[A CONTRIBUTION FROM THE DOW CHEMICAL CO., MIDLAND, MICH.]

Fundamental Properties of a Synthetic Cation Exchange Resin

BY W. C. BAUMAN AND J. EICHHORN

The fundamental study of the mechanism, equilibrium and rate of ion exchange reactions has been difficult in the case of naturally occurring exchange materials such as greensand, clay, bentonite and peat and in sulfonated coal, lignite and tannins, because of the wide variety of ion active groups and variations in the structure of individual particles. As emphasized by Myers,[1] synthesis of organic exchange resins makes it possible to obtain chemically homogeneous exchange materials with exchange activity limited to one single type of group, such as —OH, —COOH, or —SO_3H. Continuing study of the fundamental properties of these synthetic products should clarify the exact nature of the ion exchange reaction and should make possible an accurate prediction of the effectiveness of these resins in their broad field of application to the treatment of water, the separation and recovery of ions, the purification of sugar solutions, the treatment of industrial wastes, etc.

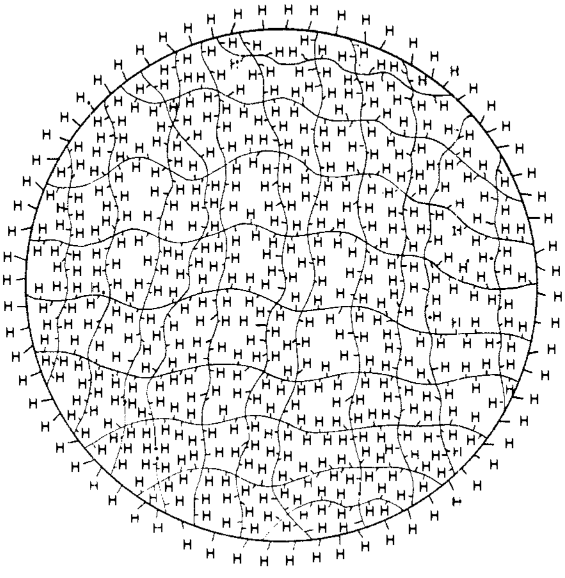

Fig. 1.—Basic structure of Dowex-50.

The subject of the present paper is the fundamental exchange properties of a newly developed synthetic cation exchange resin, Dowex 50. This product is an aromatic hydrocarbon polymer of the type described by D'Alelio in U. S. Patent 2,366,007, containing nuclear sulfonic acid groups as the sole ion active group at any pH value. This fact, combined with the stability of the hydrocarbon skeleton to strong acid, strong alkali, and oxidizing agents even at elevated temperatures, makes possible the study of the exchange properties of the sulfonic acid group over a much broader range of conditions than with the sulfonated phenol-formaldehyde resins.

Physical Form.—Dowex 50 is available in commercial quantities in the form of spherical particles with the average particle size distribution:

12–20 mesh, 0.833–1.525 mm., 50%
20–30 mesh, 0.503–0.833 mm., 35%
30–40 mesh, 0.381–0.503 mm., 12%
40–50 mesh, 0.279–0.381 mm., 2.5%
Through 50 mesh, <0.279 mm., 0.5%

For research work on special problems this product has also been made in experimental quantities in the form of smaller spheres, even down to diameters of about 0.04 micron.

By careful screening of production or experimental material it is possible to obtain uniform spheres of Dowex 50 of any diameter smaller than 1.19 mm. Spheres of larger diameter are not stable in the manufacturing process.

When working with Dowex 50 in the commercial sphere sizes it will be found that a portion of the screened material will consist of broken spheres. These are readily separated from the whole spheres by placing the sample on an inclined, polished metal plate. Gentle tapping of the plate will cause the spherical particles to roll off while the split spheres stay behind.

Chemical Constitution.—The chemical analysis of Dowex 50 in the wet sodium form, as shipped, is

Carbon	26.8%	Sodium	6%
Hydrogen	7.0%	Oxygen (by diff.)	51.3%
Sulfur	8.9%	Water	41.4%

In Figure 2 is shown the titration of 7 g. of Dowex 50 converted to the acid form, with 2 N sodium hydroxide on a glass electrode in 100 cc. of 0.01 N sodium chloride medium; 7 g. of the wet resin, when immersed under water, occupy 7.95 cc. of settled volume. The titration shows the total available capacity of Dowex 50 to be 50,500 grains $CaCO_3$/cu.ft. of settled volume or 4.92 milliequivalents of exchangeable hydrogen per gram of oven-dry hydrogen resin. The equivalent weight of the resin structure is 202. Assuming all of this capacity as sulfonic acids, as indicated by the low pH of the curve, the titration corresponds to a sulfur content of 8.4% and a sodium content of 6.0%. The excess 0.5% of sulfur in the product is probably present as sulfone cross-links.

The constitution of each spherical particle of Dowex 50 appears to be that of a homogeneous gel. In Fig. 1 is shown the basic structure of these

---

[1] R. J. Myers, "Advances in Colloid Science," Vol. I, 1942, p. 318.

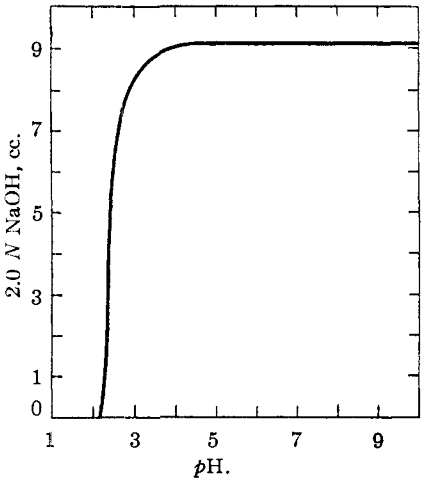

Fig. 2.—Glass electrode titration curve of 7 g. of wet Dowex-50 H-resin in 100 cc. of 0.01 N NaCl.

spherical particles. They consist of a basic hydrocarbon cross-linked skeleton which limits the linear motion of the —SO_3^- anions. The hydrogen ion, or other cation, may be considered to be completely dissociated from this skeleton—similar to the complete dissociation of a highly ionized salt in concentrated solution. Considered as a solution, the total cationic concentration of the resin phase is 3.5 mole/liter of spherical particles, or 6.7 moles/1000 g. of water within the particle.

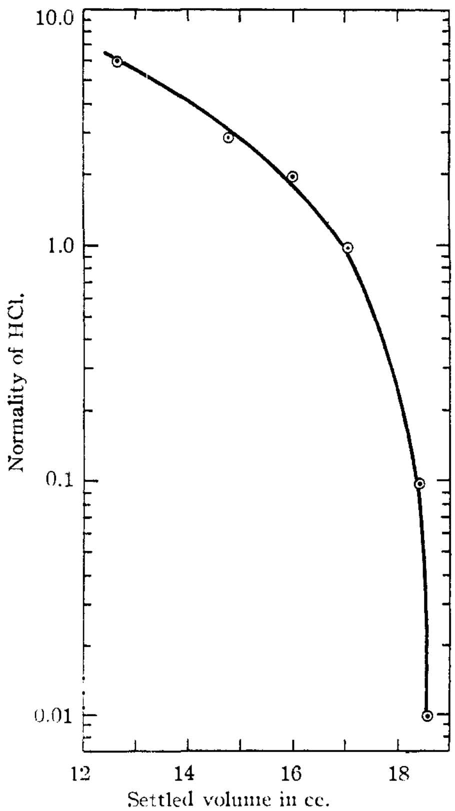

Fig. 3.—Volume changes of 10 g. of Dowex-50 in HCl solutions.

Diffusion Equilibrium: Donnan Effect.—When a sphere of the water wet acid resin is immersed in a solution of hydrochloric acid, no ion exchange takes place, but the hydrochloric acid diffuses into the water in the resin gel until an equilibrium is set up. At the same time, the sphere is found to shrink in volume as shown in Fig. 3. The hydrochloric acid concentration inside of the particle at equilibrium is always found to be less than in the solution outside the particle. This is shown in Fig. 4 for Dowex 50.

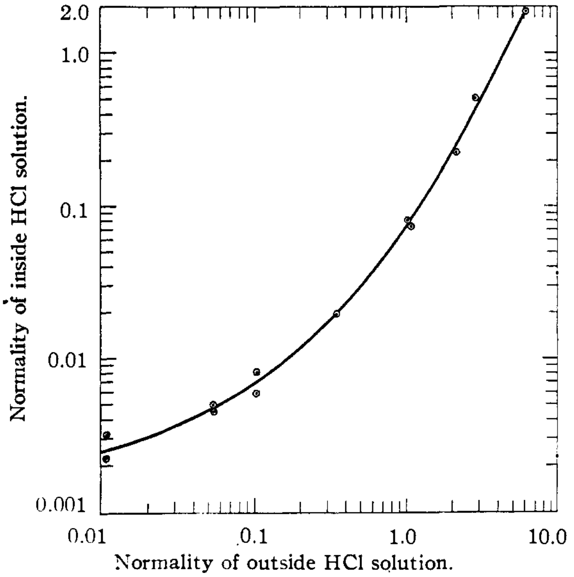

Fig. 4.—HCl concentrations inside and outside of Dowex-50 [hydrogen form].

Experimental

Dowex 50 hydrogen form was stirred with various concentrations of hydrochloric acid for one hour. The resin was removed and the supernatant liquid analyzed for hydrochloric acid. The resin particles were suction dried and then surface-dried with absorbing fibers. Of the two samples which were weighed, one was dried at 120° for eight hours and the other sample was thoroughly leached with water and the solutions titrated for hydrochloric acid. The concentration of the hydrochloric acid within the particle at equilibrium was calculated assuming that the loss in weight at 120° was entirely due to water. The method gave reproducible results.

The hydrogen and chloride ions are free to flow in and out of the resin, but the sulfonic acid groups attached to the resin structure cannot migrate into the outside solution. Applying the Donnan[2] theory to the hydrochloric acid, the sole diffusible compound in this case

$$a^i_{HCl} = a^0_{HCl} \quad (1)$$

$$a^i_{H}a^i_{Cl} = a^0_{H}a^0_{Cl} \quad (2)$$

$$\gamma^i_{H}\gamma^i_{Cl}C^i_{H}C^i_{Cl} = \gamma^0_{H}\gamma^0_{Cl}C^0_{H}C^0_{Cl} \quad (3)$$

---

[2] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1931, 2nd ed., p. 406, p. 1580.

where

a^0 = molar activity of a component in the outside solution
γ^i = molar activity coefficient of a component in the resin phase
C = molar concentration of a component
R^- = molar concentration of the —SO_3^-

But

$$C_{H}^{i} = C_{Cl}^{i} + R^- \tag{4}$$

Substituting (4) in (3) and rearranging

$$\left[\frac{C_{Cl}^0}{C_{Cl}^i}\right]^2 = \frac{\gamma_H^i\gamma_{Cl}^i}{\gamma_{Cl}^0\gamma_H^0}\left(1 + \frac{R^-}{C_{Cl}^i}\right) = \left[\frac{\gamma_{HCl}^i}{\gamma_{HCl}^0}\right]^2\left(1 + \frac{R^-}{C_{Cl}^i}\right) \tag{5}$$

In high concentration ranges, equation (5) predicts that $C_{HCl}^i/C_{HCl}^0 \rightarrow 1$; while in dilute solutions this ratio should approach zero unless γ_{HCl}^i approaches zero. For strong hydrochloric acid solutions, equation (5) represents the observed data quite closely (see Fig. 4). In the low acid concentrations, however C_{HCl}^i/C_{HCl}^0 does not approach zero at infinite dilution. Since on the basis of the activity coefficients in mixed electrolytes γ_{HCl}^i should remain high even at low HCl^0 concentration, the Donnan theory fails to explain the data for dilute HCl concentrations.

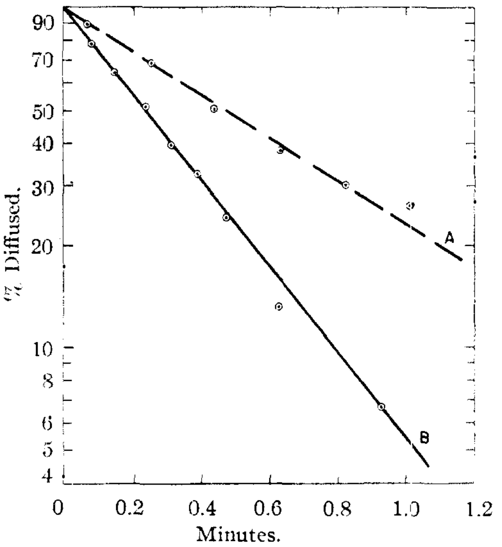

Fig. 5.—(A) diffusion into H_2O of NaCl from Dowex 50 initially contacted with 26% NaCl; (B) same; but initially contacted with 0.1 HCl.

Diffusion Rate.—The process of salt leaching from the resin or the reverse process is a problem of diffusion, the laws governing which processes having been thoroughly developed for spheres.[3] The experimental data for sodium chloride and hydrochloric acid leaching at room temperature from 20–24 mesh Dowex 50 spheres is shown in Fig. 5. The average concentration of electrolyte in a sphere immersed in pure water is given by the formula

$$\frac{\bar{C}}{C_0} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{e^{-n^2\pi^2Dt/R^2}}{n^2} \tag{6}$$

where

$\bar{C}$ = average concentration of electrolyte in sphere
C_0 = initial concentration of electrolyte
t = time in sec.
R = radius in cm.
n = any integer
D = diffusion constant, sq. cm./sec.

The experimental diffusion constants at room temperature are 2.5×10^{-6} sq. cm./sec. for sodium chloride and 5.0×10^{-6} sq. cm./sec. for hydrochloric acid. These are about one-fifth as rapid as the diffusion rates in dilute aqueous solutions.

Ion Exchange Equilibrium.—When an ion exchange resin in the hydrogen form is immersed in a sodium chloride solution, the hydrogen on the resin is replaced by sodium and the sodium chloride is converted to hydrochloric acid. The process continues until a state of equilibrium is established. The ion exchange reaction can be considered to be a heterogeneous reaction between the outside solution phase and the resin gel phase.

$$R^- \begin{matrix} Na_R^+ \\ H_R^+ \end{matrix} Cl_R^- \left\| \begin{matrix} Na_S^+ \\ H_S^+ \end{matrix} Cl_S^- \right.$$

According to the Donnan concept

$$a_{Na_R}a_{Cl_R} = a_{Na_S}a_{Cl_S} \tag{7}$$

$$a_{H_R}a_{Cl_R} = a_{H_S}a_{Cl_S} \tag{8}$$

or

$$\frac{a_{Na_R}}{a_{Na_S}} = \frac{a_{H_R}}{a_{H_S}} \tag{9}$$

or

$$\frac{C_{Na_R}C_{H_S}\gamma_{H_S}}{C_{H_R}C_{Na_S}\gamma_{Na_S}} \qquad \frac{\gamma_{H_R}}{\gamma_{Na_R}} \tag{10}$$

where

a = molar activity of a component
γ = molar activity coefficient
C = molar concentration

for dilute solutions

$$\gamma_{Na_S}/\gamma_{H_S} = 1$$

and

$$\frac{C_{Na_R}C_{H_S}}{C_{H_R}C_{Na_S}} = \frac{\gamma_{H_R}}{\gamma_{Na_R}} = K \tag{11}$$

which is the familiar mass action equation based on concentrations for the reaction

$$Na_S^+ + H_R^+ \rightleftarrows H_S^+ + Na_R^+$$

The mass action equation can also be written in terms of mole fractions.

$$\frac{X_R}{1 - X_R} = K\frac{X_S}{1 - X_S} \tag{12}$$

where

$$X_R = Na_R/C_R$$
$$X_S = Na_S/C_S$$

and

C_R = total molar exchange capacity of resin
C_S = total molar concentration of the solution

---

[3] Ingersoll and Zobel. "Math. Theory of Heat Conduction," 1913.

A plot of "X_S" against "X_R" with "K" as parameter is shown in Fig. 6.

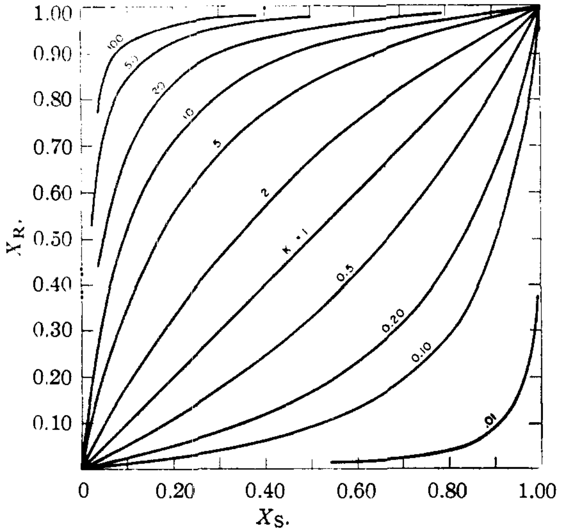

Fig. 6.—Plot of equation (12): monovalent–monovalent exchange.

Experimental

Ten grams of air-dried Dowex 50 hydrogen form was stirred with 500 cc. of salt solution for one hour. Since Dowex 50 is a fast-acting resin, equilibrium was actually attained in a much shorter period. The amount of acid liberated was determined by titration using a glass electrode. This was equivalent to the amount of metal cation on the resin. Since the capacity of the resin was known the amount of hydrogen remaining on the resin was found by difference. A careful check on the NH_4/H system for both ions showed that the procedure was entirely accurate.

The mass action equations have been checked in the NH_4/H exchange for Dowex 50 at various salt concentrations with the result:

Normality	K
0.01	1.20
0.10	1.20
1.0	1.15
2.0	0.83
4.0	0.51

Experimental data are in good agreement with the mass action law at concentrations up to 1.0 N. At higher concentrations it is not surprising that the values for "K" do not agree. A comparison of the activity coefficients for concentrated solutions of hydrochloric acid and ammonium chloride at 25° indicates that $\gamma_{HCl} > \gamma_{NH_4Cl}$; thus K should decrease as it does experimentally.

Equilibrium constants for the reaction

$$H_R + X_S \rightleftharpoons H_S + X_R$$

at 0.1 N total salt concentrations at room temperature for Dowex 50 are

Li	0.61	
Na	1.20	
NH_4	1.20	
K	1.50	
Cs	2.04	in 0.01 N solutions
Rb	2.22	
Tl	8.60	
Ag	8.70	

Lithium bromide, silver nitrate, and the chlorides of the remaining cations were used. These results were obtained in dilute solutions so that $\gamma_{X_S} = \gamma_{H_S}$ and K is then $= \gamma_{H_R}/\gamma_{X_R}$.

It is not possible to check this activity concept quantitatively since no independent determination of activity coefficients in the resin phase is available. These activity coefficients should be closely equal to those in strong solutions of nuclear sulfonic acid salts, which could be determined by standard solution methods. At present, we can check these values with the activity coefficients of the alkali halides which are available over a broad concentration range and are plotted in Fig. 7.[4] Qualitatively the K values fall in line quite well with the activity coefficients at high concentrations and in inverse order, as they should since $K \propto 1/\gamma_{X_R}$. Hence it is quite possible that ion exchange equilibrium in Dowex 50 is determined simply by the difference in activity coefficients between the outside solution and the very highly concentrated resin solution, without involving any specific affinity of $—SO_3^-$ groups for one ion over another.

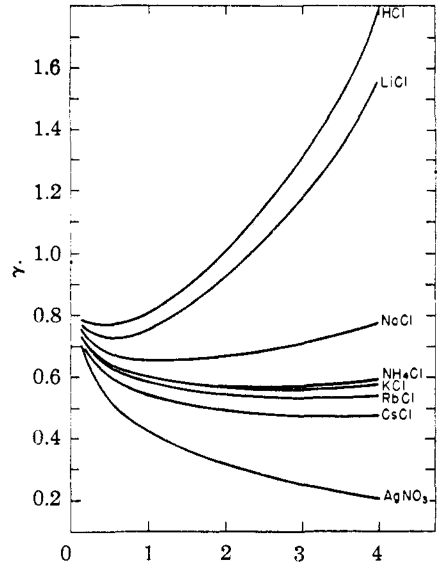

Fig. 7.—Activity coefficients of univalent halides at 25°.

The equilibrium equations in the exchange of a monovalent ion with polyvalent ions can be developed similarly to those done for monovalent exchanges. For example, in the exchange

$$Ca_S^{++} + 2H_R^+ \rightleftharpoons 2H_S^+ + Ca_R^{++}$$

---

[4] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 1943, Appendix.

$$\frac{C_{\mathrm{CaR}}C^2_{\mathrm{HS}}\gamma^2_{\mathrm{HS}}}{C^2_{\mathrm{HR}}C_{\mathrm{CaS}}\gamma_{\mathrm{CaS}}} = \frac{\gamma^2_{\mathrm{HR}}}{\gamma_{\mathrm{CaR}}} = K \tag{13}$$

and using the same notation as before

$$\frac{X_{\mathrm{R}}}{(1 - 2X_{\mathrm{R}})^2} = K\,\frac{C_{\mathrm{R}}}{C_{\mathrm{S}}}\,\frac{X_{\mathrm{S}}}{(1 - 2X_{\mathrm{S}})^2} \tag{14}$$

Figure 8 shows a plot of $2X_{\mathrm{R}}$ *versus* $2X_{\mathrm{S}}$ for various values of $KC_{\mathrm{R}}/C_{\mathrm{S}}$.

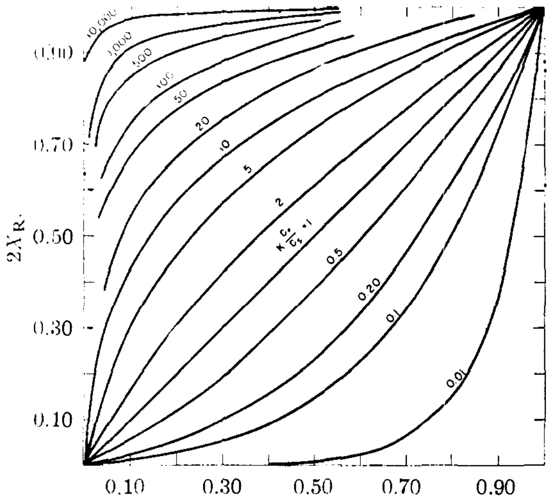

Fig. 8.—Plot of equation (14): monovalent-divalent exchange.

Of particular importance is the fact that the "selectivity" of the resin for a divalent ion over a monovalent ion varies not only with "K" and "C_{R}," which may be considered properties of the resin, but also with "C_{S}," the total salt concentration of the solution. The equation predicts, and experiment confirms, that an ion exchange resin is much more selective for polyvalent ions over monovalent ions in dilute solution than in concentrated ones. The mass action law for the Ca–H exchange at 0.1 N total salt concentration has been checked and the data are shown in Fig. 9. The straight line is drawn at the theoretical slope of 2 and agrees well with experiment.

Ion Exchange Rate.—At low solution concentrations the exchange rate has been reported[5,6] to be controlled by the rate of the chemical exchange reaction rather than by diffusion rate within the particle. For example, the rate of exchange for the reaction $\mathrm{Na_S} + \mathrm{H_R} \rightarrow \mathrm{H_S} + \mathrm{Na_R}$ is given by

$$R_{\mathrm{n}} = k_1 a_{\mathrm{NaS}} a_{\mathrm{HR}} - k_2 a_{\mathrm{HS}} a_{\mathrm{NaR}} \tag{15}$$

or

$$R_{\mathrm{n}} = k_1\gamma_{\mathrm{NaS}}\gamma_{\mathrm{HR}}C_{\mathrm{NaS}}C_{\mathrm{HR}} - k_2\gamma_{\mathrm{HS}}\gamma_{\mathrm{NaR}}C_{\mathrm{HS}}C_{\mathrm{NaR}} \tag{16}$$

At equilibrium, $k_1\gamma_{\mathrm{NaS}}\gamma_{\mathrm{HR}}C_{\mathrm{NaS}}C_{\mathrm{HR}} = k_2\gamma_{\mathrm{HS}}\gamma_{\mathrm{NaR}}\cdot C_{\mathrm{HS}}C_{\mathrm{NaR}}$. Comparing with the equilibrium equations based on the Donnan theory we find $k_1 = k_2$. Then in dilute solutions where $\gamma_{\mathrm{NaS}} = \gamma_{\mathrm{HR}} = 1$

$$R_{\mathrm{n}} = k_1\gamma_{\mathrm{HR}}C_{\mathrm{NaS}}C_{\mathrm{HR}} - k_1\gamma_{\mathrm{NaR}}C_{\mathrm{HS}}C_{\mathrm{NaR}} \tag{17}$$

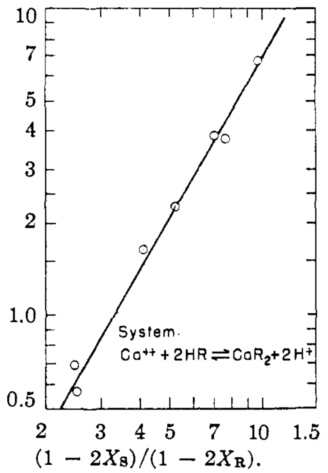

Fig. 9.—Equilibrium Ca-H exchange for Dowex-50.

Experimental

Two types of experiments were carried out in the study of reaction rates. In the stirring method 5 cc. of wet Dowex 50 resin was dumped into 1 liter of 0.001 N solutions. The change in the pH of the solution was automatically recorded. In the flow method[5] the 0.1% NaCl solution was run through a shallow bed of 5 cc. of Dowex 50 H-form in a 2.78-cm. diameter glass tube. The pH of the effluent was recorded automatically. The chart speed was 0.4 inch per minute for both methods.

The experiments were designed to check equation (17) at low solution concentrations. The linearity of the pH curves with time as shown in Figs. 10, 12, 13 (with C_{HR} or C_{NaR} constant in the stirring experiments and with C_{NaS} constant in the shallow bed experiments) proves the dependence of R_{n} on the concentrations as shown in equation (17). The study of the forward and reverse re-

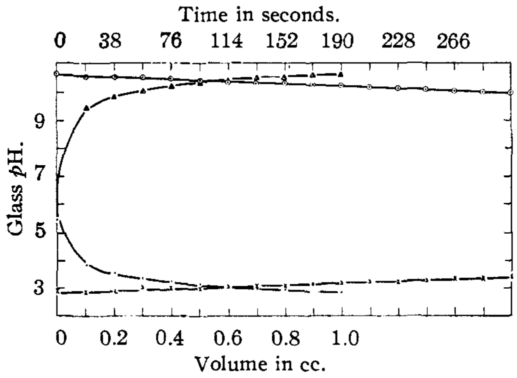

Fig. 10.—Ionic exchange rates of Na resin and H resin: ●—●, 1 cc. N HCl added to 1 liter of H_2O in 0.1 cc. increments; △—△, 1 cc. N NaOH added to 1 liter of H_2O in 0.1 cc. increments; ×—×, 5 cc. wet Na resin in 1 liter of 0.001 N HCl for five minutes; ⊙—⊙, 5 cc. wet H resin in 1 liter of 0.001 N NaOH for five minutes.

---

[5] duDomaine, Swain and Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

[6] G. P. Monet, PB-52432, Department of Commerce, Washington 25, D. C.

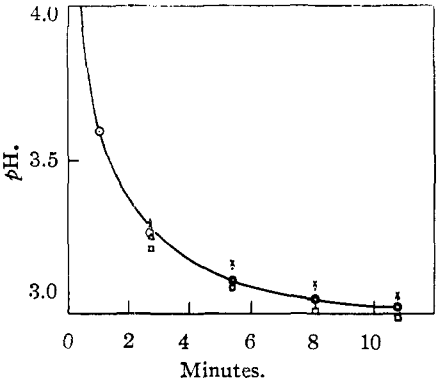

Fig. 11.—Exchange rates for $X_S + H_R$: ⊙, NaCl (calcd. from NaOH); ●, NaCl; △, NH_4Cl; ×, $AgNO_3$; □, KCl.

action rates with a variety of alkali metal ions exchanging with hydrogen ions (Fig. 11) shows that the forward rate, $X_S + H_R \rightarrow H_S + X_R$, is the same for all ions (within the experimental error of ±0.05 *p*H), as equation (17) predicts since $k_1\gamma_{H_R}$ is constant; but varies for the reverse rate (Fig. 12) $X_R + H_S \rightarrow H_R + X_S$ since $k_1\gamma_{X_R}$ is different for each of the alkali metal ions. Qualitatively the reverse rates fall in the same order as the equilibrium constants for the alkali metal ions, but the spread of the rate values is less than the equilibrium values as shown in the table.

Ion X	K from rate data	K from equilibrium data
Li	1.29	1.97
Na	1.00	1.00
NH_4	0.97	1.00
K	0.77	0.80
Ag	0.22	0.14

A part of this difference may be due to volume changes in the water swollen resin: *e. g.*, the silver form of Dowex 50 occupies only 87% of the volume of the equivalent lithium resin. The experiments, therefore, substantiate the form of equation (17) over the concentration range (0.001–0.01 molal), but indicate that the equation is not strictly quantitative over a broad range of molecular sizes.

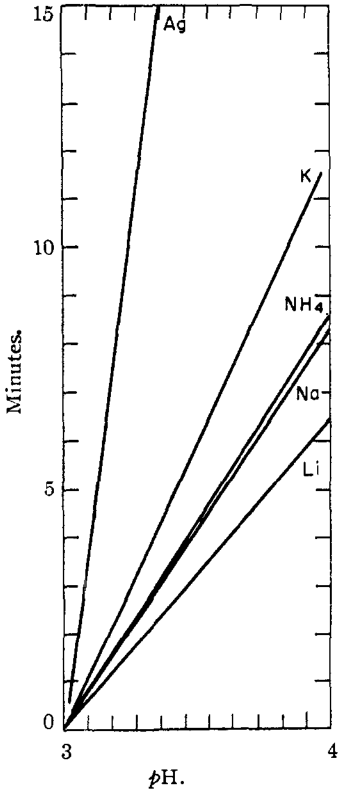

Fig. 12.—Reaction of Dowex 50 (20–24 mesh) in various cation forms with 0.01 *N* HCl solution.

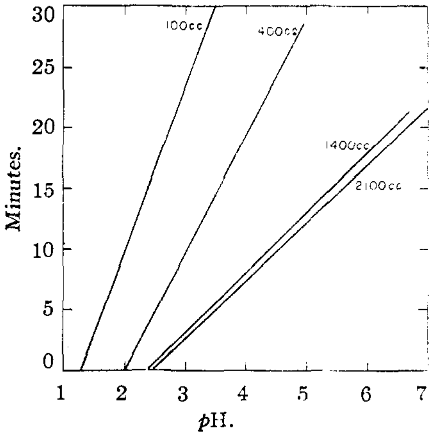

Fig. 13.—Variations of *p*H-time curves with flow rate in shallow bed run.

When R_n is expressed in terms of moles exchanged per liter of settled resin per minute, and the concentrations are expressed in moles/liter, the value of $k_1\gamma_{H_R}$ = 10–30 depending upon the experimental conditions. In the flow experiments the $k_1\gamma_{H_R}$ term increases as the cube root of the flow rate, whereas in the stirring experiments it increases only slightly with stirring rate, presumably since the particles flow with the solution. This indicates that k_1 is a dynamical constant depending upon the conditions of the experiment, such as flow rate, particle size, solution viscosity, *etc.*

Expressing the reaction rate constant in terms of a diffusion rate constant, at high stirring rate where $k_1\gamma_{H_R} = 30$, we obtain values of 6×10^{-5} sq. cm./sec. when $C_{Na_S} = 1\ N$, 6×10^{-6} when $C_{Na_S} = 0.1$ and 6×10^{-7} when $C_{Na_S} = 0.01$, *etc.* Then assuming that H^+ and Na^+ can interdiffuse at about the same rate as hydrochloric acid can diffuse through the resin structure (with a diffusion rate constant of 5×10^{-6} sq. cm./sec.), the diffusion rate should become controlling at about 0.1 *N* and higher concentrations in the Na–H exchange on Dowex 50. Under these conditions 90% of the capacity of 20–24 Dowex 50 may be exhausted in 33 sec. in the Na–H exchange.

Additional experimental work at high solution concentrations, at various temperatures, and at various particle sizes is required to complete the study of the exchange rate of Dowex 50.

Conclusions

1. Ion exchange equilibrium and rate for Dowex 50 have been shown to be consistent with the hypothesis that the resin phase is equivalent to a highly ionized salt solution.
2. Assuming activity coefficients equivalent to those in strong chloride solutions, the ion exchange equilibrium data may be interpreted by the Donnan concept of membrane diffusion.
3. The concentration of diffusible anions in the resin phase is lower than in the solution phase, as anticipated by the Donnan theory, but quantitative agreement with the theory is not obtained ni dilute solutions.
4. At low solution concentrations the exchange rate for Dowex 50 is controlled by the mass action reaction rate between the ions at the surface of the particle. The driving force is the product of the activity of one ion in the resin phase and the activity of the second ion in the solution phase. The rate constant depends on the turbulence of the solution phase at the resin surface, the surface area, etc., and hence is constant only under a specified set of experimental conditions.
5. The diffusion rate of hydrochloric acid and sodium chloride in the resin phase is about one fifth as great as in dilute aqueous solution. This rate indicates that interdiffusion of ions in the resin phase should be controlling in the exchange rate at solution concentrations above about 0.1 molal.

MIDLAND, MICH. RECEIVED JULY 16, 1947

[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics[1]

BY G. E. BOYD,[2] A. W. ADAMSON[3] AND L. S. MYERS, JR.[4]

Introduction

Although the rate factor in ion-exchange adsorption is of recognized importance in its bearing on the performance of deep adsorbent beds operating under dynamic conditions, until quite recently very little attention has been devoted to its elucidation.[5] Additional studies were deemed highly desirable since it was believed that a quantitative understanding of the kinetics of heterogeneous ion-exchange processes might reveal the mechanism of the rate controlling process, and perhaps also shed significant light on the problem of the internal physical structure of organic gel exchangers. The present investigation, therefore, was concerned first with the formulation of equations governing the velocity of ion-exchange based on diffusion and on mass action mechanisms. Three such relations were subjected to an extensive experimental testing in order to determine the validity and range of application of each of them. The alkali metal cations were employed. Depending upon the concentration existing in the aqueous phase, it was concluded that the rate of ion-exchange was determined either by diffusion in and through the adsorbent, or by diffusional transport across a thin liquid film enveloping the particle.

An important feature of the experimental work was the use of radioactive isotopes in the rate measurements. The equations were found to assume a particularly simple and readily verifiable form if the composition of the solid base-exchanger were maintained unchanged during the adsorption. In practice, this means that the cation A^+, whose adsorption is being followed, must be present in much smaller concentrations than B^+, the ion being displaced from the exchanger (*i. e.*, A^+ must be a microcomponent). This simplifying condition cannot be realized very effectively, however, owing to the paucity of highly exact general methods of trace analysis. The accurate determination of the changes in concentration of substances present in extreme dilution fortunately has been made possible by the recent feasibility of the employment of convenient radio-isotope techniques.

Also an improvement is believed to have been made in the experimental procedure used to obtain the rate data. A single stage technique, which may be termed the "shallow-bed method," made possible the determination of rates of adsorption down to very short times, a decisive advantage when the half-time for the achievement

---

[1] This work was performed under the auspices of the Manhattan District at the Clinton Laboratories of the University of Chicago and the Monsanto Chemical Company at Oak Ridge, Tennessee, during the period October, 1943, to January, 1946.

[2] On leave from the Department of Chemistry, University of Chicago. Present address: Clinton Laboratories, Oak Ridge, Tennessee.

[3] Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

[4] Present address: Institute for Nuclear Studies, University of Chicago, Chicago, Illinois.

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