

THE SEPARATION OF THE LANTHANIDES AND YTTRIUM BY CATION EXCHANGE ELUTION WITH AMMONIUM α -HYDROXYISOBUTYRATE AND LACTATE

H. DEELSTRA AND F. VERBEEK

Laboratory for Analytical Chemistry, University of Ghent (Belgium)

(Received July 24th, 1964)

INTRODUCTION

The use of ammonium α -hydroxyisobutyrate solutions for rare earth separations has been discussed by several investigators¹⁻⁵. Comparison of the relative separation factors with other eluants indicates that this eluant is so far the best².

The degree of separation for an experimental arrangement depends on variables such as temperature, type and size of the cation exchange resin particles, flow rate of the eluting agent, dimensions of the column, but for a given eluting agent the relative position of the various rare earth metals remains approximately constant. However, no attention has been given to the influence on the separation degree of the addition of an indifferent electrolyte to the eluant. The approach has been to utilize the data from elutions with and without addition of an indifferent electrolyte (in this case ammonium perchlorate), to obtain more information on the complexes present in the effluent solutions.

Since preliminary experiments indicated that the separation at 80° was not much better than at room temperature, these investigations were made at 25.0° \pm 0.1°. Only trace quantities of the lanthanides were used.

EXPERIMENTAL

Reagents and apparatus

Ion exchange resin. Dowex 50-WX 8, 200-400 mesh, was washed twice with 6 M HCl, to remove iron, and afterwards with distilled water. The colloid particles were decanted off. The resin was converted into the ammonium form with 6 M ammonium hydroxide, washed and stored in distilled water until the column was loaded.

Elution agent. Aqueous solutions of α -hydroxyisobutyric acid (Fluka) and lactic acid (BDH) were adjusted to a fixed pH value by addition of concentrated ammonium hydroxide. Commercial lactic acid often exists partially as a lactone dimer². To convert it completely to the free acid form, an aqueous solution of the lactic acid was neutralized with sodium hydroxide. The acid was regenerated by passing the solution through a bed of cation exchange resin in the hydrogen form where the sodium ions are replaced by hydrogen ions.

Tracers. The lanthanide isotopes used were obtained by neutron irradiating

of the Johnson, Matthey & Co. "spec-pure" oxides in the BR-1 reactor at a flux of $10^{12} \text{ n} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2}$.

Column. Resin columns of about 3 mm diameter and 15–20 cm in length were used. The column was surrounded by a water jacket and thermostated at $25.0^\circ \pm 0.1^\circ$.

Registration apparatus. The experiments were carried out using an apparatus similar to the one described by SPEECKE AND HOSTE⁶.

Procedure

Column experiments. The resin column was packed by pouring an aqueous slurry of the resin, previously degassed, into the column. Before each experiment, the column was washed with the eluant until the pH of the effluent and eluant were identical. The lanthanide tracers were gently placed on the top of the column and the eluant was carefully introduced to start elution. A flow rate of approximately $0.75 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ was used in all runs.

The distribution coefficients were calculated according to the method described by KRAUS AND MOORE^{7,8}.

Equilibrium experiments. The distribution coefficients K_D were also determined by equilibrium studies under conditions similar to the column experiments. K_D is defined by the expression⁶:

$$K_D = \frac{\text{activity/g resin}}{\text{activity/ml solution}} = \frac{S - E}{E} \cdot \frac{\text{ml}}{\text{g}} \quad (1)$$

where: S = activity of the solution before equilibration,

E = activity of the solution after equilibration with the resin.

The solutions of the ligand and the tracer were added in 50 ml conical flasks. Resin portions of 100 mg were weighed accurately and transferred. The flasks were agitated for 15 h in a constant temperature bath at $25.0 \pm 0.1^\circ$.

Identification. The lanthanide isotopes in the effluent were identified by taking γ -spectra with an Intertechnique 400 S.A. multichannel spectrometer or by following the half-lives by γ -counting, using a NaI(Tl) well-type scintillation detector coupled to a Tracerlab superscaler.

RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the distribution coefficients *versus* pH, using solutions of the ammonium salt of α -hydroxyisobutyric acid as eluant, 0.1 and 0.3 M respectively, without the indifferent electrolyte.

Since the concentration of the isobutyrate ion determines the elution volume and thus the distribution coefficients, these are plotted in Fig. 3 against the $\text{pL} = -\log [\text{L}^-]$ values. The anion concentration at each pH and molarity was calculated from the ionization constant of the α -hydroxyisobutyric acid: $K_A = 1.29 \cdot 10^{-4}$ and $1.33 \cdot 10^{-4}$ respectively for 0.1 M and 0.3 M of the acid⁹. The results using 1 M ammonium salt solutions of lactic acid as eluting agent are represented in Fig. 4.

The influence of increasing ionic strength on the distribution coefficient is shown in Table I. The K_D values are determined for approximately the same $[\text{L}^-]$ values using increasing amounts of ammonium perchlorate. The data for the ionization constants (column 4) are given elsewhere⁹.

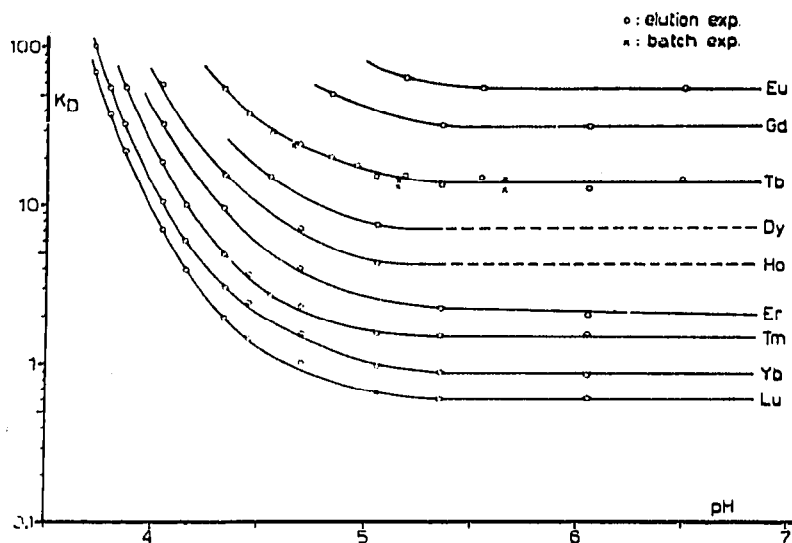


Fig. 1. Distribution coefficients *vs.* pH using 0.1 *M* ammonium α -hydroxyisobutyrate without indifferent electrolyte.

Since the stability constants of the lanthanides have been determined with α -hydroxyisobutyrate and lactate ligands in 0.2 *M* sodium perchlorate solution, a series of elution experiments in ammonium perchlorate was also performed. The results of these elutions (with 0.2 *M* ammonium perchlorate and 0.1 *M* α -hydroxyisobutyric acid) are plotted in Fig. 5.

Some points in Figs. 1 and 5 were checked by equilibrium experiments.

Because uni-negative tetra-ligand complexes are formed between the trivalent lanthanide ions and the α -hydroxyisobutyrate or lactate ions, the distribution coefficient is defined by:

$$K_D = \frac{\sum [M]_{\text{resin}}}{\sum [M]_{\text{solution}}} = \frac{[M^{3+}]_R + [ML^{2+}]_R + [ML_2^+]_R}{[M^{3+}] + [ML^{2+}] + [ML_2^+] + [ML_3] + [ML_4^-]} \quad (2)$$

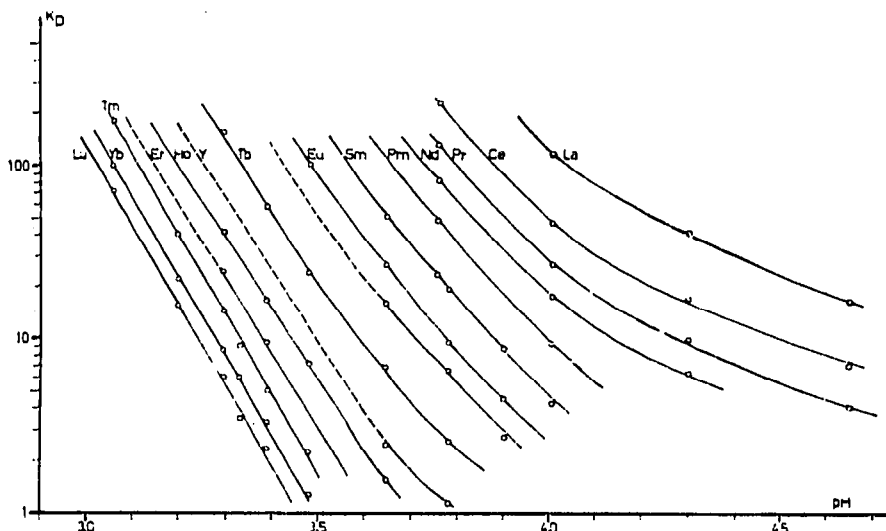


Fig. 2. Distribution coefficients *vs.* pH using 0.3 *M* ammonium α -hydroxyisobutyrate without indifferent electrolyte.

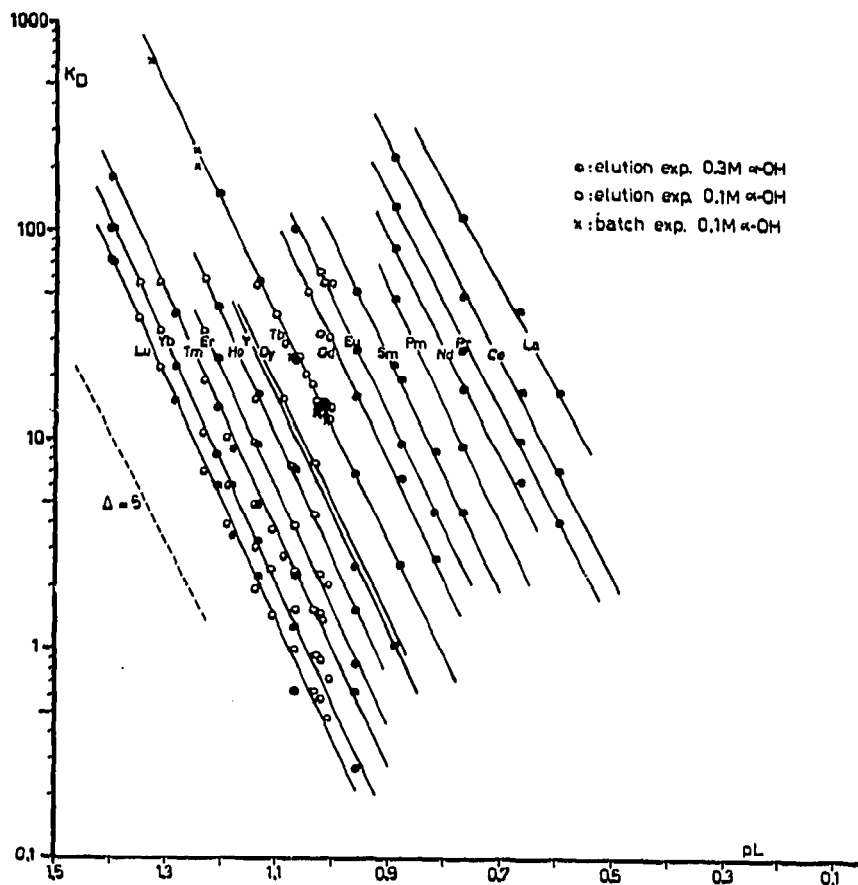


Fig. 3. Distribution coefficients *vs.* α -hydroxyisobutyrate concentration, without indifferent electrolyte.

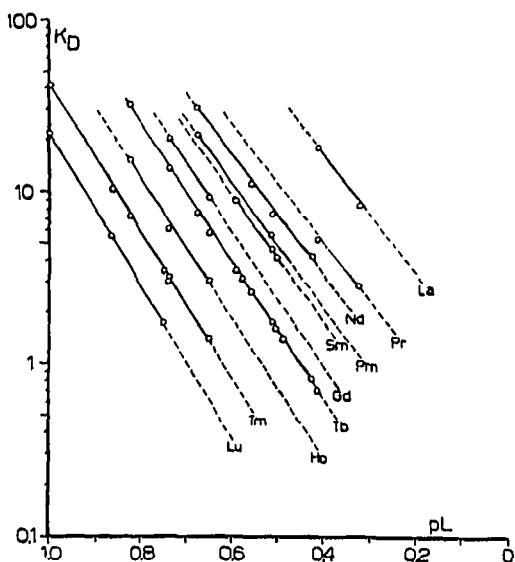


Fig. 4. Distribution coefficients *vs.* lactate concentration, without indifferent electrolyte.

TABLE I

INFLUENCE OF THE IONIC STRENGTH ON THE DISTRIBUTION COEFFICIENTS OF THE THULIUM- α -HYDROXYISOBUTYRATE COMPLEX SYSTEM

Moles NH_4ClO_4	Moles acid	pH	pK_A	$[L^-]$	I_{total}	K_D
—	0.1	3.16	3.885	0.0158	0.016	29,060
0.001	0.1	3.16	3.88	0.0160	0.017	25,815
0.01	0.1	3.16	3.875	0.0162	0.026	9,727
0.01	0.3	2.62	3.865	0.0161	0.026	8,510
0.025	0.1	3.12	3.865	0.0152	0.040	3,352
0.05	0.1	3.16	3.845	0.0171	0.067	1,057
0.075	0.3	2.57	3.82	0.0160	0.091	471
0.1	0.1	3.12	3.81	0.0169	0.117	280
0.1	0.3	2.55	3.80	0.0160	0.116	260
0.2	0.1	3.12	3.80	0.0174	0.217	35

However, in an investigation¹⁰ of some lanthanide- α -hydroxyisobutyrate complexes using FRONAEUS' cation exchange method¹¹ it was shown that the adsorption of positively charged complexes on the resin is very uncertain in the examined $[L^-]$ -concentration range, amongst other reasons because the adsorption of $M^{3+} \gg ML^{2+} \gg ML_2^+$.

Moreover these experiments were carried out in such a pL range that, according

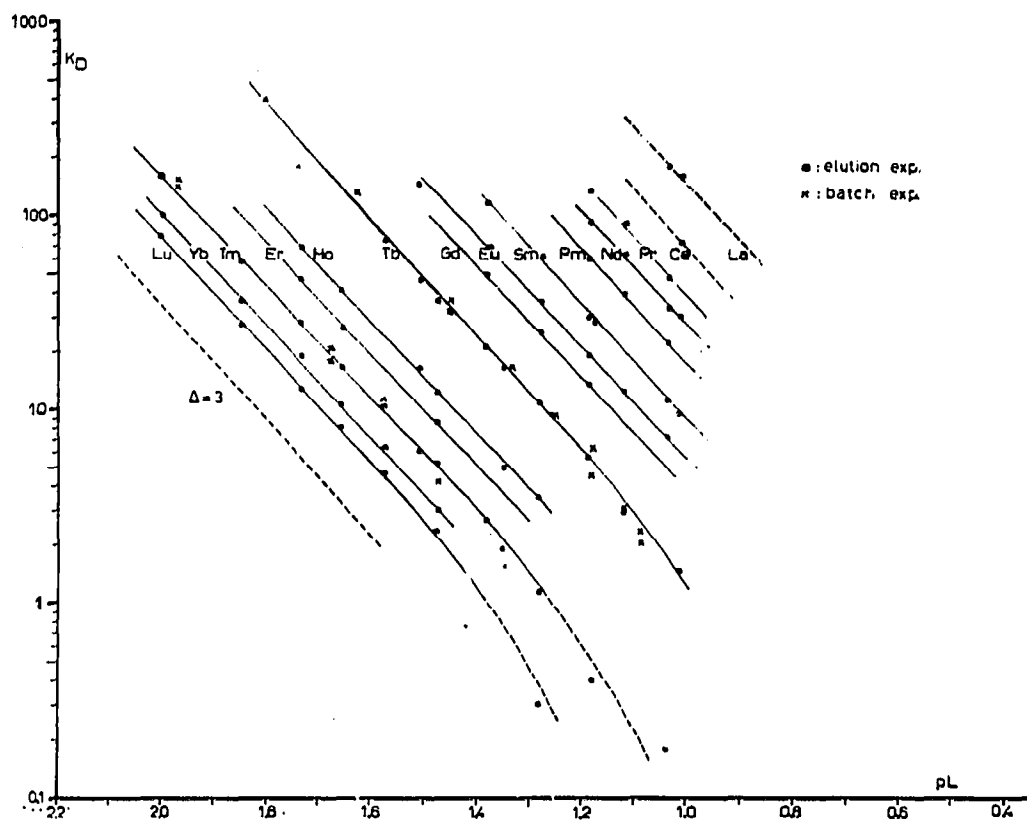


Fig. 5. Distribution coefficients vs. α -hydroxyisobutyrate concentration, in presence of 0.2 M ammonium perchlorate.

to the distribution of the complexes calculated from the stability constants, mainly ML_3 and ML_4^- complexes are formed¹². Consequently equation (2) becomes in the pL range investigated:

$$K_D \cong \frac{[M^{3+}]_R}{[M^{3+}] + [ML^{2+}] + [ML_2^+] + [ML_3] + [ML_4^-]} \quad (3)$$

Substituting ML^{2+} , ML_2^+ , ... by the respective stability constants:

$$\beta_n = \frac{[ML_n^{3-n}]}{[M^{3+}][L^-]^n} \quad (4)$$

gives:

$$K_D \cong \frac{[M^{3+}]_R}{[M^{3+}] \left(1 + \sum_{n=1}^4 \beta_n [L^-]^n \right)} \quad (5)$$

If one species is predominant in solution, the slope of a log-log plot is given by:

$$\frac{d \log K_D}{d \log [L^-]} = -n \quad (6)$$

This slope gives in fact the average number of ligands bound per metal ion. The value of $d \log K_D / d \log [L^-]$ in Fig. 3 is approximately -5 between the pL values from 0.5 to 1.4, which would lead to the assumption that the complexes in the solution present would be of the form ML_5^{2-} . These doubly charged complexes ought to be excluded from a consideration of steric factors¹³ and also from calculations using the stability constants determined by potentiometric titration¹². The deviation of the slope from -4 (complexes ML_4^-) in the absence of indifferent electrolyte is probably due to the fact that the activity coefficients do not remain constant as an effect of changing ionic strength in function of pL. The slope found by SMITH AND HOFFMAN³ using 0.5 *M* and 1 *M* solutions of the ammonium salt of α -hydroxyisobutyric acid as eluant is of the same order. HOLM and coworkers¹³ found also by anion exchange and electromigration experiments in 0.3–0.5 *M* acid that ML_4^- complexes are predominant.

Column experiments using 1 *M* ammonium lactate solutions without indifferent electrolyte (Fig. 4) give a $d \log K_D / d \log [L]$ plot with a negative slope also larger than 4, between the pL values from 0.3 to 1.0, indicating the existence of ML_4^- complexes.

However, the composition of the complexes determined from column experiments using α -hydroxyisobutyrate and lactate solutions at a constant ionic strength agrees with the composition derived from potentiometric data. The slope of the log-log plot (Fig. 5) is approximately -3 in the pL range between 1.0 and 2.0. Essentially ML_3 complexes are formed, as can also be calculated from the stability constants¹². This is also proved by calculating the stability constants β_3 from the experimental K_D values¹⁰ using SCHUBERT'S method¹⁴. These constants are in good agreement with those determined by potentiometric titration¹².

A summary of the separation of the lanthanides and yttrium is reproduced in Table II. For each eluant, column A gives the separation factor of two adjacent lanthanides with atomic numbers Z and $Z + 1$: K_D^Z/K_D^{Z+1} . Column B gives the K_D values relative to gadolinium with $K_D^{\text{Gd}} = 1.0$.

The values of column B and also the separation factors calculated from the stability constants are plotted *versus* the atomic numbers in Fig. 6. The separation factor of two adjacent lanthanides, x and y , is given by:

$$\alpha_{y^x} = \frac{K_{D_0}^x \cdot \beta_n^y}{K_{D_0}^y \cdot \beta_n^x} \cong \frac{\beta_n^y}{\beta_n^x} \quad (7)$$

where β_n^x and β_n^y are the stability constants of the complexes involved. According to POWELL AND SPEDDING¹⁵ the ratio of the K_{D_0} values for adjacent pairs of lanthanides would be less than 1.08. Similar conclusions can be drawn from distribution data of SURLS AND CHOPPIN¹⁰. The constants β_3 and β_4 were used in the calculations,

TABLE II

SEPARATION EFFICIENCY OF THE LANTHANIDES AND YTTRIUM BY CATION EXCHANGE ELUTION WITH α -HYDROXYISOBUTYRATE AND LACTATE SOLUTIONS

Element	α -Hydroxyisobutyrate				Lactate	
	With 0.2 M NH_4ClO_4		Without NH_4ClO_4		Without NH_4ClO_4	
	A	B	A	B	A	B
Lu		0.0275		0.013		0.070
Yb	1.345	0.037	1.54	0.020	—	—
Tm	1.57	0.058	1.70	0.034	—	0.15
Er	1.66	0.096	1.71	0.058	—	—
Ho	1.47	0.141	1.73	0.100	—	0.335
Dy	—	—	1.80	0.180	—	—
Tb	—	—	2.30	0.180	—	—
Tb	2.23	0.45	2.40	0.42	1.45	0.69
Gd	1.40	1.00	1.65	1.00	—	1.00
Eu	1.64	1.40	1.88	1.65	—	—
Sm	1.92	2.30	2.13	3.10	1.19	1.60
Pm	1.59	4.40	1.54	6.60	1.40	1.90
Nd	1.43	7.0	1.68	10.15	1.70	2.70
Pr	1.75	10.0	1.85	17.00	—	4.60
Ce	2.06	17.5	1.97	31.50	—	—
La		36.0		62.00	—	14.26
Y		—		0.16	—	—

respectively for the experiments with 0.2 *M* and without ammonium perchlorate.

The best eluant, as far as separation factors are concerned, is the one whose curve has the greatest slope. The improvement obtained with α -hydroxyisobutyrate as eluant in regard to lactate solutions is a result of the increase in complex stability

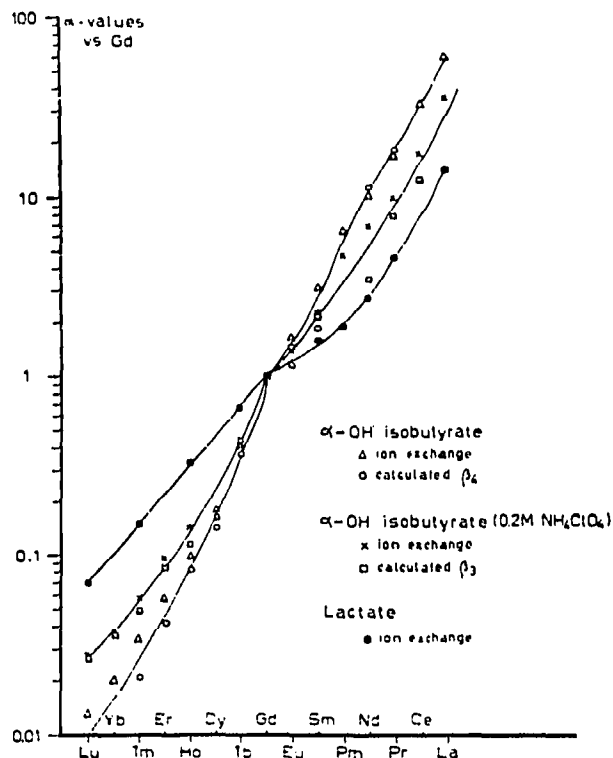


Fig. 6. Elution position of the lanthanides relative to gadolinium, determined by ion exchange measurements and by calculation from the stability constants of the respective complexes.

due to the increase of the inductive effect of the substitution of hydrogen by a methyl group in the α -carbon position¹⁷. Further introduction of larger alkyl groups does not seem to improve the separation efficiency¹⁸.

The addition of ammonium perchlorate appears to have a definite adverse effect on the separation. As practical separation of the lanthanides is only possible for K_D values less than approximately 200, it is necessary to perform elution experiments at higher pL ranges, when working at higher ionic strengths. Consequently there are less ligands bound per metal ion and the apparent stability constants, and also the separation factors α , decrease. In solutions without ammonium perchlorate the elutions are performed in a pL range approximately from 0.5 to 1.3 where mainly ML_4^- complexes occur, and in solutions with 0.2 *M* ammonium perchlorate added in a pL range approximately from 1.0 to 2.2 where mainly ML_3 complexes are formed.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Prof. Dr. J. HOSTE for his kind interest in this work, and to Mrs. F. VAN DEN ABEELE and Mrs. J. GORLÉE for technical assistance.

This investigation has partly been sponsored by the "Interuniversitair Instituut voor Kernwetenschappen", Belgium.

SUMMARY

The separation of the lanthanides and yttrium by cation exchange elution from Dowex-50 WX resin columns with α -hydroxyisobutyrate and lactate solutions has been investigated with and without addition of ammonium perchlorate. Addition of an indifferent electrolyte to the eluant decreases the practical separation efficiency. This phenomenon can be explained from complex formation data. From the variation of the logarithm of the distribution coefficient as a function of the logarithm of the ligand concentration, $[L^-]$, in absence of an indifferent electrolyte, no valid conclusion can be drawn concerning the complexes formed in solution, contrary to the measurements in presence of an indifferent electrolyte.

REFERENCES

- 1 G. R. CHOPPIN, B. G. HARVEY AND S. G. THOMPSON, *J. Inorg. Nucl. Chem.*, 2 (1956) 66.
- 2 G. R. CHOPPIN AND R. J. SILVA, *J. Inorg. Nucl. Chem.*, 3 (1956) 153.
- 3 H. L. SMITH AND D. C. HOFFMAN, *J. Inorg. Nucl. Chem.*, 3 (1956) 243.
- 4 K. E. SEYB AND G. HERMANN, *Z. Electrochem.*, 64 (1960) 1065.
- 5 D. L. MASSART AND J. HOSTE, *Anal. Chim. Acta*, 28 (1963) 378.
- 6 A. SPEECKE AND J. HOSTE, *Talanta*, 2 (1959) 332.
- 7 K. A. KRAUS AND G. E. MOORE, *J. Am. Chem. Soc.*, 71 (1949) 3855; 72 (1950) 4293; 73 (1951) 9, 13, 2900.
- 8 K. A. KRAUS, F. NELSON AND G. W. SMITH, *J. Phys. Chem.*, 58 (1954) 11.
- 9 H. DEELSTRA AND F. VERBEEK, *Bull. Soc. Chim. Belg.*, 72 (1963) 612.
- 10 H. DEELSTRA AND F. VERBEEK, *Bull. Soc. Chim. Belg.*, 73 (1964) 597.
- 11 S. FRONAEUS, *Acta Chem. Scand.*, 5 (1951) 859; 6 (1952) 1200.
- 12 H. DEELSTRA AND F. VERBEEK, *Anal. Chim. Acta*, 31 (1964) 251.
- 13 L. W. HOLM, G. R. CHOPPIN AND D. MOY, *J. Inorg. Nucl. Chem.*, 19 (1961) 251.
- 14 J. SCHUBERT, *J. Phys. Colloid Chem.*, 52 (1948) 340.
- 15 J. E. POWELL AND F. H. SPEDDING, *Chem. Eng. Progr. Symp. Ser.*, 55, No. 24 (1959) 101.
- 16 J. P. SURLS AND G. R. CHOPPIN, *J. Am. Chem. Soc.*, 79 (1957) 855.
- 17 G. R. CHOPPIN AND J. A. CHOPOORIAN, *J. Inorg. Nucl. Chem.*, 22 (1961) 97.
- 18 L. EECKHAUT, F. VERBEEK, H. DEELSTRA AND J. HOSTE, *Anal. Chim. Acta*, 30 (1964) 369.

J. Chromatog., 17 (1965) 558-566