portant negative contribution to the activation entropy. Indication of the existence of such a factor may be seen from Table XI which also exhibits the striking dependence of the self-diffusion rate on ionic charge for a constant exchanger cross-linking. Additionally, it is shown that increasing the cross-linking leads to increased differences between the *D*'s for the various ions, as expected from the relative contributions of positive and negative entropy of activation outlined above.

TABLE XI

IONIC CHARGE AND THE SELF-DIFFUSION OF CATIONS IN RELATIVELY HIGHLY CROSS-LINKED CATION EXCHANGERS

Ion	Self-diffusion coefficient (cm.^{2} sec.$^{-1}$) 0.3°	25°	Activation energy, cal. mole^{-1}	d-($e^{\Delta S^{\neq}/R}$)$^{1/2}$
Commercial Dowex-50 (5.20 m.e. per g. dry H-form)				
Na^+	1.15×10^{-7}	2.88×10^{-7}	5980	2.1
Zn^{++}	8.77×10^{-9}	2.89×10^{-8}	7830	3.1
Y^{+++}	1.01×10^{-9}	3.18×10^{-9}	7530	0.8
Th^{++++}	6.40×10^{-11}	2.15×10^{-10}	7960	0.3
Nominal 24% DVB (4.36 m.e. per g. dry H-form)				
Na^+	2.69×10^{-8}	1.00×10^{-7}	8620	12.1
Zn^{++}	5.52×10^{-10}	2.63×10^{-9}	10250	8.0
Y^{+++}	5.86×10^{-11}	2.18×10^{-10}	8620	0.6

This discussion has regarded the self-diffusion of cations in cation exchangers as analogous to that in ordinary concentrated aqueous electrolyte solutions. Other studies[35,36] have suggested, however, that exchangers are to be looked upon as cross-linked polyelectrolytes whose gel solutions are under an hydrostatic pressure exerted by the swollen polymer network. These pressures may rise to as much as 1000 atmospheres in the most highly cross-linked preparations; hence, it may be inquired if the increase in activation energy with % DVB has its origin in this factor. A pressure–volume free energy contribution to the activated complex will lower the self-diffusion coefficient according to

$$D = ed^2(kT/h)e^{\Delta S^{\neq}/R}\, e^{-(E^0_{act} + \pi\Delta V)/RT} \qquad (7)$$

where E^0_{act} is the activation energy observed at zero pressure (*i.e.*, for weakly-linked exchangers), π the swelling pressure, and ΔV is the volume increase per mole of activated state for diffusion. Studies of the pressure dependence of the viscosities of liquids[37,38] have shown that ΔV may vary between one-fifth to one-tenth the molar volume. Assuming ΔV for the sodium-form of the 24% DVB exchanger to be approximately the same fraction of its molar volume of 210 ml., and the pressure to be 1000 atm., the pressure–volume contribution will be 500 to 1000 cal. mole^{-1} to the observed activation energy of 8620 cal. mole^{-1}. Since the swelling pressure diminishes rapidly with decreasing cross-linking, the $\pi\Delta V$ increment to the activation energy may generally be taken as negligibly small.

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[35] H. P. Gregor, THIS JOURNAL, **73**, 642 (1951).

[36] E. Glueckauf, *Proc. Roy. Soc.* (*London*), **A214**, 207 (1952).

[37] R. H. Ewell, *J. Appl. Phys.*, **9**, 252 (1938).

[38] D. Frisch, H. Eyring and J. F. Kincaid, *ibid.*, **11**, 75 (1940).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Self-diffusion of Anions in Strong-base Anion Exchangers[1,2]

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Measurements of self-diffusion coefficients, *D*, for chloride, bromide, iodide, bromate, tungstate and orthophosphate anions in a strong-base anion exchanger (Dowex-2) gave values between 4.6×10^{-7} and 5.7×10^{-8} cm.^{2} sec.$^{-1}$ at 25°. The temperature variations of *D* between 0.2 and 25° gave activation energies from 6000 to 8800 cal. mole^{-1}. The dependence of *D* on ionic charge and ion exchange polymer cross-linking was not so pronounced as found previously for cations in cation exchangers. The self-diffusion of bromide ion in differently substituted quaternary ammonium type exchangers of constant polymer cross-linking indicated that the size of the exchange group was more important than its polarity in determining permeation rates. The self-diffusion of anions in anion exchangers was considered to occur with a "zone of activation." Generally, positive, *net* entropies of activation were found. Because of the relatively small hydration of the mobile anions and of the structurally-bound cationic exchange groups in anion exchangers, the sometimes appreciable negative contributions to the activation entropy observed with cation exchangers were absent.

As yet very little appears to be known about the factors governing the rate of exchange of anions in synthetic organic anion exchangers. Previously two[3,4] reports have appeared in which studies with several weakly basic; polyfunctional anion exchangers were described. Evidence for diffusion as the controlling process was given in the latter researches by the dependence of the exchange velocity on particle size, by its independence of stirring rate, by the effect of interruption after varying degrees of attainment of equilibrium, and by the activation energy, which was approximately 6600 cal. mole^{-1}. Diffusion coefficients were not derived. Indeed, from the nature of the experiments wherein frequently a considerable swelling accompanied the exchange reaction, it would have been difficult to do so.

This research, which employed the new strong-base, quaternary ammonium type anion exchangers based on polystyrene divinylbenzene copolymers,[5]

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[1] Presented before the Division of Colloid Chemistry, 120th Meeting, American Chemical Society, September 3–7, 1951, New York, N. Y.

[2] This work was performed for the Atomic Energy Commission.

[3] F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944).

[4] R. Kunin and R. J. Myers, *J. Phys. Colloid Chem.*, **51**, 1111 (1947).

[5] For examples see: G. E. Boyd, *Ann. Rev. Phys. Chem.*, **2**, 309 (1951); W. C. Bauman and R. M. Wheaton, *Ind. Engr. Chem.*, **43**, 1088 (1951); and R. Kunin and R. J. Myers, *Faraday Soc. Disc.*, **7**, 114 (1949).

was undertaken to determine diffusion rates under conditions such that swelling and other complications would be absent. Coefficients and activation energies for the self-diffusion of anions were determined in self-exchange reactions using radioactive tracers. The procedure was analogous to that already described for cation exchangers.[6]

Four groups of experiments were performed in the hope of achieving a basic interpretation of the observed rates of ionic permeation: (a) those in which the anionic size (and shape) was varied holding ionic charge and ion exchanger cross-linking constant, (b) those wherein the anionic charge was changed holding cross-linking constant, and (c) those where the ion-exchanger cross-linking was progressively increased holding the charge constant. In addition, by reason of the manner in which the quaternary ammonium anion exchangers may be prepared,[5] it was also possible to conduct a study in which the nature of the structurally-bound cationic exchange group was varied holding the polymer cross-linking constant.

Experimental Details

Rate measurements were conducted using a limited rather than an infinite bath or flow technique. Spherical ion exchange particles of accurately known diameter containing radioactively-labeled anions were stirred in a finite volume of dilute electrolyte solution containing the same anion as the exchanger. The rate of isotopic redistribution was then determined by measuring the amounts of radioactivity in the solution at known periods after the start of the self-exchange reaction. The chief advantage of this procedure was that of convenience in the measurement of temperature coefficients. The flow technique is to be preferred when the rate of attainment of equilibrium is extremely high, as with small particles or at elevated temperatures. Theoretical relations to be employed in deriving diffusion coefficients from experimental rate data from the limited bath[6] or from the flow method[7-10] have been described elsewhere.

All of the anion exchangers used in this study were obtained from the Physical Research Laboratory of the Dow Chemical Company.[11] The procedures employed in the separation of desired particle size fractions, and in the conversions to the required homo-ionic salt-forms were similar to those in studies on cation exchangers.[6] Small quantities of unreacted tertiary amine and other organic material in the anion exchangers were removed by exhaustive washing with 95% ethyl alcohol. Owing to the particle size range in the preparations available it was necessary to work with smaller than the optimum diameter particles. Further, the number of internally cracked spheres, particularly in the exchangers containing special functional groups, was sometimes higher than desired.

The anion exchangers were characterized (Tables I and II) with respect to exchange capacity by potentiometric titration of their chloride forms with silver nitrate in the presence of 1 *M* KNO_3. Moisture contents of the wet-swollen spheres were estimated from weight losses on drying in a vacuum oven at 65° over P_2O_5. Equivalental volumes were measured pycnometrically using pure water as a displacing liquid. The stability of the various salt forms seemed quite good, in contrast with the free base (*i.e.*, hydroxide) forms which appear to decompose, sometimes quite readily even at room temperatures, by Hofman degradation and other reactions. Careful *p*H titration curve studies[12] on the exchangers listed in Table II have shown all of them to contain small amounts (usually 2–4%) of weak base exchange groups.

TABLE I

SWELLING OF THE CHLORIDE FORMS OF VARIOUSLY CROSS-LINKED DOWEX-2

Nominal % DVB	Capacity, meq./g. dry Cl form	Equivalental moisture, g. H_2O/eq.	Equivalental volume, ml./eq.	V_0	V_2	Molality
1	3.77	438	659	223	226	2.3
2	3.79	287	504	218	221	3.5
3	3.54	239	474	235	239	4.2
6	3.27	172	433	261	266	5.8
8	3.09	140	409	270	280	7.2
16	2.66	98	421	323	332	10.2

TABLE II

SWELLING OF BROMIDE FORMS OF A NOMINAL 6% DVB COPOLYMER CONTAINING VARIOUS EXCHANGE GROUPS

Functional group, R = hydrocarbon matrix	Capacity, meq./g. dry Cl form	Equivalental moisture, g. H_2O/eq.	Equivalental volume, ml./eq.	V_0	V_2	Molality
$RNMe_3^+$	3.32	138	363	225	232	7.3
$RNEt_3^+$	1.51	151	722	571	575	6.6
$RNBu_3^+$	0.96	163	1090	927	927	6.1
$RNMe_2Phenyl^+$	1.31	146	788	642	640	6.9
$RNMe_2Benzyl^+$	1.47	173	745	572	574	5.8
$RNMe_2EtOH^+$	2.85	130	392	262	266	7.7
$RNMe(EtOH)_2^+$	2.17	123	492	369	366	8.1
$RNMe_2PrOH\text{-}2^+$	1.93	197	627	424	427	5.1
$RNMeMorpholinium^+$	1.87	180	600	420	432	5.6
$RNPyridinium^+$	2.04	170	556	386		5.9
$RNQuinolinium^+$	1.38	209	815	606	622	4.8

Swelling measurements (Table I) on the chloride salts of variously cross-linked Dowex-2 (benzyldimethylethanolammonium) showed that their equivalental volumes, V_e, could be related to their equivalental moisture contents, M_w, by means of the equation

$$V_e = V_0 + M_w/\rho_w \qquad (1)$$

where V_0 was 222.6 ± 3.0 ml. equiv.$^{-1}$ for the chloride salt. The extrapolated moisture-free volume, V_0, seemed invariably very slightly smaller than the true dry equivalental volume, V_2, determined experimentally on the moisture-free exchanger by displacement in a non-swelling liquid (av. V_2 = 226.5 ± 4.8 ml. equiv.$^{-1}$). The difference, $V_2 - V_0$, was also significantly smaller for the various salt forms of the strong-base anion exchanger Dowex-1 (benzyltrimethylammonium) than for the sulfonated polystyrene type cation exchanger, Dowex-50. This is explicable if ($V_2 - V_0$) is at least in part a measure of the electrostriction accompanying hydration. In anion exchangers the arylalkyl quaternary ammonium cation and the "counter-anions" are scarcely hydrated, in contrast with cation exchangers where both the sulfonate anions and "counter-cations" are strongly hydrated. A comparison of V_2 and V_0 in Table II indicates for the bromide salt forms of a variety of anion exchangers that the electrostriction effect is within experimental errors regardless of the structure of the quaternary amine.

The data of Table II are of additional interest in that they appear to show the effect of the size of the cationic exchange group on the capacity, and on V_0. With the purely alkyl-substituted quaternary ammonium exchangers as the size of the quaternizing tertiary amine increased the capacity diminished, suggesting that the reaction becomes less complete, either because of steric limitations imposed by the "mesh-size" of the polymer network, or because of a greater

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[6] G. E. Boyd and B. A. Soldano, THIS JOURNAL, **75**, 6091 (1953).

[7] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., *ibid.*, **69**, 2836 (1947).

[8] T. R. E. Kressman and J. A. Kitchener, *Faraday Soc. Disc.*, **7**, 90 (1949).

[9] J. J. Grossman and A. W. Adamson, *J. Phys. Chem.*, **56**, 97 (1952).

[10] D. Reichenberg and K. W. Pepper, THIS JOURNAL, **75**, 589 (1953).

[11] The authors express thanks to Dr. W. C. Bauman and Mr. R. M. Wheaton for their great help in this connection.

[12] H. A. Strobel and R. W. Gable, private communication, December, 1952.

activation energy involved in the Menschutkin reaction, or both. As expected, V_0 increases with the size of the exchange group. Somewhat unexpectedly, the alkanol substituted ammonium exchangers showed smaller equivalental moisture contents than the alkyl-substituted preparations. However, since the former are more weakly basic, possibly owing to the inductive effect of the hydroxyl groups which act to increase the positive charge on the nitrogen, their salts also might be expected to be less osmotically active.

The exchangers were charged with radioactive anions by treatment with aqueous solutions containing the desired isotopic types: 38.5 m Cl^{38}, 35.8 h Br,^{82} 8.0 d I^{131}, 24.1 h W^{187} and the 14.3 d P^{32}. Radiobromine-labeled bromate was obtained as a by-product from a Szilard–Chalmers reaction on crystalline $KBrO_3$.[13]

The rate experiments employed either one or five grams of exchanger in 200 ml. of aqueous solution 0.15 *N* in the desired anion. The *p*H was approximately 7 in the chloride, bromide and bromate exchanges, while with iodide ion a value of 8.5 was used to minimize hydrolysis and/or oxidation. The work with the tungstate ion was conducted at *p*H of 10, for self-diffusion measurements in pure aqueous solutions[14] had indicated the absence of polymerization to paratungstates at this alkalinity. The phosphate self-exchange experiments were performed at a *p*H of 13 to ensure a largely trivalent anion. Considerable difficulty with adsorption on the walls (Pyrex) of the reaction vessel was experienced which could not be eliminated until a pure silicate glass (Vycor) was used. The employment of these strongly alkaline solutions may have introduced a complication in that the phosphate exchanger salt probably also contained a small number of hydroxyl anions.

Radioactivity and particle diameter measurements were performed as previously described.[6] A special study showed that the particle size was independent of temperature within experimental errors. Other preliminary investigations were made to determine the influence of the ionic strength of the external aqueous solution on the self-exchange rate, and to determine if there were specific cation effects. Increasing the concentration of NaI from 0.15 to 1.0 *N* decreased the self-diffusion coefficient for iodide ion in Dowex-2 (6% DVB) from 3.46 to only 3.32 × 10^{-8} cm.^{2} sec.$^{-1}$, which is probably within experimental error.[6] A somewhat larger reduction in D to 2.82 × 10^{-8} cm.^{2} sec.$^{-1}$ was found on changing from 0.15 *N* NaI to 0.15 *N* KI. Since potassium iodide in its aqueous solutions is believed to be more associated than NaI, this last result may indicate that actually Na^+ ion enters the exchanger and acts to speed the self-exchange process. Further investigation of this type of effect seems warranted.

TABLE III

RATE OF SELF-EXCHANGE OF RADIOBROMIDE ION AT 0.2° BETWEEN 0.15 *N* NaBr SOLUTION AND THE BROMIDE FORM OF NOMINAL 6% DVB BENZYLTRIETHYLAMMONIUM ANION EXCHANGER (w = 0.0416)

Time, *t*, sec.	Fraction of equilibrium, *F*	(τ/t)
30	0.225	1.61 × 10^{-4}
60	.307	1.55
90	.363	1.52
120	.415	1.52
150	.447	1.45
190	.503	1.52
230	.537	1.50
280	.587	1.55
340	.612	1.41
400	.676	1.62
480	.697	1.48
660	.767	1.45
800	.803	1.47
950	.856	1.49
1200	.885	(1.32)

$(\tau/t)_{Av} = (1.50 \pm 0.049) \times 10^{-4}$; av. radius, $a = 3.62 \times 10^{-2}$ cm.; $D = (\tau/t)a^2 = 1.50 \times 10^{-4} \times (3.62 \times 10^{-2})^2 = 1.97 \times 10^{-7}$ cm.^{2} sec.$^{-1}$

The experimental accuracy of the self-diffusion coefficients determined for the anion exchangers was generally not as high as in our work with cation exchangers. Several factors appeared to contribute, among which the most important were: (a) the lack of spherical shape of some of the exchanger particles, (b) the sometimes extremely rapid attainment of equilibrium because of the necessity for working with relatively small particles, (c) the sometimes extensive internal cracking in the preparations as received. On occasion, however, quite good precision was realized, as shown by the illustrative calculations summarized in Table III. The derived rate constants to be reported possibly should be termed "apparent self-diffusion coefficients," for the actual anionic species responsible for the appearance of radioactivity in the external aqueous solution may not necessarily be the same as the preponderant simple species in the system. Although there was no definite evidence in any of our experiments for this type of complication, the possibility needs mention as a consideration of the system containing I^- ion will show if, for example, small amounts of I_3^- should have been present.

Experimental Results and Discussion

It will be noted first (Tables IV and V) that the orders of magnitude of the self-diffusion coefficients, D, frequency factors, D_0, and energies of activation, E_{act}, for anions are such as to suggest that the rate processes in strong-base anion exchangers are to be compared with diffusional processes in aqueous solutions. The diffusing unit in the exchanger accordingly will be taken as the hydrated ion which moves in the solvent water, or perhaps more correctly, in a mixed organic–water solvent. The structure of the solvent water in ion exchangers is very probably completely broken; however, an organic network is present and will play an important role. Since ion-exchangers are analogous to electrolyte solutions of high concentration, in addition to the ion–solvent interaction, consideration must be given to the specific interactions between ions. These two factors are, of course, not mutually independent. The specific interaction between the anions and the cationic exchange groups in an anion exchanger, for example, is influenced by the interaction between the anion and solvent molecules (*viz.*, water), and conversely.

Pursuant of the analogy between ion exchange polyelectrolytes and ordinary aqueous electrolyte solutions certain measurements on the latter will be examined to supply a background for further discussion. The self-diffusion of ions in infinitely dilute aqueous solutions will be considered first, for here only ion–solvent interactions should be present. Self-diffusion coefficients may be estimated from limiting equivalent conductances, λ^0, by use of the Nernst equation

$$D = RT\lambda^0/|Z|F^2 \qquad (2)$$

and activation energies for their temperature coefficients using the Arrhenius equation

$$E/R = -\mathrm{d}(\ln D)/\mathrm{d}(1/T) = -\mathrm{d}[\ln(\lambda^0 T)]/\mathrm{d}(1/T) \qquad (3)$$

The D values at 25° for cations decrease in the order: $Rb^+ > Cs^+ > K^+ > Na^+ > Li^+$, while for anions the sequence is: $Br^- > I^- > Cl^-$. The activation energies diminish according to: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$. At 25° these activation energies are all smaller than 4600 cal. mole^{-1}, which is the value for the self-diffusion of H_2O in pure liquid water. This fact has been

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[13] G. E. Boyd, J. W. Cobble and S. Wexler, THIS JOURNAL, **74**, 237 (1952).

[14] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, S 381 (1949).

TABLE IV

EFFECT OF ANION TYPE AND CHARGE ON APPARENT SELF-DIFFUSION COEFFICIENT AND ACTIVATION ENERGY (Dowex-2; Nominal 6% DVB; 3.27 meq./g. dry Cl form)

Ion	Equivalental moisture, g. H_2O/equiv.	Self-diffusion coefficient, cm.²/sec. 0.2°	Self-diffusion coefficient, cm.²/sec. 25°	Activation energy, cal./mole	D_0	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$	Limiting equiv. conductance, λ^0
BrO_3^-	172	1.76×10^{-7}	4.55×10^{-7}	6200	1.6×10^{-2}	3.1	55.78
Br^-	130	1.53×10^{-7}	3.87×10^{-7}	6000	9.8×10^{-3}	2.4	78.17
Cl^-	170	1.25×10^{-7}	3.54×10^{-7}	6800	3.5×10^{-2}	4.3	76.35
I^-	74	3.46×10^{-8}	1.33×10^{-7}	8800	3.8×10^{-1}	14.9	76.85
$WO_4^{=}$	179	6.00×10^{-8}	1.80×10^{-7}	7200	3.4×10^{-2}	4.5	73.8[a]
$PO_4^{\equiv}$	219	1.55×10^{-8}	5.70×10^{-8}	8700	1.4×10^{-1}	9.0	...

[a] Estimated from value of self-diffusion coefficient in aqueous solutions.

TABLE V

EFFECT OF EXCHANGER CROSS-LINKING ON THE SELF-DIFFUSION OF BROMIDE ION IN DOWEX-2

Nominal % DVB	Self-diffusion coefficient, cm.²/sec. 0.2°	Self-diffusion coefficient, cm.²/sec. 25°	Activation energy, cal./mole	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$
1	4.35×10^{-7}	9.12×10^{-7}	4800	1.3
2	2.98×10^{-7}	6.4×10^{-7}	5000	1.3
3	2.03×10^{-7}	4.52×10^{-7}	5200	1.3
6	1.48×10^{-7}	3.87×10^{-7}	6000	2.4
8	6.1×10^{-8}	2.0×10^{-7}	7740	7.4
16	6.04×10^{-8}	2.57×10^{-7}	9320	32.0

interpreted by Wang[15] as indicating that the mechanism for the diffusion of these singly-charged ions in infinitely dilute aqueous solutions probably involves the activation of the immediately surrounding solvent water molecules to get out of the way of the tracer ion. Our analysis of the recent, highly accurate values reported[16] for the limiting mobilities of the above ions has revealed the additional fact that E_{act} decreases with increasing temperature, and that, to a fair approximation, this temperature dependence in the range 10 to 50° is given by

$$E_{act} = E_0 - CRT \qquad (4)$$

The constant, C, may be identified with the quantity $(f - 1)$, in the simplest case of the theory of Barrer[17] where f is the number of degrees of freedom into which the activation energy is distributed. Since for diffusion or flow in liquids showing structure, and in numerous high polymer systems, f is found to be large, the unit transport process may be said to be accompanied by a "zone of activation." Values of f for Cl^-, Br^- and I^- ions lie between 9 and 12 with Cl^- possibly showing the largest value; approximately the same f values may be estimated for the alkali metal cations, with that for Li^+ perhaps being the largest, and that for Cs^+ the smallest. As will be seen below, the self-diffusion of ions in anion exchangers also appears to involve a "zone of activation."

The influence of specific interaction between ions on their self-diffusion in aqueous solutions may also be assessed from recently published studies.[18-20] Data are available for the self-diffusion rates of *both* ions in aqueous NaCl, NaI and Na_2SO_4 solutions out to high concentrations. Comparing D_{Na^+} for 3.0 N solutions of each of these salts one finds values of 1.02, 1.24 and $0.84_5 \times 10^{-5}$ cm.² sec.⁻¹, respectively, which show that the self-diffusion of sodium ion is increased by the faster moving I^- ion, and is decreased by the considerably slower $SO_4^{=}$ ion. While the effect of iodide ion on Na^+ ion does not become experimentally distinguishable from that also exerted by chloride ion until a concentration of 1.0N is reached, the interaction of sulfate ion is evident even at very low concentrations. These interactions are of course mutual: the mobility of the anion likewise is reduced or increased depending on whether it is faster or slower than Na^+ ion.

Both ion–solvent and ion–ion interaction effects should be apparent in the self-diffusion of ions in polyelectrolyte systems. Ionic association, in particular, should be of considerable importance, and this has been revealed by measurements of the self-diffusion of sodium ion in aqueous solutions containing linear sodium polyacrylate[21] and polystyrene sulfonate.[22] In the former, even at concentrations as low as 0.0031 N, the self-diffusion coefficient for Na^+ ion is depressed to less than 35% of its value in a sodium chloride solution of the same concentration. Effectively, more than 65% of the sodium ions are immobilized by the highly charged polyanion, and hence do not contribute to the self-diffusion. The association of mobile, weakly hydrated anions with the essentially unhydrated polycations of strong-base anion exchangers should be even greater than that of cations with a polyanion. That this factor is largely responsible for the approximately tenfold smaller self-diffusion coefficients (Table IV) of anions in these materials than in aqueous solutions of the *same concentration* is therefore not unlikely.

Differences in the degree of association of various anions with anion exchangers appear to be related to differences in their degrees of hydration. An index of relative anionic association in linear and cross-linked polyelectrolytes is given by osmotic coefficients derived from isopiestic measurements. Determinations[23] on various salt-forms of a very weakly cross-linked Dowex-1 preparation, for example, have given the following order of decreasing association: $I^- > Br^- > Cl^- > OH^- > F^-$. Equivalental moisture contents, M_w, of fully hy-

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(15) J. H. Wang, THIS JOURNAL, **74**, 1612 (1952).

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(17) R. M. Barrer, *Trans. Faraday Soc.*, **39**, 237 (1943).

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(19) J. H. Wang, *ibid.*, **74**, 1611, 1612 (1952).

(20) J. M. Nielson, A. W. Adamson and J. W. Cobble, *ibid.*, **74**, 446 (1952).

(21) J. R. Huizenga, P. F. Grieger and F. T. Wall, *ibid.*, **72**, 4228 (1950).

(22) B. A. Soldano and G. E. Boyd, unpublished results.

(23) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

drated, cross-linked anion exchangers may also be employed to assess the relative interionic attraction in anion exchangers. Thus, Table IV shows that the bromate salt form is the least associated, and that, despite its appreciable hydration and hence lower mobility, bromate ion self-diffuses fastest among the singly charged anions. While increased hydration acts to decrease the association of an anion, its mobility is also reduced owing to its increased size. The less-hydrated, mobile bromide ion accordingly self-diffuses more rapidly than the less associated, more hydrated chloride ion. The strong interaction of iodide ion with the exchanger is revealed by the small equivalental moisture of the iodide salt-form, and by the low self-diffusion coefficient and high activation energy for this ion.

Perhaps one of the most interesting features of the data of Table IV is the relatively small effect of ionic charge on the self-diffusion of anions. This is in marked contrast with results for the self-diffusion of cations in cation exchangers, where, for example, in Dowex-50 at 25°, changing from sodium to yttrium ion decreased D from 2.88×10^{-7} to 3.18×10^{-9} cm.^{2} sec.$^{-1}$ Differences in the interactions of anions and cations appear to afford a basis for understanding the relative absence of an ionic charge dependence in anion exchangers. With cation exchangers the *net* activation entropy, $\Delta S^{\ddagger}$, estimated using the absolute reaction rate equation

$$D = ed^2(kT/h) \exp(\Delta S^{\ddagger}/R) \exp(-E_{\mathrm{act}}/RT) \quad (5)$$

decreased and became negative with the most highly charged ions, because of the increasingly large negative entropy of electrostriction accompanying the charge separation to form the activated complex. This latter factor appears to be absent in anion exchangers containing usually weakly hydrated anions and essentially anhydrated cationic groups. Generally, only small, positive activation entropies from the disorder caused in the medium through which fairly large anions diffuse are observed. Since ionic size increases with charge in going from Cl^- to $\mathrm{WO}_4^{=}$ and $\mathrm{PO}_4^{\equiv}$ ions, an increasingly positive entropy acts [Eqn. (5)] to increase the self-diffusion coefficient, and thus to overcome partially the increased activation energy. It may be further seen (Table IV) that the diffusion of the relatively large iodide ion in the comparatively deswollen (*i.e.*, unhydrated) iodide salt form occurred with a large activation entropy increase. The diffusion coefficient for iodide ion, because of the positive $\Delta S^{\ddagger}$ is appreciably greater than expected for an activation energy of 8800 cal. mole.$^{-1}$ To conclude: it is the occurrence of a net positive entropy of activation which becomes greater with anionic charge which is at least partially responsible for the lack of a pronounced charge effect in the self-diffusion of anions in anion exchangers.

The self-diffusion rate of bromide ion was found to be decreased and its activation energy progressively increased by an increased ion-exchange polymer cross-linking (Table V). The decrease in D, however, was not as great as observed previously in the self-diffusion of singly-charged cations in cation exchangers. This difference again appears to be a consequence of the larger *net* positive activation entropies shown in the self-diffusion of anions. The additional factor of a progressively smaller exchange capacity (Table I) with increased cross-linking may have contributed also to the observed decrease in D. Thus, not only did the equivalental moisture decrease (Table I), but the relative amount of organic material through which the anion must diffuse became greater as the number of exchange groups diminished. The large activation energy and positive entropy found with the most highly cross-linked (*i.e.*, 16% DVB) preparation may well have resulted in part from its lower capacity.

Indications of the role of the interactions of the mobile anions with the functional groups of the exchanger were given by measurements of the self-diffusion of bromide ion in a series of diversely substituted, strong-base, quaternary ammonium type exchangers of constant cross-linking (*i.e.*, nominal 6% DVB). Although again the complication of a varying exchange capacity (Table II) was present, several observations (Table VI) can be made: Comparing the purely alkyl-substituted exchangers it is seen that the activation energy increases with exchange group size. A value greater than 16 kcal. mole^{-1}, the highest yet observed for self-diffusion in ion exchangers, was found with the benzyltributyl ammonium preparation. Concomitantly, there is an increase in the entropy, so that D does not decrease exponentially with the increase in E_{act}. With the benzyltriethylammonium exchanger, in fact, the increase in $\Delta S^{\ddagger}$ was such as to cause bromide ion to diffuse slightly more rapidly than in the benzyltrimethyl preparation. The exceptionally large $\Delta S^{\ddagger}$ of 15.1 e.u. for the benzyltributylammonium exchanger indicates that the diffusion of bromide ion in this material must occur with considerable disordering.

Substitution of a phenyl for a methyl group in the benzyltrimethylammonium exchanger appeared to give only a small increase in the activation energy and entropy. Substitution of a second, still larger benzyl group, however, increased E_{act} and gave a positive net $\Delta S^{\ddagger}$.

Changes in self-diffusion coefficients and activation energies resulting from the substitution of polar alkanol groups in general were small (Table VI). The inductive effect of the hydroxyl group is to increase the positive charge on the quaternary nitrogen and presumably to cause the bromide salt form to be more associated. Excepting for the mono-alkanol derivative, an increase in E_{act} and $\Delta S^{\ddagger}$ was observed. The effect of polar substituents on the *net* $\Delta S^{\ddagger}$ should be comprised of two parts: a negative entropy from the hydration of the exchange group in the formation of the activated complex, and a positive contribution owing to the increased size of the group. The former contribution appears to be of relatively greater importance in the benzyldimethylethanolammonium (Dowex-2) exchanger, for, although a 2.7-fold increase in D should result at the mean temperature of 12.6° from the lowered activation energy, actually, there was no change from the D for the benzyltrimethyl exchanger (Dowex-1) within experimental error.

The pyridinium exchanger showed both a small activation energy and entropy change relative to

TABLE VI

EFFECT OF CATIONIC EXCHANGE GROUP STRUCTURE ON THE SELF-DIFFUSION COEFFICIENT AND ACTIVATION ENERGY FOR BROMIDE ION

Functional group R = hydrocarbon matrix	Self-diffusion coefficient, cm.^{2}/sec. 0.2°	25°	Activation energy, cal./mole	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$	Activation free energy,[a] $\Delta F^{\ddagger}$
$RNMe_3^+$	1.38×10^{-7}	3.79×10^{-7}	6600	4.1	6310
$RNEt_3^+$	1.99×10^{-7}	6.73×10^{-7}	7940	17.5	6000
$RNBu_3^+$	4.60×10^{-9}	5.48×10^{-8}	16130	6240	7520
$RNMe_2Phenyl^+$	1.11×10^{-7}	3.33×10^{-7}	7180	6.4	6380
$RNMe_2Benzyl^+$	2.99×10^{-8}	1.15×10^{-7}	8780	15.0	7015
$RNMeEtOH^+$	1.53×10^{-7}	3.87×10^{-7}	6000	2.5	6285
$RNMe(EtOH)_2^+$	1.20×10^{-7}	3.75×10^{-7}	7440	8.5	6320
$RNMe_2PrOH\text{-}2^+$	9.42×10^{-8}	3.16×10^{-7}	7880	11.3	6435
$RNMeMorpholinium^+$	1.07×10^{-7}	3.36×10^{-7}	7420	7.9	6385
$RNPyridinium^+$	2.25×10^{-7}	5.87×10^{-7}	6270	3.9	6030
$RNQuinolinium^+$	2.38×10^{-8}	8.38×10^{-8}	8180	7.6	7185

[a] $\Delta F^{\ddagger}$ estimated using $d^2 = 10^{-15}$ cm.^{2}.

the trimethylammonium exchanger, which behavior seems consistent with the small size and lack of polarity of the quaternary ammonium cation of the former. Further increase in size of the ammonium group resulting from the employment of quinoline as the quaternizing tertiary amine gave an increase in E_{act} and a positive $\Delta S^{\ddagger}$. The results in Table VI, viewed as a whole, suggest that, in the 6% DVB exchanger at least, *the size of the quaternary ammonium cation is of greater importance than its polarity* and, hence, that it is the steric hindrance of the functional group which largely determines the self-diffusion rate of bromide ion. Specific effects from polarity in the quaternary ammonium cation, while present, do not, in general, seem to be of sufficient magnitude to give the definitely negative activation entropies sometimes found with cation exchangers.

Measurements of the self-diffusion of bromide ion in several of the exchangers listed in Table VI were conducted over a wide temperature range to determine to what extent E_{act} was temperature dependent. Some variation with temperature was expected, for it had been observed (Tables IV, V and VI) that self-diffusion of Br^- ion sometimes occurred with an appreciably positive activation entropy. The exceptionally large negative temperature coefficient which has been found for the activation energy of the benzyltributylammonium exchanger was not unexpected. However, in the highest temperature range (*i.e.*, 49.6 to 65°) E_{act} decreased to only 1300 cal. mole^{-1} suggesting that almost certainly some decomposition must have occurred. The values of 19,950, 13,500 and 4350 cal. mole^{-1} at mean temperatures of 5.3, 17.6 and 37.8°, respectively, when employed in Barrer's[17] relation: $dE_{act}/dT = -(f-1)RT$, lead to values of f of 260 and 230, indicating a quite large "zone of activation" in the movement of bromide ion through this exchanger. Considerably smaller "zones," comparable with those found for self-diffusion in cation exchangers, were indicated for the benzyldimethylethanol and benzyldimethylpropanol-2 exchangers. With the former, values of 7210 and 6470 cal. mole^{-1} at 12.7 and 37.0°, respectively, gave $f = 16$, while for the latter, values of 9120 and 6950 cal. mole^{-1} at 5.3 and 37.0°, respectively, gave $f = 34$.

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