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Polycations. 3. Coion Interactions with Quaternized Polyamines by Diffusion and Potentiometric Measurements

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ABSTRACT: Sodium and calcium coion tracer diffusion coefficients and activity coefficients were determined at 25 °C in aqueous salt solutions containing several cationic polyelectrolytes. Quaternized poly[(dimethylimino)alkyl halides] of differing linear charge densities were used as were the ring-containing ionene bromides poly(*N,N'*-dimethyl-*N,N'*-dibutylpiperazinium bromide) and poly(1,4-diazabicyclo[2.2.2]octylbutylene bromide). Poly[(vinylbenzyl)trimethylammonium chloride] and poly(diallyldimethylammonium chloride) were also studied for comparison. The equivalent concentrations both of polyelectrolyte and of salt ranged from 5×10^{-4} to 1×10^{-2} N. The results clearly indicate that the interaction of coions with cationic polyelectrolytes is negligible for the concentration range studied and is independent of the charge of the coion and charge density of the polyelectrolyte.

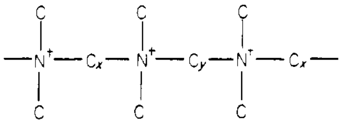
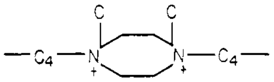
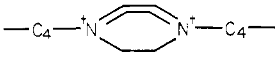
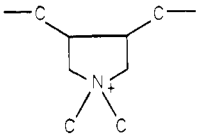
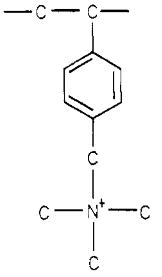
For highly charged polyelectrolytes it has long been known that counterions interact more strongly with polyelectrolytes than do coions. The higher the linear charge density parameter ξ

$$\xi = e^2/\epsilon kTb \tag{1}$$

where e is the protonic charge, ϵ is the dielectric constant of the medium, k is the Boltzmann constant, T is the absolute temperature, and b is the average axial distance between ionic charges on the backbone, the greater the interaction between the counterion and the polyelectrolyte. Experiments, of course, have borne this out. However, the interaction of coions with both anionic and cationic polyelectrolytes have only recently been investigated systematically. To study the long-range coion–polyion interaction, ion tracer diffusion coefficients and single-ion activity coefficients, being convenient measures of the interaction, were used. The effects of the charge density of the polyelectrolyte, the nature of charges on the polyion, the valence of the coion, and the concentrations of simple salt and of polyelectrolyte on the measured coefficients were of interest.

Coion tracer diffusion coefficients D_2 were found to be slightly suppressed in solutions containing an anionic polyelectrolyte when compared to their diffusion coefficients D°_2 in a polyelectrolyte-free salt solution at infinite dilution. This was found for monovalent Cl^-, divalent SO_4^{2-}, and tetravalent $Fe(CN)_6^{4-}$ ions in the presence of the sodium salts of polyacrylate,[1] poly(styrenesulfonate),[2] ι-carrageenan,[3] algin,[3] heparin,[4] dextran sulfate,[4] and DNA.[5] Generally, an ionic strength dependence of the coion diffusion coefficients was observed for the multivalent coions, which was more pronounced at the higher equivalent concentration ratios of polyelectrolyte to salt, i.e., at higher $X = N_p/N_s$ values, where N_p and N_s are the equivalent concentrations of polyelectrolyte and simple salt, respectively. Also, when extrapolated to zero ionic strength at constant X, the values of D_2/D°_2 for the multivalent coions were found to be close to the values observed for the monovalent coions. While the D_2/D°_2 values were generally found to be approximately 0.9 for monovalent coions interacting with anionic polyelectrolytes, the values of D_2/D°_2 for the Na^+ and Ca^{2+} coions in the presence of several cationic polyelectrolytes were reported[6,7] to be unity over large polyelectrolyte and salt concentration ranges. The poly[(dimethylimino)propylene, -butylene, and -hexylene bromide] polyelectrolytes, commonly referred to as the 3–3, 4–4, and 6–6 ionene bromides, were used; thus, the variation of the polyelectrolyte charge density was found to have no effect on the coion–polycation interaction.

Table I
Cationic Polyelectrolytes Used in the Present Study

polycation	symbol	ξ
	3-3 4-4 6-6	1.43 1.14 0.81
	PDMBP	1.59
	PDABOB	1.59
	PDADMA	1.25
	PVBTMA	2.85

There are several reported studies of the evaluation of the coion activity coefficient in the presence of polyelectrolytes from potentiometric measurements. Early, Nagasawa et al.[8] showed that Cl^- ion interacted with sodium poly(vinyl alcohol) sulfate to only a slight degree. This slight coion–polyion interaction was observed for chloride ion interacting with sodium and calcium (carboxymethyl)cellulose.[9] Other reported investigations indicate that the Cl^- ion activity coefficients in aqueous NaCl solutions are the same in the presence and absence of sodium poly(styrenesulfonate)[10] sodium polyphosphate,[11] sodium dextran sulfate,[11] and sodium pectinates of several charge densities.[12]

From the experimental evidence it appears that the coion–polyion interaction is negligible or almost negligible. It was desirable to further explore if these findings are general, so polycations of different structures, shown in

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Table II
Average Values of Sodium Ion Diffusion Ratios $D_{Na^+}/D^\circ_{Na^+}$ in Aqueous NaBr or NaCl Solutions Containing Cationic Polyelectrolytes at 25 °C[a]

polycation[b]	NaX concentration, N			
	0.000 50	0.0010	0.0050	0.010
3-3 ionene bromide	1.00 ± 0.01	1.01 ± 0.03	1.04 ± 0.04	1.01 ± 0.04
4-4 ionene bromide	1.04 ± 0.02	1.07 ± 0.02	1.06 ± 0.03	1.02 ± 0.04
6-6 ionene bromide	1.01 ± 0.03	1.02 ± 0.02	1.00 ± 0.02	1.00 ± 0.05
PDABOBBr	1.01 ± 0.02	1.00 ± 0.04	1.02 ± 0.03	1.00 ± 0.02
PDADMACl	0.98 ± 0.06	0.98 ± 0.04	1.02 ± 0.05	
PVBTMACl	0.98 ± 0.02	0.98 ± 0.02		0.98 ± 0.00

[a] $D^\circ_{Na^+} = 1.33 \times 10^{-5}$ cm^2 s^{-1}. [b] See Table I.

Table I, were used. In addition to linear alkyl ionene halides, where the charge group is incorporated into the backbone of the chain, linear ionene halides containing rings in the backbones were studied. These are poly(*N*,*N'*-dimethyl-*N*,*N'*-dibutylpiperazinium bromide) (PDMBPBr) and poly(1,4-diazabicyclo[2.2.2]octylbutylene bromide) (PDABOBBr). Ionene halides are useful polyelectrolytes for study because the linear charge density can be varied without changing the basic chemical structure. To compare the results obtained using ionene halides with cationic polyelectrolytes whose charges are pendant from the backbone, poly[(vinylbenzyl)trimethylammonium chloride) (PVBTMACl) and poly(diallyldimethylammonium chloride) (PDADMACl) were also used. Tracer diffusion coefficients and single-ion activity coefficients for Na^+ and Ca^{2+} ions were determined in aqueous salt solutions containing the polycations mentioned above.

Experimental Section

The preparation of PDIPBr, PDIBBr, and PDIHBr by the Menschutkin reaction has been described elsewhere.[6,7] In aqueous 0.40 N KBr, these polyelectrolytes had intrinsic viscosities of 0.13, 0.12, and 0.32 dL/g, respectively. The PDMBPBr and PDABOBBr ionenes were prepared by a similar procedure; their monomers, *N*,*N'*dimethylpiperazine, 1,4-diazabicyclo[2.2.2]octane, and 1,4-dibromobutane, were purchased from Aldrich Chemical Co. In aqueous 0.10 N NaBr, PDMBPBr had an intrinsic viscosity of 0.10 dL/g and PDABOBBr had an intrinsic viscosity of 0.11 dL/g. The PDADMACl sample, kindly supplied by Calgon Corp., had an intrinsic viscosity of 0.62 dL/g in aqueous 0.10 N NaCl, and the PVBTMACl sample, purchased from Polysciences Inc., had an intrinsic viscosity of 0.12 dL/g in aqueous 0.10 N NaCl.

Tracer diffusion measurements have been described previously.[4-6]

To determine the coion activity in cationic polyelectrolyte solutions containing NaBr or NaCl and $CaBr_2$ or $CaCl_2$, an Orion 94-11 sodium ion electrode and an Orion 93-30 calcium ion electrode were used, respectively, in conjunction with an Orion 90-02 double-junction reference electrode. The emf values were measured with an Orion Model 801A pH meter whose accuracy is 0.1 mV. The measurements were carried out in a constant-temperature bath at 25.00 ± 0.01 °C. High-purity dry-grade nitrogen gas was bubbled through all solutions at a constant rate. A potential that was constant over a 10-min period was considered a reliable emf, and a reproducibility of 0.1 mV was obtained, which corresponds to an uncertainty of 0.002 activity coefficient units. The calibration of electrodes was carried out at the beginning and at the end of each run using solutions of the appropriate simple salt in the absence of polyelectrolyte. In the concentration range studied, the slopes of the plot of emf in millivolts vs. log a_i (where a_i is the activity of species i in the concentration range studied) were always found to give values close to Nernstian behavior (±5%). The emf of polyelectrolyte solutions of the desired concentrations determined and the millivolt reading obtained were related to the corresponding activities via the sodium bromide or calcium bromide reference scale obtained from the extended Debye–Hückel equation. The activity coefficient γ_i of species i is the ratio of its activity a_i to its concentration, permitting calculation of the small ion activity coefficients. The data are reported as the ratio of the experimental ion activity coefficients in the presence of polyelectrolyte to that in the absence of polyelectrolyte at the same simple salt concentration, i.e., γ_i/γ°_i. In order to ensure accuracy in the value of the ratio γ_i/γ°_i, each emf measurement of polyelectrolyte–simple salt solution was followed by immediate checks on calibration using the appropriate standard simple salt solution.

Results and Discussion

Tracer Diffusion Coefficients. To determine the long-range interactions of monovalent and divalent coions with polycations, sodium ion tracer diffusion coefficients D_{Na^+} and calcium ion tracer diffusion coefficients $D_{Ca^{2+}}$ were determined in aqueous NaCl or NaBr and $CaCl_2$ or $CaBr_2$ solutions, respectively, containing different cationic polyelectrolytes. The tracer diffusion coefficients were determined at constant salt concentrations of 0.000 50, 0.0010, 0.0050, and 0.010 N, with the equivalent concentration of the polyelectrolyte varying from 5.0×10^{-5} to 1.0×10^{-1} N. Generally, the X values were 0.5, 1.0, 2.0, 3.0, 5.0, 8.0, and 10.0, with $X = N_p/N_s$. The reported ion diffusion coefficient at each X value is an average of at least six experimental determinations, with the reproducibility given as the standard deviation. All $D_{Na^+}/D^\circ_{Na^+}$ values are given in Table A-1.

For the 3–3, 4–4, and 6–6 ionene bromides, the average $D_{Na^+}/D^\circ_{Na^+}$ values for each salt concentration, given in Table II, were found to be independent of X. The $D_{Na^+}/D^\circ_{Na^+}$ values are close to unity for the 3–3, 4–4, and 6–6 ionene bromides and are independent of the linear charge density of the polyelectrolyte, with respective values of ξ of 1.43, 1.14, and 0.81, and independent of *both* the polyelectrolyte and salt concentrations over the large equivalent concentration range studied. It appears that the monovalent Na^+ ion is repelled from the domain of the polyelectrolyte and behaves as if the polyion were not present. Tables II and A-1 show that the same effect is obtained if the ionene bromide contains a ring with charged groups incorporated into the backbone since the $D_{Na^+}/D^\circ_{Na^+}$ values obtained for PDABOBBr ($\xi = 1.59$) are close to unity over the whole concentration range studied. Tables II and A-1 also show that the Na^+ coion has a negligible interaction with polycations whose charged groups are pendant from the backbone since the mean $D_{Na^+}/D^\circ_{Na^+}$ values for PVBTMACl ($\xi = 2.8$) and for PDADMACl ($\xi = 1.25$) are close to unity.

The sodium salts of polyacrylate,[1] poly(styrenesulfonate),[2] algin,[3] and heparin[4] showed no or little ionic strength dependence of $D_{Cl^-}/D^\circ_{Cl^-}$, while sodium dextran sulfate[4] showed a dependence. Generally, $D_{Cl^-}/D^\circ_{Cl^-}$ coion ratios were reported to decrease initially from unity as X increased and level off at approximately $D_{Cl^-}/D^\circ_{Cl^-} \simeq 0.90$ for $X > 5$. For anionic polyelectrolytes, monovalent coion tracer diffusion ratios appear to differ slightly from the unity values observed for cationic polyelectrolytes. It appears that the higher charge density Na^+ *counterions*

Table III
Average Values of Calcium Ion Diffusion Ratios $D_{Ca^{2+}}/D^{\circ}_{Ca^{2+}}$ for $X < 5$ in Aqueous $CaBr_2$ or $CaCl_2$ Solutions Containing Cationic Polyelectrolytes at 25 °C[a]

	CaX_2 concentration, N			
polyelectrolyte[b]	0.000 50	0.0010	0.0050	0.0100
3-3 ionene bromide	1.02 ± 0.04	0.96 ± 0.02	1.00 ± 0.06	1.00 ± 0.07
4-4 ionene bromide	1.04 ± 0.04	1.02 ± 0.04	1.00 ± 0.07	1.00 ± 0.07
6-6 ionene bromide	1.00 ± 0.06	0.91 ± 0.04	0.92 ± 0.04	1.00 ± 0.07
PDABOBBr	1.04 ± 0.06	1.06 ± 0.09	1.01 ± 0.06	0.96 ± 0.02
PDMBPBr	0.99 ± 0.05	0.98 ± 0.02	1.02 ± 0.03	0.98 ± 0.03
PDADMACl	1.00 ± 0.03	1.01 ± 0.04	1.03 ± 0.03	1.01 ± 0.04
PVBTMACl	0.93 ± 0.03		0.96 ± 0.03	0.96 ± 0.04

[a] $D^{\circ}_{Ca^{2+}} = 7.92 \times 10^{-6}$ cm^2 s^{-1}. [b] See Table I.

influence "their" Cl^- coions, pulling them closer to the polyanion, more than the lower charge density Cl^- *counterions* influence "their" Na^+ coions in the presence of a polycation.

Calcium ion tracer diffusion coefficients $D_{Ca^{2+}}$ were determined at 25 °C for aqueous solutions of 3-3, 4-4, and 6-6 ionene bromides, PDABOBBr, PVBTMACl, PDADMACl, and (PDMBPBr) ($\xi = 1.59$) containing $CaBr_2$ or $CaCl_2$. The equivalent concentrations of polyelectrolyte and salt and the X values were the same as used for the sodium ion diffusion experiments. All $D_{Ca^{2+}}/D^{\circ}_{Ca^{2+}}$ values are given in Table A-2 and the average of $D_{Ca^{2+}}/D^{\circ}_{Ca^{2+}}$ values for $X < 5$ for each salt concentration are given in Table III. While the diffusion coefficient ratios were found to be fairly constant for $X < 5$, lower values were observed at $X = 5.0$, 8.0, and 10.0, especially for 0.0050 and 0.10 N salt. Of course, at these higher polyelectrolyte and salt concentrations there is a greater expectancy of divalent coion-polyion and polyion-polyion interactions. Table III shows that, within experimental error, all average $D_{Ca^{2+}}/D^{\circ}_{Ca^{2+}}$ values for $X < 5$ are close to unity. This indicates that in dilute solution the divalent Ca^{2+} coion behaves like the monovalent Na^+ coion, and neither coion interacts with polycations to any significant extent.

It has been reported that divalent SO_4^{2-} coion interacts with anionic polyelectrolytes since $D_{SO_4^{2-}}/D^{\circ}_{SO_4^{2-}}$ is lower than unity over most of the range of X employed. At the lowest salt concentration (0.000 50 N), $D_{SO_4^{2-}}/D^{\circ}_{SO_4^{2-}}$ achieved fairly constant values of approximately 0.90, 0.80, 0.85, and 0.75 for the sodium salts of poly(styrenesulfonate),[2] algin,[3] carrageenan,[3] and dextran sulfate,[4] respectively, for $1.0 < X < 10$ and also, an ionic strength dependence was noted. The sodium salts of heparin[4] yielded ionic strength independent values of $D_{SO_4^{2-}}/D^{\circ}_{SO_4^{2-}}$ of approximately 0.90. The reason as to why divalent SO_4^{2-} coions interact with polyanions to some extent, while divalent Ca^{2+} coions do not interact with polycations can be rationalized as was stated previously for the monovalent coion cases. Calcium counterions are more efficient than are sulfate counterions in attracting their respective coions closer to the polyelectrolyte, resulting in larger anion-polyanion interaction compared to cation-polycation interaction.

Manning's model[13] assumes that the coions interact with the polyion to the same extent as do uncondensed counterions. The experimental diffusion results presented here and elsewhere do not agree with this. Manning's theoretical equation is

$$D_2/D^{\circ}_2 = 1 - Z_2^2 A(1,\xi^{-1}X)/3 \tag{2}$$

where Z_2 is the charge on the coion and $A(1,\xi^{-1}X)$ is the Debye-Hückel coion-polyion interaction term for $\xi_c = |Z_1|^{-1} = 1$. Figure 1 illustrates plots of eq 2 for $\xi = 1.1$ and $\xi = 2.8$, each for $|Z_2| = 1$, 2, and 3 with $|Z_1| = 1$. The predicted values obtained with $|Z_2| = 1$ are in approximate accord with the reported results for Cl^- ion interacting in polyanions of several charge densities. However, multivalent coions interact with polyanions to a much lesser extent than is predicted by eq 2. From the experimental data presented here, it can be generalized that coions do not interact with polycations since D_2/D°_2 values were always close to unity. Clearly, from Figure 1, the coion-polyion interaction is overestimated theoretically, especially for multivalent coions. To test eq 2 appropriately, values of D_2/D°_2 should be obtained for the dilute range $0 < X < 1$, i.e., for $N_p < N_s$, inasmuch as the Debye-Hückel interaction term is obtained from a truncated series expansion. Some of the data for Ca^{2+} ion diffusion in this range indicate that the percentage decrease observed at low X values is approximately the percentage decrease accounted for from the theoretical predictions. Experiments in this concentration range are being undertaken.

Table IV
Average Sodium Ion Activity Coefficient Ratios $\gamma_2/\gamma^{\circ}_2$ for $0 < X < 5$ at Constant NaBr Concentrations for Several Ionene Bromides

ionene bromide	N_s	$\gamma_2/\gamma^{\circ}_2$
3-3	0.00050	1.04 ± 0.02
	0.0010	1.02 ± 0.02
4-4	0.0010	0.99 ± 0.04
4-6	0.0010	0.96 ± 0.02
6-6	0.00050	1.01 ± 0.05
	0.0010	0.96 ± 0.01

Coion Activity Coefficients. In addition to coion tracer diffusion coefficients, single-ion activity coefficients were determined to monitor the long-range interactions between coions and cationic polyelectrolytes. Sodium ion activity coefficient ratios $\gamma_{Na^+}/\gamma^{\circ}_{Na^+}$ (or $\gamma_2/\gamma^{\circ}_2$), where γ_{Na^+} and $\gamma^{\circ}_{Na^+}$ are the sodium ion activity coefficients in the presence and absence of polyelectrolyte, respectively, and the subscript 2 is the symbol for the coion, were determined in aqueous NaBr or NaCl solutions containing the 3-3, 4-4, 4-6, and 6-6 ionene bromides and PVBTMACl. Polyelectrolyte concentrations were varied such that in constant NaBr or NaCl solutions of 0.0010, 0.0050, and 0.010 N, the values of X ranged from 0.1 to 10.0. For the 3-3 and 6-6 ionene bromides, 0.000 50 N NaBr was also used over the same range of X. The data are given in Table A-3. Except for 3-3 ionene bromide for $X < 1$ in 0.0050 and 0.10 N NaBr, it is obvious from Table A-3 that the sodium coion activity coefficient ratio is constant and close to unity for all the polyelectrolytes studied here; i.e., $\gamma_2/\gamma^{\circ}_2$ is independent of N_p and N_s for monovalent coions. Table IV shows the average $\gamma_{Na^+}/\gamma^{\circ}_{Na^+}$ values for $X < 5$ for the ionene bromides at low salt concentrations. The average value for all $\gamma_{Na^+}/\gamma^{\circ}_{Na^+}$ determinations given in Table A-3 is 0.99 ± 0.03. (It is interesting that for the 3-3 ionene bromide in 0.0050 and 0.010 N NaBr, $\gamma_{Na^+}/\gamma^\circ_{Na^+}$ was approximately unity only for $X < 1$, while $D_{Na^+}/D^\circ_{Na^+}$ was approximately unity for the whole range of X.) The values of γ_2/γ°_2 for Cl^-, Br^-, and I^- in aqueous sodium halide solutions containing sodium poly(styrenesulfonate) and sodium dextran sulfate are generally close to unity over an appreciable X range,[11] as are the reported values for Cl^- in aqueous NaCl solutions containing sodium pectinates of different charge densities.[12] Except for a few exceptions then, the coion activity coefficient results presented here and elsewhere indicate that monovalent coions are especially repelled from a greater part of the ion atmosphere of polycations and of polyanions.

Table V
Calcium Ion Activity Coefficient Ratios $\gamma_{Ca^{2+}}/\gamma^\circ_{Ca^{2+}}$ in Aqueous $CaBr_2$ Solutions Containing 3-3 Ionene Bromide

X	0.0050 N $CaBr_2$	0.0100 N $CaBr_2$
0.1	1.02	0.98
0.5	1.01	0.97
1.0	1.00	0.96
2.0	1.03	0.99
3.0	1.03	1.02
5.0	1.07	1.06
8.0	1.14	1.09
10.0	1.18	1.13

Calcium ion activity coefficient ratios $\gamma_{Ca^{2+}}/\gamma^\circ_{Ca^{2+}}$ were determined in 0.0050 and 0.010 N $CaBr_2$ containing the 3-3 ionene bromide. The data are in Table V. For $X < 5$, all the data points give $\gamma_{Ca^{2+}}/\gamma^\circ_{Ca^{2+}} = 1.00 \pm 0.02$ as a mean value. Clearly, monovalent and divalent coions appear *not* to interact with polycations to any significant extent, surely at low X values, as evidenced from the ex-

Table A-1
Sodium Diffusion Ratios $D_{Na^+}/D^\circ_{Na^+}$ in Aqueous NaBr or NaCl Solutions Containing Cationic Polyelectrolytes at 25 °C[a]

		NaX concentration, N			
polyelectrolyte	X	0.000 50	0.0010	0.0050	0.010
3-3 ionene bromide	0.1	1.02 ± 0.01	1.05 ± 0.02	1.08 ± 0.01	1.04 ± 0.03
	0.5	1.00 ± 0.02	0.99 ± 0.02	1.08 ± 0.01	1.05 ± 0.04
	1.0	0.96 ± 0.02	0.98 ± 0.01	1.06 ± 0.02	1.04 ± 0.02
	2.0	1.04 ± 0.03	1.01 ± 0.05	1.04 ± 0.03	0.94 ± 0.03
	3.0	0.99 ± 0.03	0.05 ± 0.02	1.01 ± 0.02	0.96 ± 0.02
	5.0	0.98 ± 0.03	0.96 ± 0.02	1.04 ± 0.04	1.04 ± 0.03
	8.0	1.01 ± 0.02	1.03 ± 0.01	0.96 ± 0.02	1.01 ± 0.03
	10.0	0.98 ± 0.02	1.01 ± 0.00	1.02 ± 0.03	0.96 ± 0.01
4-4 ionene bromide	0.1	1.05 ± 0.01	1.05 ± 0.02	1.05 ± 0.03	1.07 ± 0.03
	0.5	1.04 ± 0.01	1.08 ± 0.01	1.07 ± 0.01	1.04 ± 0.01
	1.0	1.03 ± 0.01	1.08 ± 0.01	1.06 ± 0.01	1.01 ± 0.02
	2.0	1.02 ± 0.03	1.09 ± 0.01	1.08 ± 0.02	0.98 ± 0.06
	3.0	1.04 ± 0.03	1.11 ± 0.03	1.11 ± 0.03	1.05 ± 0.01
	5.0	1.07 ± 0.02	1.05 ± 0.01	1.06 ± 0.03	1.06 ± 0.01
	8.0	1.04 ± 0.01	1.09 ± 0.04	1.03 ± 0.03	0.98 ± 0.02
	10.0	1.01 ± 0.03	1.04 ± 0.01	1.00 ± 0.01	0.96 ± 0.03
6-6 ionene bromide	0.1	1.00 ± 0.02	1.02 ± 0.01	1.01 ± 0.01	1.12 ± 0.03
	0.5	1.03 ± 0.03	1.00 ± 0.01	0.99 ± 0.02	1.00 ± 0.01
	1.0	0.98 ± 0.01	0.98 ± 0.01	1.02 ± 0.02	0.98 ± 0.01
	2.0	1.05 ± 0.03	1.04 ± 0.02	1.02 ± 0.01	0.99 ± 0.01
	3.0	1.01 ± 0.01	1.03 ± 0.03	0.98 ± 0.01	0.97 ± 0.02
	5.0	0.99 ± 0.01	1.01 ± 0.01	0.96 ± 0.03	0.98 ± 0.01
	8.0	1.05 ± 0.02	1.01 ± 0.02	1.03 ± 0.01	0.97 ± 0.02
	10.0	1.00 ± 0.01	1.04 ± 0.03	1.02 ± 0.01	0.96 ± 0.03
PDABOBBr	0.1	1.03 ± 0.01	1.02 ± 0.04	1.05 ± 0.01	1.02 ± 0.02
	0.5	1.04 ± 0.02	1.02 ± 0.02	0.99 ± 0.02	0.99 ± 0.01
	1.0	1.02 ± 0.01	0.95 ± 0.01	1.05 ± 0.02	1.02 ± 0.02
	2.0	0.98 ± 0.01	1.02 ± 0.03	1.03 ± 0.02	0.97 ± 0.02
	3.0	1.00 ± 0.02	1.05 ± 0.01	1.02 ± 0.01	0.96 ± 0.02
	5.0	0.99 ± 0.02	0.96 ± 0.02	1.03 ± 0.02	1.02 ± 0.01
	8.0	0.98 ± 0.01	0.97 ± 0.03	1.00 ± 0.03	1.01 ± 0.01
	10.0	1.00 ± 0.02	1.02 ± 0.02	0.98 ± 0.02	0.99 ± 0.02
PDADMACl	0.1	1.05 ± 0.02	1.03 ± 0.02	1.08 ± 0.03	
	0.5	1.06 ± 0.01	1.06 ± 0.01	0.99 ± 0.02	
	1.0	1.05 ± 0.03	0.95 ± 0.01	0.97 ± 0.03	
	2.0	0.95 ± 0.03	0.97 ± 0.03	1.01 ± 0.02	
	3.0	0.93 ± 0.01	0.94 ± 0.00	0.98 ± 0.01	
	5.0	0.94 ± 0.02	1.00 ± 0.03	1.03 ± 0.02	
	8.0	0.94 ± 0.01	0.98 ± 0.02	1.09 ± 0.02	
	10.0	0.94 ± 0.02	0.94 ± 0.02	0.97 ± 0.01	
PVBTMACl	0.1	0.96 ± 0.03	0.96 ± 0.02		0.96 ± 0.02
	0.5	0.99 ± 0.02	0.99 ± 0.03		0.99 ± 0.01
	1.0	0.98 ± 0.04	0.96 ± 0.02		0.98 ± 0.02
	2.0	1.00 ± 0.03	1.01 ± 0.05		1.00 ± 0.05
	3.0	0.95 ± 0.05	0.99 ± 0.02		0.95 ± 0.02
	5.0	0.99 ± 0.01	1.00 ± 0.04		0.99 ± 0.04
	8.0	0.97 ± 0.02	0.99 ± 0.04		0.97 ± 0.03
	10.0	0.97 ± 0.02	0.95 ± 0.01		0.97 ± 0.03

[a] $D^\circ_{Na^+} = 1.33 \times 10^{-5}\ cm^2\ s^{-1}$.

Table A-2
Calcium Ion Diffusion Ratios $D_{Ca^{2+}}/D°_{Ca^{2+}}$ in Aqueous $CaBr_2$ Solutions Containing Cationic Polyelectrolytes at 25 °C[a]

polyelectrolyte	X	CaX_2 concentration, N			
		0.000 50	0.0010	0.0050	0.010
3-3 ionene bromide	0.1	1.09 ± 0.01	1.00 ± 0.03	1.09 ± 0.02	1.05 ± 0.01
	0.5	1.04 ± 0.02	0.97 ± 0.03	1.02 ± 0.01	0.94 ± 0.02
	1.0	1.01 ± 0.02	0.95 ± 0.01	1.01 ± 0.03	0.97 ± 0.02
	2.0	1.00 ± 0.01	0.95 ± 0.01	0.92 ± 0.02	0.97 ± 0.01
	3.0	0.98 ± 0.02	0.93 ± 0.02	0.95 ± 0.02	0.97 ± 0.03
	5.0	0.97 ± 0.00	0.92 ± 0.02	0.97 ± 0.03	0.95 ± 0.03
	8.0	0.97 ± 0.01	0.92 ± 0.03	0.95 ± 0.03	0.95 ± 0.02
	10.0	0.96 ± 0.02	0.92 ± 0.01	0.96 ± 0.02	0.93 ± 0.02
4-4 ionene bromide	0.1	1.05 ± 0.01	1.07 ± 0.01	1.04 ± 0.02	1.01 ± 0.01
	0.5	1.05 ± 0.01	1.04 ± 0.01	1.06 ± 0.01	1.10 ± 0.01
	1.0	1.11 ± 0.02	0.96 ± 0.01	0.96 ± 0.02	0.91 ± 0.03
	2.0	1.00 ± 0.01	1.05 ± 0.03	1.08 ± 0.01	1.04 ± 0.03
	3.0	1.01 ± 0.01	0.99 ± 0.01	0.89 ± 0.01	0.95 ± 0.02
	5.0	1.05 ± 0.01	1.08 ± 0.01	0.99 ± 0.02	0.90 ± 0.01
	8.0	0.95 ± 0.01	1.03 ± 0.01	0.90 ± 0.02	0.91 ± 0.01
	10.0	0.98 ± 0.02	0.94 ± 0.02	0.86 ± 0.02	0.99 ± 0.04
5-6 ionene bromide	0.1	1.01 ± 0.04	0.97 ± 0.01	0.97 ± 0.01	1.07 ± 0.02
	0.5	1.10 ± 0.03	0.88 ± 0.03	0.95 ± 0.04	1.06 ± 0.03
	1.0	0.94 ± 0.01	0.91 ± 0.04	0.85 ± 0.03	1.03 ± 0.04
	2.0	0.98 ± 0.03	0.85 ± 0.03	0.89 ± 0.04	0.98 ± 0.03
	3.0	0.95 ± 0.02	0.86 ± 0.02	0.93 ± 0.04	0.87 ± 0.04
	5.0	0.93 ± 0.03	0.93 ± 0.03	0.97 ± 0.03	0.86 ± 0.03
	8.0	0.92 ± 0.03	0.95 ± 0.02	0.93 ± 0.02	0.86 ± 0.03
	10.0	0.92 ± 0.02	0.92 ± 0.03	0.93 ± 0.04	0.81 ± 0.04
PDABOBBr	0.1	1.15 ± 0.04	1.18 ± 0.03	1.11 ± 0.02	0.98 ± 0.06
	0.5	1.08 ± 0.03	1.10 ± 0.02	1.02 ± 0.03	0.97 ± 0.07
	1.0	0.99 ± 0.02	0.97 ± 0.03	0.98 ± 0.05	0.98 ± 0.03
	2.0	0.98 ± 0.01	0.98 ± 0.04	0.95 ± 0.05	0.94 ± 0.04
	3.0	1.02 ± 0.02		0.97 ± 0.02	0.95 ± 0.01
	5.0	1.01 ± 0.02	0.98 ± 0.03	0.90 ± 0.03	0.94 ± 0.03
	8.0	1.03 ± 0.02	1.08 ± 0.01	0.91 ± 0.04	0.91 ± 0.06
	10.0	0.99 ± 0.01	0.96 ± 0.03	0.90 ± 0.03	0.92 ± 0.05
PDMBPBr	0.1	1.00 ± 0.01	1.01 ± 0.00	1.07 ± 0.03	1.02 ± 0.02
	0.5	1.04 ± 0.03	0.96 ± 0.01	1.05 ± 0.03	0.99 ± 0.01
	1.0	1.03 ± 0.01	1.01 ± 0.00	0.99 ± 0.03	1.00 ± 0.02
	2.0	0.95 ± 0.02	0.98 ± 0.02	1.01 ± 0.02	0.92 ± 0.02
	3.0	0.92 ± 0.02	0.96 ± 0.01	0.99 ± 0.02	0.99 ± 0.02
	5.0	0.93 ± 0.03	0.96 ± 0.00	1.00 ± 0.02	0.94 ± 0.03
	8.0	0.97 ± 0.02	1.01 ± 0.01	1.04 ± 0.02	0.95 ± 0.02
	10.0	0.95 ± 0.01	0.95 ± 0.01	1.06 ± 0.01	0.90 ± 0.00
PDADMACl	0.1	1.03 ± 0.02	1.03 ± 0.03	1.04 ± 0.04	0.98 ± 0.01
	0.5	0.99 ± 0.01	1.09 ± 0.02	1.06 ± 0.03	1.01 ± 0.02
	1.0	0.96 ± 0.03	1.00 ± 0.02	0.97 ± 0.02	0.96 ± 0.04
	2.0	0.99 ± 0.02	0.98 ± 0.02	1.01 ± 0.03	1.05 ± 0.02
	3.0	1.02 ± 0.01	0.96 ± 0.03	1.06 ± 0.04	1.07 ± 0.02
	5.0	1.01 ± 0.01	1.08 ± 0.02	1.02 ± 0.04	1.03 ± 0.01
	8.0	1.03 ± 0.02	1.09 ± 0.03	1.02 ± 0.04	1.00 ± 0.01
	10.0	0.97 ± 0.03	1.04 ± 0.02	1.04 ± 0.04	1.04 ± 0.03
PVBTMACl	0.1	0.96 ± 0.02		0.98 ± 0.04	1.03 ± 0.03
	0.5	0.91 ± 0.03		0.99 ± 0.05	0.99 ± 0.03
	1.0	0.92 ± 0.90		0.92 ± 0.04	0.93 ± 0.02
	2.0	0.95 ± 0.04		0.94 ± 0.05	0.95 ± 0.03
	3.0	0.89 ± 0.02		0.98 ± 0.04	0.89 ± 0.03
	5.0	0.94 ± 0.04		0.94 ± 0.02	0.90 ± 0.06
	8.0	0.93 ± 0.03		0.89 ± 0.02	0.89 ± 0.03
	10.0	0.94 ± 0.02		0.98 ± 0.04	0.90 ± 0.02

[a] $D°_{Ca^{2+}} = 7.92 \times 10^{-6}$ cm^2 s^{-1}.

perimental results presented.

The condensation theory of Manning,[13] the Poisson–Boltzmann theory of Gueron and Weisbuch,[14] and the cluster theory of Iwasa and Kwak[15] predict values for the single-ion activity coefficients of small ions in the presence of polyelectrolytes. Since explicit coion activity coefficient expressions have been obtained from these theories, a brief comparison of the theoretical predictions with the experimental findings will be made.

For polyelectrolytes with $\xi > \xi_c$, the condensation theory states that coions interact with an infinite line charge of an effective $\xi_c = |Z_1|^{-1}$, just as uncondensed counterions do. The theoretical coion activity coefficient ratio $\gamma_2/\gamma°_2$ for $|Z_1| = 1$ is

$$\gamma_2/\gamma°_2 = \exp\{-\xi^{-1}|Z_2|^2/2[X/(|Z_p|\xi^{-1}X + 1 + |Z_2|)]\} \quad (3)$$

where $|Z_p|$ is the absolute charge on a monomeric unit, usually unity. Figure 2 illustrates theoretical plots of

Table A-3
Sodium Ion Activity Coefficient Ratios γ_2/γ°_2 in Aqueous NaBr or NaCl Solutions Containing Polycationic Polyelectrolytes at 25 °C

		NaX concentration, N			
polyelectrolyte	X	0.000 50	0.0010	0.0050	0.010
3-3 ionene bromide	0.1	1.05	1.02	1.03	0.97
	0.5	1.06	1.04	0.98	0.97
	1.0	1.00	1.02	0.95	0.94
	2.0	1.05	1.05	0.93	0.94
	3.0	1.03	0.99	0.90	0.93
	5.0	1.04	0.96	0.91	0.92
	8.0	1.05	0.97	0.90	0.91
	10.0	1.02	0.91	0.89	0.91
4-4 ionene bromide	0.1		1.05	1.02	1.02
	0.5		1.00	0.99	0.99
	1.0		0.97	0.98	0.97
	2.0		0.96	0.96	0.97
	3.0		0.96	0.93	0.97
	5.0		0.96	0.94	0.95
	8.0		0.96	0.97	0.96
	10.0		0.96	0.95	0.96
4-6 ionene bromide	0.5		0.97	1.00	1.00
	1.0		0.98	0.99	1.03
	2.0		0.96	1.01	1.01
	3.0		0.94	0.98	1.01
	5.0		0.98	1.01	1.00
	8.0		0.99	1.01	0.98
	10.0		0.99	1.02	0.99
6-6 ionene bromide	0.1	1.07	0.95	1.00	
	0.5	1.06	0.97	0.94	
	1.0	0.94	0.95	0.94	
	2.0	0.97	0.96	0.94	
	3.0	1.02	0.98	0.94	
	5.0	1.04	0.96	0.96	
	8.0	1.04	0.97	0.93	
	10.0	1.03	0.98	0.94	
PVBTMACl	0.1		0.96	0.99	0.99
	0.5		0.95	0.98	0.98
	1.0		0.92	0.98	1.02
	2.0		0.91	0.97	1.04
	3.0		0.93	0.97	1.03
	5.0		0.93	0.96	1.07
	8.0		0.96	1.02	1.15
	10.0		0.94	1.06	1.22

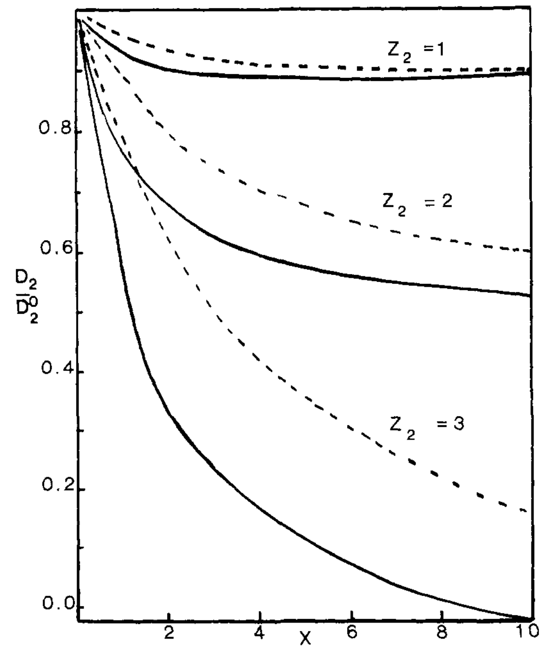

Figure 1. Plots of theoretical eq 2 for ξ_c = 1, $|Z_1|$ = 1, ξ = 2.8 (dashed lines), ξ = 1.1 (solid lines), and (from bottom to top) $|Z_2|$ = 1, 2, and 3.

γ_2/γ°_2 from X = 0 to X = 10 for 1.1, where M1, M2, I1, I2, G1, and G2 are the activity coefficient curves for Z_2 = 1 and 2 for the Manning, Iwasa, and Gueron–Weisbuch theories, respectively. The condensation theory predictions given by eq 3 for ξ = 1.1 have the γ_2/γ°_2 values decreasing from unity at X = 0 to 0.72 at X = 10 for $|Z_2|$ = 1. (While not shown in Figure 2, eq 3 predicts that the curves in Figure 2 would be displaced slightly higher for higher ξ values at each value of Z_2.) Clearly, this predicted decrease in γ_2/γ°_2 with increasing X is not in accord with the experimental results obtained for different polyelectrolytes, which show γ_2/γ°_2 to be independent of X, ξ, and Z_2. Coions must be repelled by the polyion and are not expected to interact with the polyion in a manner similar to that of uncondensed counterions, as is assumed in condensation theory.

The Poisson–Boltzmann analysis of the cell model by Gueron and Weisbuch[14] makes no special reference to the distribution of counterions near the polyelectrolyte, as does condensation theory. While the counterion activity coefficients predicted by both theories are close in value, the coion activity coefficients predicted by both theories differ. The Gueron–Weisbuch (GW) theory for the coions with $|Z_1|$ = 1 gives

$$\gamma_2/\gamma^\circ_2 = (0.7X\xi^{-1} + 1)/(0.53X\xi^{-1} + 1) \qquad (4)$$

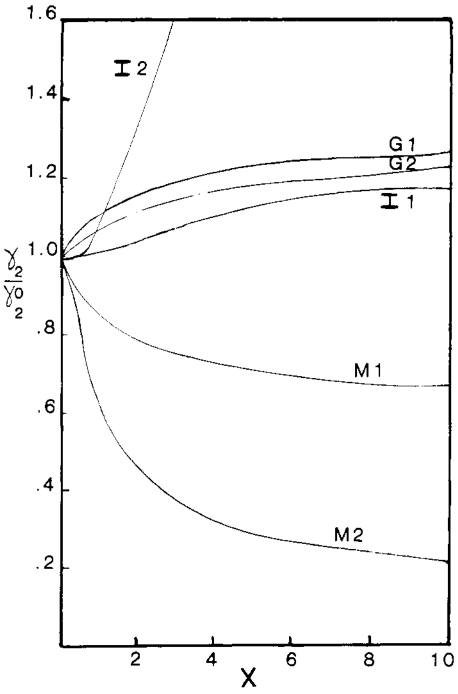

Figure 2. Plots of theoretical eq 3–5 for $\xi_c = 1$, $|Z_1| = 1$, and $\xi = 1.1$ with $|Z_2| = 1$ and 2.

where for Z_2 valent coions ξ is replaced by ξZ_2. Figure 2 shows the theoretical γ_2/γ°_2 value dependence on X for $|Z_2| = 1$ and 2 and $\xi = 1.1$, which are labeled G1 and G2, respectively, calculated from eq 4. Equation 4 predicts that γ_2/γ°_2 is greater than unity and has a value of $\gamma_2/\gamma^\circ_2 = 1.32$ for high X values, which is independent of the values of ξ and of Z_2. (While not shown in Figure 2, eq 4 predicts that the curves in Figure 2 would be displaced slightly lower for higher values of ξ and Z_2.) When the predictions of eq 4 are compared to the experimental findings, it is clear that theory is up to about 20% too high. Gueron and Weisbuch believe that the values predicted by eq 4 should be reduced by about 20% because of the interactions between ions at the cell boundary and because of the polarization of the counterion sheath.

The coion activity coefficient ratios for $\xi > \xi_c$ proposed by Iwasa and Kwak[15] was obtained by a statistical mechanical cluster technique applied to polyelectrolyte solutions. Equation 5

$$\frac{\gamma_2}{\gamma^\circ_2} = \exp\left\{\frac{\xi^{-1}X|Z_2|^2}{(1 + \xi^{-1}X)|Z_1| + |Z_2|}\left[-0.5 + 0.3906\left(\frac{(1 + X\xi^{-1})|Z_1| - |Z_2|^2}{(1 + X\xi^{-1})|Z_1| + |Z_2|} + |Z_2|\right)\right]\right\} \quad (5)$$

perhaps gives the best agreement with the experimental results for monovalent coions. From Figure 2, the I1 curve approximates unity for $X > 2$ and levels off at $\gamma_2/\gamma^\circ_2 \simeq 1.2$ for $X > 7$. For higher ξ values, the curve (not shown) is even closer to unity for monovalent coions. The theoretical divalent coion curve I2 in Figure 2 is approximately unity for $X > 1$ and then rises rapidly and continuously for $X > 1$, a prediction not in agreement with the experimental findings.

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