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

Self-diffusion of Water Molecules and Mobile Anions in Cation Exchangers

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Coefficients, *D*, and activation energies, E_{act}, for the self-diffusion of H_2O^{18} in variously cross-linked Dowex-50 type cation exchangers were measured and compared with corresponding quantities reported for pure water. The observed values for D_{H_2O}, E_{act}, and the entropy of activation, $\Delta S^{\ddagger}$, for diffusion in exchangers suggested that, as in pure water, the unit of transport is the single H_2O molecule. The lower $\Delta S^{\ddagger}$ values found were attributed to the further breaking of the structure of water in exchangers by the ions present therein. A method for distinguishing between *free* and *bound* water in exchangers was explored using the fact that two distinct rate processes involving H_2O^{18} could be measured in the Cr(III) cation exchanger salt-form. The diffusion of bromide ion, measured using 35.9 h. Br^{82} as a tracer, was found to be slower than for H_2O^{18}, but more rapid than for the self-diffusion of singly charged cations.

In recent studies[1,2] on the rates of diffusion of cations in cation exchangers, and of anions in anion exchangers, it has been assumed that the diffusing species was the hydrated ion. This hypothesis, which has appeared to be a reasonable one, quite naturally leads to the problem of the mode of transport of water in ion-exchangers. Is the water carried by the mobile ions, or, may it diffuse independently? Is *all* the water in an exchanger free to diffuse, or, only that part not associated with the ions? These, and related questions, afforded a stimulus for the present investigations of the self-diffusion rates of water molecules in cation exchangers using H_2O^{18} as a tracer. The effect of exchanger cross-linking was examined, and isotopic redistribution rates in the hydrogen, lanthanum and chromium(III) exchanger salt-forms were measured. The behavior of H_2O^{18} in exchangers containing the latter ion was of particular interest by reason of the work of Plane and Taube[3] which has shown that the water molecules of the hydrated chromic ion, $Cr(H_2O)_6^{+++}$, exchange with those in aqueous solutions with a measurably slow rate. Thus, the possibility presented itself of distinguishing between "bound" (*i.e.*, water of hydration) and "free" or solvent water in ion-exchangers on the basis of rate differences.

In addition, the rates of self-diffusion of bromide ion in variously cross-linked hydrogen-form cation exchangers were measured to determine if the mobilities of this species were comparable with those for cations and for water. Information of this sort was also of interest from the point of view of an understanding of the rate at which a Donnan equilibrium involving diffusible anions may be reached, and in connection with possible anion effects on the rate of self-diffusion of cations.

Experimental

Sulfonated polystyrene type (*i.e.*, Dowex-50) cation exchangers of nominal 4, 8 and 16% divinylbenzene (DVB) content were employed. The same general experimental techniques for self-diffusion coefficient estimations already described in detail in other studies[1] using tracers were followed in this work. Approximately 25 g. of the "wet-swollen" hydrogen-forms of the exchangers were immersed in pure water enriched[4] to 1.4% in O^{18} for a time sufficiently long to attain isotopic distribution equilibrium. After separating from the water by filtering, the exchanger was carefully blotted dry with absorbent paper to remove all surface moisture, and then was placed, together with the filtrate, in a closed vessel and allowed to come to isopiestic equilibrium with the vapor from the latter. Weighed quantities of this equilibrium exchanger containing O^{18} labeled water were rapidly introduced into a thermostated reaction flask which was subsequently closed off from the atmosphere. The isotopic redistribution of H_2O^{18} was initiated by quickly adding 60 ml. of water of natural O^{18} content (*i.e.*, *ca.* 0.20% O^{18}) to the flask after a time judged sufficient for thermal equilibrium. Approximately 300-λ aliquots of water were withdrawn at known times from the stirred reaction mixture. These were placed in ground-glass stoppered tubes and were frozen as soon as possible by immersing the tubes in acetone–Dry Ice mixtures. The samples were kept frozen until an analysis for their O^{18} contents could be performed with a mass spectrograph.[5]

An analogous procedure was followed in the experiments wherein the self-diffusion of bromide ion was measured using 35.9 h. Br^{82} as tracer. Approximately 0.5 g. of the ammonium forms of the variously cross-linked exchangers were equilibrated with 5 ml. of 1 *M* ammonium bromide solution containing radiobromide ions. After separation from this solution, and surface drying, the exchanger was placed in a closed vessel and allowed to come to isopiestic equilibrium with the aqueous solution. The redistribution reaction involving radiobromide ion was initiated by quickly adding a known weight of labeled exchanger, previously brought to constant temperature, to 200 ml. of stirred, 1 *M* NH_4Br solutions. Radioactivity determinations on 100-λ aliquots, taken from the reaction mixture at various times after the beginning of the reaction, were performed as previously described.[1]

Experimental Results and Discussion

A comparison of the coefficients, D_{H_2O}, and activation energies, E_{act}, for the self-diffusion of water in the hydrogen salt-forms of the variously cross-linked cation exchangers (Table I) with those for pure water[6] is of interest. As might be expected, D_{H_2O} is smaller in the exchanger than in pure water, and the activation energy is slightly, but apparently significantly, greater. The entropy of activation for self-diffusion $\Delta S^{\ddagger}$, measured by the quantity, $d(e^{\Delta S^{\ddagger}/R})^{1/2}$, estimated from the absolute reaction rate equation for D_{H_2O}

$$D_{H_2O} = ed^2(kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-E_{act}/RT) \quad (1)$$

using the experimental values for D_{H_2O} and E_{act}, appears to be larger in pure water than in the exchangers. This result may suggest that the ions in the latter act to break down the water structure so that self-diffusion may occur with less disturb-

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

[2] B. A. Soldano and G. E. Boyd, *ibid.*, **75**, 6099 (1953).

[3] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

[4] Obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

[5] Analyses for O^{18} were conducted by Mr. Chester Fultz, Mass Spectrographic Assay Laboratory, Y-12 Site, Oak Ridge National Laboratory, using a 60° Nier type mass spectrograph. Generally, the O^{18} content was estimated directly on the water by employing the H_2O^{+} molecule-ion.

[6] J. H. Wang, THIS JOURNAL, **73**, 4181 (1951).

TABLE I

SELF-DIFFUSION COEFFICIENTS FOR WATER MOLECULES IN CATION EXCHANGERS USING H_2O^{18} AS TRACER

Exchanger salt-form	Exchanger capacity, meq./g. dry H-form	Exchanger cross-linking, % DVB	Equivalental moisture, g. H_2O/equiv.	Self-diffusion coefficient, cm.²/sec. 3.4°	25°	Activation energy, cal./mole	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$
Pure H_2O	..	..	...	16.40×10^{-6}	30.10×10^{-6}	4410	5.5
H^+	5.16	4	408.0	4.51×10^{-6}	9.14×10^{-6}	4600	3.6
H^+	5.30	8	195.8	2.70×10^{-6}	5.40×10^{-6}	5200	4.6
H^+	5.10	16	122.2	1.10×10^{-6}	2.20×10^{-6}	5200	3.0
La^{+++}	5.30	8	150.4	8.20×10^{-7}	....	..	...

ance to the environment. The larger E_{act} observed for exchangers may also be a consequence of electrostrictive effects by the ions on the water molecules. According to eq. 1, both the lowering of $\Delta S^{\ddagger}$ because of the structure-breaking effects of the ions, and the increase in E_{act} because of electrostriction act to decrease D_{H_2O} for exchangers. Diffusion coefficients for water measured[7] in 1 N sulfuric acid and sodium sulfate solutions have also been found to be smaller than in pure water. The more than threefold decrease in D_{H_2O} for the lanthanum compared with the hydrogen exchanger may be due to the interaction of this highly charged cation with the water molecules. The rather close similarity in the values of D_{H_2O}, E_{act} and $d(e^{\Delta S^{\ddagger}/R})^{1/2}$ in Table I, however, suggests that in exchangers, as in pure water,[6] the unit of transport is a single H_2O molecule.

It is of further interest to note that the activation energies for water self-diffusion in the exchangers show only a small increase with increased polymer cross-linking. Such behavior contrasts with the appreciable increase in E_{act} usually found with ions. Thus, for sodium ion in nominal 4, 8 and 16% DVB cation exchangers the activation energies were 6500 and 8400 cal. mole^{-1}, respectively.[1] This relatively large increase may not be attributed to the increase in osmotic free energies with cross-linking.[8] A tentative conclusion, therefore, is that it probably reflects an increased electrostatic interaction of the cations with the structurally bound exchange groups.

Transport by mobile, hydrated ions probably contributes negligibly to the rate of diffusion of water molecules in and through cation exchangers, for the observed values of D_{H_2O} are almost an order of magnitude larger than the self-diffusion coefficients found for singly charged cations. It may also be inferred that the exchange of the ionic water of hydration in the hydrogen and lanthanum exchangers occurred at velocities exceeding those for diffusion, for the redistribution of H_2O^{18} initially present in these salt forms appeared to follow a single, diffusion-controlled rate process to completion. However, when hydrated chromic ion was present in the 16% DVB exchanger at 25°, two reactions were distinguishable: (a) a fast reaction leading to a fractional attainment of isotopic distribution equilibrium of 82.2% in one hour, followed by (b) a slow process which gave 96.8% exchange after six days, and complete exchange after two weeks. The total amount of water involved in the slow process could be estimated as two moles per equivalent, or, six per chromic ion, which is consistent with previous observations[3] of a slow exchange of water molecules in the $Cr(H_2O)_6{}^{+++}$ ion. Since the moisture content of the chromic exchanger salt form was 187 g., or, approximately 10 water molecules per equivalent, it may be inferred that not more than 80% of the water in the exchanger can be "free" or solvent water. The comparatively high water content of the chromic exchanger is of especial interest, for it indicates that the water of hydration is strongly bound. The lanthanum salt form, for example, possessed but 6.5 molecules per equivalent, while the hydrogen, lithium, sodium and potassium exchangers have 7.3, 7.0, 6.4 and 5.4 molecules per equivalent, respectively.

The diffusion rates of bromide ion in the hydrogen exchangers are seen (Table II) to be smaller than those for water molecules. Furthermore, this difference increases as the cross-linking increases. While bromide ion appears to diffuse more rapidly than sodium ion, it is of interest that the ratio of the diffusion coefficients for these two ions is independent of the exchanger cross-linking. This comparison, while not strictly valid because the D_{Br^-} is for bromide in an ammonium rather than in a sodium exchanger, suggests that mobile anions in cation exchangers are subject to much the same forces as are the cations. The appreciably greater mobility of bromide compared with sodium ion results, of course, partly from its greater intrinsic mobility, but mainly from the retarding action of the non-diffusible exchanger anions on the cations. It is to be expected that the presence of more highly mobile anions in cation exchangers will tend to increase the mobilities of the cations present. Anions should be particularly effective in this respect when the cationic mobilities are relatively quite small, as with highly charged types. Possible experimental indications of such an interaction have already been noted.[1]

TABLE II

COMPARISON OF THE DIFFUSION RATES OF WATER, ANIONS AND CATIONS IN VARIOUSLY CROSS-LINKED HYDROGEN-FORM CATION EXCHANGERS

Exchanger cross-linking, %DVB	Self-diffusion coefficient, cm.²/sec. × 10⁶ D_{H_2O}	D_{Br^-}	D_{Na^+}	$D_{H_2O}:D_{Br^-}$	$D_{Br^-}:D_{Na^+}$
4	4.51	3.20	0.980	1.4	3.3
8	2.70	1.11	.350	2.4	3.2
16	1.10	0.24	.066	4.6	3.6

Measurements of the diffusion of other neutral molecules (*viz.*, urea, methyl, ethyl and isobutyl

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(7) W. C. J. Orr and J. A. V. Butler, *J. Chem. Soc.*, 1273 (1935).

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

acetate, ethyl and isobutyl alcohol) in Dowex-50 have been reported[9] in which apparent diffusion coefficients approximately an order of magnitude smaller than those for water given in Table I were found. Further, apparent activation energies generally lying between 6 and 10 kcal. mole^{-1} were observed. The lower diffusion rates then are not surprising in view of the increased E_{act}. However, in contrast with the results for H_2O^{18}, diffusion in these cases appeared to be accompanied by large, positive activation entropies.

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(9) H. P. Gregor, F. C. Collins and M. Pope, *J. Colloid Sci.*, **6**, 304 (1951). In these experiments a "free diffusion" of the neutral molecule from the exchanger into an effectively infinite bath was allowed to occur. The possible dependence of the diffusion coefficient on the concentration of the neutral molecule in the exchanger was ignored. Further, the activation energies reported are for the over-all process, including desorption from the exchanger.

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

Self-diffusion of Cations in Hetero-ionic Cation Exchangers

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Diffusion coefficients, D, and activation energies, E_{act}, for the diffusion of sodium, zinc and lanthanum ions were measured experimentally and compared with corresponding values for the same ions in their pure (*i.e.*, homo-ionic) exchanger salt forms. In general, the diffusion rate of the more mobile cation was lowered, and that of the less mobile ion was increased. An interpretation of the observed diffusion coefficients was based on the equation from absolute reaction rate theory, $D = ed^2(kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-E_{\text{act}}/RT)$, according to which changes in D are governed by changes in E_{act} and $\Delta S^{\ddagger}$, the entropy of activation. An explanation of the magnitudes of the observed activation energies and derived entropies is proposed based on the hydration of the cations in the exchanger, on the extent of their association with the bound anionic exchange groups, and on the degree of hydration of the activated complex for diffusion.

This study has been concerned with the effects of ionic environment on the self-diffusion of cations in a cation exchanger of the sulfonated polystyrene type. Previous researches in this series have investigated the roles played by cationic size and charge, by ion-exchange polymer cross-linking[1] and by ion-exchange capacity[2] in determining the magnitudes of cation self-diffusion coefficients and the activation energies for self-diffusion in the pure (*i.e.*, homo-ionic) salt forms of ion exchangers. Here cation exchangers containing varying amounts of *two* different cations bearing either the same or different charges were employed, and self-diffusion rate and activation energy measurements were made for each ion using radioactive tracers. It is to be emphasized that the rate processes measured in these experiments were those which occur after a complete ion exchange equilibrium has been reached (*i.e.*, rates at dynamic equilibrium). No changes in composition either of the exchanger or of the external mixed aqueous electrolyte solution were involved, as has been the case in other reports[3-5] where a "free diffusion" of ions along concentration gradients *in the exchanger* occurred. The apparent diffusion coefficients given below, therefore, are believed to truly reflect environmental influences on ionic mobility, unmodified by thermodynamic activity coefficient gradients.

Preliminary results[6] for the diffusion of trace amounts of Na^+, UO_2^{++} and Ce^{+++} ions in an otherwise pure hydrogen form cation exchanger of another type have already indicated that diffusion rates may depend strongly on ionic charge in hetero- as well as in homo-ionic exchangers.[1]

Experimental

The well-known, commercially available sulfonated polystyrene exchangers, cross-linked with divinylbenzene (DVB) were employed in the rate measurements. Two differently linked preparations (*i.e.*, nominal 8.6% and 16% DVB) were used.[7] The general experimental procedure was closely the same as that reported in earlier studies with homo-ionic cation exchangers.[1] The desired hetero-ionic exchanger salt was prepared by repeatedly equilibrating 3.4 meq. of the hydrogen form with 200 ml. of the appropriate 0.23 *N* mixed electrolyte solution until a constant composition was achieved. The exchanger was then washed and charged with radioactively-labeled ions using an active solution of the same composition as was employed to prepare the inactive mixed salt form. The "tagged" hetero-ionic exchanger was then suspended in a well-stirred volume of pure water, and the self-exchange reaction was initiated by rapidly adding sufficient *mixed* electrolyte to give a 0.23 *N* solution containing the same relative amounts of ions as in the solution used to prepare the hetero-ionic salt form. It was, of course, necessary to employ differing diffusion theory curves in deriving self-diffusion coefficients from the rate date for each ion, owing to the ionic selectivity properties of the exchangers.

Experimental Results and Discussion

The first experiments were performed with mixed exchangers containing either two alkali metal cations, or one of these and hydrogen ion. The results (Table I) appeared to confirm the finding, reported some time ago for another cation exchanger,[8] that sodium ion diffused most slowly when present in pure sodium exchanger. Several new observations were also made:

1. The increase in D_{Na^+} when sodium diffuses in an exchanger containing another alkali cation or hydrogen ion is accompanied by a decrease in both its activation energy, E_{act}, and entropy, $\Delta S^{\ddagger}$.

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

(2) G. E. Boyd, B. A. Soldano and O. D. Bonner, to be published

(3) D. K. Hale and D. Reichenberg, *Faraday Society Disc.*, **7**, 79 (1949).

(4) T. R. E. Kressman and J. A. Kitchener, *ibid.*, **7**, 90 (1949).

(5) D. Reichenberg, THIS JOURNAL, **75**, 589 (1953).

(6) G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., *ibid.*, **72**, 4807 (1950).

(7) These Dowex-50 type cation exchangers were obtained from the Physical Research Laboratory, Dow Chemical Co., Midland, Mich.

(8) G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., THIS JOURNAL, **69**, 2836 (1947).