Equilibrium in the System Cu^{++}–Na^{+}–Dowex-50

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Equilibrium isotherms are presented for the cation exchange of copper and sodium on Dowex-50 resin in solutions from 0.01 to 4*N* in chloride content, and the equilibrium data are correlated on the basis of the Donnan equilibrium. Data are also given on the water content of the resin and the diffusible ions present in this water.

Although extensive equilibrium data for uniunivalent cation exchange are available, the published data for unipolyvalent cation exchange are relatively sparse. Gregor et al. (*7*) have listed the majority of unipolyvalent equilibrium studies, practically all of which cover only a limited concentration range and are concerned principally with relatively dilute solutions. More complete investigations have been made by Bauman and coworkers (*2*) for Ca^{++}-Na^{+} exchange and by Gregor et al. (*7*) for Mg^{++}-K^{+} exchange. These are valuable both in furthering the understanding of the fundamental mechanisms of cation exchange and in providing data for the design of ion exchange processes. Accordingly equilibrium data were obtained for the system Cu^{++}-Na^{+}-Dowex-50, a system of interest particularly at high concentrations, in various waste-treatment and recovery processes (*4, 14*). Selke and Bliss (*14*) have presented a small amount of equilibrium data for copper-hydrogen exchange at two solution concentrations, and Nayak (*11*) has studied copper-sodium and copper-hydrogen exchange at three different solution concentrations. The present investigation covered the concentration range from 0.01 to 4*N*.

THEORY

Methods for explaining and correlating ion exchange equilibrium data have generally been based on the law of mass action, adsorption theory (including statistical approaches), or Donnan equilibrium theory. As pointed out by Schubert (*13*) and Gaines and Thomas (*5*), one approach does not necessarily have a greater fundamental validity than another, as long as not too many simplifying assumptions are made. All three approaches lead to the same general form of equilibrium equation. The Donnan equilibrium principle was used to interpret the experimental data of the present investigation, because it can account for the presence of diffusible anions in the resin phase when the resin is in equilibrium with an external solution. As developed by Bauman and Eichorn (*1*), the Donnan membrane principle leads to the following expression for equilibrium in the system Cu^{++}-Na^{+}-Dowex-50:

$$\frac{a_{Na}^{2} A_{Cu}}{a_{Cu} A_{Na}^{2}} = 1 \qquad (1)$$

If activity coefficients are used, Equation (1) becomes

$$\frac{x_{Na}^{2} X_{Cu}}{x_{Cu} X_{Na}^{2}} \frac{\gamma_{Na}^{2}}{\gamma_{Cu}} \frac{f_{Cu}}{f_{Na}^{2}} = 1 \qquad (2)$$

where

$$\frac{\gamma_{Na}^{2}}{\gamma_{Cu}} = \frac{\gamma_{Na}^{2}\gamma_{Cl}^{2}}{\gamma_{Cu}\gamma_{Cl}^{2}} = \frac{\gamma_{NaCl}^{4}}{\gamma_{CuCl_2}^{3}} \qquad (3)$$

Nearly all the theoretical equations proposed for ion exchange equilibria, including those above, require data on the activities or activity coefficients of the ions in the resin and solution phases, and it is this requirement which generally limits the utility of the equations. Some data are available on the activity coefficients of single chemical compounds in aqueous solutions, and the mean ionic activity coefficients of the components in a solution containing more than one solute may be obtained from the activity coefficients of the pure components by applying the Lewis ionic-strength principle (*10*). Activity coefficients for ions in the resinous phase of an ion exchange system are exceedingly scarce; however, Schubert (*13*) has noted for several electrolytes that if the activity coefficient for the resin phase is plotted as a function of the solution strength computed from the water content of the resin, the curve for the resin-phase activity coefficient has the same shape as, but lies below, the corresponding curve for aqueous solutions of the electrolyte. If it may therefore be assumed that activity coefficients for the cations in the resin phase are proportional to the activity coefficients of these same cations in an aqueous solution of the same ionic strength as that in the resin phase, Equation (2) may be modified to

$$\frac{x_{Na}^{2} X_{Cu}}{x_{Cu} X_{Na}^{2}} \frac{\gamma_{NaCl}^{4}}{\gamma_{CuCl_2}^{3}} \frac{f^{\circ\,3}_{CuCl_2}}{f^{\circ\,4}_{NaCl}} = K \qquad (4)$$

Equation (4) requires for its use only activity coefficients in the aqueous phase.

Simplified forms of Equation (4) may be obtained by neglecting the activity coefficients in the solid phase, the activity coefficients in both phases, or the activity coefficients in both phases and the change in water content of the resin. The last of these possibilities is frequently encountered as the definition of the selectivity coefficient K_c':

$$K_c' = \frac{x_{Na}^{2} M_{Cu}}{x_{Cu} M_{Na}^{2}} \qquad (5)$$

Equation (5) predicts that the equilibrium will strongly favor the copper form of the resin for dilute external solutions but that this selectivity for copper will decrease as the external solution concentration increases (*2*).

APPARATUS AND PROCEDURE

Commercial-grade Dowex-50 cation exchange resin, 20 to 50 mesh size, 8% cross linkage, was used in the study. The resin was thoroughly pretreated, and the capacity measured with both copper and hydrogen was 5.1 ± 0.05 meq./g. of the dry hydrogen form, exclusive of "unattached" cations which might be present in the resin pores. Reagent grade copper chloride and sodium chloride were used to furnish the copper and sodium ions.

The equilibrium data were determined by the columnar technique, wherein solution of known composition is passed through a sample of the resin until equilibrium is attained, and the resin was then analyzed for chloride, copper, and water content. The resin was held in a small Pyrex tube containing a coarse fritted-glass disk near one end to serve as a resin support. The entire resin-bed unit could be attached to or removed at will from a system supplying the necessary liquid solutions. Two beds, each containing approximately 1 g. of resin, were used in the study. An accurately

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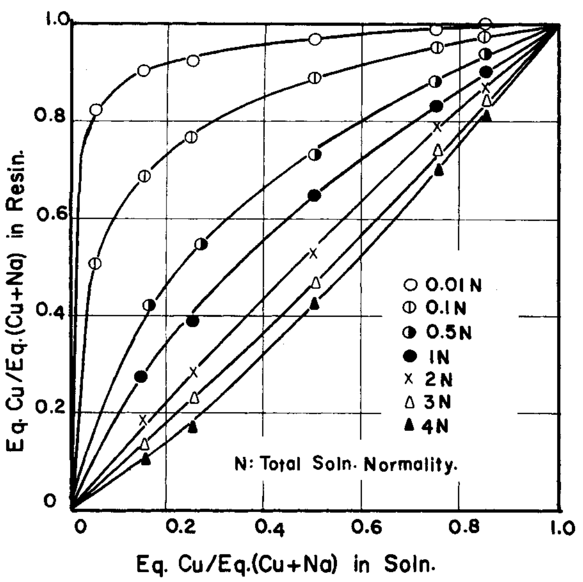

Fig. 1. Exchange isotherms (resin composition after washing).

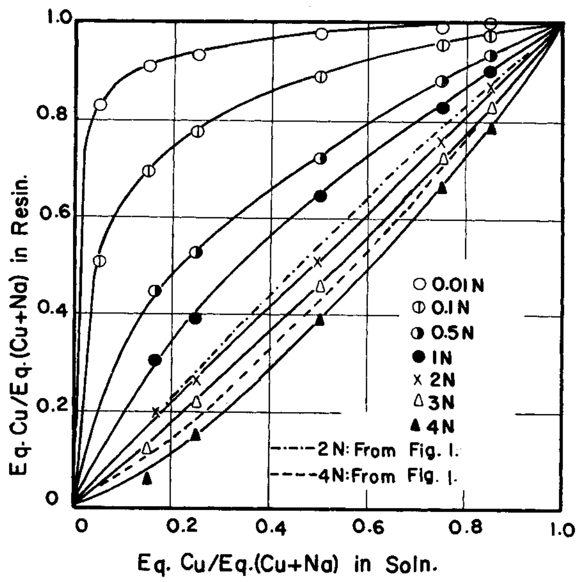

Fig. 2. Exchange isotherms (pore solution included in resin composition).

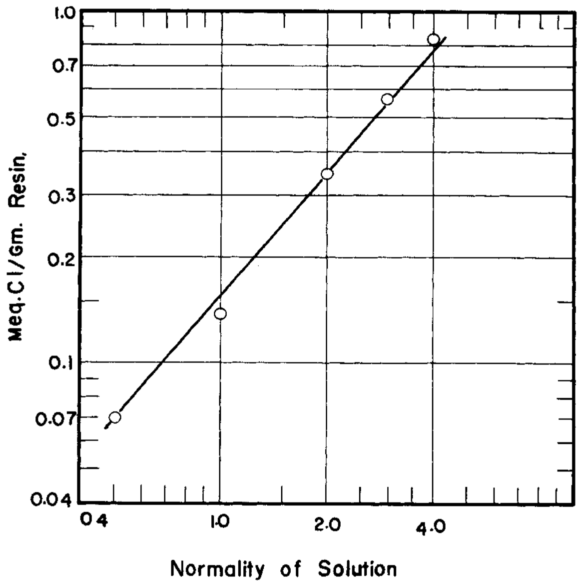

Fig. 3. Chloride content of resin (in pore solution).

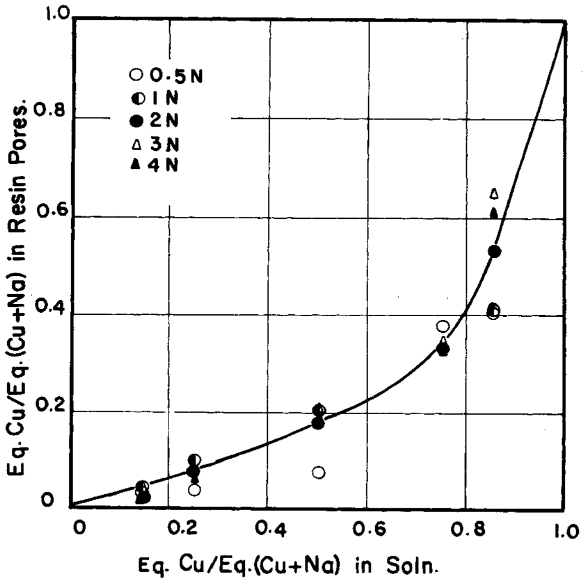

Fig. 4. Indicated copper content of pore solution.

weighed quantity of resin was placed in each bed and remained in that bed throughout the entire series of experiments.

For a given determination, 2 liters of solution of desired composition were passed through the bed at a low flow rate. Preliminary tests showed that the volume of solution and the flow rate used were generously adequate for the resin to reach equilibrium with the solution. After saturation the bed was detached from the feed system and the solution in the tube permitted to drain. The two ends of the bed were then sealed with rubber caps and the bed was centrifuged at approximately 2,000 rev./min. for 3 min., a time determined by preliminary experiments. Solution sticking to the lower end of the tube was removed by drying with filter paper and the bed was quickly weighed. After the weighing 200 ml. of distilled water was passed through the bed to elute the solution present in the pores of the resin, and the effluent wash water was analyzed for copper and chloride ions. The copper chemically combined with the resin was next eluted with 2 liters of 1*N* sodium chloride solution, which was sufficient to remove all copper from the resin. This regenerant solution was analyzed for copper content, the resin was again washed with distilled water, and the bed was ready for reuse.

The *p*H of the regenerant solutions was not measured, but solubility data, weight checks on the resin samples, and resin capacity measurements all indicated that there was no copper precipitation within the resin during regeneration.

All copper determinations were made colorimetrically, with tetraethylene pentamine as the reagent, and the chloride ion was measured turbidimetrically, with silver nitrate as the reagent.

The data obtained in the foregoing procedure, with a knowledge of the weights of the resin and Pyrex tube, are sufficient to permit calculation of the complete composition of the resin phase if electroneutrality of the resin phase is assumed and the capacity of the resin is known.

All runs were made at room temperature (22° to 25°C.). The equilibrium solution normality was varied from 0.01 to 4.0 total normality. The copper to chloride normality ratios used at each solution concentration were varied from 0.15 to 0.85, except at the 0.01 and 0.10 normality concentrations, where the copper to chloride normality ratio was extended to 0.05 to permit more accurate determination of the equilibrium isotherms. Results were computed on the basis of the oven-dry hydrogen form of the resin.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results of the study are presented in Figures 1 through 5. A complete tabulation of the original experimental data, the values used for intermediate calculations and the final results shown in Figures 1 to 6, is available in reference *15*.

Figures 1 and 2 contain the primary

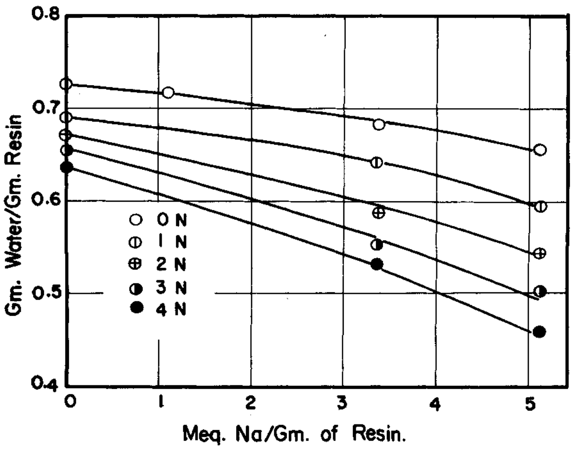

Fig. 5. Water content of resin.

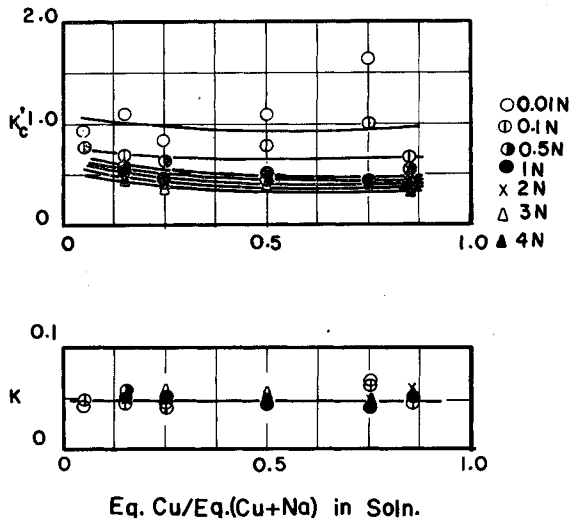

Fig. 6. Correlation of experimental data.

results and show resin composition as a function of the equilibrium-solution composition and concentration. The two figures differ only in that the exchange isotherms in Figure 2 include the ionic contents of the resin pores as part of the resin composition; whereas those of Figure 1 do not. Equivalent fractions are used as the ordinates in both figures, since cation exchange is essentially a constant normality process (at least in dilute solutions), and the data are thus presented in a form useful for design calculations and rate studies. As predicted by Equation (5), the "adsorption" of the copper is strongly favored at low solution concentrations, but this selectivity decreases as total solution normality increases and at high solution concentrations the selectivity is actually reversed. These results are also in accord with those of previous investigators of unipolyvalent exchange (*2*, *7*, *14*). The ionic content of the liquid in the resin pores has negligible effect on the equilibrium isotherms at low solution concentrations but becomes important at high concentrations, as may be noted from the comparative isotherms included in Figure 2. This effect could be significant in the design of ion exchange recovery or separations processes utilizing strong regenerants.

The magnitude of the ionic holdup in the pores of the resin is shown in Figure 3. The chloride content of the pore solution was found to be dependent only upon the total normality of the external solution and not upon the ratio of copper to sodium in the external solution. At high solution normalities the cations in the pore solution are a sizable fraction of the resin capacity. The data in Figure 3 may be expressed by the relation

$$\log q_{\mathrm{Cl}} = \log (0.198N)^{1.14} \qquad (6)$$

Whitcome et al. (*16*) found similar relations for the chloride ion content of Dowex 50 in equilibrium with pure sodium and potassium chloride solutions.

The cation composition of the pore solution as indicated by the analysis of the wash water used to elute the pore material is shown in Figure 4. Determination of the true composition of the pore solution is difficult, as the equilibrium between the resin and external solution is effectively a three-way equilibrium, involving the ions "attached" to the resin, the ions in the pore solution, and the ions in external solution. Replacement of the external solution with wash water disturbs this equilibrium and effectively brings the resin in contact with a very dilute solution. This in turn would tend to promote further take-up of copper from the pore solution by the resin. That this action does take place is possibly indicated by the data of Figure 4, which show that the copper-to-total-normality ratio is always less in the solution eluted from the pores than in the original equilibrium solution. Within the limits of experimental error for the very dilute solutions analyzed, the ratio of copper to sodium in the wash water was found to be independent of the total normality of the original equilibrium solution.

The water content of the resin (i.e., inside the resin pores) at equilibrium is shown in Figure 5 as a function of the external solution composition. The water content is higher for the copper form of the resin, and for a given total external solution normality the water content varies almost linearly with the resin composition. The water content decreases as the normality of the external solution increases. These results are in agreement with the trends found by other investigators (*3*, *8*, *12*), and the effect of solution concentration observed is to be expected from the Donnan equilibrium theory (*6*). The water content of the resin is a guide to the degree of swelling of the resin, and data on it are needed for thermodynamic analysis of the ion exchange process. In the present study the water-content data were used only for the computation of activity coefficients in the resin phase.

CORRELATION OF DATA AND USE IN DESIGN

Substitution of the experimental data into Equations (4) and (5) produces the results shown in Figure 6. A very good correlation of the data is obtained from Equation (4) (lower graph). The equilibrium constant K shows an average deviation of 8.5% and a maximum deviation of 15% from the average value of 0.047, except for four cases at high copper fractions (for the reason discussed below). The pore solution was included as part of the resin phase in computing K, as this inclusion was found to produce better constancy of K. Although K was found to vary as described above, use of Equation (4), taking the average value for K, would permit very accurate computation of equilibrium compositions, as this reverse calculation is relatively insensitive to small variations in K.

The selectivity coefficient K_c' exhibits a much greater variance than the equilibrium constant K. K_c' varies with the total solution normality and, to a lesser degree, with the copper-to-sodium ratio of the solution. Values of K_c' have an average deviation of 34% from the mean value of 0.59. The largest deviations are for the lowest normality solutions, and it may be noted that the K_c' values for these solutions show considerable scattering in the high copper region. This latter effect is caused by relatively small errors in observed copper content of the resin producing large percentage errors in the computed sodium content. K_c' is very sensitive to small changes in the value used for the sodium content of the resin, since this factor enters to the second power.

Equations intermediate to Equations (4) and (5) were also tested with the experimental data. Modification of Equation (5) by use of molalities rather than mole fractions in the resin phase actually provided a somewhat less satisfactory correlation than Equation (5). Correction

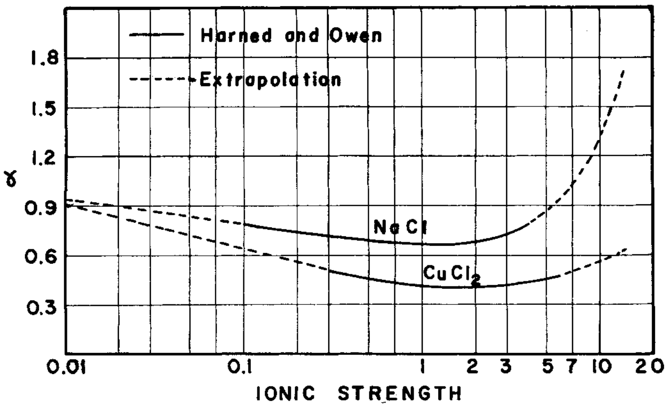

Fig. 7. Activity coefficients used in data correlation.

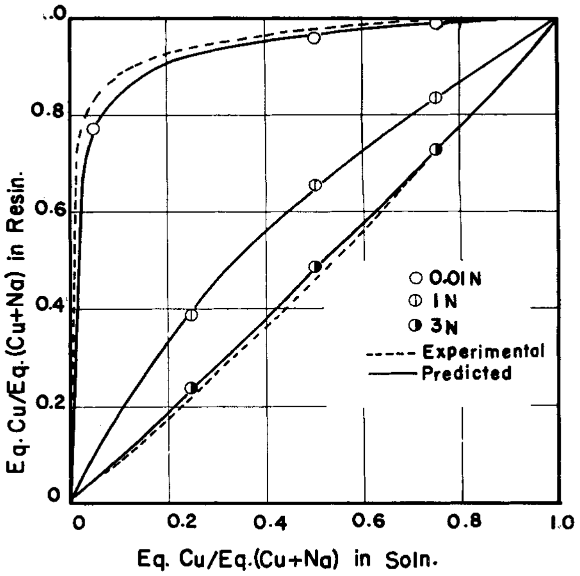

Fig. 8. Prediction of exchange isotherms from the selectivity coefficient.

for both the water content of the resin (i.e., use of molalities in the resin phase) and activity coefficients in the external solution phase resulted in a small improvement over Equation (5).

Calculation of K requires activity-coefficient data for the resin and external phases. As discussed earlier, activity coefficients in the resin phase were taken as proportional to activity coefficients in an aqueous phase having the same solution strength (based on the water content of the resin) as the resin phase. Accordingly, only activity coefficients for aqueous solutions were needed. The activity coefficients for copper and sodium chloride are available in the literature (*9*) for ionic strengths up to 6.5 and 4 respectively. These data were extrapolated as shown in Figure 7. The extrapolation was performed on a linear coordinate plot, essentially by eye, and the upward curvature of the sodium chloride curve is accentuated by the transfer of the original extrapolation to the semilog plot used in Figure 7. Relatively little attempt was made to adjust the extrapolations at high solution strengths to provide optimum agreement of K values. Such adjustment, however, could be viewed as an empirical method for defining the activity coefficient values in the resin phase. It is of interest to note that the ionic strength in the resin phase is sometimes as high as 13.6, a concentration which would not exist in an aqueous solution at room temperature.

Although values of K_c' computed from the experimental data show considerable variation, use of Equation (5) with a value of 0.5 for K_c' is generally satisfactory for design purposes. Exchange isotherms using this relation are compared with experimental results in Figure 8. The equilibrium distribution of ions between the resin and the solution predicted by this equation has a maximum error of 10% for that ion which is present in the larger amount on the resin. To obtain better agreement with experimental data, K_c' of 0.6 for solutions with concentrations up to $0.5N$ and K_c' of 0.4 for higher solution concentrations may be used. If still more accuracy is desired, Equation (4) may be used, with the proper activity coefficient corrections. However, this last procedure involves tedious trial and error.

For solution concentrations of $2N$ and higher, even simpler relations can be used to express the equilibrium for many cases. At high solution concentrations, the exchange isotherms are nearly linear, with an approximate slope of unity, as shown in Figures 1 and 2. The isotherms in Figure 1 may be approximated by the equation

$$\frac{q_{Cu}}{q_0} = \frac{N_{Cu}}{N_{total}} + B \qquad (7)$$

B is a constant for a particular solution normality, with the values 0.03, −0.02, and −0.05 for solution normalities of 2, 3, and 4 respectively. Equation (7) gives results with reasonable accuracy for N_{Cu}/N_{total} between 0.1 and 0.9.

NOTATION

A = activity of ion in resin phase
a = activity of ion in solution
B = constant in Equation (7)
f = activity coefficient of ion in resin phase
$f°$ = activity coefficient of ion in a solution whose ionic strength is the same as that in the resin phase
K = equilibrium constant defined by Equation (4)
K_c' = selectivity coefficient defined by Equation (5)
M = moles of ion per unit weight of dry hydrogen form of resin
N = normality of solution
q_{Cl} = equivalents of chloride ion per gram of dry hydrogen form of resin
q_{Cu} = equivalents of copper per gram of dry hydrogen form of resin
q_0 = total exchange capacity, equivalent per gram of dry hydrogen form of resin (exclusive of cations in the pore solution)
X = molality of ion in resin
x = molality of ion in solution
γ = activity coefficient of ion or compound in solution

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