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REVERSED-PHASE PARTITION CHROMATOGRAPHY OF RARE EARTHS WITH A MIXTURE OF ORGANIC EXTRACTANTS

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SUMMARY

The behaviour of rare earths has been investigated on papers impregnated with a mixture of thenoyltrifluoroacetone and tri-*n*-octylphosphine oxide. The mixture of these extractants effects a greater increase in the retention of the rare earth elements than any of these components alone. The maximum value for log $(1/R_F - 1)$ is obtained at a fixed composition of the mixture. The compositions of metallic complexes and the apparent equilibrium constants for certain synergistic species have also been determined.

INTRODUCTION

A mixture of organic solvents comprising a β-diketone and a neutral organophosphate has been widely used for the extraction of various metallic ions due to its effect on the enhancement of ion extraction[1-3].

The retention of metallic ions on paper impregnated with mixed solvents is considerably higher in comparison with the individual extractants, thus giving better conditions for the mutual separation of the ions[4-6].

In the present paper, the synergistic effect of a mixture of thenoyltrifluoroacetone (HTTA) and tri-*n*-octylphosphine oxide (TOPO) has been investigated with rare earths by reversed-phase chromatography. The composition of the metallic species in the organic phase and their apparent equilibrium constants have been determined.

EXPERIMENTAL

Whatman No. 1 paper strips were impregnated with a mixture of HTTA (BDH, Poole, Great Britain) and TOPO (Eastman-Kodak, New York) in carbon tetrachloride solution in the manner described earlier[4-6]. Aqueous hydrochloric acid at various concentrations was used as the mobile phase. The chromatograms were developed for 5 h at room temperature (23–25 °) by ascending chromatography. The reproducibility of the R_F values was $\pm 3\,\%$.

Investigations were performed with chloride solutions of tervalent rare earths obtained by dissolving the corresponding oxides (BDH, Poole, Great Britain, and Soyiuzchimexport, Moscow) in a small amount of concentrated HCl and by carefully drying. Solutions containing 2.5 mg of each element per millilitre in 0.1 M HCl were used. Aliquots of 0.001 ml containing about $5 \cdot 10^{-8}$ equivalents of each ion were spotted on to the paper. Ion identification was performed with a 0.1 % aqueous solution of arsenazo III reagent[7]. In addition, samarium, europium and gadolinium exhibit a red fluorescence under UV light on the paper treated with the HTTA–TOPO mixture. The fluorescence of europium is so intense that it can be used for the identification of this ion even at concentrations lower than that given above. In a recent paper[8], the fluorescence of europium, samarium and terbium in a mixture of hexafluoroacetone–tri-*n*-octylphosphine oxide solution was used for the spectrofluorimetric determination of these ions.

RESULTS AND DISCUSSION

The chromatographic papers were treated with HTTA–TOPO mixture containing various proportions of the components but with constant total molarity. The distribution of Ce(III), Sm(III) and Er(III) between 0.1 M HCl and the HTTA–TOPO mixture at a total concentration of 0.2 M is shown in Fig. 1. The value of

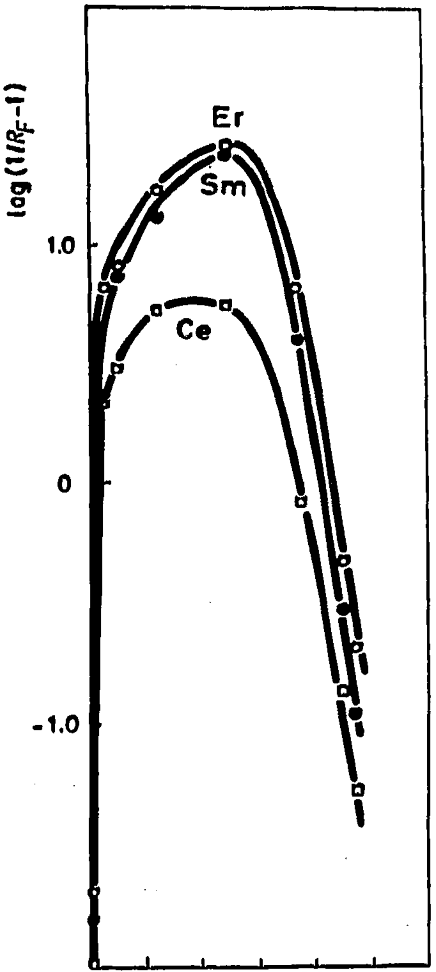

Fig. 1. Plot of log $(1/R_F - 1)$ for Ce, Sm and Er *versus* mole fraction of TOPO in a mixture with HTTA. The concentration of the mixture is 0.2 M. Eluent: 0.1 M HCl.

log $(1/R_F - 1)$ for these ions reaches a maximum at the same compositions of the organic phase fixed on the papers. Similar results were obtained for La(III) and Ce(III) with HTTA–tri-*n*-octylphosphate (TOP) and ^{241}Am(III) with HTTA–TOP and HTTA–TOPO mixtures[4,6].

The dependence of log $(1/R_F - 1)$ on the atomic number of the rare earths, with the exception of promethium, is shown in Fig. 2. A linear relationship was obtained on paper strips impregnated with a mixture of 0.15 *M* HTTA + 0.05 *M* TOPO when 0.5 *M* HCl was used as the eluent. The separation factor, $(1/R_F - 1)_{(z+1)}/(1/R_F - 1)_z$, between two adjacent rare earths was lower than the value obtained by treating the paper with dialkyl esters of phosphoric acid[9,10]. However, for the pair Ce–La, the mean value for the separation factor was 3.3 using 0.1, 0.2 and 0.3 *M* HCl.

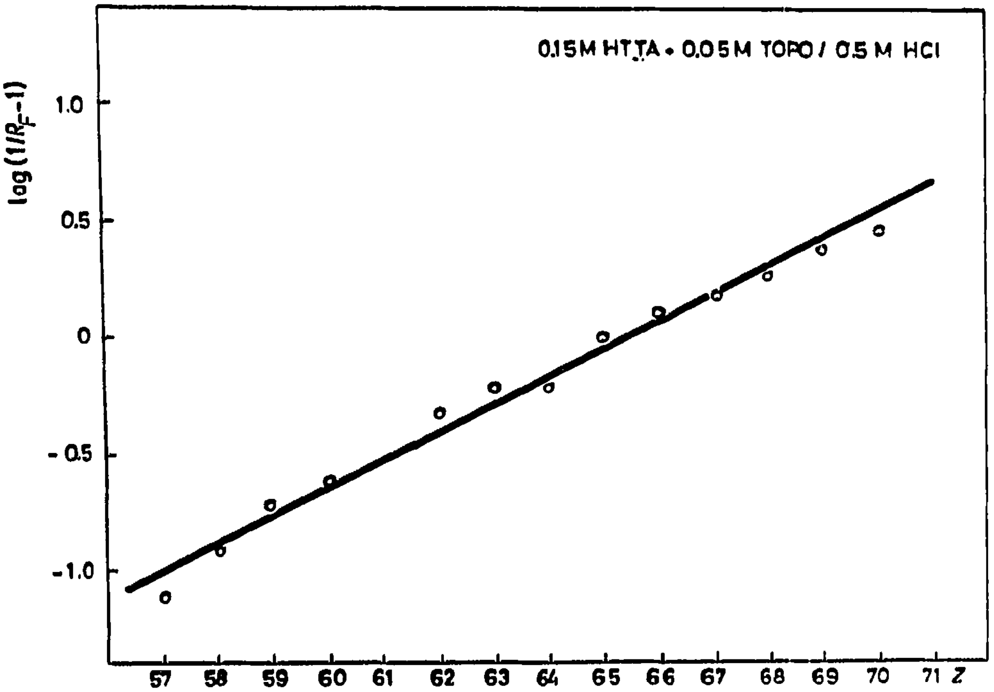

Fig. 2. Plot of log $(1/R_F - 1)$ *versus* atomic number, *Z*, for rare earths.

In all the investigations performed, lutetium remained at the starting point. The optimum conditions for the mutual separation of rare earths can be found from the results given.

The composition of metallic complexes and apparent equilibrium constants

The compositions of ternary complexes were determined for Ce, Sm and Er, which were taken as being representative members of the rare earth group.

The well known relationship

$$\log E_a^0 = \log (1/R_F - 1) + \log k \qquad (1)$$

was used in this work as it shows that the behaviour of an ion in reversed-phase partition chromatography can be correlated with its behaviour in solvent extraction[11]. The constant *k* depends on the chromatographic conditions used.

R_F values of Ce, Sm and Er were investigated as a function of the activity of the H^+ ion in the mobile phase as well as of the amounts of HTTA and TOPO on the paper. Two of the three variables were always kept constant. The activity of the H^+ ion in the eluent was calculated from the hydrochloric acid molarity[12]. In these experiments, the amounts of HTTA and TOPO on the paper, expressed in mg/cm^2, were also determined by weighing the paper before and after impregnation[4-6]. The HTTA and TOPO concentrations given on the graphs are calculated in millimoles. The dependence of log $(1/R_F - 1)$ on log a_{H^+} for Ce, Sm and Er on papers treated with a mixture of 0.15 M HTTA and 0.05 M TOPO is given in Fig. 3. The slopes of the straight lines are 2.9 for Ce and Sm and 2.6 for Er.

Fig. 4 shows a graph of log $(1/R_F - 1)$ against log [HTTA] for the given ions. The concentration of TOPO in the mixture for impregnation was always 0.04 M. With Ce and Sm, 0.1 M HCl was used as the eluent, while for Er 0.2 M HCl was used. The slope of the straight lines is about 3.

The dependence of log $(1/R_F - 1)$ on log [TOPO] is given in Fig. 5. The concentration of HTTA in the mixture with TOPO was 0.1 M. Ce and Sm were investigated with 0.1 M HCl and Er with 0.2 M HCl. The straight lines have a slope of 2.

The results obtained in these experiments suggest the following reaction:

$$M^{3+} + 3\,HTTA + 2\,TOPO \rightleftharpoons M(TTA)_3(TOPO)_2 + 3\,H^+ \qquad (2)$$

which has also been obtained by liquid–liquid extraction of some tervalent lantha-

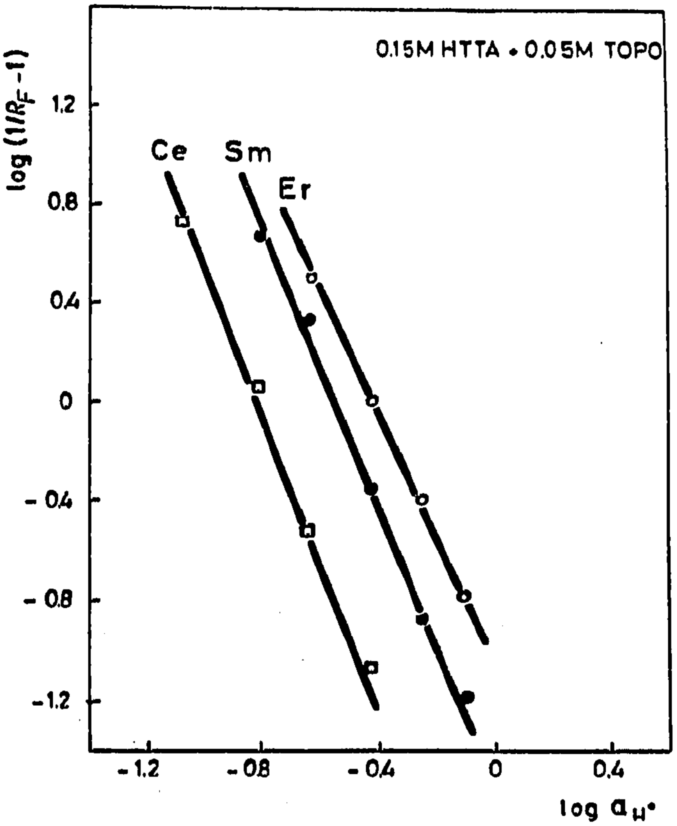

Fig. 3. Plot of log $(1/R_F - 1)$ *versus* log a_{H^+}. The slope of the straight lines is -2.9 for Ce and Sm and -2.6 for Er.

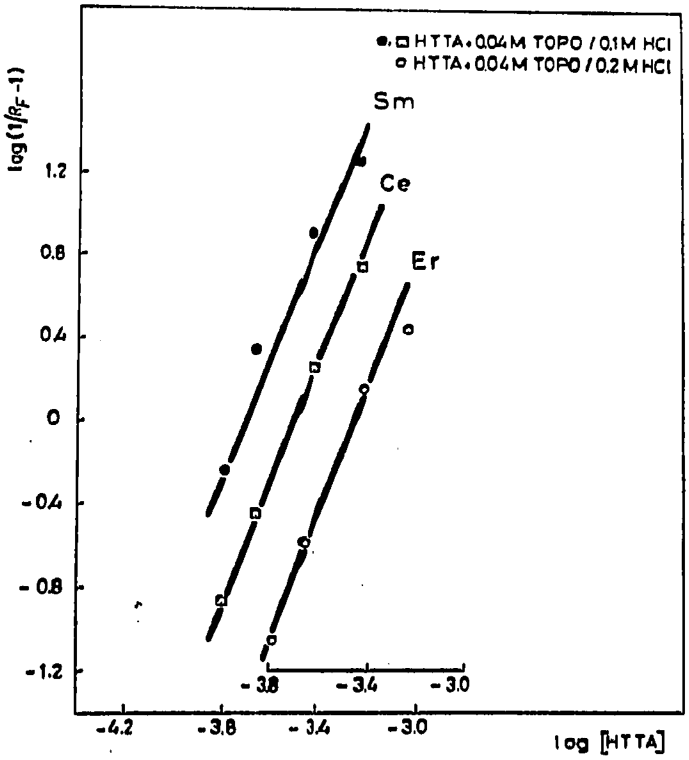

Fig. 4. Plot of log $(1/R_F - 1)$ *versus* log [HTTA] in a mixture with TOPO, for Ce, Sm and Er. The abscissa shifted to the right is for Er. The slope of the straight lines is 3.

nides and actinides with mixed solvents[1,3]. The equilibrium constant of the reaction is

$$K_e = \frac{[\mathrm{M(TTA)_3(TOPO)_2}]_{\mathrm{org}} \cdot a_{\mathrm{H^+}}^3}{[\mathrm{M^{3+}}]\,[\mathrm{HTTA}]_{\mathrm{org}}^3[\mathrm{TOPO}]_{\mathrm{org}}^2} \cdot \mathrm{f}(\gamma) \tag{3}$$

where a_{H^+} is the activity of the H^+ ion in the aqueous phase and $\mathrm{f}(\gamma)$ is the ratio of the activity coefficients of the components in the organic and aqueous phases. It can be assumed that $\mathrm{f}(\gamma)$ is constant for given experimental conditions. The extraction coefficient of the metallic complex with HTTA and TOPO ligands is

$$E_a^0 = \frac{[\mathrm{M(TTA)_3(TOPO)_2}]_{\mathrm{org}}}{[\mathrm{M^{3+}}]} \tag{4}$$

and from eqn. 1, we obtain

$$\log\,(1/R_F - 1) = 3 \log\,[\mathrm{HTTA}] + 2 \log\,[\mathrm{TOPO}] - 3 \log a_{\mathrm{H^+}} + \log K_h \tag{5}$$

where $\log K_h = \log K_e - \log \mathrm{f}(\gamma) - \log k$. The experimental results obtained enable the apparent equilibrium constant of the metallic complexes with organic ligands to be determined. Eqn. 5 can also be written in the following forms:

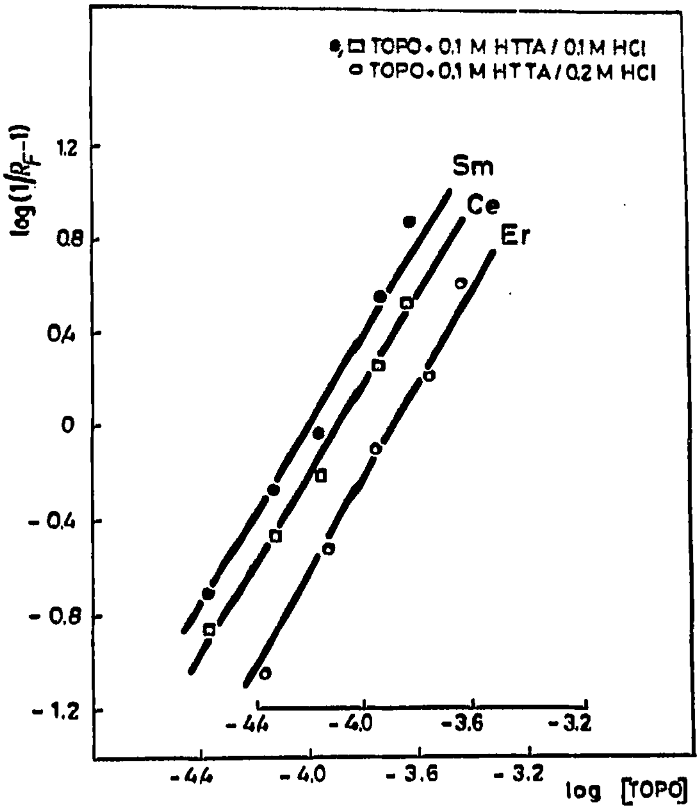

Fig. 5. Plot of log $(1/R_F - 1)$ *versus* log [TOPO] in a mixture with HTTA, for Ce, Sm and Er. The abscissa shifted to the right is for Er. The slope of the straight lines is 2.

$$\text{og}\,\frac{(1/R_F - 1)}{[\text{HTTA}]^3[\text{TOPO}]^2} = \log K_h - 3 \log a_{\text{H}^+}$$

$$\log \frac{(1/R_F - 1)\cdot a^3_{\text{H}^+}}{[\text{TOPO}]^2} = \log K_h + 3 \log [\text{HTTA}]$$

$$\log \frac{(1/R_F - 1)\cdot a^3_{\text{H}^+}}{[\text{HTTA}]^3} = \log K_h + 2 \log [\text{TOPO}]$$

These expressions are represented by a straight line on a log–log scale, as shown in Fig. 6. By extrapolating the right-hand side of the equation to zero, the apparent constant K_h can be determined from the graph. The values of log K_h of 13.88 ± 0.41 for Ce, 14.35 ± 0.45 for Sm and 14.77 ± 0.29 for Er are obtained by the least-squares method.

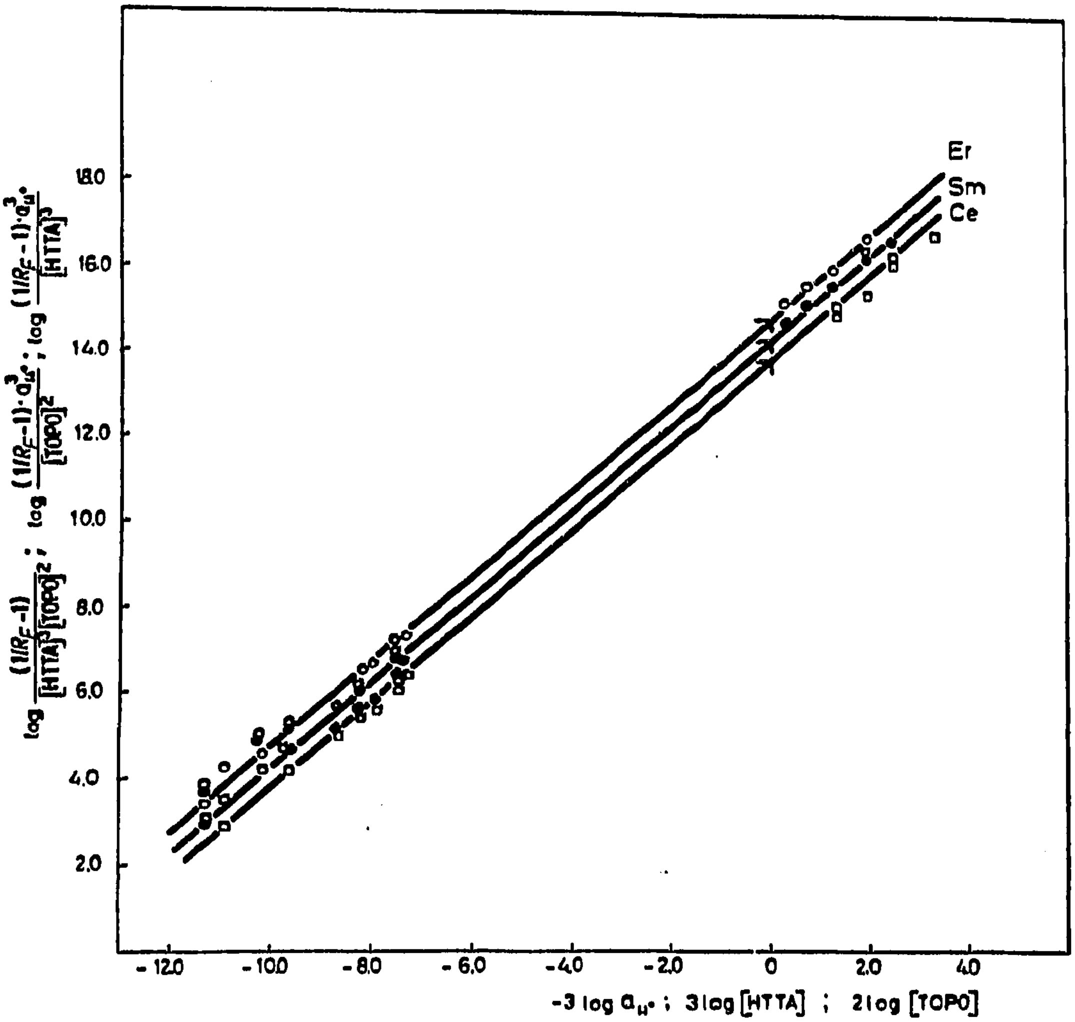

Fig. 6. Determination of log K_h for Ce, Sm and Er. The value of log K_h is obtained by extrapolation.

In the relationship $\log K_h = \log (K_e/k \cdot f(\gamma))$, k is the volume ratio between the mobile and the stationary phases. It can be determined from eqn. 1 by determining the extraction coefficient, E_a^0, for one of the investigated cations. In a previous paper[6], the extraction coefficient, E_a^0, for the radioactive isotope ^{241}Am(III) was determined by liquid–liquid distribution measurements with the same concentration of HTTA and TOPO in the organic phase and HCl in the aqueous phase as in chromatographic investigations. The value obtained from a large number of determinations is $\log k = -0.96$ ($k = 0.11$). The behaviour of Ce(III), Sm(III) and Er(III) was investigated under conditions similar to those for ^{241}Am(III) so that the same value for the constant k is applied to rare earths. Defining the apparent equilibrium constant $\log K = \log K_e - \log f(\gamma)$, values for $\log K$ of 12.92, 13.39 and 13.81 for Ce, Sm and Er, respectively, are obtained. It can be seen that $\log K$ for Sm is very close to the numerical value 13.37 obtained for Am(III)[6].

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