ANION EXCHANGE BEHAVIOUR OF LIGHT RARE EARTHS IN AQUEOUS METHANOL SOLUTIONS CONTAINING NEUTRAL NITRATES

I. SEPARATION OF CARRIER-FREE LIGHT RARE EARTHS

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The anion exchange adsorption of the rare earth elements from pure nitric acid solutions has been investigated by DANON[1,2], ICHIKOWA et al.[3] and FARIS AND BUCHANAN[4,5]. It was stated that rare earths are adsorbed only to a slight extent from pure nitric acid solutions on strongly basic anion exchangers of the quaternary amine type. Although their adsorbability increases with decreasing atomic number, it is insufficient to serve as a basis for their anion exchange separation, even in the case of the lightest rare earths. Rare earths have shown, however, an increased adsorbability from concentrated ammonium nitrate solutions[2,6] and from lithium nitrate solutions[7,8]. By using lithium nitrate solutions as an eluent MARCUS AND NELSON[7] succeeded in separating light rare earths by anion exchange chromatography. HAMAGUCHI et al. have stated in their recent work[9] that in particular the light rare earths show excellent anion exchange adsorption from magnesium nitrate solutions.

The anion exchange adsorption of the rare earth elements from nitrate solutions can be promoted considerably by replacing a part of the aqueous phase with a suitable solvent such as methanol[10,11]. Aqueous methanol solutions of nitric acid have already been used for group separation of the rare earths[12] as well as for performing other chromatographic separations[11,13,14].

In our previous work[15] the anion exchange adsorption of gadolinium and europium was investigated in aqueous methanol solutions of neutral nitrates. It was stated that neutral nitrates may in some cases be more advantageously used than nitric acid; *viz.* the employment of neutral nitrates also makes it possible to work at elevated temperatures. It was also demonstrated that anion exchange from a methanolic solution of ammonium nitrate provides a useful method for the separation of carrier-free rare earths lighter than gadolinium from macroamounts of gadolinium. In the present work these investigations are extended to all of the rare earths of the cerium sub-group.

EXPERIMENTAL

Materials

All chemicals were reagent grade and used without purification.

The radioactive isotopes of the rare earths were isolated from a tantalum target irradiated with 680 MeV protons in the Dubna synchro-cyclotron, and were purified

on a Dowex 50X8 (ammonium form) cation exchange resin bed with ammonium α-hydroxyisobutyrate.

In the anion exchange experiments the strongly basic anion exchanger Amberlite IRA-400 (nitrate form) and Dowex 1 (nitrate form) were used.

The alcoholic eluents and sorption solutions were freshly made in all cases and were acidified with nitric acid to 0.01 N

Distribution coefficients

The distribution coefficients were determined by either static or dynamic methods depending on the magnitude of their expected values. In the static experiments 0.05 g (on an oven-dry basis) of Amberlite IRA-400 (nitrate form) was shaken with 1, 2 or 3 ml of the appropriate solution containing radioactive indicator of the investigated element. After attainment of equilibrium the two phases were separated and an aliquot of the solution phase was evaporated on a platinum disk under an infra-red lamp. The radioactivity of the samples was measured with a bell-type GM counter. From the observed counts:

$$K_d = \frac{(a_t - a_l)v}{a_l m} \tag{1}$$

where:

a_t = total radioactivity of the sample;
a_l = equilibrium radioactivity of the solution phase;
v = volume of the solution phase (ml);
m = weight of the resin (g).

In the dynamic experiments the radioactive isotope of the element being investigated was added to a 2 mm × 105 mm anion exchange column in a drop of the appropriate eluent. The eluate was collected drop by drop. The radioactivity of the drops was measured with the aid of an end-window GM counter. From the peak location:

$$K_d = \frac{V_m - V_i}{m} \tag{2}$$

where:

V_m = volume of the effluent to the peak maximum (ml);
V_i = free volume of the column (ml);
m = weight of the resin (g).

Ion exchange separations

The separation of the carrier-free rare earths was investigated on a 2 mm × 105 mm Amberlite IRA-400 (nitrate form)-400 mesh or Dowex 1 (nitrate form)-400 mesh resin bed with the experimental method used for the determination of the distribution coefficients under dynamic conditions. For the separation of the entire cerium sub-group the gradient elution technique was used. The continuous change of the solute concentration was effected with a simple "exponential" mixing system containing a closed mixing chamber and a reservoir. The change of the concentration in such systems may be described by the following eqn.[16]:

$$C_V = C_1 + (C_0 - C_1) \exp(-V/V_0) \tag{3}$$

where:

C_1 = concentration in the reservoir;
C_0 = concentration in the mixing chamber;
V_0 = volume of the mixing chamber.

In anion exchange of the rare earths from methanolic nitrate solutions the eluting power of the eluent may be increased by decreasing the alcohol and/or the nitrate concentration. However, in the experiments described here only the nitrate concentration was changed. If, in accordance with our experiments, C_1 = o then eqn. (3) reduces to the form:

$$C_V = C_0 \exp(-V/V_0) \tag{4}$$

RESULTS AND DISCUSSION

Fig. 1 shows the effect of nitrate concentration on the distribution coefficient of the light rare earths in 65 % methanolic solutions of ammonium nitrate. It may be seen that the logarithm of the distribution coefficients is a linear function of the logarithm nitrate concentration, in the range examined, with a slope of near unity. This means that the variation of the distribution coefficients with nitrate concentration is described by a straight line starting from the origin. Really, a detailed analysis shows that these lines starting from the origin, after a mild curvature, take a linear form. Therefore, with a good approximation:

$$K_d = a[NO_3^-] \tag{5}$$

where a is a constant, which, under given conditions, is characteristic of individual rare earth elements. Values of a and the corresponding separation factors are summarised in Table I.

The variation of the distribution coefficient with nitrate concentration in methanolic solutions of lithium nitrate shows a different character (see Fig. 2). The reason for this has not so far been exactly explained. The main difference between the action of the two cations appears in the experimental fact that in the presence of ammonium ions the separation factor is independent, or changes only to a slight extent, with nitrate concentration while in the presence of lithium ions the separation factor increases significantly with increasing nitrate concentration. Besides, in the case of a medium containing lithium nitrate the distribution coefficients change more rapidly with nitrate concentration than in the case of ammonium nitrate.

TABLE I

VALUES OF a AND SEPARATION FACTOR FOR THE LIGHT RARE EARTHS IN 65 % $CH_3OH-NH_4NO_3-$
IRA 400 SYSTEM AT 20°

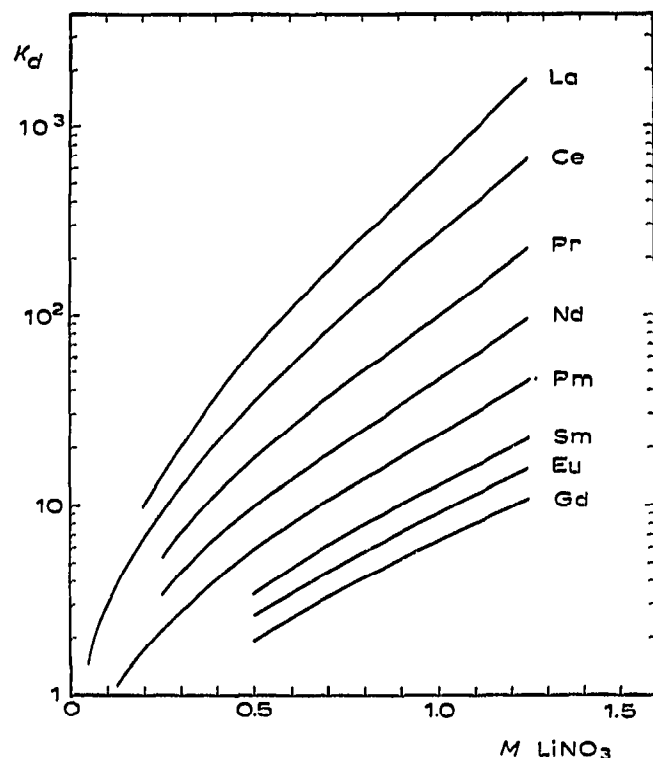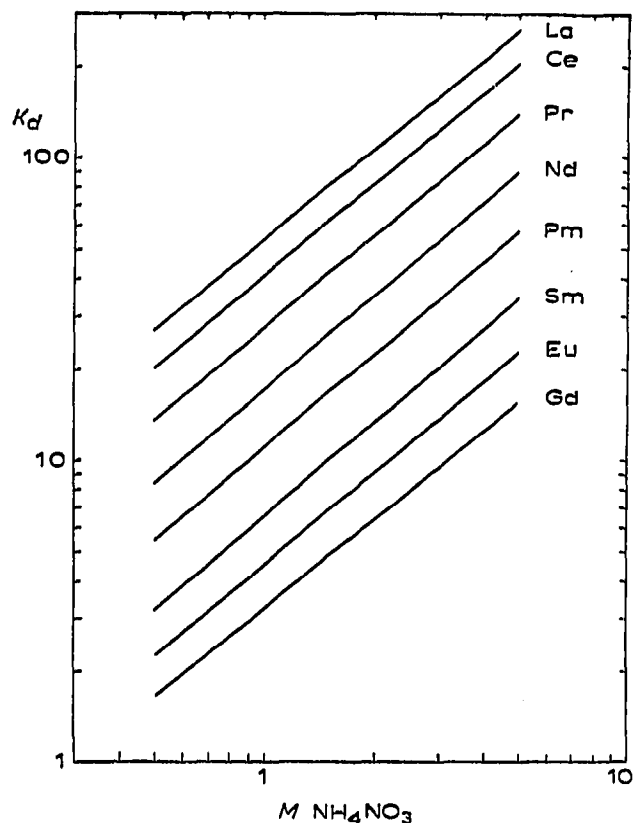| Element	Gd	Eu	Sm	Pm	Nd	Pr	Ce	La
a	3.2	4.5	6.5	11.1	17.3	27.1	40.4	53
Separation factor		1.40	1.44	1.71	1.56	1.56	1.49	1.31

Fig. 1. Variation of distribution coefficients with nitrate concentration in 65 % $CH_3OH-NH_4NO_3-$ IRA 400 system at 20°.

Fig. 2. Variation of distribution coefficients with nitrate concentration in 65 % $CH_3OH-LiNO_3-$ IRA 400 system at 20°.

The distribution coefficients of the light rare earths in 65 % CH_3OH-1 N $LiNO_3-$IRA 400 system at 20°, as well as the corresponding separation factors are shown in Table II.

Figs. 3–6 illustrate the separability of the light rare earth elements. As may be seen, using an eluent of constant eluting strength, adjacent rare earth pairs can be resolved fairly well. The HETP (height equivalent of a theoretical plate) of the column, as calculated from the praseodymium peak in Fig. 3 on the basis of GLUECKAUF's theory[17], is 0.56 mm, while from the neodymium peak in Fig. 4 it is 0.53 mm.

By using gradient elution the whole cerium sub-group can be eluted in about 400 drops (see Figs. 5 and 6). The volume corresponding to 400 drops does not much

TABLE II

VALUES OF DISTRIBUTION COEFFICIENT AND SEPARATION FACTOR FOR THE LIGHT RARE EARTHS IN 65 % CH_3OH-1 N $LiNO_3-$IRA 400 SYSTEM AT 20°

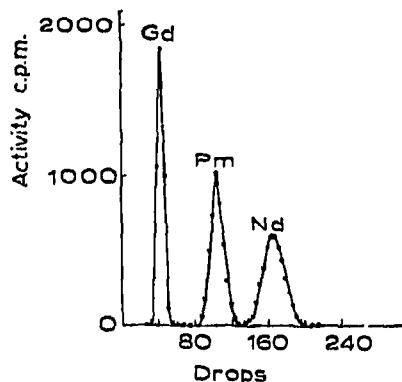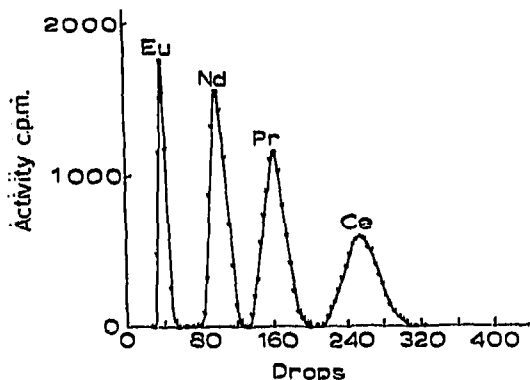| Element	Gd	Eu	Sm	Pm	Nd	Pr	Ce	La
K_d	6.4	9.0	12.5	23.2	45.5	96.6	247	586
Separation factor		1.41	1.38	1.86	1.96	2.12	2.56	2.37

Fig. 3. Separation of carrier-free Eu, Nd, Pr and Ce on a 2 mm × 105 mm Amberlite IRA 400 resin bed at 20°. Eluent: 65% CH_3OH–0.01 N HNO_3–0.5 N NH_4NO_3.

Fig. 4. Separation of carrier-free Gd, Pm and Nd on a 2 mm × 105 mm Amberlite IRA 400 resin bed at 20°. Eluent: 65% CH_3OH–0.01 N HNO_3–0.5 N $LiNO_3$.
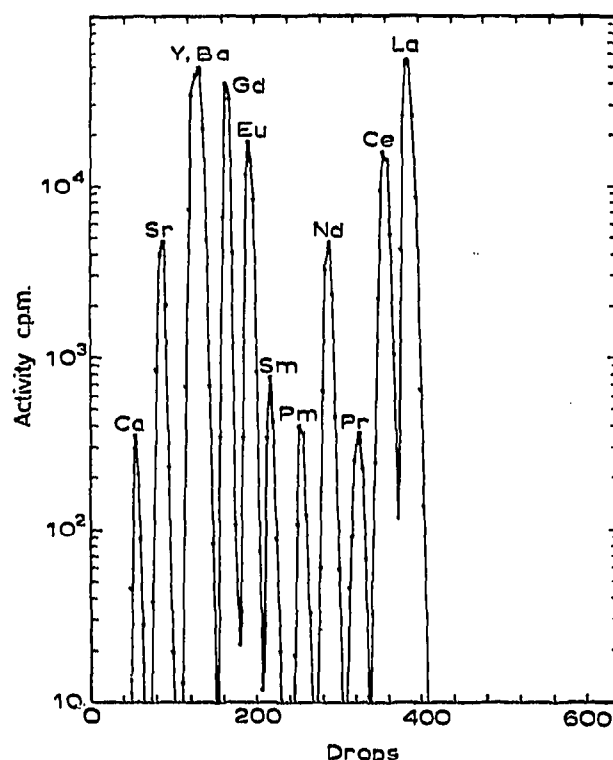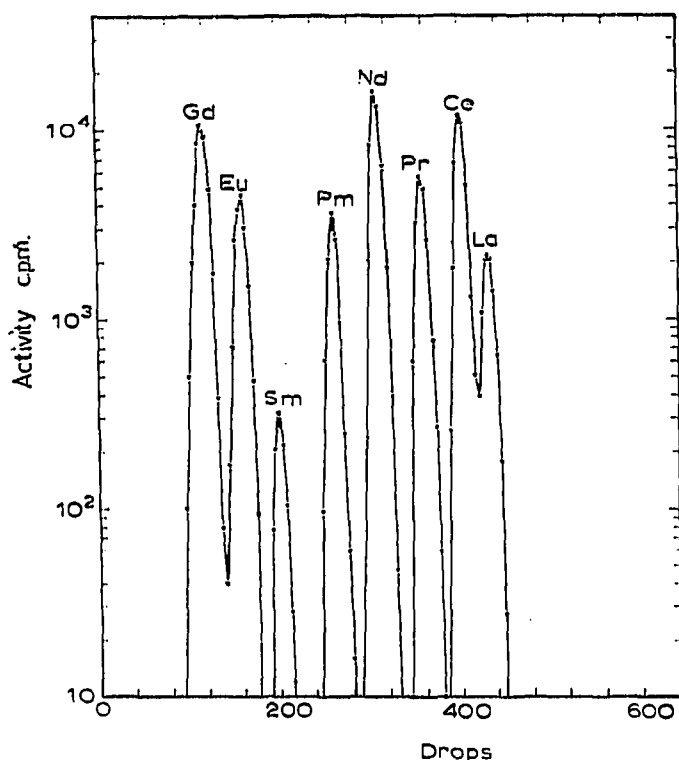
Fig. 5. Separation of carrier-free light rare earths on a 2 mm × 105 mm Amberlite IRA 400 resin bed at 50°. Eluent: 65% CH_3OH–0.01 N HNO_3–2.5 N NH_4NO_3 up to drop 100, after drop 100 gradient elution was employed. V_0 = 2.0 ml, C_0 = 2.5 N.

Fig. 6. Separation of carrier-free light rare earths on a 2 mm × 105 mm Dowex 1 resin bed at 50°. Eluent: 65% CH_3OH–0.01 N HNO_3–$LiNO_3$. Gradient elution. V_0 = 2.0 ml, C_0 = 2.5 N.

exceed the solution volume necessary for the cation exchange separation of the cerium sub-group with ammonium α-hydroxyisobutyrate. The time requirement of the present anion exchange method is about twice that of the separation with isobutyrate. We note that the separations shown in Figs. 5 and 6 were not carried out under absolutely optimal conditions. A better selection of the working conditions would improve the separation of the elements.

In Fig. 6, for the sake of comparison, the elution peaks of calcium, strontium and barium are also indicated. It can be seen that these elements, under the given elution conditions, are eluted before the gadolinium and can be separated as well. In systems containing ammonium nitrate instead of lithium nitrate their separation is hardly feasible. Under the experimental conditions corresponding to Fig. 6 barium and yttrium are eluted simultaneously. However, at room temperature barium and yttrium appear in two sharply isolated bands. The reason is that the distribution coefficient of the barium increases more rapidly with decreasing temperature than that of yttrium.

Prediction of peak locations in gradient elution

The simplicity of function (5) makes it possible to predict peak locations in gradient elution carried out with a methanolic solution of ammonium nitrate.

It follows from the elution theories that the distance l travelled by an adsorbate peak under the action of an eluent volume v is:

$$l = \frac{v}{AD} \tag{6}$$

where A is the cross-sectional area of the column and D is the volume distribution coefficient. This relationship is valid also for arbitrarily small eluent volumes and column section. Suppose that the adsorbate to be contained in a thin layer at the top of the resin bed is eluted in n steps. Let:

Δv_k = volume of eluent k;
Δl_k = distance travelled by the peak under the action of eluent k;
Δv_{tk} = free volume corresponding to Δl_k;
L = total length of the column;
V_m = effluent volume at the peak maximum;
V_t = free volume of the resin bed;
V_t = total eluent volume;
V_a = total bed volume;
m = weight of the resin in the column.

Under the effect of a volume Δv_1 of the first eluent the adsorbate moves down the column a distance Δl_1:

$$\Delta l_1 = \frac{\Delta v_1}{AD_1}$$

When the boundary between the first and second eluent and the peak meet at a distance Δl_1 from the top of the column, a solution of volume $\Delta v_1 + \Delta v_{t1}$ has al-

ready passed through the column. Similarly, the distance travelled by the peak under the action of the second eluent is:

$$\Delta l_2 = \frac{\Delta v_2}{AD_2}$$

and the volume of the solution leaving the column at the time when the peak and the boundary between the second and third eluent meet is given by:

$$\Delta v_2 + \Delta v_{i2}$$

Generally, for eluent k:

$$\Delta l_k = \frac{\Delta v_k}{AD_k}$$

and:

$$\Delta v_k + \Delta v_{ik}$$

By employing the above considerations for the whole length of the column the following result is obtained:

and:

$$\left.\begin{array}{l} L = \sum\limits_{k=1}^{n} \Delta l_k = \frac{1}{A} \sum\limits_{k=1}^{n} \frac{\Delta v_k}{D_k} \\[2mm] V_m = \sum\limits_{k=1}^{n} (\Delta v_k + \Delta v_{ik}) = V_t + V_i \end{array}\right\} \qquad (7)$$

In the case of gradient elution the concentration of the eluent changes continuously. Therefore:

$$L = \frac{1}{A} \int_0^{V_m - V_i} \frac{\mathrm{d}V}{D(V)} \qquad (8)$$

where the distribution coefficient $D(V)$ is a function of the eluent volume entering into the column.

Taking now into consideration the relationship, $D(V) = K_d(V)m/V_a$, between the distribution coefficient $D(V)$ and $K_d(V)$, eqn. (8) takes the form:

$$m = \int_0^{V_m - V_i} \frac{\mathrm{d}V}{K_d(V)} \qquad (9)$$

If the variation of K_d with eluent volume is known in a given system, eqn. (9) may be integrated and effluent volume at the peak calculated.

In our special case in which light rare earths are separated with methanolic solution of ammonium nitrate using the simple mixing system mentioned above, the function for $K_d(V)$ can be obtained from eqns. (4) and (5):

$$K_d(V) = aC_0 \exp (-V/V_0) \qquad (10)$$

From eqns. (9) and (10), after integrating, the effluent volume V_m corresponding to the peak maximum, is given by:

$$V_m = V_i + V_0 \ln \left(\frac{aC_0 m}{V_0} + 1 \right) \tag{11}$$

If the values of the constant a, relating to the individual rare earths, are known for a given resin, temperature and methanol content, with the aid of eqn. (11) the probable position of the elution peaks can be calculated, supposing that the elution is carried out under the same conditions. Fig. 7 shows a comparison of the calculated values with the experimental results. For the calculations the data of Fig. 1 were used. Although in all cases the calculated values are smaller than the experimental ones, the agreement is very good; the difference between the calculated and experimental values does not exceed 5 %.
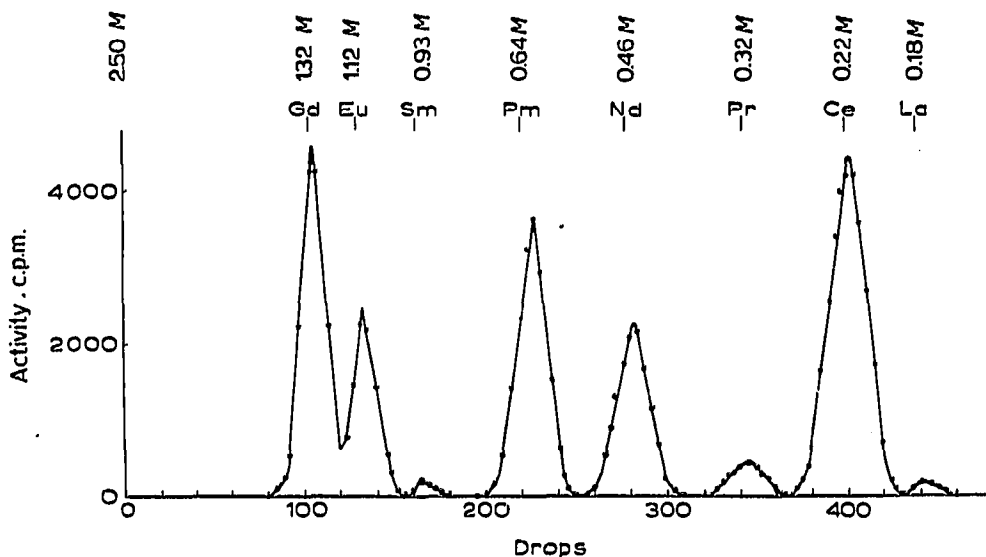

Fig. 7. Comparison of experimental peak locations with calculated values. 2 mm × 105 mm Amberlite IRA 400 resin bed. t = 20°. Eluent: 65 % CH_3OH–0.01 N HNO_3–NH_4NO_3. Gradient elution. $V_0 = 2.0$ ml, $C_0 = 2.5$ N.

Determination of distribution coefficients by means of the gradient elution technique

By using the inverse of the above treatment employed for the calculation of peak locations, the functions $K_d(C)$ of the individual elements are obtained. The elements being investigated are separated by gradient elution. From the peak positions the constants a can be calculated by:

$$a = \frac{V_0}{C_0 m} [\exp (V_m - V_i) / V_0 - 1] \tag{12}$$

This method requires much less time than the other methods of distribution coefficient determination. Since the position of the peaks can be very well reproduced the precision of the method depends mainly on the accuracy of the determination of V_i and V_m. The determination of V_i, in the case of the column used by us, is possible

TABLE III

VALUES OF a AND SEPARATION FACTOR FOR THE LIGHT RARE EARTHS IN 80 % $CH_3OH-NH_4NO_3-$
IRA 400 SYSTEM AT 20°
Determined by the gradient elution technique.

Element	Gd	Eu	Sm	Pm	Nd	Pr	Ce	La
a	17.2	26.1	42.0	81.4	156	330	631	1065
Separation factor		1.52	1.61	1.94	1.92	2.12	1.91	1.69

within ± 3–5 %. The accuracy of the determination of V_m depends on a number of different factors. Fortunately, the variation of the drop volume with nitrate concentration is negligible. Therefore the variation of the nitrate concentration in gradient elution, from this point of view, may be neglected.

In Table III, values of a, determined by the gradient elution technique, and the corresponding separation factors are shown. The relationship for K_d, drawn using the data of Table III, is shown in Fig. 8. The individual experimental points in
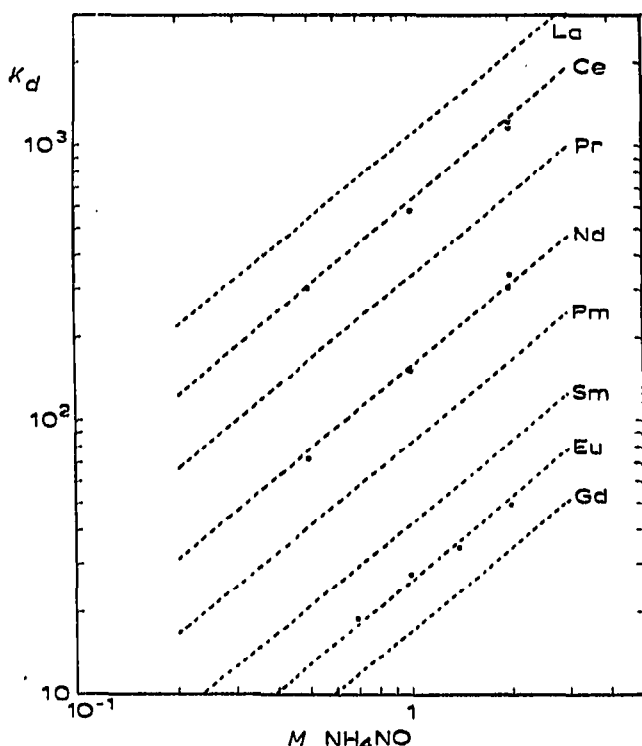

Fig. 8. Variation of distribution coefficients with nitrate concentration in 80 % $CH_3OH-NH_4NO_3-$IRA 400 system as calculated by eqn. (12).

Fig. 8 were obtained by the methods described in the "Experimental". As may be seen, the experimental points approach fairly well the corresponding curves; the differences do not exceed the spread observable with other methods for the distribution coefficient determinations.

SUMMARY

The anion exchange adsorption and separation of the cerium sub-group rare earths were investigated in $CH_3OH-NH_4NO_3-IRA$ 400, $CH_3OH-LiNO_3-IRA$ 400 and $CH_3OH-LiNO_3-Dowex$ 1 systems. It was shown that in aqueous methanol solutions of ammonium nitrate the distribution coefficients of the light rare earths are linear functions of the nitrate concentration. Based on this, a simple scheme for the calculation of the probable location of the peaks in gradient elution, as well as a method for the determination of the distribution coefficients by means of gradient elution are presented.

REFERENCES

1 J. DANON, *J. Inorg. Nucl. Chem.*, 5 (1958) 237.
2 J. DANON, *J. Inorg. Nucl. Chem.*, 7 (1958) 422.
3 F. ICHIKOWA, S. URUNO AND H. IMAI, *Bull. Chem. Soc. Japan*, 34 (1961) 952.
4 J. P. FARIS AND R. F. BUCHANAN, *Anal. Chem.*, 36 (1964) 1157.
5 R. F. BUCHANAN AND J. P. FARIS, *Conf. Use Radioisotopes Phys. Sci. and Ind., Copenhagen, 1960*, Paper RICC-173.
6 K. A. KRAUS AND F. NELSON, *Symp. Ion Exchange Chromatog. Anal. Chem., 1956*, Am. Soc. for Testing Materials, Spec. Pub. No. 195.
7 Y. MARCUS AND F. NELSON, *J. Phys. Chem.*, 63 (1959) 77.
8 Y. MARCUS AND I. ABRAHAMER, *J. Inorg. Nucl. Chem.*, 22 (1961) 141.
9 H. HAMAGUCHI, I. HIKAWA AND K. KURODA, *J. Chromatog.*, 18 (1965) 556.
10 J. KORKISCH AND F. TERA, *Anal. Chem.*, 33 (1961) 1265.
11 J. P. FARIS AND J. W. WARTON, *Anal. Chem.*, 34 (1962) 1077.
12 R. A. EDGE, *Anal. Chim. Acta*, 29 (1963) 321.
13 J. S. FRITZ, H. WAKI AND B. B. GARRALDA, *Anal. Chem.*, 36 (1964) 900.
14 V. A. BOCHKAREV AND E. N. VOEWODIN, *Radiokhimiya*, 7 (1965) 461.
15 F. MOLNÁR, A. HORVÁTH, V. A. KHALKIN AND V. A. VOLKOV, *JINR Preprint, E-1921*, Dubna, 1964; *Radiokhimiya*, 8 (1966) 183.
16 B. DRAKE, *Arkiv Kemi*, 8 (1955) 1.
17 E. GLUECKAUF, *Trans. Faraday Soc.*, 51 (1955) 34.