DISTRIBUTION OF SPECIES ALONG A BAND IN SEPARATIONS BY DISPLACEMENT CHROMATOGRAPHY

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INTRODUCTION

Of the different theoretical treatments to explain the chromatographic phenomena in columns, the plate theory originally developed by MARTIN AND SYNGE[1] and later extended by MAYER AND TOMPKINS[2] and by GLUECKAUF[3] has been most successful. These authors have applied the plate theory mainly to elution chromatography where bell-shaped elution curves are obtained. In recent years, displacement chromatography, characterised by flat-topped elution curves has acquired some prominence, especially in the field of rare earth separations[4,5] and in the separation of the isotopes of nitrogen[6] and those of lithium[7], using cation exchange resins. In the course of investigations on the separation of the isotopes of nitrogen, SPEDDING, POWELL AND SVEC[6] observed a plateau region (where the composition was uniform and equal to the initial composition) in the middle of the band separating the two ends where the separation of the species occurred. However, no successful attempts appear to have been made to predict quantitatively the concentration distribution of the species in the region following and preceding this plateau. In the present paper detailed calculations are given to determine the concentration distribution of the species along the length of the band during the course of separation and the calculated values are experimentally verified.

THEORETICAL

Consider two species M_1 and M_2 distributed uniformly (initially) along the length of the band of length L. For the sake of simplicity let us assume that the species are ions of equal charge. If the mole fraction of M_1 is N_0 then that of M_2 is $1 - N_0$. According to the concepts of the plate theory this band may be assumed to consist of a number of plates, say, n, of equal height h, so that $n \cdot h = L$. In the chromatographic separation process the eluant will gradually displace the adsorbed species at the rear boundary and the solution will come to equilibrium with the rest of the species during its movement along the band and redeposit the species on the resin at the front boundary. Two special features of displacement chromatography are: (1) the formation of sharp rear and front boundaries, and (2) the constancy of the length of the band under equilibrium conditions irrespective of the distance of elution. Separation is possible only if there is equilibrium between the species according to the exchange reaction:

$$M_1^r + M_2^s \rightleftharpoons M_1^s + M_2^r \tag{1}$$

where the superscripts r and s refer to the resin and solution phases respectively. The distribution of species between the solution and resin phases at any point on the band, at equilibrium, is governed by the relation:

$$\frac{N^s}{1 - N^s} = \alpha \frac{N^r}{1 - N^r} \tag{2}$$

in which N^s and N^r denote the mole fractions of M_1 in the solution and resin phases respectively, and α is the equilibrium constant of reaction (1). α is sometimes also called the separation factor. If $\alpha > 1$, M_1 will concentrate at the front edge and if $\alpha < 1$, it will concentrate at the rear edge. There will be no separation when $\alpha = 1$. When one of the species tends to concentrate at one end of the band, the other species tends to concentrate at the other end and in the middle section the composition remains the same as in the original mixture. This plateau region will disappear when the separation is complete.

Rear section

Let AB (Fig. 1) represent the resin phase, divided into a number of theoretical plates, R_1, R_2... R_n, of equal height, h, and CD be the solution phase, the corresponding plates in equilibrium with the resin phase being S_1, S_2,.... S_n. Initially let the resin phase contain a mixture of M_1 and M_2 in the mole fraction ratio of N_0 to $1 - N_0$, distributed uniformly throughout the length of the band. As a result of elution allow the con-
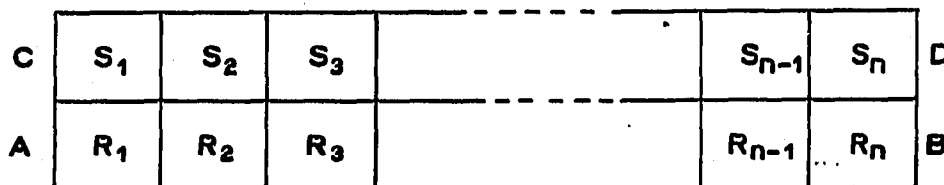

Fig. 1. "Plates" along the resin column.

tents of plate R_1 to go to the solution phase plate S_1. Since the whole of the contents of R_1 is transferred to S_1 the composition of the two plates will remain the same. Transfer the solution to S_2 and now $N_{R_1} = N_{S_1} = N_{S_2}$, which symbols represent the mole fractions of M_1 in R_1, S_1 and S_2 respectively. Allow this solution to come to equilibrium with the resin phase R_2. Let the composition of the resin and solution phases after equilibration be $N_{R_2}^E$ and $N_{S_2}^E$ respectively. Then from material balance considerations the following relation holds good:

$$N_{S_2} + N_{R_2} = N_{R_2}^E + N_{S_2}^E \tag{3}$$

and since there is equilibrium between the two phases:

$$\frac{N_{S_2}^E}{1 - N_{S_2}^E} = \alpha \frac{N_{R_2}^E}{1 - N_{R_2}^E} \tag{4}$$

Transfer the solution from S_2 to S_3 and allow it to come to equilibrium with R_3, then again:

$$\frac{N_{S_3}{}^{E}}{1 - N_{S_3}{}^{E}} = \alpha \, \frac{N_{R_3}{}^{E}}{1 - N_{R_3}{}^{E}} \tag{5}$$

This process of equilibration can be continued throughout the band. From eqns. (4) and (5):

$$N_{R_2}{}^{E} = \frac{N_{S_2}{}^{E}}{\alpha + (1 - \alpha)N_{S_2}{}^{E}} \tag{6}$$

$$N_{S_2}{}^{E} = \frac{\alpha \, N_{R_2}{}^{E}}{1 + (\alpha - 1)N_{R_2}{}^{E}} \tag{7}$$

$$N_{R_3}{}^{E} = \frac{N_{S_3}{}^{E}}{\alpha + (1 - \alpha)N_{S_3}{}^{E}} \tag{8}$$

$$N_{S_3}{}^{E} = \frac{\alpha \, N_{R_3}{}^{E}}{1 + (\alpha - 1)N_{R_3}{}^{E}} \tag{9}$$

and from material balance:

$$N_{S_3}{}^{E} + N_{R_3}{}^{E} = N_{R_3} + N_{S_2}{}^{E} \tag{10}$$

Rearranging eqn. (10) and substituting the value of $N_{S_2}{}^{E}$ from eqn. (7) we have:

$$N_{S_3}{}^{E} = \frac{\alpha \, N_{R_2}{}^{E}}{1 + (\alpha - 1)N_{R_2}{}^{E}} + \Delta \, N_{R_3}{}^{E} \tag{11}$$

where:

$$\Delta \, N_{R_3}{}^{E} = N_{R_3} - N_{R_3}{}^{E}$$

Substituting the value of $N_{S_3}{}^{E}$ in eqn. (8) one obtains:

$$N_{R_3}{}^{E} = \frac{[\alpha N_{R_2}{}^{E} + \Delta \, N_{R_3}{}^{E}\{1 + (\alpha - 1)N_{R_2}{}^{E}\}]}{\alpha \{1 + (\alpha - 1)N_{R_2}{}^{E}\} + (1 - \alpha)[\alpha N_{R_2}{}^{E} + \Delta \, N_{R_3}{}^{E}\{1 + (\alpha - 1)N_{R_2}{}^{E}\}]} \tag{12}$$

or in general, the equilibrium composition of the resin phase of any particular plate, R_n, is related to that of the immediate next plate, R_{n+1}, by the relation:

$$N_{R_{n+1}}{}^{E} = \frac{[\alpha N_{R_n}{}^{E} + \Delta \, N_{R_{n+1}}{}^{E}\{1 + (\alpha - 1)N_{R_n}{}^{E}\}]}{\alpha \{1 + (\alpha - 1)N_{R_n}{}^{E}\} + (1 - \alpha)[\alpha N_{R_n}{}^{E} + \Delta \, N_{R_{n+1}}{}^{E}\{1 + (\alpha - 1)N_{R_n}{}^{E}\}]} \tag{13}$$

where:

$$\Delta \, N_{R_{n+1}}{}^{E} = N_{R_{n+1}} - N_{R_{n+1}}{}^{E}$$

If $\alpha > 1$, $\Delta \, N_{R_{n+1}}{}^{E} \geqslant 0$, and if $\alpha < 1$, $\Delta \, N_{R_{n+1}}{}^{E} \leqslant 0$. Both at the rear and front sections of the band there is overall mass transfer between the solution and resin phases and therefore $\Delta \, N_{R_n}{}^{E} >$ or < 0, depending on the value of α. At the plateau region $\Delta \, N_{Rn}{}^{E} = 0$, and eqn. (13) reduces to $N_{R_{n+1}}{}^{E} = N_{Rn}{}^{E}$.

At the rear section of the band the value of $\Delta \, N_{Rn}{}^{E}$ varies continuously until it becomes 0 at the plateau region. If we repeat the cycle of plate equilibration starting with the contents of the second plate, R_2, a similar type of relation will be obtained

for the composition of any two successive plates. For a given and particular value of N_0 different curves can be plotted representing the actual concentration distribution of the species on the band during the separation process. A typical set of curves is given in Fig. 2, calculated for $\alpha = 2$ and $N_0 = 0.5$. Each curve represents the
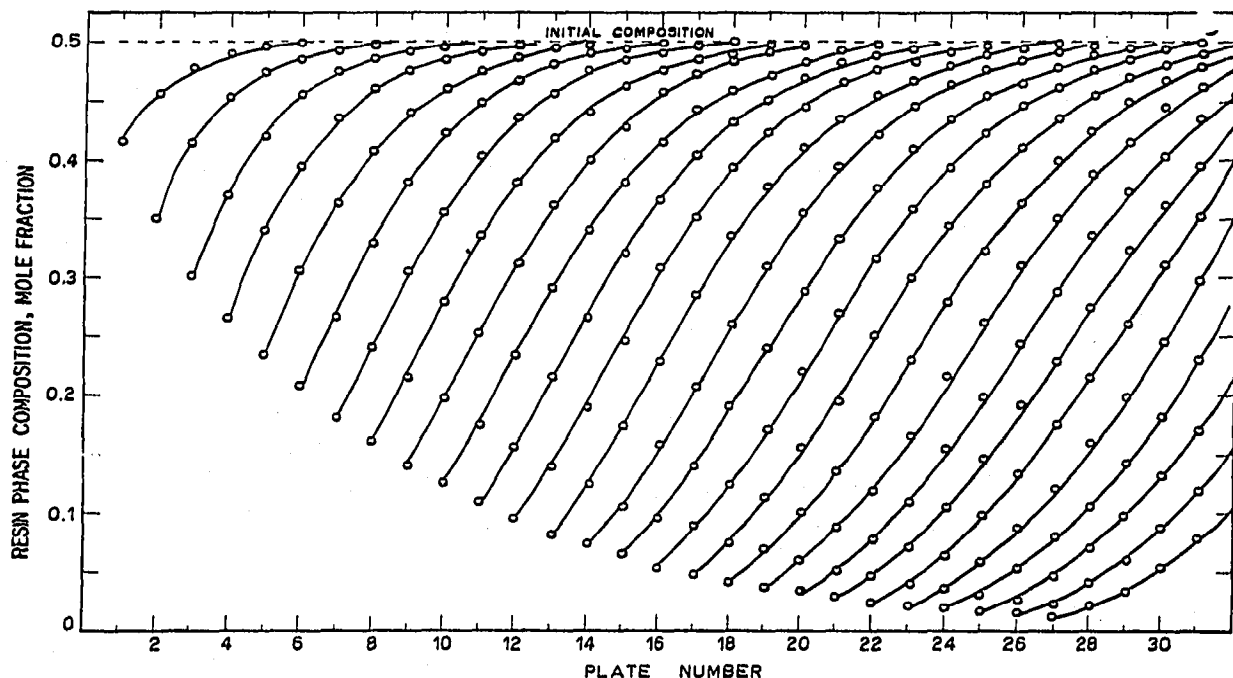

Fig. 2. Theoretical curves representing the concentration distribution of species in the rear section of the band during the course of separation for $\alpha = 2$ and $N_0 = 0.5$.

concentration distribution in different plates for a particular cycle of equilibration. If the height of a theoretical plate (HETP) is known the actual concentration variation along the length of the band, as a result of elution through a known distance, can be computed.

Front section

The general equation (13) will hold good also for the front section of the band. However, the following points have to be considered before applying the equation:

(1) The composition of the first plate, which is formed as a result of the transfer of species from the rear edge of the band through the plateau, will be the same as the composition of the solution at the plateau, *i.e.* equal to:

$$\frac{\alpha N_0}{1 + (\alpha - 1)N_0}$$

(2) The net mass transfer between the solution and resin phases during further development of the band starts from this plate.

(3) The composition of the resin phase in the last plate of the band is equal to the composition of the equilibrium solution in the preceding plate.

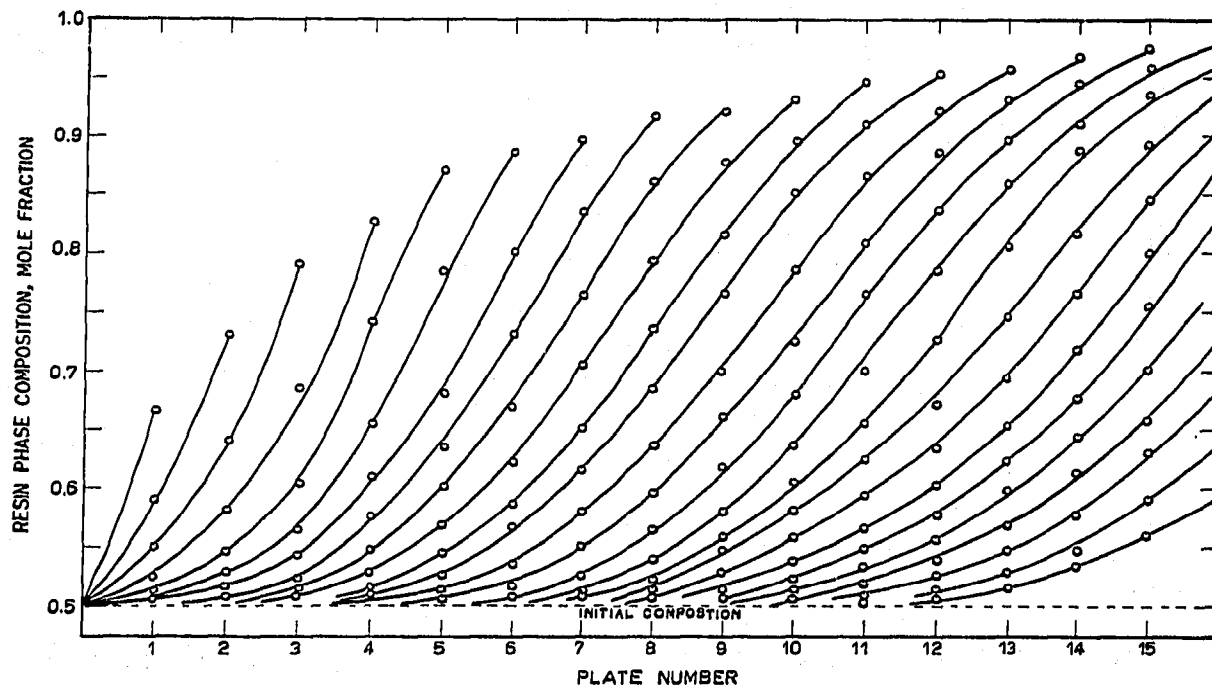Bearing these points in mind, curves representing $N_{R_n}{}^E$ at different values of "n"

Fig. 3. Theoretical curves for the concentration distribution in the front section of the band, $\alpha = 2$, and $N_0 = 0.5$.

can be plotted for any given value of α and N_0. A typical set of curves is given in Fig. 3, for $N_0 = 0.5$ and $\alpha = 2$, each curve representing a particular set of equilibration.

Plateau region

It has been pointed out earlier that in the plateau region the composition of the resin phase remains constant. A general overall picture of the composition of the rear, the plateau and the front regions of the band, and those of the corresponding solution phases in equilibrium with the resin phase, for $\alpha = 2$ and $N_0 = 0.5$, is given in Fig. 4. The fraction of the band occupied by the plateau region depends on α and the number of band displacements. For an ideal case, the length l_1 of the rear section and l_2 of the front section, where separations have taken place, can be calculated for any band displacements. The length of the plateau will then be equal to $L - (l_1 + l_2)$. So long as the plateau region exists, the composition, $N_P{}^S$, of the solution which is going to the front region through the plateau is related to N_0 by the equation:

$$N_P{}^S = \frac{\alpha N_0}{1 + (\alpha - 1)N_0} \tag{14}$$

The net amount of M_1 transferred through this region (since $\alpha > 1$) when the band moves v band lengths is $v \cdot L(N_P{}^S - N_0) \cdot C$, where C is the capacity of the resin per unit length of the column. Suppose that as a result of this mass transfer there develop bands of length l_1 at the rear and of length l_2 at the front section, then from material balance considerations we have[*]:

$$(N_P{}^S - N_0) \cdot v \cdot L \cdot C = N_0 \cdot l_1 \cdot C = (1 - N_0) \cdot l_2 \cdot C \tag{15}$$

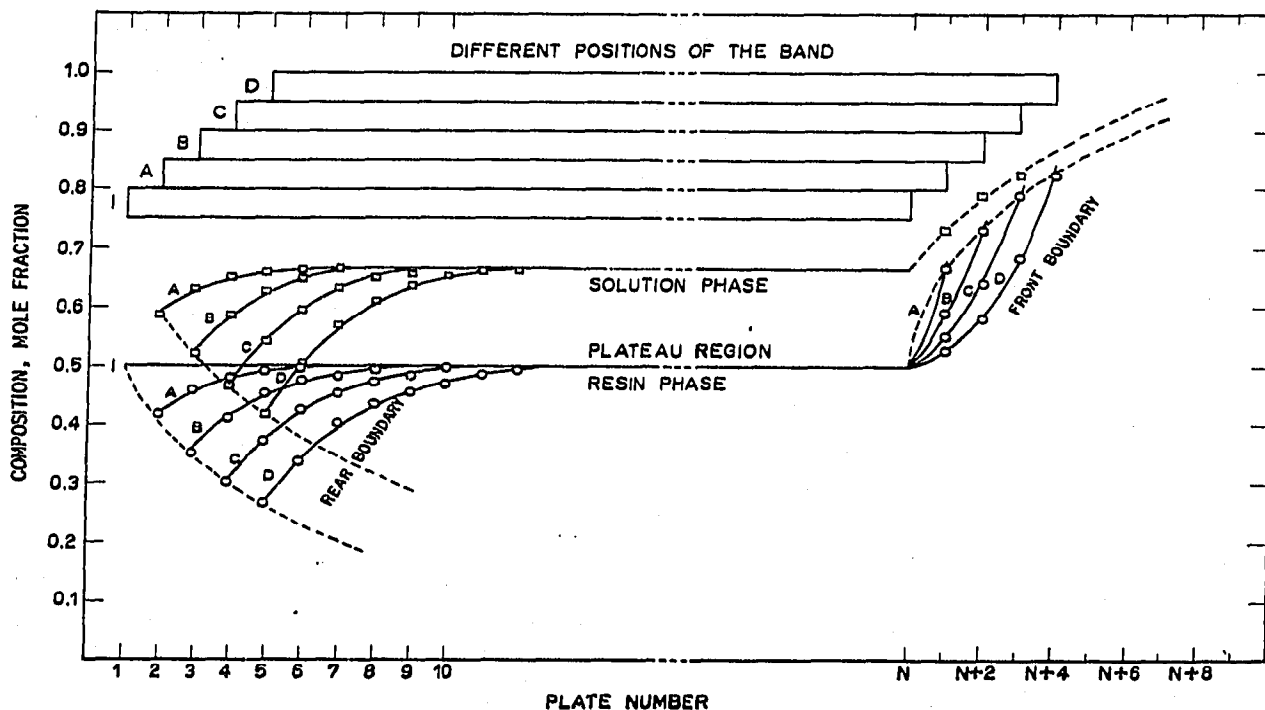[*] This is true only if the length of the band is large compared to the mixing zone.

Fig. 4. Theoretical curves for the concentration distribution in the solution and resin phases along the length of the band.

Substituting the value of $N_P{}^S - N_0$ from eqn. (14) into eqn. (15) and rearranging gives:

$$l_1 = \frac{(1 - N_0)\,(\alpha - 1)\cdot v\cdot L}{1 + (\alpha - 1)N_0} \tag{16}$$

$$l_2 = \frac{N_0(\alpha - 1)\cdot v\cdot L}{1 + (\alpha - 1)N_0} \tag{17}$$

and the length of the plateau region:

$$L - (l_1 + l_2) = L\left[1 - \frac{v\cdot(\alpha - 1)}{1 + (\alpha - 1)N_0}\right] \tag{18}$$

When the plateau disappears, $L = l_1 + l_2$, and then it follows from eqn. (18) that:

$$v = \frac{1 + (\alpha - 1)N_0}{(\alpha - 1)} \tag{19}$$

This value of v also represents the minimum number of band displacements required for the separation of two species. A similar equation was obtained by SPEDDING et al.[6] by a different approach, but expressions for l_1 and l_2 were not derived.

<center>EXPERIMENTAL</center>

Height equivalent to a theoretical plate (HETP)

For the experimental verification of the theoretical predictions made in the preceding

section one should know the height of a theoretical plate. SPEDDING, POWELL AND SVEC[6] have shown that HETP (h) can be calculated using the relation:

$$h = \log \alpha \cdot \frac{\Delta L}{\Delta \log (r)} \qquad (20)$$

where $\Delta L/\Delta \log (r)$ is the slope of the L–log (r) line, L and r being the length and the corresponding ratio of the two species in the band at the steady state. In the present case the value of α is equal (for all practical purpose) to the ratio of the stability constants of the complexes involved. From the results of SCHWARZENBACH, GUT AND ANDEREGG[8], α is 3.38 for the Nd–Sm–EDTA system and 1.62 for the Pr–Nd–EDTA system.

An equimolar mixture of samarium and neodymium was absorbed on a cation exchange resin, Dowex-50W, X-8, 200 mesh, contained in a 2 cm diameter glass column to a height of about 5 cm. After saturation the resin was thoroughly washed with deionised water. This rare earth mixture was then eluted with EDTA solution, 0.01 M, pH adjusted to 8.3, at the rate of 0.2 ml/min using 40 cm length of copper retaining bed. As the rare earth band came out of the column the eluate was collected in different fractions and the corresponding lengths of the band were noted. The rare earths in the eluate were precipitated as oxalates, ignited to oxide, and analysed
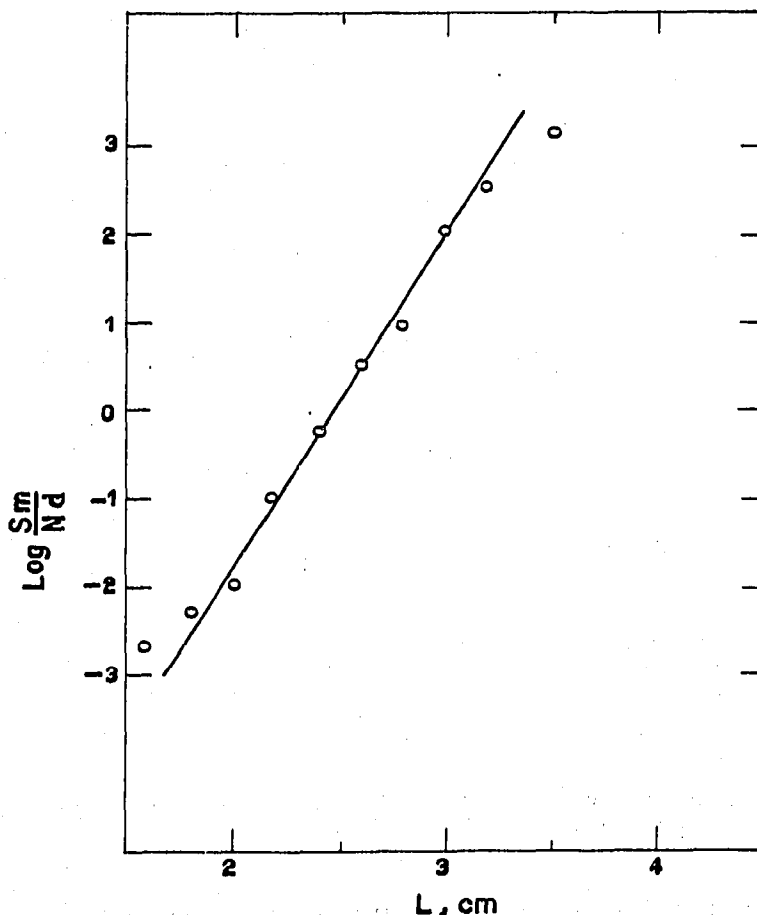

Fig. 5. Height equivalent to a theoretical plate.

for their Nd and Sm contents by the method described by BANKS AND KLINGMAN[9].
The results are plotted in Fig. 5. The HETP, calculated from these plots using eqn. (20)
gave a value of 0.14 cm.

Distribution of species along the band during separation

The actual concentration distribution of the species on the resin phase before the
steady state is reached cannot be determined correctly by analysing the eluate,
because the composition of the resin phase is continuously changing while the solution
is passing through the column. Therefore, a static approach was made to determine
the resin phase composition during the separation.

A glass column, about 30 cm long, was fitted with a sintered glass disc (with a
rim of thin rubber band) at the bottom in such a way that it can be moved smoothly.
The bottom end of the column was closed with a rubber stopper containing a glass
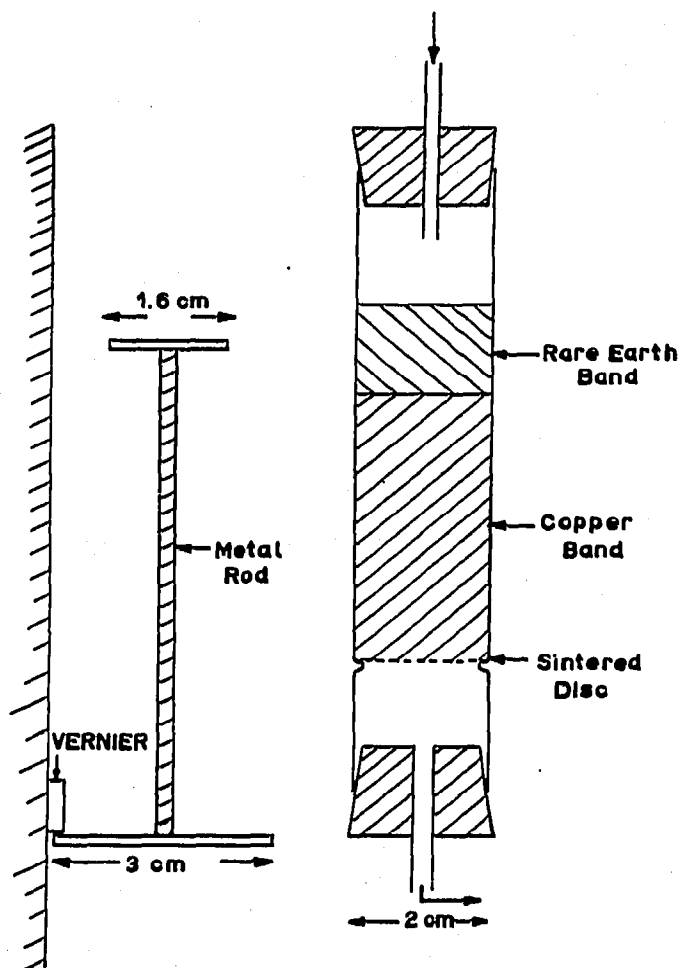tube which served as outlet for the solution (Fig. 6). The column was filled to a height

Fig. 6. Experimental set-up for the determination of the concentration distribution during the
separation of neodymium and samarium.

of 20 cm with the copper form of the resin and then the rare earth form of the resin
containing equal amounts of neodymium and samarium was poured in to a height of

5 cm and pressed gently. Special care was taken to avoid mechanical mixing at the copper–rare earth boundary. EDTA solution, 0.01 M, adjusted to pH 8.3 with ammonia, was passed through the column at a rate of 0.2 ml/min until the required amount of NH_4^+ band was formed at the top of the rare earth band. The displacement was 0.45 cm in expt. I, 1.4 cm in expt. II, and 20 cm in expt. III where the steady state was reached. After the required amount of displacement of the band, the solution was drained off by suction. The rubber stopper at the bottom of the column was removed and the sintered glass disc was raised carefully by means of a metal rod, with two discs attached to it, one at the top and another at the bottom (Fig. 6). The movement of this rod was measured using the bottom disc with a vernier scale correct to 0.05 cm. As the resin bed moved up the column the NH_4^+ band, which could be recognised by its white colour, was cut off from the top with a sharp blade. Afterwards the rare earth band was raised and was cut off every 0.2 cm length, and each time the length of the band cut was determined from the movement of the disc at the bottom. The rare earth from each portion of the band was extracted from the resin by repeated treatment with EDTA solution, precipitated as oxalate, ignited to oxide and analysed as before. The results of the three experiments along with the theoretical predictions are given in Fig. 7. It can be seen that within the limits of
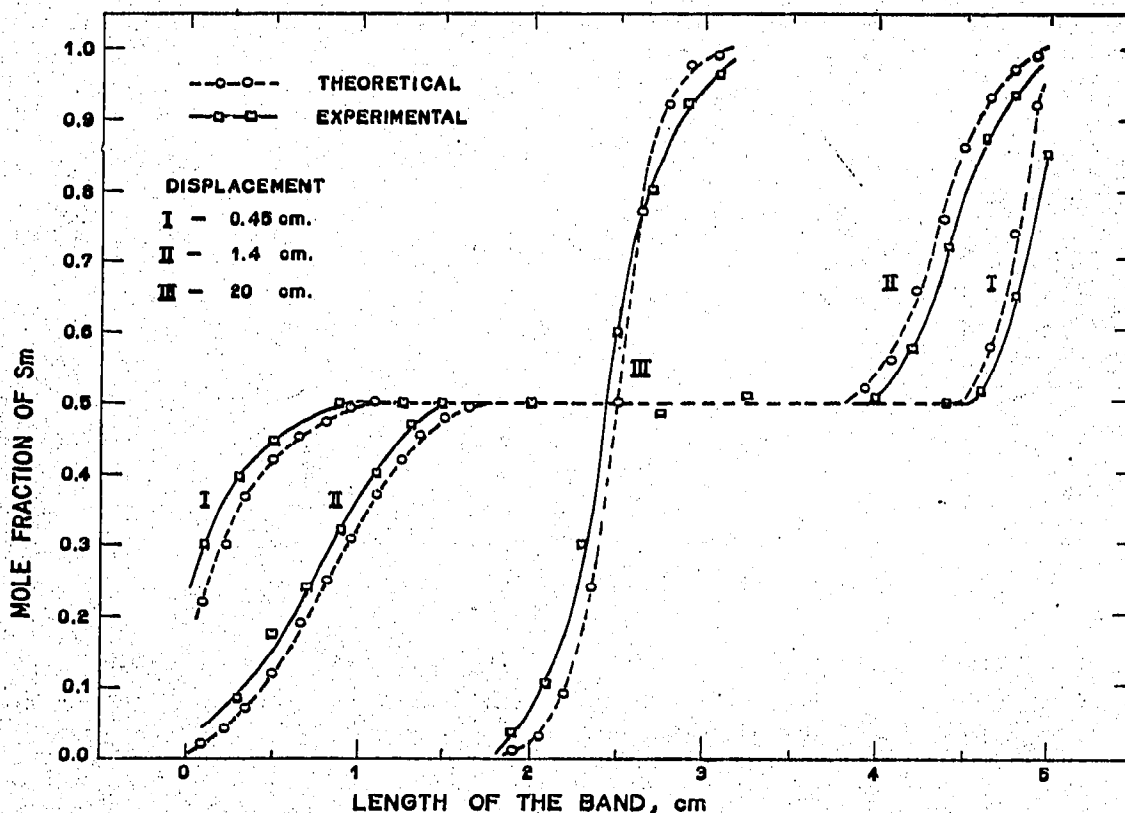

Fig. 7. Comparison of theoretical and experimental results for the separation of neodymium and samarium.

experimental error the agreement between theoretical and experimental values are reasonably good.

Verification of equations (16) and (17)

For verifying eqns. (16) and (17) it is preferable to take coloured rare earths so that the lengths of the rear and front sections of the band can be measured during the course of separation. A mixture of Pr and Nd was used for verifying eqn. (16) and a mixture of Nd and Sm for eqn. (17).

An equimolar mixture of praseodymium and neodymium was absorbed on the cation exchange resin in a 1 in. diameter column to a height of about 40 cm. It was then eluted with EDTA, 0.01 M adjusted to pH 8.3, at a rate of 0.5 ml/min using copper retaining bed. When separation occurred the praseodymium band could be identified by its green colour. The distance of elution was measured from the movement of the center of the rare earth band and at the same time the length of the praseodymium band was also measured. The length of the Pr band expected theoretically from eqn. (16) was calculated. When separation is complete the length of the Pr band will remain constant and will be equal to half the total length of the rare earth band. The experimental and theoretical results are given in Fig. 8.
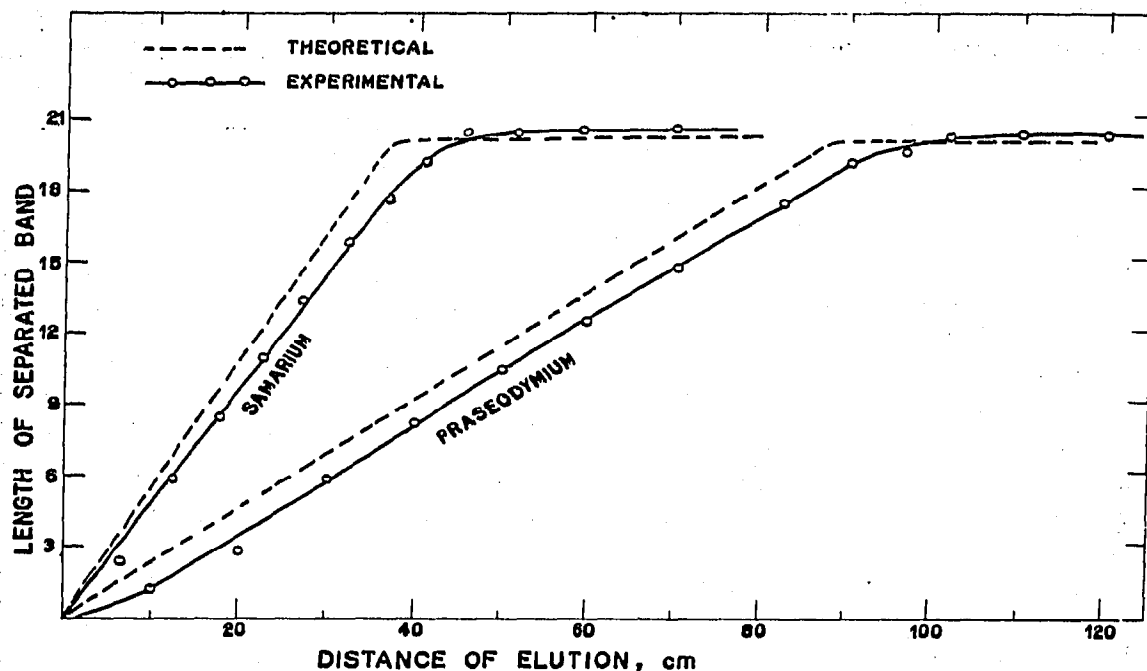

Fig. 8. Verification of equations (17) and (18).

Similar experiments were also carried out with a mixture of Nd and Sm in order to verify eqn. (17). The results are given in Fig. 8. In both cases good agreement is observed between theory and experiment.

SUMMARY

The distribution of species along the band during separation by displacement chromatography is discussed from a theoretical view point, using the concepts of the plate theory. Detailed calculations are presented for the determination of the concentration distribution in the rear and the front regions of the band, for the separation

of two species originally present in equal amount and having a separation factor of 2. An experimental procedure is described for verifying the theoretical results. Data obtained for the separation of neodymium and samarium and of praseodymium and neodymium, using EDTA as eluant and copper as retaining ion confirmed the validity of the theoretical treatment.

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