

ELUTION REQUIREMENTS FOR THE RESOLUTION OF TERNARY RARE-EARTH MIXTURES*

J. E. POWELL AND H. R. BURKHOLDER

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Ia. (U.S.A.)

AND

D. B. JAMES

Michigan Chemical Corporation, St. Louis, Mich. (U.S.A.)

(Received September 4th, 1967)

INTRODUCTION

Since 1959, it has been customary to compute the minimum number of band lengths of displacement by elution required on cation-exchange columns to isolate the components of a binary rare-earth mixture by the POWELL-SPEDDING equation¹⁻³, namely,

$$\nu = \frac{1 + \varepsilon A_0}{\varepsilon} = 1/(\alpha_B^A - 1) + A_0 \quad (1)$$

where:

ν = the minimum number of band length displacements required to achieve resolution of an A-B mixture into essentially "pure" A and "pure" B components, the assumption being made that the sorbed band is sufficiently long, the separation factor α_B^A sufficiently large, and the theoretical plate height h sufficiently small that the inherent overlap between the developed pure A and B bands at the steady state can be neglected ($L = 4 h/\log \alpha_B^A$, $6 h/\log \alpha_B^A$ or $8 h/\log \alpha_B^A$, depending upon whether > 99 , > 99.9 or > 99.99 % A and B products are taken to be pure).

A_0 = the mole fraction of A (the component which elutes more readily) in the original A-B mixture sorbed on the cation-exchange system.

α_B^A = the A-B separation factor for the system, defined as the ratio of A to B in the solution phase divided by the ratio of A to B in the resin phase when complete equilibrium exists between the two phases.

$\varepsilon = (\alpha_B^A - 1)$ = the amount the A-B separation factor exceeds unity.

The POWELL-SPEDDING equation has been applied satisfactorily to at least one multicomponent system in which a single component (yttrium) comprised 75 mole % of the rare-earth species present¹. While the estimated ν , based on the

* This work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2173.

assumption that dysprosium (5 mole %) and the lanthanons heavier than dysprosium (10 mole %) could be treated as a single component A ($A_0 = 0.15$), turned out to be very close to the requirement established experimentally, the outcome was largely fortuitous, due to the fact that two adjacent elements Y and Dy comprised 80 % of the species present.

Minor constituents of complex mixtures are generally recovered as binary or ternary mixtures from ion-exchange plants designed to obtain 90–95 % yields of one or more major constituents. For example, in the commercial production of yttrium, Lu–Yb, Yb–Tm–Er, Er–Ho–Dy, Dy–Y, Y–Tb–Gd, Gd–Eu–Sm, etc. fractions are commonly encountered. These valuable enriched concentrates may be processed further on columns of smaller diameter immediately or allowed to accumulate from a number of primary runs, combined and reprocessed on the primary column system. In either case the resorbed material must provide an adequate sorbed band length (in excess of $6h/\log \alpha_B^A$ centimeters with binary mixtures and in excess of $6h(\log \alpha_B^A + \log \alpha_C^B)/(\log \alpha_B^A \cdot \log \alpha_C^B)$ with ternary mixtures) if > 99.9 % pure products are desired. The retaining bed requirement for all binary mixtures is, of course, $1/(\alpha_B^A - 1)$ times the length of the sorbed band (see eqn. 1), but the requirements for ternary mixtures are complex and need to be discussed. It is the intent of the authors to extend the classical POWELL–SPEDDING treatment for binary mixtures to the case of ternary mixtures.

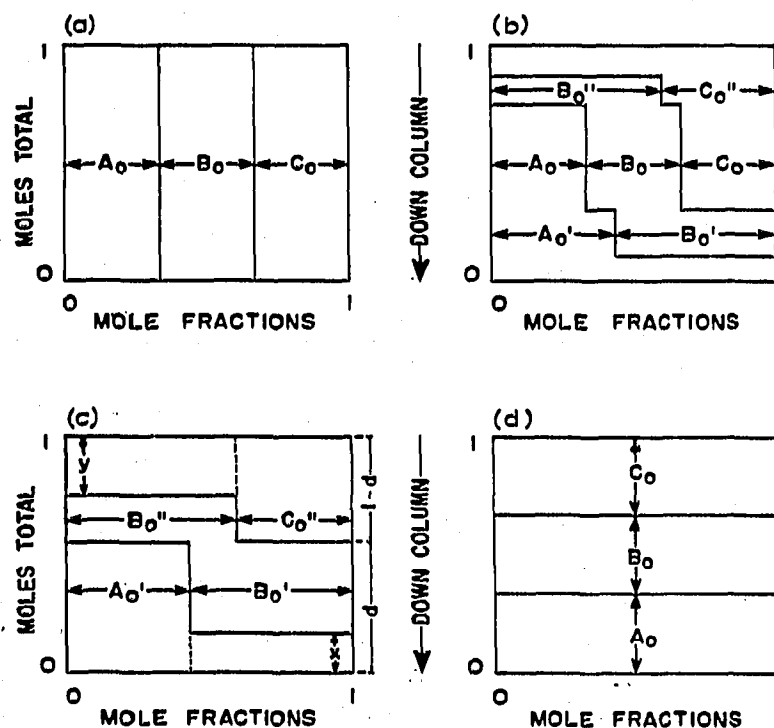


Fig. 1. Progressive stages (idealized) in the elution of ternary mixtures by displacement chromatography. (a) Three component charge of rare-earth mixture sorbed on a non-selective cation-exchange bed. (b) Course of development as ternary rare-earth mixture is displaced down the system by eluant. (c) Intermediate stage of development at which components A and C disengage after ν_A band lengths of displacement. (d) Final distribution of components at the steady state reached after ν_A or ν_C band lengths, whichever is the greater.

THEORY

For obvious reasons, we shall stipulate (as did POWELL AND SPEDDING *loc. cit.*) that the sorbed material span sufficient theoretical plates of the resin bed system that the inherent overlaps between developed bands at the steady state (characteristic of displacement chromatography) are negligible compared to the resolved bands of pure A, B, and C. Thus the regions of transition between plateaus of constant composition during development, and between resolved pure bands at the steady state (see Fig. 1), can be treated as abrupt steps rather than regions in which mole fraction gradients exist.

Further conditions include maintenance of a compact band of sorbed components and employment of sufficiently dilute eluant that virtually all cations of the charge are in a sorbed state at any time. In elutions with 0.015 M EDTA down Dowex 50 beds at pH 8.5, for example, > 99% of the cations reside in the resin phase within any cross section of the column at all times.

When one mole of rare-earth mixture (comprised of A_0 , B_0 , and C_0 moles of components A, B, and C, respectively) are sorbed on a non-selective resin bed system, the distribution of cations is uniform and the situation may be represented as in Fig. 1a. As the sorbed band of mixture is eluted with an efficient selective eluant (such as ammonium EDTA at pH 8.5) down additional resin bed originally loaded with a suitable retaining cation, the rare-earth cations are desorbed and complexed at the rear edge of the band, percolate through the sorbed mixture, and are redeposited at the front edge of the band. As the components desorbed at the rear percolate through the additional mixture of composition A_0 , B_0 , C_0 , exchange of cationic species between the resin and solution phases occurs so that the following equilibria are achieved in a short distance:

$$\begin{aligned}\frac{A}{B} &= \alpha_B^A \cdot \frac{A_0}{B_0} = (1 + \varepsilon_1) \frac{A_0}{B_0} \\ \frac{B}{C} &= \alpha_C^B \cdot \frac{B_0}{C_0} = (1 + \varepsilon_2) \frac{B_0}{C_0} \\ \frac{A}{C} &= \alpha_C^A \cdot \frac{A_0}{C_0} = (1 + \varepsilon_3) \frac{A_0}{C_0}\end{aligned}$$

where A , B , and C represent the mole fractions of components A, B, and C in the solution phase, A_0 , B_0 , and C_0 are the mole fractions originally sorbed on the resin, α_B^A , α_C^B , and α_C^A are the respective separation factors, and ε_1 , ε_2 , and ε_3 are the amounts the respective separation factors α_B^A , α_C^B , and α_C^A exceed unity. By definition $A + B + C = A_0 + B_0 + C_0 = 1$, and since $\alpha_C^A = \alpha_B^A \cdot \alpha_C^B$, it can be shown that

$$\varepsilon_3 = \varepsilon_1 + \varepsilon_2 + \varepsilon_1\varepsilon_2 \quad (2)$$

As the sorbed materials progress down a bed system, the sorbed band can be viewed from any point within the band itself as a typical counter-current system operating in total reflux. That is to say, for every mole of mixture that percolates down through a cross section of the band (transported by the aqueous phase), a mole of mixture of different but definite composition moves upward in the resin phase.

Of course, the latter mixture actually is affixed to the stationary bed as the band is eluted by.

Component A moves forward across the A_0, B_0, C_0 plateau region at a fixed rate of $(A - A_0)$ moles per mole of downward displacement of the sorbed charge. At the same time component C moves to the rear across the same ternary plateau at a fixed rate of $(C_0 - C)$ moles per mole of over-all band displacement. The net movement of component B, either forward or backward across the ternary region, depends upon whether $(C_0 - C)$ or $(A - A_0)$ is the greater, since by definition $(B - B_0) = (C_0 - C) - (A - A_0)$. A diminishing region of original ternary mixture persists within the band system until disengagement of components A and C occurs (after v_d displacements of the over-all band of sorbed material) at a point located d moles back from the leading edge of the band (see Fig. 1c). It is clear that the disengagement of components A and C must occur within the region which ultimately is to be occupied by a pure B band, B_0 moles in width (see Fig. 1d).

From Figs. 1a-c it can be seen that $C_0 d$ moles of component C must be transported to the rear and $A_0 (1 - d)$ moles of component A must be transported forward across the diminishing A_0, B_0, C_0 plateau (Fig. 1b) for disengagement of A and C to occur at point d . Since the rates of transport of C to the rear and of A to the fore are, respectively, $(C_0 - C)$ and $(A - A_0)$ moles per mole of displacement,

$$v_d = \frac{C_0 d}{C_0 - C} = \frac{A_0 (1 - d)}{A - A_0} \quad (3)$$

thus

$$d = \frac{A_0 (C_0 - C)}{AC_0 - A_0 C} \quad (4)$$

From the definitions of mole fractions in a ternary system and the equilibria described above, it can be shown that

$$A = \frac{\alpha_C^A A_0}{\alpha_C^A A_0 + \alpha_C^B B_0 + C_0} \quad (5)$$

and that

$$C = \frac{C_0}{\alpha_C^A A_0 + \alpha_C^B B_0 + C_0} \quad (6)$$

Substituting these equalities for A and C in eqns. (3) and (4), and using the definitions $\alpha_C^B = (1 + \varepsilon_2)$ and $\alpha_C^A = (1 + \varepsilon_3)$, first d , then v_d can be found by standard algebraic operations,

$$d = A_0 + \frac{\varepsilon_2}{\varepsilon_3} B_0 \quad (7)$$

$$v_d = \frac{1 + \varepsilon_3 A_0 + \varepsilon_2 B_0}{\varepsilon_3} = \frac{1}{\varepsilon_3} + d \quad (8)$$

While the system is developing to the point of disengagement of components A and C, some A also moves forward across a binary A_0' , B_0' plateau at the rate of $(A' - A_0')$ moles per mole of displacement, forming a pure A band at the rate of $(A' - A_0')/B_0'$ moles per mole of displacement of the sorbed charge. Meanwhile, C moves to the rear across a similar binary B_0'' , C_0'' plateau at the rate of $(C_0'' - C'')$ moles per mole of displacement, forming a "pure" C band at a rate of $(C_0'' - C'')/B_0''$ moles per mole of band travel. A_0' and B_0' , and B_0'' and C_0'' represent the mole fractions of A, B and C in the separate intermediate binary plateau regions which form as a consequence of mutual movement of components C and A out of the ternary mixed region. A' , B' , B'' , and C'' represent the corresponding mole fractions of components A, B, and C in the solution phases which are in dynamic equilibrium with the binary A_0' , B_0' and B_0'' , C_0'' resin phase compositions. The equilibrium conditions are, of course,

$$\frac{A'}{B'} = \alpha_B^A \cdot \frac{A_0'}{B_0'} = (1 + \varepsilon_1) \frac{A_0'}{B_0'}$$

$$\frac{B''}{C''} = \alpha_C^B \cdot \frac{B_0''}{C_0''} = (1 + \varepsilon_2) \frac{B_0''}{C_0''}$$

where $(A' + B') = (A_0' + B_0') = (B'' + C'') = (B_0'' + C_0'') = 1$. In dynamic systems of this kind it should be remembered that equilibrium is achieved between the solution and resin phases at points which do not exactly coincide but are displaced from each other by one theoretical stage or plate of height h .

Before proceeding further with the theoretical development, let us consider the import of eqn. (7). It is seen that, if the rate $(A' - A_0')$ should be exceed $(A - A_0)$, an A_0' , B_0' plateau could never develop, and the A_0' , B_0' composition would then represent but a single point on a composition gradient between the A_0 , B_0 , C_0 mixture and a pure A band. In such a case, the controlling rate of transfer of A would be $(A - A_0)$ moles per mole from the beginning up to the point of disengagement of components A and C (disappearance of the ternary region), *i.e.* the point d would fall exactly A_0 moles from the leading edge of the band system after a displacement of v_d moles (band lengths). For such an event to occur, according to eqn. (7), either B_0 or ε_2 must of necessity equal zero, reducing the problem to the case of a binary mixture. The value $\varepsilon_2 = 0$ (or $\alpha_C^B = 1$) infers that components B and C are identical with respect to their elution behavior.

It can only be concluded that $(A - A_0)$ always exceeds $(A' - A_0')$ with ternary mixtures; and that an intermediate plateau of composition A_0' , B_0' forms at a rate of $(C_0 - C)/C_0 - (A' - A_0')/B_0'$ moles of said mixture per mole of displacement, from the beginning until the system has undergone v_d displacements down the bed. From that point on, the A_0' , B_0' plateau is consumed at a constant rate of $dx/dN = (A' - A_0')/B_0'$ moles per mole of displacement until all of the A component present has migrated into the "pure" component region (Fig. 1d).

The important point of these arguments is that the pure A band simply grows at a rate of $dx/dN = (A' - A_0')/B_0'$ moles per mole of displacement from start

(Fig. 1a) to finish (Fig. 1d). By similar reasoning it may be seen that the pure C band also grows throughout the development at a constant rate, $dy/dN = (C_0'' - C'')/B_0''$ moles per mole of displacement. Consequently,

$$B_0' \int_0^{A_0} dx = (A' - A_0') \int_0^{v_A} dN \quad (9)$$

and

$$B_0'' \int_0^{C_0} dy = (C_0'' - C'') \int_0^{v_C} dN \quad (10)$$

where dx and dy represent the respective numbers of moles of pure A and pure C derived from dN moles of displacement of the sorbed system down a resin bed.

Carrying out the indicated integrations one obtains the relationships

$$v_A = \frac{B_0' A_0}{A' - A_0'} = \frac{(1 - A_0') A_0}{A' - A_0'} \quad (11)$$

$$v_C = \frac{B_0'' C_0}{C_0'' - C''} = \frac{(1 - C_0'') C_0}{C_0'' - C''} \quad (12)$$

Substituting $A_0'(1 + \varepsilon_1)/(1 + \varepsilon_1 A_0')$ for A' in eqn. (11) and $C_0''/\{1 + \varepsilon_2(1 - C_0'')\}$ for C'' in eqn. (12),

$$v_A = \frac{A_0}{A_0'} \left\{ \frac{1}{\varepsilon_1} + A_0' \right\} \quad (13)$$

and

$$v_C = \frac{C_0}{C_0''} \left\{ \frac{1}{\varepsilon_2} + B_0'' \right\} \quad (14)$$

Most generally resolution of the intermediate A_0', B_0' mixture does not coincide with resolution of the B_0'', C_0'' mixture so that v_A and v_C are rarely equal.

It can be seen from inspection from Figs. 1a-c that the area

$$A_0' d = A_0 - B_0' x \quad (15)$$

and since

$$x = \int_0^x dx = \frac{(A' - A_0')}{B_0'} \int_0^{v_A} dN = \frac{(A' - A_0') v_A}{B_0'} \quad (16)$$

then

$$A_0' d = A_0 - (A' - A_0') v_A \quad (17)$$

Substituting the values of d and v_d from eqns. (7) and (8) and the readily derived equivalent of $(A' - A_0')$, namely, $\varepsilon_1 A_0' (1 - A_0') / (1 + \varepsilon_1 A_0')$, into eqn. (17) and carrying out the obvious algebraic manipulations,

$$\varepsilon_1 (A_0')^2 - \{\varepsilon_3 A_0 + \varepsilon_2 B_0 + \varepsilon_1 + \varepsilon_1 \varepsilon_2 B_0\} A_0' + \varepsilon_3 A_0 = 0 \quad (18)$$

Eqn. (18) can be reduced to a more elegant form by substituting the quantity $(\varepsilon_3 - \varepsilon_1 - \varepsilon_2)$ for $\varepsilon_2 \varepsilon_1$ (obtained from eqn. (2)) and then substituting $(A_0 + C_0)$ for the quantity $(1 - B_0)$.

$$\varepsilon_1 (A_0')^2 - \{\varepsilon_3 (A_0 + B_0) + \varepsilon_1 (A_0 + C_0)\} A_0' + \varepsilon_3 A_0 = 0 \quad (19)$$

Eqn. (19) is of the form $ax^2 + bx + c = 0$.

It can also be seen by inspection of Figs. 1a-c that the area

$$C_0'' (1 - d) = C_0 - B_0'' y \quad (20)$$

Now

$$y = \int_0^y dy = \frac{(C_0'' - C'')}{B_0''} \int_0^{v_d} dN = \frac{(C_0'' - C'') v_d}{B_0''} \quad (21)$$

so that

$$C_0'' (1 - d) = C_0 - (C_0'' - C'') v_d, \quad (22)$$

and substituting the values of d and v_d from eqns. (7) and (8) and the easily derived equivalent of C'' , equal to $C_0'' / (1 + \varepsilon_2 - \varepsilon_2 C_0'')$, into eqn. (22), one arrives (after some laborious manipulations) at the expression

$$\varepsilon_2 \alpha_C^A (C_0'')^2 - \{\varepsilon_3 + \varepsilon_2 \varepsilon_3 + \varepsilon_2 + \varepsilon_2 \varepsilon_3 C_0 - \varepsilon_3 A_0 - \varepsilon_2 B_0\} C_0'' + \varepsilon_3 \alpha_C^B C_0 = 0 \quad (23)$$

When the value $(1 - B_0 - C_0)$ is substituted for A_0 and the equation is divided through by $\alpha_C^B (= 1 + \varepsilon_2)$, eqn. (24) results

$$\varepsilon_2 \alpha_B^A (C_0'')^2 - \left\{ \varepsilon_3 C_0 + \varepsilon_2 \alpha_B^A + \frac{\varepsilon_3 - \varepsilon_2}{1 + \varepsilon_2} B_0 \right\} C_0'' + \varepsilon_3 C_0 = 0 \quad (24)$$

From eqn. (2), $\varepsilon_1 = (\varepsilon_3 - \varepsilon_2) / (1 + \varepsilon_2)$, so that

$$\varepsilon_2 \alpha_B^A (C_0'')^2 - \{\varepsilon_3 C_0 + \varepsilon_2 \alpha_B^A + \varepsilon_1 B_0\} C_0'' + \varepsilon_3 C_0 = 0 \quad (25)$$

This equation is likewise in the form $ax^2 + bx + c = 0$.

CONCLUSIONS

The elution requirements for ternary mixtures in displacement chromatographic processes can be fully evaluated for any combination of mole fractions and

separation factors by first solving eqns. (19) and (25) by the quadratic formula, and then solving eqns. (13) and (14). One would like to express ν_A and ν_C more neatly in terms of A_0 , B_0 , C_0 , ϵ_1 , ϵ_2 and ϵ_3 , but to do so algebraically is a burdensome task, due to the complexity of the a , b and c coefficients of the quadratic eqns. (19) and (25). The reader will surely appreciate that it is much simpler in any given case to make numerical substitutions before combining eqns. (19) and (13), or eqns. (25) and (14).

SUMMARY

The treatment employed by POWELL AND SPEDDING to establish the minimum number of displacements by displacement chromatography needed to resolve the components of binary rare-earth mixtures has been extended rigorously to the case of ternary mixtures.

NOTE ADDED IN PROOF

It has come to the attention of the authors that SILLÉN⁴ has derived a general solution to the problem by a different approach. His results are compatible with the above.

REFERENCES

- 1 J. E. POWELL AND F. H. SPEDDING, *Chem. Eng. Progr. Symp. Ser.*, 55 (1959) 101.
- 2 J. E. POWELL AND F. H. SPEDDING, *Trans. Met. Soc. AIME*, 215 (1959) 457.
- 3 J. E. POWELL, in L. EYRING (Editor), *Progress in the Science and Technology of the Rare Earths*, Vol. 1, Pergamon Press, Oxford, 1964, p. 62.
- 4 L. G. SILLÉN, *Arkiv Kemi*, 2 (1950) 477.

J. Chromatog., 32 (1968) 559-566