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Comparison Between Some Simple Computer-Calculated and Experimental Ion Exchange Elutions¹

EDWARD H. WARD, LARRY G. MCRAE, AND
RUSSELL W. MAATMAN

Abstract. A method for calculating the elution curves for certain ion exchange columns is given. Equilibrium is assumed to be achieved in theoretical plates of finite height. Predicted and experimental elutions agree where it is possible to circumvent non-equilibrium factors by use of the plate concept. Methods are given for elutions both where there is and where there is not co-ion reaction with counter-ion. The mathematical solutions are lengthy because approximations are avoided, necessitating the use of a high-speed computer. Comparisons with experimental results, using Amberlite CG-120 columns, are given for band elution of Na^+ by HNO_3 , elution by NaNO_3 of the resin entirely in the acid form, and elutions by HNO_3 and acetic acid of the resin entirely in the Na form. In all but the acetic acid elution the elution curve was correctly predicted by assuming 13-18 plates per centimeter; with acetic acid the curve shape was correctly predicted and shown to be almost insensitive to the number of plates assumed.

The mathematical prediction of the behavior of ion exchange columns has received considerable attention. (1) Usually the procedure involves assuming the system is simpler than it actually is. A frequently-used simplification is the assumption that solution flow is equivalent to equilibrations of the solution in successive "theoretical plates" of finite height, as first proposed by Martin and Synge. (2) The concept of a finite-height plate is used to circumvent kinetic effects. If there are no kinetic effects, i.e., if equilibrium is attained locally, the plate height is infinitesimal. Under such conditions, concentration changes along the column can be obtained by integrating the change in the plate of infinitesimal height. In the present work concentration changes are predicted by assuming equilibrations in successive finite plates. The analogy with mathematical integration is thus only approximate. An additional reason the finite plate method is only approximate is that the HETP is empirical and a sensitive function of many variables, e.g., column and particule geometry, ion distribution coefficient, ion diffusivity, flow rate, etc. It is the purpose of this article to show that in spite of these difficulties with the finite plate height method, it is possible to predict, using a computer, the shapes of some elution curves.

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The method is general enough to study the effect of several variables of the ion exchange equilibrium. Some of these variables are those arising from competing solution reactions and non-constant distribution coefficients. In this article the general method is described, the effect of introducing a competing reaction is given, and comparison of calculated and experimental curves is given for cases where there is and where there is not a competing solution reaction.

In earlier mathematical treatments (some using computers) of column adsorption and ion exchange the systems studied and/or the comparisons with experimental results were different from ours. (3-10) Certain insights into the nature of column adsorption and exchange were gained from these studies. The position taken here is that although some of the information obtained by use of the present method has been obtained in some of these other studies, the method presented can also be used to obtain new insights. For example, among the elution curves which can be predicted by this method are those in which reaction between counter-ion and co-ion affect the curve shape. This perturbation of the ion-exchange equilibrium is usually avoided in mathematical treatments, although experimentally it is a very real and often useful effect.

METHODS AND RESULTS

Systems without Co-ion Reaction

The problem to be solved is the calculation of the equilibrium concentrations of the mobile ions in the last plate for each of the successive volumes (where a volume is the volume of the solution in contact with one plate) which moves through the column. The method used applies to columns in which the resin exchange behavior can be characterized at a given ion concentration by an exchange site density and an equilibrium constant. In the experimental systems described here the exchange "constant" does not vary with the ion concentration, although the method presented in general in that it does not require this constancy.

First, the concentrations in one plate are determined by considering the reaction with resin RX,



where U and X are monovalent ions. The following equations are used to solve for the various concentrations after equilibration in a plate:

$$K_1 = \frac{(RU)(X)}{(RX)(U)} \quad (1)$$

$$(X) + (U) = A \quad (2)$$

$$(X) + Q(RX) = B \quad (3)$$

$$(RU) + (RX) = 1 \quad (4)$$

where

K_1 = equilibrium constant for reaction (I), previously determined from batch equilibration (for convenience this symbol is written K_1 instead of the conventional " ∞ ");

(RU) , (RX) = mole fractions of the exchange sites in the two forms;

(X) , (U) = ion molar concentrations;

A = initial molar concentration of eluent;

Q = milliequivalents of exchange sites contacting void per milliliter of void volume, previously determined;

B = milliequivalents of ion X per milliliter of void at the beginning of equilibration either in solution or on surface, determined from the previous history of the plate.

The activity coefficients of both mobile and resin phase ions are incorporated (equation (1)) into K_1 . In our systems K_1 so defined (see experimental section) is constant over the concentration range of interest. (Where K_1 is not constant, equations (1) - (4) can be solved by successive approximations using in the successive steps the value of K_1 called for by the previous solution). Equations (2) and (4) state the condition of electro-neutrality in the solution and resin phases, respectively; equation (3) states the conservation of ion X in a plate during the process of equilibration.

Solving equations (1)-(4),

$$(X) = \frac{-K_1A - K_1B - Q + B \pm \sqrt{[(K_1A + K_1B + Q - B)^2 + 4K_1AB(1 - K_1)]^{1/2}}}{2(1 - K_1)} \quad (5)$$

Determination of (U) , (RU) , and (RX) is then straight-forward.

Second, this calculation is repeated for each plate and for each volume of liquid passing through. Thus, in our columns for the first volume equilibrating in the first plate, $B=Q$, since initially $(RX) = 1$ and $(X) = 0$. For each succeeding equilibration in the first plate $B \neq Q$ because (RX) is decreasing, and for each equilibration in plates beyond the first, $B \neq Q$ because both (X) and (RX) may vary. However, B is always calculable from the previous history of the plate and the solution; therefore all concentrations in all plates can be determined. Obviously, calculations can be made assuming various initial con-

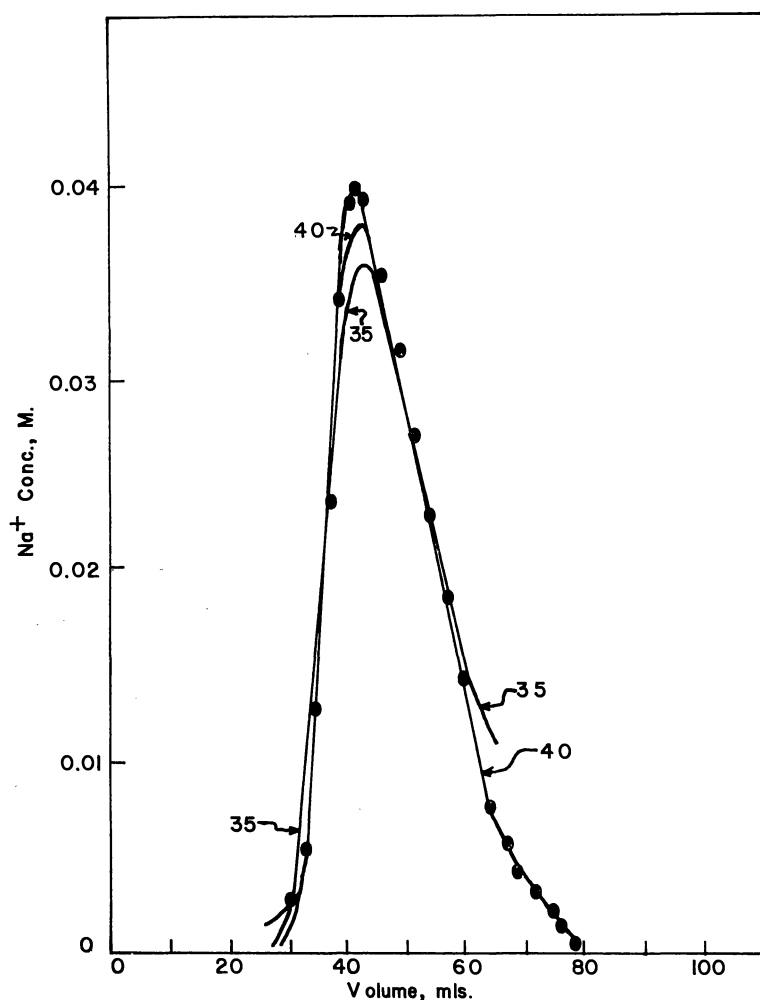


Figure 1. Experimental and calculated elution of Na^+ from 1.00 g. Amberlite CG 120, with first 20% in Na^+ form, by 0.100 M. HNO_3 . $Q = 2.54$ meq./ml. and $K_1 = 1.50 \text{ M}^{-1}$ Plate numbers for the entire column indicated for calculated curves.

ditions of the column. In the present work are reported (1) cases in which the upper part of the column is in the RX form and the remainder is in the RU form and (2) cases in which the entire column is in the RX form.

Elution curves were calculated using the IBM 1620 Data Processing System. (11) In a computer run, for a given set of system parameters, the elution curve of (X) vs. volume number for many plates was produced. When an experimental column is assumed to contain a certain number of plates, the abscissa

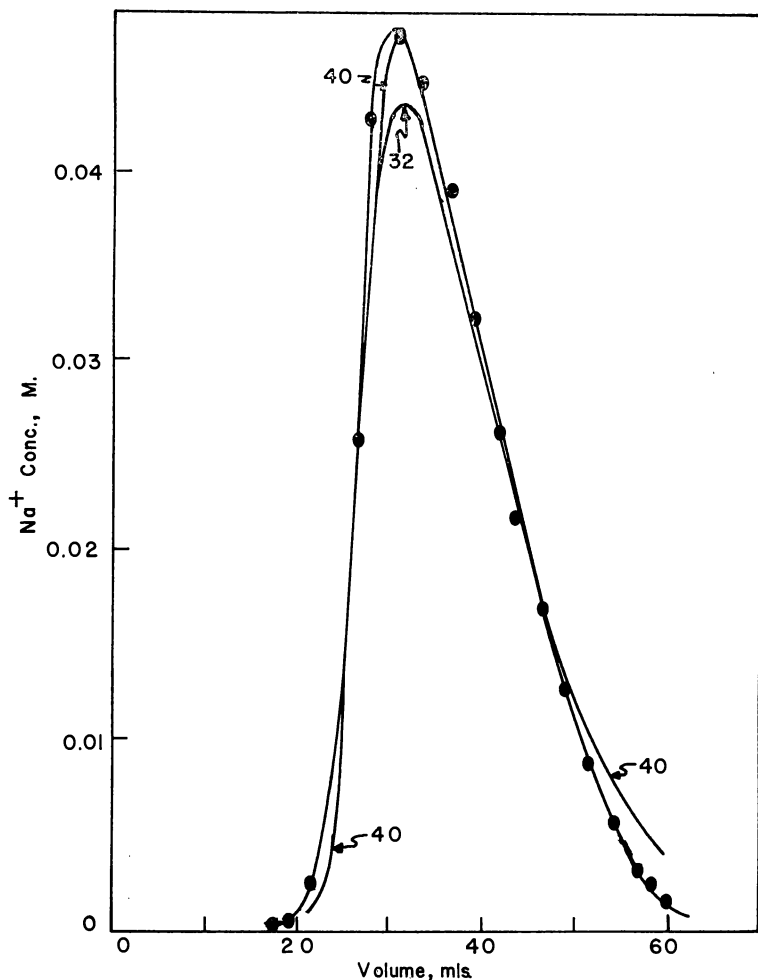


Figure 2. Same as Figure 1, but 0.800 g. resin with 25% in Na⁺ form.

of the calculated curve is converted from volume number to milliliters by equating the assumed number of plates to the void volume (see experimental section) of the column. In Figure 1-4 are shown downward-flow elutions by tenth-molar nitric acid of Na⁺ from Amberlite CG-120 (sulfonic acid) resin, with the first part of the column in the sodium form and the remainder in the acid form. The calculated curves are indicated by the number of plates assumed. There is reasonable agreement with the experimental curves. The approximate number of plates per centimeter (for all columns the cross section is 0.79 cm², with lengths about 2.8 cm/g) in the four columns, respectively,

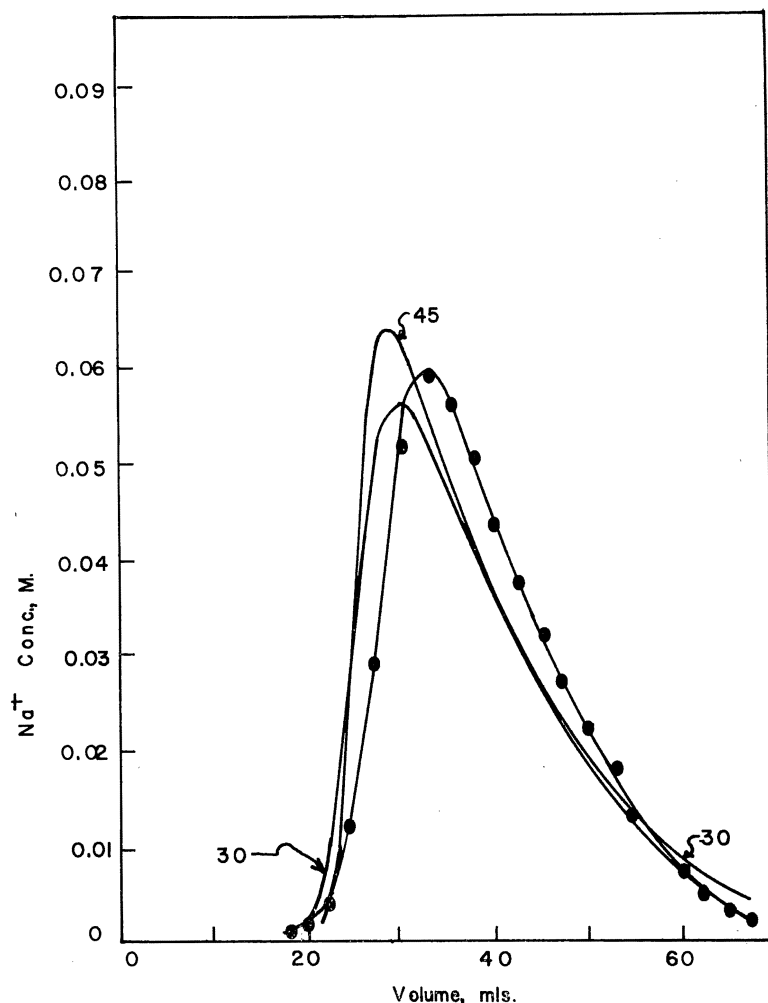


Figure 3. Same as Figure 1, but 0.900 g. resin with 83% in Na^+ form.

is calculated to be 16, 18, 15, and 14, with an HETP of 0.055-0.071 cm. (For the first two columns slight extrapolation beyond 40 plate calculation for the entire column was made.)

In Figure 5 are given the calculated and experimental curves for tenth-molar sodium nitrate elution of acid from a 1.0 g column initially in the acid form. Here the 35-plate calculated curve (13 plates per centimeter) matches the experimental, in fair agreement with the 14-18 plates per centimeter found with the other systems.

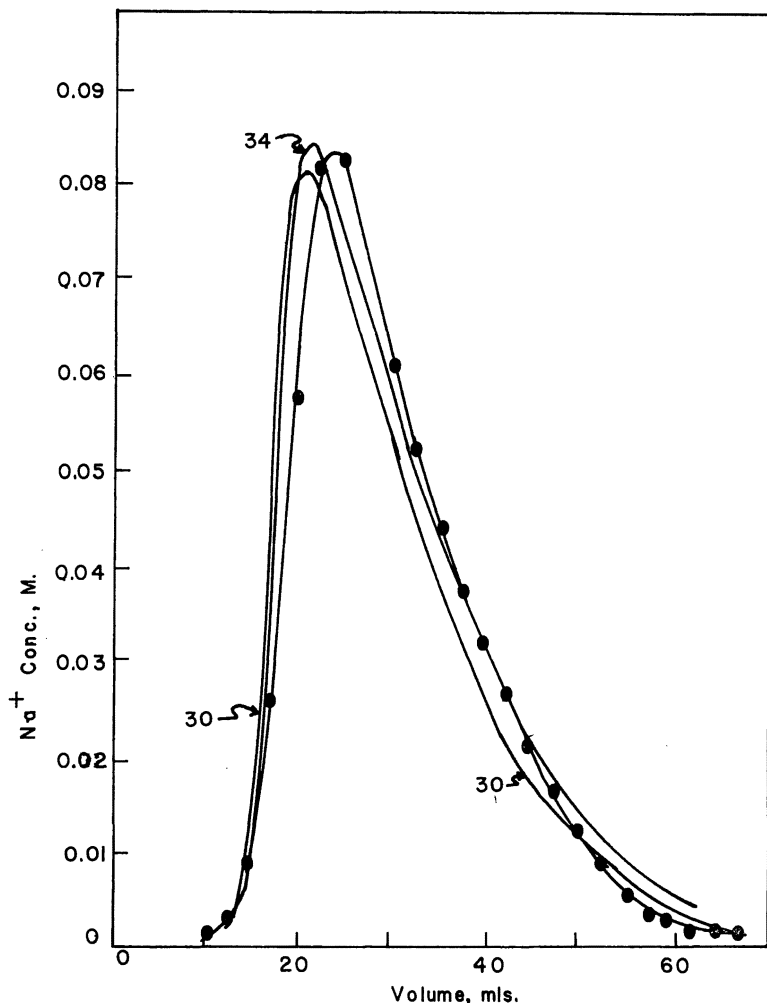
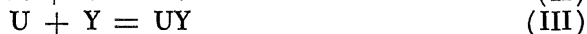
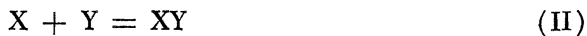


Figure 4. Same as Figure 1, but 0.800 g. resin with 50% in Na^+ form.

Systems with Co-Ion Reaction

In some elutions the co-ion—in our elutions, the eluent anion—combines with one or both of the counter-ions. Then reaction (I) is influenced by



where Y is the co-ion. Equilibrium concentrations in each plate are found by solving simultaneously equations (1), (4), and the following:

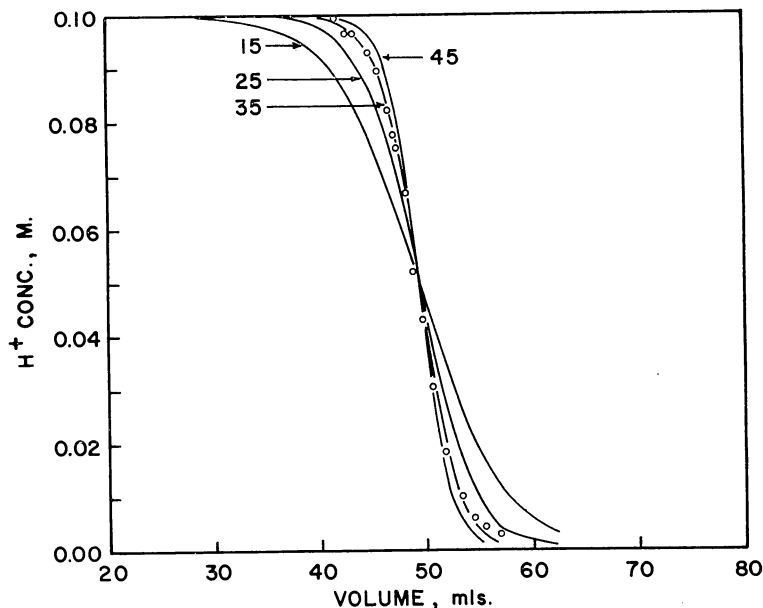


Figure 5. Experimental and calculated elution of H^+ from 1.00 g. Amberlite CG-120, completely in acid form, by 0.100 M. $NaNO_3$. Plate numbers indicated for calculated curves.

$$K_2 = \frac{(XY)}{(X)(Y)} \quad (6)$$

$$K_3 = \frac{(UY)}{(U)(Y)} \quad (7)$$

$$(XY) + (UY) + (Y) = A \quad (8)$$

$$(XY) + (X) + Q(RX) = B \quad (9)$$

$$(X) + (U) = (Y) \quad (10)$$

where K_2 and K_3 are association equilibrium constants, defined here in terms of concentrations, which range from extremely dilute to tenth-molar. Note that A and B have the same meaning as earlier but that they are no longer defined by equations (2) and (3). Equations (8) and (9) state, respectively that Y and X ions are conserved during the equilibration process; equation (10) states the condition of electroneutrality in the solution phase. Equations (1), (4), and (6)-(10) can be rearranged to

$$C(X)^5 + (D + BD')(X)^4 + (E + BE')(X)^3 + (F + BF' + B^2F'')(X)^2 + (BG + B^2G')(X) + B^2H = O \quad (11)$$

The constants in equation (11) are defined as follows:

$$\begin{aligned}
C &= K_2 K_3^2 - K_1 K_2 K_3^2 - K_2^2 K_3 + K_1 K_2^3 - K_1^2 K_2^3 + K_1^2 K_2^2 K_3 \\
D &= K_3^2 - K_2 K_3 - K_1^2 K_2^3 A - K_1 K_2^3 + K_2 K_3^2 Q + 2 K_1 K_2^2 + K_1 K_2^3 A - K_2^2 K_3 A + K_1 K_2^3 Q - \\
&\quad K_2^2 K_3 Q - 2 K_1^2 K_2^2 + 2 K_1^2 K_2 K_3 - K_1 K_2^2 K_3 - K_1 K_2^2 K_3 Q + K_1^2 K_2^2 K_3 A \\
D' &= K_1 K_2 K_3^2 - K_2 K_3^2 - K_1 K_2^3 + K_2^2 K_3 + K_1^2 K_2^3 - K_1^2 K_2^2 K_3 \\
E &= 2 K_3^2 Q - K_1 K_3^2 Q + K_1 K_2 - K_1 K_3 - K_1 K_2^2 A - K_1 K_2 + 2 K_1 K_2^2 Q - 2 K_1 K_2 K_3 Q - K_2 K_3 Q \\
&\quad + K_1^2 K_3 - K_1^2 K_2 K_3 A \\
E' &= 2 K_1 K_3^2 - 2 K_3^2 - 2 K_1 K_2^2 + 2 K_1 K_2 K_3 + K_2 K_3 - 3 K_1^2 K_2 K_3 + 2 K_1^2 K_2^2 \\
F &= K_1^2 K_2^2 A^2 + K_3^2 Q^2 + K_1^2 K_2 A - K_1^2 K_3 A + K_1 K_2 Q - K_1 K_3 Q + 2 K_1 K_2 K_3 A Q \\
F' &= K_1 K_2^2 Q - 2 K_3^2 Q - K_1 K_2 + 2 K_1 K_3 - K_1^2 K_2^2 A - 2 K_1^2 K_3 + K_1^2 K_2 + K_1 K_2 K_3 Q + K_1^2 K_2 K_3 A \\
F'' &= K_3^2 - K_1 K_2 K_3 - K_1 K_3^2 + K_1^2 K_2 K_3 \\
G &= 2 K_1^2 K_3 A + K_1 K_2 Q - K_1^2 K_2 A \\
G' &= K_2^2 K_3 - K_1 K_3 \\
H &= K_1^2 K_3 A
\end{aligned}$$

The ultimate computer calculation was that of total concentration of X in solution, i.e., $(X) + (XY)$, in the last plate at equilibrium. As with the systems without co-ion reaction the successive approximation method can be used if K_1 is a function of ion concentration.

Elutions by tenth-molar acetic acid and tenth-molar nitric acid of the sodium form of the column used in the Figure 5 experiment are shown in Figure 6. The values of K_2 and K_3 in

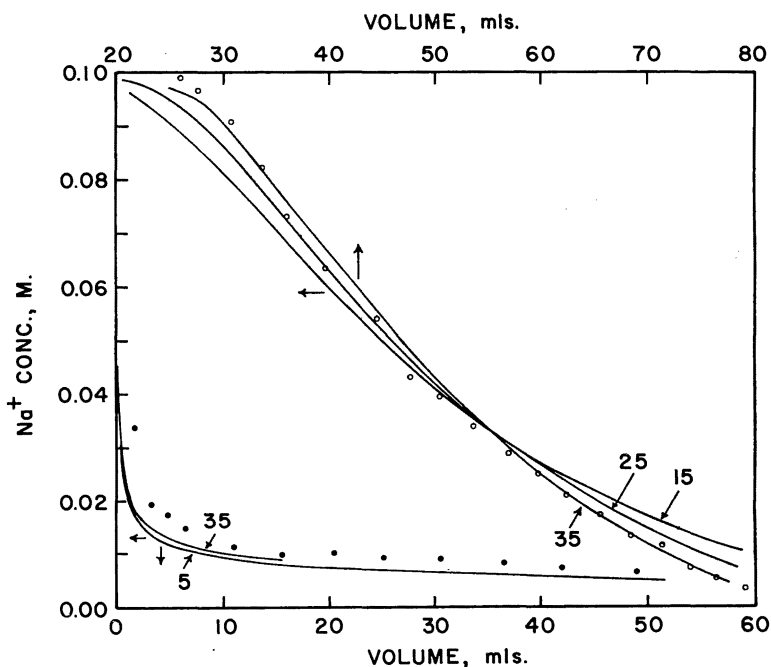


Figure 6. Experimental and calculated elution of Na⁺ from Figure 5 column initially in Na⁺ form by 0.100 M. HNO₃ (upper) and 0.100 M. CH₃COOH (lower). Plate numbers indicated for calculated curves.

the acetic acid calculation are 1.1 and $5.7 \times 10^{-4} \text{M}^{-1}$, respectively (12); in the nitric acid calculation, 0.25 and 0.05M^{-1} , respectively. (13-14) (Because the calculated curves are insensitive to K_2 and K_3 when they are no more than the order of unity, the calculated nitric acid curve of Fig. 6 can be produced by assuming $K_2 = K_3 = 0$.) Both calculated and experimental curves show that the nature of the co-ion has a profound effect on the shape of the elution curve. With nitric acid elution the best match is again obtained with the 35-plate calculation, with 13 plates per centimeter. With acetic acid elution the shape of the experimental curve is correctly predicted by calculation, but no decision concerning the number of plates can be made.

In some cases, e.g., in the sodium nitrate and sodium acetate elutions of this resin in the acid form, the nature of the co-ion has essentially no effect on the experimental curve. There are here other factors not considered in the simple model and the calculated curves do not make a correct prediction. Even where kinetics is not a factor, the improvements in the model needed for the more complex cases include the introduction of (1) the dependence of the electrolyte invasion of the resin phase upon electrolyte concentration and (2) activity coefficients, especially for the resin phase.

EXPERIMENTAL

Materials

The sulfonic acid resin used was Amberlite CG-120 received in the sodium form. To prepare the acid form about 300 g was exhaustively eluted with one molar nitric acid, washed with deionized water, dried at 110° for 24 hours, and screened; the 100-200 mesh fraction was stored for use. Other materials were reagent grade.

Determination of K_1

To determine K_1 approximately 1 g resin in the acid form was equilibrated with 200 ml of a sodium perchlorate solution, with frequent shaking, for a week. The value of K_1 was calculated from the amounts used and the amount of acid in an aliquot at equilibrium, with a correction made for the amount of acid produced when water instead of electrolyte solution was used. (The origin of this acid was apparently the slight decomposition accompanying the 110° treatment.) There was no trend in twenty-four K_1 determinations between equilibrium sodium ion concentrations of $2.5 \times 10^{-4} \text{M}$. and 0.0647M ., and between

7.0 and 77.1% sodium coverage of the exchange sites. The value of K_1 used was 1.50 (error, ± 0.10).

Column Preparation and Use

All the columns of height 2.8 - 3.0 cm, were established in 50 ml burets, with a bed cross-section of 0.79 cm². The resin was supported on a glass wool plug; a similar plug covered the bed to prevent entering solutions from disturbing it. All columns were washed with deionized water.

The exchange capacity, determined by exhaustive elution with one molar sodium nitrate and titration of eluate acid with sodium hydroxide, was 4.97 meq./g, based on the resin weight in the hydrogen form. The exchange capacity on the basis of void volume, Q , was 2.54 meq./ml. The void volume of the column was found by determining the volume of water between the lower and upper glass wool plugs when the bed was packed.

Resin beds were just covered with water as elutions began. Flow rates were 0.4-2.0 ml./min. To determine elution curves fractions of about one milliliter were taken, with the exact size of the fraction determined by weighing. The acid concentration of the fraction was determined by titration with sodium hydroxide. Eluent sodium concentration was obtained by subtracting eluent acidity from eluate acidity.

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