Polycations. 1. Sodium, Calcium, and Sulfate Ion Diffusion Coefficients in Aqueous Salt Solutions Containing Ionene Bromides

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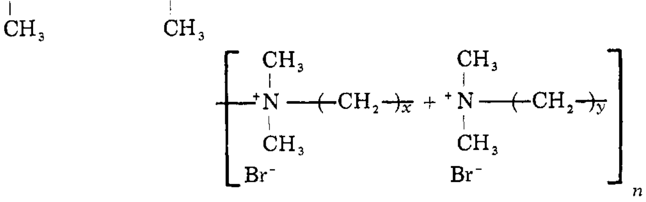
ABSTRACT: Tracer diffusion coefficients for Na^+, Ca^{2+}, and SO_4^{2-} ions were determined in aqueous solutions of the 3–3 and 4–4 ionene bromides, i.e., poly[(dimethylimino)propylene bromide] and poly[(dimethylimino)butylene bromide], respectively. The ionene bromide concentration ranged from 5.0×10^{-5} to 1.0×10^{-1} N, and the simple salt concentration ranged from 5.0×10^{-4} to 1.0×10^{-2} N. It was found that the diffusion coefficients for Na^+ and Ca^{2+} ions had their same respective values in the presence and absence of polyelectrolyte. The SO_4^{2-} ion diffusion coefficients exhibit similar behavior as do divalent Ca^{2+} counterions in solutions containing polyanions. The experimental values of the diffusion coefficients are correlated with those predicted by the Manning theory of polyelectrolyte solutions.

It is theoretically predicted and substantiated from experimental results that there are two predominant interactions between small ions and polyelectrolytes. A fraction of the counterions bind or condense onto the polyion if the linear charge density of the polyion is above a critical value. The remaining uncondensed counterions and the uncondensed coions are in the ionic atmosphere and interact with the polyion by Debye–Huckel forces.

Polyelectrolytes of relatively high charge density, having average distances between charged groups on the polyion between 1.7 and 4 Å, have been used experimentally to examine polyelectrolyte theories. Thus, the amount of counterions condensed onto the polyion chain is large, which causes the contribution of the condensation term in the theoretical expressions to be relatively large as compared to the Debye–Huckel interaction term. Hence, it is of interest to study the interactions of small ions with a polyelectrolyte whose charge density could be varied so that its values are close to the critical charge density.

All systematic investigations have been done with polyanions. To elucidate polyelectrolyte behavior further, polycations should be investigated. Quaternized polyimines, referred to as ionenes, are being used in our current study. One of the advantages of using quaternized polyimines is that the charge density can be varied by changing the number of methylene groups between the quaternized nitrogens. The linear polyquaternary ammonium compounds can be prepared by the reaction of ditertiary amines with dihalides (Menshutkin reaction)[1,2]



$$(CH_3)_2N\text{—}(CH_2)_x\text{—}N(CH_3)_2 + A(CH_2)_yA \rightarrow \left[\text{—}{}^+N(CH_3)_2\text{—}(CH_2)_x\text{—}{}^+N(CH_3)_2\text{—}(CH_2)_y\text{—}\right]_n \; Br^- \; Br^-$$

where A = Br or Cl. To study the interactions between small ions and polycations, the 3–3 and 4–4 ionene bromides, i.e., $x = y = 3$ and 4, were chosen initially for study because of the ease of preparation and because the distance between the charged groups in the respective polyion chains is about 0.50 and 0.63 nm when the chains are stretched to their contour length. The presence of the methyl groups on the nitrogens is to avoid any complications due to hydrogen bonding with water if hydrogen atoms were on the nitrogens.

Here we present the Na^+, Ca^{2+} and SO_4^{2-} tracer diffusion coefficients in aqueous solutions of the 3–3 and 4–4 ionene bromides, i.e., poly[(dimethylimino)propylene bromide] (PDIPBr) and poly[(dimethylimino)butylene bromide] (PDIBBr), respectively.

Experimental Section

Preparation. The 3–3 and 4–4 ionene bromides were prepared in the same manner. To two separate 100-mL mixtures of equivolumes of dimethylformamide and methanol, 0.3 mol of tetramethyldiaminopropane (or tetramethyldiaminobutane) and 0.3 mol of dibromopropane (or dibromobutane) were added. The two solutions were mixed and left undisturbed at room temperature for 1 week. The resulting white precipitate was filtered, dissolved in water, filtered, and precipitated from aqueous solution by adding acetone. This process was repeated several times, and the final product was dried under vacuum at 40 °C.

The NMR spectra of the prepared 3–3 and 4–4 ionene bromides in D_2O were found to be similar to the reported spectra.[1] Carbon, hydrogen, nitrogen and bromine analyses by the Schwarzkopf Microanalytical Laboratory indicated that the 3–3 and 4–4 ionene bromide samples prepared were the desired products, having equivalent weights of 166 and 180 g, respectively. The 3–3 and 4–4 ionene bromides gave intrinsic viscosity values of 0.13 and 0.12 dL/g, respectively, at 25 °C in 0.40 N KBr. From the reported Mark–Houwink equation for the 3–3 ionene bromide,[1] its molecular weight is 21 000, and the 4–4 ionene bromide is crudely approximated to be 19 000 from the Mark–Houwink equation for the 3–3 ionene bromide.

Results and Discussion

The capillary tracer diffusion measurements by the open-end capillary method were described in previous papers.[3-5] Self-diffusion coefficients could be determined by measuring the radioactive activity of the capillary contents after a known, measured time t, denoted as C_t, and the radioactive activity of the filled capillary at the start of diffusion, C_0. The relevant expression under the boundary conditions of this experiment is[6]

$$C_t/C_0 = 8\pi^{-2} \sum_{n=0}^{\infty} 1/(2n + 1)[\exp(-(2n + 1)^2\pi^2 Dt/4L^2)] \tag{1}$$

where D is the phenomenological self-diffusion constant for the labeled species and L is the capillary length. Equation 1 was inverted, with the aid of a computer, to obtain D for a given C_t/C_0 measurement. If $C_t/C_0 > 0.5$, a simple approximate inversion of eq 1 gives[7]

$$D = \pi 4^{-1}[1 - (C_t/C_0)]^2 L^2/t \qquad C_t/C_0 > 0.5 \tag{2}$$

Each reported value of a diffusion coefficient was based on at least six individual determinations of C_t and at least

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Table III
Sodium Ion Diffusion Coefficient Ratios $D_{Na^+}/D^0_{Na^+}$ in Aqueous NaBr Solutions Containing PDIPBr and PDIBBr[a]

X	0.00050 N NaBr	0.0010 N NaBr	0.0050 N NaBr	0.010 N NaBr
		PDIPBr		
0.1	1.02	1.05	1.08	1.04
0.5	1.00	0.99	1.08	1.05
1.0	0.96	0.98	1.06	1.04
2.0	1.04	1.01	1.04	0.94
3.0	0.99	1.05	1.01	0.96
5.0	0.98	0.96	1.04	1.04
8.0	1.01	1.03	0.96	1.01
10.0	0.98	1.01	1.02	0.96
		PDIBBr		
0.1	1.05	1.05	1.05	1.07
0.5	1.04	1.08	1.07	1.04
1.0	1.03	1.08	1.06	1.01
2.0	1.02	1.09	1.08	0.98
3.0	1.04	1.11	1.11	1.05
5.0	1.07	1.05	1.06	1.06
8.0	1.04	1.09	1.03	0.98
10.0	1.01	1.04	1.00	0.96

[a] $D^0_{Na^+} = 1.33 \times 10^{-5}$ cm²/s.

Table IV
Calcium Ion Diffusion Coefficient Ratios $D_{Ca^{2+}}/D^0_{Ca^{2+}}$ in Aqueous $CaBr_2$ Solutions Containing PDIPBr and PDIBBr[a]

X	0.00050 N $CaBr_2$	0.0010 N $CaBr_2$	0.0050 N $CaBr_2$	0.0100 N $CaBr_2$
		PDIPBr		
0.2	1.09	1.00	1.09	1.15
1.0	1.05	0.97	1.02	0.94
2.0	1.01	0.95	1.01	0.97
4.0	1.00	0.95	0.92	0.97
6.0	0.98	0.93	0.95	0.97
10.0	0.97	0.92	0.87	0.95
16.0	0.97	0.92	0.95	0.95
20.0	0.96	0.91	0.96	0.93
		PDIBBr		
0.2	1.05	1.07	1.04	1.01
1.0	1.05	1.04	1.06	1.10
2.0	1.11	0.96	0.96	0.91
4.0	1.00	1.05	1.08	1.04
6.0	1.01	0.99	0.89	0.95
10.0	1.05	1.08	0.99	0.80
16.0	0.95	1.03	0.90	0.91
20.0	0.98	0.94	0.86	0.99

[a] $D^0_{Ca^{2+}} = 7.92 \times 10^{-6}$ cm²/s.

five values of C_0. In general, the standard error in each diffusion coefficient reported did not exceed ±3%.

Tracer diffusion coefficients for Na^+, Ca^{2+}, and SO_4^{2-} ions were determined at 25 °C in aqueous solutions of 3–3 ionene bromide (PDIPBr) and 4–4 ionene bromide (PDIBBr) containing 0.00050, 0.0010, 0.0050, and 0.010 N NaBr, $CaBr_2$, and Na_2SO_4. The experimental diffusion coefficients and their reproducibilities are presented in Tables I and II in the supplementary material.[8] Tables III and IV contain the experimental data represented as the diffusion coefficient ratio D_i/D^0_i, where D_i and D^0_i are the diffusion coefficients of ion i in the presence of polyelectrolyte and in the absence of polyelectrolyte at infinite dilution, respectively. The concentration parameter X is the ratio of the normality of polyelectrolyte n_p to the *molarity* of simple salt n_s. The values $D^0_{Na^+} = 1.33 \times 10^{-5}$, $D^0_{Ca^{2+}} = 7.92 \times 10^{-6}$, and $D^0_{SO_4^{2-}} = 1.06 \times 10^{-5}$ cm²/s were used.[6,9] It is convenient to define a structural linear charge density parameter ξ

$$\xi = e^2/\epsilon kTb \qquad (3)$$

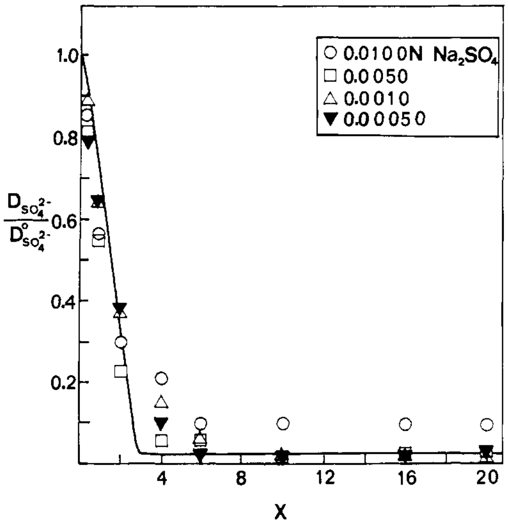

Figure 1. The sulfate ion diffusion ratio dependence on X in aqueous salt solutions containing poly[(dimethylimino)propylene bromide].

where e is the protonic charge, ξ is the dielectric constant, k is the Boltzmann constant, T is the temperature, and b is the average axial distance between charges on the polyelectrolyte. At 25 °C in water, ξ is 1.43 and 1.14 for PDIPBr and PDIBBr, respectively.

It is immediately obvious from Tables III and IV that the coion diffusion ratios approximate unity for the whole concentration range of the polyelectrolyte and of the simple salt studied. Also, this appears to be true for both PDIPBr and PDIBBr, polyelectrolytes of different linear charge densities. Coion diffusion ratios at the lowest simple salt concentration or extrapolated to infinite dilution have been reported to approximate a value of 0.8–0.9 for $X > 2$ for several polyelectrolytes of higher charge densities. This is reported for sodium poly(styrene sulfonate),[3] sodium ι-carrageenan, and sodium alginate,[4] where Cl^-, SO_4^{2-}, and $Fe(CN)_6^{4-}$ are the coions, for sodium heparin and sodium dextran sulfate,[5] where Cl^- and SO_4^{2-} are the coions, and for sodium polyacrylate,[10] where Cl^- is the coion. It should be noted that these polyanions have pendant sulfonate, sulfate, or carboxyl groups, indicating that the coion–polyion interaction is independent of the nature of the pendant charge group.

While no trend is indicated in Table III for the sodium ion diffusion ratios, a slight trend appears in Table IV for the calcium ion diffusion ratios. For each simple salt concentration, $D_{Ca^{2+}}/D^0_{Ca^{2+}}$ decreases slightly as X increases, roughly about 10% over the range of X used. Because divalent calcium ions would be expected to interact with the polyion to a greater extent, than sodium ions, the trend may be due to coion–polyion interaction.

For $S < 1$, the diffusion ratios for both sodium and calcium ions are slightly above unity. It is tempting to attribute this accelerated diffusion in the presence of the polyelectrolyte to water–polyion interaction, i.e., to the water structure making ability of the alkyl portion of the polyion.

To evaluate the counterion–polyion interaction, tracer diffusion coefficients were determined for SO_4^{2-} ion in the presence of PDIPBr and PDIBBr; the respective results are shown in Figures 1 and 2. For $X < 2$ it appears that the SO_4^{2-} ion diffusion ratio decreases linearly as X increases, followed by a levelling off as X is further increased. This trend has been reported for polyelectrolytes that are polyanions.[3-5,9,12,13] The PDIPBr shows small ionic strength dependence on the sulfate ion diffusion ratio, while the

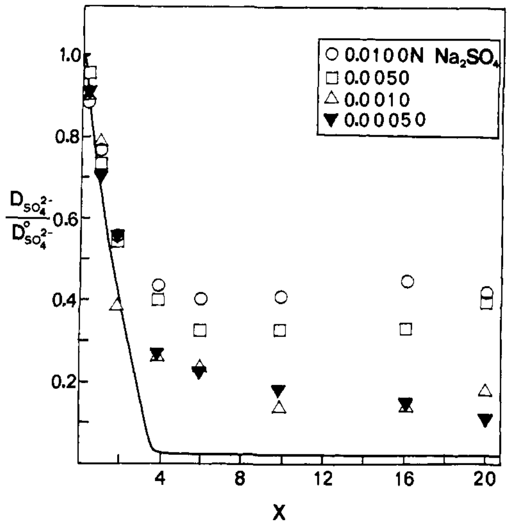

Figure 2. The sulfate ion diffusion ratio dependence on X in aqueous salt solutions containing poly[(dimethylimino)butylene bromide].

values for PDIBBr show a larger dependence. The levelling off values at the higher values of X are 0.03 and 0.1 for PDIPBr and PDIBBr, respectively. These values could be compared to analogous divalent calcium counterion diffusion ratios for chondroitin sulfate, whose structural ξ values is 1.40, for dextran sulfate (ξ = 2.85), and for heparin (ξ = 3.0). The levelling off values of the calcium ion diffusion ratios at high X values are 0.044, 0.2, and 0.1 for chondroitin sulfate, dextran sulfate, and heparin, respectively. It is interesting that PDIPBr and chondroitin sulfate which have similar ξ values have similar levelling off values for the divalent counterion diffusion ratios, while the higher charge density polyelectrolytes have larger values. Also, the larger values obtained for PDIBBr may indicate a larger effective ξ value than its structural ξ value due to coiling.

The Manning model[14-17] for the polyelectrolyte is an infinite line charge characterized by a linear charge density parameter ξ defined by eq 3. If ξ is greater than its critical value ξ_c of $|z_1|^{-1}$, where z_1 is the valence of the counterion, counterion condensation occurs so as to reduce ξ to its effective value ξ_c. When the simple salt and the polyelectrolyte have a common counterion, the concentration of the dissociated counterions is $(\xi z_1)^{-1}n_p$, which together with the counterions and the coions of the simple salt interact with the polyion of Debye–Huckel forces. If $\xi < \xi_c$, no counterion condensation occurs and *all* small ions interact with the fully charged polyion by Debye–Huckel forces. For PDIPBr and PDIBBr in aqueous NaBr and $CaBr_2$ solutions, ξ_c = 1, and the coion (subscript 2) diffusion ratio is given by

$$D_2/D^0_2 = 1 - z_2^2 A/3 \tag{4}$$

where A is given by

$$A = \sum_{-\infty}^{\infty}\sum_{(m,n\neq 0)}[\pi(m^2 + n^2) + |z_1| + (|z_1| + |z_2|)\xi X^{-1}]^{-2} \tag{5}$$

where z_1 and z_2 are the counterion and coion charges, respectively, and A is the contribution of the Debye–Huckel interactions of all uncondensed small ions with the polyion which is a function of ξ_c and the effective value of X. Since eq 4 is a limiting law, it is more fitting to correlate the theoretical values with the experimental ones at the lowest simple salt concentration or at an average value if the points at an X value are bunched together. Clearly eq 4 is not in accord with the data for Na^+ and Ca^{2+} ions presented in Tables III and IV. The data indicate that the values of the coion diffusion ratios are independent of the coion charge and independent of X, while eq 4 predicts the opposite. It has been pointed out previously that eq 4 overemphasizes the coion–polyion interaction when correlated with the data obtained for polyanions.[3,5]

When Na_2SO_4 is adding to an ionene bromide, monovalent and divalent counterions are present, and Manning's equations are modified.[11,12,14] Simply, in salt-free solutions, PDIPBr and PDIBBr have an effective ξ_c = 1 and a charge fraction, i.e., the fraction of structural polyelectrolyte charge uncompensated by associated counterions, of $(z_1\xi)^{-1}$. Gradually adding SO_4^{2-} ion to the polyelectrolyte solutions at a constant effective ξ_c = 1 results in a continuous replacement of the condensed monovalent Br^- ions by divalent SO_4^{2-} ions. When all of the condensed Br^- ions are replaced by the added SO_4^{2-} ions, the effective ξ_c value becomes $\xi_c = |z_1|^{-1} = {}^1/_2$, and further addition of SO_4^{2-} ions results in condensation of SO_4^{2-} ions onto the polyion until this effective ξ value is reached. At this critical point the value of X is $4\xi/(2\xi - 1)$, and the charge fraction of the polyelectrolyte is $(\xi z_1)^{-1}$ and $\xi^{-1}/2$. Further addition of SO_4^{2-} ions results only in uncondensed SO_4^{2-} ions, Br^- ions, and coions interacting with the polyion by Debye–Huckel forces. At X values lower than this critical point of $4\xi/(2\xi - 1)$, $D_{SO_4^{2-}}$ is that of the uncondensed SO_4^{2-} ions, while above this value the diffusion coefficient is constant and equal to that of the salt-free sulfate polyelectrolyte polyion itself, since all of the SO_4^{2-} ions are assumed to be condensed on it. For $X < 4\xi/(2\xi - 1)$, Manning's theoretical relationship is

$$D_1/D_1^0 = (1 - X/2 + \xi^{-1}X/4)(1 - 4A_1/3) \tag{6}$$

where subscript 1 represents SO_4^{2-}

$$A_1 = \sum_{-\infty}^{\infty}\sum_{(m,n\neq 0)}[2\pi(m^2 + n^2) + 2 - 2\xi + 12\xi X^{-1}]^{-2} \tag{7}$$

The series in eq 7 converges rapidly and contributes insignificantly to eq 6, and the values for D_2/D^0_2 are determined by the condensation term.

With no experimental values for the diffusion of the polyions available, the theoretical curves were constructed using values obtained from eq 6 for $0 < X < (4\xi/2\xi - 1)$, joined to a horizontal line for X values greater than $4\xi/2\xi - 1$. From Figures 1 and 2, it is evident that the Manning lines are in accord with the experimental results below X = 2 for both polyelectrolytes studied and in accord with the PDIPBr results over the whole concentration range. The values for PDIBBr in Figure 2 seem to indicate that the exchange of SO_4^{2-} ions for Br^- ions is not as complete as the theory predicts.

Since the Manning theory should be most applicable at low polyelectrolyte concentration, i.e., at low X values, it is of interest to compare the experimental values of the limiting slopes in Figures 1 and 2 with those predicted by eq 6. A regression analysis of the $D_{SO_4^{2-}}/D^0_{SO_4^{2-}}$ values below X = 2 gives slopes of −0.29 and −0.21 for PDIPBr and PDIBBr, respectively, which compare favorably with their respective limiting slopes of −0.33 and −0.28 obtained from eq 6. It is believed that the Manning theory should be compared with experimental results only at low X values; however, the experimental error in this range is greatest.

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Supplementary Material Available: Experimental diffusion coefficients of Na^+, Ca^{2+}, and SO_4^{2-} (Tables I and II) (2 pages). Ordering information is given on any current masthead page.

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Effect of Chain Length Distribution on Elastomeric Properties. 2. Comparisons among Networks of Varying Degrees of Randomness[1]

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ABSTRACT: Three poly(dimethylsiloxane) polymers were prepared, all with 0.5 mol % methylvinylsiloxane units. In the first polymer the potentially reactive vinyl groups were randomly distributed, in the second they were segregated in groups but slightly separated from one another, while in the third the vinyl groups were strictly segregated and adjacent. Networks were prepared from each of the polymers and from mixtures thereof. They were characterized in terms of their stress–strain isotherms in elongation and their degree of equilibrium swelling. Previous observation showed that networks prepared by selectively cross-linking through segregated vinyl sites resulted in relatively large values of the molecular weight M_c between cross-links. The present study showed that the cross-linking agent 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane is considerably more selective toward vinyl groups than is benzoyl peroxide, in that it does yield networks which reflect the segregated vinyl distribution. Relatively large values of M_c persist even when the vinyl groups are somewhat separated, thus implicating the elastic ineffectiveness of very short network chains (rather than a reduced reactivity of cross-linking sites when situated on every Si atom in a portion of the chain). The ratio $M_c(f)/M_c(v_{2m})$ of the values of M_c from stress–strain and swelling measurements was also found to depend on the nonrandomness of the cross-link distribution.

In two previous studies,[3,4] elastomeric networks were prepared from two samples of poly(dimethylsiloxane) (PDMS), both with 0.57 mol % methylvinylsiloxane units. In the first polymer, the potentially reactive vinyl groups were randomly distributed

–x———x——x–x———x——x————x–x———x——x–

while in the second they were completely segregated, in adjacent repeat units,

—xxxxx————————————————————————xxxxx—

at the two end of the chains. The networks were prepared from both polymers and from various mixtures thereof, using γ radiation and benzoyl peroxide (which are not selective for vinyl groups) and a silicon hydride cross-linking agent $Si[OSi(CH_3)_2H]_4$ (which is very highly selective).[5-7] They were characterized in terms of their stress–strain isotherms in elongation and their degree of equilibrium swelling in benzene.[4] The networks which had been prepared by selectively cross-linking through the segregated vinyl sites were found to have relatively large values of the molecular weight M_c between cross-links, thus indicating that very short chains have significantly reduced contributions to the elastomeric properties of a network. The ratio $M_c(f)/M_c(v_{2m})$ of the values of M_c from the stress–strain isotherm and degree of equilibrium swelling was generally found to be close to the expected value of unity. The values of the ratio for the very nonrandom networks suggested, however, that the very short chains contributed even less to the swelling response than they did to the modulus in elongation.[4]

The present study addresses two related aspects of this general problem of characterizing the effect of chain length distribution on elastomeric properties and serves in a sense to check the conclusions reached in the previous studies.[3,4] The first aspect involves the use of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane $[CH_3C(CH_3)(OOC_4H_9)CH_2-]_2$ (DBPH) as a cross-linking agent for the same two PDMS polymers. Free radicals generated from it are much less reactive than those generated from benzoyl peroxide and, as a result, do have a significant selectivity for vinyl groups.[6,7] Networks thus prepared should therefore have properties similar to those of the networks prepared by the previously employed highly selective cross-linking

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