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Notes

Polycations. 5. Sulfate Ion Tracer Diffusion Coefficients in Solutions Containing Poly[(dimethylamino)hexylene bromide], a 6–6 Ionene

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The Manning theory[1–6] of polyelectrolyte solutions has been the dominant model used by many researchers. Limiting laws have been derived for equilibrium and transport properties using an infinite line charge model. For a polyelectrolyte whose value of the charge density parameter ξ

$$\xi = e^2/\epsilon kTb \qquad (1)$$

where e is the protonic charge, ϵ is the dielectric constant of the medium, k is the Boltzmann constant, T is the temperature, and b is the average axial distance between charges on the polyelectrolyte, is above a critical value of the charge density parameter ξ_c

$$\xi_c = |Z_1|^{-1} \qquad (2)$$

where Z_1 is the counterion charge, counterion condensation is predicted so as to bring ξ to its effective ξ_c value, and the remaining uncondensed counterions interact with the polyion by Debye–Hückel forces. When $\xi < \xi_c$ no condensation is predicted to occur, and all uncondensed counterions interact with the polyion by Debye–Hückel forces. A noticeable transition is predicted for an appropriate solution property as the values of ξ decrease from above ξ_c to below it.

From small-ion tracer diffusion studies in polyelectrolyte solutions containing simple salt,[7–17] it has been shown that the Manning model is a good representation for monovalent and divalent counterions that interact with polyelectrolytes having values greater than approximately 1.4. Recently, it was shown from diffusion studies[15,17] that for polyelectrolytes with $\xi > \xi_c$, the fraction of the counterions associated with the polyelectrolyte, i.e., the fraction of stoichiometric charges neutralized by counterions, was constant over large concentration ranges of polyelectrolyte and simple salt for excess salt, as is predicted by the Manning theory. Other experimental evidence for counterion condensation and the constancy of the charge fraction for a given counterion valence and polyelectrolyte charge density was discussed.[3,4,18]

When systematic measurements are performed that monitor the long-range interactions between the counterions and the polyion, results not in accord with the Manning theory have been found. Recently, Kowblansky and Zema[19] found using fully neutralized polyacrylamides hydrolyzed to different charge densities that for the range $0.02 < \xi < 2.84$, $\gamma_{\mathrm{Na^+}}/\gamma^\circ_{\mathrm{Na^+}}$, where $\gamma_{\mathrm{Na^+}}$ and $\gamma^\circ_{\mathrm{Na^+}}$ are the sodium ion activity coefficients with and without polyelectrolyte present, respectively, varied linearly with $\xi^{1/2}$ over the *whole* range of ξ studied. Their analysis of reported counterion activity coefficient data for sodium pectinate[20] and sodium polymethacrylate[21] over large ranges of ξ indicated that the same linear functionality is obeyed above and below ξ_c, as is observed for the hydrolyzed polyacrylamides. The discontinuities at ξ_c predicted by the theory were not observed, and the experimental values were always observed to be lower compared to the values predicted from the theory, which only considers long-range Debye–Hückel interactions for $\xi < \xi_c$. This must mean a short-range interaction, perhaps of the consideration type, occurs for $\xi < \xi_c$.

Table I
Sulfate Ion Diffusion Coefficient Ratios $D_{\mathrm{SO_4^{2-}}}/D^\circ_{\mathrm{SO_4^{2-}}}$ in Salt-Free Aqueous Solutions of 3–3 and 6–6 Ionene Bromides[a]

N_p	3–3	6–6
0.00010	0.052	0.046
0.0050	0.050	0.073
0.0010	0.055	0.077
0.0050	0.060	0.091
0.009	0.082	0.152
0.010	0.118	0.238
0.050	0.163	0.423
0.090	0.186	0.508

[a] $D^\circ_{\mathrm{SO_4^{2-}}} = 1.06 \times 10^{-5}$ cm^2/s.

Small-ion tracer diffusion coefficients in the presence of polyelectrolytes provide a useful measure of the small ion–polyanion interactions. Here, SO_4^{2-} ion tracer diffusion coefficients in aqueous and aqueous Na_2SO_4 solutions containing (dimethylamino)hexylene bromide (PDIHBr) (6–6 ionene bromide) are compared with analogous results for similar solutions containing (dimethylamino)propylene bromide (PDIPBr) (3–3 ionene bromide). Thus, the effect of polyelectrolytes with similar structures but differing charge densities, $\xi = 0.81$ for PDIHBr and $\xi = 1.43$ for PDIPBr, can be noted.

Experimental Section

The preparations of the ionenes followed the procedure of Rembaum et al.,[22] which was described previously.[13,14] The NMR spectra of the products compared favorably with the reported spectra.[23,24] An intrinsic viscosity of 0.32 dL/g in 0.40 M KBr was obtained for the 6–6 ionene bromide sample. Radioactive tracer diffusion measurements have been described in detail.[10–15] Dilutions in simple-salt solution were made at constant simple-salt concentration by varying the polyelectrolyte concentration and hence, X, where $X = N_p/N_s$ the ratio of the equivalent concentration of polyelectrolyte, N_p, to that of simple salt, N_s.

Results and Discussion

It was of interest to note if added SO_4^{2-} ions could bind to the 6–6 ionene halide ($\xi = 0.81$) and hence migrate with the polyelectrolyte. The reported good correlation[13] between the experimental results and those predicted by the Manning theory for the SO_4^{2-} ion tracer diffusion coefficients $D_{\mathrm{SO_4^{2-}}}$ in aqueous Na_2SO_4 solutions containing the 3–3 ionene bromide ($\xi = 1.43$) indicates that sulfate counterion condensation takes place when SO_4^{2-} ion is added to the polyelectrolyte. A comparison of the SO_4^{2-} ion tracer diffusion coefficients $D_{\mathrm{SO_4^{2-}}}$ in *salt-free* solutions containing the 3–3 ionene and 6–6 ionene halides should relate whether SO_4^{2-} ion is or is not condensed onto the 6–6 ionene bromide. These data are given in Table I. The $D^\circ_{\mathrm{SO_4^{2-}}}$ value of 1.06×10^{-5} cm^2/s is the infinitely dilute SO_4^{2-} ion diffusion coefficient for polyelectrolyte–free-salt solution. It should be noted from Table I that the $D_{\mathrm{SO_4^{2-}}}/D^\circ_{\mathrm{SO_4^{2-}}}$ ratios obtained in the N_p range 1.0×10^{-4} to 5.0×10^{-3} N for the 6–6 ionene in salt-free solutions are

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Table II
Sulfate Ion Tracer Diffusion Coefficients (cm²/s) in Aqueous Na_2SO_4 Solutions Containing Poly [(dimethylamino)hexylene bromide][a]

	0.00050 N Na_2SO_4			0.0010 N Na_2SO_4		
N	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1\mathrm{eff}}/D^\circ_1$
0.10	8.59	8.51	0.80	8.48	8.38	0.79
0.50	7.31	7.01	0.66	7.21	6.83	0.64
1.0	5.41	4.95	0.47	5.62	5.05	0.48
2.0	3.82	3.21	0.30	0.60	2.84	0.27
3.0	2.97	2.19	0.20	3.18	2.32	0.22
5.0	2.44			3.07		
8.0	2.44			2.97		
10.0	2.33			2.96		

	0.0050 N Na_2SO_4			0.010 N Na_2SO_4		
X	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$
0.10	9.12	8.96	0.85	9.43	9.23	0.87
0.50	7.31	7.12	0.67	8.16	7.44	0.70
1.0	6.15	5.26	0.50	6.53	5.46	0.52
2.0	5.19	4.01	0.38	5.62	4.00	0.38
3.0	5.09	3.67	0.31	5.72		
5.0	4.66			5.62		
8.0	4.66			5.72		
10.0	4.66			5.72		

[a] $D^\circ_{SO_4^{2-}} = 1.06 \times 10^{-5}$ cm²/s.

Table III
Sulfate Ion Tracer Diffusion Coefficients (cm²/s) in Aqueous Na_2SO_4 Solutions Containing Poly[(dimethylamino)propylene bromide][a]

	0.00050 N			0.0010 N		
X	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$
0.1	9.37	9.35	0.88	9.33	9.31	0.88
0.5	6.78	6.72	0.63	6.78	6.71	0.63
1.0	4.13	4.05	0.38	4.03	3.93	0.37
2.0	0.975	0.86	0.08	1.59	1.46	0.14
3.0	0.392	0.27	0.03	0.721	0.58	0.05
5.0	0.265			0.350		
8.0	0.254			0.281		
10.0	0.254			0.274		

	0.0050 N			0.010 N		
X	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$	$D_{1,\mathrm{obsd}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}} \times 10^6$	$D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$
0.1	9.75	9.72	0.92	9.12	9.05	0.85
0.5	5.83	5.73	0.54	6.15	5.90	0.56
1.0	2.44	2.30	0.22	3.18	2.61	0.27
2.0	0.700	0.51	0.05	2.23	1.74	0.16
3.0	0.710	0.49	0.05	1.06		
5.0	0.477			1.17		
8.0	0.413			1.17		
10.0	0.435			1.17		

[a] $D^\circ_{SO_4^{2-}} = 1.06 \times 10^{-5}$ cm²/s.

close in values to those obtained for the 3–3 ionene at the same concentrations. Also, the fairly constant diffusion ratios have very low values. It appears from the data that the SO_4^{2-} ion condenses on the 6–6 ionene bromide as it condenses on the 3–3 ionene bromide, and the diffusion coefficients of the condensed SO_4^{2-} ions are a measure of the diffusion of the polyelectrolyte.

Table II lists the observed sulfate ion diffusion coefficients $D_{1,\mathrm{obsd}}$ or $D_{SO_4^{2-},\mathrm{obsd}}$ in aqueous solutions containing PDIHBr in 0.00050, 0.0010, 0.0050, and 0.010 N Na_2SO_4. These values of $D_{1,\mathrm{obsd}}$ are *not* corrected for the diffusion of the polyelectrolyte if it is assumed that the SO_4^{2-} counterions interact strongly enough with the polyelectrolyte to migrate with it. The trends of the $D_{1,\mathrm{obsd}}$ values for SO_4^{2-} are similar for each Na_2SO_4 concentration: an initial decrease in $D_{1,\mathrm{obsd}}$ as X increases from 0 to 3, followed by a leveling off as X increases to 10. These trends are similar to those found for the sulfate ion diffusion coefficients in aqueous Na_2SO_4 solutions containing the 3–3 ionene bromide,[13] whose ξ value is 1.43, and for the calcium ion diffusion coefficients in aqueous Na_2SO_4 solutions containing polyanions.[11,12,15]

A comparison of the $D_{1,\mathrm{obsd}}$ values in Table II for the 6–6 ionene bromide can be made with the data in Table III for the $D_{1,\mathrm{obsd}}$ values in aqueous Na_2SO_4 solutions containing the 3–3 ionene bromide. The trends in the $D_{1,\mathrm{obsd}}$ values for the 6–6 ionene bromide are similar to those for the 3–3 ionene bromide inasmuch as both polyelectrolytes have values that decrease with increasing X in the range $0 < X < 3$, followed by a leveling off for $X > 3$, with limiting $D_{1,\mathrm{obsd}}$ values for $X > 3$ increasing with increasing salt concentration. The limiting $D_{1,\mathrm{obsd}}$ values for the 6–6 ionene are higher than those for the 3–3 ionene. It appears that at higher X values, where there is an excess of polyelectrolyte to salt, SO_4^{2-} ions condense onto both polyelectrolytes so that $D_{1,\mathrm{obsd}}$ for $X > 3$ is the diffusion

Table IV
Limiting Values for N_p-N_s Solutions Used for $D^{(c)}_1$ in Eq 4

N_s, N	$D_{SO_4{}^{2-}} \times 10^6$, cm²/s 3-3 ionene	6-6 ionene
0.00050	0.26	2.40
0.0010	0.30	3.00
0.0050	0.44	4.66
0.100	1.14	5.68

coefficient of the polyelectrolyte. The higher $D_{1,\mathrm{obsd}}$ values for the 6-6 ionene as compared to the 3-3 ionene are believed to be due to a coiling of the more flexible polycation due to divalent counterion condensation. As X is decreased from about $2 < X < 3$ to $X = 0.1$, $D_{1,\mathrm{obsd}}$ increases. This is probably due to both the $SO_4{}^{2-}$ ions in the ionic atmosphere and the condensed $SO_4{}^{2-}$ ions since the equivalent concentration ratio of salt to polyelectrolyte increases as X decreases. Thus, the tracer and nonradioactive $SO_4{}^{2-}$ ions are distributed between the polyelectrolyte and the simple salt at low X values according to their weighted concentrations.

It is desirable to obtain the counterion tracer diffusion coefficient for those ions in the ionic atmosphere, for this is a measure of the long-range ion-polyion interaction. For high molecular weight polyelectrolytes with diffusion coefficients very much smaller than those for small ions, the condensed radioactive small ions would not contribute appreciably to the measured counterion tracer diffusion coefficients. If the diffusion coefficient of the polyelectrolyte is *not* negligible compared to that of the counterions and if counterion condensation takes place, then the measured counterion diffusion coefficient $D_{1,\mathrm{obsd}}$ is

$$D_{1,\mathrm{obsd}} = D^{(c)}_{1,\mathrm{eff}} + D^{(u)}_{1,\mathrm{eff}} \tag{3}$$

where $D^{(c)}_{1,\mathrm{eff}}$ and $D^{(u)}_{1,\mathrm{eff}}$ are the effective diffusion coefficients of the condensed counterions and uncondensed counterions, respectively. To determine the desired quantity $D^{(u)}_{1,\mathrm{eff}}$, the weighted concentration average of $D^{(c)}_{1,\mathrm{eff}}$ is used, i.e., $D^{(c)}_1(1 - (Z_1\xi)^{-1})N_p/(N_p + N_s)$, giving

$$D_{1,\mathrm{obsd}} = D^{(c)}_1(1 - (Z_1\xi)^{-1})X/(X + 1) + D^{(u)}_{1,\mathrm{eff}} \tag{4}$$

where $D^{(c)}_1$ is the diffusion coefficient of the condensed counterions and hence of the polyelectrolyte. Values of $D^{(c)}_1$ can be obtained from tracer diffusion measurements of divalent (or higher valent) counterions when they are added to a polyelectrolyte whose counterions are monovalent. Recently, direct evidence has been reported[25] that shows that tracer amounts of radioactive Ca^{2+} ion condensed onto sodium heparin, and the values observed for $D_{Ca^{2+}}$ were very close to the values obtained for the tracer diffusion coefficient of the polyelectrolyte itself. Also the replacement of monovalent counterions by trace amounts of divalent and trivalent counterions has been confirmed indirectly from tracer diffusion measurements[7,8,11-16] and from potentiometric measurements.[26,27] In the absence of direct experimental information pertaining to the charge fraction of the ionene halides, an assumption had to be used in eq 4 to evaluate the weighted contribution of counterions dissociated from the polyelectrolyte. The validity of the Manning theoretical charge fraction of the polyelectrolyte was assumed for $\xi > \xi_c$, i.e., $(1 - (Z_1\xi)^{-1})$.[17]

To determine the appropriate values to use for $D^{(c)}_1$ in eq 4, it is noted from Table II that in the range $3 < X < 10$, fairly constant $D_{1,\mathrm{obsd}}$ values for $SO_4{}^{2-}$ are observed. At high X values, where there is an excess of polyelectrolyte to salt, the small amounts of $SO_4{}^{2-}$ ions replace the condensed Br^- ions, so that the measured diffusion is due to the diffusion of the polyelectrolyte in this region. Then $D^{(c)}_1 = D_{1,\mathrm{obsd}}$ in the range $3 < X < 10$. These values are the ones listed in Table IV and are used in eq 4 to calculate $D^{(u)}_{1,\mathrm{eff}}$. For comparison with theory the data are also presented as $D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$, where $D^\circ_1 = 1.06 \times 10^{-5}$ cm²/s for $SO_4{}^{2-}$ ion. With this correction, it should be noted from Tables II and III that below $X = 3$ (excess salt to polyelectrolyte solutions), $D^{(u)}_{1,\mathrm{eff}}/D^\circ_1$ appears to be fairly independent of salt concentration for each X value, which is predicted by the Manning theory.

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Registry No. (1,6-Dibromohexane)·(*N,N,N',N'*-tetramethyl-1,6-hexanediamine) (copolymer), 29322-35-8; 6-6 ionene bromide, 31622-88-5.

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Crossover Behavior for the Directed Lattice Animals Model of Anisotropic Polymers[†]

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I. Introduction

Recently, Daoud et al.[1] have examined the collapse and phase separation of linear and randomly branched polymers by a scaling analysis. In this note, the analysis of

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