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Tributylphosphate (TBP) is one of the phosphororganic compounds most frequently employed for the separation of rare earth elements (REE). At the same time it has a number of drawbacks: high solubility in water (0.39 g/l), the possibility to form the third phase upon saturation of TBP, diluted with saturated hydrocarbons, with REE nitrates and others.

The present work is concerned with the study of the properties of triisomylylphosphate (TiAP), extractant devoid of the above drawbacks, its properties are compared to those of TBP.

Triisomylylphosphate containing more than 98% of the basic component ($d = 0.952 \text{ g/cm}^3$, $n_D^{20} = 1.4275$, $t_{\text{boil}} = 143-146^\circ\text{C}$ (3-4 mmHg), content of acid impurities 0.002%) was used as an extractant.

The data on the REE extraction with TiAP are scanty and refer, mainly, to the extraction of microquantities of REE [1,2]. Primary attention in this work is paid to the study of those regularities of REE extraction with TiAP, which are of important for its practical application (isotherms of lanthanide extraction, the influence of REE concentration and concentration of salting out agents in the aqueous phase on the values of REE distribution and separation coefficients, effect of HNO_3 concentration and others.)

General regularities of the REE extraction with TiAP and other NPOC are analogous. For example, the shape of the dependence of the REE distribution coefficients on the HNO_3 concentration in the aqueous phase is typical of NPOC. It is related to the REE extraction by two mechanisms with the formation of $\text{Ln}(\text{NO}_3)_3 \cdot 3\text{S}$ compounds over the range of moderate HNO_3 concentrations and $\text{HxLn}(\text{NO}_3)_{3+x}$ HNO_3 concentrations higher than 10 M. A decrease in the values of REE distribution coefficients over the acidity range 4-9 M is due to the HNO_3 extraction (Fig. 1). By analogy with TBP TiAP extracts well HNO_3 (Fig. 2), the formation of the solvates $\text{HNO}_3 \cdot \text{S}$ and $(\text{HNO}_3)_2 \cdot \text{S}$ being possible. A considerable increase in the volume of the organic phase (up to 30%) is observed during extraction. The extraction isotherms (Fig. 3) happen to be the main characteristics during the REE extraction with NPOC. The shape of the isotherms is typical of all the NPOC, Sm having the highest distribution coefficient among them. A shift of the Y position in the REE extractability row upon the change of their concentrati-

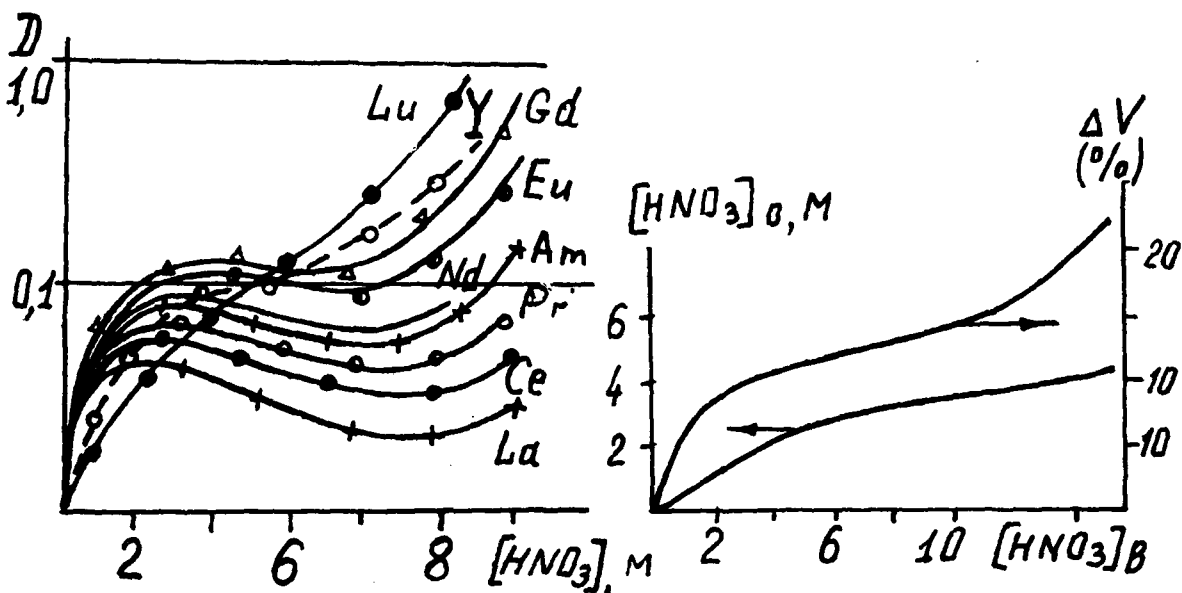


Fig. 1. Dependence of REE distribution coefficients on the HNO_3 concentration

Fig. 2. Isotherm of the HNO_3 extraction and the increase in the volume of the organic phase

on in the aqueous phase is observed. The volume of the organic phase increases up to 7% in the range of the maximum saturation, when it is saturated with lanthanide nitrates. Molar ratios $\text{TiAP}:\text{REE} = 3:1$. Similar data were obtained by the delution method, which supports the formation of trisolvate $\text{Ln}(\text{NO}_3)_3 \cdot 3\text{S}$.

The use of the diluted TiAP (up to 25%), in contrast to TBP, did not result in the formation of the third phase (Fig. 4). The REE distribution coefficients regularly decline with increasing the diluent polarity (Table 1).

At the $\text{Li}(\text{NO}_3)$ concentrations equal to or exceeding 2 M the extraction order is dodecane TCB TCE toluene.

The existence of salting out agents in the aqueous phase increases the distribution coefficients of lanthanides (Fig. 5), the separation coefficients also go up, which is due to the great difference in the values of activity coefficients of lanthanides in aqueous and organic phases.

The extraction ability of TiAP is close to that of TBP (Table 2), but TiAP has a higher selectivity during the extraction of cerium REE as distribution coefficients on their ordinal number is typical of NPOC, the maximum of the distribution coefficients falls on samarium (Fig. 6-7), in any case the yttrium position shifts to the lanthane side during the extraction from more diluted solutions.

The obtained data lead us to conclude:

- TiAP is a typical representative of NPOC, its extraction properties are close to those of TBP, but it has certain advantages over the latter.

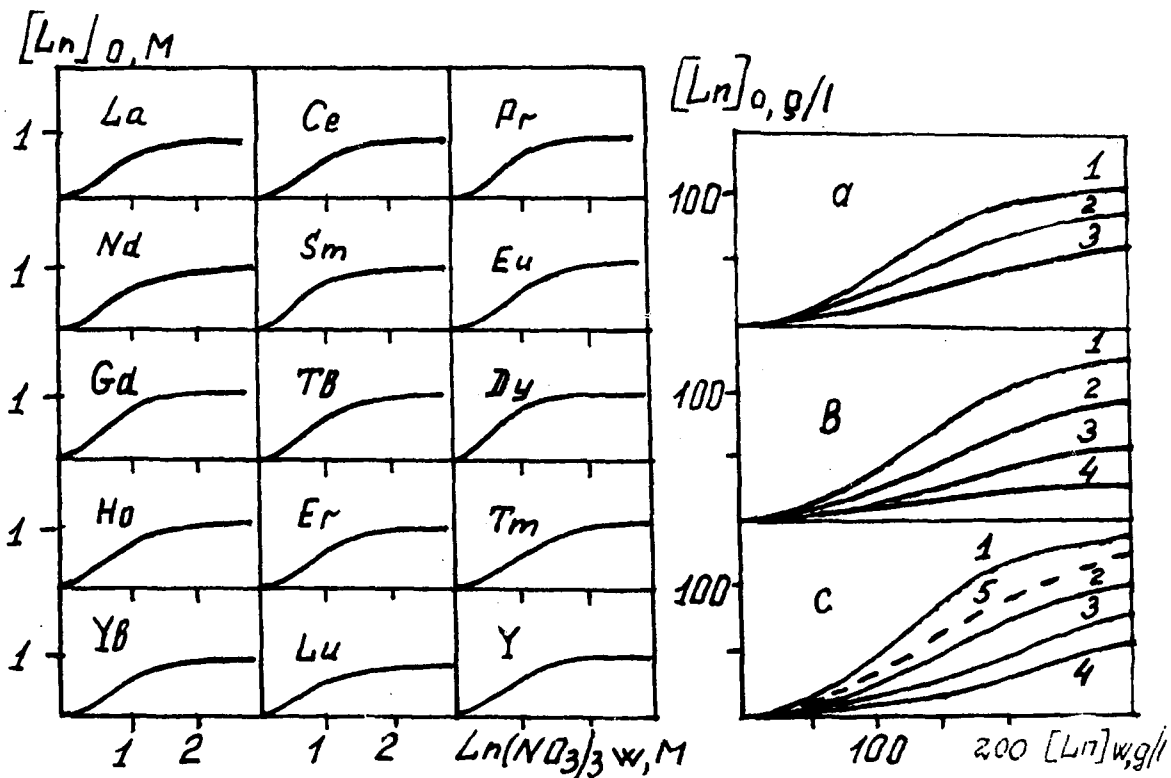


Fig. 3. Isotherms of REE with triisoamylphosphate up to 7% in the range of maximum separation

Fig. 4. Isotherms of La and Ce, Nd extraction with TiAP solutions

(%) in: a) dodecane 1-100%, 2-66%, 3-50%;

b) CCl₄ 1-100%, 2-66%; 3 50% 4)25%; c-dodecane 1-100% (25°C),
5 - 100% (80°C); 2 - 66%; 3 - 50%; 4 - 25%

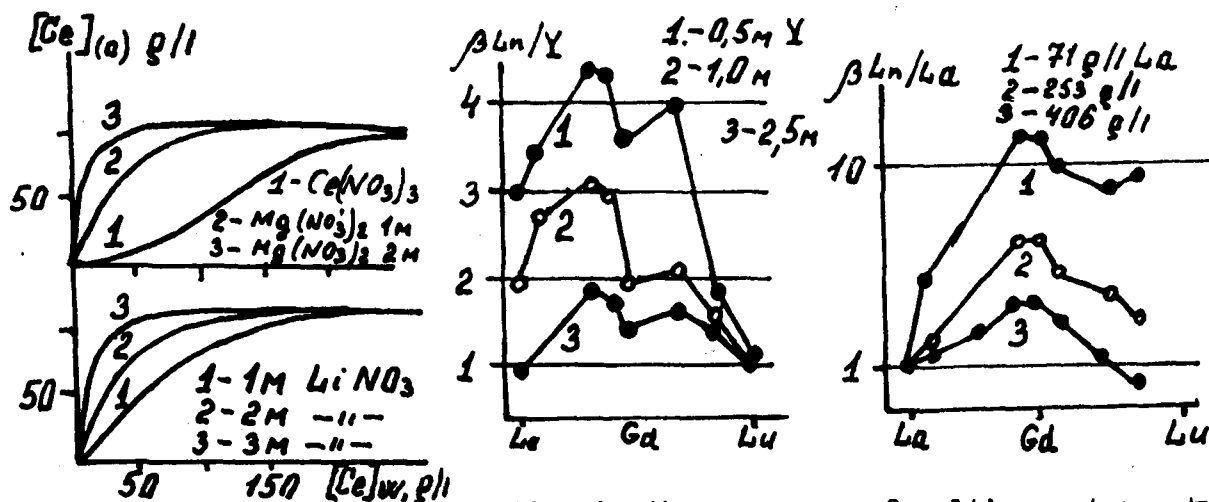


Fig. 5. Isotherms of Ce extraction in the presence of salting out agents

Fig. 6. Values of distribution coefficients of REE as related to Y

Fig. 7. Values of distribution coefficients of REE as related to lanthane

Table 1. Influence of Diluents on the Values of Eu Distribution Coefficients in the System: Aqueous Phase $\text{LiNO}_3 + 5 \text{ g/l Eu}(\text{NO}_3)_3$. Organic phase: 0.5 M TiAP Solutions in Diluents

Diluent	LiNO_3 , M					
	1.0	1.5	2.0	3.0	4.0	5.0
Dodecane 2.014	0.039	0.11	0.34	0.96	7.25	37.1
TCB -	0.051	0.079	0.16	0.66	2.8	11.0
TCE 2.3	0.02	0.027	0.099	0.54	2.26	9.82
Toluene 2.379	0.036	0.036	0.07	0.35	0.84	1.76

Table 2. Values of Distribution Coefficients of Eu Microquantities during the extraction with 0.5 M NPOC Solutions in Toluene in the Aqueous Phase Containing LiNO_3

Extractant	LiNO_3 , M					
	1.0	1.5	2.0	3.0	4.0	5.0
TRP	0.019	0.038	0.1	0.4	1.1	2.9
TiAP	0.024	0.036	0.07	0.35	0.84	1.75
DiOMP	0.15	0.35	0.81	5.17	-	-
TOPO	51.2	161.0	269.0	919.0	-	-
T1MHPO	26.2	36.9	87.0	145.0	-	-

- The third phase during the saturation of TiAP of any concentration in saturated hydrocarbons with REE nitrates is absent.

Table 3. Separation Coefficients of Binary Lanthanide Mixtures. Concentration $\text{Ln}_I + \text{Ln}_{II} = 350-450 \text{ g/l}$ in Terms of REE Oxide

Extractant	Ce - La	Nd / Pr	Sm / Nd
TiAP	2-2.3	1.3-1.8	1.8-2.3
TBP	1.9-2.0	1.3-1.6	1.8-2.0

- Higher selectivity of TiAP during the separation of lanthanides of the cerium group is not observed.

- The TiAP losses are lower than those of TBP due to lower TiAP solubility in water.

References

1. Eremin G.K., Kamenev A.I., Martynenko L.I. // Zh. Neorg. Khim. 1961. N 16. P. 1487-1488.
2. Danilov N.A., Karavayeva S.A., Utkina O.B. // Radiokhimiya. 1984. N 6. P. 778-783.