

ANION EXCHANGE BEHAVIOUR OF THE RARE EARTH COMPLEXES WITH *trans*-1,2-DIAMINOCYCLOHEXANE-N,N'-TETRAACETIC ACID

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The anion exchange of metal complexes with multidentate organic ligands is a relatively little explored domain. In previous papers from this Laboratory¹⁻³, it was shown that rare earth complexes with EDTA of the LnY^- type, (where Y^{4-} stands for the EDTA anion) show an unusual sequence of affinity to strongly basic anion exchangers. The affinity first increases when going to higher atomic numbers, passes through a maximum, and decreases with the further increase of atomic number. This non-monotonical sequence was interpreted in terms of change in the degree of hydration of LnY^- ions in dependence of the kind of Ln cation. For lanthanum, Y^{4-} acts more like a pentadentate than a hexadentate ligand and the presence of a relatively free carboxyl group renders the $[\text{LnY}(\text{H}_2\text{O})]^-$ ion strongly hydrated. As the radius of the central ion decreases (as when going from La to the medium rare earths) the tendency of the EDTA ligand to occupy six coordination places gradually increases with the simultaneous decrease in hydration. Optimum packing conditions (at room temperature) occur in Eu. With a further increase of atomic number (and decrease of central ion radius) down to Lu, steric hindrances appear, the carboxyl group becomes progressively more and more free and hydration of the complex ion again increases.

Separation factors of adjacent rare earths, at least for some groups of elements (e.g. in the La-Ce-Pr and Eu-Gd-Tb-Dy-Er-Tm series), were quite promising and ion exchange chromatography in the system Amberlite IRA-400 $[\text{H}_2\text{Y}^{2-}] - \text{Na}_2\text{H}_2\text{Y}$ aq. in conjunction with neutron activation has been used for the determination of Lu, Ho and Dy in spectrally pure Er_2O_3 ⁴, Pr and Ce in spectrally pure La_2O_3 ⁵, and La, Pr, Ce, Nd, Ho and Dy in Misch metal⁶. The rather unusual elution position of yttrium in this system (apparent atomic number of Y here amounts to $67\frac{1}{2}$) offered the possibility of determining of traces of Dy in Y_2O_3 ⁶ and Sm, Eu and Gd in Y_2O_3 ⁷.

The thermodynamics of anion exchange of the rare earth complexes with EDTA, also shows some peculiarities. Exceptionally high entropy and heat capacity changes were noted for some exchange reactions⁸. In view of all that has been said above it seemed interesting to investigate the anion exchange behaviour of rare earth complexes with a ligand structurally similar to the EDTA anion. *trans*-1,2-Diaminocyclohexane-N,N'-tetraacetic acid (H_4DCTA or H_4Z) seemed ideally suited for this purpose. It is a structural analogue of EDTA, the only difference between the two reagents being that in DCTA, C atoms of the ethylenediamine grouping are bound into a cyclohexane ring. This acid forms strong complexes with rare earth elements. Their stability constants are more than an order of magnitude higher than correspond-

ing values for the analogous EDTA complexes. The plots of $\log K$ for both complex-forming agents *vs.* atomic number of the lanthanide are nearly parallel to each other¹². It might be expected therefore that a comparison of the anion exchange behaviour of rare earth complexes with both ligands would reveal some similarities due to the analogous arrangement of functional groups, as well as differences due to the presence or absence of the bulky cyclohexane ring in the molecule.

EXPERIMENTAL

Resin

Dowex 1 X4 (styrene base, containing quaternary ammonium functional groups) was used. The air-dried resin [Cl⁻]-form was ground in a ball mill and sieved. The fraction of particle size ≤ 0.07 mm diameter was then further separated by gradual sedimentation of resin suspension in water². Martin's diameter (arithmetical mean of the distance between opposite sides of the particle, measured crosswise) as determined from microscopic measurements was used to specify the exact particle size¹³. For each fraction the Martin's diameter of 100 randomly chosen particles was determined, five of the smallest and five of the greatest results being subsequently rejected to give finally the effective particle size with a 90% probability. The resin was placed in a column and conditioned by passing successively 1 *N* NaOH, water and 1 *N* HCl solution in large excess. Finally the resin was converted into the [H₂Z²⁻] form by passing 0.1 *M* disodium 1,2-diaminocyclohexane-N,N'-tetraacetate (Na₂H₂Z) solution until no chloride could be detected in the effluent. Then the ion exchanger was washed with deionized water and air dried. The exchange capacity was determined by displacing H₂Z²⁻ ions from a known weight of resin with 1 *M* NaCl solution followed by titration of the effluent with standard zinc solution in the presence of Eriochrome Black T.

The water content of the air-dried resin was determined by drying at 105° to constant weight. The exchange capacity thus determined was found to be: $Z_s = 2.40$ mval/g of the dry resin [H₂Z²⁻]. The bed density (d_z) was determined by measuring the volume of the bed formed by a known weight of the exchanger in distilled water. It amounted to: $d_z = 0.305$ g of the dry resin [H₂Z²⁻]/ml of the bed.

Tracers and reagents

The following radioactive tracers were used: ¹³⁴Cs ($T_{1/2} = 2.2$ y); ¹⁴⁰La ($T_{1/2} = 40.2$ h); ¹⁴²Pr ($T_{1/2} = 19.2$ h); ¹⁴⁷Pm ($T_{1/2} = 2.6$ y); ¹⁵³Sm ($T_{1/2} = 1.96$ d); ^{152,154}Eu ($T_{1/2} = 13-16$ y); ¹⁵³Gd ($T_{1/2} = 236$ d); ¹⁶⁰Tb ($T_{1/2} = 73$ d); ¹⁶⁵Dy ($T_{1/2} = 2.3$ h); ¹⁶⁶Ho ($T_{1/2} = 27.3$ h); ¹⁷⁰Tm ($T_{1/2} = 127$ d); ¹⁷⁷Lu ($T_{1/2} = 6.8$ d); ⁴⁶Sc ($T_{1/2} = 85$ d); ⁹⁰Y ($T_{1/2} = 65$ h). The ¹⁴⁷Pm and ¹⁵³Gd tracers were supplied by Soyuzchimexport, Soviet Union.

The ¹³⁴Cs was prepared by irradiation of CsCl of spectral purity followed by purification of the tracer from ³²P and ³²S (formed as result of reaction with fast neutrons) on a cation exchange column¹⁴.

All the other isotopes were prepared by neutron irradiating the appropriate spectrally pure grade of oxides or nitrates (Johnson Matthey "Specpure") in the Polish reactor EWA and were used without further purification.

A stock solution of 0.1 *M* disodium 1,2-diaminocyclohexane-N,N'-tetraacetate

($\text{Na}_2\text{H}_2\text{Z}$) was prepared by titrating the suspension of 17.33 g of H_4Z (Fluka A.G.) in deionized water with NaOH solution to $\text{pH} = 4.8$ and diluting to 500 ml with deionized water. Solutions of lower concentration were made from the stock solution by diluting with an appropriate amount of deionized water. The exact concentration of the solution was determined by titration with standard Zn solution in the presence of Eriochrome Black T.

Apparatus

The apparatus used in this work was essentially the same as described previously^{2,8}. Jacketed glass columns of approximately 2 mm internal diameter were employed.

The resin bed of the desired height rested on a glass-wool plug. Constant temperature ($\pm 0.2^\circ$) was maintained by passing water from the Höppler ultra-thermostat through the jacket of the column.

The eluant solution was supplied to the column from a burette under a mercury column pressure regulated so as to get a flow rate of 0.5–1.0 cm/min.

The effluent was collected in drops on a moving paper band. The drops were then automatically dried when passing under an infra-red lamp.

Procedure

The column was filled with an aqueous slurry of the Dowex 1 X4 [H_2Z^{2-}] resin and after the exchanger settled down, it was rinsed with a few ml of eluant solution. After the temperature was established, the level of the liquid in the column was adjusted to the upper level of the resin bed. The solution of radioactive tracers of rare earths (in HCl) together with a small quantity of ^{134}Cs was evaporated to dryness in a glass crucible, then enough $\text{Na}_2\text{H}_2\text{Z}$ solution to complex all rare earth ions was added, and the solution evaporated gently to dryness again. The residue was dissolved in 75 μl of the eluant and 25 μl of this solution were introduced onto the top of the bed by means of pipet with a capillary end. The total rare earth content in the "load" did not exceed 0.3 % of the exchange capacity of the resin in the column.

The load was forced through the column by applying slight overpressure. After washing the walls of the column with two to three 20- μl portions of the eluant solution, the burette containing the eluant was connected to the column and the elution carried out in the usual manner. The volume of a drop was determined by noting burette readings corresponding to a known number of drops of eluant. The dried drops were cut out of the band with the aid of a special cutter, placed in standard aluminium holders and their GM counting rate was measured using an automatic sample changer (NZQ 615). The elements corresponding to a particular maxima on the elution curve were identified by determining the half-life, maximum energy of β -radiation or by γ -ray spectrometry.

RESULTS AND DISCUSSION

Theoretical

H_4DCTA is a tetrabasic acid, its dissociation constants according to MOELLER AND HSEU¹⁰ being as follows: $\text{p}K_1 = 2.40$; $\text{p}K_2 = 3.55$; $\text{p}K_3 = 6.14$; $\text{p}K_4 = 11.70$.

From these data the percentage contents of various dissociation forms have

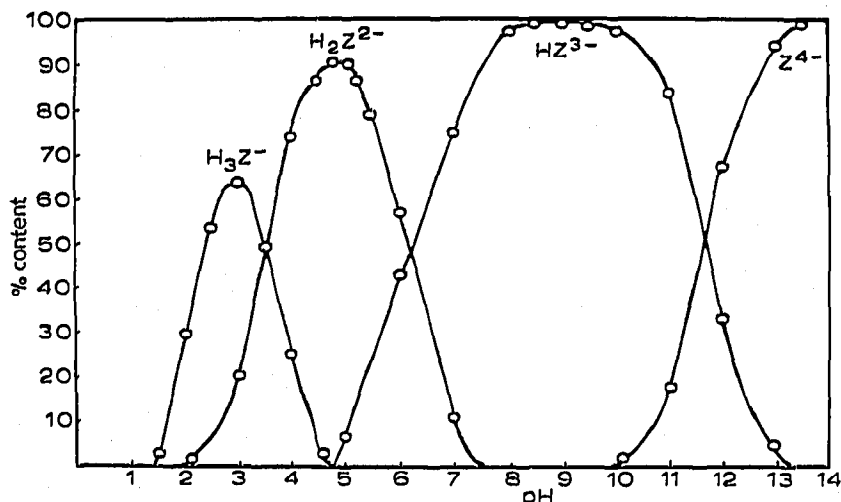
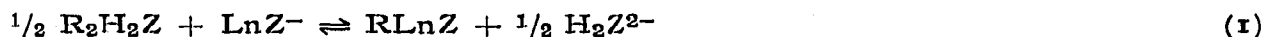


Fig. 1. The percentage content of various DCTA dissociation forms as a function of pH.

been calculated and the results are presented in Fig. 1. As can be seen from Fig. 1, at pH 4.8, 91% of DCTA is in the form of H₂Z²⁻ anion. At this pH practically 100% of all the lanthanides should be in the complexed form. Assuming that only 1:1 complexes are formed, the ion exchange reaction can be then written as:



The selectivity coefficient (equilibrium quotient) for this reaction defined as:

$$k_{H_2Z^{2-}}^{LnZ^-} = \frac{N_{RLnZ} \cdot m_{H_2Z^{2-}}^{1/2}}{N_{R_2H_2Z}^{1/2} \cdot m_{LnZ^-}} \quad (2)$$

(where N is the mole fraction of the ion in the resin phase and m is molality of the solution), and is related to the weight distribution coefficient λ_{LnZ^-} (amount per g of the dry resin [H₂Z²⁻]/ amount per ml of the solution) by the equation¹⁵:

$$k_{H_2Z^{2-}}^{LnZ^-} = \frac{\lambda_{LnZ^-} \cdot m_{H_2Z^{2-}}^{1/2} \cdot d}{C_r} \quad (3)$$

were:

C_r = concentration of the resin phase (mmole per g of dry resin [H₂Z²⁻])

d = density of the solution.

Distribution coefficients were determined from the elution curve by the formula²:

$$\lambda = \frac{U_{max} - (U_0 + V)}{m_j} \quad (4)$$

where:

U_{max} = volume of the eluant at which the concentration of a given ion reached its maximum

U_0 = dead volume of the column

V = free volume of the resin bed

m_j = weight of the dry ion exchange resin in the column.

It follows from eqn. (3) that:

$$\frac{d \log \lambda_{\text{LnZ}^-}}{d \log m_{\text{H}_2\text{Z}^{2-}}} = -1/2 \quad (5)$$

Experimentally determined dependence of λ_{LnZ^-} on the concentration of $\text{Na}_2\text{H}_2\text{Z}$ for several rare earth elements is presented in Fig. 2. It can be seen that linear plots, with a slope of -0.50 ± 0.02 , were obtained for all the elements investigated. This indicates that, at pH 4.8, all the rare earths form with DCTA only one kind of complex ion of the same charge (-1), *i.e.* the LnZ^- ion. This is in agreement with the results of potentiometric and polarographic studies by other workers^{9,10}.

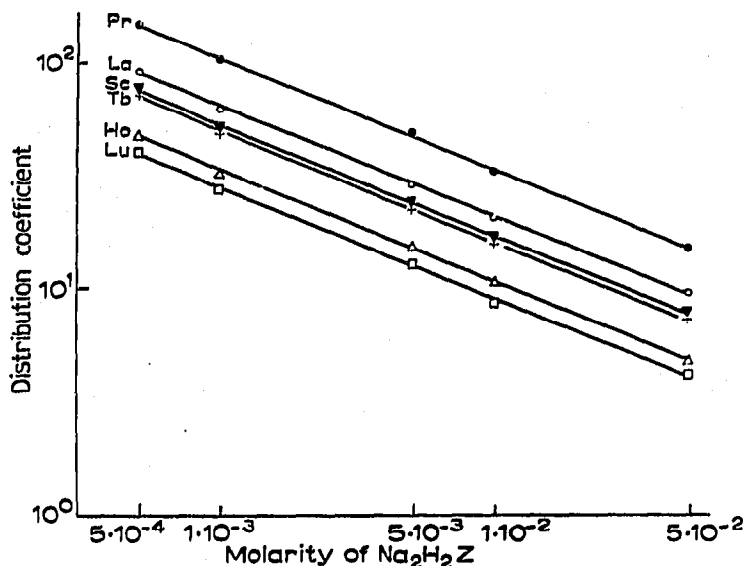


Fig. 2. Distribution coefficients of the rare earths in the system Dowex 1 X4 $[\text{H}_2\text{Z}^{2-}]$ - $\text{Na}_2\text{H}_2\text{Z}$.

Selectivity and structure of the complex ions

The dependence of selectivity coefficient (as calculated from eqn. (3) on the atomic number of the lanthanide is illustrated in Fig. 3. For comparison, the analogous plot for the EDTA system (Dowex 1 X4 $[\text{H}_2\text{Y}^{2-}]$ - $\text{Na}_2\text{H}_2\text{Y}$ aq.)¹⁶ is also given. The similarities and differences of these two plots are apparent.

The general trend in changes of selectivity coefficient with the atomic number (or ionic radius) of the central ion is similar for both systems. The ion exchange affinity of the complex first increases with the increasing atomic number (or decreasing ionic radius) of the central atom, passes through a maximum corresponding to optimum packing of the ligand functional groups around the central atom (*cf.* also ref. 2 and 8) and decreases with a further increase of atomic number when new steric hindrances appear. The maximum on the $\log k$ - Z plot, which for the EDTA system occurs in Eu, is shifted towards the lower atomic numbers for DCTA, and occurs in Pm. This would mean that DCTA needs a central ion of greater radius for realisation of optimum packing than does EDTA, which is conceivable in view of the more rigid structure and the presence of the bulky cyclohexane ring in the molecule of the former. It is apparent from Fig. 3 that selectivity coefficients of lanthanide complexes in the DCTA system are relatively very low. This means that the differences in ion exchange affinity between the Ln-DCTA complexes and dibasic DCTA anion are much smaller than the corresponding figures for EDTA. Also the differences in the properties of the

LnZ^- ions depending on the central atom radius are rather small. The greatest and the smallest selectivity coefficient of LnZ^- complexes in the DCTA system differ by a factor of 4.3, while the corresponding figure for the EDTA system is 28.7 (*cf.* Fig. 3). Evidently the ability of the ligand molecule to rotate freely along the C-C axis is necessary to assure such kind of packing around the central ion that the resultant complex is much less hydrated than the free ligand anion. If this rotation is impossible as in the case of the C-C bond in the cyclohexane ring, the ability of the complexing agent to act as a hexadentate ligand is much more limited. Thus, one carboxyl group is relatively more free in DCTA than in EDTA complexes, and the former complex being more hydrated shows a smaller affinity to the anion exchange resin.

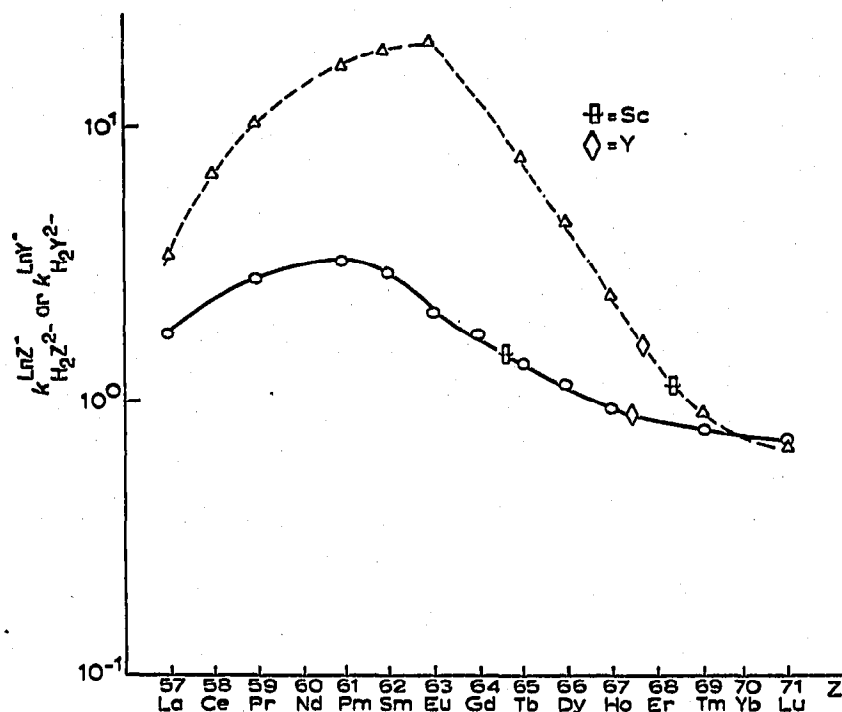


Fig. 3. Selectivity coefficients of the lanthanides as a function of atomic number. —○—○—○ Dowex 1 X4 $[\text{H}_2\text{Z}^{2-}] - \text{Na}_2\text{H}_2\text{Zaq}$ system. —△—△—△ Dowex 1 X4 $[\text{H}_2\text{Y}^{2-}] - \text{Na}_2\text{H}_2\text{Yaq}$ system, 25°.

The position of the "quasi-lanthanides", *i.e.* Sc and Y is of interest. In the EDTA system on Dowex 1 X4 $[\text{H}_2\text{Y}^{2-}]$ at 25°, Y has an apparent atomic number of 67½, and Sc 68½ similarly on Amberlite IRA-400 $[\text{H}_2\text{Y}^{2-}]$ resin^{3,8}. In the DCTA system, the apparent atomic number of Y is also 67½ but that of Sc amounts to 64½.

These values do not agree with the position of the elements in the series of crystallographic radii¹⁷ or with the available data on the position of Y in the series of stability constant with DCTA⁹⁻¹¹. This would mean that the bond between the rare earth cation and the DCTA anion is not of purely ionic character.

The form of the $\log k-Z$ plot is temperature dependent as a consequence of different values of enthalpy change accompanying separate ion exchange reactions. The thermodynamics of anion exchange of rare earth-DCTA complexes will be dealt with in another paper¹⁸.

TABLE I

SEPARATION FACTORS OF THE RARE EARTHS IN THE SYSTEMS: DOWEX 1 X4 [H₂Z²⁻]-Na₂H₂Z aq. AND DOWEX 1 X4 [H₂Y²⁻]-Na₂H₂Y aq. AT 25°.

Element	Atomic number (Z)	Dowex 1 X4 [H ₂ Z ²⁻]-Na ₂ H ₂ Z aq.			Dowex 1 X4 [H ₂ Y ²⁻]-Na ₂ H ₂ Y aq.		
		α_{Lu}^{Ln}	α_{Z+1}^Z	α_{Z+1}^{Z+1}	α_{Lu}^{Ln}	α_{Z+1}^Z	α_{Z+1}^{Z+1}
La	57	2.31	0.75 ₀	1.31 ₀	5.05	0.50 ₀	1.98
Ce	58	3.05*	0.80 ₀	1.24 ₀	9.98	0.65 ₀	1.52
Pr	59	3.78	0.89 ₂	1.12 ₁	15.20	0.75 ₅	1.33
Nd	60	4.24*	0.97 ₀	1.02 ₄	20.17*	0.82 ₀	1.22
Pm	61	4.35	1.07 ₀	0.92 ₀	24.60	0.89 ₄	1.12
Sm	62	4.03	1.37 ₀	0.72 ₅	27.55	0.96 ₀	1.04
Eu	63	2.92	1.22 ₈	0.81 ₄	28.70	1.49	0.67 ₀
Gd	64	2.38	1.27 ₀	0.78 ₃	19.25*	1.67	0.59 ₈
Tb	65	1.86	1.24 ₂	0.80 ₄	11.51	1.74	0.57 ₄
Dy	66	1.50	1.19 ₂	0.83 ₈	6.62	1.86	0.54 ₀
Ho	67	1.26	1.08 ₈	0.90 ₇	3.55	1.76	0.56 ₇
Er	68	1.15*	1.09 ₀	0.91 ₇	2.02*	1.54	0.65 ₀
Tm	69	1.06	1.02 ₀	0.97 ₂	1.31	1.21	0.82 ₇
Yb	70	1.03*	1.03 ₂	0.97 ₁	1.08 ₅ *	1.08 ₅	0.92 ₁
Lu	71	1.00			1.00		
Sc	21	1.95			1.67		
Y	39	1.22			2.36		

* Separation factors for these elements were calculated from the selectivity coefficients estimated by interpolation in log *k*-*Z* plot (Fig. 3).

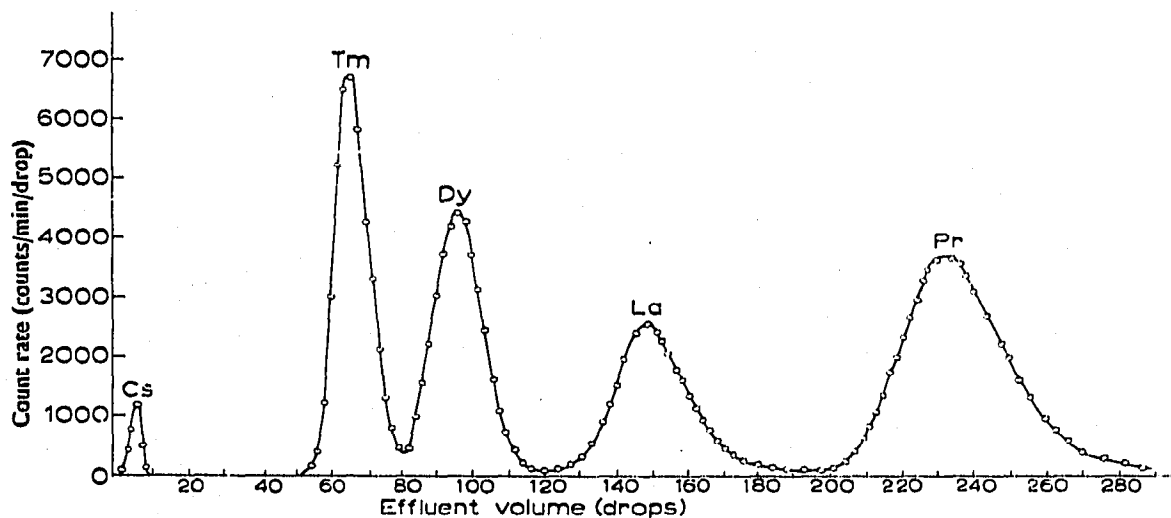


Fig. 4. Separation of Tm, Dy, La and Pr. Column: 9.90 cm × 0.0314 cm²; Dowex 1 X4 [H₂Z²⁻](9-40 μ). Eluant: 0.0011 M DCTA, pH 4.8, temp. 25°. Flow rate: 1.0 · 10⁻² ml/sq.cm.sec. *H*_{Tm} = 0.62 mm; *H*_{Dy} = 0.56 mm; *H*_{La} = 0.45 mm; *H*_{Pr} = 0.39 mm.

Separations

The separation factors of the rare earths (with respect to lutetium) and the separation factors of adjacent lanthanides in the system examined are given in Table I. For comparison, the data for analogous systems with EDTA are also given¹⁰. As can be seen in the Dowex 1 X4 [H₂Z²⁻]-Na₂H₂Z aq. system, the ion exchange affinity of rare earths decreases in the series: Pm > Nd > Sm > Pr > Ce > Eu > Gd > La > Sc >

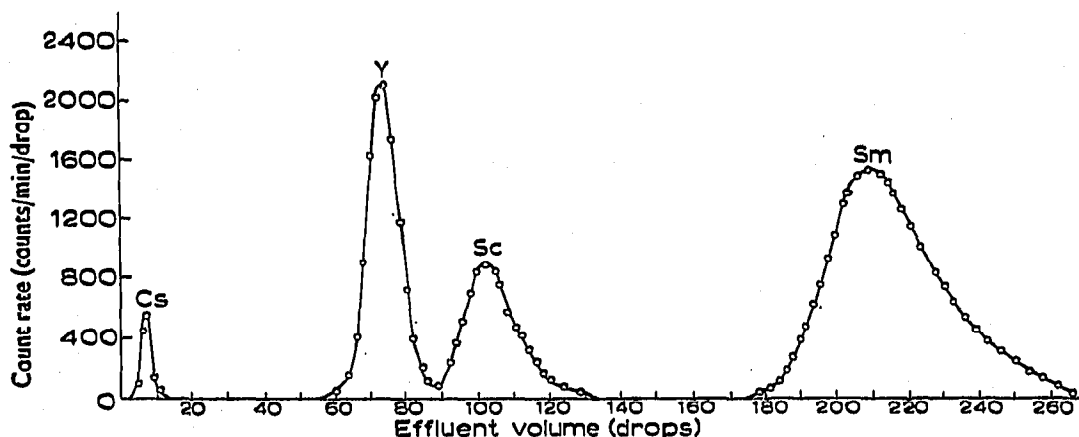


Fig. 5. Separation of Y, Sc and Sm. Column: 9.90 cm \times 0.0314 sq. cm; Dowex 1 X₄ [H₂Z²⁻] (9-40 μ). Eluant: 0.0011 M Na₂H₂Z, pH 4.8, temp. 25°. Flow rate: 1.1 \cdot 10⁻² ml/sq.cm \cdot sec. $H_Y = 0.61$ mm; $H_{Sc} = 0.71$ mm; $H_{Sm} = 0.55$ mm.

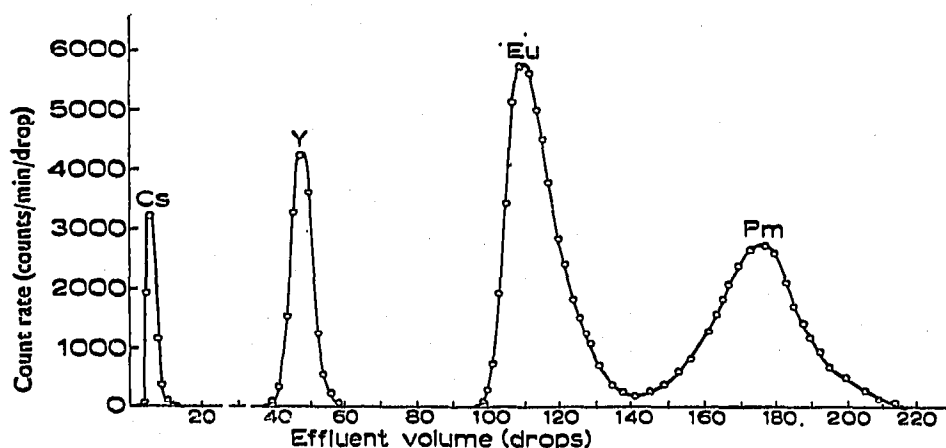


Fig. 6. Separation of Y, Eu and Pm. Column: 9.90 cm \times 0.0314 sq.cm; Dowex 1 X₄ [H₂Z²⁻] (9-40 μ). Eluant: 0.0025 M Na₂H₂Z, pH 4.8, temp. 30°. Flow rate: 9 \cdot 10⁻³ ml/sq.cm \cdot sec. $H_Y = 0.42$ mm; $H_{Eu} = 0.40$ mm; $H_{Pm} = 0.50$ mm.

Tb > Dy > Ho > Y > Er > Tm > Yb > Lu. The separation factors are substantially smaller than the corresponding values for the Dowex 1 X₄ [H₂Y²⁻]-Na₂H₂Y aq. system. Some separations, however, are still possible. Several experimental elution curves are presented in Figs. 4-6. The plate heights H , corresponding to particular elution curves, have been calculated from the formula¹⁰:

$$H = \frac{L}{N} = \frac{LW(C+1)}{8(U_{\max} - U_0)^2 C} \quad (6)$$

where besides the symbols defined earlier:

L = column length

N = number of the theoretical plates

C = distribution ratio, *i.e.* ratio of the quantity of a substance in the resin to the quantity in the solution on one theoretical plate

W = peak width for the ordinate $M = 0.368 M_{\max}$

and are given in each figure as H_{Ln} . These values are approximately twice greater than the corresponding figures for the EDTA system¹⁶, indicating that ion exchange

kinetics are considerably less favourable for rare earth-DCTA complexes. To summarize what has been said above, it should be underlined that even small changes in the complexone ligand structure can have a profound influence on the properties of the metal complexes formed by the ligands in question and specifically on their anion exchange behaviour. Further work on the anion exchange of metal chelate compounds is in progress.

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SUMMARY

The anion exchange behaviour of the rare earth elements in the system: Dowex 1 X4 $[H_2Z^{2-}]$ -aqueous solution of disodium salt of *trans*-1,2-diaminocyclohexane-*N,N'*-tetraacetic acid (Na_2H_2Z) has been studied. All the lanthanides, Sc and Y form under these conditions (pH 4.8) complexes of the LnZ^- type. Ion exchange affinity in the lanthanide series increases in a regular manner from lanthanum to promethium and then decreases with further increase of atomic number. Apparent atomic numbers of Sc and Y in this system are $64\frac{1}{2}$ and $67\frac{1}{2}$, respectively. Separation factors of adjacent lanthanides are substantially smaller than corresponding values for the Dowex 1 X4 $[H_2Y^{2-}]$ - Na_2H_2Y aq. system (when Y^{4-} stands for the EDTA anion). Some separations however can still be achieved. Heights equivalent to a theoretical plate are greater than in the corresponding EDTA system, indicating that ion exchange kinetics in a DCTA system are less favourable.

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