The Effect of Ionic Strength on Equilibrium in Silver–Sodium Ion Exchange[1]

By G. Elizabeth Wilson,[2] Arthur W. Davidson and William J. Argersinger, Jr.

From data for exchange equilibrium at 25° between Dowex 50 and aqueous silver nitrate–sodium nitrate solutions at five ionic strengths ranging from 0.01 to 1 M, values were determined for the separation factor K_m (the equilibrium quotient, uncorrected for activity coefficients, for replacement in the resin of sodium by silver). Activity coefficients, γ, for these electrolytes in aqueous solution being unknown, values of the equilibrium constant K_a, defined as $K_m(\gamma_{NaNO_3}/\gamma_{AgNO_3})^2$, were calculated on the assumption of the validity of a modified form of the ionic strength principle. From plots of log K_a against resin composition, the activity coefficients, f, of the resin components, and the equilibrium constant $K = K_a f_{AgRes}/f_{NaRes}$ were determined. Up to 0.3 M ionic strength, the several K values so obtained are fairly concordant. By linear extrapolation to infinite dilution, on plots of log K_m against molality for fixed resin composition, a series of values were found for log K^0_m, defined as log K − log f_{AgRes}/f_{NaRes}; and from these values the thermodynamic equilibrium constant K has been calculated to be 6.54.

Introduction

In previous papers from this Laboratory,[3-5] a method was described for the calculation of the thermodynamic equilibrium constant for cation exchange on a synthetic resin, and applied to the sodium–hydrogen and silver–hydrogen exchange systems on Dowex 50 of 10.5% divinylbenzene content. In the present work a similar method was used for the investigation of the silver–sodium system at several ionic strengths. In this case, experimental values for activity coefficients in the mixed aqueous solutions of silver and sodium nitrates are not yet available; the activity coefficient ratio may, however, be estimated, at least for the more dilute solutions, with considerable accuracy.

The silver–sodium exchange on Dowex 50 samples of 8 and 16% divinylbenzene content has been studied by Bonner and Rhett,[6] in 0.1 M solutions only; in their work the activity coefficient ratio in the aqueous solution was assumed to be unity.

Experimental Methods

For each series of determinations, samples of from 4 to 10 g. of either the sodium or the silver form of the resin were agitated at 25° for two hours or more with measured volumes of a solution of silver nitrate, sodium nitrate or a mixture of the two, at a fixed ionic strength. In some of the studies with the more dilute solutions, a mixed resin was equilibrated with silver nitrate solution. After the resin had settled, the supernatant liquid was decanted through filter paper, and the remaining resin was thoroughly washed with water and then dried. The density of the equilibrium solution was determined by means of a pycnometer, and appropriate samples were taken for analysis.

In the more concentrated solutions, silver was determined gravimetrically as chloride. In the moderately dilute solutions, silver was titrated with potassium iodide solution in the presence of ceric ammonium sulfate, as described by Bloom and McNabb,[7] and in the 0.01 molal solutions, the titration with potassium iodide solution was carried out potentiometrically.

In every case, silver was precipitated from the solution before analysis for sodium. In all but the most dilute solutions, sodium was determined gravimetrically in appropriate

portions of the filtrate as sodium zinc uranyl acetate; in the 0.01 molal solutions, uranium in this precipitate was reduced to the tetrapositive state and titrated potentiometrically with potassium dichromate solution in the presence of ferric chloride and phosphoric acid, in a slight modification of the method described by Kolthoff and Lingane.[8]

For analysis of the equilibrium resin, the samples were subjected in most cases to exhaustive exchange by means of 8 N nitric acid, and the effluent solution was evaporated to dryness. The silver content of the residue was determined as silver chloride; after removal of the silver, sodium was determined in the filtrate as above. In the case of resins containing only a small amount of silver, samples other than those to be used for the sodium analysis were exhaustively exchanged by means of a nearly saturated solution of sodium nitrate, and the silver was determined as already described.

Calculations

Writing the equation for the exchange reaction as

$$Ag^+ + NaRes = Na^+ + AgRes$$

we may define the separation factor, or uncorrected equilibrium quotient, K_m, by means of the equation

$$K_m = \frac{m_{Na^+} N_{AgRes}}{m_{Ag^+} N_{NaRes}}$$

in which m denotes equilibrium molality in the aqueous solution and N equilibrium mole fraction in the resin phase. The corrected equilibrium quotient K_a, previously designated[4,5] as the apparent equilibrium constant, is defined by

$$K_a = K_m \left(\frac{\gamma_{NaNO_3}}{\gamma_{AgNO_3}}\right)^2$$

where γ is the mean activity coefficient of the electrolyte. An approximate value of the correction factor may be found by the application of the ionic strength principle[9] in a modified form which follows from Guggenheim's extension[10] of the Debye–Hückel limiting law. This modification may be stated as follows: the ratio of the activity coefficients of two given strong electrolytes of the same valence type is the same in all dilute solutions of the same ionic strength; and in the case of two uni-univalent electrolytes with a common ion, this ratio is the square root of the ratio of the activity coefficients of the electrolytes in their own pure solutions at the same ionic strength.[11] On the basis of

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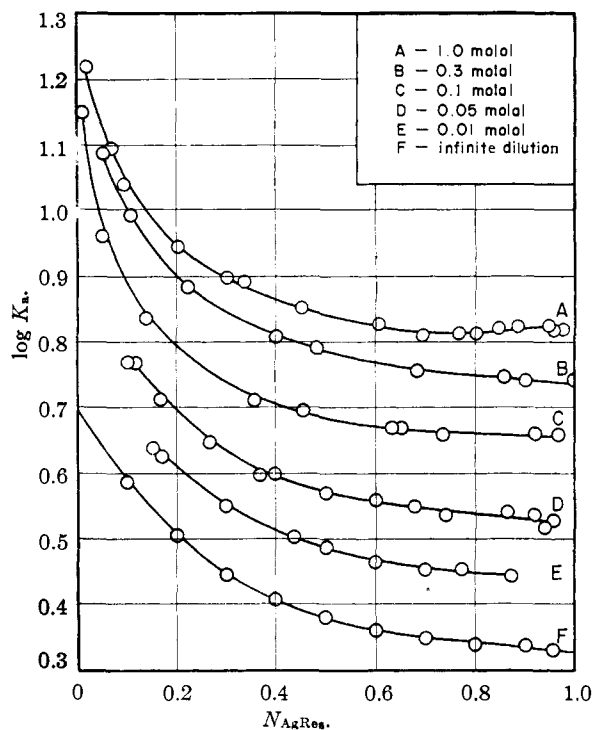
Fig. 1.—Silver–sodium exchange at several ionic strengths; for curves C, D, E and F, add 0.1, 0.2, 0.3 and 0.4, respectively, to ordinate scale.

this principle, the values of K_a may be found by the multiplication of each of the corresponding K_m values by a factor, constant for a given ionic strength, which is, in fact, simply the ratio of the activity coefficients of the electrolytes in their own solutions. These correction factors, for the several ionic strengths used, are as follows[12]

Ionic strength	1.0	0.3	0.1	0.05	0.01	0
$\gamma_{NaNO_3}/\gamma_{AgNO_3}$	1.280	1.101	1.037	1.019[a]	1.004[a]	1

[a] Extrapolated values.

From plots of log K_a against resin composition values were determined, by the method previously described,[3] for the activity coefficients, f, of the resin components, and for the equilibrium constant K, defined by

$$K = K_a \frac{f_{AgRes}}{f_{NaRes}}$$

In view, however, of the uncertainty of the aqueous activity coefficients in all but the most dilute solutions, another method was used also for the determination of K. Plots were made, for each of ten selected resin compositions, of log K_m vs. total ionic strength, and each of these was linearly extrapolated by the method of least squares to infinite dilution, to give a series of values designated as log K^0_m. Since at this limit the aqueous activity coefficient ratio is unity, it follows that each value of K^0_m should be equal to the apparent equilibrium constant for the resin composition in question; that is

$$\log K^0_m = \log K_a = \log K - \log \frac{f_{AgRes}}{f_{NaRes}}$$

(12) Reference 11, pp. 563–564.

From a plot of log K^0_m vs. N_{AgRes}, then, there were determined what are believed to be the best values both of the activity coefficients of the resin components and of the thermodynamic equilibrium constant.

Results

Plots of log K_a vs. N_{AgRes} are shown in Fig. 1, curves A through E. The values of log K^0_m at selected resin compositions are listed in Table I, and these values, also, are plotted in Fig. 1, curve F.

TABLE I

EXTRAPOLATED VALUES OF LOG K^0_m

N_{AgRes}	log K^0_m	N^0_{AgRes}	log K^0_m
0.1	0.966	0.6	0.758
.2	.903	.7	.748
.3	.844	.8	.739
.4	.807	.9	.734
.5	.780	.96	.730

The activity coefficients of the resin components, as calculated from the plots of Fig. 1 for solutions of 0.1, 0.05 and 0.01 M ionic strength, as well as from the plot of extrapolated values, are presented in Table II. It will be noted that all of the values for either of the components at a given resin composition are fairly concordant, although at 0.1 M ionic strength marked divergence, especially in the f_{Ag} values, becomes apparent for resins of low silver content, where long extrapolations are necessary. Data for still more concentrated solutions yield in this range even somewhat more discordant values (not included in the table); this fact may be attributed in large part, it is believed, to the inadequacy of the ionic strength principle at ionic strengths
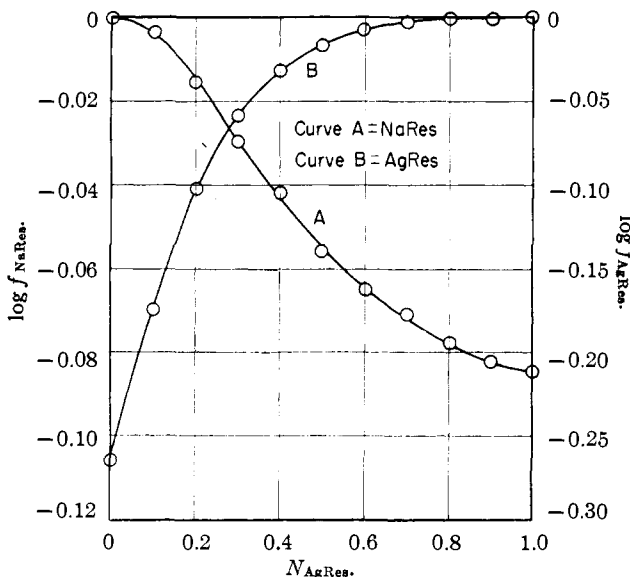

Fig. 2.—Activity coefficients of resin components.

above 0.1 M. The logarithms of the activity coefficients, taken from the last two columns of Table II, are plotted, in Fig. 2, against resin composition.

The values of the equilibrium constant calculated from the curves of Fig. 1 are listed below.

Ionic strength	1.0 M	0.3 M	0.1 M	0.05 M	0.01 M	0
K	7.6	6.83	6.78	6.40	6.63	6.54

The value 6.54, obtained from the extrapolated data, is believed to be the best as yet available for the thermodynamic equilibrium constant for silver–sodium exchange on this resin.

TABLE II

Ionic strength N_{AgRes}	0.1 M		0.05 M		0.01 M		0 M	
	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}
0.0	1.000	0.382	1.000	0.532	1.000	0.564	1.000	0.544
.1	0.974	.699	0.990	.668	0.990	.687	0.992	.670
.2	.942	.840	.961	.801	.964	.802	.965	.790
.3	.918	.911	.928	.892	.933	.885	.934	.875
.4	.895	.953	.903	.939	.897	.924	.908	.927
.5	.876	.977	.883	.968	.883	.962	.878	.961
.6	.863	.990	.869	.982	.859	.989	.861	.983
.7	.854	.997	.855	.991	.846	.997	.849	.992
.8	.848	1.000	.846	.996	.840	.999	.836	.998
.9	.846	1.000	.835	.999	.835	1.000	.828	1.000
1.0	.846	1.000	.826	1.000	.832	1.000	.823	1.000

This value may be compared with two others for the same equilibrium quotient. The data of Bonner and Rhett[6] for resins of 8 and 16% divinylben-zene content yield, by linear interpolation (a procedure which appears justifiable in view of experimental results in the sodium–hydrogen system), a figure of 5.86 for 10.5% divinylbenzene; corrected for the activity coefficient ratio at 0.1 M ionic strength, this becomes 6.08. The value calculated from the ratio of equilibrium constants for silver–hydrogen and sodium–hydrogen exchanges,[13] previously determined in this Laboratory for the same sample of Dowex 50, is 7.31. In view of the wide diversity of their sources, the approximate concordance of the three values is not without interest.

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The Exchange Reaction between Chromous and Chromic Ions in Perchloric Acid Solution

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The rate of the chromium(II)–chromium(III) exchange reaction has been measured in perchloric acid solutions and shown to be first order in chromous ion and first order in chromic ion. In 1.00 f $HClO_4$ the second-order rate constant is 0.440 f^{-1} hr.$^{-1}$ at 24.5°, and the experimental activation energy is 22 ± 2 kcal./mole. If the data obtained by varying the hydrogen ion concentration at approximately constant ionic strength are interpreted in terms of exchange reactions between Cr^{++} and the species Cr^{+++} and $Cr(OH)^{++}$, the second-order rate constants at 24.5° are $\leq 0.07 f^{-1}$ hr.$^{-1}$ and $\simeq 2.5 \times 10^3 f^{-1}$ hr.$^{-1}$, respectively. No catalysis by chloride ion was observed. The separation method used was a novel one based on the fact that chromous ion could be converted to a chromic complex which did not exchange with, and could be separated from, $Cr(H_2O)_6^{+++}$.

Rates of the exchange reactions between only a few simple, hydrated +2 and +3 ions have been measured. The Fe(II)–Fe(III) reaction has been studied in some detail,[3] and preliminary data on the kinetics of the Co(II)–Co(III) reaction have been obtained.[4] The two reactions appear to be very similar in rate and general behavior. King and Garner[5] have obtained evidence indicating that the V(II)–V(III) reaction rate may be of the same order of magnitude as the iron and cobalt reactions.

Meier and Garner[6] have found that in contrast to the above reactions, the Eu(II)–Eu(III) reaction is quite slow. Plane and Taube[7] have reported that the Cr(II)–Cr(III) reaction is also slow.

This paper describes some preliminary studies of the kinetics of the Cr(II)–Cr(III) reaction in perchloric acid solution using a simpler and more direct procedure than that of Plane and Taube.

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Experimental

Chromium Tracer.—Chromium metal containing 28-day Cr^{51} was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. It was dissolved in HCl and converted to CrO_3 by fuming with perchloric acid. The CrO_3 was dissolved in water, a small amount of ferric chloride added, and ferric hydroxide precipitated by the addition of ammonia. The chromium was then extracted into ethyl ether from acid solution as the blue peroxychromate. After back-extraction into dilute ammonia it was fumed with nitric and perchloric acids to destroy ammonium ion. It was finally diluted with water to a perchloric acid concentration of 1 f and reduced to $Cr(H_2O)_6^{+++}$ with hydrogen peroxide. The excess peroxide was catalytically decomposed on platinum black. The tracer for the exchange experiments was taken directly from this solution. In order to test for undecomposed peroxide, about 1 ml. of the solution was added to a dilute iodide solution and shaken with benzene. No iodine color was observed.

The purified material was checked for radiochemical purity by counting a sample of it in solution on a gamma counter at intervals for 108 days. The half-life observed was 27.6 days. Another sample was converted to $BaCrO_4$ and counted from time to time on an X-ray counter over a period of 68 days. This sample gave a half-life of 27.3 days. Both values are in satisfactory agreement with the published value of 27.8 days.[8]

Specific Activity Measurements.—In runs numbered 2, 5, 6 and 10, the samples whose specific activities were to be measured were converted to chromate by oxidation with

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