1.75 ± 0.04	0.92 ± 0.03	0.45 ± 0.01
	7.50	1.82 ± 0.03	0.94 ± 0.01	0.45 ± 0.02
	10.00	1.79 ± 0.06	0.91 ± 0.03	
0.001 00 N	0.50	1.67 ± 0.02	0.84 ± 0.02	0.55 ± 0.03
	1.00	1.63 ± 0.05	0.88 ± 0.01	0.54 ± 0.03
	2.00	1.74 ± 0.03	0.88 ± 0.01	0.50 ± 0.01
	3.00	1.72 ± 0.03	0.88 ± 0.03	0.45 ± 0.01
	5.00	1.75 ± 0.01	0.90 ± 0.02	0.44 ± 0.01
	7.50	1.77 ± 0.02	0.88 ± 0.01	0.40 ± 0.01
	10.00	1.69 ± 0.03	0.90 ± 0.03	
0.005 00 N	0.50	1.79 ± 0.02	0.91 ± 0.02	0.49 ± 0.01
	1.00	1.72 ± 0.02	0.84 ± 0.02	0.52 ± 0.01
	2.00	1.77 ± 0.01	0.85 ± 0.01	0.41 ± 0.02
	3.00	1.76 ± 0.03	0.85 ± 0.02	0.37 ± 0.01
	5.00	1.71 ± 0.03	0.80 ± 0.04	0.36 ± 0.02
	7.50	1.70 ± 0.03	0.79 ± 0.04	0.36 ± 0.01
	10.00	1.70 ± 0.01	0.81 ± 0.01	
0.010 0 N	0.50	1.72 ± 0.01	0.87 ± 0.02	0.46 ± 0.01
	1.00	1.70 ± 0.04	0.82 ± 0.02	0.49 ± 0.01
	2.00	1.74 ± 0.03	0.80 ± 0.02	0.39 ± 0.01
	3.00	1.72 ± 0.02	0.78 ± 0.01	0.36 ± 0.02
	5.00	1.72 ± 0.03	0.75 ± 0.04	0.41 ± 0.03
	7.50	1.76 ± 0.03	0.75 ± 0.02	0.32 ± 0.05

on the polyion and of the linear charge density of the polyion, at least for charge densities above unity. At a given X value, $D_{SO_4^{2-}}/D_{SO_4^{2-}}{}^0$ for NaCarr increases as the simple salt concentration decreases. This effect is pronounced at higher X values and is hardly noted at lower X values where the diffusion ratio is fairly independent of salt concentration. Similar results were obtained for $D_{SO_4^{2-}}/D_{SO_4^{2-}}{}^0$ for sodium polyacrylate and sodium poly(styrenesulfonate).[33] The same initial decrease for $D_{SO_4^{2-}}$ with increasing X values is noted for NaAlg in Figure 3, where the curve also levels off as the X values increase. At a given X value, however, the effect of increasing $D_{SO_4^{2-}}/D_{SO_4^{2-}}{}^0$ with decreasing salt concentration is much less pronounced with the points clustering for all four simple salt concentrations as compared to NaCarr, sodium poly(styrenesulfonate), and sodium polyacrylate.

The most pronounced simple salt concentration dependence of the coion diffusion ratio occurred with the tetravalent ferrocyanide ion for both the NaAlg and NaCarr solutions as is shown in Figures 5 and 6, respectively. Both polysaccharide solutions show similar characteristics with $D_i/D_i{}^0$ for $Fe(CN)_6{}^{4-}$ for each $Na_4Fe(CN)_6$ concentration leveling off at approximately $X > 4$, the leveling off values of the diffusion ratio being approximately 0.63 and 0.65 for NaAlg and NaCarr, respectively, at 0.000 500 0 N $Na_4Fe(CN)_6$, the lowest salt concentration used. For sodium poly(styrenesulfonate) solutions containing $Na_4Fe(CN)_6$ the general characteristics are similar to those mentioned here for the ionic polysaccharides, a leveling off of the coion diffusion ratio for $X > 10$ of 0.83. Thus, the $Fe(CN)_6{}^{4-}$ ion appears to interact with NaAlg and NaCarr to a greater extent than with sodium poly(styrenesulfonate).

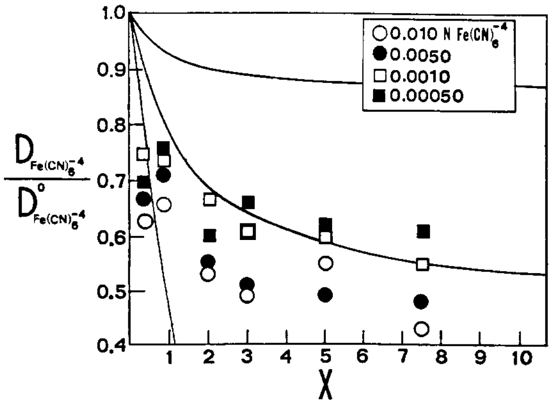

Figure 6. The dependence of the self-diffusion ratio of ferrocyanide ion in sodium carrageenan solutions containing $Na_4Fe(CN)_6$ on X. The solid lines are predicted from Manning's theory for monovalent, divalent, and tetravalent coions for $\xi = 1.66$.

To determine the effect of the coion on the interaction of sodium ions with ionic polysaccharides, the Na^+ ion self-diffusion coefficients were determined in solutions of NaAlg containing 0.001 00, 0.005 00, and 0.010 0 N NaCl and 0.0100 N Na_2SO_4. The results are listed in Table III. As is illustrated in Figure 7, $D_{Na^+}/D_{Na^+}{}^0$ for $X > 1$ are close in value for 0.0100 N NaCl and Na_2SO_4, indicating a negligible effect of the nature of the coion on the interaction of the counterion. Such an effect has been observed previously.[33] The general shape of the Na^+ ion diffusion curve in Figure 7 is similar to those reported for sodium polyacrylate[34] and sodium poly(styrenesulfonate).[33] In the present study, $D_{Na^+}/D_{Na^+}{}^0$ decreases with increasing X values and levels off approximately at $X > 5$. At a constant X value for $X > 5$, $D_{Na^+}/D_{Na^+}{}^0$ decreases with decreasing simple salt concentration, which is probably due to a decrease in the screening of the polyion charges with a decrease in salt concentration. It is interesting that the sodium ion activity coefficients for solutions of NaAlg containing NaCl were found to level off at high X values and decrease with decreasing simple salt concentration at constant X values.[37]

Table III
Self-Diffusion Coefficients of Na$^+$ in Aqueous Sodium Alginate Solutions Containing NaCl and Na_2SO_4 at 25 °C

n_s	X	$D_{Na^+} \times 10^5$, cm^2/s
0.000 500 N NaCl	0.10	1.18 ± 0.03
	0.50	1.01 ± 0.04
	1.00	0.93 ± 0.02
	2.00	0.90 ± 0.01
	3.00	0.82 ± 0.01
	5.00	0.76 ± 0.01
	8.00	0.72 ± 0.04
	10.00	0.71 ± 0.03
0.001 00 N NaCl	0.10	1.11 ± 0.03
	0.50	0.99 ± 0.02
	1.00	1.05 ± 0.02
	2.00	0.92 ± 0.01
	3.00	0.81 ± 0.02
	5.00	0.79 ± 0.01
	8.00	0.79 ± 0.01
	10.00	0.79 ± 0.01
0.005 00 N NaCl	0.10	1.16 ± 0.04
	0.50	1.05 ± 0.01
	1.00	1.01 ± 0.01
	2.00	0.86 ± 0.04
	3.00	0.90 ± 0.02
	5.00	0.87 ± 0.02
	8.00	0.86 ± 0.01
	10.00	0.86 ± 0.04
0.010 0 N NaCl	0.10	1.19 ± 0.05
	0.50	0.99 ± 0.03
	1.00	0.93 ± 0.04
	2.00	0.94 ± 0.02
	3.00	0.93 ± 0.03
	5.00	0.89 ± 0.02
	8.00	0.74 ± 0.04
	10.00	0.80 ± 0.03
0.010 0 N Na_2SO_4	1.00	0.94 ± 0.02
	3.00	0.90 ± 0.03
	5.00	0.87 ± 0.03
	8.00	0.82 ± 0.02

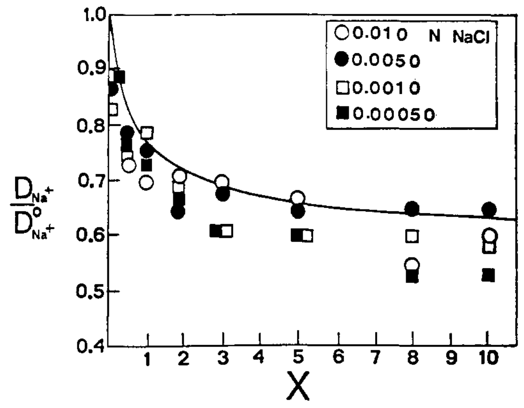

Figure 7. The dependence of the self-diffusion ratio of sodium ion in sodium alginate containing NaCl on X. The solid line is predicted from Manning's theory for monovalent counterions for $\xi = 1.43$.

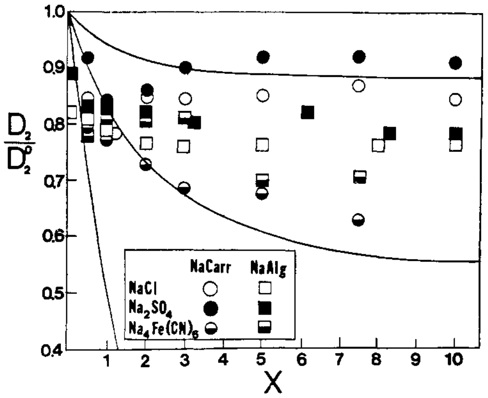

Figure 8. A comparison of the experimental coion self-diffusion ratio extrapolated to zero ionic strength. The solid lines are predicted from Manning's theory for monovalent, divalent, and tetravalent coions for $\xi = 1.66$.

Central to Manning's theory of polyelectrolyte solutions is the linear charge density parameter ξ of the polyelectrolyte $\xi = e^2/\epsilon kTb$, where the symbols have their usual designations and b is the distance between adjacent charge groups on the polyion. Above a critical value $\xi_c = |z_p z_1|^{-1}$, where z_p is the charge of a single charge-site on the polyion and z_1 is the charge of the counterion, ions condense onto the polyion to reduce ξ to ξ_c and the uncondensed counterions and coions interact with the polyion by Debye–Hückel forces. For NaAlg and NaCarr $\xi = 1.43$ and $\xi = 1.66$, respectively, and $\xi_c = 1$ for both ionic polysaccharides. For coions, designated by the subscript 2, *no* condensation onto the polyion can take place and from the theory[29–31]

$$D_2/D_2^0 = 1 - (Z_2^2/3)A(1,\xi^{-1}X) \qquad (2)$$

where $A(1,\xi^{-1}X)$ is a rapidly converging series dependent on ξ_c, which is equal to unity for NaAlg and NaCarr, and the effective X value, $\xi^{-1}X$, since ξ^{-1} is the fraction of uncondensed counterions of the polyion. Equation 2 cannot be valid for highly charged coions at large X values since negative values of D_2/D_2^0 would result. Hence, it is probably best to correlate eq 2 with the experimental data only at low X values, where the polyelectrolyte concentration is low and the limiting laws would be most applicable. In Figures 3 to 6, where the solid lines represent the predicted theoretical values, it is noted that for $X < 1$ for the SO_4^{2-} and $Fe(CN)_6^{4-}$ ions accord between theory and experiment is good, but for $X > 1$ the correlation is poor. It can be seen in Figures 1 to 6 that generally the coion values of D_i/D_i^0 increase as the concentration of simple salt decreases. By extrapolating D_i/D_i^0 to zero simple salt concentration at a constant X value, the limiting value of D_i/D_i^0 at zero total ionic strength is obtained. Such values are shown in Figure 8; when the points for a given X value approximated one another, however, an average value was used. The extrapolated values for the Cl$^-$ ion diffusion ratio for NaCarr approximate the monovalent theoretical curve closely at higher X values but do not follow the theoretical upward trend at lower values of X. Those for NaAlg are approximately 10% lower than those observed for NaCarr. It is interesting that the limiting diffusion ratio for the SO_4^{2-} over the whole range of X for NaAlg is about 7% below the theoretical *monovalent* line, while for NaCarr the correlation with the theoretical monovalent line is excellent. For $Fe(CN)_6^{4-}$, extrapolated diffusion ratios are similar to the results obtained for NaAlg and NaCarr, with a slight decrease in the extrapolated diffusion ratios with increasing X values and a leveling off at approximately $X > 3$. These values are about 20% below the theoretical monovalent line predicted by Manning for the range of X studied. At infinite dilution, the Cl$^-$ and $Fe(CN)_6^{4-}$ appear to interact with both ionic polysaccharides to approximately the same extent, while the SO_4^{2-} ion interacts with the NaAlg to a slightly greater extent than with NaCarr. Also, each coion closely resembles the behavior of the limiting diffusion ratio predicted over the range of X, although the experimental values are slightly lower. The good correlation between the interaction of multivalent coions and polyions at infinite dilution and the theoretical line for *monovalent* coions has been reported previously for sodium polyacrylate and sodium poly(styrenesulfonate).[33] Clearly, while coion interaction with the polyion does take place in the Debye–Hückel atmosphere, the theory overemphasizes the electrostatic effect of the coion charge.

From the theory of Manning, counterions condense onto the polyion if $\xi > \xi_c$ and the uncondensed counterions interact with the polyion. The equation for monovalent counterions is

$$D_1/D_1^0 = [(\xi^{-1}X + 1)][X + 1]^{-1}[1 - \tfrac{1}{3}A(1;\xi^{-1}X)] \quad (3)$$

where the subscript 1 refers to the counterions. From Figure 7 it can be seen that the solid line predicted from Manning's theory is in good accord with the experimental results below $X = 1$, and for the two highest concentrations of simple salt, 0.005 00 N and 0.010 0 N, over the whole range of X. Since limiting laws are derived from the theory, it would be expected that at the lowest polyelectrolyte and simple salt concentrations, i.e., at low X values, the best correlation of the experimental findings with the theory would result. While such is generally manifest in Figure 7, the experimental results show negative deviations from the theory for the lowest NaCl concentration by as much as 20%.

Acknowledgment. The assistance of Dr. M. Kowblansky is gratefully appreciated. This project was supported by Grant No. GM 21234, awarded by the Public Health Service, DHEW.

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Critical Permeation Size of Dextran Molecules

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Received July 8, 1976

ABSTRACT: The chromatographic behavior of dextran fractions on glass of narrow pore size distribution has been studied. Since the pore size of such glasses can be measured very accurately by mercury intrusion, the permeation behavior of macromolecules into the pores of such glass allows their characterization by a new size parameter, "the critical permeation size". The "critical permeation size" is defined as the pore size of the controlled pore glass at which the elution coefficient becomes zero. Two plotting procedures are shown which effectively linearize the molecular weight vs. elution coefficient and the pore diameter vs. elution coefficient relations. These plotting procedures can be used for extrapolations when the calculation of the critical permeation size from a limited number of chromatographic determinations is desired.

Gel permeation chromatography[2,3] has, over the past 15 years, become a well established procedure for the fractionation and characterization of high polymers of synthetic and natural origin. Characterization consists usually in comparing the elution behavior of the unknown sample with the behavior of substances with known molecular weight. Within several years, controlled pore glass[4] has joined the rank of substances for permeation chromatography. Rigidity and chemical inertness make it particularly useful for applications where high speed,[5] sterilizability,[6,7,8] long life,[9] resistance against chemically reactive[10–13] or hot eluants,[14] and the ability of covalent surface derivatization[15–17] are of importance. As a result of its rigidity and the fact that its pore size is not affected by the presence of gases, liquids, or vacuum, the pore size of controlled pore glass (CPG) can be measured by electron microscopy and mercury intrusion analysis.[4] This has been found very valuable in the reproducible preparation of CPG, in comparing experimental results, and, to a lesser extent, in the investigation of the mechanism underlying permeation chromatography itself.[3,18–22]