

# SEPARATION OF RARE EARTHS ON ANION EXCHANGE RESINS

## IV. INFLUENCE OF TEMPERATURE ON ANION EXCHANGE BEHAVIOUR OF THE RARE EARTH ETHYLENEDIAMINETETRAACETATES\*

RAJMUND DYBCZYŃSKI

*Analytical Chemistry Division of the Institute of Nuclear Research,  
Warsaw (Poland)*

(Received July 11th, 1963)

Raising the temperature in order to improve the quality of separation has often been applied in ion exchange chromatography. The rise of temperature causes the diffusion coefficients to increase in the solution as well as in the resin phase and accelerates the stabilisation of local equilibrium, and hence the height ( $H$ ) equivalent of the theoretical plate diminishes. The smaller  $H$  is, the narrower are the elution curves of the separate components of the mixture, and the better the separation.

Most of the previous work in which increased temperatures were applied, *viz.* in chromatography of rare earths and actinides on cation exchange resins with the use of organic acids as eluants, concerned systems in which separation is brought about by differences in the stability constants of complexes formed by the metal ions with eluant ions and not by differences in the affinity of ions for the ion exchange resin.

In such systems the change of temperature only effects the absolute values of the distribution coefficients while the ratio of the distribution coefficients, the separation factor ( $\alpha$ ) remains practically unchanged<sup>1,2</sup>. In this case, the positive influence of the rise of temperature is exclusively concerned with decreasing the height equivalent of the theoretical plate.

In systems in which the different rates of migration of the components of a mixture down the column are due to the differences in the individual affinity of the ions for the ion exchange resin, the change of temperature has a double effect:

(a) the height equivalent of the theoretical plate ( $H$ ) diminishes with rise of temperature as usual; and

(b) the values of the distribution coefficients of the individual ions undergo changes in accordance with the values and signs of the enthalpies of the ion exchange reaction, and hence the separation factor ( $\alpha$ ) changes as well.

This second aspect of the influence of temperature has not yet been explained in the literature.

Up to now, it has been tacitly assumed that the exchange reactions' enthalpies are so small that changes of temperature cannot be of any great consequence for the course of separation.

However, when dealing with ions with very similar distribution coefficients, even small changes of the separation factor can be of great practical importance. The

\*For Part III, see ref.<sup>11</sup>.

values of the enthalpies of ion exchange reactions are of the order of several kcal<sup>3-7</sup>. This means that in the universally accessible range of temperature of 0–100°C the value of the distribution coefficient of a given ion can increase (or decrease) several times. At the same time the separation factor of two ions can increase several times especially when the enthalpy signs of the two ion exchange reactions are opposite. Rise of temperature still has one favourable effect, namely, it decreases the viscosity of solutions and thus diminishes the hydraulic resistance and permits the use of greater flow rates. In previous papers<sup>8-11</sup>, a new method of separation of rare earths on anion exchange resins was discussed which took advantage of differences in the affinity of rare earth complexes with ethylenediaminetetraacetic acid (H<sub>4</sub>Y) to ion exchange resin.

The preliminary experiments have already proved that a change of temperature has a great influence on the separation factor for particular rare earths, and in some cases the sequence of elution is even reversed. The detailed results of the investigation of the thermodynamics of anion exchange of the rare earth ethylenediaminetetraacetates have been given in another paper<sup>6</sup>.

The present publication deals with analytical aspects of the separation of rare earths in the system: Amberlite IRA-400 [H<sub>2</sub>Y<sup>2-</sup>]-Na<sub>2</sub>H<sub>2</sub>Y aq.

#### EXPERIMENTAL

##### *The ion exchange resin*

The strongly basic anion exchange resin Amberlite IRA-400 [Cl<sup>-</sup>] was ground in a ball-mill, sieved and the fraction of particle size < 0.07 mm (200 mesh) was collected. This resin was further separated into fractions according to their settling time in water. In this way a fraction was collected in which the diameter of more than 95 % of the particles was within the range of 10–35 μ, as shown by microscopic examination.

This ion exchange resin was successively treated in a glass column with a large excess of 1 N NaOH and 1 N HCl. After washing with water, the resin was transformed into ethylenediaminetetraacetate [H<sub>2</sub>Y<sup>2-</sup>] form by passing 0.2 M disodium-ethylenediaminetetraacetate solution (Na<sub>2</sub>H<sub>2</sub>Y) down the column until no chlorides could be detected in the effluent. Then ion exchanger was washed with deionized water and air dried.

In order to determine the exchange capacity a known weight of the resin was put in the column; the [H<sub>2</sub>Y<sup>2-</sup>] ions were eluted with 1 M NaCl solution and determined by titration with a standard solution of magnesium chloride in presence of Eriochrome Black T. The quantity of water in the anion exchange resin was determined by drying at 105°C constant weight.

The exchange capacity was found to be  $Z_s = 2.38$  mval/g of the dry ion exchange resin [H<sub>2</sub>Y<sup>2-</sup>].

The bed density has been previously determined and amounted to  $\bar{d}_2 = 0.326$  g of the dry ion exchange resin [H<sub>2</sub>Y<sup>2-</sup>]/ml of the bed.

##### *Reagents*

Disodium-ethylenediaminetetraacetate was prepared from commercial Na<sub>2</sub>H<sub>2</sub>Y·2H<sub>2</sub>O by purifying it by the method of BLAEDEL AND KNIGHT<sup>12</sup>. Solutions of the required concentration were prepared by dissolving the appropriate quantity of pure Na<sub>2</sub>H<sub>2</sub>Y·2H<sub>2</sub>O in deionized water. The exact concentration of the solution

was determined by titrating it with standard solution of magnesium chloride in presence of Eriochrome Black T. Since in most cases very dilute  $\text{Na}_2\text{H}_2\text{Y}$  solutions were used, the density values of pure water given in the literature were applied in order to convert molarity into molarity. The pH values of the  $\text{Na}_2\text{H}_2\text{Y}$  aq. solutions were within the range of 4.55-4.70.

#### *Radioactive tracers*

The following radioactive tracers were used:  $^{134}\text{Cs}$  (half life = 2.2 years);  $^{140}\text{La}$  (half life = 40 h);  $^{144}\text{Ce}$  (half life = 285 days);  $^{142}\text{Pr}$  (half life = 19.2 h);  $^{147}\text{Pm}$  (half life = 2.6 years);  $^{152,154}\text{Eu}$  (half life = 12.2 years);  $^{159}\text{Gd}$  (half life = 18.0 h);  $^{160}\text{Tb}$  (half life = 73.5 days);  $^{166}\text{Ho}$  (half life = 27.3 h);  $^{170}\text{Tm}$  (half life = 127 days);  $^{177}\text{Lu}$  (half life = 7.0 days);  $^{48}\text{Sc}$  (half life = 85 days);  $^{90}\text{Y}$  (half life = 65 h).

The radioactive tracers  $^{144}\text{Ce}$ ,  $^{147}\text{Pm}$  and  $^{152,154}\text{Eu}$  were supplied by Sojuzchim-Export, USSR.

The others were prepared by irradiating the appropriate spectral pure grade of oxides or chlorides (Johnson Matthey "Specpure") with neutrons in the Polish reactor EWA.

#### *Apparatus*

The apparatus used here was similar in principle to that described in a previous paper<sup>10</sup>. The only substantial difference consisted in using the jacketed columns. The temperature was maintained constant within the limits of  $\pm 0.4^\circ\text{C}$  by passing water from a Höppler ultrathermostat through the jacket. The internal diameter of the actual column was 2.1-2.7 mm. The height of the ion exchange resin bed was altered according to actual needs.

#### *Procedure*

The column filled with Amberlite IRA-400 [ $\text{H}_2\text{Y}^{2-}$ ] was rinsed with several millilitres of the eluant (the  $\text{Na}_2\text{H}_2\text{Y}$  solution of the known molarity). When the desired temperature had been obtained and the column brought to thermal equilibrium the level of the liquid in the column was adjusted to the upper level of the resin bed.

The solution of the radioactive tracers of rare earths (in HCl) together with a small quantity of  $^{134}\text{Cs}$  was evaporated to dryness in a glass crucible, then the theoretical quantity of  $\text{Na}_2\text{H}_2\text{Y}$  solution necessary to form complexes with all the rare earths was added to the crucible which was again evaporated to dryness. The residue was dissolved in 75  $\mu\text{l}$  of the eluant, and 25  $\mu\text{l}$  of this solution were introduced into the column. The total rare earth content in the "load" did not exceed 0.3 % of the exchange capacity of the ion exchange resin in the column. After the solution has passed into the resin bed, the walls of the column were rinsed with two 10  $\mu\text{l}$  portions of the eluant. A burette was connected to the column and the flow rate adjusted to about 1 ml/cm<sup>2</sup>/min. The volume of a drop was determined by noting burette readings corresponding to a known number of drops of eluant. The drops previously dried on paper were cut out with the aid of a special cutter, placed in standard plexiglass holders, and their activity was measured under identical geometrical conditions with the aid of an end-window Geiger-Müller counter. The elements corresponding to particular maxima on the elution curve were identified by determining the half life or the maxi-

imum energy of radiation, or by comparing them with the elution curves obtained for single elements under identical conditions.

The fractional free volume of the ion exchange resin bed,  $i = v/v_b$  (the ratio of the free volume to the bed volume), was determined from the changes of the peak position of the  $^{134}\text{Cs}$  ion, for which the distribution coefficient,  $\lambda$ , in the given system is equal to 0:

$$i = \frac{U_{\max 2} - U_{\max 1}}{v_{b2} - v_{b1}},$$

where  $U_{\max 2}$  and  $U_{\max 1}$  are the effluent volumes corresponding to the maxima of the caesium peak for the volumes of the ion exchange resin bed  $v_{b2}$  and  $v_{b1}$  respectively.

The fractional free volume thus determined amounts to  $i = 0.42$ .

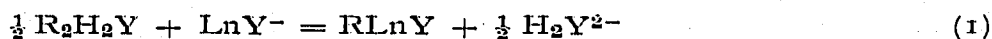
The method of determining the free volume (formula (2)<sup>10</sup>) previously applied gave results which were distinctly too high.

Although strongly basic anion exchange resins in the "salt" form are more resistant to the effects of higher temperatures than they are in the hydroxide form<sup>13</sup>, the ion exchange resin in the column was changed after each experiment where the temperature exceeded 45°C in order to avoid any complications caused by possible degradation of the functional groups<sup>14</sup>.

## RESULTS AND DISCUSSION

### *Formulation of fundamental relations*

Previous work<sup>6,9-11</sup> has shown that in  $\text{Na}_2\text{H}_2\text{Y}$  aq. solution (pH = 4.55 — 4.70) practically 100 % of all the rare earths appear in the form of their respective monovalent negative  $[\text{LnY}(\text{H}_2\text{O})]^-$  complexes. Under these conditions nearly 100 % of ethylenediaminetetraacetic acid also appears in the form of the  $\text{H}_2\text{Y}^{2-}$  anion. The ion exchange reaction (with respect to one equivalent) can be expressed as follows:



where R is the cationic part of the anion exchange resin.

Without taking into consideration the activity coefficients, the equilibrium constant of the exchange reaction, or the so called "selectivity coefficient", is given by the equation:

$$k = \frac{N_{\text{RLnY}} \cdot m_{\text{H}_2\text{Y}^{2-}}^{\frac{1}{2}}}{N_{\text{R}_2\text{H}_2\text{Y}}^{\frac{1}{2}} \cdot m_{\text{LnY}^-}} \quad (2)$$

where  $N$  is the mole fraction of the ion in the ion exchange resin and  $m$  is molality.

When the separated ions (in this case the  $\text{LnY}^-$  ions) are present in trace amounts *i.e.*  $N_{\text{R}_2\text{H}_2\text{Y}} \cong 1$ , the selectivity coefficient  $k$  is related to the weight distribution coefficient,  $\lambda$  (amount per 1 g of the dry ion exchange resin  $[\text{H}_2\text{Y}^{2-}]$ /amount per 1 ml of the solution), by the following expression<sup>6</sup>:

$$k_{\text{LnY}^-}^{\text{H}_2\text{Y}^{2-}} = \frac{\lambda_{\text{LnY}^-} \cdot m_{\text{H}_2\text{Y}^{2-}}^{\frac{1}{2}} \cdot d}{C_r} \quad (3)$$

where  $d$  = the density of the eluant solution, and

$C_r$  = the concentration of the resin phase in the units of mmol./g of the dry ion exchange resin [ $H_2Y^{2-}$ ]; ( $C_r = 1/2 Z_s$ ).

The distribution coefficient can easily be determined from the elution curve<sup>10</sup> by the formula:

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

where  $U_{\max}$  = volume of the eluant at which the concentration of the given ion reaches its maximum;

$U_0$  = dead volume of the column;

$V$  = free volume of the ion exchange resin bed; and

$m_j$  = mass of the dry ion exchange resin in the column (in grams).

Since the  $Cs^+$  ions do not form any complexes with  $H_4Y$  and are not retained by the anion exchange resin in the ethylenediaminetetraacetate form<sup>10, 15</sup>;

$$\lambda_{LnY^-} = \frac{U_{\max(LnY^-)} - U_{\max(Cs^+)}}{m_j} \quad (5)$$

The  $k$  values, determined experimentally for several temperatures, can be used to compute the respective changes of free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ). Strictly speaking the thermodynamic functions so obtained are partial molal values for  $X_{LnY^-} \cong 0$  ( $X_{LnY^-}$  is the equivalent fraction of the  $LnY^-$  ion in the ion exchange resin).

The method of computation and the exact values of  $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$  for temperatures within the range 2–92°C have been given in another paper<sup>6</sup>. As a of interest, the values of these functions for the temperature 298°K (25°C) is shown in Table I.

TABLE I

THE THERMODYNAMIC FUNCTIONS FOR THE ION EXCHANGE REACTION:  
 $1/2 R_2H_2Y + LnY^- \rightleftharpoons RLnY + 1/2 H_2Y^{2-}$

<i>Ln</i>	Atomic number <i>Z</i>	$\Delta G^*_{298^\circ K}$ kcal/equiv.	$\Delta H^*_{298^\circ K}$ kcal/equiv.	$\Delta S^*_{298^\circ K}$ cal/equiv.	$\Delta C^*_p$ cal/equiv. °K
Sc	21	—0.270	—0.135	0.45	14.1
Y	39	—0.561	—2.079	— 5.09	36.2
La	57	—1.017	2.251	10.97	7.8
Ce	58	—1.526	1.721	10.89	—0.7
Pr	59	—1.716	2.318	13.54	—33.6
Nd*	60	—1.896	2.172	13.65	—58.9
Pm	61	—2.027	1.962	13.39	—82.1
Sm*	62	—2.087	1.059	10.56	—81.8
Eu	63	—2.118	—0.225	6.35	—70.6
Gd	64	—1.961	—0.467	5.01	—73.5
Tb	65	—1.678	—1.177	1.68	—55.6
Dy*	66	—1.289	—2.016	— 2.44	—20.2
Ho	67	—0.915	—2.359	— 4.85	2.7
Er*	68	—0.526	—2.153	— 5.46	21.5
Tm	69	—0.189	—2.073	— 6.32	43.6
Yb*	70	—0.132	—1.857	— 5.79	41.8
Lu	71	—0.070	—1.998	— 6.47	42.4

\* The thermodynamic functions for these elements were calculated by the method previously described<sup>6</sup> from the values of selectivity coefficients estimated by interpolation in the  $\log k-Z$  curves (Fig. 3).

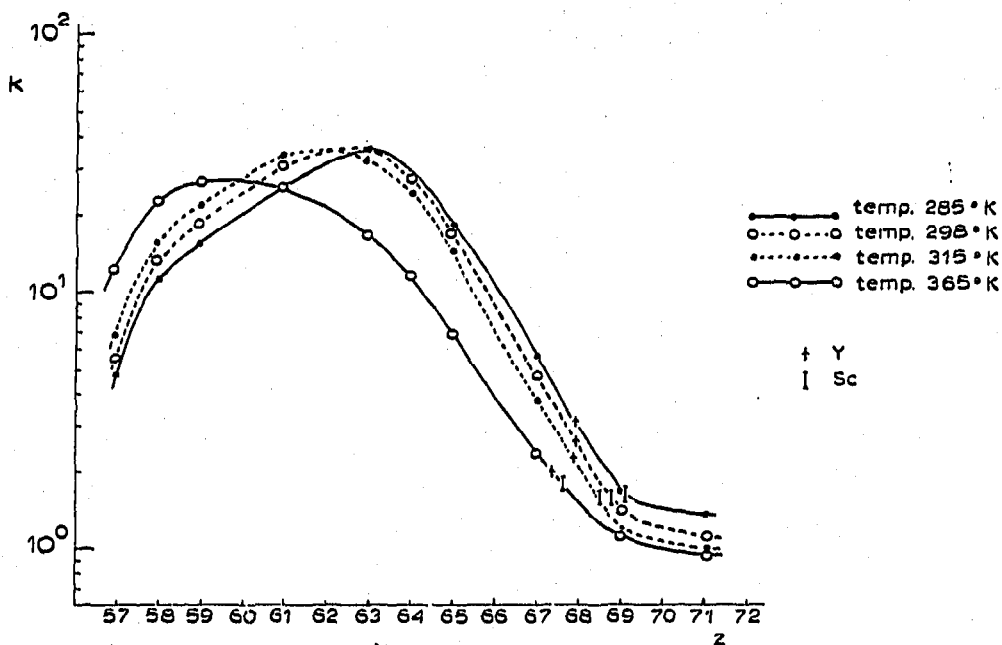


Fig. 1. Selectivity coefficients for the ion exchange reaction:  $\frac{1}{2} R_2H_2Y + LnY^- \rightleftharpoons RLnY + \frac{1}{2} H_2Y^{2-}$ , as a function of temperature. Points = experimental values; solid lines are calculated by the least squares' method<sup>6</sup>.

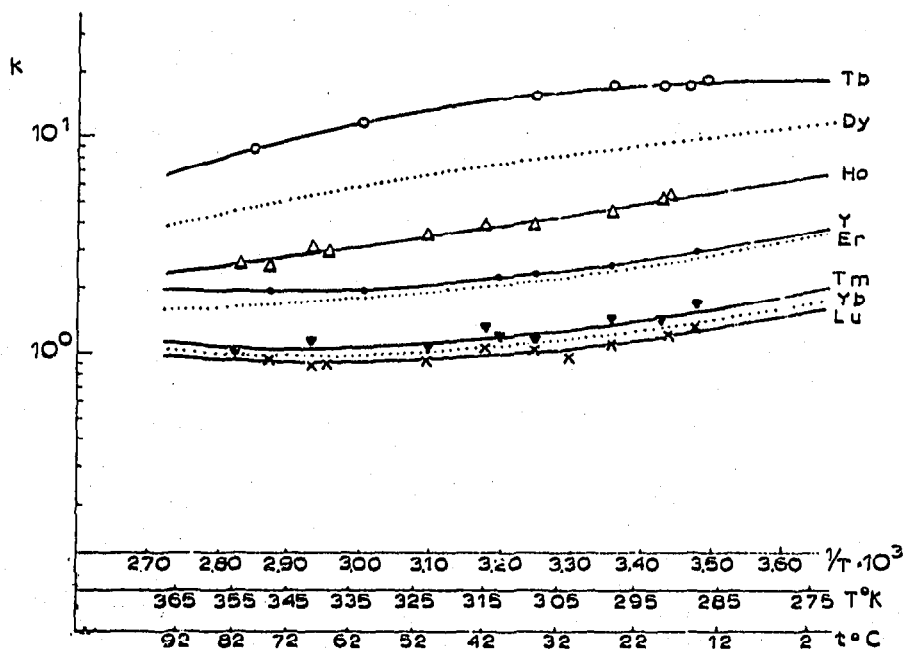


Fig. 2. Selectivity coefficients for the ion exchange reaction:  $\frac{1}{2} R_2H_2Y + LnY^- \rightleftharpoons RLnY + \frac{1}{2} H_2Y^{2-}$ , as a function of temperature. Points = experimental values; solid lines are calculated by the least squares' method<sup>6</sup>.

The  $\log k$  values for separate exchange reactions as the function of  $1/T$  are given in Figs. 1 and 2.

Fig. 3 shows the plot of  $\log k$  vs. the atomic number of the lanthanide  $Z$ .

As can be seen from Fig. 3 the  $\log k - Z$  curves consist as it were of two slopes within which  $\log k$  increases or decreases monotonically with increase of  $Z$ .

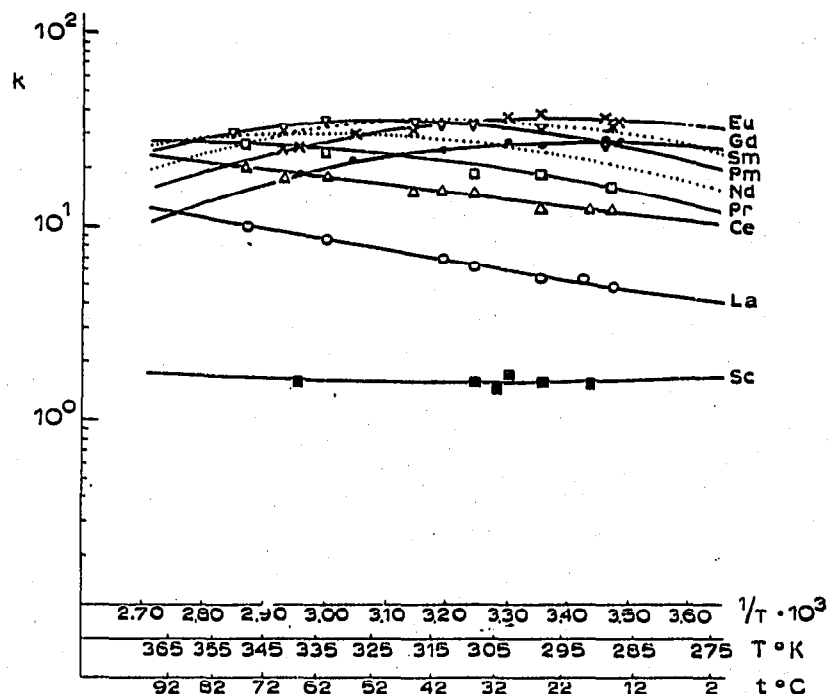


Fig. 3. Selectivity coefficients of the lanthanides in the system: Amberlite IRA-400  $[\text{H}_2\text{Y}_2^-]$ - $\text{Na}_2\text{H}^2\text{Y}$  aq., as a function of atomic number.

Owing to this, the values of  $\log k$  for the elements which were not investigated (Nd, Sm, Dy, Er, Yb) could be determined with reasonable accuracy. These results are shown in Figs. 1 and 2 by broken lines.

#### Separation factors

The separation factor  $\alpha$  (the ratio of the distribution coefficients of the components being separated) is a value of fundamental importance in ion exchange chromatography. With an increase in the separation factor a less efficient column *i.e.* the column of a smaller number of theoretical plates, is sufficient to carry out the separation required<sup>16-17</sup>.

From equation (3) the following ratio is obtained:

$$\alpha_{\text{Ln}(1)/\text{Ln}(2)} = \frac{\lambda_{\text{Ln}(1)} \text{Y}^-}{\lambda_{\text{Ln}(2)} \text{Y}^-} = \frac{K_{\text{H}_2\text{Y}_2^-}^{\text{Ln}(1)\text{Y}^-}}{K_{\text{H}_2\text{Y}_2^-}^{\text{Ln}(2)\text{Y}^-}} \quad (6)$$

From the data shown in Figs. 1 and 2 the separation factor can be computed for a deliberately chosen pair of rare earths at a given temperature. The values of the separation factors of the rare earths (with respect to europium) are given in Table II,

TABLE II  
SEPARATION FACTORS OF THE RARE EARTHS IN THE SYSTEM  
AMBERLITE IRA-400 [H<sub>2</sub>Y<sup>2-</sup>]-Na<sub>2</sub>H<sub>2</sub>Y aq. AT DIFFERENT TEMPERATURES

Element	Atomic number Z	$\frac{L_n}{\alpha_{Eu}}$										$\frac{Z}{\alpha_{Z+1}}$				
		2°	22°	42°	62°	82°	92°	2°	22°	42°	62°	82°	92°			
La	57	0.12 <sub>6</sub>	0.15 <sub>5</sub>	0.20 <sub>9</sub>	0.32 <sub>9</sub>	0.54 <sub>0</sub>	0.72 <sub>6</sub>	0.39 <sub>9</sub>	0.43 <sub>4</sub>	0.44 <sub>8</sub>	0.48 <sub>3</sub>	0.52 <sub>2</sub>	0.54 <sub>4</sub>			
Ce	58	0.31 <sub>6</sub>	0.35 <sub>6</sub>	0.46 <sub>7</sub>	0.68 <sub>1</sub>	1.05	1.34	0.83 <sub>5</sub>	0.73 <sub>6</sub>	0.70 <sub>7</sub>	0.73 <sub>1</sub>	0.78 <sub>8</sub>	0.83 <sub>1</sub>			
Pr	59	0.37 <sub>8</sub>	0.48 <sub>4</sub>	0.66 <sub>1</sub>	0.93 <sub>2</sub>	1.34	1.61	0.75 <sub>6</sub>	0.73 <sub>9</sub>	0.76 <sub>9</sub>	0.82 <sub>5</sub>	0.82 <sub>4</sub>	0.99 <sub>4</sub>			
Nd	60	0.59 <sub>0</sub>	0.65 <sub>5</sub>	0.86 <sub>0</sub>	1.13	1.45	1.62	0.80 <sub>9</sub>	0.80 <sub>1</sub>	0.82 <sub>7</sub>	0.89 <sub>7</sub>	1.01	1.07			
Pm	61	0.61 <sub>8</sub>	0.81 <sub>6</sub>	1.04	1.26	1.43	1.51	0.78 <sub>1</sub>	0.88 <sub>1</sub>	0.95 <sub>4</sub>	1.05	1.16	1.20			
Sm	62	0.79 <sub>1</sub>	0.92 <sub>8</sub>	1.07	1.20	1.23	1.26	0.79 <sub>1</sub>	0.92 <sub>9</sub>	1.09	1.20	1.23	1.26			
Eu	63	1.00	1.00	1.00	1.00	1.00	1.00	1.27	1.30	1.34	1.38	1.42	1.44			
Gd	64	0.78 <sub>9</sub>	0.76 <sub>7</sub>	0.74 <sub>8</sub>	0.72 <sub>5</sub>	0.70 <sub>4</sub>	0.69 <sub>2</sub>	1.41	1.60	1.69	1.73	1.71	1.68			
Tb	65	0.55 <sub>9</sub>	0.47 <sub>9</sub>	0.44 <sub>2</sub>	0.42 <sub>0</sub>	0.41 <sub>1</sub>	0.41 <sub>0</sub>	1.57	1.89	1.96	1.93	1.80	1.72			
Dy	66	0.35 <sub>6</sub>	0.25 <sub>4</sub>	0.22 <sub>5</sub>	0.21 <sub>8</sub>	0.22 <sub>8</sub>	0.23 <sub>8</sub>	1.77	1.87	1.96	1.90	1.80	1.71			
Ho	67	0.20 <sub>1</sub>	0.13 <sub>6</sub>	0.11 <sub>5</sub>	0.11 <sub>5</sub>	0.12 <sub>7</sub>	0.13 <sub>9</sub>	1.89	1.94	1.80	1.69	1.54	1.48			
Er	68	0.10 <sub>7</sub>	0.070 <sub>f</sub>	0.063 <sub>8</sub>	0.068 <sub>2</sub>	0.082 <sub>6</sub>	0.094 <sub>2</sub>	1.76	1.75	1.78	1.65	1.51	1.41			
Tm	69	0.060 <sub>9</sub>	0.040 <sub>0</sub>	0.035 <sub>9</sub>	0.041 <sub>2</sub>	0.054 <sub>8</sub>	0.066 <sub>6</sub>	1.17	1.10	1.11	1.10	1.06	1.08			
Yb	70	0.052 <sub>1</sub>	0.036 <sub>3</sub>	0.032 <sub>2</sub>	0.037 <sub>3</sub>	0.051 <sub>5</sub>	0.057 <sub>8</sub>	1.07	1.11	1.08	1.07	1.11	1.09			
Lu	71	0.048 <sub>6</sub>	0.032 <sub>6</sub>	0.029 <sub>9</sub>	0.034 <sub>7</sub>	0.046 <sub>6</sub>	0.056 <sub>9</sub>									
Sc	21	0.950 <sub>5</sub>	0.044 <sub>2</sub>	0.048 <sub>0</sub>	0.061 <sub>0</sub>	0.085 <sub>4</sub>	0.10 <sub>4</sub>									
Y	39	0.11 <sub>3</sub>	0.074 <sub>9</sub>	0.067 <sub>0</sub>	0.075 <sub>3</sub>	0.097 <sub>3</sub>	0.11 <sub>6</sub>									



together with the separation factors of adjacent elements computed for 20-degree intervals within the range of temperature of 2–92°C.

It can be seen in Table II that the separation factors of rare earths in the Amberlite IRA-400 [H<sub>2</sub>Y<sup>2-</sup>]-Na<sub>2</sub>H<sub>2</sub>Y aq. system depend to a high degree on the temperature. This is an undisputed consequence of the fact that the value and sign of enthalpies:

$$\Delta H^* = -2.303 R \frac{d \log k}{d\left(\frac{1}{T}\right)},$$

of the exchange reaction expressed by equation (1) are different for particular rare earths (see Figs. 1 and 2, and Table I); also  $\Delta H^*$  is a function of temperature<sup>9</sup>. ( $\Delta H^* = \Delta H_0^* + \Delta C_p^* \cdot T$ ) and the heat capacities  $\Delta C_p^*$  are different for different rare earths (cf. Table I). The separation factors relative to europium, which are  $< 1$  for all the rare earths at lower temperatures, can have the values  $> 1$  as the temperature rises (in case of the lanthanides of the cerium group). For some elements the sequence of the elution has been shown to be reversed. The maximum on the  $\log k$ - $Z$  curve, which for low temperatures occurs in the position of europium ( $Z = 63$ ), moves along the axis as the temperature rises to smaller values of  $Z$ , and at 365°K it occurs in the region of the Pr-Nd pair ( $Z = 59$ -60). In the light of these findings, it becomes clear that the selectivity coefficient values given previously<sup>10, 11</sup> must be of dubious value since the room temperature at which those measurements were made was not precisely defined and it could change by as much as 10–15 degrees according to the season.

The fact that the course of the  $\log k$ - $1/T$  curves is quite different for particular rare earths is very interesting when one considers the well known similarity of these elements and the fact that they form complexes of identical stoichiometric composition with H<sub>4</sub>Y. The discussion on the values of thermodynamic functions<sup>9</sup> seems to have proved the hypothesis<sup>9, 10</sup> put forward previously as to the structural changes of the LnY<sup>-</sup> complex with respect to the changes of the central ion radius. The properties of the complex ion are likely to depend not only on the dimensions on the central ion but also on its electronic structure, and hence on the presence or absence of the 4f electrons. From the analytical point of view it is important that by changing the temperature it is possible to influence the separation factors of particular rare earths and in some cases to reverse the sequence of elution.

#### *The number of theoretical plates and the resolution*

The number of theoretical plates  $N$  in the column can be computed with the aid of the theory of MAYER AND TOMPKINS<sup>18</sup> from the formula derived previously<sup>19</sup>:

$$N = 8 \left( \frac{C}{C + 1} \right) \frac{(U_{\max} - U_0)^2}{W^2} \quad (7)$$

where apart from the symbols already explained,

$C$  = distribution ratio, *i.e.* the ratio of the concentration of the substance in the ion exchange resin to the concentration in the solution on one theoretical plate;

$W$  = width of the peak for the  $M = M_{\max}/e = 0.368 \cdot M_{\max}$  ordinate.

The expression  $C/(C + 1)$  for  $C > 10$ , *i.e.* for the majority of cases given in this paper, is close to 1 and formula (7) takes the form:

$$N = 8 \frac{(U_{\max} - U_0)^2}{W^2} \quad (8)$$

Formula (8) is identical with the formula computed by GLUECKAUF<sup>16</sup> when taking advantage of the "continuous flow" model instead of the "discontinuous flow" model applied by MAYER AND TOMPKINS. According to the theory, the elution curves of particular components (peaks) have the form of the normal Gaussian distribution curves. As a result of the properties of normal diffusion:

$$w = \sqrt{2} \cdot 2\sigma \quad (9)$$

where  $\sigma$  is the dispersion (standard deviation) of the peak.

Substituting the above equation in the equation (8), we have:

$$N = \frac{(U_{\max} - U_0)^2}{\sigma^2} \quad (10)$$

The height equivalent of the theoretical plate  $H$  can now easily be obtained from the formula:

$$H = \frac{L}{N} = \frac{L \sigma^2}{(U_{\max} - U_0)^2} \quad (11)$$

where  $L$  is the length of the column.

The value of  $H$  can also be derived from the theoretical formula<sup>20, 21</sup>:

$$H = 1.64 r + \frac{\lambda'}{(\lambda' + i)^2} \cdot \frac{0.142 r^2 u}{D_s} + \frac{(\lambda')^2}{(\lambda' + i)^2} \cdot \frac{0.266 r u}{(1 - i) D_L (1 + 70 r u)} \quad (12)$$

where  $r$  = the radius of the ion exchange resin particle,  
 $\lambda'$  = the bed distribution coefficient ( $\lambda' = \lambda - dz$ ),  
 $i$  = the fractional free volume of the bed,  
 $D_s, D_L$  = the diffusion coefficients in the ion exchange resin and in the solution respectively, and  
 $u$  = the linear flow rate of the eluant solution.

It can be seen from (12) that in the case when the deciding factor for the reaction time is the diffusion in the ion exchange resin phase, then the height equivalent to the theoretical plate is a function of the distribution coefficient and diminishes as  $\lambda'$  increases.

The dispersion (standard deviation) for the elution curve is given by the formula<sup>21</sup>:

$$\sigma = S\sqrt{L} \sqrt{1.64 r (\lambda' + i)^2 + \frac{0.142 \lambda' r^2 u}{D_s} + \frac{0.266 (\lambda')^2 r^2 u}{(1 - i) D_L (1 + 70 r u)}} \quad (13)$$

where  $S$  is the area of the column cross section.

It is well known that the diffusion coefficients increase with rise of temperature.

According to (12) and (13) the rise of temperature should bring about diminution of  $H$  as well as of  $\sigma$ .

Fig. 4 represents the experimentally determined relation between  $H$  and the distribution coefficient at different temperatures. It is easy to see from Fig. 4a that for a given value of the distribution coefficient and flow rate the height equivalent of the theoretical plate decreases, as the temperature increases. Simultaneously the value of  $H$  diminishes as the distribution coefficient increases, and this effect is particularly noticeable for small values of  $\lambda$ .

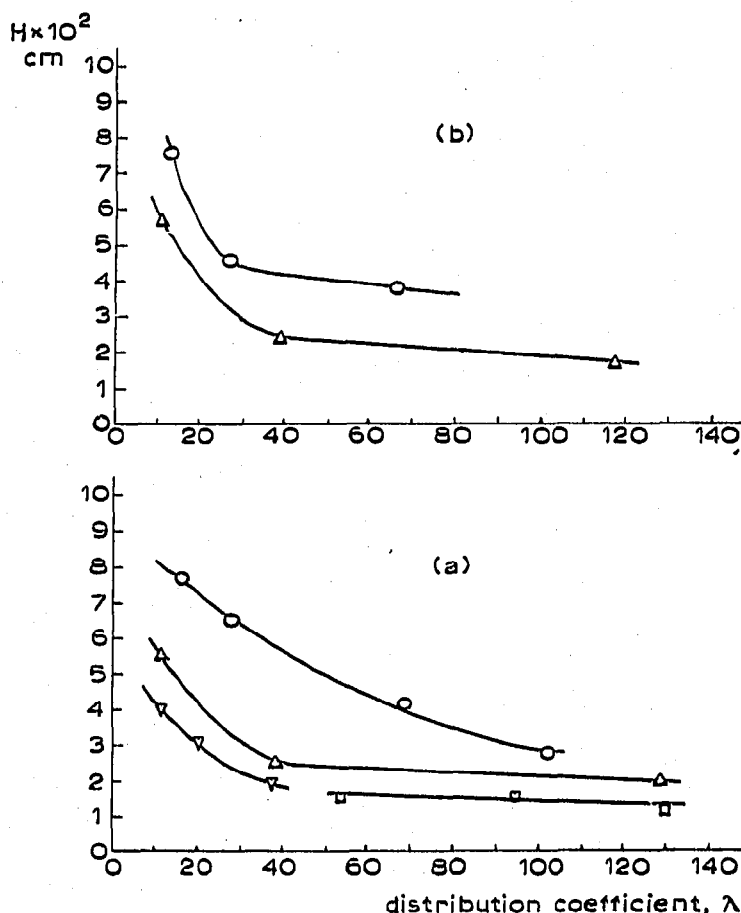


Fig. 4. Height equivalent to a theoretical plate as a function of distribution coefficient for various temperatures and flow rates. (a) —○—○— elution of Y, La, Ce and Pr; temp. 18°; —△—△— elution of Y, La and Pr; temp. 50°; —□—□— elution of Tb, Gd and Eu; temp. 55°; —▽—▽— elution of Lu, Sc and Ho; temp. 65°;  $u = 1.8-2.1 \cdot 10^{-2}$  ml/cm<sup>2</sup>/sec. (b) —○—○— elution of Y, La and Ce;  $u = 1.82 \cdot 10^{-2}$  ml/cm<sup>2</sup>/sec; —△—△— elution of Tm, La and Tb;  $u = 1.06 \cdot 10^{-2}$  ml/cm<sup>2</sup>/sec.; temp. 25°.

Fig. 4b shows the influence of the flow rate on the height equivalent of the theoretical plate. According to equation (12) as the flow rate decreases so does the value of  $H$ . All the data given above prove that the ion exchange reaction expressed by equation (1) is at least in part controlled by particle diffusion.

It can be shown from equation (10) that the greater the number of theoretical plates, the smaller the value of  $\sigma$  *i.e.* the narrower the peaks of separate components and the smaller their overlap.

The resolution of two components,  $R$  depends on the interval between the maxima as well as on the dispersions of the peaks themselves.

In gas chromatography the separation is generally deemed to be adequate when the interval between the maxima amounts to  $4\sigma$ <sup>22-23</sup>; it is often assumed that the dispersion of both peaks is practically identical  $\sigma_1 \cong \sigma_2 = \sigma$ .

This problem has recently been considered in a more general way, the "resolution  $N\sigma$ " being taken as the criterion for the separation, the value of  $N$  being chosen according to the actual problem.

In ion exchange chromatography the assumption that the dispersions of neighbouring peaks are identical is generally far from being true. The resolution can thus be defined in general terms as follows:

$$R_n = \frac{U_{\max(2)} - U_{\max(1)}}{n(\sigma_1 + \sigma_2)} = \frac{\Delta U_{\max}}{n(\sigma_1 + \sigma_2)} \quad (14)$$

where  $n$  is an arbitrary number greater than 0.

In the present paper the separation of two components is taken as being complete if:

$$\Delta U_{\max} \geq 3(\sigma_1 + \sigma_2) \text{ i.e. } R_3 \geq 1 \quad (15)$$

This means that after having divided the effluent into fractions at the point  $U = U_{\max(1)} + 3\sigma_1$  at least 99.86 % of each of the components is in its appropriate fraction, and the impurity amounts to at most 0.14 % of the peak of the contiguous component.

It should be stressed, however, that for analytical purposes, *e.g.* for quantitative determinations effected directly from the elution curve by means of the previously described method<sup>19</sup>, the condition that  $R_2 \geq 1$ , ( $R_2 = 1.5 R_3$ ) is in many cases sufficient.

#### *Analysis of the elution curves*

In Figs. 5-9 several experimental elution curves are shown which illustrate influence of temperature on the separation of rare earths. For each pair of peaks the separation factors  $\alpha_1^2$  are given (computed from formula (7)), as well as the resolutions  $R_3$  computed from formula (14).

As has been shown above, as the temperature rises the number of the theoretical plates in the column increases. Simultaneously the separation factor changes on account of thermodynamic changes in the distribution coefficients of the components being separated.

For a certain limited range of temperature three cases are possible, *viz.*:

- (a)  $\alpha_1^2$  increases as the temperature rises;
- (b)  $\alpha_1^2$  remains practically constant;
- (c)  $\alpha_1^2$  decreases as the temperature rises.

Case (a) is illustrated, among others, by the elution curves of the pairs Tb-Pm (Fig. 6), Eu-Pm (Fig. 7), Lu-Sc (Fig. 8) and Y-La (Fig. 9).

On account of the accumulation of the effects of the simultaneous increase of  $N$  and  $\alpha_1^2$  the resolution increases very rapidly as the temperature rises. In case (b) where the separation factor remains constant or changes only very slightly, the resolution increases far more slowly; *cf.* the elution curves of the pairs Gd-Eu (Fig. 5) and Ce-Pr (Fig. 9).

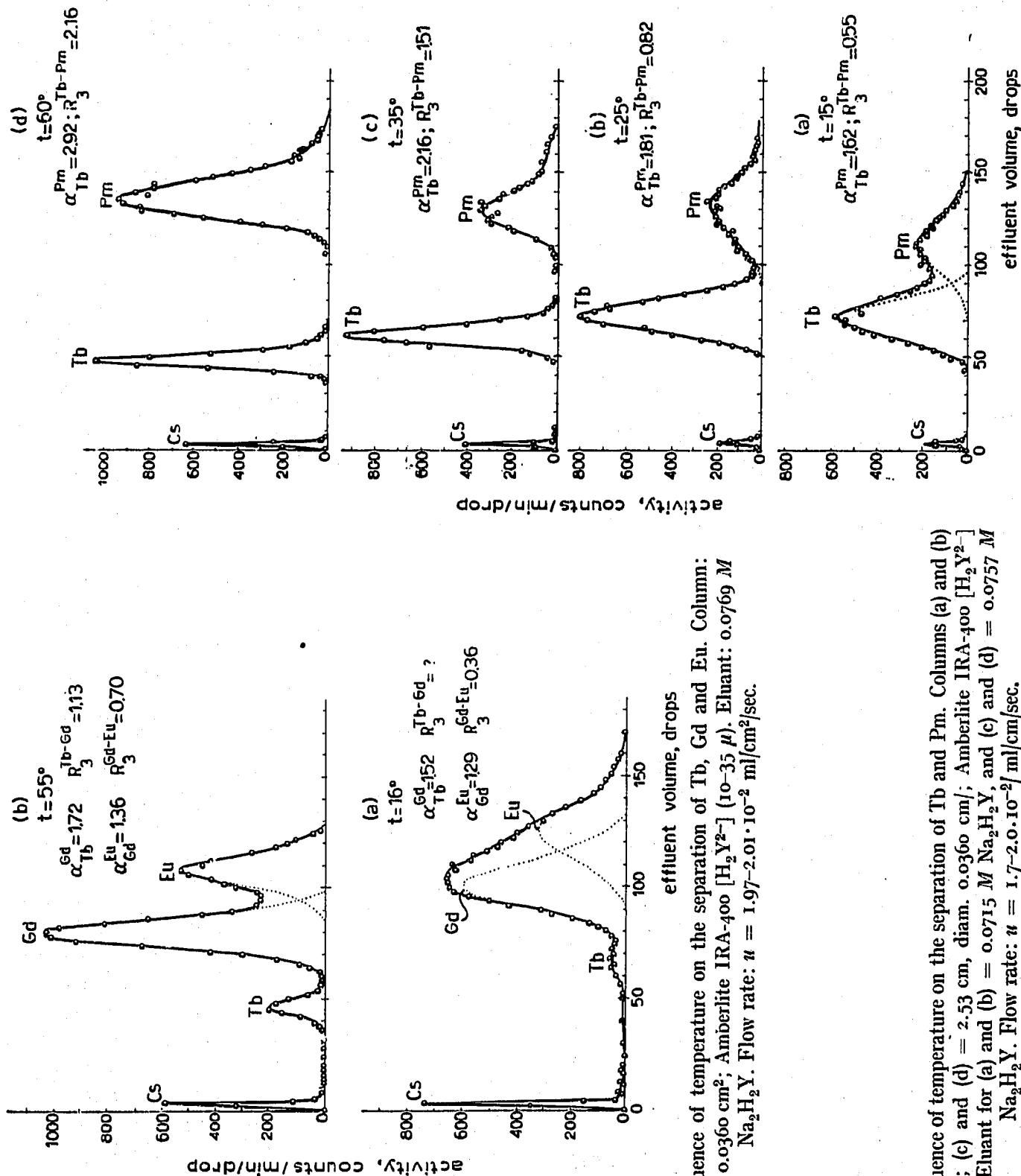


Fig. 5. Influence of temperature on the separation of Tb, Gd and Eu. Column:  $2.50 \text{ cm} \times 0.0360 \text{ cm}^2$ ; Amberlite IRA-400  $[\text{H}_2\text{Y}^{2-}]$  (10-35  $\mu$ ). Eluant: 0.0769 M  $\text{Na}_2\text{H}_2\text{Y}$ . Flow rate:  $u = 1.97-2.01 \cdot 10^{-2} \text{ ml/cm}^2/\text{sec}$ .

Fig. 6. Influence of temperature on the separation of Tb and Pm. Columns (a) and (b) = 2.50 cm; (c) and (d) = 2.53 cm, diam. 0.0360 cm; Amberlite IRA-400  $[\text{H}_2\text{Y}^{2-}]$  (10-35  $\mu$ ). Eluant for (a) and (b) = 0.0715 M  $\text{Na}_2\text{H}_2\text{Y}$ , and (c) and (d) = 0.0757 M  $\text{Na}_2\text{H}_2\text{Y}$ . Flow rate:  $u = 1.7-2.0 \cdot 10^{-2} \text{ ml/cm}^2/\text{sec}$ .

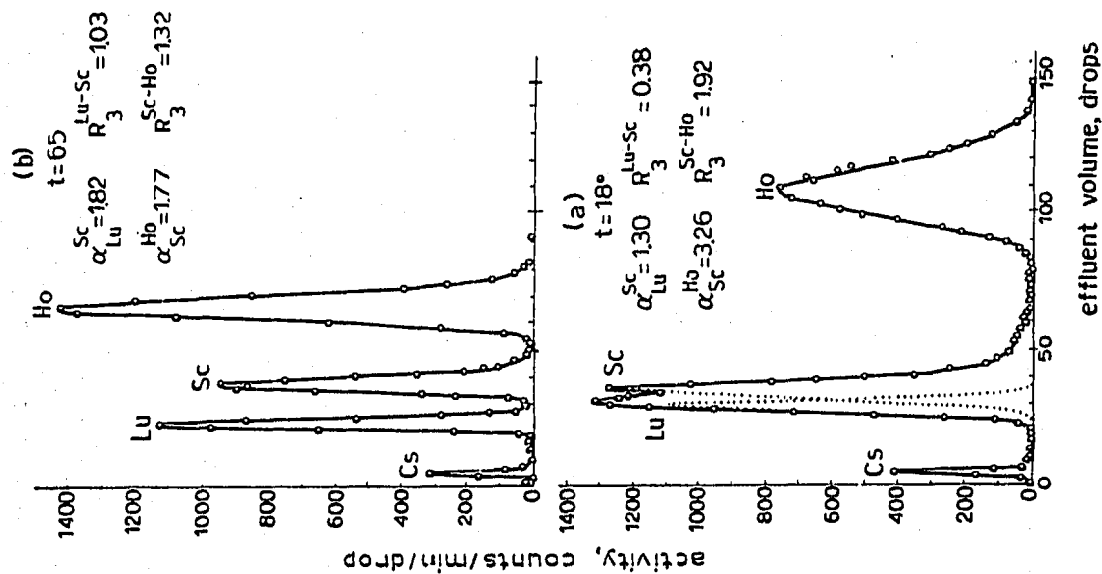


Fig. 8. Influence of temperature on the separation of Lu, Sc and Ho. Column:  $4.65 \text{ cm} \times 0.0360 \text{ cm}^2$ ; Amberlite IRA-400 [ $\text{H}_2\text{Y}^2-$ ] ( $10\text{-}35 \mu$ ); Eluant:  $0.0089 \text{ M Na}_2\text{H}_2\text{Y}$ ; Flow rate:  $u = 1.8\text{-}2.1 \cdot 10^{-2} \text{ ml/cm}^2/\text{sec}$ .

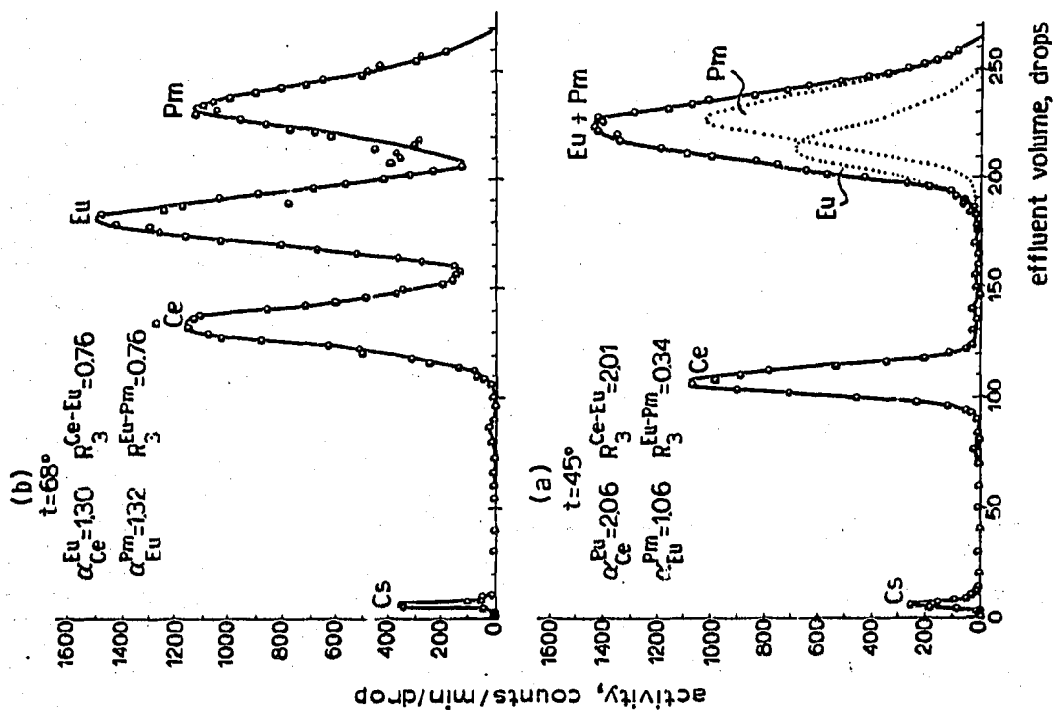


Fig. 7. Influence of temperature on the separation of Ce, Eu and Pm. Column:  $2.90 \text{ cm} \times 0.0556 \text{ cm}^2$ ; Amberlite IRA-400 [ $\text{H}_2\text{Y}^2-$ ] ( $10\text{-}35 \mu$ ); Eluant:  $0.0761 \text{ M Na}_2\text{H}_2\text{Y}$ ; Flow rate:  $u = 1.05\text{-}1.14 \cdot 10^{-2} \text{ ml/cm}^2/\text{sec}$ .

The last case (c) is perhaps the most interesting where changes of both factors affecting the final value of the resolution run in opposite directions. Depending on which of them prevails, the resolution can either decrease, *e.g.*, elution of the pairs Ce–Eu (Fig. 7) and Sc–Ho (Fig. 8), or increase, *e.g.* elution of the pair La–Ce (Fig. 9).

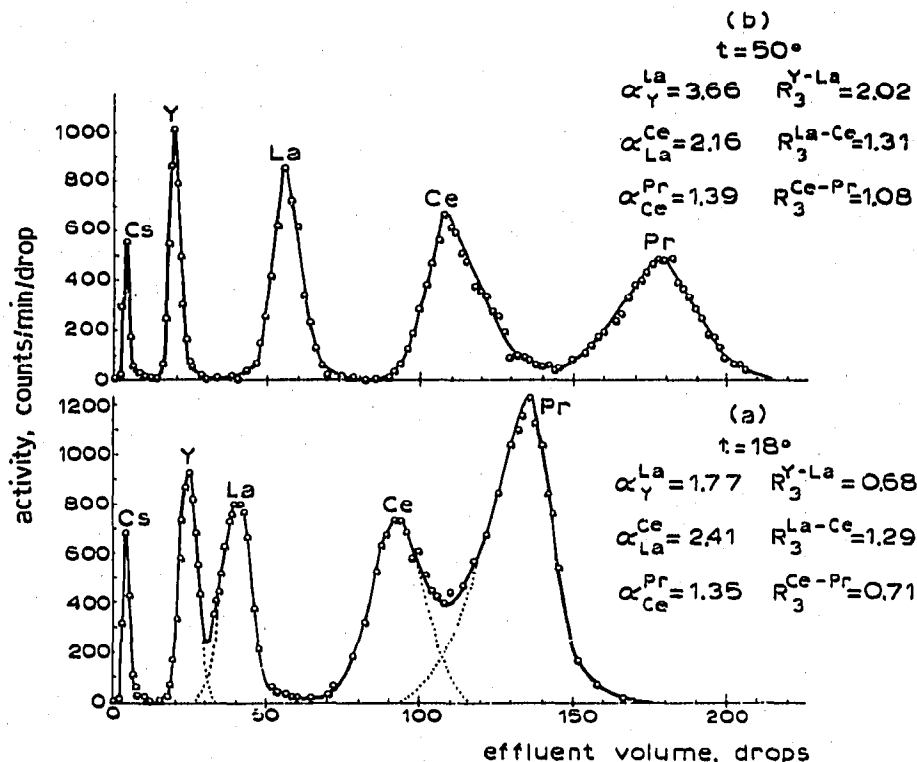


Fig. 9. Influence of temperature on the separation of Y, La, Ce and Pr. Column: 4.20 cm  $\times$  0.0360 cm<sup>2</sup>; Amberlite IRA-400 [H<sub>2</sub>Y<sup>2-</sup>] (10–35  $\mu$ ); Eluant: 0.0447 M Na<sub>2</sub>H<sub>2</sub>Y; Flow rate:  $u = 1.82-1.88 \cdot 10^{-2}$  ml/cm<sup>2</sup>/sec.

It, must however, be said that sometimes it is worth discarding very good resolution in order to considerably reduce the time of separation.

This is illustrated by the following example. At 18°C good resolution ( $R_3^{Sc-Ho} = 1.92$ ) was obtained for the pair Sc–Ho, yet at the same time the separation of lutetium from scandium is unsatisfactory (see Fig. 8) and the time needed rather long. With an increase of temperature to 65°C,  $R_3^{Sc-Ho} = 1.32$ , the separation of scandium from holmium continues to be complete according to the assumed criterion (15), but on the other hand their separation time is nearly half. In addition to this, at 65°C the separation of lutetium from scandium is also complete ( $R_3^{Lu-Sc} = 1.03$ ).

#### Other aspects of the changes of temperature

As has already been mentioned temperature influences also the separation time. The rate of movement of the band of the component down the column  $u_x$ , and strictly speaking the speed with which the peak maximum moves, is given by the formula<sup>25</sup>:

$$u_x = \frac{u}{\lambda' + i} \quad (16)$$

The speed of the movement of the band is approximately inversely proportional

to the distribution coefficient. Since the distribution coefficient is also a function of temperature hence the latter expresses (other conditions remaining unchanged) the time of separation.

The diminution of the dispersion of the peak as the temperature increases may also be important.

When using an ion exchange resin of very fine particles the flow of the liquid in the column is hindered considerably, and it can sometimes be very difficult to achieve an adequately high flow rate. The rise of temperature diminishes the hydraulic resistance and consequently a higher flow rate or the required flow rate at a lower pressure can be achieved.

As can be seen from Fig. 10 the pressure which must be applied for a given column in order to achieve the required flow rate decreases as the temperature rises and is also dependent upon the changes of viscosity of the water<sup>26</sup>.

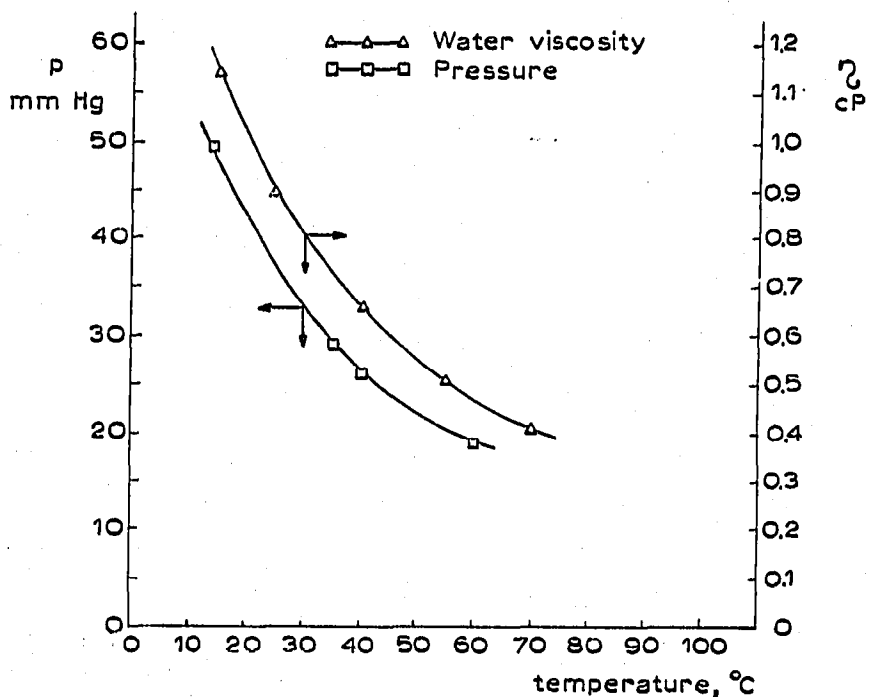


Fig. 10. Pressure which must be applied to obtain the desired flow rate, as a function of temperature. Column: 2.62 cm  $\times$  0.0360 cm<sup>2</sup>; Amberlite IRA-400 [H<sub>2</sub>Y<sup>2-</sup>] (10-35  $\mu$ ); Eluant: 0.0754 M Na<sub>2</sub>H<sub>2</sub>Y; Flow rate:  $u = 1.73-1.77 \cdot 10^{-2}$  ml/cm<sup>2</sup>/sec.

#### *New possibilities of qualitative analysis*

In a given chromatographic system the distribution coefficient is the characteristic feature of a substance and can help to identify it in a mixture. In ion exchange chromatography such a characteristic value can be the distribution coefficient, for a given concentration of the eluant, as well as the selectivity coefficient which in principle is independent from the concentration of the eluant; *cf.* equation (3). Conclusions drawn as to the presence or absence of a substance from  $\lambda$  or  $k$  values computed from the elution curve are not specific, since different substances can have identical or very similar distribution coefficients. Because of this, it has been suggested<sup>27</sup> that the



value of the selectivity coefficient should not be taken as a criterion of identification but its change as a function of temperature.

As has been shown in the present paper (Figs. 1 and 2) and in the literature<sup>4, 5, 21</sup> the  $\log k-1/T$  curves have a different course for the seemingly similar substances. On account of this determination of selectivity coefficients from the elution curves for several discreet temperature intervals and comparison of these data with the previously determined  $\log k-1/T$  curves of the substances of interest should be a more specific method. As far as the analysis of rare earths in the system discussed here is concerned this method allows identification of trace amounts of separate elements in a mixture, with a prevailing excess of other components. In this way it is possible to identify radioactive rare earths in such small amounts that the half-lives cannot be determined precisely<sup>27</sup>.

#### ACKNOWLEDGEMENTS

The author is indebted to Prof. Dr. J. MINCZEWSKI for valuable discussions and observations and to Mrs. M. MARECKA for her help in carrying out the experiments.

#### SUMMARY

The influence of temperature on the anion exchange behaviour of the rare earth elements in the system: Amberlite IRA-400 [ $H_2Y^{2-}$ ]-aq. solution of disodium ethylenediaminetetraacetate ( $Na_2H_2Y$ ) has been investigated. In the system examined the change of temperature has a double effect: (1) the height equivalent to a theoretical plate decreases with a rise of temperature; (2) the distribution coefficients of the individual ions undergo changes according to the enthalpy values of the ion exchange reactions. As the enthalpies of the ion exchange reactions differ in magnitude and sign for different rare earths, the separation factors (ratio of distribution coefficients) may undergo considerable changes with a change of temperature. Both effects contribute to the final resolution value; for some elements the order of elution is even reversed.

New possibilities in qualitative analysis, resulting from the determination of the selectivity coefficient of an exchange reaction for a given ion at different temperatures, have been pointed out.

#### REFERENCES

- <sup>1</sup> B. H. KETELLE AND G. E. BOYD, *J. Am. Chem. Soc.*, 69 (1947) 2800.
- <sup>2</sup> G. R. CHOPPIN AND R. J. SILVA, *J. Inorg. Nucl. Chem.*, 3 (1956) 153.
- <sup>3</sup> O. D. BONNER AND R. R. PRUETT, *J. Phys. Chem.*, 63 (1959) 1417 and 1420.
- <sup>4</sup> K. A. KRAUS AND R. J. RARIDON, *J. Phys. Chem.*, 63 (1959) 1901.
- <sup>5</sup> K. A. KRAUS, R. J. RARIDON AND D. L. HOLCOMB, *J. Chromatog.*, 3 (1960) 178.
- <sup>6</sup> R. DYBCZYŃSKI, *Roczniki Chem.*, 37 (1963) 1411.
- <sup>7</sup> E. H. CRUICKSHANK AND P. MEARES, *Trans. Faraday Soc.*, 53 (1957) 1289.
- <sup>8</sup> R. DYBCZYŃSKI, *Mitteilungsblatt der Chemischen Gesellschaft in der DDR*, Sonderheft 1960, Analytische Chemie, p. 393-401.
- <sup>9</sup> J. MINCZEWSKI AND R. DYBCZYŃSKI, *Chem. Anal. (Warsaw)*, 6 (1961) 275.
- <sup>10</sup> J. MINCZEWSKI AND R. DYBCZYŃSKI, *J. Chromatog.*, 7 (1962) 98.
- <sup>11</sup> J. MINCZEWSKI AND R. DYBCZYŃSKI, *J. Chromatog.*, 7 (1962) 568.
- <sup>12</sup> W. J. BLAEDEL AND H. T. KNIGHT, *Anal. Chem.*, 26 (1954) 741.
- <sup>13</sup> R. M. WHEATON AND W. C. BAUMAN, *Ind. Eng. Chem.*, 43 (1951) 1088.
- <sup>14</sup> R. DYBCZYŃSKI, *Przemysł Chem.*, 38 (1959) 216.
- <sup>15</sup> F. NELSON, *J. Am. Chem. Soc.*, 77 (1955) 813.

- <sup>16</sup> E. GLUECKAUF, *Trans. Faraday Soc.*, 51 (1955) 34.  
<sup>17</sup> F. W. CORNISH, *Analyst*, 83 (1958) 634.  
<sup>18</sup> S. W. MAYER AND E. R. TOMPKINS, *J. Am. Chem. Soc.*, 69 (1947) 2866.  
<sup>19</sup> J. MINCZEWSKI AND R. DYBCZYŃSKI, *Chem. Anal. (Warsaw)*, 6 (1961) 725.  
<sup>20</sup> E. GLUECKAUF, *Ion Exchange and its Applications*, Society of Chemical Industry, London, 1958.  
<sup>21</sup> P. B. HAMILTON, D. C. BOGUE AND R. A. ANDERSON, *Anal. Chem.*, 32 (1960) 1782.  
<sup>22</sup> *Gas chromatography*, D. H. DESTY, Editor, Butterworths Scientific Publications, London, 1958, p. xi.  
<sup>23</sup> D. AMBROSE, A. T. JAMES, A. I. M. KEULEMANS, E. KOVÁTS, H. RÖCK, C. ROUIT AND F. H. STROSS, *Pure and Applied Chemistry*, 1 (1960) 169.  
<sup>24</sup> H. STRICKLER AND E. sz. KOVÁTS, *J. Chromatog.*, 8 (1962) 289.  
<sup>25</sup> F. HELFFERICH, *Ion Exchange*, Mc. Graw-Hill Book Company Inc., New York, 1962, p. 455.  
<sup>26</sup> *Kalendarz Chemiczny*, Part. I, PWT, Warsaw, 1954, p. 280.  
<sup>27</sup> R. DYBCZYŃSKI, *Anal. Chim. Acta*, 29 (1963) 369.

*J. Chromatog.*, 14 (1964) 79-96