REVERSED-PHASE PARTITION CHROMATOGRAPHY WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID AS THE STATIONARY PHASE

PART II. FACTORS AFFECTING THE HEIGHT OF THE PLATE

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In Part I of this series[1], results were reported of the use of di-(2-ethylhexyl) orthophosphoric acid (HDEHP) retained on kieselguhr for the separation of rare earths. The aim of the present work is the detailed study of the factors affecting the height of the plate in reversed phase partition chromatography with HDEHP as extracting agent.

EXPERIMENTAL

Column material and methods of preparation were the same as previously described[1]. The inner diameter of the columns was 3 mm and the length of the bed was 10 cm in all experiments. The weight ratio of HDEHP to kieselguhr was 1:10. For runs at elevated temperatures columns were fitted with water jackets fed from a thermostat. Heating up to 70° did not change the mechanical properties of the bed, although some bubble formation was observed.

RESULTS AND DISCUSSION

The effect of flow rate and temperature on the height of the plate

It is generally assumed that the effective height of the plate (H) is the sum of three independent components:

$$H = H_O + H_D + H_T$$

where the finite thickness of the grains is responsible for H_O, the longitudinal diffusion for H_D and some slow step in the mass transfer between the two phases for H_T. Provided the flow rate (v) is not too slow H_O is independent of flow rate, whereas H_D decreases and H_T increases with increasing flow rate. At constant flow rate, an increase in temperature causes the value of H_D to increase and that of H_T to decrease. Study of the effect of temperature and flow rate should provide evidence on which component is the most important in determining the overall height of the plate. Experiments on the effect of flow rate and temperature were performed for Eu, Tb and Tm in HNO_3 and HCl. The results obtained are shown in Figs 1, 2, 3, 4, 5 and 6. The main conclusions are as follows:
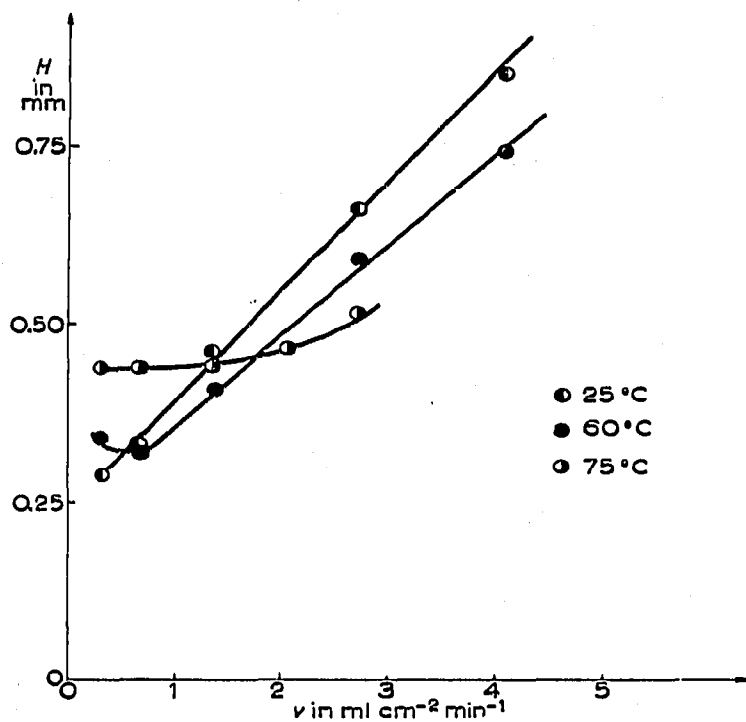
Fig. 1. The effect of flow rate and temperature on the height of the plate. Elution of Eu with 0.36 M HNO$_3$.
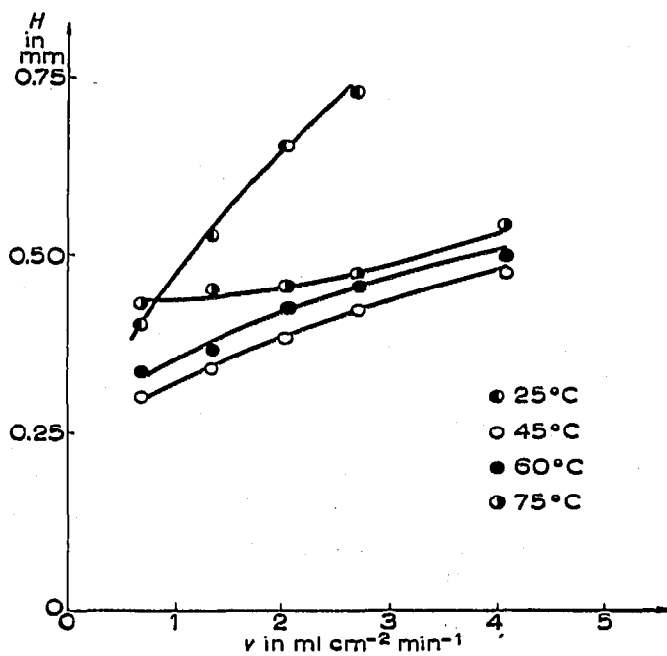

Fig. 2. The effect of flow rate and temperature on the height of the plate. Elution of Eu with 0.36 M HCl.
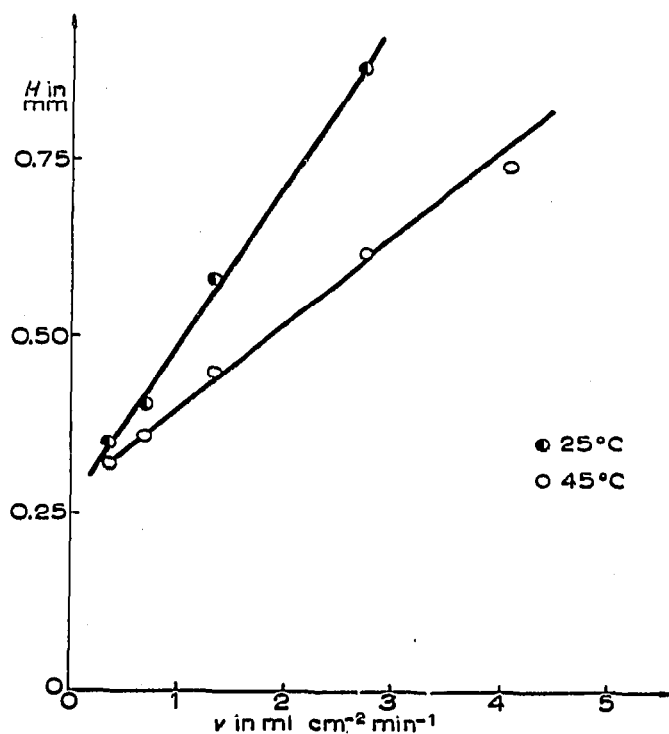
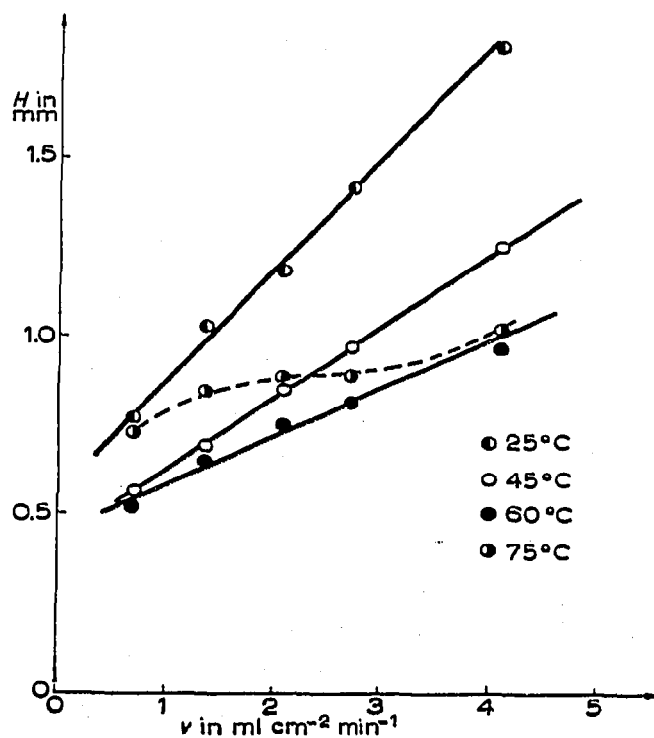Fig. 3. The effect of flow rate and temperature on the height of the plate. Elution of Tb with 0.86 M HNO$_3$.

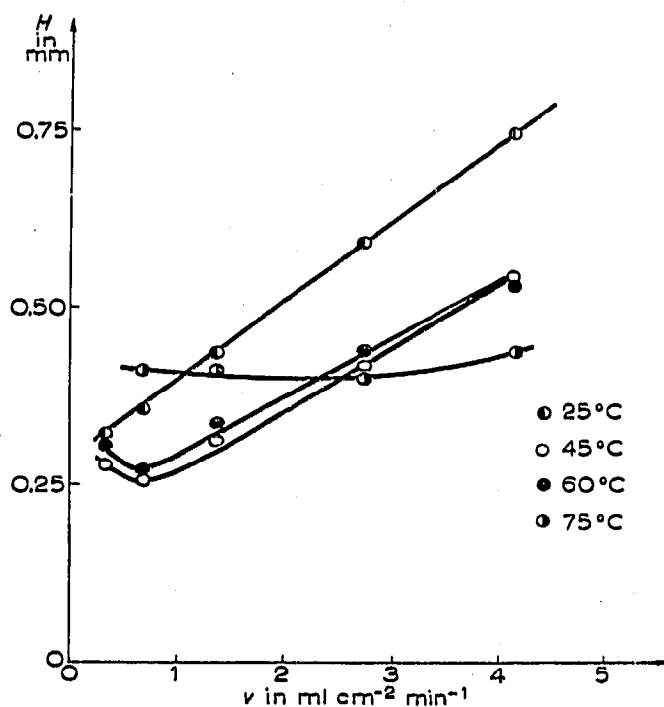Fig. 4. The effect of flow rate and temperature on the height of the plate. Elution of Tb with 0.86 M HCl.

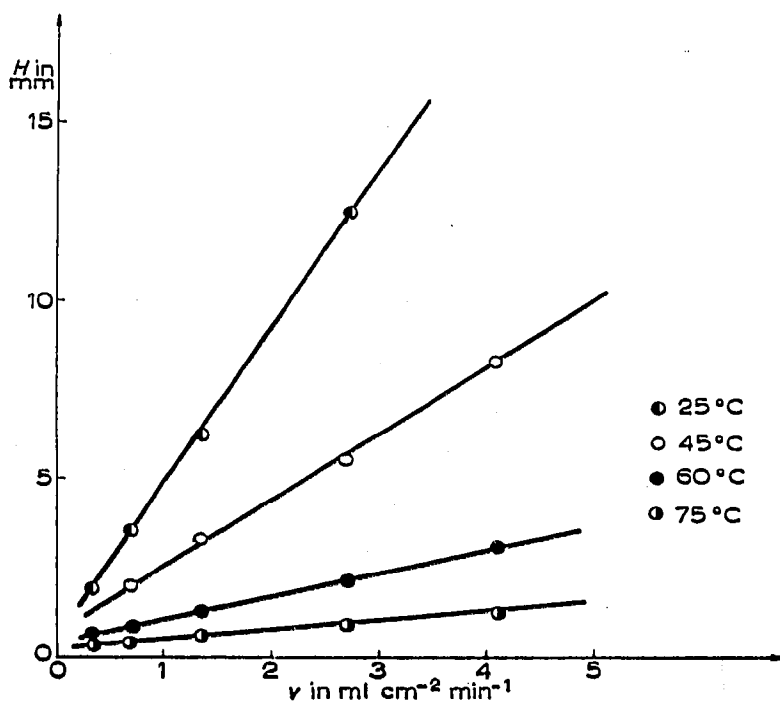Fig. 5. The effect of flow rate and temperature on the height of the plate. Elution of Tm with 4.52 M HNO$_3$.

Fig. 6. The effect of flow rate and temperature on the height of the plate. Elution of Tm with 4.50 M HCl.

1. Elution of Eu, Tb, Tm with HNO$_3$ and elution of Eu with HCl. These systems differ in some details but have several important features in common:

The height of the plate is relatively low.

The height of the plate increases approximately linearly with flow rate at 25°, 45° and 60° but the slope of the line is rather small. At 75° the height of the plate is practically independent of flow rate. In the case of Eu, Tb and Tm in HNO$_3$ there is some indication of a minimum in the $H = f(v)$ curve at very low flow rates.

The influence of temperature on the height of the plate is small. An increase in temperature from 25° to about 45° at constant flow rate in most cases decreases the height of the plate. There is little change in H between 45° and 60°, whilst a change in temperature from 60° to 75° decreases the height of the plate at high flow rates and increases it at low flow rates.

The results show that at 25°, 45° and 60° the total height of the plate is the sum of two factors only: H_O and H_T. The contribution of each of these factors depends on flow rate. The longitudinal diffusion component contributes substantially only at 75° and to a very much smaller extent at 60° and 45° at very low flow rates. Since $H_T \to 0$ when $v \to 0$ it should be possible to determine H_O by extrapolation, provided the temperature is sufficiently low so that the contribution of H_D can be neglected. The value of H_O obtained by extrapolation from different plots is very near to 0.25 mm. According to GIDDINGS[2] $H_O = 2ar_O$, where r_O is the radius of the grain and a is the so-called packing constant: $1 < a < 6$. Since the r_O of the grains of kieselguhr used in this work is about 0.0075 mm, one gets a value for $a \approx 17$ for the packing constant. This is rather a high value indicating that either the grain size is larger because of aggregation, or that there is very uneven flow due to channelling.

2. Elution of Tm with HCl. The height of the plate was found to be very great, especially at low temperatures, and it increases linearly with flow rate at all temperatures and is much more pronounced than in previous systems.

A change in temperature from 25° to 75° very markedly decreases the height of the plate at each flow rate. The influence of temperature explains why earlier workers did not observe the effect of the eluting acid since most of their work was carried out at elevated temperature.

The results for Tm in HCl indicate that the overall height of the plate is determined only by H_T except at very high temperatures and very low flow rates. The extrapolated value of H_O lies between 0.25 and 0.5 mm, which is very near to that obtained in previous cases.

3. Elution of Tb with HCl. The behaviour of Tb in HCl is intermediate to that of Tb or Eu in HNO$_3$ and that of Tm in HCl. The total height of the plate is the sum of H_O and H_T. Generally $H_T > H_O$. The extrapolated value of H_O is about 0.5 mm. The longitudinal diffusion contributes to the total height of the plate only at 75° and with low flow rates.

The study of the effect of flow rate and temperature on H has revealed that at low and moderate temperatures and not too low flow rates the total height of the plate is chiefly determined by H_T. The different behaviour of heavy rare earths in HCl and HNO$_3$ as eluting agents must therefore be caused by different values of H_T. The value of H_T is determined by the slowest stage in the mass transfer between the two phases. In most cases this slow stage is the diffusion process, but it can also be a comparatively slow chemical reaction, accompanying the mass transfer. The com-

parison of the height of the plates for Tm in HNO_3 and HCl at 25° and $v = 3$ ml·cm⁻²·min⁻¹ shows that H is about 22 times greater in HCl. Such an enormous difference in plate heights cannot be caused by the difference in diffusion coefficients of the Tm-containing species in the aqueous or organic phases. The inevitable conclusion is that the high value of H in HCl for all the rare earths starting from Tb is caused by some slow chemical stage in the formation or dissociation of the extractable complex.

The effect of electrolyte on the height of the plate

The results of changing flow rate and temperature have shown that the high value of H for Tm in HCl is caused by some slow stage in the overall process of transfer between the mobile and stationary phases. To study this effect in more detail, first the value of H in HCl and HNO_3 was determined, as a function of the atomic number (Z) of the rare earth element. The results, including measurements for some rare earths eluted with H_2SO_4 and $HClO_4$, are shown in Table I from which the following conclusions can be drawn:

In the case of HNO_3 as eluent the height of the plate does not depend on Z. H is somewhat higher in $HClO_4$ than in HNO_3 and also seems to be independent of Z.

In the case of HCl as eluent, H is independent of Z for the light rare earths and is practically the same as in HNO_3. H increases several times between Gd and Er and remains approximately constant for the last four rare earths. The behaviour of rare earths in H_2SO_4 seems to be similar to that in HCl.

The four acids studied can be thus divided into two groups. The first group includes nitric and perchloric acids, the second group includes hydrochloric and sulphuric acids. These two groups differ in the height of the plate for heavy rare earths. It can be argued that an increase in H is caused by the increase in concentration of the acid needed to elute heavy rare earths, and not by the change in chemical properties with increasing Z. This possibility was ruled out by an experiment in which Eu was eluted with a solution containing 0.38 M HCl and 2.36 M NaCl. The value of H found in this experiment was 0.38 mm, only slightly different from that in the solution of low chloride content. In a solution of approximately the same chloride content (2.3 M HCl), the height of the plate for Er is about 4 mm. It should also be noted that when Eu and Tb were eluted with HCl of the same concentration the values of H nevertheless differed fairly appreciably (see Table I). Since the increase in H starts at Tb, it is possible that this is a half-filled shell effect. Such effects are frequently encountered in the chemistry of rare earths. But this possibility is ruled out owing to the behaviour of yttrium, which is characterised by a very high value of H.

A priori, two explanations can be offered for the strange behaviour of the heavy rare earths in HCl and H_2SO_4. According to the first, the complexes of these rare earths with HDEHP differ in their composition when extracted from acids belonging to different groups. This possibility is excluded by the experiments carried out by PEPPARD, MASON AND HUCHER[3] and PIERCE, PECK AND HOBBS[4]. These experiments proved that inorganic anions such as Cl⁻, NO_3⁻ and ClO_4⁻ are absent in the species which are extracted into the organic phase. This must be also true for sulphates since the elution peak of a rare earth element in sulphuric acid lies between those for nitric and perchloric acids.

According to the second explanation the high value of H for the heavy rare earths

TABLE I

THE DEPENDENCE OF THE HEIGHT OF THE PLATE ON THE ATOMIC NUMBER OF THE RARE EARTH ELEMENTS

H in mm; flow rate $v = 0.7$ ml$\cdot$cm$^{-2}\cdot$min^{-1}, room temperature.

|	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
HNO$_3$	0.31	0.33	—	0.33	0.32	0.32	0.34	0.31	0.33	0.39	0.36	0.36	0.32	0.33	0.32	—
HCl	0.30	0.29	0.34	0.35	0.35	0.36	0.33	0.31	0.78	1.4	1.7	4.0	3.6	6.0	4.4	6.0
HClO$_4$	—	0.36	—	—	—	—	0.40	—	0.45	—	—	0.50	0.45	—	—	—
H$_2$SO$_4$	—	0.37	—	—	0.46	—	0.45	—	0.75	—	—	5.0	7.5	—	—	—

in HCl and H_2SO_4 may be caused by different degrees of complexing which, in turn, may result in some sluggishness in establishing extraction equilibrium. To study this possibility the ratio of the mean molal stoichiometric activity coefficients ($\gamma_\pm$) of the trace amounts of rare earths salts in 1:1 electrolytes (HNO_3, HCl, $HClO_4$) was determined. Since $\gamma_\pm$ is calculated under assumption of complete dissociation of a salt, its value reflects any association which can take place in a solution (low value of $\gamma_\pm$ means high association). From the extraction equilibrium the following equations can be easily derived:

$$D = A \frac{m^3{}_E}{m^3{}_H} \cdot \frac{\gamma^4{}_{\pm MX_3}}{\gamma^3{}_{\pm HX}} \quad \text{or} \quad \gamma^4{}_{\pm MX_3} = D \frac{m^3{}_H \cdot \gamma^3{}_{\pm HX}}{A \cdot m^3{}_E}$$

where D = the extraction coefficient, m_E = the molality of extracting agent, m_H = the molality of hydrogen ions, $\gamma_\pm$ = the mean molal stoichiometric activity coefficient. MX_3 denotes a rare earth salt, and HX an acid, and A is a constant.

The following equation was assumed to represent the extraction process:

$$\text{MeX}_3 + 3 \text{ HDEHP} \rightleftharpoons \text{Me(DEHP)}_3 + 3 \text{ HX}$$
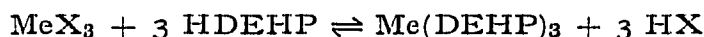
Since the value of D can be easily determined from the position of the peak, and m_H, m_E and $\gamma_{\pm HX}$ are known, the ratio of the activity coefficients of the salts can be calculated. Results are shown in Tables II, III, IV and V. The main conclusions are as follows:

The association between cation and anion is somewhat lower for Eu, Tb and Er in hydrochloric than in nitric acid of the same concentration, and is much lower in

TABLE II

THE ASSOCIATION OF EUROPIUM SALTS IN VARIOUS ACIDS

Flow rate v = 0.7 ml·cm^{-2}·min^{-1}; room temperature.

	$HClO_4$	HCl	HNO_3	H_2SO_4
Molality of acid m	0.87	0.85	0.86	—
Position of the peak in free volumes V_{max}-V_0	1.66	0.91	0.82	1.4
Activity coefficient of acid $\gamma_{\pm HX}$	0.80	0.79	0.72	—
Ratio of the activity coefficients of salts $\gamma^4{}_\pm$ Eu(ClO$_4$)$_3$: $\gamma^4{}_\pm$ EuCl$_3$: $\gamma^4{}_\pm$ Eu(NO$_3$)$_3$	1.0	0.53	0.36	—
Height of the plate H in mm	0.40	0.33	0.33	0.45

TABLE III

THE ASSOCIATION OF TERBIUM SALTS IN VARIOUS ACIDS

Flow rate v = 0.7 ml·cm^{-2}·min^{-1}; room temperature.

	$HClO_4$	HCl	HNO_3	H_2SO_4
Molality of acid m	0.87	0.85	0.86	—
Position of the peak in free volumes V_{max}-V_0	13.3	6.8	6.9	11.5
Activity coefficient of acid $\gamma_{\pm HX}$	0.80	0.79	0.72	—
Ratio of the activity coefficients of salts $\gamma^4{}_\pm$ Tb(ClO$_4$)$_3$: $\gamma^4{}_\pm$ TbCl$_3$: $\gamma^4{}_\pm$ Tb(NO$_3$)$_3$	1.0	0.49	0.38	—
Height of the plate H in mm	0.45	0.78	0.33	0.75

TABLE IV

THE ASSOCIATION OF ERBIUM SALTS IN VARIOUS ACIDS

Flow rate v = 0.7 ml·cm^{-2}·min^{-1}; room temperature.

	$HClO_4$	HCl	HNO_3	H_2SO_4
Molality of acid m	2.44	2.30	2.35	—
Positions of the peak in free volumes V_{max}-V_0	7.23	1.84	3.65	4.88
Activity coefficient of acid $\gamma_{\pm HX}$	1.21	1.09	0.83	—
Ratio of the activity coefficients of salts $\gamma^4_\pm Er(ClO_4)_3:\gamma^4_\pm ErCl_3:\gamma^4_\pm Er(NO_3)_3$	1.0	0.18	0.16	—
Height of the plate H in mm	0.50	4.0	0.36	5.0

perchloric acid. This conclusion is in full agreement with the results of PEPPARD[3] who also found that NO_3^- and Cl^- ions have approximately the same complexing properties toward rare earths in dilute solutions.

The association between the Tm cation and the anions in concentrated solutions of the acids decreases in the order: $HNO_3 > HCl > HClO_4$.

The comparison of the ratio of activity coefficients with the height of the plate clearly indicates the absence of any correlation between the degree of association and the value of H. This conclusion remains true also when H_2SO_4 is taken into account.

TABLE V

THE ASSOCIATION OF THULIUM SALTS IN VARIOUS ACIDS

Flow rate v = 0.7 ml·cm^{-2}·min^{-1}; room temperature.

	$HClO_4$	HCl	HNO_3	N_2SO_4
Molality of acid m	5.65	5.05	5.22	—
Position of the peak in free volumes V_{max}-V_0	3.15	0.94	1.72	2.33
Activity coefficient of acid $\gamma_{\pm HX}$	4.08	2.43	1.10	—
Ratio of the activity coefficient of salts $\gamma^4_\pm Tm(ClO_4)_3:\gamma^4_\pm TmCl_3:\gamma^4_\pm Tm(NO_3)_3$	1.0	0.06	0.01	—
Height of the plate H in mm	0.45	3.6	0.32	7.5

It was not possible to compare the degree of association in H_2SO_4 with other acids on the basis of activity coefficients, because H_2SO_4 is a 2:1 electrolyte, but there is little doubt that the SO_4^{2-} anion is a relatively strong complexing agent towards rare earths. Assuming that the complex-forming tendency of H_2SO_4 is higher or approximately the same as that of HNO_3 one gets the following order for the increasing association in the aqueous phase: $HClO_4 < HCl < HNO_3 < H_2SO_4$. The order of the plate height is quite different: $H_{HNO_3} < H_{HClO_4} < H_{HCl} \approx H_{H_2SO_4}$.

The height of the plate must nevertheless be related in some manner to the complex formation in the aqueous phase, although it is not related to the degree of association. This conclusion is supported by experiments with mixtures of electrolytes. Table VI shows the effect of increasing concentration of $NaNO_3$ on the height of the plate for Tb in 0.75 M HCl. The addition of NO_3^- ions which are somewhat stronger complexing agent than Cl^- ions shifts the equilibrium toward formation of $[TbNO_3]^{2-}$ and, as a result, the plate height decreases. A reversed effect is observed when NaCl

is added to the weakly complexing perchloric acid. A marked decrease in the height of the plate of Tb is also observed when 1.8 M NaNO$_3$ is added to 0.9 M H$_2$SO$_4$.

The results discussed so far have eliminated two possible explanations for the column behaviour of the heavy rare earths, these are: different composition of the extractable species, and different degree of the complexing in the aqueous phase, depending on the acid used for elution. It was also established that this behaviour is in some way connected with the complex formation in the aqueous phase. In the authors' opinion there is no contradiction between these two statements, since the height of the plate is a kinetic effect resulting from the kinetic stability of the complex.

TABLE VI

THE EFFECT OF THE CONCENTRATION OF NaNO$_3$ ON THE PLATE HEIGHT OF TERBIUM IN 0.75 M HCl
Flow rate v = 0.7 ml·cm^{-2}·min^{-1}; room temperature.

$NaNO_3$ M	0	0.1	0.25	0.5	0.75	2.0
H in mm	0.8	0.7	0.61	0.49	0.41	0.36

This stability is not always related to the thermodynamic stability. It is difficult to formulate a satisfactory explanation for the behaviour of the heavy rare earths in various acids on the basis of existing experimental material, but it is possible to make some suggestions. To do this two additional points should be taken into account. First, it should be noted that the light rare earths are only slightly complexed at low concentrations of mineral acids (this follows from the stability constants determined by PEPPARD and coworkers[3]), and, at the same time, the values of the height of the plate for the light rare earths are low. This means that the process of column extraction in which the hydrated cations of the light rare earths are involved is a fast process. The second point is that the column extraction of light and heavy rare earths from perchloric acid is also a comparatively fast process since the value of H is rather low for HClO$_4$, although not as low as for HNO$_3$. Now, it is generally assumed that the ClO$_4^-$ anion is a weak complexing agent and that cations retain their hydration layer in perchlorate solutions. It was shown for instance that the association between the Ce^{3+} cation and the ClO$_4^-$ anion is caused by hydrogen bonding between water molecules in the first coordination shell of the cation and the ClO$_4^-$ anion in the second coordination shell[5]. These facts would suggest that the column extraction equilibrium may be established quickly even for the heavy rare earth cations, provided the inner coordination shell of the cation is occupied by water molecules only. If this explanation is correct the NO$_3^-$ anions should be also coordinated in the second coordination layer, although the complexes formed by nitrates are relatively strong. On the contrary the Cl$^-$ and SO$_4^{2-}$ anions would be able to replace water molecules and enter the inner coordination shell of the cation. These two types of complexes differ for some unknown reason in their kinetic stability which results in the different height of the plate. Clearly, further and independent experiments are necessary to decide whether the difference in the hydration, or other differences in the structure between the various complexes are responsible for the observed difference in the height of the plate. Work with this aim in view is in progress.

SUMMARY

The effect has been studied of the atomic number of the lanthanide, of the eluting acid, the flow rate and temperature on the height of the plate in reversed phase partition chromatography with HDEHP as the stationary phase. It has been shown that the height of the plate is chiefly determined by the mass transfer between the aqueous and organic phases. In the case of elution of the heavy rare earths with HCl and H_2SO_4 the mass transfer is a slow process because of some slow chemical stage in the overall process of extraction.

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