SEPARATION OF RARE EARTHS ON ANION EXCHANGE RESINS

II. ANION EXCHANGE BEHAVIOUR OF THE RARE EARTH COMPLEXES WITH ETHYLENEDIAMINETETRAACETIC ACID*

JERZY MINCZEWSKI AND RAJMUND DYBCZYŃSKI

Analytical Chemistry Division of the Institute of Nuclear Research of the Polish Academy of Sciences, Warsaw (Poland)

The history of the separation of the rare earth elements is closely related to the development of ion exchange chromatography. Separation on cation exchange resins by elution with the aid of complexing agents[1-3] was fully investigated by several authors and has already become a standard method of identification and isolation for pure lanthanides and actinides[4]. The behaviour of rare earths on anion exchange resins has until now been little investigated, probably because of the weak tendency of these metals to form complexes with inorganic ligands. Lanthanides are not absorbed by strongly basic anion exchange resin from solutions in HCl[5], or from solutions in HNO_3 and H_2SO_4, over a whole range of concentrations[6]. Only a rather weak sorption was observed from solutions of such salts as sulphites[7], sulphates, thiosulphates, nitrites and nitrates[8], and thiocyanates[9]. Rare earth elements form strong complexes, mostly of negative charge, with several organic ligands. This fact opens up the possibility of separating lanthanides on anion exchange resins. As is known, in citrate solutions of pH 1.8–2.1 the sequence of elution from the anion exchange resin in citrate form is in concordance with the order of increasing atomic number[10,11]. A similar sequence has been obtained in the case of elution of lanthanides with 0.13 M citric acid from Dowex-1 anion exchange resin in the form of disodium ethylenediaminetetraacetate (Na_2H_2Y)[12]. When using a Na_2H_2Y solution adjusted to pH 11.7 and Dowex-1 resin (pretreated with the same solution) HIGGINS AND BALDWIN[13], however, ascertained that yttrium is eluted before europium, as in the case of elution from cation exchange resins.

In earlier work[14] it was found that when Na_2H_2Y solution in acetate buffer of pH 3.6 and Amberlite IRA-400 anion exchange resin pretreated with the same solution were used, cerium was separated from promethium, cerium appearing first in the eluate. An attempt was made to explain this sequence of elution from the point of view of the stability constants of the rare earth complexes with ethylenediaminetetraacetic acid (H_4Y), which—as is known[15]—increase monotonically from lanthanum to lutecium. Further investigations[16] carried out as static equilibrations as well as

column experiments have corroborated the fact that in this system the distribution coefficients of the lanthanides of the cerium group increase as the atomic numbers increase: La < Ce < Pm < Eu. Yet, the separation factor (the ratio of the distribution coefficients of two elements) has proved to be almost independent of the pH value (Fig. 1). This indicates that an agent other than the differences between the
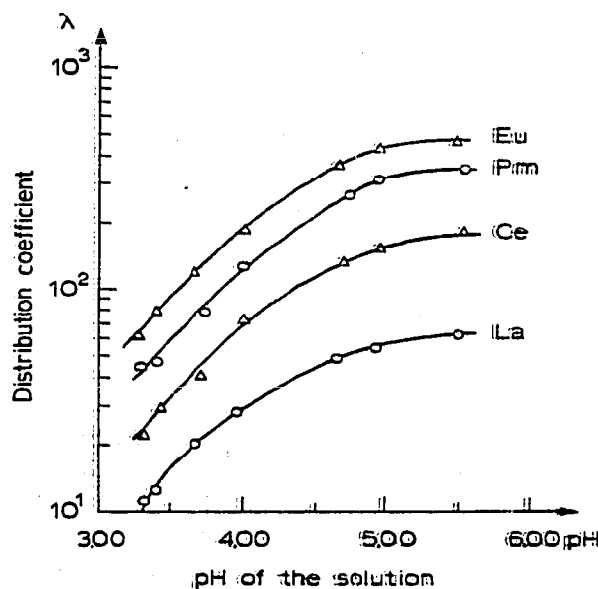

Fig. 1. Distribution coefficients of some lanthanides as a function of the pH of the solution. Solution: 0.02 M Na_2H_2Y, 0.02 M CH_3COONa, x M CH_3COOH. Anion exchange resin: Amberlite IRA-400 pretreated with the above-mentioned solution. From ref.[16].

stability constants of complexes plays the main role. Moreover, for the yttrium group, it has been found[17] that in these conditions the affinity to the ion exchange resin increases in the order Yb < Y < Ho < Tb, i.e. according to the decrease of the atomic number. The differences between the values of the distribution coefficient observed were unexpectedly great. Work has been undertaken in order to characterize more fully the behaviour of the rare earth group elements in Na_2H_2Y aq. medium. The results of the preliminary experiments have been published in a letter to the editor of *Chemia Analityczna*[18].

<div align="center">EXPERIMENTAL</div>

The ion exchange resin

The strongly basic anion exchange resin Amberlite IRA-400 of the styrene–divinylbenzene type, possessing functional groups of the $-N^+(CH_3)_3$ type, was used. The exchange capacity of the strongly basic groups (Z_s) and the total exchange capacity (Z_c) had been determined previously[16] and had been found to be 3.70 and 3.76 mequiv./g of the dry resin [Cl$^-$] respectively. These data show that the Amberlite IRA-400 used here contained only a very small admixture of the weakly basic groups and could be regarded as monofunctional. At first the ion exchange resin, in its chloride form, was dried in the air, ground in a ball-mill, sieved and fractionated

to a particle size of $\varnothing$ < 0.07 mm (—200 mesh). From this fraction a suspension in distilled water was prepared in a big beaker. Four fractions were collected according to the time of settling: within 0 – 8, 8 – 15, 15 – 30 and 30 – 60 min. This last fraction was used for all the experiments. In order to eliminate possible impurities, the ion exchange resin was treated successively with excess of 1 N HCl, 1 N NaOH, 1 N HCl, washed with deionized water and transformed to the [H_2Y^{2-}] form by passing 0.2 M of Na_2H_2Y solution until no Cl^- ions could be detected in the effluent. The density of the dry ion exchange resin (d_j) was determined by the pycnometric method (with benzene); it amounted to 1.21 g of the dry resin [H_2Y^{2-}] per ml. The bed density (d_z) was determined by measuring the volume of the bed formed in a graduated cylinder from a known weight of the dry ion exchange resin after it had been submerged in distilled water. This density amounted to 0.326 g of the dry resin [H_2Y^{2-}] per ml of the bed.

Reagents

Disodium ethylenediaminetetraacetate was prepared from commercial $Na_2H_2Y \cdot 2H_2O$ by purifying it with the aid of the BLAEDEL AND KNIGHT method[19]. A stock 0.2 M solution was prepared by dissolving 37.21 g of pure $Na_2H_2Y \cdot 2H_2O$ in 500 ml of deionized water. Solutions of other concentrations were prepared from the stock solution by dilution. All the other reagents were of Analytical Grade. The pH values of the Na_2H_2Y solutions were within the range 4.55 – 4.70.

Radioactive tracers

The following radioactive tracers were used:

[137]Cs ($T_{1/2}$ = 30 y), [24]Na (15.0 h), [90]Y (65 h), [140]La (40 h), [144]Ce (285 d), [142]Pr (19.2 h), [147]Pm (2.6 y), [152,154]Eu (12.2 y), [159]Gd (18.0 h), [160]Tb (73.5 d), [166]Ho (27.3 h), [170]Tm (127 d), [169,175]Yb (33 d; 4.2 d) and [177]Lu (7.0 d).

The radioactive tracers: [137]Cs, [144]Ce, [147]Pm and [152,154]Eu were supplied by Soyuzchim-export, Soviet Union. The others were prepared by irradiating the appropriate oxides of spectral purity (Johnson, Matthey "Specpure") with neutrons in the Polish reactor "EWA".

Apparatus

The column was made of a glass tube 2.2 mm in diameter, of which the lower end was thinner; a piece of polyethylene pipe was attached to this end. The ion exchange resin bed was supported by a glass-wool plug which extended exactly to the upper edge of the thinner part of the column. At the top the column was widened to facilitate introduction of the mixture to be separated. The height of the ion exchange resin bed was altered according to actual needs. The scheme of the drop collector is shown in Fig. 2. The top of the column (K) was connected by a rubber pipe to a burette (E) containing the eluant. The eluant was supplied to the column under a pressure approximately equal to the difference between the levels of mercury in the separating funnels (W) and (R). The drops leaving the column were collected on an impregnated

paper band (P) set in motion by means of a small electric motor, and which moved with a constant speed of 2 cm/min.* The drops were then automatically dried by passing under infra-red lamps (L).
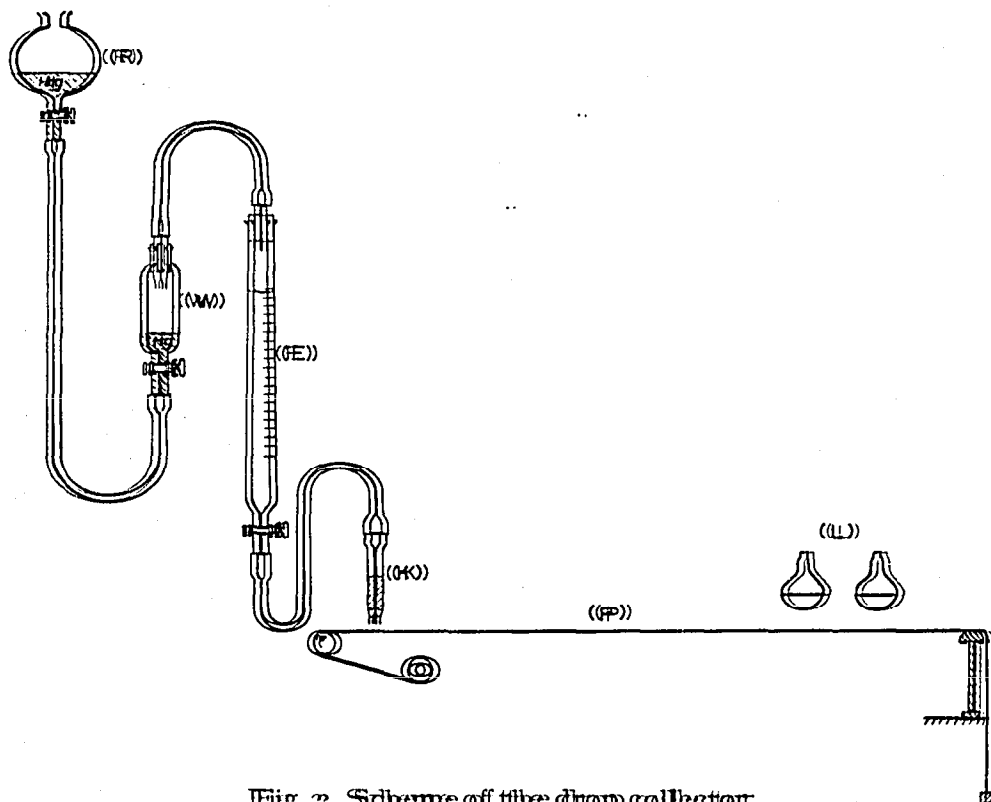

Fig. 2. Scheme of the drop collection.

Procedure

All the experiments were carried out at room temperature. The column was filled with ion exchange resin, washed with some millilitres of the eluant, and then the level of the liquid was adjusted to the upper level of the bed. The mixture of radio-active tracer was evaporated to dryness in a small glass or quartz crucible. Then the amount of Na_2H_2Y solution was added that is theoretically necessary to form complexes with all the lanthanides (on the assumption that complexes are formed with the mole ratio 1:1), after which the solution was again evaporated to dryness. The contents of the crucible were dissolved in 90 μl of the eluant, and 30 μl of this solution was applied to the top of the column. The lanthanide content of the "load" did not exceed 0.3 % of the total exchange capacity of the resin bed. By applying a slight overpressure, the "load" was made to pass down the column. The first drop was collected as Drop No. 0. The walls of the column were rinsed twice or thrice with small portions (10–20 μl) of the eluant. The column was filled up with the eluant, connected to the burette and the pressure regulated so that the rate of flow was 0.7–1 ml/cm²/min. At the moment when one of the first drops appeared, the level in

* The idea of application of ordinary temperature recorder as a drop receiver was devised by Dr. M. Wald (private information).

the burette and the time were noted. By making a similar note at the end of the experiment the volume of the drop and the exact flow rate could be calculated. The dried drops were numbered, cut out from the band by means of a pattern and placed in standard plexiglass holders. The activity was measured with the aid of an end-window Geiger-Müller counter. The elements corresponding to particular maxima of the elution curve were identified by determining $T \frac{1}{2}$ and the maximum energy of β particles or by comparison with elution curves obtained under similar conditions for single elements.

<div align="center">RESULTS AND DISCUSSION</div>

Distribution coefficients and the charge of complex ions

If the ion, whose ion exchange is being investigated, is present in trace amounts the exchange isotherm is as a rule linear. Then, on the basis of the elution curves obtained in conditions of complete equilibrium between the ion exchange resin and the solution, the distribution coefficients of the substances being separated can be calculated with the aid of the plate theory[20, 21]. The weight distribution coefficient (the amount of the substance per gram of the dry ion exchange resin divided by the amount of the substance per millilitre of the solution) is given by the equation:

$$\lambda = \frac{U_{max} - (U_0 + V)}{m} \tag{1}$$

where U_{max} = volume of the effluent when the concentration of the substance reaches its maximum

U_0 = dead volume of the column (the amount of the solution between the lower level of the resin bed and the outlet of the column)

V = free volume of the resin bed

m = mass of the dry ion exchange resin in the column (in g).

The free volume V is[20] the volume occupied by the liquid phase in the resin bed and can be calculated from the equation:

$$V = V_z \left(1 - \frac{d_z}{d_j}\right) \tag{2}$$

where V_z = volume of the resin bed (in ml)

d_z = density of the bed (gram of dry resin per millilitre of the bed)

d_j = density of the dry resin (gram of dry resin per millilitre).

If we assume that only one species of complex ions (X^{v-}) is present in the solution and that the ion exchange resin is completely saturated with A^{a-} ions, then the exchange reaction can be expressed by the following equation:
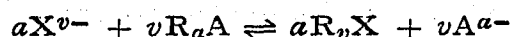
$$aX^{v-} + vR_aA \rightleftarrows aR_vX + vA^{a-}$$

The expression for the stability constant is then:

$$K = \frac{[R_vX]^a [A^{a-}]^v \gamma^a R_vX \gamma^v A^{a-}}{[X^{v-}]^a [R_aA]^v \gamma^v R_aA \gamma^a X^{v-}} \tag{3}$$

Activity coefficients in the resin phase are difficult to compute; their ratio, however, should be an approximately constant value under given conditions, so that they can be grouped together with the stability constant. Activity coefficients in dilute solutions are nearly equal to unity so that:

$$- \frac{[R_v X]^a \, [A^{a-}]^v}{[X^{v-}]^a \, [R_a A]^v} = K_c = \left[K \cdot \frac{\gamma^v R_a A}{\gamma^a R_v X} \right]$$ (4)

If the concentration in a solution is expressed as mole per litre and the concentration in the ion exchange resin phase as mole per litre of the bed then:

$$\frac{[R_v X]}{[X^{v-}]} = D,$$

is the volume distribution coefficient (the amount of the substance per ml of the bed divided by the amount of the substance per ml of the solution). It is easy to see that $[R_a A] =$ constant in view of the fact that the X^{v-} ion is present in trace amounts. By re-grouping and differentiating equation (4) the expression:

$$\frac{d \lg D}{d \lg[A^{a-}]} = - \frac{v}{a}$$ (5)

is obtained, and from this the charge of the investigated complex ion can be determined.

This method, which was given by KRAUS AND NELSON[5], has also been applied repeatedly by other authors[22].

Because the relation $D = \lambda d_z$ is given, equation (5) can be rewritten in the form:

$$\frac{d \lg \lambda}{d \lg [A^{a-}]} = - \frac{v}{a}$$ (6)

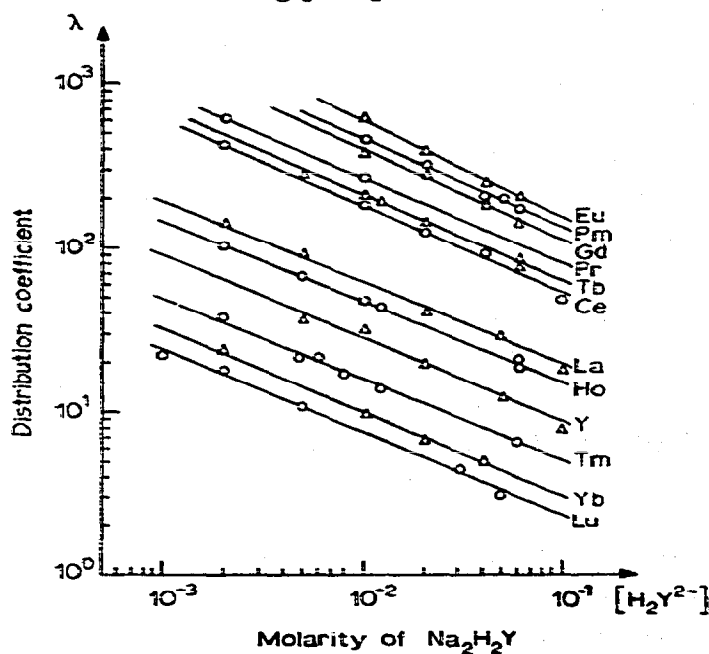Fig. 3. Distribution coefficients of the lanthanides in the system: Amberlite IRA-400 ($H_2 Y^{2-}$) – $Na_2 H_2 Y$ aq.

A plot of lg λ vs. lg [A^{a-}] should be a straight line with a slope equal to:

$$-\frac{v}{a}.$$

As can be seen in Fig. 3, for all the lanthanides the relation between lg λ and lg [H_2Y^{2-}] is linear with a slope equal to 0.50 $\pm$ 0.01. For europium the absolute value of the slope is slightly greater and amounts to —0.58. Hence it follows that with Na_2H_2Y at pH 4.55—4.70 all the lanthanides form only one kind of complex ion with the same charge equal to —1. They are evidently ions of the LnY^- type, which is in agreement with the results of the spectrophotometric and potentiometric investigations carried out by MOELLER et al.[23, 24].

Selectivity

The exchange affinity of the ion to the ion exchange resin depends in the first place on its charge and on the radius of the hydrated ion. In the system anion exchange resin–solution of metal ions + reagent forming complexes of negative charge with the ions, differences between the distribution coefficients can in principle be expected in three cases:

(a) When certain metals form complex ions of different charge.

(b) When under given conditions the position of the equilibrium between a free metallic ion and a complex ion (dissociation of the complex) is different for different components of the mixture.

(c) When metallic ions form complexes of equal charge but of different degrees of hydration.

Under the conditions prevailing in the present work (pH = 4.55–4.70) practically 100 % of every lanthanide exists in the form of a complex ion. Moreover—as shown above—all the lanthanides form complex ions of the same charge: —1.

Differences observed between the distribution coefficients would indicate greatly differing degrees of hydration of complex ions LnY^-.

In Fig. 4 the logarithms of the distribution coefficients of the lanthanides (in 0.01 M Na_2H_2Y) are plotted as a function of the atomic number.

We quote for comparison the relative values of the distribution coefficients obtained on elution of lanthanides from the Dowex-50 X12 cation exchange resin with α-hydroxyisobutyric acid at 87°[3], and the solubilities of complex salts NaLnY given by MARSH[25].

The behaviour of the lanthanides in the system Amberlite IRA-400–Na_2H_2Y aq. is rather unusual.

The distribution coefficients of the cerium group increase according to the increase of the atomic number, and for the yttrium group they decrease in the same direction. Thus there is no monotonical relation between the distribution coefficient and the atomic number or the ionic radius respectively, which is the case in the separation of lanthanides on cation exchange resins. It is interesting to note the distinct correlation between the values of the distribution coefficients and the solubility of the salts of

the Me(I) LnY type (Me(I)—alkali metal). According to MARSH[25], the solubility of such salts first diminishes and then increases according to the increase of the atomic number, in the order: La > Ce > Pr > Nd > Sm < Gd < Dy < Y < Er < Yb, with a minimum in the vicinity of Sm–Eu (see Fig. 4). The cation of Amberlite
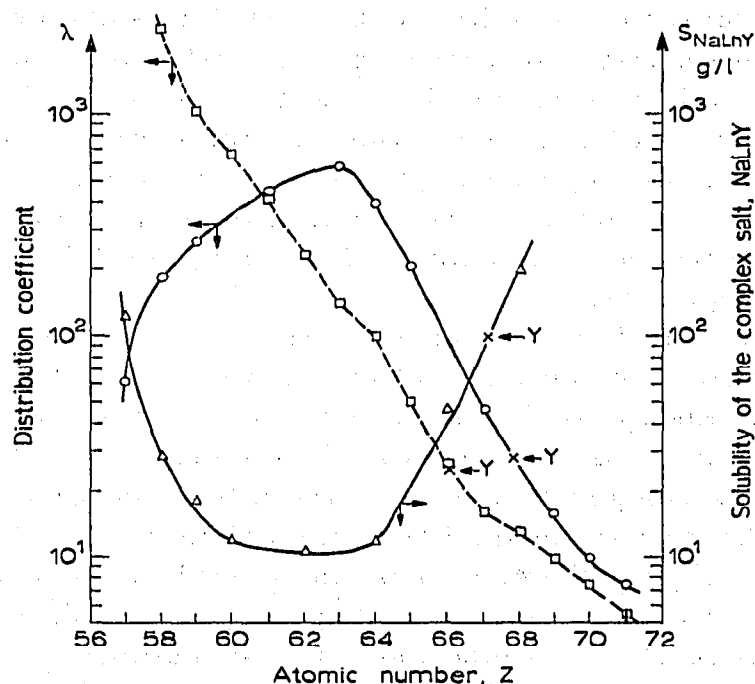

Fig. 4. Some properties of the lanthanides as a function of the atomic number. —O—O—O— Distribution coefficients in the system: Amberlite IRA-400 (H_2Y^{2-}) – 0.01 M Na_2H_2Y aq. –□– –□– –□– Relative distribution coefficients (Gd taken as standard), in the system: Dowex 50 X12 – α-hydroxyisobutyric acid aq. at 87°. From ref.[3]. —△—△—△— Solubility of the complex salts NaLnY. From ref.[25].

IRA-400 resin is of the —$N^+(CH_3)_3$ type, thus being a quaternary ammonium base. Bearing in mind the known analogies between alkali metals and ammonium ions as well as their alkyl derivatives, it can be assumed that the trend of solubility altera-tions of salts of the $RN(CH_3)_3LnY$ and Me(I) LnY types should be similar. It is very evident that the maximum affinity to the ion exchange resin corresponds to the minimum solubility. An analogous correlation between the affinity of the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} to the sulphonic cation exchange resin and the solubility of the sulphates of these metals has been observed by GREGOR AND FREDERICK[26].

If, in a series of lanthanides some properties are discussed as a function of the atomic number then a break at $Z = 64$ often occurs. Amongst other properties, this has been observed for the values of the crystal ionic radii[27], the distribution coefficients for the extraction with the system tributyl phosphate–HNO_3 aq.[28], stability constant values of complexes with H_4Y, 1,2-diaminocyclohexanetetraacetic acid and nitrilotri-acetic acid[15, 29], and for the positions of maxima on the elution curves from cation exchange resins[4]. This has generally been brought into relation with the effect of the half-filled $4f$ shell of gadolinium. As can be seen in Fig. 4, the break in the order of the distribution coefficients in the system examined in the present work is very

sharp. It occurs, however, at the position of europium, and gadolinium clearly belongs to the yttrium group. The unusual course of the curve lg λ–Z is undoubtedly connected with the changes of such properties of the complex ion that are responsible for the affinity to the anion exchange resin. On the basis of the data quoted above concerning the solubility of the Me(I) LnY salts it can be assumed that the interaction between water molecules and the LnY$^-$ ion is strongest for the extreme lanthanides, and weakest for the middle members of the series. The most strongly hydrated ions are at the same time the most weakly absorbed by the ion exchange resin, which is in agreement with the theory of GREGOR[30]. The reason for the great differences between the degree of hydration of the complex ions is not quite clear. As is known[31] trivalent lanthanides differ only very slightly in their affinity for the cation exchange resins.

Should the LnY$^-$ ions have an identical structure for all the rare earths, it could be expected that their distribution coefficients would be very similar. Yet, these differences are in fact unexpectedly great (*e.g.* the distribution coefficients of europium and lutecium differ from each other by two orders of magnitude). From what has been said above it may be concluded that the structure of the LnY$^-$ ion may undergo some changes with respect to the quality of the central ion.

The anion of ethylenediaminetetraacetic acid is a potentially hexadentate ligand. WHEELWRIGHT *et al.*[15] pointed out that when the stability constant values of LnY$^-$ complexes are plotted as a function of atomic number a break in the curve is observed at the position of gadolinium. They have put forward the assumption that Y^{4-} acts as a hexadentate ligand for light lanthanides (up to and including Gd), and for the remaining ones as a pentadentate ligand, while the sixth coordination place is occupied by a water molecule. On the basis of investigations carried out with the aid of several physicochemical methods and, among others, of investigations of dehydration of compounds of the Me(I) LnY and HLnY types, and of the interpretation of absorption spectra in the infra-red, MOELLER *et al.*[24] have come to the conclusion that in these complexes a free carboxyl group occurs and that the complex anion can be represented by the formula [LnY(H$_2$O)]$^-$. Investigations of the spectra in the infra-red, however, were carried out only for neodymium and yttrium compounds. A comparison of the data from the literature with the results of the present work has led us to put forward the following hypothesis of the structural changes of the complex ion and the affinity to the ion exchange resin.

From the statistical point of view Y^{4-} is, in principle, for lanthanum, a pentadentate ligand, the sixth coordination place being occupied by a water molecule. Owing to the presence of a free carboxyl group with hydrophilic properties in the [LnY(H$_2$O)]$^-$ ion, this ion is strongly hydrated and its ion exchange affinity is small. According to the rise of the atomic number of the lanthanide, the radius of the central ion decreases and the tendency of Y^{4-} to occupy all the six coordination places becomes progressively greater. Free movements of the free carboxyl group become continually more limited, the complex ion becomes less and less hydrated and its ion exchange affinity increases. Optimal conditions for the "packing" of all the func-

tional groups of the ligand around the central ion appear in europium. With a further rise of the atomic number and a corresponding decrease of the radius of the central ion new steric hindrances appear, the carboxyl group becomes progressively more
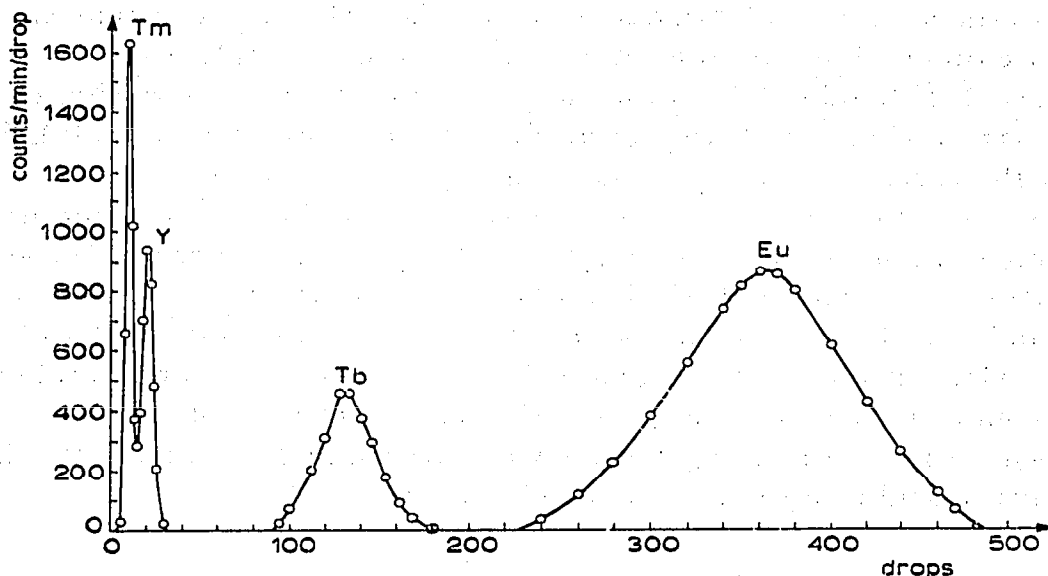

Fig. 5. Separation of Tm, Y, Tb, and Eu. Column: 1.63 cm × 0.0375 cm²; Amberlite IRA-400 (H_2Y^{2-}) (ø < 0.07 mm, settling time 30–60 min). Eluant: 0.01 M Na_2H_2Y, pH = 4.65. Flow rate: 0.94 ml. sq. cm⁻¹. min ⁻¹.
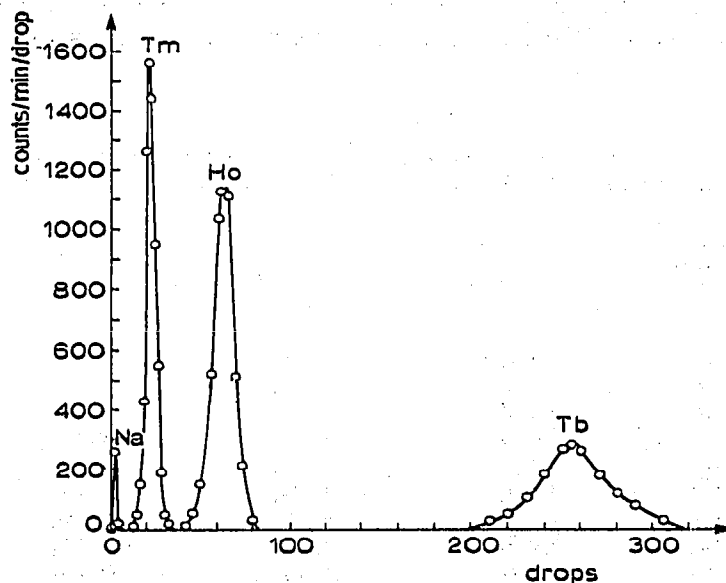
Fig. 6. Separation of Na, Tm, Ho, and Tb. Column: 2.50 cm × 0.0375 cm²; Amberlite IRA-400 (H_2Y^{2-}) (ø < 0.07 mm, settling time 30–60 min). Eluant: 0.005 M Na_2H_2Y, pH = 4.70. Flow rate: 0.78 ml. sq. cm⁻¹. min ⁻¹.

free, the hydration degree of the complex ion increases and its affinity to the ion exchange resin continually decreases.

The position of yttrium is interesting. As can be seen in Fig. 4 the distribution coefficient for the complex ion of yttrium occupies an intermediate place between

the complexes of holmium and erbium, so that it can be ascribed an "apparent atomic number" of $67\frac{1}{2}$. Yttrium occupies an identical position within the solubility range of the NaLnY salts. Unfortunately, reliable data regarding the radius of the Y^{3+} ion as compared to the ion radii of lanthanides are missing. The various values published in the literature differ widely from each other. The recent complete summary of the ion radii values of lanthanides[27] contains no values for yttrium. According to earlier indications[1], yttrium occupies the position between dysprosium and holmium. Elution from the cation exchange resins with organic hydroxyacids showed — according to several authors[1, 3, 32] — various positions of yttrium corresponding to the "apparent atomic numbers" of $64\frac{1}{2}$, $65\frac{1}{2}$ and $66\frac{1}{2}$. In the order of the stability constant values of complexes with H_4Y, yttrium occupies the place between terbium and dysprosium[15]. In the case of 1,2-diaminocyclohexanetetraacetic acid and nitrilotriacetic acid, yttrium occupies the places between gadolinium and terbium, and between europium and gadolinium[29] respectively. The change of place of yttrium seems to indicate that the bonding between lanthanide and the anion of ethylenediaminetetraacetic acid is not of fully ionic character.

Separations

The most important parameter for the separation of two ions with the aid of ion exchange chromatography is the separation factor, defined as the ratio of their distribution coefficients ($\alpha_2^1 = \lambda_1/\lambda_2$). In Table I the values of the separation factors of lanthanides (with respect to europium), and the separation factors of the neighbouring

TABLE I

SEPARATION FACTORS OF THE LANTHANIDES IN THE SYSTEM
AMBERLITE IRA-400(H_2Y^{2-})–Na_2H_2Y aq.

Element	Atomic number Z	$\alpha_{Eu}^{Ln} = \dfrac{\lambda_{Ln}}{\lambda_{Eu}}$	α_{Z+1}^{Z}	α_Z^{Z+1}
La	57	0.10_4	0.34_3	2.92
Ce	58	0.30_4	0.67_0	1.49
Pr	59	$0.45_3'$	0.74_5	1.34
Nd	60	0.60_9 *	0.78_6	1.27
Pm	61	0.77_4 *	0.86_8	1.15
Sm	62	0.89_1 *	0.89_1	1.11
Eu	63	1.00	1.51	0.66_4
Gd	64	0.66_4	1.90	0.52_6
Tb	65	0.34_9 *	2.24	0.44_7
Dy	66	0.15_6 *	1.95	0.51_4
Ho	67	0.080_0	1.85	0.54_0
Er	68	0.043_2 *	1.61	0.64_0
Tm	69	0.026_8	1.59	0.63_1
Yb	70	0.016_9	1.32	0.75_8
Lu	71	0.012_8		
Y	39	0.047_1		

* The distribution coefficient of these elements were estimated by interpolation in the lg λ–Z curve (Fig. 4).

elements are given. Using these data the separation factors of two arbitrary elements can be computed from the formula:

$$\alpha_{Ln_2}^{Ln_1} = \alpha_{Eu}^{Ln_1} \Big/ \alpha_{Eu}^{Ln_2} \qquad (7)$$

As can be seen from Table I and Fig. 4 the sequence of the elution of lanthanides under given conditions is: Lu, Yb, Tm, Er $\cong$ Y, Ho, La, Dy, Ce, Tb, Pr, Nd, Gd, Pm,
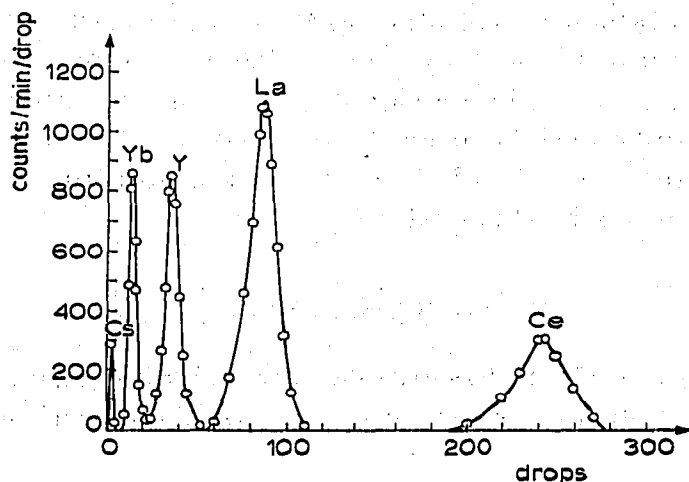

Fig. 7. Separation of Cs, Yb, Y, La, and Ce. Column: 2.85 cm $\times$ 0.0375 cm^2; Amberlite IRA-400 (H$_2$Y^{2-}) (ø $<$ 0.07 mm, settling time 30–60 min). Eluant: 0.005 M Na$_2$H$_2$Y, pH $=$ 4.70. Flow rate: 0.79 ml. sq. cm^{-1}. min^{-1}.
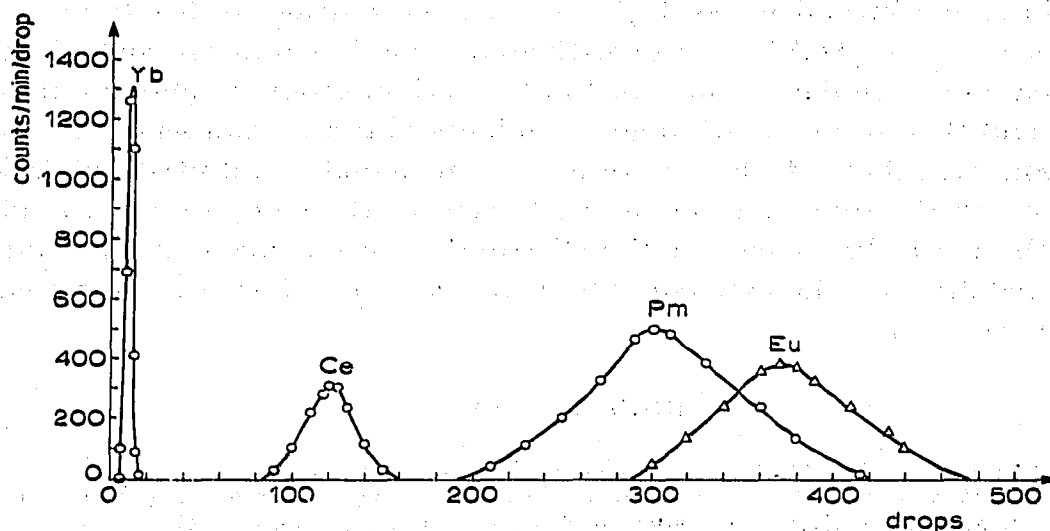

Fig. 8. Separation of Yb, Ce, Pm, and Eu. Column: 2.8 cm $\times$ 0.0375 cm^2; Amberlite IRA-400 (H$_2$Y^{2-}) (ø $<$ 0.07 mm, settling time 30–60 min). Eluant: 0.02 M Na$_2$H$_2$Y, pH $=$ 4.67. Flow rate: 0.85 ml. sq. cm^{-1}. min^{-1}.

Sm, Eu. Separation of all the rare earths by means of one elution with the aid of the method described above would certainly cause considerable difficulty, due to the fact that the distribution coefficients of Gd, Tb and Dy are within the same range as the distribution coefficients of the cerium group. In practice, however, it is seldom

necessary to deal simultaneously with all the lanthanides. The data given in Table I indicate very favourable conditions, particularly for certain pairs and groups of lanthanides to be separated. The values of α_{Ce}^{La} and α_{Z+1}^{Z} for nearly the whole yttrium group are higher than the best results obtained on cation exchange resins. The α value is also relatively good for the Gd–Eu pair, which are generally difficult to separate. In Figs. 5–8 typical elution curves obtained on relatively very short columns are presented. It should be stressed that—as shown in Figs. 6 and 7—under these conditions alkali metals are not taken up by the resin (they are eluted with the first free volume of the column), and they do not obscure the picture of the separation of the rare earths, in contrast to the elution from cation exchange resins[1]. These investigations are being continued in order to investigate the influence of the cross-linking of the ion exchange resin and that of the temperature on the distribution coefficients of the lanthanides in this system.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. S. SIEKIERSKI for valuable discussions and to Miss M. TYMIENIECKA for her help in carrying out some of the experiments.

SUMMARY

The anion exchange behaviour of the lanthanides in the system strongly basic anion exchange resin Amberlite IRA-400 ($H_2Y_2^-$)–aqueous solution of disodium ethylenediaminetetraacetate (Na_2H_2Y), was investigated. The distribution coefficients were found to increase in a regular manner within the cerium group, reaching a maximum at europium, and then to decrease on going to higher atomic numbers. The charge of the complex ions was shown to be —1 for all the lanthanides and yttrium. A possible explanation, based on differences in the hydration of the complex ions, is given to account for the large differences of the distribution coefficients in the lanthanide series. The possibility of achieving efficient separations on relatively short columns is also demonstrated.

REFERENCES

[1] B. H. KETELLE AND G. E. BOYD, *J. Am. Chem. Soc.*, 69 (1947) 2800.
[2] D. C. STEWART, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, Vol. 7 (1956) 321.
[3] G. R. CHOPPIN AND R. J. SILVA, *J. Inorg. & Nuclear Chem.*, 3 (1956) 153.
[4] J. J. KATZ AND G. T. SEABORG, *The Chemistry of the Actinide Elements*, Methuen & Co. Ltd., London, 1957.
[5] K. A. KRAUS AND F. NELSON, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, Vol. 7 (1956) 113.
[6] L. R. BUNNEY, H. E. BALLOU, J. PASCUAL AND S. FOTI, *Anal. Chem.*, 31 (1959) 324.
[7] R. C. VICKERY, *J. Chem. Soc.*, (1955) 2360.
[8] Y. MARCUS AND F. NELSON, *J. Phys. Chem.*, 63 (1959) 77.
[9] J. P. SURLS, Jr. AND G. R. CHOPPIN, *J. Inorg. & Nuclear Chem.*, 4 (1957) 62.
[10] E. H. HUFFMAN AND R. L. OSWALT, *J. Am. Chem. Soc.*, 72 (1950) 3323.
[11] G. M. KOLOSOVA AND M. M. SENYAVIN, *Redkozemelnye Elementy*, Izdat. A.N., S.S.S.R., Moskva, 1959, p. 138.

[12] A. A. POZDNYAKOV AND A. K. LAVRUKHINA, *Trudy Komisii po Analiticheskoi Khimii*, 9 (1958) 161.

[13] C. E. HIGGINS AND W. H. BALDWIN, *Nuclear Sci. Abstr.*, 5 (1951) 542.

[14] R. DYBCZYŃSKI, *Chem. Anal. (Warsaw)*, 4 (1959) 531.

[15] E. J. WHEELWRIGHT, F. H. SPEDDING AND G. SCHWARZENBACH, *J. Am. Chem. Soc.*, 75 (1953) 4196.

[16] R. DYBCZYŃSKI, *Mitteilungsblatt der Chemischen Gesellschaft in der DDR*, Sonderheft 1960, *Analytische Chemie*, p. 393–401.

[17] R. DYBCZYŃSKI, unpublished data.

[18] J. MINCZEWSKI AND R. DYBCZYŃSKI, *Chem. Anal. (Warsaw)*, 6 (1961) 275.

[19] W. J. BLAEDEL AND H. T. KNIGHT, *Anal. Chem.*, 26 (1954) 741.

[20] S. W. MAYER AND E. R. TOMPKINS, *J. Am. Chem. Soc.*, 69 (1947) 2866.

[21] J. BEUKENKAMP, W. RIEMAN III AND S. LINDENBAUM, *Anal. Chem.*, 26 (1954) 505.

[22] M. WALD AND T. SCHÖNFELD, *Monatsh.*, 89 (1958) 526.

[23] T. MOELLER AND J. C. BRANTLEY, *J. Am. Chem. Soc.*, 72 (1950) 5447.

[24] T. MOELLER, F. A. J. MOSS AND R. H. MARSHALL, *J. Am. Chem. Soc.*, 77 (1955) 3182.

[25] J. K. MARSH, *J. Chem. Soc.*, (1955) 451.

[26] H. P. GREGOR AND M. FREDERICK, *Ann. N. Y. Acad. Sci.*, 57 (1953) 87.

[27] D. H. TEMPLETON AND C. H. DAUBEN, *J. Am. Chem. Soc.*, 76 (1954) 5237.

[28] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN AND S. McCARTY, *J. Inorg. & Nuclear Chem.*, 4 (1957) 326.

[29] G. SCHWARZENBACH AND R. GUT, *Helv. Chim. Acta*, 39 (1956) 1589.

[30] H. P. GREGOR, *J. Am. Chem. Soc.*, 70 (1948) 1293.

[31] J. P. SURLS, Jr. AND G. R. CHOPPIN, *J. Am. Chem. Soc.*, 79 (1957) 855.

[32] F. H. SPEDDING AND J. L. DYE, *J. Am. Chem. Soc.*, 72 (1950) 5350.