

## Tracer Diffusion Coefficients of Counterions in Homo- and Heteroionic Poly(styrenesulfonate) Resins

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The tracer diffusion coefficients of  $\text{Na}^+$  and  $\text{Ba}^{2+}$  ions in especially synthesized poly(styrenesulfonate) resins with 2.3% cross linking were determined at 25 °C. These data were employed to evaluate the various contributions to the ionic mobilities in such media, i.e. tortuosity effect and electrostatic interactions. Yasuda's equation is found to describe adequately the tortuosity effect in the range 0.1–0.8 of the resin volume fraction ( $V_p$ ). It is concluded that electrostatic interactions are important even at large  $V_p$ , but the value of the acting electrostatic potential surrounding the charged chains is different from that calculated with theories of dilute polyelectrolyte solutions. The probable mechanism of transport of ions in resins is also discussed in terms of the values found for the activation energies for ionic transport.

### Introduction

The transport of small mobile particles through polymeric materials bearing fixed charges is of importance in a variety of processes which are related to the permeability of synthetic or natural membranes as well as to the kinetics of ion exchange. In the past, it was common to interpret thermodynamic and transport properties of ion-exchange resins in terms of those of concentrated electrolyte solutions. However, it is now generally accepted that polyelectrolyte solutions are the correct homogeneous analogues of the resin systems.<sup>1–4</sup> Solutions of linear polyelectrolytes are in every way similar to the corresponding cross-linked resins at the same concentration of fixed charges; a difference, however, exists in that the resins cannot be indefinitely "diluted" with solvent because it is impossible to stretch the chemical bonds linking two polymeric chains beyond a certain limit, thus the "infinite dilution limit" cannot be experimentally achieved in cross-linked resins.

The transport of small ions in dilute polyelectrolyte solutions is governed by the strong electrostatic interactions between the polymeric chains and the mobile counterions and coions. According to Manning<sup>5</sup> and to Katchalsky and co-workers,<sup>6</sup> these electrostatic interactions depend mainly on the distance between adjacent charges along the backbone, and very little on the concentration of the polyelectrolyte. On the other hand, when the concentration of macromolecules is sufficiently high, the displacements of the mobile species, which always occur through the regions containing water in the macroionic solution, will be hampered by the polymeric chains. This situation has the effect of lengthening the real path of the moving particles which travel through the macromolecular medium. This tortuosity effect<sup>7</sup> is fundamentally related to the volume fraction of resin,  $V_p$ .

Thus, it may be said quite generally that the tracer diffusion coefficients of ions ( $D_i$ ) in resins or polyelectrolyte solutions may be expressed for all  $V_p$  by

$$D_i = D_i^{(el)} f(V_p) \quad (1)$$

where

$$D_i^{(el)} = D_i^0 g(\Phi)/z_i \quad (2)$$

and  $f(V_p)$  represents the tortuosity effect,  $\Phi$  is the reduced electrostatic potential,  $z_i$  is the charge of the moving ion, and  $D_i^0$  denotes the tracer diffusion coefficient of ion  $i$  in pure water which is proportional to the absolute mobility of the ion.

The present work reports measurements of tracer diffusion coefficients in homo- and heteroionic poly(styrenesulfonate) resins. The results were employed in order to clarify the nature of the various terms appearing in eq 1 and 2 and evaluate their general applicability.

### Experimental Section

**Preparation of the Resin Strips.** The poly(styrenesulfonate) resin strips employed in the present work were synthesized from styrene (PASA S.A.) using divinylbenzene (Fluka technical grade) as the cross-linking agent. The styrene was washed with 5% NaOH and then distilled under reduced pressure (0.1 Torr) to eliminate any residual polymerization inhibitor. The precise content of divinylbenzene in the commercial product, which also contained ethylvinylbenzene and diethylbenzene, was established by vapor phase chromatography.

The polymerization was carried out<sup>8</sup> in such a way that the final resin was in the form of thin strips of 200  $\mu\text{m}$  thickness. A mixture of the monomers with 15% of toluene and 0.66% of azobis(isobutyronitrile) was prepared in a large test tube. A number of glass slides separated from each other by thin glass plates was tightly tied together and immersed in the reaction mixture. The glass slides had to be scrupulously clean to enable the preparation of smooth homogeneous strips. The test tube was sealed and the polymerization proceeded for successive periods of 24 h at 40, 70, and 100 °C.

The strips obtained were sulfonated at 100 °C in concentrated  $\text{H}_2\text{SO}_4$  containing 0.2%  $\text{Ag}_2\text{SO}_4$  as a catalyst. The sulfonation proceeded for a time which depended on the degree of cross linking of the resin; the end of the sulfonation occurred when the resins did not swell any more and their surfaces appeared smooth. In order to avoid a destructive osmotic shock when the sulfonated resins were immersed in water, it was necessary to equilibrate them successively in a series of  $\text{H}_2\text{SO}_4$  solutions of decreasing concentration. All the syn-

TABLE I

$V_p$	$10^7 D_i / \text{cm}^2 \text{ s}^{-1}$									
	Na <sup>+</sup>	Ba <sup>2+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>	Na <sup>+</sup>	Ba <sup>2+</sup>
0.785	0.303									
0.724		0.0107							0.0851	0.00262
0.686	1.36	0.0399	0.880	0.209	0.678		0.594	0.0156	0.482	0.0217
0.659	2.21									
0.630	3.82	0.259	2.87	0.152	2.08	0.109	1.78	0.0906	2.49	0.238
0.582	8.52	0.747	5.64	0.421	3.89	0.268	3.39	0.255	5.56	0.527
0.558	9.96	1.15	7.60		5.03		4.22		7.67	0.681
$X_{\text{Ba}^{2+}}$	0.00		0.20		0.50		0.80		1.00	

thesized resins were subjected to various cycles of ion exchange with HCl, NaCl, and BaCl<sub>2</sub> before being employed.

The exchange capacity of the resins resulted between 96 and 100% of the calculated theoretical capacity for poly(styrenesulfonate) resins. Electron-scan microscopy of the material obtained showed the resins were very smooth and homogeneous if the samples for microscopy were carefully dried; otherwise when the solvent desorbed abruptly from the strips, it damaged severely the surface of the resin.

Various strips were completely exchanged with <sup>22</sup>NaCl and then they were cut in small pieces which were found to have the same radioactivity per unit length; this showed that the resin strips had a constant thickness throughout their entire length.

**Water Absorption Isotherms.** The resin strips were isopiastically equilibrated inside a vacuum desiccator containing either saturated electrolyte solutions or solutions of sulfuric acid of such concentrations that the desired relative humidity could be obtained. The desiccators were provided with electromechanical devices that enabled stirring of the solutions from the outside of the thermostat when necessary. The isopiastic equilibration required between 5 and 7 days to be completed; all determinations were made in duplicate. The water content of the resins at each relative humidity was determined gravimetrically; the weight of dry resin was obtained after drying for 48 h at 120 °C.

**Heteroionic Resins.** They were obtained by equilibrating the resins with a solution containing a mixture of NaCl and BaCl<sub>2</sub> in a variable ratio. The ionic composition of the resin was established by exchanging the cations with HCl and by subsequent determination of the sodium content by flame photometry.

**Tracer Diffusion Measurements.** For the diffusion runs, the strips were cut to a size of 0.3 by 3.0 cm. When the isopiastic equilibration of the resin strips was completed, they were hung from a stainless steel hook mounted onto a micrometer screw which allowed moving the strips up or down, so that they could be made to just touch the solution containing the desired radioactive isotope (<sup>22</sup>Na<sup>+</sup> or <sup>133m</sup>Ba<sup>2+</sup> in carrier-free chloride solutions (CNEA, Argentina)) in order to seed the strips. In this way the seeding process could be carried out in a very short time and produced a very convenient thin and straight front of radioactive solution in the strips. The seeded strips were then placed in test tubes containing solutions of the appropriate relative humidity. The test tubes were kept in a thermostat at 25.0 ± 0.1 °C during the period required to complete the diffusion run. The strips were then taken out of the tubes and put between two pieces of adhesive tape which were tightly sealed together.<sup>8</sup> With an especially designed guillotine, the strips were cut into sections of 0.237 cm, their length always being checked with a mea-

suring microscope. The radioactivity in each section was determined by a scintillation counter (Nuclear). From each strip section a value of the tracer diffusion coefficients was calculated<sup>8</sup> from the accumulative fraction of radioisotope,  $f_i$ , and the distance  $x_i$  of the section from the origin of the strip according to the equation which gives the solution of Fick's differential equation for this experimental situation. The expression results:

$$f_i = \text{erf}(x_i^2/4Dt)^{1/2}$$

where erf is the error function to be found in mathematical tables and  $t$  is the diffusion time. The dispersion of the data obtained in every strip was never greater than 3% from the averages which are reported here.

## Results

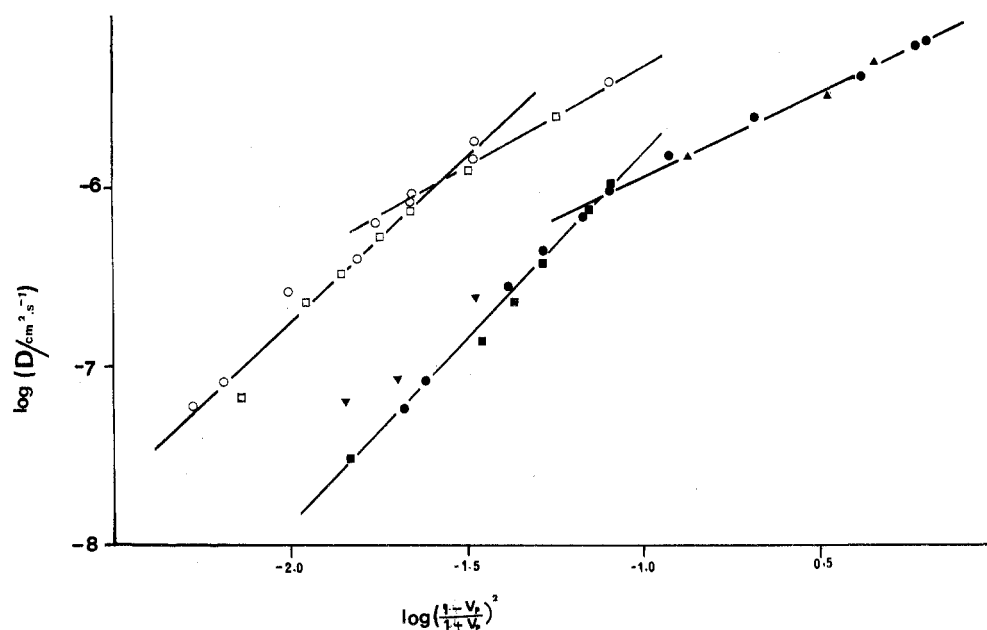
It was important to carry out the measurements of tracer diffusion in the whole series of resin ionic composition at constant  $V_p$  (cf. Discussion). Hence the measured water absorption isotherms at each ionic composition were converted into plots of  $V_p$  against relative humidity. With these plots the relative humidity necessary to achieve the desired values of  $V_p$  could be determined for each ionic composition. These relative humidities were obtained by careful adjustment of the concentration of H<sub>2</sub>SO<sub>4</sub> aqueous solutions.

In order to calculate the volume fraction, we assumed that the partial molar volume of water was 17 cm<sup>3</sup> mol<sup>-1</sup> for the resins at all ionic compositions; this choice is based on data reported in the literature for various poly(styrenesulfonates)<sup>9</sup> and for films of sodium deoxyribonucleic acid.<sup>10</sup> With this value and the measured density of the various dry resins,  $V_p$  was calculated from the water content of the resins determined gravimetrically.

Table I summarizes the data obtained for the tracer diffusion coefficients of Ba<sup>2+</sup> and Na<sup>+</sup> in homo- and heteroionic poly(styrenesulfonate) resins with 2.3% cross linking. The ionic composition of the resin is denoted by  $X_{\text{Ba}^{2+}}$  which is equal to the fraction of barium ion equivalents in the resin.

## Discussion

In order to establish the nature of the functions appearing in eq 1 and 2, we shall deal first with  $f(V_p)$ . There are several models proposed to account for the tortuosity effect. In 1955 Mackie and Meares<sup>7</sup> derived an expression for  $f(V_p)$  employing a model that considers the hydrated resin as a lattice through which the ions diffuse. The lattice sites which are occupied by the polymeric chains are assumed not to be available for the displacement of the mobile particles. The magnitude of the obstruction produced by the polymeric chains was evaluated in terms of the probability of polymer occupancy of the lattice sites. This probability was related



**Figure 1.** The tortuosity effect in poly(styrenesulfonate) systems according to Mackie and Meares<sup>7</sup> where  $f(V_p)$  is given by eq 3.  $\text{Na}^+$ : (●) linear polyelectrolyte;<sup>9</sup> (■) present work 2.3% cross linking; (▲) commercial resins with 1.7, 4, and 8% cross linking; (▼) 2.3% cross linking.<sup>8</sup>  $\text{Cs}^+$ : (○) 4.5% cross linking; (□) 2.4% cross linking.<sup>8</sup>

directly to the volume fraction of resin. The resulting expression was

$$f(V_p) = \frac{(1 - V_p)^2}{(1 + V_p)^2} \quad (3)$$

The theory of Mackie and Meares has been employed successfully for the diffusion of ions and small neutral solutes through membranes of gelatin, cellulose, and poly(vinyl) compounds,<sup>11</sup> as well as for ion-exchange resins.<sup>12</sup> Equation 3 has been found to work for cases where  $V_p \leq 0.5$ ; for the case of ions it was necessary to introduce also an electrostatic interaction to account for the experimental  $D_i$  values.<sup>3</sup>

In order to test this and other expressions for the tortuosity effect we have selected the relatively abundant tracer diffusion data for the sodium ion in poly(styrenesulfonate) aqueous systems. Data are available for the linear polymer,<sup>9</sup> for commercial ion-exchange resins of various degrees of cross linking,<sup>2</sup> and for resins synthesized by Lagos<sup>8</sup> and those employed in the present work. Figure 1 illustrates the plot of  $\log(D_i)$  against  $\log(f(V_p))$  according to eq 3; the data cover the range 0.1–0.8 of  $V_p$ . In Figure 1 we have also included the data of  $D_{\text{Cs}^+}$  in poly(cesium styrenesulfonate) resin obtained by Lagos.<sup>8</sup> It may be seen that the data for each ion may be represented by *two* straight lines, one for the region of low  $V_p$  with slopes of 0.9 and 1.0 for  $\text{Na}^+$  and  $\text{Cs}^+$ , respectively, and the other for high  $V_p$  having slopes of 1.9<sub>6</sub> and 1.7<sub>5</sub>. According to eq 3 the double logarithmic plots in Figure 1 should give straight lines with slopes of unity for the entire range of  $V_p$ , hence it may be said that the theory of Mackie and Meares is closely verified for  $D_{\text{Na}^+}$  up to  $V_p = 0.55$  and for  $D_{\text{Cs}^+}$  up to 0.68. For larger  $V_p$  values eq 3 underestimates the decrease of  $D_i$  with  $V_p$  probably due to the fact that at very high concentration of polymeric material there exists a significant number of polymer chain configurations which completely surround the solvent regions, such that the diffusing species which enter those regions have to move against a chemical potential gradient in order to escape from them and advance then in the direction of the existing chemical potential gradient.

Yasuda et al.<sup>13</sup> showed that the permeability of NaCl passing through hydrophilic membranes could be correctly accounted for by an expression derived by them from the free volume theory of Cohen and Turnbull<sup>14</sup> for mass transport in glasses and polymeric systems. Yasuda et al. considered that in a hydrophilic membrane the free volume may be additively expressed by that of water and that of the resinous material. Considering, furthermore, that the moving particles cannot permeate through the regions occupied by the resinous matrix, they concluded that the free volume of the system is given by the fraction of water<sup>22</sup> times its free volume. Thus

$$f(V_p) = \exp(-bV_p/(1 - V_p)) \quad (4)$$

This rather straight forward extension of Cohen and Turnbull's theory is not extent of criticism, e.g., the free volume of water in the resin is taken to be the same as that in pure water. Hence the physical significance of the constant  $b$  in eq 4 is rather obscure. Figure 2 is a plot of the tracer diffusion data for  $\text{Na}^+$  and  $\text{Cs}^+$  ions in poly(styrenesulfonate) resins already plotted in Figure 1. It may be seen that the data covering the whole range of  $V_p$  are correctly represented by a single straight line as predicted by eq 4. The least-squares analysis of the data is summarized in Table II. Equation 4 has been reported<sup>11</sup> to apply for  $V_p \leq 0.5$  as well as eq 3 for the diffusion of neutral molecules through various hydrophilic membranes, and it also applies for  $\text{Na}^+$  tracer diffusion in concentrated films of the sodium salt of deoxyribonucleic acid where the slope is almost parallel to that reported in Table II for  $\text{Na}^+$  in poly(sodium styrenesulfonate).<sup>10</sup> On the other hand, the values of  $D_i^{(\text{el})}$  in Table II are significantly smaller than  $D_i^0$  indicating the existence of an electrostatic effect ( $D_{\text{Na}^+}^0 = 1.333 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $D_{\text{Cs}^+}^0 = 2.057 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

The change in the tracer diffusion coefficients of  $\text{Na}^+$  and  $\text{Ba}^{2+}$  with the resin ionic fraction in heteroionic resins was employed to evaluate the electrostatic contribution to eq 1. First, let us consider the change in diffusion coefficients that would be predicted by polyelectrolyte theory when the  $\text{Na}^+$  counterion is replaced by  $\text{Ba}^{2+}$ . Due to the preferential condensation of multivalent counterions<sup>5</sup> when  $\text{Ba}^{2+}$  ions are

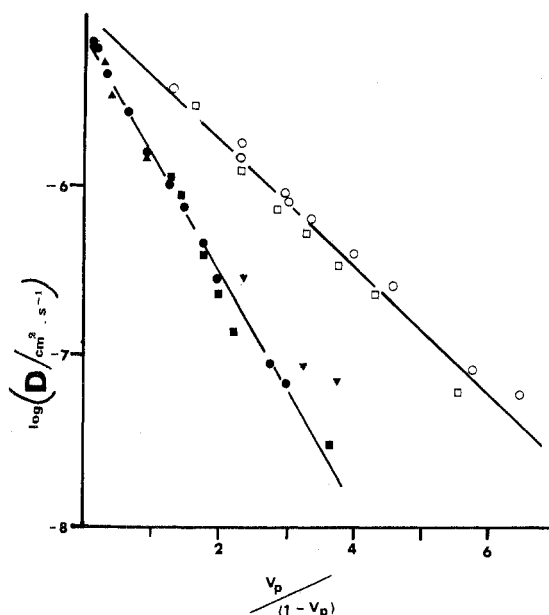


Figure 2. The tortuosity effect in poly(styrenesulfonate) systems according to Yasuda et al. where  $f(V_p)$  is given by eq 4. Symbols are the same as in Figure 1.

present in the resin only as a trace, they will be strongly attracted by the macroion as well as a fraction of the sodium counterions. When  $X_{Ba^{2+}}$  increases, a fraction of barium ions becomes relatively free and the fraction of free  $Na^+$  also increases. Consequently, the tracer diffusion coefficients of both ions would be expected to increase with  $X_{Ba^{2+}}$  at constant  $V_p$ , i.e., with the fraction of free counterions.<sup>15</sup>

In an important and classical study, Soldano and Boyd<sup>16</sup> have observed the opposite behavior in  $Na^+/Zn^{2+}$  heteroionic poly(styrenesulfonate) resins. Nevertheless, their measurements were carried out under conditions which maintained the water activity almost constant, and it is a well-known fact verified in the present work that at the same water activity the bivalent resin has a lower water content than the sodium resin; in other words, at constant water activity  $V_p$  increases with the fraction of bivalent counterion in the resin. This implies an increased tortuosity and may be deemed responsible for the observed behavior of the tracer diffusion coefficients in the work of Soldano and Boyd.<sup>16</sup> For this reason we have measured the values of  $D_{Na^+}$  and  $D_{Ba^{2+}}$  in various heteroionic resins at constant  $V_p$ , a condition that proved to be experimentally tedious and difficult to carry out (cf. Results). Figure 3 is a plot of the data reported in Table I for both ionic tracer diffusion coefficients at constant  $V_p$  as a function of  $X_{Ba^{2+}}$ . Figure 3 shows that, from the point of view of "dilute polyelectrolytes", the behavior is still anomalous in spite of the fact that a minimum in the curves is observed which appears to shift to lower  $X_{Ba^{2+}}$  values as  $V_p$  decreases, suggesting that the predictions of polyelectrolyte theory might be verified at low  $V_p$ .

In view of the results illustrated in Figure 3, it is tempting to argue that in sufficiently concentrated ion-exchange resins, the electrostatic effect is not a relevant quantity. This would be the case if under such conditions the counterions moved along the chains of the polymeric backbone through essentially equipotential paths. In this case the electrostatic polyelectrolyte effect would not be acting since it really accounts for the decrease in ionic mobility when the ions travel from positions near the chains in the polymeric domains toward the

TABLE II

Ion	$10^5 D_i^{(el)}/cm^2 s^{-1}$	$b_i$	Std deviation
$Na^+$	0.56 <sub>9</sub>	1.42	3%
$Cs^+$	1.0 <sub>9</sub>	0.87 <sub>6</sub>	2%

$V_p = \text{const.}$

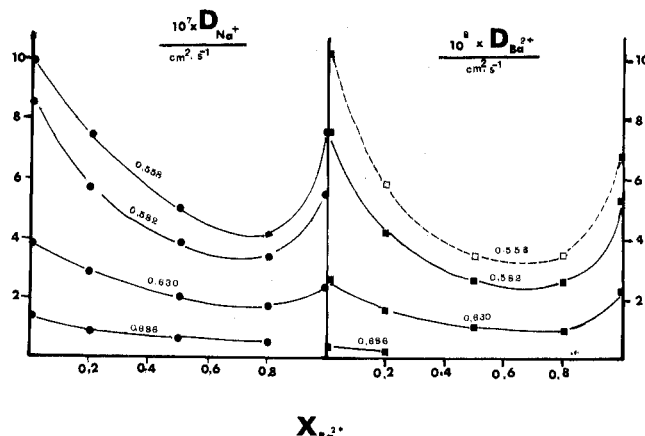


Figure 3. Tracer diffusion coefficients of  $Na^+$  and  $Ba^{2+}$  against  $X_{Ba^{2+}}$  in  $Na^+/Ba^{2+}$  heteroionic poly(styrenesulfonate) resins at constant  $V_p$ . For  $D_{Ba^{2+}}$  at  $V_p = 0.558$  the open symbols were obtained by extrapolation of the data at other  $V_p$  values.

domain boundaries.<sup>3,17</sup> Consequently, if counterions moved along electrostatic equipotential paths close to the chains,  $D_i^{(el)}$  in eq 2 should equal  $D_i^0$  and, furthermore, the counterions would follow closely the contour of the resin chains so that the slowest counterions would block the paths to the fastest ones; i.e., since  $Ba^{2+}$  has the largest hydrated radius,  $D_i$  would decrease with  $X_{Ba^{2+}}$ .

In order to check this hypothesis, the  $\log(D_i)$  values for sodium and barium ions in the heteroionic resins are plotted in Figure 4 against  $V_p/(1 - V_p)$  according to eq 4. The slope of  $\log(D_{Na^+})$  for the pure sodium resin is somewhat different from that in Figure 3 where all available data for poly(sodium styrenesulfonate) systems were plotted. This discrepancy is attributed to experimental uncertainties which are smoothed out when data in a wider  $V_p$  range are considered.

It is surprising to note that according to Figure 4 and Table III the data for  $X_{Ba^{2+}} \leq 0.8$  give straight lines which are almost exactly parallel for each diffusing ion at all ionic compositions of the resin. The values of  $b_i$  reported in Table III indicate that this parameter in eq 4 depends on the nature of the moving ion but is independent of the particular ionic composition of the resin, an interesting conclusion which also supports our previous contention that the slope  $b_i$  in eq 4 has in these media a different meaning to that in the theory of Cohen and Turnbull.

The data for the pure barium resin do not fall on straight lines as illustrated in Figure 4. No satisfactory explanation could be found for this fact; a careful analysis of the corresponding runs make it unlikely that a systematic error may have affected the data.

A consequence of eq 1 and 2 is that the ratios

$$\frac{D_{Na^+}^{(el)}/D_{Na^+}^0}{D_{Ba^{2+}}^{(el)}/D_{Ba^{2+}}^0} = \frac{z_{Ba^{2+}}}{z_{Na^+}} = 2$$

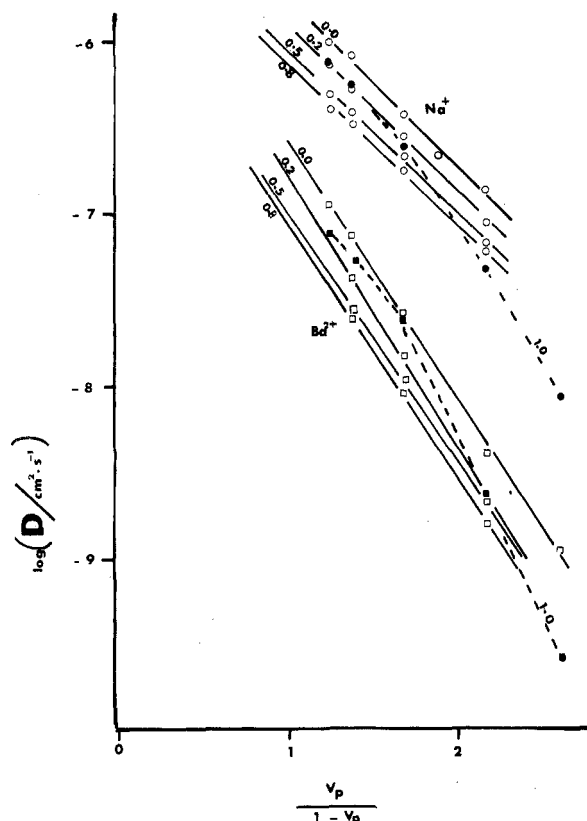


Figure 4. Tracer diffusion coefficients of  $\text{Na}^+$  and  $\text{Ba}^{2+}$  against  $V_p/(1 - V_p)$  in  $\text{Na}^+/\text{Ba}^{2+}$  heteroionic poly(styrenesulfonate) resins. Full symbols correspond to  $X_{\text{Ba}^{2+}} = 1.0$ .

for each ionic composition. The ratios obtained from the lines drawn in Figure 4 are reported in Table III, the average value of the ratios being  $1.7 \pm 0.3$ . This would imply that the electrostatic field around the chains is a relevant quantity in determining the diffusion of ions at high  $V_p$  values, but the value of  $\Phi$  would not correspond to that calculated from theories that apply to dilute polyelectrolyte solutions.

Finally it is important to analyze whether it is possible to consider that the absolute mobility of the ions in the resins at high  $V_p$  is the same as that in pure water, i.e., that  $D_i^0$  in eq 2 is the tracer diffusion coefficient of ion  $i$  at infinite dilution. There are a variety of data on the activation energy for ionic mobilities in resins which show in general that these are of the same order of magnitude as in pure water, except when the diffusing species is large enough to be affected by a sieve effect. In Table IV some recent activation energy data for ionic transport in poly(styrene) resins are compared to those in water; column two of the Table IV gives the degree of cross linking of the resins. It may be observed that the activation energies are only slightly larger than in water except for  $\text{I}^-$  and for  $\text{NMe}_4^+$ ; for the latter ion Boyd<sup>19</sup> considers that sieve effect is operative and responsible for the rather large activation energy.

When the data in Table IV are compared to those for alkali metal ions in glasses<sup>21</sup> which are several times larger, they seem to indicate that the mechanism of transport in ion-exchange resins is akin to that in water and quite different from those in anhydrous ionic viscoelastic media.

## Conclusions

(1) The variation of ionic tracer diffusion coefficient in ion-exchange resins with  $V_p$  is well represented by eq 4.

TABLE III: Counterion Tracer Diffusion Coefficients in Heteroionic Resins and Parameters of the Equation:  $D_i = D_i^{(el)} \exp(-b_i V_p / (1 - V_p))$ <sup>a</sup>

$X_{\text{Ba}^{2+}}$	$b_{\text{Na}^+}$	$b_{\text{Ba}^{2+}}$	$\frac{D_{\text{Na}^+}^{(el)}/D_{\text{Na}^+}^0}{D_{\text{Ba}^{2+}}^{(el)}/D_{\text{Ba}^{2+}}^0}$
0.0	2.3	3.45	1.46
0.2	2.3	3.65	1.43
0.5	2.3	3.45	1.87
0.8	2.3	3.45	1.98
			$1.7 \pm 0.3$

$$^a D_{\text{Na}^+}^0 = 1.333 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}; D_{\text{Ba}^{2+}}^0 = 0.846 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}.$$

TABLE IV: Activation Energies of Ionic Mobilities in Poly(styrene) Type Resins

Ion	% cross linking	$E^\ddagger$	$E^\ddagger_{\text{H}_2\text{O}}$ <sup>a</sup>	Ref
$\text{Na}^+$	8	5.2	4.20	19
$\text{Na}^+$	30	5.3 <sub>9</sub>	4.20	18
$\text{Cs}^+$	30	4.15	3.65	18
$\text{Sr}^{2+}$	30	4.82	4.76	18
$\text{Mg}^{2+}$	30	4.87	4.48	18
$\text{NMe}_4^+$	8	7.0	3.46	19
$\text{Cl}^-$	4	2.51	3.92	20
$\text{Cl}^-$	8	3.56	3.92	20
$\text{Cl}^-$	16	5.17	3.92	20
$\text{I}^-$	6	8.7	3.84	20

<sup>a</sup> Calculated from the conductivity at infinite dilution data in R. A. Robinson and R. H. Stokes in "Electrolyte Solutions", Butterworths, London, 1959.

(2) The slope  $b_i$  in eq 4 depends on the nature of the moving ion and not on the nature of the ionic matrix of the resin. Thus eq 1 becomes

$$D_i = D_i^{(el)} f(b_i, V_p) \quad (5)$$

(3) The electrostatic predictions of polyelectrolyte theories are not met in heteroionic resins at large  $V_p$ . However, the electrostatic potential still plays an important role.

(4) The activation energy data for ionic transport in resins suggests that the real friction coefficient is closely related to that in dilute aqueous solutions.

**Acknowledgment.** We thank the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for partial financial support.

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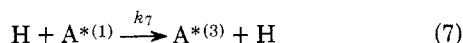
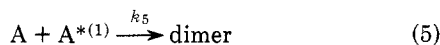
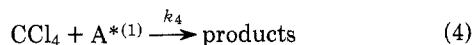
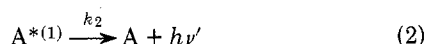
## COMMUNICATIONS TO THE EDITOR

### Multiplicity of the Reacting State in the Photoaddition of Carbon Tetrachloride to Anthracene

Publication costs assisted by the National Institutes of Health

Sir: The photochemical addition of carbon tetrachloride to anthracene has been known for some time.<sup>1</sup> Although it has been assumed to be a reaction occurring from the excited singlet state of anthracene,<sup>1-3</sup> Hardwick concluded from flash spectroscopic studies of triplet quenching<sup>6</sup> that the reaction is very likely to take place entirely from the anthracene triplet state.<sup>7</sup>

Because of our interest in quenching of excited triplet states<sup>8</sup> and in heavy atom elucidation of photochemical and photophysical processes,<sup>9,10</sup> we have investigated the photoaddition of carbon tetrachloride to anthracene in benzene solutions containing varying concentrations of bromobenzene as a heavy atom additive. Assuming that the only effect of bromobenzene is to convert anthracene excited singlets to triplets,<sup>11</sup> the following kinetic scheme may be written for the case in which the photoaddition takes place from the anthracene singlet state.<sup>12</sup>



If this formulation is correct, the Stern-Volmer slope for bromobenzene quenching of anthracene fluorescence (from plots of  $F'/F$  vs. [bromobenzene], where  $F'$  and  $F$  are the fluorescence intensities (both in the presence of  $CCl_4$ ) in the absence and presence of bromobenzene, respectively) and the Stern-Volmer slope for bromobenzene quenching of anthracene disappearance (from plots of  $\Phi_d'/\Phi_d$  vs. [bromobenzene], where  $\Phi_d'$  and  $\Phi_d$  are the disappearance quantum yields in the absence and presence of bromobenzene, respectively) should be the same.

Using solutions of  $2.4 \times 10^{-3}$  M anthracene and 0.13 M  $CCl_4$  in benzene, with bromobenzene concentrations of 0, 1.2, 1.52, 1.9, and 2.3 M and following the photochemical reaction by monitoring the decrease of anthracene absorbance at 378 nm, we observed a Stern-Volmer slope of  $0.68 \text{ M}^{-1}$  (standard deviation, 0.02) for fluorescence quenching and a Stern-Volmer slope of  $0.72 \text{ M}^{-1}$  (standard deviation, 0.06) for reaction quenching. Since these slopes are the same within experimental error, we conclude that the photochemical reaction of anthracene with carbon tetrachloride takes place entirely from the singlet state of anthracene.

At our experimental concentrations we observed a 480- $\mu\text{s}$  lifetime for the anthracene triplet in the absence of carbon tetrachloride and a  $k_q$  for  $CCl_4$  quenching of anthracene triplets of  $1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with the  $k_q$  value determined by Hardwick.<sup>6</sup> At the  $CCl_4$  concentration used in this study, half of the anthracene triplets were quenched by carbon tetrachloride. Since photochemical adduct formation does not appear to follow, we conclude that the net result of triplet quenching is enhanced radiationless decay of the triplet excited state.

Charge transfer interactions have been proposed in the  $CCl_4$  quenching of naphthalene triplets by Schulte-Frohlinde.<sup>13</sup> In the present case, an electron transfer complex can be calculated from the equation of Weller<sup>14</sup> and from anthracene and  $CCl_4$  redox data<sup>15</sup> to lie  $1.97 \pm 0.1 \text{ eV}$  above the ground state. Since this is slightly higher than the 1.82-eV energy of the anthracene triplet, electron transfer would require thermal activation. In that case homolysis of the C-Cl bond, which is thought to lead to adduct formation,<sup>1,2</sup> may be less likely than other processes which lead to ground states.