

SELF-DIFFUSION OF SODIUM ION IN A CATION-EXCHANGE RESIN¹BY DAVID RICHMAN AND HENRY C. THOMAS²*Contribution from Sterling Chemistry Laboratory, Yale University, New Haven, Conn.**Received July 25, 1955*

By means of a procedure based on diffusion from a well-stirred bath into a long rod, the coefficient of self-diffusion of sodium in a cation-exchange resin at chemical equilibrium has been measured. Evidence is presented for the absence of a liquid film effect. The results at two temperatures indicate at least two mechanisms for the transport through the resin: in the absence of Donnan electrolyte an exchange between sites with activation energy about 10 kcal./mole, and a diffusion involving free anion with activation energy about 2 kcal./mole.

The diffusion of ions within the matrix of a solid cross-linked polyelectrolyte must be a very complicated process. In the study of such a process it is of course advantageous to simplify the situation as much as is consistent with retaining its essential features. Much simplification is obtained by limiting the study to self-diffusion and this in a material at chemical equilibrium. We have carried out such a study with the cation exchanger Nepton CR-51,³ a phenolsulfonic acid-formaldehyde copolymer. The resin was obtained in the form of nearly cylindrical rods about 5 mm. in diameter. This simple and well-defined shape made possible an especially simple diffusion experiment: the measurement of diffusion from a limited bath into the end of an infinite uniform rod.

The solution of the equation for isotopic diffusion, with no gradient of excess chemical potential, *i.e.*, no gradient of activity coefficient, for the case of a well-stirred limited bath into an infinite rod with no boundary liquid film and with isotopic equilibrium at the interface is

$$\theta/\theta_0 = \exp(\alpha^2 A^2 Dt/V^2) \operatorname{erfc}(\alpha A \sqrt{Dt}/V)$$

Here θ/θ_0 is the relative isotopic content (relative radioactivity in our case) of the bath at time t , the rods being initially free of marked isotope; $\alpha = q/c$ is the distribution coefficient of the diffusing isotopic species, being merely the ratio of the equilibrium values of the volume concentrations (exchanger)/(solution); A , the total area of the ends of the rods exposed to the solution; V , the volume of the solution; and D , the coefficient of self-diffusion in the solid. It will be shown that a significant liquid film was absent under the conditions of our experiments.

Rods of length about 20 cm. were used. That these rods are effectively of infinite length is easily shown. The fraction of the activity initially in the bath which has diffused by time t beyond the point $x = \xi$ measured from the input end (of an infinite rod) is

$$\operatorname{erfc}(\xi/2\sqrt{Dt}) - \exp(\kappa^2 Dt + \kappa\xi) \times \operatorname{erfc}\{(\xi/2\sqrt{Dt}) + \kappa\sqrt{Dt}\}$$

in which κ has been written for $\alpha A/V$. With moderately pessimistic estimates for the various quantities, in particular if we put $D = 10^{-6}$ (more than

twice our largest measured value) and $t = 10^5$ sec. (the average duration of a run), and $\xi = 10$ cm., this fraction turns out to be of the order 10^{-12} ; *i.e.*, radiosodium never reached the ends of our rods.

Experimental

The procedure consisted in pumping continuously the radioactive bath solution through a jacketed Geiger-Mueller counter. A small glass centrifugal pump served to move the solution, and very vigorous stirring resulted. The solution, on entering the reaction chamber, was caused to impinge directly against the ends of the rods to eliminate as far as possible a static liquid film.

The counter ran continuously and was followed by a conventional scale-of-4096 circuit. The cumulative count and time were recorded at intervals of 100×4096 counts. Background and resolving time corrections were applied. If the cumulative count divided by the initial counting rate be called R , then because of the simple nature of the diffusion problem we have the following relation between R and its time derivative $dR/dt = \theta/\theta_0$

$$k^2 R - 2k\sqrt{t/\pi} - dR/dt + 1 = 0$$

in which $k = \alpha A \sqrt{D}/V$. Thus the determination of D results directly from the solution of a quadratic equation involving the experimental record and its time derivative. For each run some fifteen to twenty values of k were computed, the slope dR/dt being taken as $409600/\Delta t$ at $t + \Delta t/2$.

To obtain sufficiently large effects a group of three rods was used in each experiment. One end of each rod was flattened with a fine jeweler's file, and the surface area exposed to the solution was determined by several measurements of the diameter. Two groups of three rods were used, with satisfactory agreement between the groups (*vide infra*). The rods were soaked in concentrated NaCl solution to remove activity from previous experiments and then for several hours in distilled water. The equilibration with the desired solution was accomplished by slowly passing over the rods 2-4 liters of the solution during a period of 24-40 hours.

The ends of the rods to be exposed to the solution were defined by forcing the rod through a pin-hole in a piece of dental dam, the sides of the rods being protected by taping the rubber sheet into place.

Thermostat water (at 30 or 50°) was circulated around the chamber containing the radioactive solution and rods.

The exchange capacities of the polymer were determined by an isotopic dilution in the following manner. Small pieces of about 2-ml. volume were equilibrated with the desired solution (many hours rotation in the thermostat). The resin volume was then determined by weighing in a pycnometer filled with the appropriate solution, and, after wiping dry, quickly weighing the resin itself. The density of the solution and the volume of the pycnometer being known, the necessary information was available. The bits of resin were then placed in aliquots of a solution, carrying sodium-22 tracer, of the same gross concentration as the solution with which the rods were equilibrated. The rods were agitated in this solution for 10-20 hours in the thermostat. The initial activity of the solution and the activity after isotopic equilibrium was reached give immediately the total capacity of the resin under the conditions of the experiment. Typical results at 30° are as follows: three pieces of resin in 0.01 *N* NaCl gave 0.873, 0.897, 0.891 meq./ml.; three pieces in 0.05 *N* NaCl gave 0.944, 0.953, 0.954

(1) This paper is based on work done by D.R. as part of the requirement for the degree of Bachelor of Science with Honors from Yale University. The work was in part supported by the Department of Nuclear Engineering of Brookhaven National Laboratory, to which we express our thanks.

(2) To whom any communications may be addressed.

(3) This material was very kindly given to us by its manufacturer, Ionics Incorporated, Cambridge, Massachusetts.

meq./ml. The capacity of the exchanger in its dependence on the concentration of the external solution is sufficiently well reproduced by the linear relation

$$q = 0.865 + 1.73c$$

This relation is, of course, not consistent with the usual formulation of the Donnan effect, $q(+)q(-)/c^2 = 1$, which requires that in the limit of low concentration q be linearly related to c^2 . Only below 0.03 N do our results show approximately this proportionality. Within the precision of our experiments no effect of temperature is discernible. This point, however, needs more careful study.

A preliminary experiment was designed to show any effect due to diffusion through a static liquid film at the end of the rods. A metal baffle was placed in the reaction chamber so that on changing its position (by means of a glass rod extending to the outside) the agitation of the solution in the neighborhood of the resin was materially reduced. No change in the course of the R vs. t curve was detected when the position of the baffle was changed. This fact coupled with a consideration of the values of D obtained show that liquid film diffusion was negligible.

Values of $k = \alpha A \sqrt{D}/V$ should, of course, be constant throughout a run. Typical results are shown in Table I. It is difficult to estimate how much scatter to expect in these results depending as they do in such a complicated manner on the results of radioactivity counting. After the initial stages of a run no trends are observable in the values of k . In the first two runs k failed to reach a steady value until after 25,000 sec. This effect appears to have been due to a partial drying at the ends of the rods. In subsequent experiments the ends of the rods were kept moist at all times during the handling, and k assumed essentially constant values after 5,000–10,000 sec.

TABLE I

COURSE OF SELF-DIFFUSION OF Na^+ FROM 0.03 N NaCl INTO NEPTON CR-51

t , sec.	$k \times 10^{-4}$	t , sec.	$k \times 10^{-4}$	t , sec.	$k \times 10^{-4}$
12300	4.80	60700	4.98	88000	4.74
29600	5.38	65900	4.90	92700	4.94
47400	5.09	70800	4.74	129500	4.74
51600	5.02	76700	4.54	132700	4.81
56300	5.03	83500	4.67	140100	4.82

Independent experiments at 30° with 0.01 N solutions using different groups of rods, differing by a factor of two in total exposed area, gave 1.34×10^{-6} and 1.23×10^{-6} cm.²/sec. for D . Perhaps the largest sources of error are in the capacity determinations and in the definition of the exposed surface. Errors due to lack of definition (smoothness) of the ends of the rods are impossible to estimate. The capacity determinations depend on differences in counting rates and are subject to errors of 2 to 5%. A 5 to 10% uncertainty in D seems reasonably pessimistic under the circumstances.

The experiments at 50° were beset with difficulties not met near room temperature. Among other things we found that warm neutral sodium chloride solutions will etch pinholes through the walls of thin stainless steel Geiger counters. Our results on the temperature effect are by no means as complete as could be desired.

The results of this work are summarized in Table II.

TABLE II

CAPACITY AND COEFFICIENT OF SELF-DIFFUSION FOR Na^+ IN NEPTON CR-51 AT CHEMICAL EQUILIBRIUM

Bath N NaCl	Capacity, meq. $\text{Na}/\text{ml. resin}$		$D \times 10^6$, cm. ² /sec.	
	30°	50°	30°	50°
0.0025	...	0.860
.01	0.891	.964	1.32	3.79
.02	.912	...	2.43	...
.03	.930	...	4.69	...
.05	.954	...	4.88	...
.07974	...	6.01
.10	1.036	...	4.77	...

Discussion

When the diffusion coefficient is plotted against the concentration of the external solution, the curve obtained rises sharply up to 0.03 M after which it is nearly horizontal. The nature of this curve suggests immediately that at least two mechanisms are responsible for the transfer of the cation through the resin matrix. This effect was apparently first found and discussed by R. Schlögl.⁴ In the leached state in which no free anions are present, the transfer must be an exchange between relatively widely separated sulfonic acid groups. This mechanism is characterized by a low diffusion coefficient, about 1×10^{-6} cm.²/sec. As the free anion content of the resin increases an easier path for the transfer becomes available through the presence of the negative carrier. This mechanism is characterized by the considerably larger coefficient, 4.8×10^{-6} cm.²/sec. The runs at 50° bear out these ideas both as to the relative magnitude of the constants and as to the temperature coefficients. Calculating activation energies from the formula $D = A \exp(E/RT)$, we obtain at 0.01 N , $E = 10.3$ kcal. and at 0.07 N , $E = 2.2$ kcal. Thus the formation of the activated state for the exchange between neighboring sulfonic groups requires much more energy than that for the exchange taking place through the medium of the free anion, as would certainly be expected.

According to the calculations of Wang⁵ the activation energy for self-diffusion of Na^+ in NaCl solution (at infinite dilution) is 4.4 kcal. Our value of 10.3 kcal. (at 0.01 N) implies again that the process is not one of diffusion through a film of solution at the end of the rod.

There is little in the literature with which to compare these results. Spiegler and Coryell⁶ find 1.95×10^{-6} cm. for the D of Na^+ in a sample of Nepton. Their experiment was carried out in an entirely different manner and on a different batch of resin; it is possible to state only that our results are not inconsistent with theirs. The extensive work of Boyd and Soldano,⁷ where it is comparable with ours, produced results of the same order of magnitude. Their experiments are complicated by the fact that in most cases the exchanger was not initially at chemical equilibrium with the bath. Furthermore, in order to avoid effects of film diffusion Boyd and Soldano worked at higher concentrations and found no effect due to change in external concentration.

If one considers two mechanisms for transfer of ions through the resin which interact only to produce local isotopic equilibrium of the diffusing species, and are characterized simply by two coefficients, D_0 for interchange between fixed sites and D_1 for diffusion in the Donnan electrolyte, the relation between these coefficients and the observed value of D is⁸

$$D = D_0(q_0/q) + D_1(1 - q_0/q)$$

(4) R. Schlögl, *Z. Elektrochem.*, **57**, 195 (1952).

(5) J. H. Wang, *J. Am. Chem. Soc.*, **74**, 1612 (1952).

(6) K. S. Spiegler and C. D. Coryell, *This Journal*, **57**, 687 (1953).

(7) G. E. Boyd and B. A. Soldano, *J. Am. Chem. Soc.*, **75**, 6091 (1953).

(8) This relation results immediately from the condition of conservation of the diffusing ion at local isotopic equilibrium.

in which q_0 is the concentration of fixed charges in the resin and q is the total concentration of gegenion. This formulation cannot account quantitatively for the observed dependence of D on the concentration of the external electrolyte; it gives much too gentle an increase in D . The picture, however, is evidently oversimplified. A rapid exchange between free and bound ions within the resin would certainly not be unaccompanied by a marked alteration of the field between bound ions. The presence of free ion pairs will act to decrease the activation energy for an exchange between sites. This ef-

fect will cause an exponential increase in the value of D_0 itself, leading to a rapid increase in the observed value of D . An exact formulation of this idea would be a very involved problem for the concentrated systems with which we are concerned; we do not attempt it.

It should be remarked that these considerations do not appear to apply to the results of the work of Schlögl,⁴ who finds a rather slow increase in D with increase in concentration of the Donnan electrolyte. Evidently more work with a variety of well-characterized exchangers is much to be desired.

THE EQUILIBRIA BETWEEN TRI-*n*-OCTYLAMINE AND SULFURIC ACID

By KENNETH A. ALLEN

Oak Ridge National Laboratory, Oak Ridge, Tennessee

Received August 1, 1955

Benzene solutions of tri-*n*-octylamine have been equilibrated with aqueous sulfuric acid at 25°. The amine sulfate and bisulfate species remain in the organic phase, and the data are interpreted on the basis of polymerization of these salts. Equilibrium constants for the formation of the normal sulfate and for sulfate-bisulfate exchange within the colloid are evaluated, and a hypothesized distribution of free amine between solvent and colloid is shown to lead to a relation of the form of a solubility product for the reaction between free amine and sulfuric acid.

I. Introduction

The long chain amines have been shown to be efficient extractants of mineral acids. Smith and Page¹ used tertiaries such as methyldi-*n*-octylamine in chloroform or nitrobenzene to effect the quantitative separation of strong acids from water-soluble organics such as glycine and glutamic acid. There are other examples of similar applications of these amines; very little has been done, however, toward the elucidation of the fundamental processes which occur. It has been shown that the latter are by no means simple,² and considerable unpublished information on the reactions between benzene solutions of di-*n*-decylamine and aqueous sulfuric acid indicates polymerization of the amine salts in the organic phase.³ The present investigation with a tertiary amine generally corroborates the qualitative conclusions obtained from the earlier work and has provided a quantitative theoretical treatment for the case of tri-*n*-octylamine.

II. Experimental

Materials.—The tri-*n*-octylamine (hereinafter this amine will be referred to as TOA) used in this work was from a special preparation supplied by Carbide and Carbon Chemicals Company. Its neutralization equivalent was 354 ± 1 (theor., 353.7) and its tertiary amine content was $100 \pm 1\%$.⁴ A sample subjected to fractional distillation boiled at constant temperature with the exception of a trace of lower boiling forerun, and the neutralization equivalents of the first, middle and tail fractions were in excellent agreement with the theoretical value given above. Fischer titrations showed the water content of this amine to be less than one-half gram per mole, and a weighed sample exposed to the laboratory atmosphere for three days showed only a 0.1%

loss in weight, precluding any possibility of extensive take-up of water or carbon dioxide.

Standard solutions of TOA in benzene were prepared on a weight basis, diluted to the mark at $25.00 \pm 0.05^\circ$ and stored in the 25° thermostat throughout their period of use. All other reagents used were of the standard C.P. reagent grade furnished by the large chemical supply houses. The distilled water was subjected to de-ionization⁵ immediately before use and usually showed a pH of around 6.

Apparatus.—The only equipment of a specialized nature used in this work was a shaking apparatus. This assembly accommodated six separatory funnels in a thermostat regulated at $25.0 \pm 0.1^\circ$ and the degree of agitation could be changed by means of a variable drive motor. A standard speed of agitation was determined from a few preliminary experiments and adhered to throughout the investigation. A series of rate studies with 0.5 and 0.05 *M* TOA equilibrated with widely varying sulfuric acid concentrations for shaking times of one-half, one and two hours showed that equilibrium was attained in all cases in a half hour. The data reported below are based on shaking times of one hour or more.

Procedure and Analyses.—A series of six 60-ml. separatory funnels were used for the equilibrations. In a typical run 20 ml. of water, varying amounts of standard sulfuric acid and 10 ml. of the appropriate amine solution were pipetted into each funnel. After agitation at 25° the funnels were usually allowed to stand in the bath overnight to allow complete phase separation. Each aqueous layer was then drained into a clean, dry beaker from which aliquot portions were pipetted for titration with standard base. In the low acid range 0.01 *N* NaOH was used, the samples being titrated to pH 7 on a meter. The higher acidities were measured with tenth normal base using phenolphthalein. The technique for the determination of H_2SO_4 adsorbed into the organic phases was as follows: 3–5 ml. of the benzene solution was pipetted directly from the funnel into a 150-ml. beaker, 20–25 ml. of acetone added, and one drop of the usual phenolphthalein indicator solution. The magnetically stirred solution was then titrated with standard aqueous base to a faint permanent pink. The solutions usually became quite cloudy during the titration; rapid stirring and strong illumination were necessary for good results. Checks run on 5-ml. portions of amine solutions to which known amounts of H_2SO_4 had been added were in excellent agreement with the calculated values.

(1) E. L. Smith and J. E. Page, *J. Soc. Chem. Ind. (London)*, **67**, 48 (1948).

(2) K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis and J. G. Moore, Classified Report ORNL-1734.

(3) K. A. Allen, C. F. Baes, Jr., and W. J. McDowell, unpublished report.

(4) These analyses were performed by J. G. Moore, of this Laboratory, using standard techniques.

(5) An "Ilco-Way" research model de-ionizer made by the Illinois Water Treatment Co., Rockford, Illinois, was used according to the manufacturer's directions.