

CHROM. 3402

SYNERGISM IN THE REVERSED-PHASE PARTITION CHROMATOGRAPHY OF AMERICIUM, CERIUM AND LANTHANUM

N. CVJETIĆANIN

Hot Laboratory Department, Boris Kidrič Institute of Nuclear Sciences, Beograd (Yugoslavia)

(Received January 18th, 1968)

SUMMARY

Retention of the ions of $^{241}\text{Am}^{3+}$, Ce^{3+} and La^{3+} in reversed-phase chromatography is considerably higher on paper treated with a mixture of HTTA and TOP than if each extractant is used separately. The value for $\log (1/R_F - 1)$ for all three ions reaches a maximum at a fixed composition of components in the mixture. Thus a synergistic effect occurs not only in the liquid-liquid extraction process but also in the reversed-phase partition chromatography.

The composition of the metallic species formed in the organic phase is determined by correlating $\log (1/R_F - 1)$ with the amount of HTTA and TOP fixed on the paper and with the concentration of H^+ ions in the mobile phase at constant ionic strength. The results imply that species of composition $\text{M}(\text{TTA})_3(\text{TOP})_2$ are formed, which is in agreement with the data obtained by solvent extraction on the same system.

Reversed-phase partition chromatography with various organic solvents as the stationary phase has proved to be a very useful method of investigating the behaviour and separation of metallic ions. Previous results obtained by this method suggest an analogy with solvent extraction processes¹⁻⁷.

Taking into account the similarity of these two processes, it would be interesting to know whether the synergistic effect, so often found in solvent extraction⁸⁻¹⁰, also occurs in chromatographic processes.

Our previous investigation¹¹ on the behaviour of rare earths on papers impregnated with tri-*n*-octylphosphate (TOP) showed a very low affinity towards this solvent and consequently a low retention on the stationary phase. In the present paper the behaviour of Am(III), Ce(III) and La(III) on papers treated with a mixture of thenoyltrifluoroacetone (HTTA) and TOP was examined. A considerable increase in the retention, *i.e.* decrease in the R_F value, appears for all three trivalent ions. This behaviour closely follows the synergistic effect found in solvent extraction^{9,10}. The composition of the complexes and the optimal conditions for mutual separation of the ions were determined from the results obtained.

EXPERIMENTAL

Impregnation of the chromatographic paper with a mixture of a TOP (Fluka, Buchs, Switzerland) and HTTA (BDH, London) solution in carbon tetrachloride was carried out as described previously^{6,7}. An aqueous hydrochloric acid solution of selected concentration was used as the mobile phase.

Investigations were carried out with chloride solutions of La^{3+} , Ce^{3+} and $^{241}\text{Am}^{3+}$. In the case of La^{3+} and Ce^{3+} , 0.010 ml aliquots containing about $5 \cdot 10^{-7}$ equivalents of each ion were spotted on the paper. To check the R_F values, the radioisotope cerium-144 (Ce^{3+}) was used in some runs. The R_F values of $^{241}\text{Am}^{3+}$ were determined radiometrically with a γ -scintillation NaI (Tl) counter.

The experiments were carried out on Whatman No. 1 paper strips, 2×35 cm, in glass cylinders 14×40 cm, by ascending development. The chromatograms were developed for 4-5 h at room temperature.

RESULTS AND DISCUSSION

The chromatographic papers were impregnated with solvents having different molar ratios of HTTA to TOP, but the total concentration of the two extractants was kept constant at 0.2 M. Table I gives the R_F values of La^{3+} , Ce^{3+} and Am^{3+} , while Fig. 1 shows $\log(1/R_F - 1)$ versus the molar concentrations of HTTA and TOP in the mixture. La^{3+} and Ce^{3+} were run with 0.01 M HCl and Am^{3+} with 0.05 M HCl at ionic strength $\mu = 0.1$ Na(H)Cl. The R_F values were determined relative to the acid front. When impregnated papers are treated with dilute mineral acids as the mobile phase, it is possible that acid is absorbed by the paper. Therefore it is convenient to

TABLE I

R_F VALUES FOR Am^{3+} , La^{3+} AND Ce^{3+}

Paper impregnated with a mixture of HTTA and TOP. The mobile phase for La^{3+} and Ce^{3+} is 0.01 M HCl and for Am^{3+} 0.05 M HCl; $\mu = \text{Na(H)Cl}$.

Mixture of organic extractants		R_F		
		Am^{3+}	La^{3+}	Ce^{3+}
TOP	0.20 M	0.99	0.97	0.96
HTTA	0.02 M	0.98	0.95	0.81
TOP	0.18 M			
HTTA	0.05 M	0.66	0.55	0.12
TOP	0.15 M			
HTTA	0.10 M	0.14	0.14	0.03
TOP	0.10 M			
HTTA	0.15 M	0.16	0.21	0.05
TOP	0.05 M			
HTTA	0.18 M	0.28	0.39	0.15
TOP	0.02 M			
HTTA	0.02 M	0.98	0.97	0.97

define the acid front as the distance between the starting line and the line where the acid no longer appears on the paper. The acid free zone is immediately behind the solvent front¹².

From the results presented it is seen that the R_F values for all three ions are nearly equal to unity when the paper is impregnated only with 0.2 M HTTA or 0.2 M TOP. A mixture of these extractants causes a considerable increase in the retention of all three ions. A maximum value for $\log (1/R_F - 1)$ is obtained at a certain composition of the mixture.

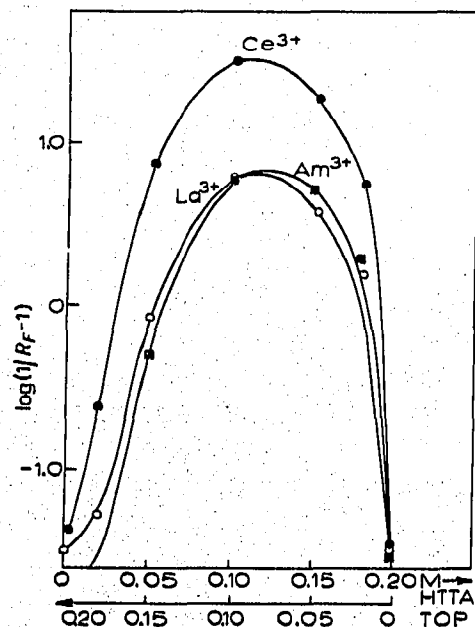


Fig. 1. Plot of $\log (1/R_F - 1)$ for Am^{3+} , La^{3+} and Ce^{3+} as functions of molar concentrations of HTTA and TOP in the mixture.

To determine the composition of the complexes we used a relation which allows us to correlate reversed-phase partition chromatography with solvent extraction. If the aqueous and organic phases in both processes are identical the following equation is valid^{1, 13}

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

where E_a^0 is the extraction coefficient, and k is a constant depending on the chromatographic experimental conditions.

The dependence of the R_F values for La^{3+} , Ce^{3+} and Am^{3+} on the H^+ ion concentration and on the amount of HTTA and TOP was examined. In these experiments two variables out of three were always kept constant. Fig. 2 shows the plot of $\log (1/R_F - 1)$ against $\log [\text{H}^+]$. The chromatographic paper strips were impregnated with a mixture of 0.15 M HTTA + 0.05 M TOP.

The behaviour of Am^{3+} , La^{3+} and Ce^{3+} has been investigated as a function of the amount of HTTA at constant TOP concentration in the organic phase and at constant H^+ ion concentration in the mobile phase. The amount of HTTA, mg/cm², is determined by weighing the paper before and after impregnation. It has been

proved that the weight increases obtained by treating the paper with a mixture of HTTA and TOP are additive compared with the values obtained by impregnation only with HTTA or with TOP. On the graphs, the HTTA and TOP concentrations are expressed in millimoles.

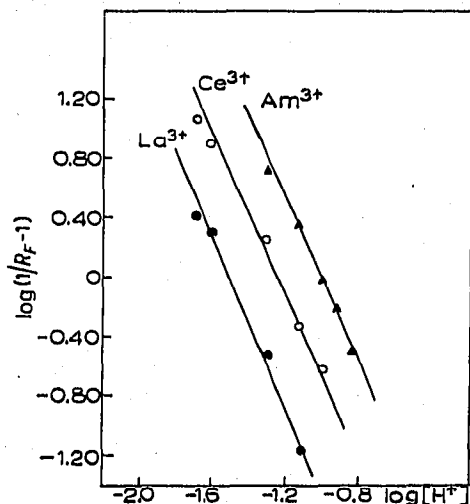


Fig. 2. Plot of $\log (1/R_F - 1)$ vs. $\log [H^+]$ for La^{3+} , Ce^{3+} and Am^{3+} . The slope of the straight lines is -3 .

Fig. 3 shows $\log (1/R_F - 1)$ versus $\log [HTTA]$ for Am^{3+} , La^{3+} and Ce^{3+} . The TOP concentration in the impregnation mixture was always $0.05 M$. The eluent for La^{3+} and Ce^{3+} was $0.01 M$ HCl and for Am^{3+} $0.05 M$ HCl at constant ionic strength, $\mu = 0.1$ Na(H)Cl.

The dependence of $\log (1/R_F - 1)$ on $\log [TOP]$ for La^{3+} , Ce^{3+} and Am^{3+} was investigated in the same way (Fig. 4). The HTTA concentration in the mixture with

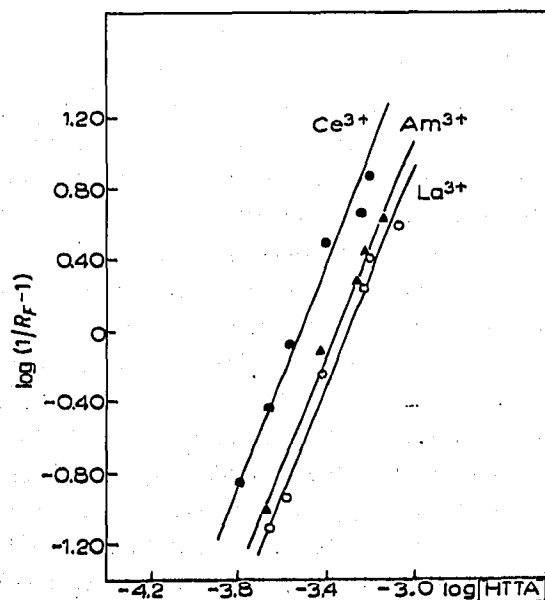


Fig. 3. Plot of $\log (1/R_F - 1)$ vs. $\log [HTTA]$ in a mixture with TOP for Am^{3+} , La^{3+} and Ce^{3+} . The slope of the straight lines is 3 .

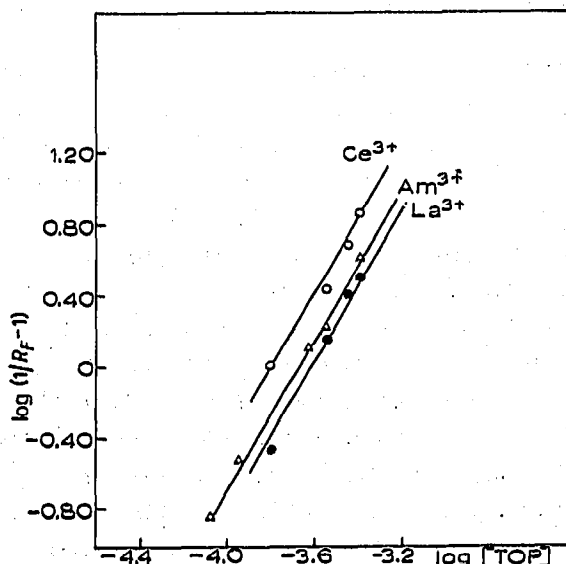
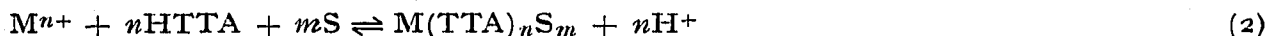


Fig. 4. Plot of $\log (1/R_F - 1)$ vs. $\log [TOP]$ in a mixture with HTTA for Am^{3+} , La^{3+} and Ce^{3+} . The slope of the straight lines is 2 .

TOP was 0.15 *M*. The concentration of hydrochloric acid for La³⁺, Ce³⁺ and Am³⁺ was the same as in the preceding graph.

If synergistic effects^{10,14} occur in the extraction of metallic ions with a mixture of two organic extractants (in the present case, one is HTTA which forms chelates with metallic ions, and the other is a ternary organophosphate, TOP) the over-all reaction may be represented in the following way:



where S is the organic electron donor molecule.

Taking into account the valency of the ions, one obtains:



The equilibrium constant of this reaction is:

$$K_e = \frac{[M(\text{TTA})_3(\text{TOP})_2]_{\text{org}}[\text{H}^+]^3}{[M^{3+}][\text{HTTA}]_{\text{org}}^3[\text{TOP}]_{\text{org}}^2} \times f(\gamma) \quad (4)$$

where $f(\gamma)$ is the ratio of the activity coefficients of the components. For certain experimental conditions it is assumed that $f(\gamma)$ is constant. The extraction coefficient of the metallic species is then:

$$E_a^0 = \frac{[M(\text{TTA})_3(\text{TOP})_2]_{\text{org}}}{[M^{3+}]} \quad (5)$$

combining these with eqn. (1), one obtains:

$$\log (1/R_F - 1) = 3 \log [\text{HTTA}] + 2 \log [\text{TOP}] - 3 \log [\text{H}^+] + \text{const.} \quad (6)$$

The term "const." includes K_e , $f(\gamma)$ and h . Taking into account the slopes of the straight lines in Figs. 2, 3, and 4, the extracted complexes fixed on the impregnated paper are in the form of $M(\text{TTA})_3 \cdot (\text{TOP})_2$. The results are in accordance with the data for the extraction of some trivalent lanthanides and actinides with a mixture of HTTA and ternary organophosphate¹⁰. The synergistic effect noted is in agreement with the assumption that an increased solubility of metallic chelates in the organic phase is caused by the formation of an adduct molecule with the ternary organophosphate^{15,16}.

The behaviour of other trivalent lanthanides (Pr, Nd, Sm, Eu) was also investigated on paper impregnated with the aforementioned mixture of extractants. The R_F values obtained have shown that the retention of these ions increases with the increase of their atomic number or with the decrease of their crystalline ionic radius.

The separation factor $(1/R_F - 1)_{z-1} / (1/R_F - 1)_z$ for ${}_{55}\text{Ce}$ – ${}_{57}\text{La}$ can be calculated from Fig. 2. The mean value for the separation factor for this pair of lanthanides with HCl in the concentration range of 0.01–0.075 *M* ($\mu = 0.1$) is 4.5. When compared with their separation factor obtained on paper treated with acid esters of phosphoric acid^{1,6} this value is more than twice as high.

Conditions for separation of Am³⁺, Ce³⁺ and La³⁺ can be chosen from Fig. 2. The best separation is obtained with 0.05 and 0.075 *M* HCl.

ACKNOWLEDGEMENTS

Thanks are due to Prof. Dr. M. ŠUŠIĆ for helpful discussions and to Dr. I. GAL for his interest in this work.

The author is grateful to the Yugoslav Federal and Serbian Research Funds for financial support.

REFERENCES

- 1 E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
- 2 E. CERRAI, in M. LEDERER (Editor), *Chromatographic Reviews*, Vol. 6, Elsevier, Amsterdam, 1964, p. 129.
- 3 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 24 (1966) 383.
- 4 C. TESTA, *Anal. Chem.*, 34 (1962) 1556.
- 5 J. W. O'LAUGHLIN, G. J. KAMIN AND C. V. BANKS, *J. Chromatog.*, 21 (1966) 460.
- 6 N. CVJETIĆANIN, *Bull. Boris Kidrič Inst. Nucl. Sci.*, (Beograd), 15 (1964) 201.
- 7 N. CVJETIĆANIN, *J. Chromatog.*, 32 (1968) 384.
- 8 C. A. BLAKE, C. F. BAES, K. B. BROWN, C. F. COLEMAN AND J. C. WHITE, *Proc. 2nd. Intern. Conf. Peaceful Uses At. Energy, Geneva*, 28 (1958) 289.
- 9 H. IRVING AND D. N. EDGINGTON, *J. Inorg. Nucl. Chem.*, 15 (1960) 158.
- 10 T. V. HEALY, *J. Inorg. Nucl. Chem.*, 19 (1961) 314.
- 11 N. CVJETIĆANIN, J. ČVORIĆ AND I. OBRENOVIĆ-PALIGORIĆ, *Bull. Boris Kidrič Inst. Nucl. Sci. (Beograd)*, 14 (1963) 83.
- 12 J. W. O'LAUGHLIN AND C. V. BANKS, *U.S. At. Energy Comm. Rept. IS-737*, 1963.
- 13 R. CONSDEN, A. H. GORDON AND A. J. P. MARTIN, *Biochem. J.*, 38 (1944) 224.
- 14 A. M. POSKANZER AND B. M. FOREMAN, *J. Inorg. Nucl. Chem.*, 16 (1961) 323.
- 15 W. R. WALKER AND N. C. LI, *J. Inorg. Nucl. Chem.*, 27 (1965) 411.
- 16 N. C. LI, S. M. WANG AND W. R. WALKER, *J. Inorg. Nucl. Chem.*, 27 (1965) 2263.

J. Chromatog., 34 (1968) 520-525.