[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

Ion Exchange as a Separations Method. IV. A Theoretical Analysis of the Column Separations Process[1]

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Introduction

Considerable success has been achieved in the separation of elements of very similar characteristics by the use of a method developed for the separation of the products of uranium fission. This method, which is similar to chromatographic analysis, consists of adsorbing a mixture of cations in a narrow band at the top of an ion exchange column and subsequently eluting these cations stepwise with solutions of complexing agents. The separation depends upon differences in the affinity of the exchanger for the cations and differences in the dissociation constants of their complexes. The two competing reactions may be represented by the equations:

$$(1)\quad M^{+n} + nR^{-} \rightleftarrows MR_n; \text{ and}$$

$$(2)\quad M^{+n} + yH_xA^{-x} \rightleftarrows M(H_xA)_y^{-s}$$

in which M^{+n} is a cation, R^- is the ion exchanger anion, H_xA^{-x} some complex forming anion and *s* is the final charge on the complex.

Although this method of separation of the fission products and later of the rare earths was developed empirically it gave very satisfactory results. The empirical approach was, however, very time consuming and, at best, resulted in the selection of a set of conditions for the column operation which were acceptable, since the true optimum conditions required too much time to evaluate.

This difficulty was partially resolved by a series of equilibrium studies of the column reactions.[2] As a result of that study, it was possible to evaluate the effects of various factors on the distribution of a cation between the resin and solution phases at equilibrium. In order that the equilibrium data could be applied to column conditions, a satisfactory theory of column operation was necessary.

Wilson[3] had attempted a theoretical approach to chromatographic analysis in 1940. He based his development on the assumption that the band width of an adsorbed substance does not change during the chromatographic development. When he noted that the band did actually widen and the boundaries did become diffuse, he ascribed this to diffusion and lack of equilibration of the solute between the two phases. DeVault[4] extended Wilson's treatment but still failed to predict fully the actual behavior of the solutes during the chromatographic development process.

A theory of mass transfer, first proposed by Beaton and Furnas[5a] has been quantitatively extended to adsorbent beds by G. E. Boyd, *et al.*,[5b,c] but not to computation of the degree of separation.

About a year after Wilson's publication, Martin and Synge[6] described a treatment based on the assumption that the chromatographic columns are similar in operation to distillation and extraction fractionating columns. They considered the column as consisting of a number of theoretical plates, within each of which equilibrium between the two phases occurred. They found that under the limited conditions in which the distribution coefficient did not change with the change in concentration of a solute, the width of the band, as predicted by their theory, was very similar to that observed experimentally.

The theoretical approach described below is also based on the analogy of the ion exchange separations column to the fractionating distillation or extraction column. The notations used to express the various factors (particularly the use of solution volume and resin mass rather than area and height for expressing the elements in each plate) allow a simpler representation of several of the expressions than those used by Martin and Synge. Also, this approach is directly applicable to the determination of the composition of the eluate as well as predicting the distribution of the various substances on the column.

Notation of Symbols to be Used.—The column is considered as being made up of a number of theoretical segments or plates, *p*, each plate having an equivalent mass of resin, *m*, and volume of solution, *v*. As flow is started through the column, these *v*'s of solution progress down the column from plate to plate. Other notations which will be used are:

V = (pv) = volume of solution in the column.
n = number of *v*'s that have entered into a plate up to any given time.
F = (n/p) = number of *V*'s that have passed through the column.
L = the fraction of a solute in any *v* of solution.
S = the fraction of a solute in the solid phase of the column in any plate.
$L_{n,p}$ = the fraction of solute in solution which is in contact with plate *p* when the *n*'th *v* has equilibrated in that plate.
$S_{n,p}$ = the fraction of solute in the solid phase in plate *p* when the *n*'th *v* has equilibrated in the plate.

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[2] E. R. Tompkins and S. W. Mayer, THIS JOURNAL, **69**, 2859 (1947).

[3] J. N. Wilson, *ibid.*, **62**, 1583 (1940).

[4] D. DeVault, *ibid.*, **65**, 532 (1943).

[5] (a) R. H. Beaton and C. C. Furnas, *Ind. Eng. Chem.*, **33**, 1501 (1941); (b) G. E. Boyd and A. W. Adamson, THIS JOURNAL, **69**, 2836 (1947); (c) G. E. Boyd, L. S. Myers and A. W. Adamson, *ibid.*, **69**, 2849 (1947).

[6] A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 1385 (1941).

Development of the Theory.—The distribution of solute in any plate may be expressed as

$$S_{n,p}/L_{n,p} = C \qquad (1)$$

where C represents the distribution of the solute between the solution and the resin in a plate, p. To maintain material balance

$$L_{n,p} + S_{n,p} = L_{n,p-1} + S_{n-1,p} \qquad (2)$$

As mentioned above, the separation procedure developed in this laboratory consists of adsorbing a mixture of cations in a narrow band at the top of the column and then eluting them differentially by the use of a complexing agent in aqueous solution. As the first increment of volume v enters the column it will come in contact with the portion of exchanger on which the cations to be separated are adsorbed. This part of the column will be designated as plate zero and the quantity of the cation on it will be considered as unity. Then, from (1) and (2), when the first volume v has equilibrated in plate zero

$$L_{1,0} + S_{1,0} = 0 + 1$$
$$S_{1,0}/L_{1,0} = C$$
$$\therefore S_{1,0} = C/(1 + C);\ L_{1,0} = 1/(1 + C)$$

Similarly

$$L_{2,0} + S_{2,0} = 0 + \frac{C}{1 + C};\ \frac{S_{2,0}}{L_{2,0}} = C$$

and

$$S_{2,0} = \frac{C^2}{(1 + C)^2};\ L_{2,0} = \frac{C}{(1 + C)^2}$$

In general

$$S_{n,0} = \frac{C^n}{(1 + C)^n};\ L_{n,0} = \frac{C^{n-1}}{(1 + C)^n}$$

For the first theoretical plate

$$L_{1,1} + S_{1,1} = L_{1,0} + S_{0,1} = \frac{C^0}{(1 + C)} + 0;\ \frac{S_{1,1}}{L_{1,1}} = C$$
$$\therefore L_{1,1} = \frac{C^0}{(1 + C)^2};\ S_{1,1} = \frac{C}{(1 + C)^2}$$

and

$$L_{2,1} + S_{2,1} = L_{2,0} + S_{1,1} = \frac{C}{(1 + C)^2} + \frac{C}{(1 + C)^2};\ \frac{S_{2,1}}{L_{2,1}} = C$$
$$\therefore L_{2,1} = \frac{2C}{(1 + C)^3};\ S_{2,1} = \frac{2C^2}{(1 + C)^3}$$

In general

$$L_{n,1} = \frac{nC^{n-1}}{(1 + C)^{n+p}};\ S_{n,1} = \frac{nC^n}{(1 + C)^{n+p}}$$

$L_{n,p}$ can be similarly calculated for $p = 2,3,4, \cdots$, to give the general equations

$$L_{n,p} = \frac{(n + p - 1)!}{(n - 1)!\, p!} \frac{C^{n-1}}{(1 + C)^{n+p}} \qquad (3)$$

and

$$S_{n,p} = \frac{(n + p - 1)!}{(n - 1)!\, p!} \frac{C^n}{(1 + C)^{n+p}} \qquad (4)$$

For large values of n and p not given in tables of factorials, Stirling's approximation may be used, (*i. e.*, $n! = e^{-n}n^n\sqrt{2\pi n}$)

$$L_{n,p} = \frac{1}{\sqrt{2\pi}} \frac{(p + n - 1)^{p+n-1/2}}{(n - 1)^{n-1/2}p^{p+1/2}} \frac{C^{n-1}}{(1 + C)^{p+n}} \qquad (5)$$

(When $p = 75$ and $n = 26$, Stirling's approximation gives a value of 2.434×10^{23} for the above coefficient whereas the value of the coefficient in equation (3) equals 2.425×10^{23}.)

It can be shown that $L_{n,p}$ in equation (5) has its maximum at $n = pC$

$$L_{\text{max.}} = L_{p,p} = [2\pi pC(1 + C)]^{-1/2} \qquad (6)$$

Furthermore

$$F_{\text{max.}} = n_{\text{max.}}/p$$

But

$$C = n_{\text{max.}}/p$$

Consequently

$$F_{\text{max.}} = C$$

Application of the Theory to Previous Separations.—The usual elution curve for these separations is a plot of the concentration of one of the elements being separated in the effluent (as ordinate) against the volume of eluting solvent that has passed through the column (as abscissa). Therefore, the plot of L, for the last plate of the column versus n as abcissa (as n varies from zero to its value at the termination of the separation) is a theoretical elution curve.

In Fig. 1, a typical experimental elution curve for rare earth separations[7] is compared with the calculated elution curve. The data for the peak of this experimental curve were used to calculate p and C employing equation (6) and the simple relationship derived above, showing that $C = F$ at the peak. The degree of correlation between the experimental and calculated elution curves indicates the degree of applicability of the developed theory to this experimental column run. It will be noted that both the experimental and theoretical elution curves are non-symmetrical, and in all cases the peak occurs before one-half

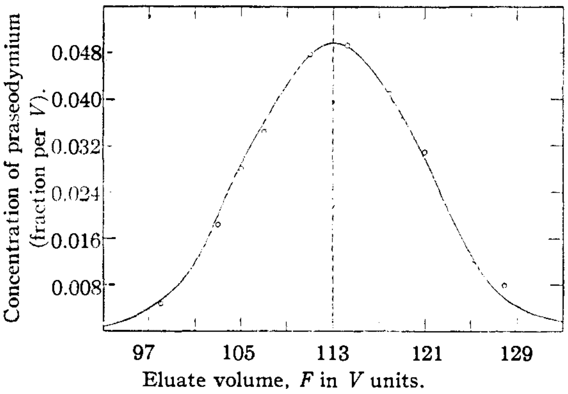

Fig. 1.—Correlation of experimental and theoretical elution curves: The full curve is calculated from (3) for $p = 240$ and $C = 113$. The experimental points are for the Pr-Ce-2 separation.[7] From the location and magnitude of the maximum Pr concentration found in the eluate, it was calculated (from equation (6)) that $p = 240$ and $C = 113$.

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[7] D. H. Harris and E. R. Tompkins, THIS JOURNAL, **69**, 2792 (1947).

the material has been eluted. It is obvious, however, that the asymmetry is greater in this experimental curve than in the curve predicted by the theory.

Analysis of the Separations.—The degree of separation of two or more solutes during their elution depends upon the differences in their distribution coefficients. Determination of F at the peaks gives the corresponding C's of the materials being separated, since F and C are numerically equal at any peak. Therefore, the intervals between the peaks of the elution curves will be a measure of the differences between their C's in units of F. No matter how complete the separations may be, there will be some overlapping between the elution curves since the column must be infinitely long or the C's must differ by infinity to secure complete separation. A convenient graphical method has been developed for determining the fraction of one material present in the other (*i. e.*, the degree of separation) at any point on the elution curves. Using primes to distinguish between solute 1 and solute 2, we can write from (3)

$$\frac{L'_{n,p}}{L''_{n,p}} = \frac{\dfrac{(n+p-1)!}{(n-1)!\,p!}\,\dfrac{C'^{n-1}}{(1+C')^{n+p}}}{\dfrac{(n+p-1)!}{(n-1)!\,p!}\,\dfrac{C''^{n-1}}{(1+C'')^{n+p}}}$$

or

$$\frac{L'_{n.p}}{L''_{n.p}} = \text{antilog}\left[\log\frac{C'^{n-1}}{(1+C')^{n+p}} - \log\frac{C''^{n-1}}{(1+C'')^{n+p}}\right] \tag{7}$$

Inasmuch as p is constant in any given separation, each of the logarithmic expressions is a linear function of n (as is also their difference). Therefore, the complete curve for each of the logarithmic expressions (or the difference between them) can be drawn as a straight line when any two points have been calculated.

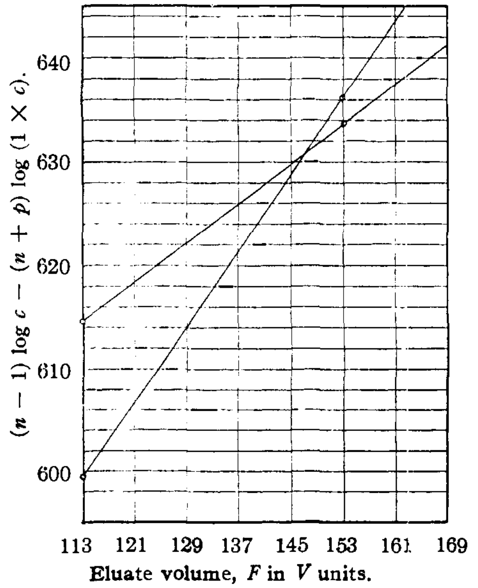

Fig. 2.—Calculated degree of separation for Pr-Ce-2.[7]

In Fig. 2, plots of the pair of lines have been made for the separation of praseodymium and cerium, by Harris and Tompkins.[6] Here $C_{Pr} = 113$ and the estimated $C_{Ce} = 193$. (The pH was changed at $F = 165$, so that C_{Ce} had to be estimated.) p was calculated to be 240. The two values of n plotted in this figure are $F = 113$ and 153. The ordinate axis is logarithmic, and the ratio $L'_{n,p}/L''_{n,p}$ is equal to the anti-logarithm of the ordinate distance between the pair of lines at points of equal F. (To calculate the quantity ratio, the ratio of fractions L'/L'' must be multiplied by the ratio of the initial quantities of the two substances put on the column.)

From Fig. 2, it is apparent that the maximum fraction of impurity occurs at $F = 147$, where $L'_{n,p} = L''_{n,p}$ Analytical data on the eluate showed that overlapping occurred in the range from $F = 146$ to 151. If it is assumed that the spectrographic method used will just detect 1% Pr in the presence of Ce (or *vice versa*) in the milligram quantities of rare earth obtained in that center portion of the elution curve, there will be detectable impurity when the pair of lines in Fig. 2 are less than two units apart at equal F. It can be seen that the lines are within two ordinate units of each other over a range of five column free-volumes of solution. This calculation is in agreement with the above analytical data. On the other hand, if 0.1% purity can be detected in this eluate, the calculated range will be 7.5.

The graphical method for calculating separation can be applied to conditions which approach those for the separation of isotopes. A calculation was made for the case where $C' = 50$, $C'' = 51$; $p = 180$, 900, and the criterion was a tenfold enrichment of one isotope in the other. For 180 plates the maximum enrichment (at the very beginning of the effluent) is 14 and the 90% isotope is obtained for 0.34 of the distance to the first peak. For 900 plates, however, the maximum enrichment is 10^7, and the 90% isotope is obtained for 0.77 of the distance to the first peak.

The expression for the volume of eluate that is cross-contaminated may be derived as follows. Any given ratio $L'_{n,p}/L''_{n,p}$ may be selected as the criterion for cross-contamination. and log $L'_{n,p}/L''_{n,p}$ will be designated by the symbol I. The limits of the cross-contamination flow are determined by two values of $n{:}n_1$ (when solute one begins to be contaminated with solute two); n_2 (when cross-contamination of solute two by one stops). From (7)

$$\log\frac{L'_{n,p}}{L''_{n.p}} = (n-1)\log C' + (n+p)\log(1+C'') - (n-1)\log C'' - (n+p)\log(1+C') \tag{8A}$$

$$I = n_1[\log C' + \log(1+C'') - \log C'' - \log(1+C')] + \{-\log C' + p\log(1+C'') - \log C'' + p\log(1+C')\}$$

or $+I = n_1K + J$, where K and J are constants equal to the quantities in the brackets and braces, respectively. Similarly, $-I = n_2K + J$. The cross contaminated flow, $n_{\text{cc.}} = n_2 - n_1 = -2I/K$. But $n = pF$. Therefore

$$F_{\text{cc.}} = \frac{-2I}{pK} \tag{8B}$$

where $F_{\text{cc.}}$ denotes the cross contaminated flow.

The above derivation shows that the fraction of eluate in which insufficient separation has occurred varies inversely as the number of theoretical plates, or (other conditions being equal) inversely as the column length. Therefore, increasing the number of theoretical plates increases separation. But the relationship showing that the maximum concentration varies as $[\sqrt{2\pi}Cp(1+C)]^{-1/2}$ leads to the conclusion that the maximum concentration obtainable varies as $p^{-1/2}$. Accordingly, the longer the column, the smaller the maximum concentration. In addition, increasing the length of the column increases the time required for separation inasmuch as the rate of eluate flow is maintained constant.

Calculation of Material Eluted.—Since an elution curve is a plot of concentration *vs.* volume, the total material eluted is represented by the area under the elution curve. As has been pointed out by Martin and Synge[6] the normal curve of error can be used to approximate the theoretical elution curve, the approximation becoming closer as p and C become larger and as the column operating conditions approach equilibrium. Tables of the area under the normal curve of error are readily available. These tables give the area corresponding to values of the sigma unit t (t is defined as n/σ, with the peak at the origin). The ordinate of the normal curve at the peak $= [\sigma\sqrt{2\pi}]^{-1}$. The ordinate of the theoretical elution curve at the peak $= \{2\pi pC(1 + C)]^{-1/2}$. Equating, $\sigma = [pC(1 + C)]^{1/2}$, and therefore

$$t = \frac{n - n_{\text{max.}}}{[pC(1 + C)]^{1/2}} \tag{9}$$

where n max is the value of n at the peak of the elution curve. Since $n_{\text{max.}} = pC$, this equation may be written in the form

$$t = \frac{p(F - C)}{[pC(1 + C)]^{1/2}} = \frac{p^{1/2}(F - C)}{[C(1 + C)]^{1/2}} \tag{10}$$

When C is large, C and $1 + C$ are almost equal, and

$$t = p^{1/2}(F - C)/C \tag{11}$$

Since problems involving the use of the column very frequently revolve about the questions of the degree of separation and the fractions of materials recovered, the application of equation (9) in conjunction with equation (7) is useful. As an illustration, we may refer to the previous example of calculations for isotope separation where $p = 900$, and the 90% isotope is obtained through 0.77 of the distance to the first peak. If we wished to know the quantity of 90% isotope recoverable in such a column, we can proceed as follows: $n_{\text{max.}} = pC = 900 \times 50 = 45{,}000$. $n = 0.77 \times 45{,}000$. Substituting in (9), we have $t = -6.9$. From a published table, it can be seen that this value of t corresponds to an area of less than 10^{-10}, so that a negligible portion of the isotope will be eluted 90% pure.

To calculate the enrichment factor of one isotope in the eluate when one per cent. of that isotope has been eluted, the procedure is as follows. From the table we see that t is -2.33 when the area under the curve is 0.01. Substituting in (9), we find that $n - n_{\text{max.}} = 3535$. Therefore $n = 41{,}465$. Substituting this value in (7), gives a value of 3.4 for the enrichment factor. By a comparable calculation, it is possible to ascertain the length of a column necessary to produce any fraction of each of the cations of the original mixture in any desired purity.

In the praseodymium and cerium separation of Harris and Tompkins[7] referred to above, F at the point where impurities are less than 0.01% is equal to 141. Therefore, from (11), $t = 240\,(141 - 113)/113 = 3.8$. Thus, the recovery of Pr in a purity greater than 99.99% is calculated to be 99.99%. In another separation, Nd-Pr-Ce-1, there was a relatively long flow of eluate between the praseodymium and cerium peaks in which the eluate contained less than 0.001% of the rare earth per ml.[7] To see whether the calculated recoveries agree with this experimental observation, one proceeds as follows (after making corrections for pH changes in the elutrient). The value for p, as calculated from the heights of the neodymium and praseodymium peaks (the Ce fractions obscured its peak), is 230 and 235, respectively. The flow between $F = 164$ and $F = 197$ contained less than 0.001% rare earth per ml. At $F = 164$, $t_{\text{Pr}} = 7$. Therefore, less than 0.01% of the Pr remained to be eluted. At $F = 197$, $t_{\text{Ce}} = -3.0$, and therefore only 0.13% of the Ce had been eluted when $F = 197$. Thus, the calculations show that only 0.14% of the two rare earths was eluted in the 1070 ml. of eluate between $F = 164$ and $F = 197$.

Table I was calculated from (7) and (9) for the conditions of a typical rare earth separation where $C' = 100$ and $C'' = 150$. It gives the per cent. of the rare earth that has been eluted before an eluate of less than the tabulated purity is obtained.

TABLE I

PER CENT. OF RARE EARTH ELUTED IN GIVEN PURITY

p	>99.9% purity	>99.99% purity
100	33	21
250	99.77	97.6
500	99.99999	99.9999
1000	99.99.....(to 15 places)	99.99...(to 10 places)

From these calculations it appears that in the rare earth separations described by Harris and Tompkins[7] (where $p \cong 250$), 97.6% of one rare earth was eluted before 0.01% impurity of the second appeared in the eluate.

Distribution on the Column.—The quantity of material in any plate may be calculated from the following expression

$$S_{n,p} + L_{n,p} = \frac{(1 + C)\,(p + n - 1)^{p+n-1/2}}{\sqrt{2\pi}\,(n - 1)^{n-1/2}\,p^{p+1/2}}\;\frac{C^{n-1}}{(1 + C)^{n+p}} \tag{12}$$

From equation (12) the band width of a substance on the column may be obtained by determining the range of p's over which not less than any given fraction (0.1% for example) is present.

The theory leads to the following picture of material movement through the column during elution. The material with the lowest C will travel through most rapidly. The fraction of the column traversed by the band of any of the materials $= F/C$. The rate of movement of the band down the column is Dr/C where $D =$ length of the column, and $r =$ rate of flow in V's per unit of time. The distance between bands equals $DF(1/C' - 1/C'')$. The fraction of that distance in which any selected degree of overlapping occurs is proportional to p^{-1}(8B). Thus the bands separate as the flow of eluting solution moves them down the column. However, each band broadens out as it moves through the column, the maximum concentration varying as $p^{-1/2}$(6). The maximum concentration also varies as C^{-1} so that when several materials are eluted from a column, the heights of the successive peaks represent successively smaller fractions of the initial quantities of the corresponding materials. From the initial data on band movements near the top of the column, the values of C can be estimated and predictions can be made as to separation of two or more substances.

Test of the Theory for Near Equilibrium Column Operation

Although the fit of the experimental curve shown in Fig. 1 is fairly good, it is somewhat more asymmetrical than would be predicted by the theory. Most of the elution curves obtained in the rare earth separations are even less symmetrical than the one shown here. Some previous work by Harris and Tompkins on the Amberlite resins had shown the relationship of flow rate to the shape of the elution curve of a solute. As the rate was decreased the curves became more and more symmetrical, approaching a limit at rates of 0.05 to 0.10 ml. per sq. cm. per minute. For this reason, it seemed probable that the failure of the experimental curves to fit the one predicted from the theory might be due chiefly to nonequilibrium conditions within the column. Further substantiation of this hypothesis was found in the general observation of several investigators here and elsewhere that decreasing the resin particle size would increase the efficiency of separation.

From the above considerations, it seemed that column runs at much slower rates, using resin of very fine mesh size, should be made to test the theory under conditions approximating equilibrium. Operating at very slow rates has the disadvantage of requiring a long time for each run. An alternative to this is to operate the columns at higher temperatures which is possible with Dowex 50.[8] The advantages of operating columns at higher temperatures was demonstrated by Ketelle[9] who was working on the separation and identification of the radioisotopes of the heavy group of rare earths. The separation of these elements, which was obtained by operating the columns at 100°, was much better than any previous separations of this group of elements. Furthermore, the elution curves were very nearly symmetrical. The chief disadvantage of using the higher temperature is the difficulty of keeping air from condensing in the column. It is necessary to remove almost completely the dissolved air from the influent solutions or the column will soon become "air bound" and the flow will stop.

Recently some additional samples of Dowex 50, consisting of agglomerates of colloidal particles, were obtained.[10] Examination of this material by the electron microscope showed that the size of the individual particles was about 0.05 micron. Since the material was obtained in agglomerates varying widely in size, it was possible to separate a fraction of the agglomerates of any mesh size desired. Such a fraction, in the range of 250 to 300 mesh, was prepared and used in some preliminary experiments designed to test its effectiveness as an exchanger for the column separations. These experiments showed that the separations which could be made by using the agglomerates of colloidal resin at room temperature were comparable, or somewhat superior, to those obtained by the use of ordinary Dowex 50 resin (with particle size about equal to that of the agglomerates) at 100°

Apparatus and Method.—The column separations were made in the usual manner[7] with the exception that conditions which would give considerable overlap of the elution curves of the cations being studied were chosen. The columns used in these studies were about 10 cm. and 15 cm. in length. The rare earth pairs Ce, Pr, and Eu, 61 were used in the two series reported here. To facilitate the study, radioisotopes of the rare earth elements were employed. The effluent from the column was passed through a device which continuously monitored and recorded the concentration of activity in this solution. The recorded curve (which was a plot of solute concentration in the eluate versus time) was the usual elution curve, since the flow rate was constant. In the study of cross contamination, samples were collected frequently, the time of their collection being marked on the recorded elution curve. This permitted a good comparison of the purity of

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[8] L. A. Matheson, private communication.

[9] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, 69, 2800 (1947).

[10] Through the courtesy of W. C. Bauman, The Dow Chemical Co.

each sample, as determined experimentally, with that predicted from theory.

The degree of cross-contamination, was determined by a differential counting technique similar to that described earlier.[7] When Eu^{154} and 61^{147} were used a considerable degree of precision was possible since the former has a gamma radiation while the latter has only a weak beta radiation.[11]

Effect of Flow Rate and Particle Size on Separations.—From the theory, the relative positions of the peaks of two rare earths being separated by elution from a column would not be expected to vary appreciably with flow rate, unless the rates of the reactions of the two elements were considerably different. On the other hand, it was expected that the actual position and height of each peak and the degree of asymmetry of the elution curves would be very dependent on the flow rate. To test this and to determine the conditions necessary for near-equilibrium column operation, a series of preliminary column runs were made.

In these preliminary experiments, a column 0.855 sq. cm. × 15 cm. of colloidal agglomerates and another of equivalent size, utilizing the regular Dowex 50 resin of similar mesh size, were employed. A mixture of Pr^{143} and Ce^{141} were eluted from these columns under identical conditions and the elution curves from the two columns compared. The results of this study are shown in Fig. 3. The elution was made under conditions usually considered very unfavorable for the separation[12] (*i. e.*, 5% citrate at *p*H 3.5) and yet considerable fractionation of the two elements occurred. A careful study of the elution curves 1, 2 and 3 shows their close approximation to symmetry. Increase in the flow rate or resin particle size resulted in asymmetry and poorer separations as evidenced by curves 4, 5 and 6.

After the conditions for near-equilibrium column operation had been ascertained (Fig. 3), another separation, designed to test the theory, was made. For this experiment radioisotopes of the rare earth elements europium and 61 (in trace concentrations) were used, since they are easily determined in the presence of each other by differential counting, due to the difference in the characteristics of their radiations. They were first adsorbed at the top of the bed and then eluted with citrate of 0.25 *M* concentration at a *p*H of 2.90. The solution was 0.294 *M* in NH_4^+.

These studies were made with a column 1.0 sq. cm. × 10.4 cm. of colloidal agglomerates of Dowex 50. The weight of the resin (oven-dried basis) was 2.83 g., its density 1.45 g./cc. Thus the volume of solution, *V*, in the bed was 81.9% of the total bed volume or 8.84 ml. It has been shown[2] that

$$K_d = \frac{M_s}{M_l} \times \frac{\text{solution volume (ml.)}}{\text{resin mass (g.)}} = C \times \frac{\text{ml. of solution}}{\text{grams of resin}} \quad (13)$$

Hence

$$C \text{ will be equal to } K_d \times \frac{\text{grams of resin}}{\text{ml. of solution}} = K_d\,\frac{2.83}{8.84} \quad (14)$$

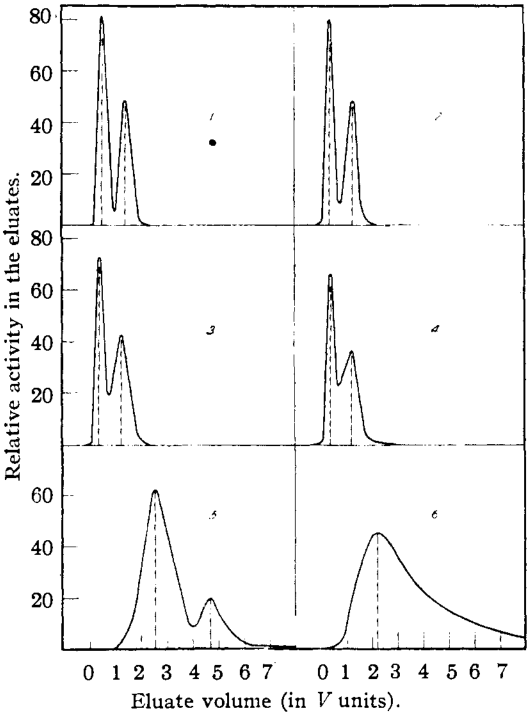

Fig. 3.—The effect of resin particle size and flow rate on the separation of Pr and Ce[a]: elutrient solution, 0.25 *M* citrate, *p*H 3.50; columns, 0.867 sq. cm. × 15 cm., Dowex 50 ammonium form, (1) colloidal agglomerates of Dowex 50, (2) Dowex 50, 170–200 mesh. In the following designations the first number represents the column used and the second the number of the run on that column.

DESIGNATIONS OF CURVES

		Flow rate, ml./sq.cm./minute
1.	Pr-Ce-1-2	0.053
2	Pr-Ce-1-5	0.207
3	Pr-Ce-1-3	0.627
4	Pr-Ce-1-4	1.152
5	Pr-Ce-2-2	0.026
6	Pr-Ce-2-1	0.230

[a] In runs Ce-Pr-2 to 5, a 50-mg. Al absorber was used during the Pr elution. This reduced the heights of the Pr curves to 43% of the value which would have been obtained if the absorber had not been used.

To determine K_d at equilibrium, 0.275 g. and 0.278 g., respectively, of this resin was shaken with 1.0 ml. of the elutrient solution containing Eu and 61 tracers. The values obtained for the K_d's were 29.9 for 61 and 19.4 for Eu. Thus the predicted values for the *C*'s were 9.56 for 61 and 6.20 for Eu. Since $C = F_{\text{max.}}$, it was possible to test the theory by these elutions at near-equilibrium conditions. Figure 4 shows the elution curves for Eu and 61 from this column, when they were eluted separately. The values for the *C*'s determined by the elution were 9.41 for 61 and

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(12) E. R. Tompkins, J. X. Khym, W. E. Cohn, *ibid.*, **69**, 2769 (1947).

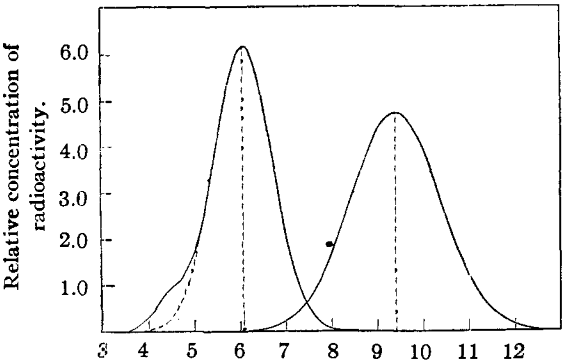

Fig. 4.—Elution curves of europium and element 61.

6.08 for Eu. The ratio of the distribution coefficients (K_d 61/K_d Eu) as determined at equilibrium was 1.542, while that determined by the column run was 1.548. A further comparison was made between the values for K_d, found here, and those in the equilibrium experiments in which Dowex 50 of 40–60 mesh was used.[2] The results of these comparisons (when corrections for differences in NH_4^+ concentration have been made) check within 3%.

To test the applicability of the theory for predicting the cross-contamination of one rare earth with the other, a further column run, in which both elements were eluted simultaneously, was made. Figure 5 shows a reproduction of the continuously recorded curves in this elution, the dotted line extensions being calculated from the theory. Conditions which would give a sufficient overlap to test the theory were chosen. It can be seen that the shapes of these curves closely approximate those for the two elements eluted separately (Fig. 4).

It is necessary to calculate the number of theoretical plates in the column to determine how nearly the degree of cross-contamination observed in this experiment conforms with that predicted from the theory. From equation (6), at the maximum

$$L_{C_{p,p}} = \frac{1}{p^{1/2}\sqrt{2\pi C(1 + C)}} \text{ and } pL_{C_{p,p}} = \frac{p^{1/2}}{\sqrt{2\pi C(1 + C)}}$$

From Fig. 4, for element 61, $C = 9.41$ and

$$pL_{C_{p,p}} = \frac{4.75 \times 1.00}{4602 \times 0.0025}$$

Thus $p = 103$. Calculation of p for the europium elutions gave results agreeing to within 2%.

Table II shows the comparison between the composition of each of the fractions in the over-lap region of the curves, as determined experimentally, with the values calculated from equation (7). As may be seen, there is good agreement.

The number of V's of solution in which detectable over-lap occurs may now be calculated as shown above, (8B). The criterion selected is that degree of impurity which is just detectable by the differential counting technique used here. This is 1%.

$$F_{co.} = \frac{2 \times 2}{103[\log 6.08 + \log 10.41 - \log 9.41 - \log 7.08]}$$
$$= \frac{4}{103 \times 0.0223} = 1.74$$

Thus 1.74 V's of solution contain cross-contaminated rare earths. Figure 5 shows 1.71 V's of cross-contaminated solution. The yields of each of the two elements in a purity of 99% may be calculated from equations (7) and (10) and show that 97.3% of element 61, and 95.8% of the europium were recovered in this purity.

Table III shows the comparison between the experimental values for the fraction of solute in succeeding eluate volumes and those values calculated from (10).

Discussion

The resin bed of an exchange column consists of a highly cross-linked organic matrix with attached

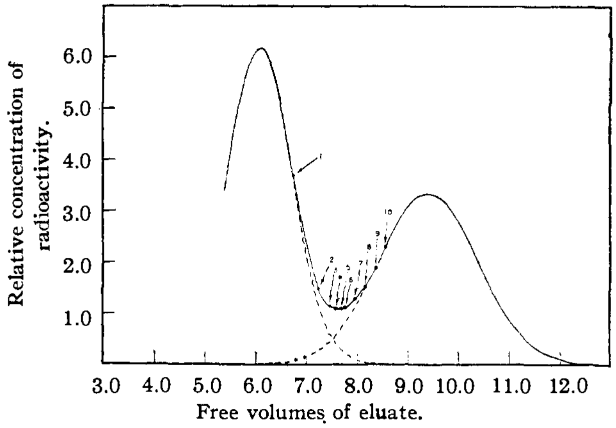

Fig. 5.—Cross-contamination in the eluates of europium and element 61.

Table II

Cross-Contamination—Comparison of Experimental Data with Theory

	Volume (V) of eluate, free-vols.	Observed ratio of Eu to 61	Fractional ratios of Eu/61 Experimental[a]	Theoretical
1	6.74	>100	>80	110
2	7.23	8.18	6.7	8.0
3	7.47	2.45	2.0	2.14
4	7.57	1.50	1.22	1.3
5	7.67	.762	.62	.74
6	7.73	.423	.34	.48
7	7.98	.164	.133	.135
8	8.18	.064	.052	.050
9	8.36	.024	.020	.021
10	8.57	.006	.005	.007

[a] Corrected for original ratio of Eu to 61.

TABLE III

AREA UNDER THE ELUTION CURVE—COMPARISON OF EXPERIMENTAL DATA WITH THEORY

(Element 61)

Volume of eluate, free-volumes		Area units under experimental curve	Fraction of total area under curve	
From	To		Experimental	Theory
6.0	6.5	4	0.0009	0.0011
6.5	7.0	25	.0054	.0054
7.0	7.5	85	.0185	.0182
7.5	8.0	215	.0467	.0485
8.0	8.5	470	.1021	.1027
8.5	9.0	748	.1625	.1610
9.0	9.5	927	.2014	.1987
9.5	10.0	880	.1912	.1899
10.0	10.5	652	.1417	.1418
10.5	11.0	370	.0804	.0809
11.0	11.5	152	.0330	.0352
11.5	12.0	58	.0126	.0122
12.0	12.5	13	.0028	.0032
12.5	13.0	3	.0007	.0007
		Total 4602	1.00	1.00

sulfonic acid groups which provide points of combination for cations. The number of these exchangeable positions in any column is the product of the number of equivalents of exchanger times Avogadro's number. If a cation, M^+, is first adsorbed on an exchange position at the top of a resin bed of NR and then a solution of cations, N^+ is passed through the column, one of these N^+ ions will replace the M^+ from the MR; M^+ will then be carried down the column by the flowing solution. As it passes other exchange positions, NR, there will be a tendency for the reverse reaction to take place and so for it to be readsorbed. This ion, M^+, will therefore proceed down the column, being successively adsorbed and desorbed, until it finally appears in the eluate from the bottom of the column bed.

In describing the behavior of the M^+ ion in its route through the column, it is necessary to determine the number of times the exchange reactions take place. This will be governed by such factors as the rates of the exchange reactions themselves, the rates of diffusion of the ions and the rate of the movement of the solution through the column. Thus, as the ion passes any possible point of attachment there will be some finite probability that it will exchange. When large numbers of ions are eluted simultaneously, each will behave individually according to the same probability, which is dependent upon the rate factors named. Thus, it is to be expected that in the usual elution, in which more than 10^{10} ions are eluted by chromatographic development through the column, the shape of the elution curve will approach that of the probability curve (or the normal curve of error) as the flow rate approaches zero and, therefore, as equilibrium conditions are approximated. This expectation has been amply demonstrated experimentally in the series of elutions of trace quantities of several rare earths from colloidal resin columns, in which near-equilibrium conditions prevailed throughout the column.

When the quantity of solute is very small as compared to the possible exchange positions in the resin bed, it may be adsorbed originally in a very narrow band at the top of the column. As the elution is started and these ions move down the column there is an upper limit to the number of exchanges that can take place, *viz.*, the average number of exchange positions passed by each ion as it moves down the column. In the usual column separation, the number of transfers of an ion is only a very small fraction of this limiting value. As equilibrium in the column is approached, this number of transfer units, or plates approaches a limit. When this number of plates and the equilibrium distribution coefficient are known for an elution under any given set of conditions, the elution curve may be calculated as demonstrated above.

When the quantity of solute is so small as to saturate a very small fraction (*e. g.*, less than 10^{-6}) of the column area. On the other hand, when the quantity of solute is relatively large, an increase in the column area should benefit the separation, as has been previously demonstrated by a number of investigators.

In those cases where the quantity of solute is sufficient to saturate an appreciable fraction of the resin bed, each ion will undergo fewer transfers per unit length of the column, during its elution. This is a consequence of the increased competition for the available exchange positions in any horizontal plane of the resin bed. Thus, the separation between two solutes (which depends upon the number of such transfers of the solute ions) will be poorer than in the case where the solutes are present in trace concentrations. In addition, if the concentration of the solute ions in the solution exceeds a certain critical value (3×10^{-4} M for Dowex 50 and 4×10^{-7} M for IR-1), the equilibrium distribution coefficient is affected,[2] still further decreasing the degree of separation of the two solutes.

The importance of the use of a complexing agent in increasing the separation of relatively large quantities of solutes has been amply demonstrated. In some of the rare earth separations, described in an earlier paper,[7] as much as 15 to 20% of the column bed was saturated with the solute. The separation in these cases was still very good as long as the concentration of the solute ions in the liquid phase did not exceed the critical value given in the preceeding paragraph. Because the dissociation constants of the complexes of the rare earth citrates are small, the total rare earth concentration in the eluates from these columns was several orders of magnitude larger than their combined ionic concentration.

For laboratory experiments and other small scale separations, it is possible to operate columns under conditions approaching equilibrium. In such cases, the theory described above predicts the degree of separation which may be expected. Its present limitations do, however, decrease its applicability to large scale industrial processes in which columns must be operated in such a way that the distribution coefficient may not remain constant throughout the bed and equilibrium conditions are not approached. To be generally useful for the development of such large scale, industrial separations processes, it will be necessary to extend this theory by a further study of the kinetics of column reactions and the rates of diffusion of the various substances entering into these reactions.

Summary

A simple theoretical analysis of the ion exchange column separations process has been developed for the case in which the distribution coefficient of the solute between the solid and liquid phases remains constant throughout the column. Application of this theory to the rare earth separations, reported earlier by one of the authors, and for the prediction of separation in another column separation, demonstrates its usefulness. The elution curves derived from the theory fit the observed data within the limits of experimental error when near-equilibrium conditions prevail in the column. The theory is also applied to determine the purities of the rare earths separated by this process. The general applicability of the theory to processes of this type is discussed.

P. O. BOX W, OAK RIDGE, TENN. RECEIVED JULY 14, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE RESINOUS PRODUCTS AND CHEMICAL CO.]

The Anion Exchange Equilibria in an Anion Exchange Resin

BY ROBERT KUNIN AND ROBERT J. MYERS

The equilibria involved in ion exchange phenomena have received considerable attention since the early work of Thompson[1] and Way[2] in 1850. However, although considerable information has been obtained for the cation exchange phenomena, outside of the studies of Mattson and his students[3,4] and Jenny[5] in the field of soils, until recently, comparatively little information has been published for the anion exchange phenomena. The recent availability of durable and high capacity anion exchange resins has stimulated much work on this phenomenon during the past few years.

Mattson and his students[3,4] and Jenny[5] have shown that many silicates have the ability to exchange anions as well as cations. Jenny[6] and Sussman[7] have indicated that amine type exchange resins behave as true exchange substances. However, Schwartz, Edwards, and Boudreaux[8] have indicated that the amine type resins merely adsorb acids molecularly instead of exchanging anions. Bishop[9] considers the mechanism of the adsorption of acids by ion exchange resins to be one of covalent adsorption. Myers, Eastes and Urquhart[10] and Bhatnagar and his co-workers[11] have examined the adsorption isotherms for the adsorption of acids by various amine type resins. Wiklander[12] recently has investigated briefly some of the anion exchange reactions for Wofatit M and has concluded that this amine resin behaves as a true exchange substance exchanging anions in a manner quite analogous to cation exchangers. Griessbach[13] also considers Wofatit M to be a true anion exchange resin. However, considerable data are lacking for the acid–base character of these resins and the nature and mechanism of the various exchange equilibria involved in many anion exchange systems. This work was undertaken in an attempt to study these factors in a typical anion exchanger resin.

Experimental

Preparation of Resins.—The resin chosen for this study was Amberlite IR4B, an amine type resinous exchanger containing 14% nitrogen in the hydroxyl form of the exchanger. The hydroxyl form of the resin was prepared by repeated treatments with a normal solution of sodium hydroxide and subsequent rinsing of the resin with distilled water until a suspension of the resin remained neutral after twenty-four to forty-eight hours. Samples of the resins whose exchangeable ions were other than the hydroxyl ion were prepared by treating the hydroxyl form of the resin several times with an excess of the required acid (molar solutions) followed by several rinses with distilled water. Due to the hydrolysis of the salt forms of the resin, rinsing was discontinued when the *p*H of the suspension was about 3.5. The amount of excess acid remaining after the rinse was much below 10% of the total capacity. This value may be obtained from the data presented graphically in Figs. 5–9. Since the acid liberated upon equilibration with water was approximately 10%, the amount of uncombined anion must be below this value since this value includes hydrolytic acidity. The capacity of the hydroxyl form of the resin toward HCl, H_2SO_4, H_3PO_4 and CH_3-

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