Studies of the Cation Exchange System Fe^{+++}-H^+

I. Equilibrium Studies

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Equilibrium data are presented for the exchange of Fe^{+++} and H^+ on a sulfonated polystyrene exchanger. The data cover solution concentrations from 0.05 *N* to 2 *N* in total cation for solutions having either nitrate or perchlorate ion as the common anion. The nitrate system shows irregular behavior because of complex ion formation, but for composition where such behavior is absent the equilibrium data can be correlated by equations based on the law of mass action. Equilibrium compositions for the perchlorate system can be correlated over the entire range studied by a single equation based on the law of mass action. Methods based on the law of mass action are presented for correlating or predicting equilibrium compositions for both systems.

Equilibrium studies with cation exchange materials are important for increasing the understanding of the fundamental nature of these exchange materials. Equilibrium investigations have yielded valuable information about the mechanism of ion exchange (*2, 7, 16*), the selectivity of the resin for various cations as a function of solution composition (*5, 8*), and the properties of the ions in contact with the exchange material, such as hydrated radii (*2, 7*), activity coefficients (*3, 4, 6, 13*), and complex-ion formation (*10, 19*). Equilibrium data are also necessary for the study and interpretation of ion exchange rate data, and from a practical viewpoint equilibrium studies aid in understanding and predicting the performance of industrial ion exchange units. Despite the importance of ion exchange equilibrium data, relatively few studies covering a wide range of compositions and concentrations have been reported. Most of the available comprehensive studies deal with uniunivalent exchange (for example, *11, 14, 18*), a few are available for diunivalent exchange (*1, 5, 16*), but none have previously been presented for monotrivalent exchange. Accordingly the equilibrium data for the cation exchange system $Fe^{+++} - H^+$, which were obtained preliminary to a study of the kinetics of this system, are presented in this paper.

EXPERIMENTAL PROCEDURE

A previous ion exchange study (*12*) had indicated that ferric ions in nitric acid solutions are essentially noncomplexing over the concentrations ranges used in that study, and nitrate was initially selected for the common anion in the present study. Subsequent experimental work revealed large amounts of complexing with the nitrate ion, an undesirable feature for rate studies, and so additional equilibrium studies were carried out with perchlorate as the common anion. The latter anion did not exhibit complexing with the iron.

Analytical grade ferric nitrate, ferric perchlorate, nitric acid, and perchloric acid were used to prepare the necessary solutions. Nitrate solutions were aged at least 6 hr. before use to prevent erratic results. The cation resin employed was Dowex-50, X-8, 20- to 50-mesh particle size, a cation exchange resin extensively used in industry. The cation resin was preconditioned by three preliminary saturation-regeneration cycles, and the moisture content of the resin was obtained by drying samples at 105°C. for 24 hr. The resin-exchange capacity was determined by passing a solution of barium chloride through a weighed amount of the resin in hydrogen form and titrating the effluent with standardized sodium hydroxide solution. The barium was then eluted from the bed and measured gravimetrically. The capacity as determined by these methods was 5.2 meq./g. of dry hydrogen-form resin.

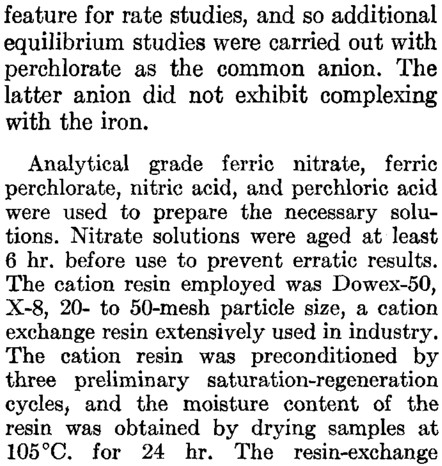

Fig. 1. Exchange isotherms for nitrate system, *q/a*, equivalent fraction iron on the resin, vs. C/C_0, equivalent fraction iron in external solution. The area to the right of the dotted line represents systems exhibiting a high degree of coloration from colloidal ferric chloride.

The equilibrium data were obtained with small beds of exchange material through which equilibrating solutions were passed. Each bed consisted of approximately 1 g. of exchange material supported on a sintered-glass filter mounted in 12-mm. glass tubing. The ends of the glass tubing above the bed and below the filter were drawn to permit ready attachment to Tygon tubing. Another sintered-glass filter was mounted upstream of the bed section to serve as a filter for the equilibrating solution and to prevent loss of resin during preliminary steps of the runs. Tygon tubing was used to connect the bed to reservoirs containing the various solutions needed.

For an equilibrium measurement 2 to 4 liters of solution of accurately known composition was passed through the bed at 5 to 10 ml./min. These conditions were found by preliminary work to be overgenerous for attainment of equilibrium. After passage of the equilibrating solution the glass tube containing the resin bed was detached from the system, and most of the excess solution remaining between the resin particles in the bed was removed by passing air through the bed. The remainder was removed by centrifuging for 5 min. at 2,000 rev./min., these conditions also having been determined by exploratory study. The tube and resin were weighed, the resin was washed with 100 ml. of distilled water to remove the solution from within the resin pores, and the wash water was analyzed for iron content. One liter of 3 to 4 *N* acid was then passed through the bed at a low flow rate and the effluent analyzed for iron content. After the washing the bed was ready for reuse. All runs were at room temperature.

In most runs the resin was initially in the hydrogen form; however in a few runs the resin was started in the iron form, and these gave results identical to those obtained by approaching equilibrium from the hydrogen side. In some runs with nitrate as the common anion hydrochloric acid rather than nitric acid was used as the regenerant solution, so that nitrate complexes present on the resin at equilibrium might be measured.

Both iron and nitrate ion were determined colorimetrically, with potassium thiocyanate and brucine used respectively.

The data obtained with this procedure permitted computation of the amount of iron present on the resin and the amount of solution present in the pores of the resin, as well as an estimate of the amount of iron present in the pore solution.

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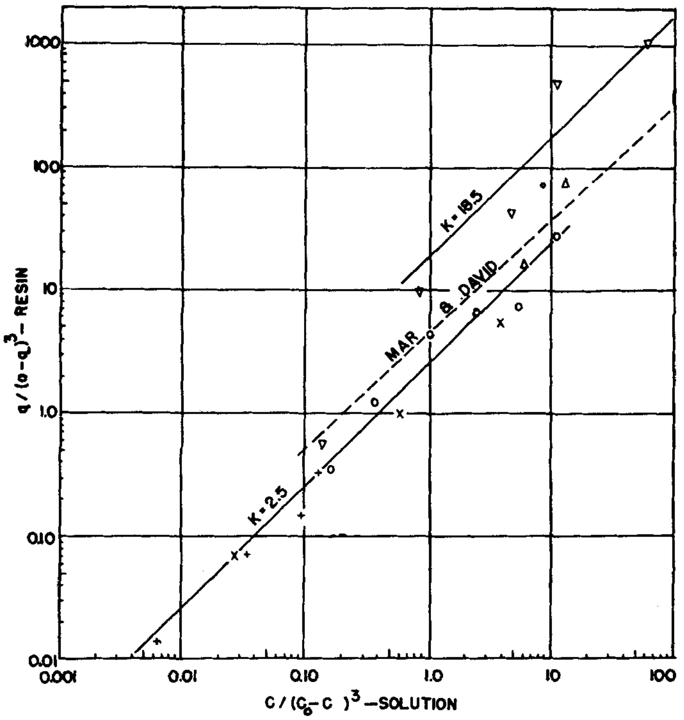

Fig. 2. Nitrate system equilibrium data plotted according to Equation (3); symbols are the same as in Figure 1.

EQUILIBRIUM RESULTS WITH NITRATE AS THE COMMON ANION

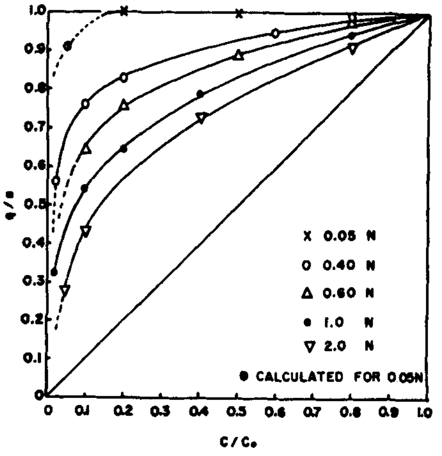

Fig. 4. Exchange isotherms for perchlorate system.

The equilibrium data obtained when the nitrate ion was used as the common anion are shown in Figure 1.* In this figure q/a, the milliequivalents of iron per gram of resin (when one assumes all iron on the resin to be trivalent) divided by the total milliequivalent capacity per gram of resin, is plotted vs. C/C_0, the equivalent fraction of iron in the equilibrating solution. Since only negligible amounts of iron were found in the pore solution (see discussion below), the ordinate represents both total iron content and the chemically exchanged iron content of the resin. As is to be expected for trimonovalent exchange (*2*, *8*), the results in Figure 1 show that the equilibrium on the resin is highly favorable for iron take-up. Most of the data fall on normally shaped ion exchange isotherms, but at low solution concentrations and/or high iron-to-hydrogen ratios in the solution, the curves show abnormal behavior characteristized either by q/a larger than 1 or a sudden upturn in the equilibrium curve. (Points on these portions of the curves are shown in solid symbols.) The equilibrium curves for the 1.0 N and 2.0 N solutions were obtained only for the C/C_0 values shown, as at higher C/C_0's plugging of the sintered-glass filter by colloidal ferric hydroxide was encountered.

The exchange of trivalent iron in solution for hydrogen on an ion exchange resin may be represented by the equation

$$\mathrm{Fe}^{+++} + 3\,\mathrm{H}R \rightleftarrows \mathrm{Fe}R_3 + 3\,\mathrm{H}^+ \quad (1)$$

By application of the law of mass action the equilibrium constant for this system may be defined by

$$K = \frac{[\mathrm{Fe}R_3][\mathrm{H}^+]^3}{[\mathrm{Fe}^{+++}][\mathrm{H}R]^3} \quad (2)$$

wherein the terms in brackets represent activities of the components. If the necessary data were available, these activities could be replaced in terms of concentrations and activity coefficients, but since activity coefficients are lacking for ferric salts in either ordinary solutions or in ion exchange resins, it is

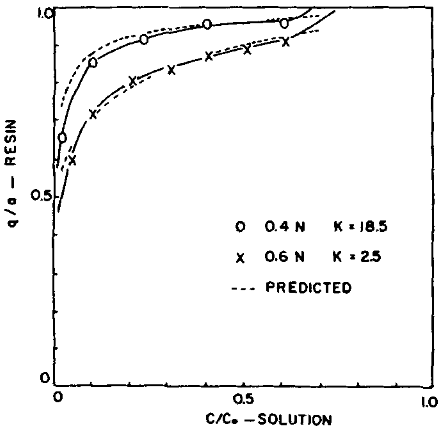

Fig. 3. Prediction of exchange isotherms for the nitrate system.

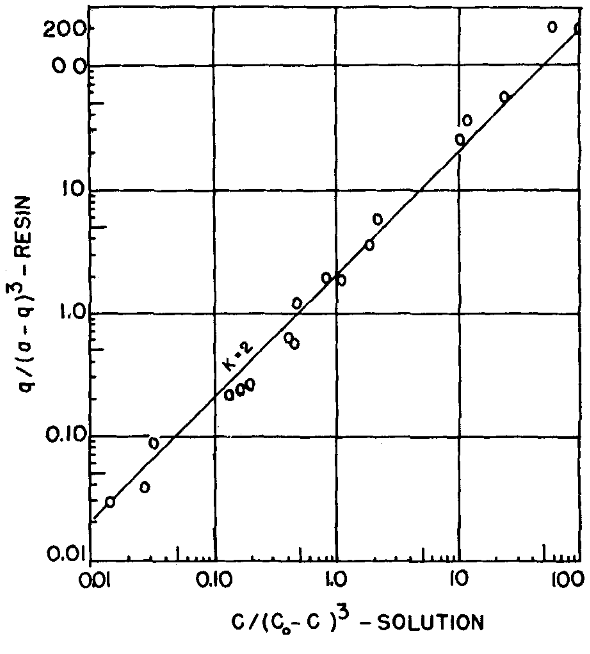

Fig. 5. Perchlorate system equilibrium data plotted according to Equation (3).

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*A complete tabulation of original data and computed results is given in the Ph.D. thesis of R. C. Vasishth, University of Washington, Seattle, Washington.

Table 1. Results of Equilibrium Studies for the System $Fe^{+++} - H^+$ with Perchlorate as the Common Anion

Run number	C_0 milliequivalents	C/C_0	q/a	K	Calculated q/a ($K = 2.0$)	% Dev.
1	0.4	0.2	0.83	2.65	0.815	+1.84
2	0.6	0.2	0.755	1.71	0.765	−1.3
3	1.0	0.1	0.545	1.57	0.576	−5.38
4	1.0	0.4	0.798	2.02	0.795	+0.37
5	1.0	0.8	0.943	2.01	0.941	+0.21
6	2.0	0.4	0.72	2.6	0.70	+2.86
7	2.0	0.05	0.273	1.815	0.276	−1.08

necessary to approximate Equation (2) with Equation (3), wherein the activities are approximated by concentrations

$$\frac{q}{(a-q)^3} = K \frac{C}{(C_0 - C)^3} \qquad (3)$$

where C_0 is the total solution normality and C is the iron normality in solution.

The equilibrium data from the normally-shaped portions of the curves in Figure 1 are replotted in Figure 2 in accordance with Equation (3). Data from Mar and David (*12*) are also included in this plot and agree well with the data of the present studies. From Equation (3), the data should determine a straight line on the log-log plot, with a slope of unity. The value of K determined from the intercept of this line is 6. However the data tend to cluster into two groups, one above and one below the single line; most of the points lying above represent dilute solutions and solutions containing large proportions of iron to hydrogen. If these points are considered separately, they indicate a value of K of 18.5, and the remaining points have a value of K of 2.5. Lines corresponding to these K values are shown on Figure 2. The higher value of K for the one group of points may simply reflect changes in activity coefficients, or it may result in part from complex formation, as discussed later.

Predicted equilibrium-resin compositions determined by the use of the values of K listed above are compared in Figure 3 with experimentally determined values. For solutions 0.1 to 0.4 N the equilibria are represented well by the K value of 18.5. For more concentrated solutions the value of $K = 2.5$ provides good agreement. Thus most of the equilibrium data for the nitrate system may be adequately correlated by equations based on the law of mass action.

The abnormally high iron take-up on the resin in equilibrium with very dilute solutions or solutions containing large iron-to-hydrogen ratios presumably could result from either physical adsorption of colloidal ferric hydroxide or from the exchange of iron present in lower valence complexes, such as $Fe(NO_3)^{++}$, $Fe(OH)^{++}$, $Fe(NO_3)_2^+$, etc. Almost all ferric solutions are hydrolyzed to some extent, and in the present study those solutions with C/C_0's to the right of the dashed line on Figure 1 contained sufficient colloidal ferric hydroxide to exhibit a high degree of coloration from this source. Ferric ions also have a tendency to form complexes with most anions, and available data for ferric nitrate (*17*) and ferric chloride (*15*) solutions indicate the probability of a high degree of nitrate complexing in the concentration ranges where unusually high iron take-up on the resin was noted. Other data (*9*) indicate that appreciable quantities of $Fe(OH)^{++}$ might be present in the solutions. Color effects in the solutions and on the resin militated for the presence of complex ions in the system and against the adsorption of colloidal ferric hydroxide. Subsequent studies with hydrochloric acid used as regenerant showed that for cases where high resin capacity for iron existed, sufficient nitrate ion also existed in the resin phase (as part of the exchanged ions) to account for the major portion of the increased resin capacity. Hence nitrate complexes undoubtedly are responsible for much of the abnormal behavior of the equilibrium for this system.

EQUILIBRIUM RESULTS WITH PERCHLORATE AS THE COMMON ANION

The presence of complexes in the ferric nitrate solutions made these solutions undesirable for use in ion exchange rate studies, and accordingly a ferric system without complexing was sought. Several workers (*15, 19*) have reported that the degree of complexing in dilute ferric perchlorate solutions is almost negligible, even at low hydrogen ion concentrations, and a few test runs indicated that this was also true at higher concentrations. Equilibrium data were then obtained for $Fe^{+++} - H^+$ exchange with perchlorate as the common anion. Figure 4 presents the results. The equilibrium isotherms are normal in shape, and no abnormally high take-up of iron on the cation exchange resin was observed.

As with the nitrate system, only negligible amounts of iron were detected in the solution contained in the pores of the resin particles. This situation might result from further take up of iron on the resin during the washing step, since during this step the resin is effectively in contact with a very dilute solution, but the results are in striking contrast to the pore solution compositions reported in studies of $Cu^{++} - Na^+$ exchange on the same type of resin (*16*). From a practical viewpoint it is immaterial whether the iron is completely exchanged onto the resin initially or whether part of the iron remains within the pores until the washing step and is then exchanged onto the resin.

The data for the perchlorate system were plotted in accordance with Equation (3), as shown on Figure 5, and show very little scatter on this plot as compared with the nitrate system. The value of K obtained from the graph is 2, and typical calculated values of equilibrium resin compositions with this value of K used are compared in Table 1 with experimentally measured resin compositions. The average deviation between experimental and computed values is only 2.5%, and hence K of 2 may be recommended for use for design calculations with this system.

That Equation (3) correlates the equilibrium data so well for the perchlorate system is somewhat surprising in view of the variations of the activity coefficients which might be expected for the components of the system.

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