The prediction of elution maxima in the gradient elution of rare earths

Several authors[1-6] have used α-hydroxy-isobutyric acid (α-IHBA) as the eluting agent for ion exchange separations of rare earths (R.E.). The time needed for such a separation can be much shortened with a gradient elution technique[5,6]. It was thought to be of interest to develop a method that would allow the calculation of the effect of proposed gradients on the separation.

Theoretical development

The dependence of the distribution coefficient on the ligand concentration is given by eqn. (1):

$$\log K_D = a \log c + b \tag{1}$$

where:

c = ligand concentration,
K_D = distribution coefficient,
a and b = constants characteristic for each R.E. element.

The distribution coefficient is defined according to KRAUS AND MOORE[7-10] as the quantity of chromatographed substance per gram dry stationary phase divided by the quantity per millilitre mobile phase:

$$K_D = \rho \left(\frac{V}{A h} - i \right) \tag{2}$$

where:

ρ = specific volume of the column,
V = volume of eluant necessary to elute the maximum of the elution peak,
A = cross-section of the column,
h = height of the column,
i = interstitial fraction, *i.e.* the volume fraction of the column occupied by the mobile phase.

a and b have been determined by a least squares method on results published by DEELSTRA[22]. These values are given in Table I.

Gradients can be obtained by the use of a constant volume mixing chamber, yielding an exponential gradient; or with a communicating vessels device, which yields linear, concave or convex gradients depending on the ratio of the cross-sections of the mixing vessel and the reservoir. Equations relating the eluting agent concentration to the volume which has passed through the column have been published by several authors (eqn. 3: exponential gradient; eqn. 4: linear, concave or convex gradients[11-16]).

$$c = c_0 + (c_L - c_0)e^{-V_x/V_t} \tag{3}$$

$$c = c_0 + (c_L - c_0) \left(\frac{V_x}{V_t} \right)^x \tag{4}$$

TABLE I

VALUES OF CONSTANTS a AND b

	a	b		a	b
Lu	—5.73	—6.15	Gd	—5.54	—4.07
Yb	—5.67	—5.89	Eu	—5.45	—3.76
Tm	—5.66	—5.66	Sm	—5.43	—3.46
Er	—5.60	—5.37	Pm	—5.69	—3.38
Ho	—5.81	—5.36	Nd	—5.19	—2.65
Y	—5.56	—4.89	Pr	—4.97	—2.32
Dy	—5.46	—4.73	Ce	—5.12	—2.19
Tb	—5.27	—4.19	La	—4.88	—1.67

where:

c_0 = initial ligand concentration in the mixing chamber,
c_L = ligand concentration in the reservoir,
V_x = volume of eluate,
V_t = volume of mixing chamber (eqn. 3); total initial volume in the communicating vessels (eqn. 4),
$\varkappa$ = ratio of the cross-sections of reservoir and mixing chamber.

Combining eqns. (3) and (4) with eqn. (1), one obtains eqns. (5) and (6):

$$\log K_D = a \log \left[c_0 + (c_L - c_0)e^{-V_x/V_t} \right] + b \tag{5}$$

$$\log K_D = a \log \left[c_0 + (c_L - c_0)\left(\frac{V_x}{V_t}\right)^{\varkappa} \right] + b \tag{6}$$

From eqns. (5) and (6) it is clear that K_D changes continually as a function of V_x. One can, however, calculate an apparent distribution coefficient K_D' as defined by eqn. (2).

To predict K_D', consider a small volume increment of eluting agent passing through the column. The length of migration of the maximum of the chromatographic peak, Δh_1, is given by eqn. (7):

$$(\Delta h)_1 = \frac{(\Delta V_x)_1}{(K_D)_1 + i\rho} \cdot \rho/A \tag{7}$$

Similarly, for a second volume increment:

$$(\Delta h)_2 = \frac{(\Delta V_x)_2}{(K_D)_2 + i\rho} \cdot \rho/A \tag{8}$$

The total length of migration after the first two volume increments, is given by eqn. (9):

$$(\Delta h)_1 + (\Delta h)_2 = \rho/A \left[\frac{(\Delta V_x)_1}{(K_D)_1 + i\rho} + \frac{(\Delta V_x)_2}{(K_D)_2 + i\rho} \right] \tag{9}$$

After n volume increments:

$$\sum_{v=1}^{n} (\Delta h)_v = \sum_{v=1}^{n} \frac{(\Delta V_x)_v}{(K_D)_v + i\rho} \cdot \rho/A \tag{10}$$

If $\sum_{v=1}^{n} (\Delta h)_v$ equals h, then:

$$h = \rho/A \int_{V_x=0}^{V_x=\overline{V}} \frac{\mathrm{d}(V_x)}{K_D + i\rho} . \tag{11}$$

From eqn. (2) follows:

$$h = \rho/A \cdot \frac{\overline{V}}{K_D + i\rho} \tag{12}$$

Combination of eqns. (11) and (12) yields eqn. (13):

$$\frac{\overline{V}}{K_{D'} + i\rho} = \int_0^{\overline{V}} \frac{\mathrm{d}V_x}{K_D + i\rho} = \frac{Ah}{\rho} \tag{13}$$

K_D' is the root of function $\varphi(z)$:

$$\varphi(z) \equiv \int_0^{(Ah/\rho)\,(z+i\rho)} \frac{1}{K_D + i\rho} \mathrm{d}V_x - \frac{Ah}{\rho} \tag{14}$$

and can be calculated by different methods.

FREILING[17,18] has obtained a migration equation for gradient elution by an analogous development. Other authors have also published equations that can be reduced to the same formula[19,21].

Calculation

In addition to the simple gradients described in eqns. (3) and (4), many other gradients can be obtained. Therefore no attempt was made to calculate analytically the integral from eqn. (14). Instead a Fortran program was written to calculate the integral numerically on an IBM-1620 ordinator. This procedure makes it possible to predict the results of other more complex gradients where the integral would certainly become incalculable by analytical means.

The method that is used here consists in enclosing the root K_D' of eqn. (14) between two narrowing limits, until two numbers, z_L and z_U, are obtained, with four identical meaningful figures, and so that:

$$\varphi(z_L) < 0, \qquad \varphi(z_U) > 0$$

Because of the monotonously increasing character of φ one can then conclude that:

$$z_L < K_D' < z_U$$

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL K_D'-VALUES

$c_0 = 0$ (250 ml); $c_L = 0.375$ (250 ml); $V_t = 2 \times 250$ ml $= 500$ ml; $Ah = 5.40$; $\varrho = 2.11$; $i = 0.44$.

	K_D' calculated	K_D' experimental	
		Expt. 1	Expt. 2
Ho	44.6	43.7	46.0
Tb	54.8	—	54.1
Gd	63.2	60.3	62.2
Eu	68.4	64.5	67.2
Sm	75.4	72.2	75.2
Ce	110.1	109.1	114.6

This procedure involves the numerical integration of the integral in eqn. (14). The integration interval $(0, \overline{V})$ is split up in n equal smaller intervals:

$$\int_0^{\overline{V}} f(V_x)\mathrm{d}V_x = \int_0^k f(V_x)\mathrm{d}V_x + \int_k^{2k} f(V_x)\mathrm{d}V_x + \cdots + \int_{jk}^{(j+1)k} f(V_x)\mathrm{d}V_x + \cdots + \int_{(n-1)k}^{nk} f(V_x)\mathrm{d}V_x \qquad (15)$$

where $f(V_x)$ obviously represents the integrand in eqn. (14) and $k = \overline{V}/n$.

To each of these intervals the six-point Newton-Cotes' formula is applied:

$$\int_{jk}^{(j+1)k} f(V_x)\mathrm{d}V_x \cong \frac{k}{288} [19f(jk) + 75f(jk + \delta) + 50f(jk + 2\delta) + 50f(jk + 3\delta) + 75f(jk + 4\delta) + 19f(j + 1)k] \qquad :(16)$$

where $\delta = k/5$.

The calculations were performed once with a number $n = 8$ of intervals and once with $n = 16$. From the comparison of both results it appears that splitting up the integration interval in eight smaller intervals is sufficient to obtain a K_D' value with a precision of four figures.

Comparison of calculated and experimental K_D' values

Several R.E. separations were achieved by means of a linear gradient. The K_D' values were predicted by calculation and compared with those experimentally found. The results are shown in Tables II–IV.

Discussion

From the results in Tables II–IV it appears that the described calculation method allows a reasonably accurate prediction of K_D' and is thus a useful tool in the planning of R.E. separations or any other separation where $K = f(c)$ is known. Its value is, however, lessened by the large dependence of K_D on the mass of R.E. brought on the column[6]. Therefore only the elution maxima of R.E. traces can be

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL K_D' VALUES

$c_0 = 0$ (250 ml); $c_L = 0.300$ (250 ml); $V_t = 2 \times 250$ ml $= 500$ ml; $Ah = 4.53$; $\varrho = 2.11$; $i = 0.44$.

	K_D' calculated	K_D' experimental
Ho	54.0	50.1
Tb	66.25	59.5
Gd	76.5	69.4
Sm	91.6	83.1
Eu	82.8	74.8
Ce	133	117.5

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL K_D' VALUES

$c_0 = 0.0334$ (550 ml); $c_L = 0.292$ (550 ml); $V_t = 1100$ ml; $Ah = 4.53$; $\varrho = 2.11$; $i = 0.44$.

	K_D' calculated	K_D' experimental		K_D' calculated	K_D' experimental
Lu	42	43	Gd	150	142
Yb	49	48	Eu	168	—
Tm	59	58	Sm	194	184
Er	70	68	Pm	228	214
Ho	84	81	Nd	258	241
Y	94	90	Pr	275	266
Dy	96	—	Ce	312	—
Tb	117	113	La	363	—

predicted. Furthermore to compute the efficiency of the separation one would need to calculate also the shape of the elution peaks.

In the case of the separations in Tables II–IV the apparent number of plates was from 1000 to 5000, while on the same column one obtains only 200 plates when eluting with constant ligand concentrations.

After completing this work, OHASHI AND KOGUCHI[23] and MOLNAR et al.[24] published articles relating to methods of calculation of the position of the elution peaks in gradient elution analysis.

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