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DISPLACEMENT ION-EXCHANGE SEPARATION OF TERNARY RARE EARTH MIXTURES WITH CHELATING ELUANTS

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SUMMARY

The separation of a ternary mixture of rare earths by displacement cation-exchange chromatography with chelating eluants can be described by constructing a distance-time diagram. The original composition of the mixture and the separation factors are the only inputs to the calculation. The points of complete separation of each of the three components or the point of any partial separation can be determined. Two methods of operation are considered, *viz.* loading of the unchelated mixture prior to elution, and chelation of the mixture prior to its introduction to the resin.

INTRODUCTION

The rare earths are separated in ton quantities in high purity by cation-exchange displacement chromatography with chelating eluants. The process was developed by POWELL, SPEDDING AND CO-WORKERS¹. (A complete bibliography is given in Ref. 1.) A theory for the calculation of the minimum number of displacements of the sorbed mixture necessary to separate the components of a binary mixture was described by POWELL AND SPEDDING². Recently, the same approach was used to extend the treatment to three-component mixtures³.

SILLÉN presented results⁴ in 1950 from which the POWELL-SPEDDING equations can be easily obtained. Both the SILLÉN and the POWELL-SPEDDING treatments are equilibrium theories; they assume infinite mass-transfer rates. Rare earth separations are usually conducted in a manner so that the inherent overlap between developed pure regions is small compared to the width of the pure regions, making the equilibrium assumption a reasonable one. Both theoretical treatments further assume constant separation factors between components; the validity of this assumption in rare earth separations was effectively argued by POWELL AND SPEDDING²; they also showed that the separation factors for adjacent pairs of rare earths can be accurately approximated by the ratio of their chelate stability constants. In this discussion the general approach of SILLÉN will be extended and applied to separations of ternary rare earth

mixtures, leading to more general results than those derived using the POWELL-SPEDDING approach³.

In the displacement-chromatographic, cation-exchange separation of rare earths, the sorbed mixture is eluted down a column with a chelating eluant such as 0.015 *M* EDTA, pH 8.5. The process is schematically shown in Fig. 1 for the separation of a binary mixture. As the constant-length charge moves down the column, regions containing a pure single component grow at the front and rear at the expense of a region in the center containing the original binary composition. When the binary

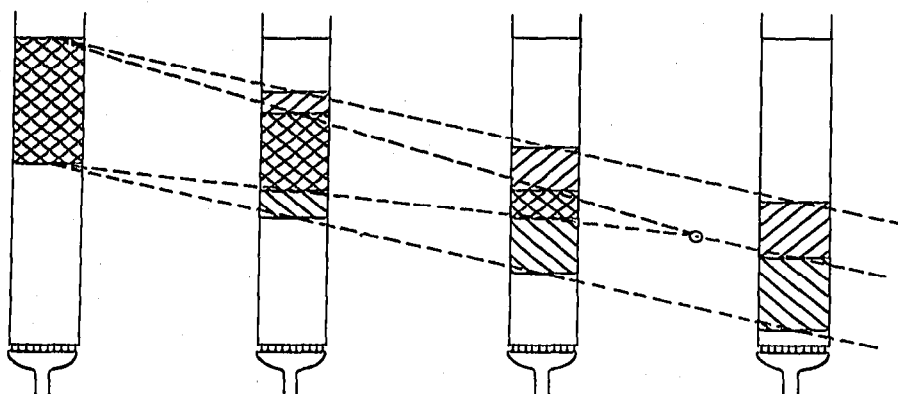


Fig. 1. Displacement chromatographic separation of a binary rare earth mixture.

composition is entirely consumed, the separation is complete. To describe the behavior of the system we must determine the rates at which the boundaries between these regions migrate down the column. Thus the coordinates of interest are time of elution (or volume of eluant) and distance down the resin bed measured from the inlet.

It simplifies the mathematics to express distance in units of length of the sorbed mixture and time in units of time to elute mixture through its length:

$$\zeta = z/z_0, \quad \tau = t/t_0 \quad (1)$$

where:

- ζ = distance from the inlet (band lengths)
- z = distance from the inlet (cm)
- z_0 = length of sorbed mixture (cm)
- τ = time to elute mixture through its length (band displacements)
- t = time of elution (h)
- t_0 = time to elute mixture through its length (h).

An expression for the velocity of any boundary can be derived by considering a material balance across a boundary of thickness dz . Matter conservation of any species *i* requires that the change in the concentration of species *i* across the boundary be equal to the difference of what flows in and what flows out of the boundary.

$$(\Delta C_1 + \Delta \bar{C}_1)qdz = U_0(C_1 + \Delta C_1)qdt - U_0C_1qdt, \quad (2)$$

where

- U_0 = linear fluid flow (cm/h)
- C_1 = fluid concentration of species *i* (moles/l of column)
- \bar{C}_1 = resin concentration of species *i* (moles/l of column)
- q = column cross-section (cm²).

From eqn. (2) the velocity of the boundary is

$$\frac{dz}{dt} = \frac{U_0 \Delta C_1}{\Delta C_1 + \Delta \bar{C}_1} \quad (3)$$

In rare earth separations solubilities of the rare earth chelate complexes usually limit C_1 so that $\Delta \bar{C}_1 \gg \Delta C_1$. Therefore,

$$\frac{dz}{dt} \cong U_0 \cdot \frac{\Delta C_1}{\Delta \bar{C}_1} \quad (3')$$

Converting all concentrations to mole fractions,

$$x_1 = C_1 / \sum_1 C_1, \quad y_1 = \bar{C}_1 / \sum_1 \bar{C}_1 \quad (4)$$

and substituting eqns. (1) and (4) into (3') yields the velocity, U_Δ , of any boundary where species i changes by Δx_1 and Δy_1 :

$$U_\Delta = \frac{d\zeta}{d\tau} = \frac{dz/z_0}{dt/t_0} = \frac{\Delta x_1}{\Delta y_1} \quad (5)$$

In displacement chromatography all boundaries are between two zones, one of which has one, and only one, more species present than are present in the other zone. If it is species j which disappears across the boundary then

$$U_\Delta = \frac{x_j}{y_j} \quad (6)$$

where x_j and y_j are the mole fractions of j in each phase on that side of the boundary where j is present.

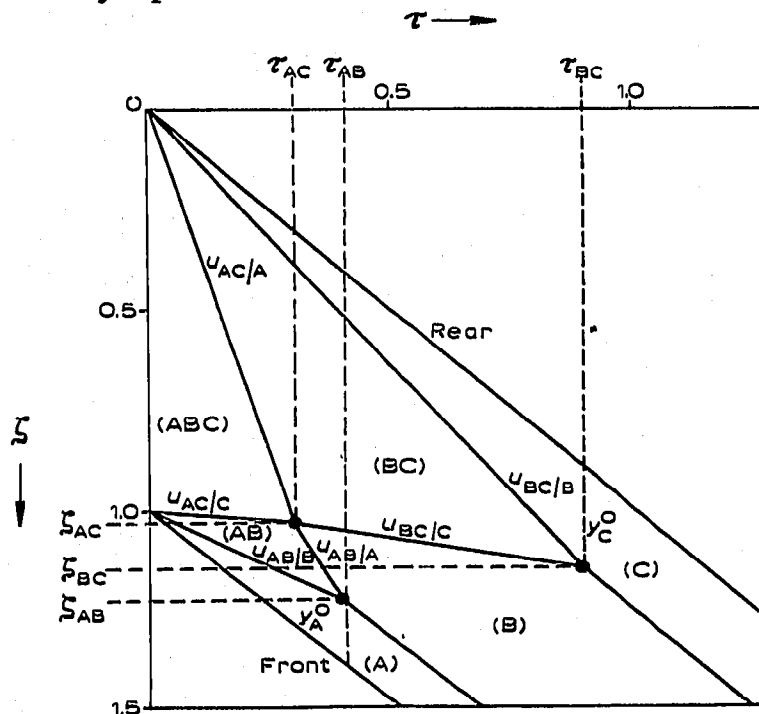


Fig. 2. Displacement chromatographic separation of a uniformly loaded, ternary rare earth mixture.

The displacement development of a uniformly loaded, ternary mixture of rare earths is shown in Fig. 2*. If the order of decreasing chelate stability is $A > B > C$, then the separation factors between A and B, α_{BA} , and between A and C, α_{CA} , are greater than unity;

$$\alpha_{BA} = \frac{y_B x_A}{x_B y_A}, \quad \alpha_{CA} = \frac{y_C x_A}{x_C y_A} \quad (7)$$

As elution proceeds the original mixture is consumed as a zone of pure C and a zone containing a mixture of B and C grow behind it, and a zone of pure A and a zone containing a mixture of A and B grow ahead of it. As shown in the preceding discussion the boundaries between these zones migrate down the column at velocities given by the ratio of the mole fractions of that species which disappears across each boundary. The velocities of the front and rear boundaries are unity because only one species exists on either side of them.

From Fig. 2 it is clear that

$$U_{AC/A} = \frac{x_A^0}{y_A^0} = \frac{\zeta_{AC}}{\tau_{AC}} \quad (8)$$

and

$$U_{AC/C} = \frac{x_C^0}{y_C^0} = \frac{\zeta_{AC} - 1}{\tau_{AC}} \quad (9)$$

where y_A^0 and y_C^0 are the resin mole fractions in the initial loaded ternary mixture and x_A^0 and x_C^0 are eluant mole fractions in equilibrium with y_A^0 and y_C^0 . The time τ_{AC} and distance ζ_{AC} required to separate A from C is determined from eqns. (7) through (9);

$$\zeta_{AC} = \frac{\alpha_{CA}}{\alpha_{CA} - 1} \quad (10)$$

$$\tau_{AC} = (\zeta_{AC}) \left(y_A^0 + \frac{y_B^0}{\alpha_{BA}} + \frac{y_C^0}{\alpha_{CA}} \right) \quad (11)$$

The times and distances for the complete separation of A from B and B from C can be determined from a similar argument. Considering first the AB separation point, (τ_{AB}, ζ_{AB})

$$U_{AB/A} = \frac{\zeta_{AB} - \zeta_{AC}}{\tau_{AB} - \tau_{AC}} = \frac{x_A^{AB}}{y_A^{AB}} \quad (12)$$

$$U_{AB/B} = \frac{\zeta_{AB} - 1}{\tau_{AB}} = \frac{x_B^{AB}}{y_B^{AB}} \quad (13)$$

$$U_{Front} = \frac{\zeta_{AB} - 1 + y_A^0}{\tau_{AB}} = 1 \quad (14)$$

* The use of distance-time diagrams and boundary velocities in this treatment was stimulated by F. HELFFERICH who disclosed a general, as yet unpublished theory on this basis.⁵

where $x_A^{AB} + x_B^{AB} = 1 = y_A^{AB} + y_B^{AB}$ describes the composition of the binary mixture AB that appears between the zone containing the original mixture and the zone containing pure A. Combining eqns. (7) and (12) through (14) produces a quadratic equation

$${}_2K_{AB}p_{AB}^2 + {}_1K_{AB}p_{AB} + {}_0K_{AB} = 0 \quad (15)$$

where

$${}_2K_{AB} = a_{BA} - 1 \quad (16)$$

$${}_1K_{AB} = (a_{BA} - 1)y_A^\circ - a_{BA}\tau_{AC} + \zeta_{AC} - 1 \quad (17)$$

$${}_0K_{AB} = y_A^\circ(\zeta_{AC} - 1) \quad (18)$$

$$p_{AB} = \zeta_{AB} - 1 = \tau_{AB} - y_A^\circ \quad (19)$$

For simplicity the coefficients are given here in terms of the coordinates of the AC separation point (ζ_{AC} , τ_{AC}). They can be calculated from eqns. (10) and (11). After eqn. (15) is solved for p_{AB} the coordinates (ζ_{AB} , τ_{AB}) for the AB separation point can be calculated from eqn. (19).

Similarly the BC separation point (ζ_{BC} , τ_{BC}) is determined from

$$U_{BC/B} = \frac{x_B^{BC}}{y_B^{BC}} = \frac{\zeta_{BC}}{\tau_{BC}} \quad (20)$$

$$U_{BC/C} = \frac{x_C^{BC}}{y_C^{BC}} = \frac{\zeta_{BC} - \zeta_{AC}}{\tau_{BC} - \tau_{AC}} \quad (21)$$

$$U_{Rear} = \frac{\zeta_{BC} - y_C^\circ}{\tau_{BC}} = 1 \quad (22)$$

where $x_B^{BC} + x_C^{BC} = 1 = y_B^{BC} + y_C^{BC}$ describes the composition of the binary mixture BC that appears between the zone containing the original mixture and the zone containing pure C.

As with the other point we obtain a quadratic equation,

$${}_2K_{BC}p_{BC}^2 + {}_1K_{BC}p_{BC} + {}_0K_{BC} = 0 \quad (23)$$

where

$${}_2K_{BC} = a_{CB} - 1 \quad (24)$$

$${}_1K_{BC} = \tau_{AC} - (a_{CB} - 1)y_C^\circ - a_{CB}\zeta_{AC} \quad (25)$$

$${}_0K_{BC} = a_{CB}\zeta_{AC}y_C^\circ \quad (26)$$

$$p_{BC} = \zeta_{BC} - 1 = \tau_{BC} + y_C^\circ \quad (27)$$

It is interesting to consider also the problem when the rare earth mixture is complexed by the eluant prior to its introduction into the column. With these initial conditions the distance-time diagram takes the form shown in Fig. 3. Arguments, similar to those developed for the case of initially loading the resin, yield the following results:

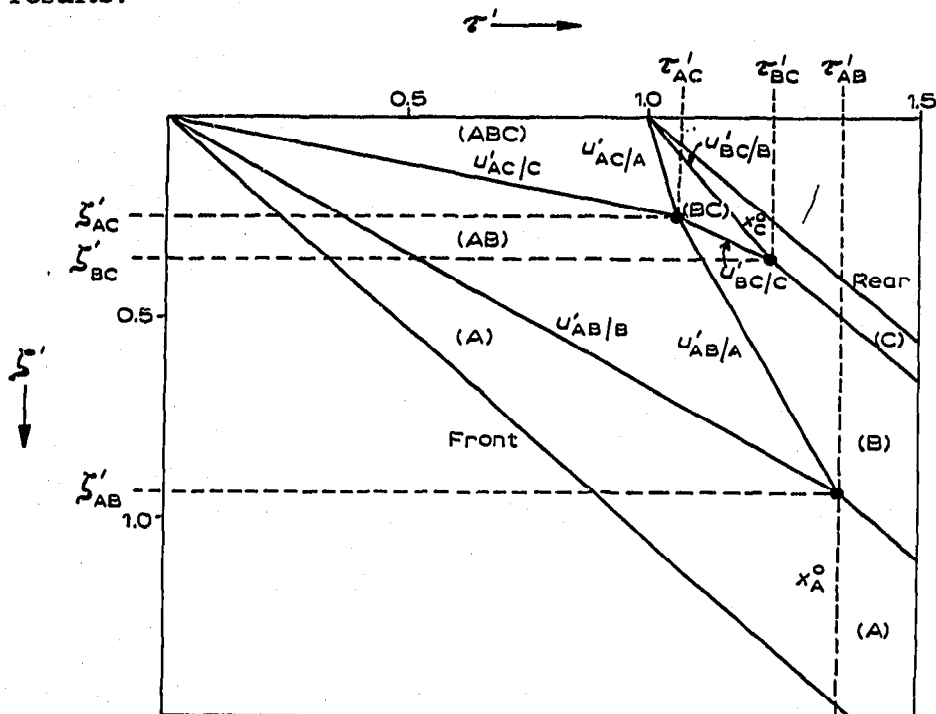


Fig. 3. Displacement chromatographic separation of an initially complexed, ternary rare earth mixture.

(a) the AC separation point,

$$\tau'_{AC} = \frac{\alpha_{CA}}{\alpha_{CA} - 1} \quad (28)$$

$$\zeta'_{AC} = \tau'_{AC} \left(\frac{x_A^0}{\alpha_{CA}} + \frac{x_B^0}{\alpha_{CB}} + x_C^0 \right) \quad (29)$$

(b) the AB separation point,

$$2K'_{AB}(p'_{AB})^2 + 1K'_{AB}p'_{AB} + 0K'_{AB} = 0 \quad (30)$$

where

$$2K'_{AB} = \alpha_{AB} - 1 \quad (31)$$

$$1K'_{AB} = (\alpha_{BA} - 1)x_A^0 - \alpha_{BA}\tau'_{AC} + \zeta'_{AC} \quad (32)$$

$$0K'_{AB} = \zeta'_{AC}x_A^0 \quad (33)$$

$$p'_{AB} = \zeta'_{AB} = \tau'_{AB} - x_A^0 \quad (34)$$

(c) and the BC separation point

$${}_2K'_{BC}(p'_{BC})^2 + {}_1K'_{BC}p'_{AB} + {}_0K'_{BC} = 0 \quad (35)$$

where

$${}_2K'_{BC} = \alpha_{CB} - 1 \quad (36)$$

$${}_1K'_{BC} = \tau'_{AC} - 1 - \alpha_{CB}\zeta'_{AC} - (\alpha_{CB} - 1)x_C^0 \quad (37)$$

$${}_0K'_{BC} = + \alpha_{CB}\zeta'_{AC}x_C^0 \quad (38)$$

$$p'_{BC} = \zeta'_{BC} = \tau'_{BC} + x_C^0 - 1 \quad (39)$$

In these equations x_A^0 and x_C^0 describe the initial composition of the chelated mixture that is percolated through the system.

The results from eqns. (28) through (39) can be compared with the results from eqns. (10), (11), (15) through (19), and (23) through (27) to evaluate the best method of operation, unchelated loading or initial chelation. Qualitatively, the unchelated-loading method of operation requires more resin but less time or eluant to effect the same separation.

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