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

Self-diffusion of Cations in and through Sulfonated Polystyrene Cation-exchange Polymers[1]

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Coefficients, D, for the self-diffusion of nine cations in sulfonated polystyrene–divinylbenzene type cation exchangers were determined as a function of temperature and polymer cross-linking. A strong dependence of D on the formal cationic charge was observed at all cross-linkings: In Dowex-50 at 25° values of 2.88×10^{-7} for Na^+, 2.89×10^{-8} for Zn^{++}, 3.18×10^{-9} for Y^{+++} and 2.15×10^{-10} for Th^{++++} ion were observed. Increased cross-linking, measured by the nominal divinylbenzene (% DVB) content, resulted in a sharply lowered self-diffusion rate. The coefficient at 25° for Zn^{++} in 1% DVB was 1.06×10^{-6} compared with 2.63×10^{-9} cm.^{2} sec.$^{-1}$ in a 24% DVB exchanger. Activation energies, E_{act}, which were temperature but not charge dependent, increased with cross-linking from *ca.* 4700 to 10,000 cal. mole^{-1}.

A qualitative interpretation of the variations of D was attempted based on absolute reaction rate theory modified by Barrer to explain observed temperature variations of E_{act}. The derived entropy of activation, $\Delta S^{\neq}$, was regarded as the resultant of two opposing effects: (a) a positive contribution from the disturbance created in its environment by the diffusing ion; and (b) a negative contribution from the electrostriction of water accompanying the separation of charge in forming the activated complex.

Ion-exchange rate processes in the synthetic organic ion-exchange polymers are of interest for several reasons. Firstly, reaction velocity studies may reveal features of the basic physical chemistry of these novel materials not disclosed by thermodynamic measurements on exchange equilibria. Further, reaction velocity constants enter in an important way into the theory of ion-exchange chromatography from which it may be demonstrated that rate as well as equilibrium processes determine the efficiency with which ion-exchange separations of interest to analytical and preparative chemistry may be accomplished. Finally, since the monofunctional organic exchangers may be, to some degree at least, prototypes of naturally occurring ion-exchange bodies such as silk, wool, proteins, cell membranes, nerve fibers, etc., it has seemed that careful studies of their permeation by ions might be of general significance.

Published literature on cation-exchangers has consisted of: (a) those contributions[3,4] in which the exchange velocity was thought to be governed by a chemical rate mechanism based on the law of mass action, and (b) those[5–8] wherein diffusional processes were considered to be rate controlling. Although the possibility continues that chemically controlled processes may occasionally govern ion-exchange rates, an increasing weight of evidence[9] favors the view that diffusion is the more usual mechanism. Ionic diffusion may be either of two types, or a mixture thereof: (a) "film diffusion" in which ions are transported across a concentration gradient between the bulk of an aqueous solution and the surface of an ion-exchange particle, or, (b) "particle diffusion" wherein a permeation of ions through the polymeric structure of the exchanger occurs. The rate constant for (a) is independent of the nature of the ion-exchange polymer but is related to the diffusion coefficients for the electrolyte solution. Particle diffusion rates, however, are independent of the external aqueous solution and appear to depend on the nature and ionic composition of the exchanger. Both types of diffusion controlled exchange rates depend on the ionic charge.[10] Preliminary measurements[5,7] have sug-

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(1) Presented before the Division of Physical and Inorganic Chemistry, 118th Meeting, American Chemical Society, Sept. 3–8, 1950, Chicago, Ill.

(2) Fulbright Advanced Research Scholar for The Netherlands, 1952–1953.

(3) F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944); **67**, 629 (1945).

(4) W. Juda and M. Carron, *ibid.*, **70**, 3295 (1948).

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

(6) W. C. Bauman and J. Eichorn, *ibid.*, **69**, 2830 (1947).

(7) T. R. E. Kressman and J. A. Kitchener, *Faraday Society Discussions*, **7**, 90 (1949).

(8) D. K. Hale and D. Reichenberg, *ibid.*, **7**, 79 (1949).

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

(10) G. E. Boyd, L. S. Myers, Jr., and A. W. Adamson, THIS JOURNAL, **72**, 4807 (1950).

gested that the activation energy for particle diffusion may be somewhat higher than for the film mechanism.

This work was undertaken to obtain quantitative information about the diffusion of cations in cation-exchangers of the sulfonated polystyrene variety.[11,12] Self-exchange rates were determined rather than rates of attainment of exchange equilibrium in which the composition of the exchanger varied. Since only a redistribution of isotopic species was involved, a rate characteristic of the system at equilibrium was measured. Complications such as from alterations in the particle size during the exchange reaction owing to swelling or deswelling and from activity coefficient effects on the rate arising from a changing environment along the path of diffusion were thereby avoided.

Apparent self-diffusion coefficients were estimated for a variety of cations to establish the effect of ionic size and charge, and, for a number of variously cross-linked ion-exchangers to determine the influence of polymer structure. Measurements were made at several temperatures to find the activation energy for self-diffusion, and to evaluate its dependence on cationic size and charge and polymer structure. A stirred-bath technique was employed in which radioactively labeled, spherical cation-exchange particles of accurately known diameter were placed in a dilute electrolyte solution containing the same cation as the exchanger. The rate of isotopic redistribution was determined by measuring the amounts of radioactivity in small aliquots of solution withdrawn at known periods after the start of the reaction. Apparent self-diffusion coefficient values were then derived from the observed time-dependence of the fractional attainment of equilibrium using diffusion theory.

Theory of the Method

A known mass of spherical exchanger particles each containing an initially uniform distribution of radioactive "counter-ions" is immersed in a well-stirred electrolyte solution of known concentration initially devoid of radioactivity, but otherwise in equilibrium with the exchanger. Suppose the entire solution to be divided equally among the total spheres, each of radius, a, such that every particle is surrounded by a shell of solution of radius, b, of uniform concentration. Let additional variables be: V^r, the volume of exchanger and V, the volume of solution in the spherical shell; and c and q, the concentrations of radioisotope in the solution and in the exchanger at any time, t, respectively. The rate of loss of radioactivity from the exchanger will be described by the radial diffusion equation

$$\partial(Rq)/\partial t = D\partial^2(Rq)/\partial R^2 \qquad (1a)$$

The concentration, q, at a distance R from the center of the sphere will be given by the solution to eq. 1a subject to the following boundary conditions: Sphere initially at constant concentration

$$q = q_0 \text{ for } R < a, t = 0 \qquad (1b)$$

Solution initially devoid of radioactivity

$$c = 0 \text{ for } R > a, t = 0 \qquad (1c)$$

Surface of the sphere in equilibrium with the solution (*i.e.*, "steady state" at surface)

$$q = kc \text{ for } R = a, t > 0 \qquad (1d)$$

Conservation (*i.e.*, Fick's first law of diffusion)

$$(\mathrm{d}c/\mathrm{d}t) = -(4\pi a^2 D/V)(\partial q/\partial R)_{R=a} \text{ for } t > 0 \qquad (1e)$$

Combining (1d) and (1e)

$$(\mathrm{d}q/\mathrm{d}t)_{R=a} = -(3wD/a)(\partial q/\partial R)_{R=a} \qquad (1f)$$

where $w = kV^r/V$. Upon substituting $R/a = r$; $Dt/a^2 = \tau$; $Rq/aq_0 = u$ and $c/q_0 = u'$, eqs. (1) become

$$(\partial u/\partial\tau) = (\partial^2 u/\partial r^2) \text{ for } r < 1, \tau = 0 \qquad (2a)$$

$$u = r \text{ for } r < 1, \tau = 0 \qquad (2b)$$

$$u' = 0 \text{ for } r > 1, \tau = 0 \qquad (2c)$$

$$u = ku' \text{ for } r = 1, \tau > 0 \qquad (2d)$$

$$-3w(\partial u/\partial r - u/r) + (\mathrm{d}u/\mathrm{d}\tau) = 0 \text{ for } r = 1, \tau > 0 \qquad (2e)$$

Equations 2, which also arise in the problem of the cooling of a solid sphere in a well-stirred fluid, may be solved by classical methods to give a series solution. Thus, for the fractional attainment of isotopic distribution equilibrium, F, at any time, t

$$F = 1 - {}^2/_3 w\sum_1^\infty e^{-\lambda_n^2\tau}/[1 + \lambda_n^2/9w(1 + w)] \qquad (3a)$$

where the λ_n's are the roots of the transcendental equation

$$\lambda_n \cot \lambda_n = 1 + \lambda_n^2/3w \qquad (3b)$$

obtained by substituting the particular solution for eq. 2a

$$u = \sin(\lambda_n r)e^{-\lambda_n^2\tau} \qquad (3c)$$

into eq. 2e. The convergence of the series in eq. 3a for $\tau < 0.1$ is quite poor, and it is therefore tedious to use in self-exchange rate studies with the organic exchangers where the magnitudes of D and a are such that $Dt/a^2 < 0.1$. Fortunately, Paterson[13] has given a detailed mathematical treatment of this problem. A solution which holds with good accuracy for $\tau \leq 0.1$, and which is susceptible to ready numerical evaluation is

$$F = (w + 1)/w\{1 - (1/(\alpha - \beta))[\alpha e^{\alpha^2\tau}(1 + \operatorname{erf} \alpha\sqrt{\tau}) - \beta e^{\beta^2\tau}(1 + \operatorname{erf} \beta\sqrt{\tau})]\} \qquad (3d)$$

where α and β are the roots of the equation

$$X^2 + 3wX - 3w = 0 \qquad (3e)$$

A typical (F, log τ) plot constructed for several values of w using eq. 3d is given in Fig. 1. Since w is simply the ratio of total milliequivalents of ion in the exchanger to that in the external solution, its numerical value may be determined by measurement of the equilibrium partition of radioactivity between the exchanger and solution. Apparent self-diffusion coefficients, D, may then be derived from experimentally determined rate curves using Fig. 1 to determine τ for any given fractional attainment of equilibrium, F, at time, t. Since $D = a^2\tau/t$, numerical values follow when the particle radius, a, is known.

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[11] G. d'Alelio, U. S. Patent 2,366,007 (Dec. 26, 1944).

[12] W. C. Bauman, J. R. Skidmore and R. H. Osmun, *Ind. Eng. Chem.*, **40**, 1350 (1948).

[13] S. Paterson, *Proc. Phys. Soc.*, **59**, 50 (1947).

Experimental

All measurements were conducted using variously cross-linked polystyrene sulfonic acid cation exchangers of the Dowex-50 type.[14] Preparations consisting of spheres of the largest possible diameter were desirable because of the dependence of the rate on the square of the particle radius (*cf.* eq. 3a and d), and because of the relatively large diffusion coefficients encountered. Unfortunately, the fraction of defective particles (*i.e.*, cracked spheres, ellipsoids, "pop-corn" polymer, etc.) also increased with the particle size, so that, depending on the cross-linking, an optimum size was selected. After a preliminary microscopic examination to establish the usability of each preparation, approximately 200–400 g. quantities of the sodium form (NaR) were wet-screened to procure fractions of 20/30, 30/40, 40/50 and 60/70 mesh size, respectively. These fractions were examined and any defectives were removed. Sodium, potassium, rubidium, cesium, silver, zinc, strontium, lanthanum, yttrium and thorium salt-forms were prepared separately. Approximately 5–10 g. aliquots of sized NaR exchanger were converted to the hydrogen form with a large excess of 6 N HCl. The exchanger was then treated with a concentrated aqueous solution of the desired cation, after rinsing with deionized water until a negative chloride test was obtained. The excess of reagent grade salt to exchanger on an equivalent basis was at least 15:1, and occasionally was as high as 30:1, except with yttrium, where the scarcity of pure chemical permitted only a 5:1 excess. In this latter instance, the solution from the exchanger was recycled until no change in *p*H between influent and effluent was observed. Very low flow rates were employed throughout. Finally, the exchanger salts were washed with many bed-volumes of deionized water to remove all occluded electrolyte. Where necessary, the *p*H of the wash was adjusted to eliminate possible hydrolysis of the salt-form. The washed, homoionic preparations were suction-dried in air and then stored in glass-stoppered bottles. The completeness of the conversion was confirmed in several cases either by titration for residual hydrogen ion in the exchanger, or by neutron activation analysis[15] of the salt form.

The preparations were characterized with respect to exchange capacity (Table I) by accurate electrometric *p*H titration of their hydrogen forms. Their nominal divinylbenzene (DVB) contents, however, afforded only a rough indication of their cross-linking. Accordingly, equivalental volumes, V_e, of the hydrogen and the salt-forms of the various preparations in water were determined using conventional 5-ml. capillary-neck pycnometers. Equivalental volumes of the moisture-free forms, V_m, were also measured pycnometrically using an inert organic liquid as the displacing medium. A correlation between these quantities and the nominal percentage DVB could be achieved using the empirical equation

TABLE I

CHARACTERIZATION OF CATION EXCHANGERS USED IN RATE STUDIES

Nominal % DVB	Exchange capacity, m.e. per g. dry H-form	Equivalental moisture, g. H₂O per equiv.	Equivalental volume, ml. per equiv.
		1947	
8	4.95	198	326
16	4.83	100.3	232
24	4.36	95.5	....
Commercial Dowex-50	5.20	143	268.6
		1949	
2	5.20	786	909.5
4	5.32	359	480
8	4.80	194	327
8.6	5.25	193	320
16	5.16	94.3	216.6
		1950–1951	
1	5.32	1901	2034
2	5.26	935	1064
4	5.16	408	536
8	5.26	208.5	325
16	5.10	116	247
Commercial Dowex-50	5.25	188	311

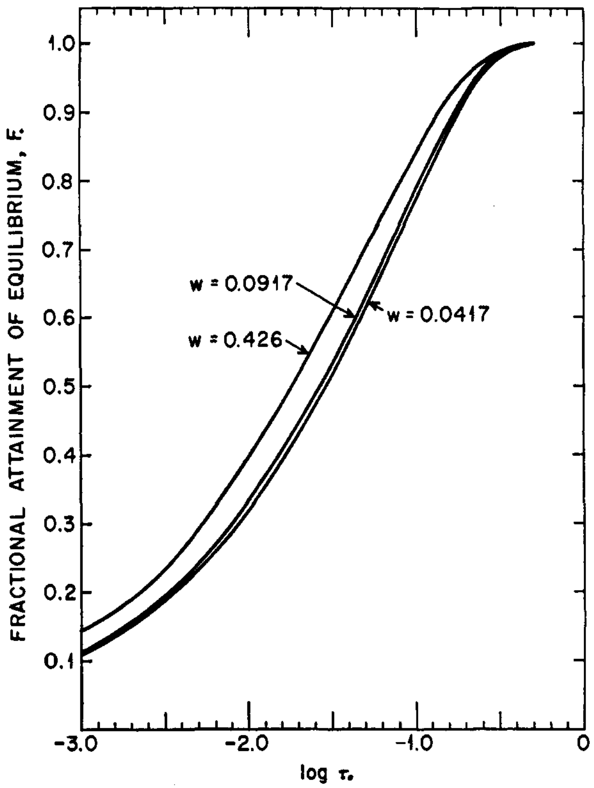

Fig. 1.—Curves from diffusion theory for representative cases of the diffusion of cations in cation-exchangers.

$$(V_e/V_m - 1) = k/(\%\text{DVB}) \quad (4)$$

where k is a constant for a given salt-form. The relative volume swelling, $(V_e/V_m - 1)$, was accurately proportional to the inverse first power of the percentage DVB for nominal contents varying from 1–25%. Equation 4 was obeyed not only by our data, but also quite well by that from other laboratories.[16,17] Values of k on the hydrogen forms from our work for the pre- and post-1950 exchangers, and from that of Pepper, Reichenberg and Hale[17] were 10.8, 13.7 and 10.7, respectively, while values for the lithium, potassium, ammonium and tetramethylammonium forms derived from the data of Gregor, Gutoff and Bregman[16] were 11.8, 9.1, 9.2 and 5.2, respectively. Our swelling data for the post-1950 exchangers therefore suggest that these were less highly cross-linked than those of Pepper and co-workers by a factor of about 1.3. This apparent variance may rest in differences between the methods of analysis for DVB. One notable exception to eq. 4 was observed with two shipments of pre-1950 nominal 1% DVB exchanger. Here the relative swelling was much smaller than expected and corresponded to a nominal DVB content of ~2.5%. It is considered possible that a misidentification may have occurred. Since our exchangers were received from the Dow Chemical Company over a period of several years, we have employed

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[14] The authors are indebted to the very helpful coöperation of W. C. Bauman and R. M. Wheaton of the Physical Research Laboratory of the Dow Chemical Company who supplied all of the exchangers used in this study.

[15] G. E. Boyd, *Anal. Chem.*, **21**, 335 (1949).

[16] H. P. Gregor, F. Gutoff and J. I. Bregman, *J. Coll. Sci.*, **6**, 245 (1951). Owing to the variable exchange capacity of these preparations all volumes were first corrected to an arbitrary capacity of 5.20 m.e./g.

[17] K. W. Pepper, D. Reichenberg and D. K. Hale, *J. Chem. Soc.*, 3129 (1952).

eq. 4 to establish an internally consistent cross-linking (*i.e.*, % DVB) scale.

One- to four-gram aliquots of the above described exchanger salts were charged with radioactivity prior to a rate experiment by placing the desired preparation in an aqueous solution containing an isotopic activity. After a time sufficient to allow the radioisotope ion to distribute itself uniformly throughout the exchanger the tracer solution was separated. The exchanger was thoroughly washed and then suspended in 150 ml. of pure water contained in a three-neck, round-bottom flask which was submerged in a 50-l. water-bath held to ±0.10° of the desired temperature. Sometimes a small amount of activity (*ca.* 10 to 50 c./m./ml.) appeared in the aqueous phase. This was interpreted as indicating that the washing away of occluded radioactivity had been incomplete. Inasmuch as the final activities in solution were usually *ca.* 5000 c./m./ml., or more, only a small correction was needed.

After stirring for several hours to ensure complete thermal equilibrium, the self-exchange reaction causing radioactive ions to appear in the external solution was initiated by adding as rapidly as possible to the reaction vessel (*i.e.*, *ca.* 1-3 seconds) 50 ml. of an electrolyte solution at the same temperature and containing the same cation as the exchanger. The external ionic strength after mixing was sufficiently low (usually *ca.* 0.2 *N*) that little or no deswelling of the exchanger occurred. The reaction zero-time was taken when one-half of the electrolyte had been added. Aliquots of 50 λ were withdrawn from the mixture at predetermined times read to 0.1 second until the radioactivity of the fluid remained constant. The time for equilibrium varied from several minutes to days. The final (equilibrium) radioactivity of the solution was of such importance that four aliquots were taken to guarantee a reliable measurement.

Radioactivity assays were performed either with a 4 π geometry scintillation counter[18] or with conventional mica end-window Geiger counters depending on whether or not a γ-ray was emitted by the radioisotope employed. γ-Radioactivity determinations were made on the 15.1 h Na^{24}, 12.5 h K^{42}, 19.5 d Rb^{86}, 37 y Cs^{137}, 270 d Ag^{110}, 250 d Zn^{65}, and 40 h La^{140} activities, while the 53 d Sr^{89}, 57 d Y^{91} and 24.1 d Th^{234} were beta counted. A considerably higher reproducibility may be achieved on solids or liquids with γ- than with β-detection techniques principally owing to difficulties in sample mounting in the latter instance. To measure the γ-activities of the 50 λ aliquots mentioned earlier, the contents of the 50 λ micropipets were transferred to small glass tubes containing 100 λ of water, and the micropipets were then rinsed twice to bring the volume up to 250 λ. The tube was placed as shown in Fig. 2, and the activity measured to a statistical error of 0.5%. β-Activities were estimated to a 1% error on 50 λ aliquots evaporated onto small glass discs which were mounted in a manner already described.[19] Because of its high detection geometry and large intrinsic efficiency for γ-activity detection, the 4 π geometry scintillation counter makes for either a very large saving in time, or for a much greater statistical accuracy, or both, when compared with the Geiger counter as a means for radioactivity assay. It no longer need be usual that the largest source of error in a physical chemical experiment using radioactive tracers be the statistical error in the activity estimation. Further, not the least time-saving advantage in the scintillation counter is the elimination of the need for elaborate source preparations.

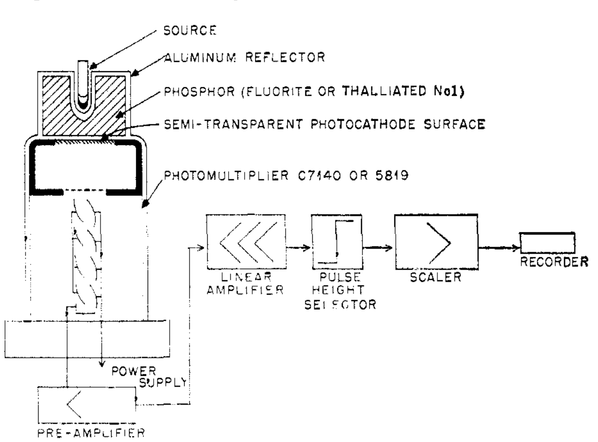

Fig. 2.—Schematic arrangement of 4π geometry scintillation counter for the measurements of γ-ray emitting radioactive tracers.

Measurements of the average radius of the spherical exchanger particles used in a given rate determination were performed photomicrographically. At the conclusion of an experiment, an aliquot of the exchanger *plus* equilibrium aqueous solution were transferred to a cylindrical insert in a thick microscope slide which was covered to prevent evaporation, and then placed on a microscope stage. Photomicrographs were taken with a Zircon light source using a 32 mm. microscope objective and a 10× ocular. The magnification was set accurately at 50× by means of a stage micrometer. Eastman Kodak Co. 4 × 6 inch Metallographic plates were employed and these were developed with Dektol to obtain good contrast.[20] Usually 400 to 500 particles were measured on several plates using a millimeter scale. The average radius was derived by computing the relative accumulations, plotting the same on arithmetic probability paper, drawing the best straight line through the points, and then visually estimating the radius corresponding to 50% accumulation. This procedure assumes that a normal distribution of particle sizes will be obeyed; most of the time this was the case.

Possible variations of particle diameter with temperature were investigated using a heated microscope stage. No changes were found within the experimental error (*ca.* 1%) between 0 and 60°. This finding appears to be in agreement with an earlier report[21] that the swelling of a weakly cross-linked exchanger was temperature independent. In one instance (Nominal 16% DVB) a small amount of distortion was noted upon cooling from 25 to 0°. It cannot be stated, however, that this effect is general for highly cross-linked cation exchangers, since only this particular preparation showed a distortion.

An illustration of the numerical evaluation of the self-diffusion coefficient is afforded by Table II taken from a representative experiment.

TABLE II

RATE OF SELF-EXCHANGE OF RADIOZINC AT 0.3° BETWEEN 0.22 *N* $Zn(NO_3)_2$ SOLUTION AND THE ZINC FORM OF NOMINAL 8% DVB DOWEX-50 EXCHANGER ($w = 0.0417$)

Time (t), seconds	Fraction of equilibrium (F)	log τ (Fig. 1)	$(\tau/t) \times 10^4$
30	0.270	−2.16	2.30
60	.360	1.875	2.22
90	.430	1.70	2.22
180	.582	1.362	2.41
300	.675	1.18	2.20
360	.715	1.105	2.18
590	.800	0.950	1.90

$$(\tau/t)_{\text{Av.}} = (2.20 \pm 0.09) \times 10^{-4}$$

Average radius, $a = 9.70 \times 10^{-3}$ cm.

$$D = (\tau/t)a^2 = 2.06 \times 10^{-8} \text{ cm.}^2 \text{ sec.}^{-1}$$

It may be seen, taking the uncertainty in the measurements of the average radius to be ±1%, that the average deviation in the numerical value of the self-diffusion coefficient was ±5%. In some experiments as many as 15 points (each of which gives a value of *D*) were taken. Never fewer than 5 points were used in the estimation of the final value, except in those relatively infrequent cases where the half-time for self-exchange was less than 5 seconds.

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[18] R. S. Stone and C. J. Borkowski, Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949, ORNL-607, p. 168.

[19] G. E. Boyd and D. N. Hume, "Analytical Chemistry of the Manhattan Project," National Nuclear Energy Series, Volume VIII, Ch. 28, McGraw-Hill Book Co., Inc., New York, N. Y., 1946.

[20] The authors wish to thank Mr. T. E. Willmarth for his help in this phase of our research.

[21] O. Samuelson, The Royal Swedish Institute for Engineering Research, Proceedings Nr. 179, Stockholm, 1945.

Values for the apparent activation energy of self-diffusion, E_{act}, were computed using the usual Arrhenius formula. The variation of log D with $1/T$ may be employed, or, since the particle radius was independent of temperature, somewhat more accurate estimates may be made by comparing the times for the attainment of a given F at two or more temperatures. The average uncertainty in E_{act} is believed to be ±200 cal. mole^{-1}.

Several preliminary studies were conducted to ensure the proper experimental conditions for a particle diffusion controlled process. As shown in previous studies,[5,9] among other things, the diffusion mechanism obtaining depends upon the equilibrium ratio of ions in the exchanger to those in solution. This ratio is measured by the parameter, w, and it was found that a particle diffusion process was followed when w was less than unity. This fact necessitated starting with the activity in the resin. Variations of w in the range $0 < w < 1$ did not change D. In a study of the self-diffusion of Zn^{++} ion in a nominal 24% DVB preparation the amount of exchanger was increased from 1 to 5 g. in 200 ml. of aqueous $Zn(NO_3)_2$ solution thereby changing w from 0.05 to 0.3. The values of D were 2.52 and 2.63 × 10^{-9} cm.^{2} sec.$^{-1}$, respectively. In another experiment the concentration of Zn^{++} in solution was increased twofold, holding the weight of exchanger constant, without any change in D.

The theory outlined above assumes that the transfer of radioactive ions from the exchanger takes place into a well-stirred liquid (*i.e.*, no concentration gradients at the particle surface). The effects of variations in stirring rate were determined, and it was established that rates greater than 500 r.p.m. gave efficient mixing. Actually, a rate of 1000 r.p.m. was used; higher rates tended to cause a mechanical attrition of the exchanger.

That particle diffusion was truly rate governing was of course implied by the constant values of D (*cf.* Table II) obtained. However, further proof was supplied by showing that F depended on the particle size according to eq. 3. This equation would require that rates for particle radii of 53 and 83 μ should stand in the ratio of 2.5:1. The observed ratio was 2.55:1, and the derived self-diffusion coefficients were 3.24 and 3.18 × 10^{-9} cm.^{2}sec.$^{-1}$, respectively.

It was found that with the very weakly and with the highly cross-linked exchangers the observed (F,t) curves frequently did not give a constant D as the self-exchange proceeded to completion. Rather, a trend was exhibited such that with the 16 and 24% DVB preparations D became progressively smaller as equilibrium was approached, while, with the 1% DVB exchanger, D increased initially and then became quite constant. The distribution in particle sizes in the former preparations was considered as a possible cause, for the initial exchange rate might be that for the smallest particles whereas the final rate would be governed by the largest spheres. A highly monodisperse preparation of the 24% DVB exchanger was obtained, and the rate of self-diffusion of Zn^{++} ion in it was compared with that in a relatively unsized preparation holding other variables constant. The same decrease of D with increasing F was observed in both experiments. This result seemed to indicate some non-homogeneity within the highly cross-linked exchanger particles. Either there may be a non-uniformity in cross-linking along the diameters of the particles or their centers are less highly sulfonated than the outer portions. The exchange capacity of the 24% DVB exchanger (4.36 m.e. per g. dry H-form) is appreciably smaller than that for a monosulfonic acid. Visual examination of the particles from this preparation under a polarizing microscope revealed the presence of mechanical strain not seen in the less highly linked exchangers. The values of D reported later were arbitrarily selected for $F = 0.5$. Typical examples of the behavior of the 16% and 24% DVB systems are given in Table III.

Table III

The Apparent Effects of Non-homogeneity on Self-diffusion Coefficients

F	Self-diffusion coefficient cm.^{2} sec.$^{-1}$ × 10^9 for zinc resinate at 24% nominal DVB at 25°	F	Self-diffusion coefficient cm.^{2} sec.$^{-1}$ × 10^8 for zinc resinate at 16% nominal DVB at 50.1°
0.254	2.89	0.366	1.70
.3695	2.74	.490	1.57
.484	2.66	.684	1.15
.570	2.50	.810	0.84
.894	2.37		

Other preliminary investigations were made to determine if changes in the ionic strength of the external electrolyte solution would be reflected in the self-diffusion rates. Two possible influences might be anticipated: (a) the deswelling action of an increased amount of external electrolyte would increase the density of the spherical exchange particle and would lower the rate; (b) diffusible *anions* from the external solution would enter the exchanger (Donnan distribution) and these might act to lower the activation energy for, and hence increase, the self-diffusion. A small, apparently real increase was found in the self-diffusion of Na^+ ion at 25° in a nominal 8.6% DVB exchanger, where, for an electrolyte concentration of 0.22 N, $D = 9.44 \times 10^{-7}$, while for 1.0 N, $D = 11.1 \times 10^{-7}$ cm.^{2} sec.$^{-1}$. In the diffusion of Y^{+++} ion in a commercial Dowex-50 exchanger, on the other hand, when the ionic strength of YCl_3 was increased from 0.26 to 0.53 molar the self-diffusion coefficient decreased from 3.18 to 2.83 × 10^{-9} cm.^{2} sec.$^{-1}$. A search for possible specific effects from diffusible anions in the external electrolyte was made keeping the ionic strength constant (Table IV). It has appeared that nitrate ion caused a definite lowering of the activation energy for the self-diffusion of silver, but not for lanthanum ion. In the attempt to minimize anion effects, the self-diffusion measurements in this paper employed the chloride salts, except for silver, zinc and thorium, and a constant electrolyte concentration of 0.22 N.

Table IV

Influence of Anion in the External Electrolyte on Self-diffusion of Cations in Cation Exchangers

(Concentration 0.22 N)

External electrolyte	Nominal % DVB	Self-diffusion coefficient, cm.^{2} sec.$^{-1}$ 0.3°	25°	Activation energy, cal. mole^{-1}
$AgClO_4$	16	9.30 × 10^{-8}	2.85 × 10^{-7}	6980
$AgNO_3$	16	10.10 × 10^{-8}	2.62 × 10^{-7}	6220
$La(ClO_4)_3$	8	3.01 × 10^{-9}	9.20 × 10^{-9}	7300
$La(NO_3)_3$	8	3.09 × 10^{-9}	9.28 × 10^{-9}	7340

Finally, a comparison (Table V) was made between the self-exchange rate of radiolanthanum ion and the rate when an ordinary ion-exchange of lanthanum occurs. In this latter experiment, 8% DVB exchanger was converted to the tagged sodium-form, and the exchange reaction with lanthanum was initiated by making the external electrolyte 0.22 N in lanthanum ion, as in the self-exchange experiment. The exchange with the sodium-form was found to occur approximately 25-fold times more rapidly than the self-exchange, and there was also an appreciable lowering of the activation energy. These results reveal the "averaging-down" of exchange rates where two or more ions are involved, and therefore emphasize that *self-diffusion rate measurements* afford a much more sensitive tool for the elucidation of ion-exchange phenomena.

Table V

Comparison of the Rate of Self-exchange of La^{+++} Ion with the Rate of Its Exchange with Na^+ Ion in a Nominal 8% DVB Cation Exchanger

Exchange reaction	Self-diffusion coefficient, cm.^{2} sec.$^{-1}$ 0.3°	25°	Activation energy, cal. mole^{-1}
$La^*R + La^{+++}$	3.09 × 10^{-9}	9.28 × 10^{-9}	7340
$Na^*R + La^{+++}$	8.47 × 10^{-8}	2.20 × 10^{-7}	6210

Results and Discussion

Self-diffusion coefficients were determined as a function of ion-exchange polymer cross-linking keeping ionic charge constant, as a function of ionic charge keeping cross-linking constant, and as a function of ionic size keeping both charge and cross-

TABLE VI

COEFFICIENTS OF SELF-DIFFUSION FOR ALKALI AND SILVER IONS IN A NOMINAL 8.6% DVB CATION EXCHANGER (5.25 E./G. DRY H-FORM)

Diffusing Ion	Self-diffusion coefficient (cm.^{2} sec.$^{-1}$ × 10^7) 0.3°	25°	Activation energy, cal. mole^{-1}	D_0, cm.^{2} sec.$^{-1}$ × 10^2	$d(e^{\Delta S^{\neq}/R})^{1/2}$ × 10^8, cm.	$(Ve/N)^{1/3}$ × 10^8, cm.	λ°	Activation energy,[a] cal. mole^{-1}
Ag^+	2.62	6.42	5895	1.4	3.0	9.0	61.90	..
Na^+	3.50	9.44	6500	3.44	5.7	9.8	50.15	4390
K^+	6.28	13.4	5220	0.90	2.3	9.45	73.50	3990
Rb^+	6.36	13.8	5140	.81	2.2	9.7	77.81	3950
Cs^+	6.61	13.7	4790	.45	2.1	9.8	77.26	3860

[a] Activation energies are for the self-diffusion of ions in aqueous solutions at infinite dilution.

TABLE VII

SELF-DIFFUSION RATES IN VARIOUS MEDIA

System	Self-diffusion coefficient (cm.^{2} sec.$^{-1}$)	°C.	Activation energy, cal. mole^{-1}	D_0, cm.^{2} sec.$^{-1}$	$d(e^{\Delta S^{\neq}/R})^{1/2}$ × 10^8 cm.	Reference
Na^+ in NaR	9.44×10^{-7}	25	6500	3.4×10^{-2}	5.7	This work, Table VI
Na^+ in 0.0 *M* NaCl	1.33×10^{-5}	25	4390	2.2×10^{-2}	3.6	22
Na^+ in 1.0 *M* NaCl	1.26×10^{-5}	25	5840	2.4×10^{-1}	11.9	23
Na^+ in NaCl(c)	8.0×10^{-13}	350	17,700	1.2×10^{-6}	...	24
H_2O^{18} in H_2O	3.01×10^{-5}	25	4410	5.0×10^{-2}	5.5	25
C_2H_5OD in C_2H_5OH	1.25×10^{-5}	30	4500	2.1×10^{-2}	3.5	26
C_6H_5D in C_6H_6	2.28×10^{-5}	30	2100	7.3×10^{-4}	0.66	26
C_2H_4DBr in C_2H_5Br	3.78×10^{-5}	22.5	1200	2.9×10^{-4}	.41	26
Hg in Hg	1.79×10^{-5}	23.0	1160	1.3×10^{-4}	.28	27
CH_4 in natural rubber (7.15% S)	1.03×10^{-6}	60	10,600	8.3	70.3	28

linking constant. The results (Table VI) from this last series determined with Na^+, K^+, Rb^+, Cs^+ and Ag^+ ions will be considered first. A comparison (Table VII) of the value for the self-diffusion coefficient of Na^+ ion in a moderately linked commercial cation exchanger with its coefficients for other systems shows that this ion diffuses in the exchanger an order of magnitude more slowly than in aqueous NaCl solutions of approximately the same molality, and with an appreciably greater activation energy. However, the movement of Na^+ ion in the exchanger is not to be compared with that in crystalline NaCl, even at temperatures approaching the melting point of the latter. The magnitudes of the quantity D_0 (Table VII) appearing in the equation $D = D_0 \exp(E_{act}/RT)$, also support the view that the diffusion of the singly charged cations in the nominal 8.6% DVB exchanger is to be compared with diffusion in aqueous or alcoholic media rather than in ionic crystals, or possibly in non-polar organic liquids.

The self-diffusion rates of the alkali cations are seen to be in the order: $Cs^+ \geq Rb^+ > K^+ > Na^+$, with the activation energies at 25° showing the reverse sequence. This same general type of behavior is exhibited (Table VI) by the ionic mobilities, λ°, at infinite dilution[29] and by the activation energies estimated from their temperature variations.[30] This analogy suggests that the diffusing species in the exchanger is the same (hydrated ion) as in ordinary aqueous solutions.

According to Eyring[31] self-diffusion coefficients are governed by the equation

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

where *e* is the base of the natural logarithms, *k* the Boltzman constant, *h* Planck's constant, *d* the average distance between equilibrium positions in the process of diffusion, $\Delta S^{\neq}$ the entropy of activation, and E_{act} is the experimental energy of activation. In the absence of information as to the correct value of *d*, eq. 5 may be applied to estimate the quantity, $d(e^{\Delta S^{\neq}/R})^{1/2}$ (Table VI)

Either abnormally large, or small, values of this function may give an indication of the mechanism of diffusion. Large positive values of $\Delta S^{\neq}$ may suggest[31] that the diffusion is accompanied by breakage of bonds, or by significant structural changes, while appreciable negative values may imply a partial mobilization of the diffusing species, or solvent effects. In some cases reliable estimates for *d* may be computed from molar volume data. As may be seen in Table VI, average distances of *ca.* 10 Å. separate the anionic exchange groups in the exchanger employed. This "jump-distance" appears rather too great for free-diffusion in a condensed medium. The value, *d* = 1.5 Å., for pure water derived by Wang from self-diffusion and dielectric data seems much more reasonable. Hence, it is inferred that $\Delta S^{\neq}$ for the diffusion of K^+, Rb^+, Cs^+ and Ag^+ ions is close to zero. Since all four ions are either unhydrated or weakly hydrated, and thus are approximately the same size, the larger E_{act} for silver ion may be attributed to the stronger interaction it shows with the structurally-bound

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sulfonate anion. This stronger interaction is also revealed by equilibrium selectivity measurements which show the silver ion to possess a large affinity for the exchanger, and by isopiestic measurements where the Ag form shows a small osmotic coefficient. By reason of its specific interaction, the silver ion diffusivity does not follow its limiting ionic conductance, as do the alkali cations. In contrast with silver, the even larger activation energy and the positive activation entropy for the sodium appear to be a consequence of the greater size of this hydrated ion.

An important observation in this study was the apparent temperature dependence of the activation energy which was found in all cases where measurements were made over a sufficiently wide range (Fig. 3). Tangents to the curve for the diffusion of Na^+ ion in the 8.6% DVB exchanger give E_{act} as 7100, 6280 and 4640 cal. mole^{-1} at 6.0, 18.35 and 36.9°, respectively. Similar variations of E_{act} for the self-diffusion of Na^+ ion at infinite dilution may be estimated from the temperature variation of the product, $T\lambda^0$. Accurate data[29] show in this case a decrease from 5200 at 2.5° to 3470 cal. mole^{-1} at 50°. The activation energy for the diffusion of Cs^+ ion, both in pure water and in the 8.6% DVB exchanger, decreases considerably less rapidly. For the latter, E_{act} was 4790 at 12.65° compared with 4440 cal. mole^{-1} at 36.9°.

Variations of the activation energy with temperature are not unusual for reactions in liquids; moreover, they have been reported for the diffusion of sucrose through collodion membranes[32] and for the diffusion of various inert gases though vulcanized natural rubber membranes.[28] Frenkel,[33] who discusses this question, has suggested that the temperature dependence of the activation energy for diffusion in liquids can be described by

$$E_{\text{aot}} = E_0 - \gamma RT \qquad (6a)$$

Barrer[34] in his "zone of activation" formulation of the statistical theory of rate processes has shown that E_{act} should decrease with temperature in the simplest case according to

$$\mathrm{d}E_{\text{aot}}/\mathrm{d}T = -(f - 1)R \qquad (6b)$$

where f is the number of degrees of freedom into which the activation energy may be accumulated. Our data appeared to obey eq. 6 and a value, $f = 39$, was estimated for the self-diffusion of Na^+ ion in the 8.6% DVB exchanger which may be compared with $f = 15$ estimated for the self-diffusion of this ion at infinite dilution in water. The self-diffusion of Cs^+ ion appeared to take place with approximately the same size of "zone of activation" in the exchanger and in water for $f = 10$ in both cases within experimental error. It is perhaps not surprising that the diffusion of large ions in an exchanger should occur with more local disturbance than in pure water. Further, since f for Na^+ ion is approximately as large as that for the diffusion of methane in a natural rubber vulcanized with 1.7% S (f = 30 to 40),[28] an appreciable interaction with the ion-exchange polymer network may be suggested.

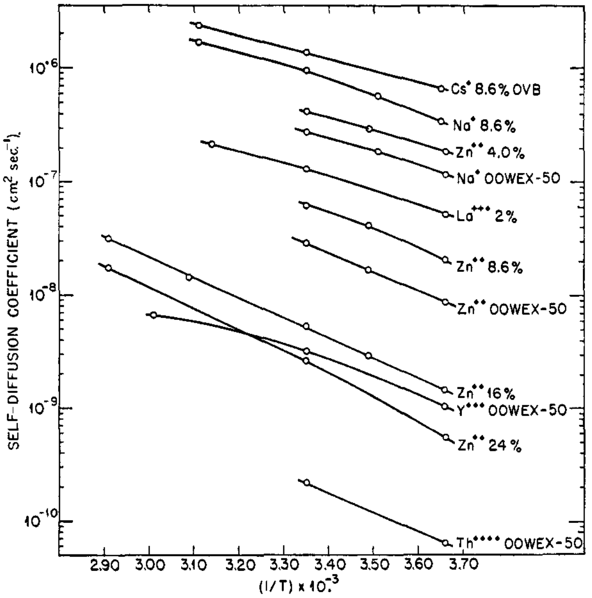

Fig. 3.—Temperature dependence of self-diffusion coefficients.

If the difference between the activation energy for the self-diffusion of Na^+ ion in an ordinary electrolyte (*cf.* Table VII) and in an ion-exchanger is at least partly a result of the higher concentrations usually existing in the latter, then, a dependence of the activation energy, and hence diffusion rate, on cross-linking is to be expected. This expectation appears to be confirmed (Table VIII) in that D decreases and E_{act} increases with the nominal % DVB. With silver and cesium ions the decrease in the self-diffusion coefficient seems almost entirely governed by the increase in activation energy. However, with sodium ion in the 24% and probably in the 16% DVB preparations there appears to

TABLE VIII

EXCHANGER CROSS-LINKING AND THE SELF-DIFFUSION COEFFICIENTS FOR SINGLY-CHARGED CATIONS

Nominal % DVB	Exchange capacity m.e. per g. dry H-form)	Self-diffusion coefficient (cm.² sec.⁻¹) 0.3°	25°	Activation energy, cal. mole⁻¹	d-$(e^{\Delta S^{\neq}/R})^{1/2}$ $\times 10^8$ cm.
		Sodium			
4	5.32	6.66×10^{-7}	1.41×10^{-6}	4930	1.9
8.6	5.25	3.50×10^{-7}	9.44×10^{-7}	6500	5.7
Dowex-50	5.20	1.15×10^{-7}	2.88×10^{-7}	5980	2.1
16	5.10	6.58×10^{-8}	2.40×10^{-7}	8400	
16	5.16	3.75×10^{-8}	1.10×10^{-7}	7070	3.3
24	4.36	2.69×10^{-8}	1.00×10^{-7}	8620	12.1
		Silver			
8.6	5.25	2.62×10^{-7}	6.42×10^{-7}	5895	3.0
16	5.10	1.00×10^{-7}	2.75×10^{-7}	6590	3.5
24	4.36	3.76×10^{-8}	1.13×10^{-7}	7200	3.6
		Cesium			
8.6	5.25	6.61×10^{-7}	1.37×10^{-6}	4790	2.1
24.0	4.36	3.32×10^{-8}	7.33×10^{-8}	5205	0.5

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be positive net entropy of activation. This factor acts (eq. 5) to increase D, and hence to diminish the retarding effect of increased cross-linking at high % DVB. A further consequence, possibly, of its net positive $\Delta S^{\neq}$ is that Na^+ ion diffuses more rapidly at 25° in the 24% DVB exchanger than does cesium ion.

Self-diffusion coefficients for the doubly-charged cations of zinc and strontium (Table IX) showed an even more pronounced dependence on the cross-linking than did the singly-charged ions, and the tendency toward becoming relatively independent of cross-linking at high % DVB remained. The E_{act} for the strongly hydrated zinc cation was also found to decrease with increasing temperature. Measurements were carried to as high as 70.8° with the 16 and 24% DVB exchangers. Values of 8580, 8440 and 7500 cal. mole^{-1} were observed at mean temperatures of 6.6, 19.0 and 37.5°, respectively, for the former preparation, while values of 10,200 and 8420 cal. mole^{-1} were found at 12.6 and 47.9°, respectively, for the latter. These variations correspond to an average f of approximately 25.

Table IX

Exchanger Cross-linking and the Self-diffusion Coefficients for Doubly-charged Cations

Nominal % DVB	Exchange capacity (m.e. per g. dry H-form)	Self-diffusion coefficient (cm.² sec.$^{-1}$) 0.3°	25°	Activation energy, cal. mole^{-1}	d-$(e^{\Delta S^{\neq}/R})^{1/2}$ × 10^8 cm.
Zinc					
1	5.32	4.26×10^{-7}	1.01×10^{-6}	5640	3.0
2	5.26	2.95×10^{-7}	7.37×10^{-7}	6020	3.5
8	4.80	2.06×10^{-8}	6.30×10^{-8}	7340	3.2
Dowex-50	5.20	8.77×10^{-9}	2.89×10^{-8}	7830	3.1
16	5.10	3.12×10^{-9}	1.16×10^{-8}	8520	3.8
16	5.16	1.47×10^{-9}	5.37×10^{-9}	8500	2.5
24	4.36	5.52×10^{-10}	2.63×10^{-9}	10250	8.0
Strontium					
4	5.32	9.67×10^{-8}	2.28×10^{-7}	5640	1.6
Dowex-50	5.20	9.58×10^{-9}	3.38×10^{-8}	8280	5.1
16	5.16	5.59×10^{-10}	2.98×10^{-9}	10980	16.1

The rate of decrease of D for the trivalent lanthanum and yttrium ions with increasing % DVB (Table X) was even greater than that for the divalent ions, whereas the "leveling-off" at the highest cross-linking was proportionately the least among the cations thus far mentioned. In the two cases examined, the activation energy decreased with increasing temperature, and a value of $f = 25$ was estimated for the diffusion of La^{+++} ion in the 2% DVB exchanger. However, a net negative entropy of activation seems to be required to explain the one-tenth smaller diffusion coefficients for these ions, for their activation energies are approximately the same as those for uni- and divalent ions. The origin of such a contribution may reside in the strong interaction, indicated by thermodynamic measurements, of the rare earth cations with the structurally-bound sulfonate anion of the exchanger. If these cations must *dissociate* to form the activated complex, it seems possible that the charge separation will be accompanied by an electrostriction of water molecules giving an appreciable negative entropy change.

Table X

Exchanger Cross-linking and the Self-diffusion Coefficients for Tricharged Cations

Nominal % DVB	Exchange capacity (m.e. per g. dry H-form)	Self-diffusion coefficient (cm.² sec.$^{-1}$) 0.3°	25°	Activation energy, cal. mole^{-1}	d-$(e^{\Delta S^{\neq}/R})^{1/2}$
Yttrium					
2	5.20	4.10×10^{-8}	1.14×10^{-7}	6700	2.5
4	5.32	2.66×10^{-8}	7.46×10^{-8}	6770	2.1
Dowex-50	5.20	1.01×10^{-9}	3.18×10^{-9}	7530	0.8
24	4.36	5.86×10^{-11}	2.18×10^{-10}	8620	0.6
Lanthanum					
1	5.32	7.45×10^{-8}	1.88×10^{-7}	6080	1.9
2	5.26	5.18×10^{-8}	1.30×10^{-7}	6040	1.5
4	5.16	2.96×10^{-8}	6.85×10^{-8}	5520	0.7
8	5.30	3.01×10^{-9}	9.20×10^{-9}	7310	1.2
16	5.10	1.53×10^{-10}	5.10×10^{-10}	7870	0.4

Although the diffusion of cations in cation exchangers appears to take place with a "zone of activation," evidently, this may also occur with either a positive or negative net entropy of activation. Data from other systems also suggest that the presence of a zone does not necessarily require a net positive activation entropy, for, while the diffusion of inert gases in vulcanized natural rubber[28] apparently occurs with a relatively large, positive $\Delta S^{\neq}$, the diffusion of sucrose through collodion[32] shows a relatively large, negative value. Further, a small net $\Delta S^{\neq}$ does not of necessity require the absence of a zone of activation, although for the self-diffusion of water[25] and of liquid mercury[27] this appears to be the case since here the activation energies are also largely temperature independent. All factors considered, however, it seems natural to suppose that in the absence of strong specific interactions with the environment a positive $\Delta S^{\neq}$ will accompany zone formation. As a corollary, then, it will be assumed that whether the activation entropy is positive or negative for diffusion in ion-exchangers will depend upon the degree of such specific interaction of the ion with the exchange groups. The *net* entropy of activation is then regarded as the resultant of two opposing effects: (a) a positive contribution arising from the disturbance in its environment by the diffusing ion and (b) a negative contribution from the electrostriction of water accompanying the separation of charge in forming the activated complex. Effect (a) may be expected to predominate when the diffusing ion is large, and when its association with the anionic exchange group is slight. When most of the water, as in highly cross-linked exchangers, is water of ionic hydration, the polymer network may participate in the "zone of activation" with a large $\Delta S^{\neq}$. Association with the sulfonate group may increase as the ionic charge increases so that effect (b) becomes increasingly evident despite effect (a) as with the rare earth cations.

Application of the foregoing argument to the example afforded by tetravalent thorium ion leads to the expectation in this case of an even more important 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

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

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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OAK RIDGE, TENN.

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

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

BY B. A. SOLDANO AND G. E. BOYD

RECEIVED MAY 21, 1953

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.

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