

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Factors Involved in Cation Exchange Equilibria^{1,2}BY OSCAR D. BONNER,³ WILLIAM J. ARGERSINGER, JR., AND ARTHUR W. DAVIDSON

Studies of the NH_4^+-H^+ and Ag^+-H^+ exchanges on Dowex 50 at 25° in solutions of unit ionic strength have shown that the equilibrium composition of solid and liquid phases is determined by (a) the extent of simple equivalent ion exchange, which may be regarded as a chemical reaction, (b) the absorption or desorption of water by the resin, (c) the adsorption of electrolyte by the resin, and (d) the apparent molal volume change of the solute. Water absorption is a linear function of resin composition, but electrolyte adsorption depends in a more involved fashion on both resin and solution composition. New data for the Na^+-H^+ exchange on Dowex 50 in solutions of ionic strength 1.0 and 0.3 *M* have been combined with solution activity coefficient ratios from the literature to obtain, by a method of graphical integration, the activity coefficients of the resin components and the true exchange equilibrium constant. The activity coefficients, less than unity, agree well for the two ionic strengths. The value of the equilibrium constant at 25° is 1.70 ± 0.03 .

Introduction

In cation exchange investigations it has often been the practice to assume that only simple equivalent exchange occurs in a solution of constant volume, and to calculate, from the measured change in concentration of one ion in solution and the initial amount of resin, the equilibrium compositions of both solution and resin phases. In previously reported work in this Laboratory⁴ in which concentration changes of both ions were determined directly, it was found that computations based upon this simple hypothesis are not generally valid. The experimental observation that in an exchange of ions of the same valence the ionic strength of the solution is not constant, sufficed to indicate at least a volume change during exchange; the nature of the apparent discrepancy and its variation with composition indicated some other non-exchange process as well.

In a study of the factors determining the equilibrium composition at 25° of the NH_4^+-H^+ and Ag^+-H^+ exchange systems with the sulfonic acid-substituted polystyrene resin exchanger known as Dowex 50, the previous observations have been verified and interpreted. It has been found that

the error in the simple computation of equilibrium compositions may arise from any or all of three factors ordinarily neglected in the calculation: absorption or desorption of water by the resin; take-up of electrolyte by the resin by some non-exchange process which will be referred to as adsorption; and change in volume of the solution accompanying exchange of electrolytes of different apparent molal volume.

Experimental

The Nature of the Over-all Exchange Process.—Samples of both pure and mixed resins were thoroughly soaked in water, removed by filtration, lightly dried with filter paper, and weighed. These weighed samples were then dried to constant weight at 115°, and the loss of weight taken as the total absorption capacity. Each pure resin was found to have a specific reproducible total capacity for water of the order of 100–150 ml. per gram-equivalent of resin. This total absorption capacity is independent of particle size and of the degree of drying before determination. For mixtures of two forms of resin, however, the capacity, as shown in Fig. 1 for NH_4^+-H^+ resins, is a linear function of the composition of the mixture.

When partially dried pure resins are immersed in solutions of electrolytes with which no change can occur (*e.g.*, hydrogen resin in hydrochloric acid), or in general when partially dried resins are used in exchange experiments, net absorption of water, with consequent decrease in solution volume, is observed. Since even with equivalent exchange the concentration of the external solution is thus altered, it is not possible correctly to calculate the extent of exchange merely from the change in concentration of one ion in solution. On the other hand, the amount of water absorbed from a solution by the resin may be computed from the observed change in total concentration. The results of such calculation of total water absorption for a series of NH_4^+-H^+ resins in solutions of 1 molar total concentration are in agreement within 2–4% with the direct determinations plotted in Fig. 1.

The liquid taken up within the particles of the resin contains electrolyte in excess of that retained in the resin as a result of ion exchange. This electrolyte, termed "adsorbed," can be almost entirely removed by thorough washing with water. In experiments in which, for example, pure ammonium resin was treated with ammonium chloride solution, the amount of adsorbed ammonium chloride was found to be far from negligible. In these experiments an exact material balance, within a very small experimental error, was obtainable only when both the adsorbed electrolyte (defined as that amount removed by thorough washing of the resin, after it had been superficially dried by pressure between filter papers) and the change in concentration of the solution arising from absorption of water by the resin, were taken into account. The amount of electrolyte adsorption depends on the particular exchange system studied, and is a function of the equilibrium composition of the resin. The experimentally determined adsorptions are shown for the NH_4^+-H^+ exchange at unit total molarity in Table I, and for the Ag^+-H^+ exchange at the same ionic strength in Fig. 2.

It may be seen that, in general, adsorption is much more pronounced in the Ag^+-H^+ system than in the NH_4^+-H^+ system; further, that in the former case it is also a much

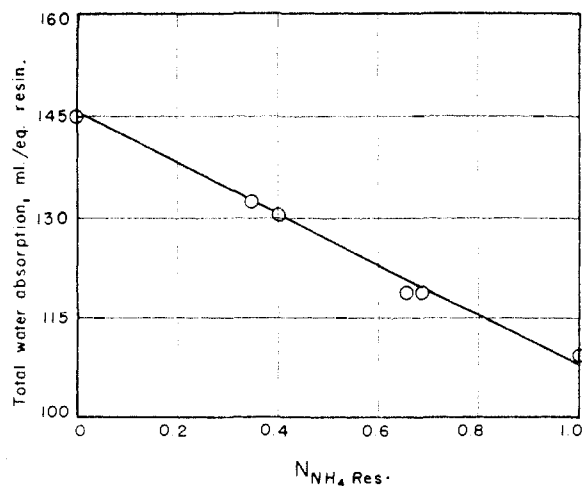


Fig. 1.—Water absorption capacity of NH_4^+-H^+ resins.

(1) From a portion of a thesis presented to the Graduate School of the University of Kansas by Oscar D. Bonner in partial fulfillment of the requirements for the Ph.D. degree, 1951.

(2) Presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

(3) du Pont Fellow, 1950–1951.

(4) W. K. Lowen, R. W. Stoenner, W. J. Argersinger, Jr., A. W. Davidson and D. N. Hume, *THIS JOURNAL*, **73**, 2666 (1951).

TABLE I
ELECTROLYTE ADSORPTION IN $\text{NH}_4^+ - \text{H}^+$ EXCHANGE

Initial resin	Mole fraction of NH_4^+ resin at equilibrium	Equivalent of HCl adsorbed per eq. resin	Equivalent of NH_4Cl adsorbed per eq. resin	Total equivalent adsorbed per eq. resin
H Res	0.000	0.020	...	0.020
H Res	.413	.028	0.009	.037
H Res	.520	.028	.016	.044
H Res	.649	.014	.015	.029
H Res	.850	.008	.023	.031
NH_4 Res	.262	.020	.005	.025
NH_4 Res	.551	.018	.011	.029
NH_4 Res	.647	.019	.017	.036
NH_4 Res	.746	.013	.021	.034
NH_4 Res	1.000032	.032

more sensitive function of resin composition, the adsorption becoming quite large for resins of high silver content. The ratio of the amounts of the two electrolytes adsorbed varies, as would be expected, with the equilibrium composition of the solution.

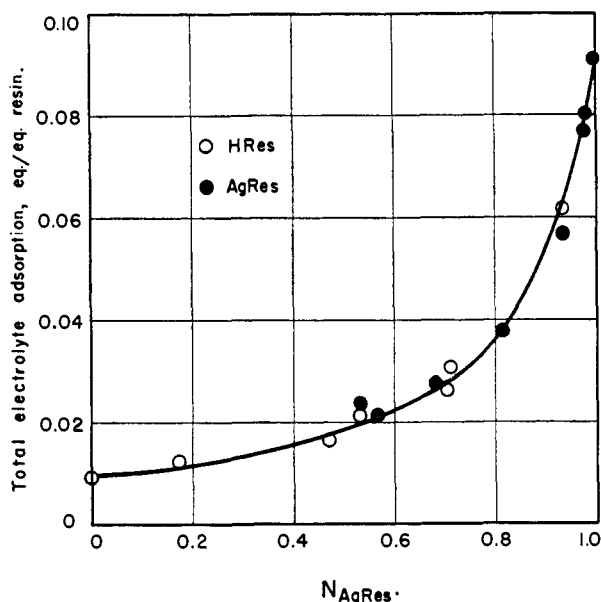


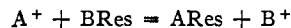
Fig. 2.—Electrolyte adsorption on Ag-H resins.

In experiments in which exchange occurs, a third factor must be considered: namely, the variation of apparent molal volume during exchange. In the $\text{NH}_4^+ - \text{H}^+$ system at unit total molarity, complete replacement of ammonium chloride by hydrochloric acid is accompanied by a decrease in volume of approximately 2%, partial exchange by a proportionately smaller volume decrease. Hence, in the calculation of water absorption from change in total concentration, the equilibrium concentrations must in general be corrected also for this volume effect. The apparent molal volume effect is found to be negligible, however, in the exchange of silver nitrate for nitric acid at unit total molarity, as it will be for any exchange of electrolytes of nearly identical apparent molal volumes at the concentration of interest.

Thus, in general, when a partially dried resin is immersed in an electrolyte solution, the equilibrium composition of both resin and solution phases is determined by four factors: (a) the extent of simple equivalent ion exchange; (b) the absorption or desorption of water by the resin; (c) the adsorption, in excess of simple exchange, of both electrolytes by the resin; (d) the apparent molal volume change of the solute.

Obviously, then, measurements of solution concentrations alone are not sufficient to determine the extent of exchange, nor the equilibrium constant for the process. Hence in all our subsequent investigations, in order to avoid specific consideration of these complicating factors, and since the

object was always to obtain the equilibrium constant itself, the equilibrium concentrations of all components in both phases were determined experimentally. Such data give directly the equilibrium quotient, K_m , for the exchange



$$K_m = \frac{m_{\text{B}^+}}{m_{\text{A}^+}} \times \frac{N_{\text{ARes}}}{N_{\text{BRes}}}$$

in which m represents molality in the solution and N mole fraction in the resin.

Exchange Equilibrium Experiments.—The general exchange procedure consisted of the equilibration of weighed samples of partially dried pure resin with definite volumes of accurately analyzed solutions of the two exchanging cations at a constant total ionic strength of approximately 1 molal. After a two-hour equilibration period in a thermostat at $25.0 \pm 0.2^\circ$, aliquot samples of the equilibrium solution were removed and analyzed for the two cations by appropriate procedures. The resin was removed by filtration with suction, and thoroughly washed with water. The composition of the washed equilibrium resin was also determined, by means of exhaustive exchange with a solution of a third electrolyte, followed by appropriate analyses of the effluent solution.

The $\text{NH}_4^+ - \text{H}^+$ exchange on Dowex 50 at 1 molal ionic strength and 25° was carefully reinvestigated by this method. No hysteresis was observed, and the K_m values, ranging from 1.1 to 2.1, are in very close agreement with previous results from this Laboratory. The new data are shown in Fig. 3.

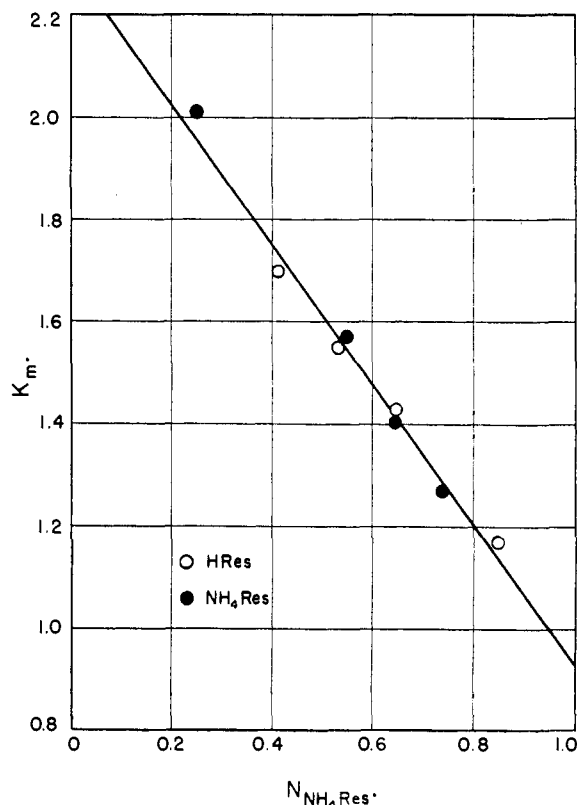


Fig. 3.—Ammonium-hydrogen exchange.

$$K_m = \frac{m_{\text{H}^+}}{m_{\text{NH}_4^+}} \times \frac{N_{\text{NH}_4\text{Res}}}{N_{\text{HRes}}}$$

The reinvestigation of the $\text{Ag}^+ - \text{H}^+$ exchange on Dowex 50 in nitrate solutions at unit ionic strength and 25° revealed the inadequacy of previous calculations of extent of exchange, which had been based entirely upon analysis of the equilibrium solutions, together with postulated constant water absorption and adsorption of silver nitrate alone. The results are shown in Fig. 4.

These K_m values, determined directly by analysis for all equilibrium concentrations, range from 6 to about 20, as

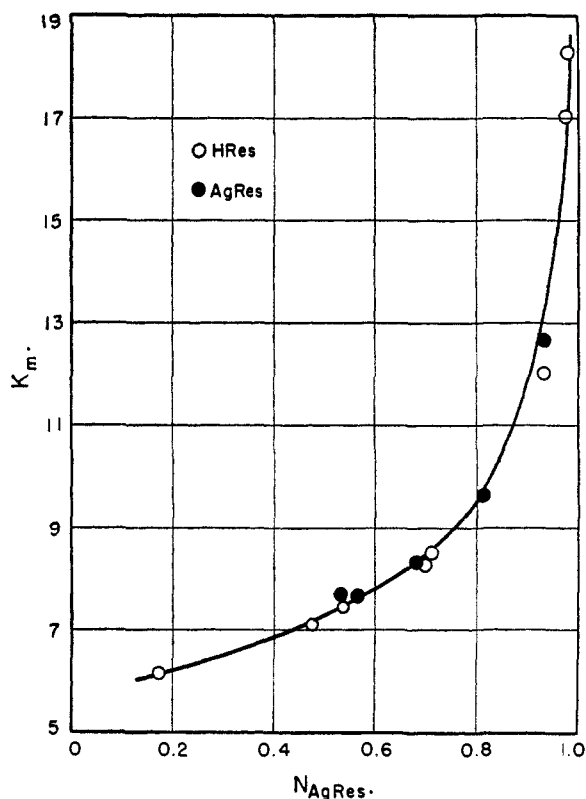


Fig. 4.—Silver-hydrogen exchange.

$$K = \frac{m_{H^+}}{m_{Ag^+}} \times \frac{N_{AgRes}}{N_{HRes}}$$

compared to the range of 5 to 9 previously computed indirectly. The present values, however, are in substantial agreement, except for resins of very low silver content, with the recently reported figures of Högfeldt, Ekedahl and Sillén.⁵ The slight discrepancy at high silver resin compositions may well be due in part to electrolyte adsorption. In order to confirm if possible the unexpected results of these authors (a sharp increase in K_m) at the other end of the concentration range, work is now in progress to extend the detailed investigation to very low equilibrium mole fractions of silver resin.

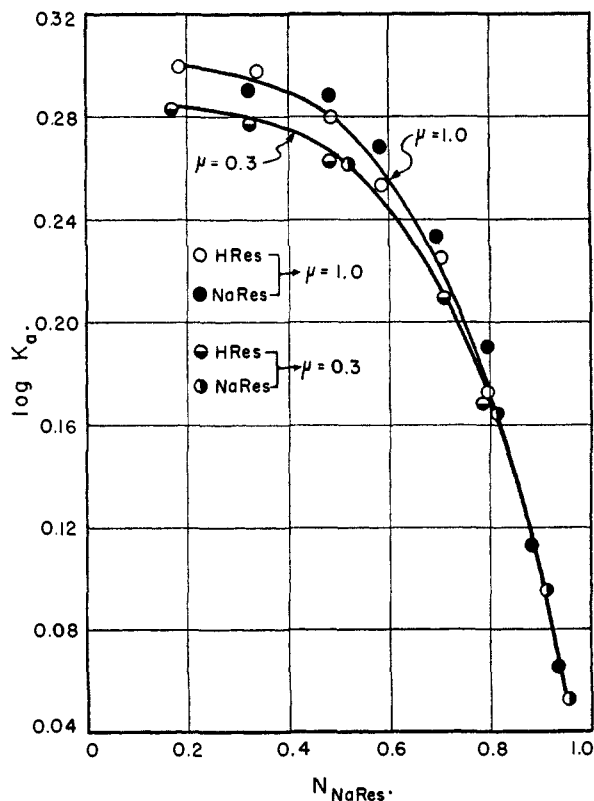
Evaluation of the True Equilibrium Constant in $Na^+ - H^+$ Exchange.—The calculation of true equilibrium constants for exchange processes from the experimentally determined equilibrium quotients requires a knowledge of activity coefficients both of the electrolytes in solution and of the components of the equilibrium resin. In a few cases activity coefficients are known as a function of composition for electrolytes in mixed aqueous solutions, but for the most part these are solutions of alkali halides with hydroxides or halide acids, and hence of limited applicability in ion exchange investigation. It has been customary, therefore, either to ignore solution activity coefficients (as has been done by Högfeldt, Ekedahl and Sillén⁵), or to approximate them by the values for the separate pure electrolytes in solution, on the assumption of the validity of the ionic strength principle even at high ionic strengths.⁴ For the resin phase, similar approximations are used if the solid phase is considered a concentrated electrolyte solution with fixed anions but labile cations; in this case, however, the error seems quite large. If the resin phase is considered to be a solid solution of the two forms of the resin, as had been done in the work at this Laboratory, then usually the assumption of ideal solid solution behavior in the mixed resin has been made.

It seemed that exchange experiments themselves might offer exactly the requisite data from which activity coefficients of resin components might be determined, at least in those systems for which solution activity coefficients are

(5) E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 1471 (1950).

known as functions of composition.^{6,7} Accordingly, the $Na^+ - H^+$ exchange on Dowex 50 was studied over a wide range of equilibrium resin compositions by the complete analysis method, in two series of experiments at approximately constant ionic strengths of 1.0 and 0.3 *M*. The equilibrium resin was washed, air-dried, and separated into two samples of known weight. One sample was analyzed for the hydrogen form of the resin by addition of a concentrated solution of sodium chloride and titration with standard sodium hydroxide solution. The other sample was placed in a micro-exchange column, and the sodium ion was completely replaced by passage of 6 *M* hydrochloric acid through the column. Aliquot portions of the effluent were evaporated to dryness and ignited, and the residues were weighed directly as sodium chloride. The concentration of sodium ion in the equilibrium solutions was determined in a similar manner, and that of hydrogen ion by titration with standard base.

There is no hysteresis, and at 1.0 *M* ionic strength the values of K_m , the equilibrium quotient, ranging from 0.9 to 1.7 as a function of equilibrium resin composition, are in good agreement with the results previously reported from this Laboratory.⁴ No earlier data exist with which the very slightly lower values of K_m at 0.3 *M* ionic strength may be compared. In Fig. 5 are shown the calculated values of $\log K_a$, the apparent equilibrium constant obtained by combining the K_m values with solution activity coefficient ratios from the literature.⁸

Fig. 5.—Sodium-hydrogen exchange at ionic strengths of 1.0 and 0.3 *M*.

$$K_a = K_m \left(\frac{\gamma_{HCl}}{\gamma_{NaCl}} \right)^2$$

The ion exchange process, regardless of its mechanism, is necessarily susceptible to ordinary thermo-

(6) W. J. Argersinger, Jr., A. W. Davidson and O. D. Bonner, *Trans. Kansas Acad. Sci.*, **53**, 404 (1950).

(7) E. Ekedahl, E. Högfeldt and L. G. Sillén, *Acta Chem. Scand.*, **4**, 556 (1950).

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 467-468.

dynamic formulation. The corresponding equilibrium constant, K , defined in terms of activities, then must be truly constant, independent of the variation of composition of the resin phase. In view of this fact, then, the relationship between K_a and K , the true thermodynamic equilibrium constant, *i.e.*

$$K = K_m \left(\frac{\gamma_{\text{HCl}}}{\gamma_{\text{NaCl}}} \right)^2 \frac{f_{\text{Na}}}{f_{\text{H}}} = K_a \frac{f_{\text{Na}}}{f_{\text{H}}}$$

may be combined with the Gibbs-Duhem equation to yield the following results⁶

$$\ln K = \int_0^1 \ln K_a dN_{\text{Na}}$$

$$\ln f_{\text{Na}} = -(1 - N_{\text{Na}}) \ln K_a + \int_{N_{\text{Na}}}^1 \ln K_a dN_{\text{Na}}$$

$$\ln f_{\text{H}} = N_{\text{Na}} \ln K_a - \int_0^{N_{\text{Na}}} \ln K_a dN_{\text{Na}}$$

In these expressions N_{Na} is the equilibrium mole fraction of sodium resin, and f_{Na} and f_{H} are the activity coefficients of sodium and hydrogen resins, respectively. The indicated integrations may be carried out graphically on plots of $\log K_a$ vs. N_{Na} like those in Fig. 5. The results of such graphical integration of the data for the $\text{Na}^+ - \text{H}^+$ exchange at 1.0 M and 0.3 M ionic strengths at 25° are given in Table II.

The true exchange equilibrium constant, and the activity coefficients of the resin components at a given resin composition, should in theory be independent of the concentration of the solution, unless the nature of the resin is radically changed during the exchange process by some such means as excessive electrolyte adsorption. Experiments indicate very slight adsorption in the $\text{Na}^+ - \text{H}^+$ system, and no other important complicating factors. The results for the equilibrium constant and the resin activity coefficients in the two series

TABLE II
EQUILIBRIUM CONSTANT AND RESIN ACTIVITY COEFFICIENTS
IN $\text{Na}^+ - \text{H}^+$ EXCHANGE

N_{Na}	Ionic strength 1.0 M , $K = 1.73$		Ionic strength 0.3 M , $K = 1.68$	
	f_{Na}	f_{H}	f_{Na}	f_{H}
0.0	0.865 ^a	1.000	0.879 ^a	1.000
.1	.867	0.999	.879	1.000
.2	.870	.999	.879	1.000
.3	.876	.996	.883	0.997
.4	.884	.992	.887	.995
.5	.894	.983	.899	.984
.6	.909	.963	.917	.960
.7	.933	.916	.940	.917
.8	.964	.836	.966	.847
.9	.986	.720	.989	.735
1.0	1.000	.532 ^a	1.000	.583 ^a

^a Extrapolated values.

of experiments at different ionic strengths agree fairly well, the discrepancies being no greater than the uncertainty in the values used for the solution activity coefficients. Work now in progress in solutions at a constant ionic strength of 0.1 M appears to offer further corroboration of this independence of solution concentration.

The method of calculation of resin activity coefficients and true exchange equilibrium constants here used may, as has been shown,⁶ be extended to the general case of exchange of ions of any valence, provided solution activity coefficients are available. Although quite independently derived, the method is essentially the same as that of Ekedahl, Högfeldt and Sillén,⁷ who have recently applied it to the computation of activity coefficients in the $\text{Ag}^+ - \text{H}^+$ and $\text{Ba}^{++} - \text{H}^+$ systems.⁹

(9) E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 828, 829 (1950).

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Activity Coefficient Ratios of Nitric Acid and Silver Nitrate, and their Application to Ion Exchange Equilibria^{1,2}

By OSCAR D. BONNER,³ ARTHUR W. DAVIDSON AND WILLIAM J. ARGERSINGER, JR.

Electromotive force measurements on cells of the type: $\text{Ag} | \text{AgCl} | \text{HCl} (0.2 M) | \text{glass} | \text{HNO}_3 (m_1), \text{AgNO}_3 (m_2) | \text{Ag}$ were used for the calculation of the ratios of activity coefficients at 25° of nitric acid and silver nitrate in solutions of varying acid-salt ratio and of total ionic strengths ranging from 0.1 to 1.0 molal. These activity coefficient ratios were combined with ion exchange data for the $\text{Ag}^+ - \text{H}^+$ equilibrium on Dowex 50. By means of graphical integration on a plot of the logarithm of the apparent equilibrium constant against the mole fraction of silver resin in the equilibrium mixed resin, the activity coefficients of the resin components and the true thermodynamic equilibrium constant for the exchange reaction were calculated. The activity coefficients in the mixed resins proved to be greater than unity. The value of the equilibrium constant at 25° was found to be 13.7.

Introduction

In a previous paper from this Laboratory,⁴ it has been shown that although the total interaction between a solution of an electrolyte and a resinous

cation exchanger is more complex than has generally been supposed, the exchange process proper may nevertheless be regarded as a simple chemical reaction, subject to the law of chemical equilibrium.

An extensive investigation, from this viewpoint, of the $\text{Ag}^+ - \text{H}^+$ exchange on Dowex 50 was made by Högfeldt, Ekedahl and Sillén,⁵ and a study of this equilibrium has been reported also in our previous

(1) From part of a thesis submitted by Oscar D. Bonner in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1951.

(2) Presented at the Cleveland Meeting of the American Chemical Society, April, 1951.

(3) du Pont Fellow, 1950-1951.

(4) O. D. Bonner, W. J. Argersinger, Jr., and A. W. Davidson, *This Journal*, **74**, 1044 (1952).

(5) E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 1471 (1950).