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CHEMISTRY AND TECHNOLOGY OF RARE, TRACE,  
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## Binary Extraction of Lanthanides (III) Nitrates with Carboxylates and Dialkylphosphates of Secondary and Tertiary Amines

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**Abstract**—The separation of lanthanide (III) ions with binary extractants based on carboxylates, di-(2-ethylhexyl)phosphates of secondary and tertiary amines and their mixtures has been studied. The parameters of lanthanide nitrates extraction from the aqueous phase by solutions of these substances in nonpolar diluents have been found to fit the binary extraction mechanism. For systems containing di-(2-ethylhexyl) phosphate and caprate of dioctylammonium and trioctylammonium, synergistic effects have been observed.

**Keywords:** binary extraction, REE, distribution isotherm, di-(2-ethylhexyl) phosphoric acid, capric acid, synergistic effect

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### INTRODUCTION

The purification and separation of lanthanides is a complex chemical-technological problem, as naturally occurring REM compounds contain 15 elements with very similar physicochemical properties. Precipitating, extraction and ion exchange chromatography methods are used for preparative separation and purification of lanthanides [1]. In various methods, the separation factors of a single stage of separation process for the lanthanide pairs neighboring in the periodic table does not exceed ten and is often close to one [1, 2]. Extraction is the most effective and selective process. However, for a pure metal to be obtained, up to 50 separation stages should be carried out in extraction–reextraction cycles. This process is usually carried out using countercurrent extraction cascades containing several dozen successive extractors. Organophosphorus extractants, such as TBP, di-(2-ethylhexyl) phosphoric acid (D2EHPA), dialkylphosphinic, dialkyldithio phosphinic and carboxylic acids are mainly used to produce REM [3–8].

Cation exchange extractants based on dialkyl-substituted esters of phosphoric acid, such as D2EHPA, are among the most selective in the separation of lanthanides. However, these extractants are characterized by fairly high distribution coefficients of lanthanides, which require the use of concentrated mineral acids to strip the metals. This problem can be solved by using binary extracting agents based on D2EHPA and, in some cases, the metal reextraction is carried out by water [9].

Binary extractants are salts formed by an organic acid and an organic base. Thus, the binary extractants

can be prepared from stoichiometric mixtures of the known cation and anion exchange extractants. For these extraction systems a coupled interfacial transfer of a cation and an anion of the extracted inorganic salt occurs, so re-extraction by water is possible. The selectivity of binary extractants is determined by the nature of organic acids and bases.

The selectivity of the separation metal cations using binary extractants is comparable to selectivity via cation exchanging precursors of binary extractants. The distribution factor of an inorganic salt depends on the nature of an anion and cation of the extracted salt.

Hence, it is possible to vary the distribution factor of the cation using different inorganic anions [10]. For binary extraction the initial section of the isotherms of interfacial distribution of the salts is typically linear. In a high concentration section, a decrease in the isotherm slope is observed due to the saturation of the extractant.

Another problem of D2EHPA-based extractant is the formation of poorly soluble compounds in the organic phase at concentrations of lanthanides above 0.005 mol/L. Carboxylic acids and their salts formed by organic amines, i.e., carboxylates, are effective solvating additives that increase the solubility of di-(2-ethylhexyl) phosphates of lanthanides. Moreover, the extraction of REM salts by amine carboxylates via the binary extraction mechanism is also possible. At the same time, the selectivity of the extraction of lanthanides with carboxylic acids is significantly lower compared to phosphorus-containing extractants. In our previous paper, the extraction of REM chlorides in these systems was studied in detail [11]. In the present

paper, the extraction of REM nitrates with dialkyl phosphates and carboxylates of tertiary and secondary amines, as well as their mixtures, was studied. The dependence of selectivity of lanthanides extraction on the organic phase composition was discussed.

## EXPERIMENTAL

### Reagents

Reagents of chemically pure grade were used. The initial solutions of lanthanide nitrates were prepared by dissolving the corresponding salts in water, followed by titrimetric determination of the exact concentration [12]. Technical D2EHPA was purified by recrystallization of the salt  $\text{Cu}(\text{D2EHPA})_2$  according to the conventional technique [13]. Binary extractants, i.e., di-(2-ethylhexyl) tri and dioctylammonium phosphates ( $\text{R}_3\text{NHA}$  and  $\text{R}_2\text{NH}_2\text{A}$ ), were prepared by dissolving equimolar amounts of D2EHPA and the appropriate amine in toluene. Binary extractants based on amine caprates were prepared similarly. These extractants will be further referred to as tri- and dioctylammonium caprates, i.e.,  $\text{R}_3\text{NHB}$  and  $\text{R}_2\text{NH}_2\text{B}$ , respectively.

### Experimental Technique

Extraction equilibria were studied at  $25 \pm 1^\circ\text{C}$ . Extraction and stripping were carried out in a separatory funnel with equal volumes of organic and aqueous phases. The duration of mixing was 10 min and the time of establishing equilibrium in the system was 3–5 min.

To study the selectivity of lanthanide extraction, solutions of lanthanide nitrates with equal molar concentrations of 14 metals were used. The initial and equilibrium metal concentrations were determined titrimetrically in solutions that contain only one lanthanide using EDTA in the presence of a xylenol orange indicator [12].

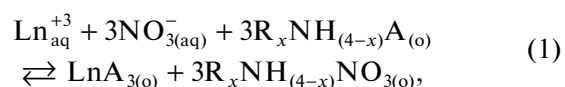
The concentration of lanthanide in the organic phase was determined by the difference between the concentrations in the initial solution and in the aqueous phase after extraction. In the case of low distribution coefficients, lanthanide concentrations in the organic phase were determined after stripping with 0.2 mol/L  $\text{HNO}_3$  solution. The concentration of metal in the aqueous phase less than 0.001 mol/L was determined using a spectrophotometer or by potentiometric titration with EDTA [14]. A platinum electrode was used as the indicator and a silver chloride electrode EVL 1M1 was used as the reference. Titration was carried out in an acetate buffer solution (pH 5.5) in the presence of trace amounts of divalent iron ions.

To determine the pH values of solutions and other potentiometric measurements, an Expert 001 pH-meter-ionomer was used. Spectrophotometric measurements were carried out using an AvaSpec-2048L

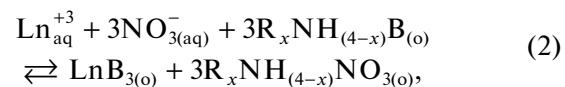
device. When extracting the lanthanide mixture, the concentrations of elements in the aqueous phase were measured using a mass spectrometer with inductively coupled plasma ICP-MS Agilent 7500A.

## RESULTS AND DISCUSSION

In our previous studies, the process of extracting the inorganic lanthanide salts (chlorides, bromides, nitrates) by di-(2-ethylhexyl) phosphates of secondary and tertiary organic amines and quaternary organic bases was shown to take place in accordance with binary extraction mechanism [15, 16]. Binary extraction of lanthanide nitrates by di-(2-ethylhexyl) phosphates of organic amines can be described by the following equation of the main heterogeneous reaction with no specific interactions in the organic phase, in particular taking into account the solvation processes:



where  $\text{R}_x\text{NH}_{4-x}\text{A}$  is di-(2-ethylhexyl) phosphate of di- or trioctylammonium and the symbols (o) and (aq) are the organic and aqueous phase, respectively. According to the binary extraction mechanism, the extraction of lanthanide salts with amine carboxylates can be described by the heterogeneous reaction equation



where  $\text{R}_x\text{NH}_{4-x}\text{B}$  is di- or trioctylammonium carboxylate.

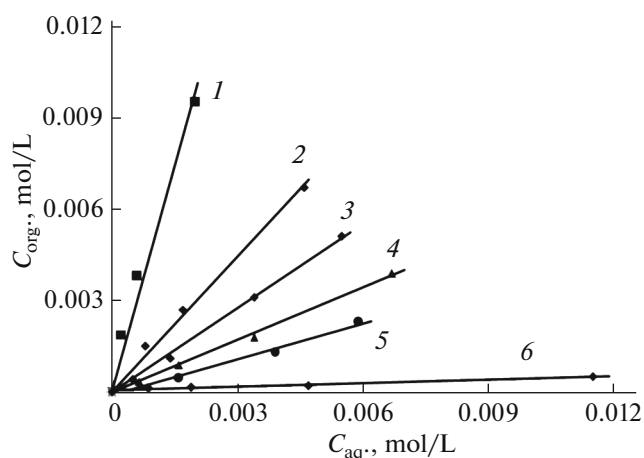
According to the above equations binary extraction has a number of features:

1. Similar to the extraction of salts by neutral extractants, the stoichiometric ratio of a cation and an anion is extracted into the organic phase.

On one hand, this phenomenon makes the extraction of metal salts in the presence of salting-out agents more efficient. On the other hand, the salts can be reextracted from the organic phase with water.

2. It is possible to salt out metals from the organic phase by adding amine nitrate due to the formation of two compounds during extraction, i.e.,  $\text{LaA}_3$  and  $\text{R}_x\text{NH}_{4-x}\text{NO}_3$ . This distinguishes binary extraction from metal extraction with neutral extractants. Moreover, the same factor results in the linearity of the initial section of the extraction isotherm (if there are no salting-out additives in the aqueous or organic phases)

3. In contrast to cation exchange extraction, the coefficients of metal distribution in these systems depend slightly on the pH of aqueous solutions, at least in a quite wide pH range. For D2EHPA systems, this range is equal to 3.5–6. At lower pH values, com-



**Fig. 1.** Isotherms of  $\text{La}(\text{NO}_3)_3$  extraction for the extractants based on secondary and tertiary amines: (1) mixed binary extractant 0.1 mol/L D2EHPA–0.3 mol/L of capric acid–0.4 mol/L dioctylamine in toluene; (2) mixed extractant 0.1 mol/L D2EHPA–0.3 mol/L of capric acid–0.4 mol / l of N, N–dioctylmethylamine in toluene; (3) 0.1 mol/L dioctylammonium caprate in toluene; (4) 0.1 mol/L of di-(2-ethylhexyl) phosphate of dioctylammonium in toluene; (5) 0.1 mol/L of di-(2-ethylhexyl) phosphate of trialkylammonium in toluene; 6. 0.3 mol/L of capric acid in toluene.

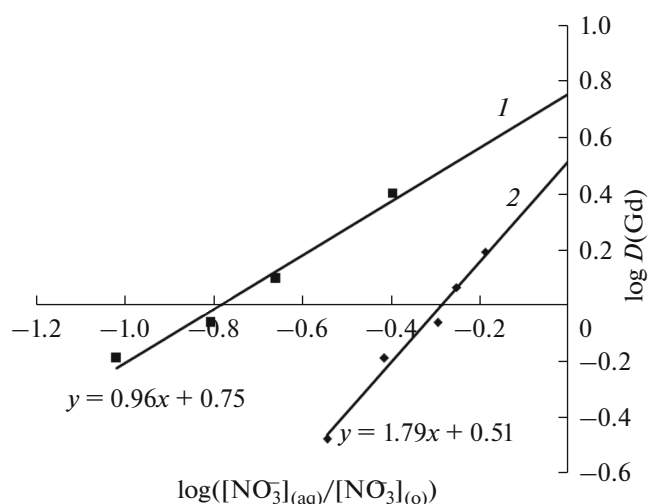
petitive binary extraction of  $\text{HNO}_3$  [17] is possible, while at higher values, the formation of metal hydroxocomplexes takes place.

4. The selectivity of the binary extraction of metals is determined by the nature of the organic acid of the binary extractant being used, while that of anions is determined by the nature of the amines being used.

The experimental isotherms of the extraction of the lanthanum salts with di-(2ethylhexyl) phosphate and di- or trioctylamine carboxylate, as well as their mixtures in various ratios, are shown in Fig 1. In these systems, the stoichiometric transfer of the cation and anion to the organic phase is observed with a ratio of 1 : 3, which is consistent with Eqs. (1) and (2). The isotherms in the initial section are almost linear.

For extractants  $\text{NR}_x\text{H}_{4-x}\text{A}$  and  $\text{NR}_x\text{H}_{4-x}\text{B}$ , as well as their mixtures, the pH value of the aqueous phase stays almost unchanged during the process of metal extraction, i.e., the initial pH is 5.2, while the final pH is 4.8–5.1.

The logarithmic dependences of the distribution coefficients for gadolinium nitrates on the ratio of nitrate ion concentration in the aqueous and organic phases are shown in Fig. 2. It can be seen that, for these extractants, the increase in nitrate ion concentration in the organic phase results in the suppression of the extraction of lanthanides. It can be said that salts are salted out into the aqueous phase in accordance with equilibrium described by Eq. (2).



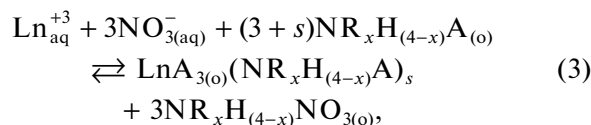
**Fig. 2.** Logarithmic dependence of  $D_{\text{Gd}}$  on the ratio of the equilibrium concentrations of nitrate ions in the aqueous and organic phases. ( $C_{\text{Cd}(\text{NO}_3)_3} = 0.0028$  mol/L): (1) 0.5 mol / L trioctylammonium caprate in toluene–Gd ( $\text{NO}_3$ ) $_3$  with the addition  $\text{NR}_3\text{HNO}_3$  in the range of 0–0.1 mol/L; (2) 0.1 mol/L dioctylammonium caprate in toluene–Gd( $\text{NO}_3$ ) $_3$  with the addition of  $\text{NR}_2\text{H}_2\text{NO}_3$  in the range of 0–0.02 mol/L.

The presented data show that, in the studied systems, the interphase metal distribution at least qualitatively follows the regularities of the binary extraction of metal salts. Moreover, as a rule, the quantitative description of this type of processes is not simple, since extraction is accompanied by various secondary interactions in the organic phase that in uence the extraction dependences. The following should be classified among these interactions:

–the solvation of organic metal salt by the excess of the binary extractant with the formation of  $(\text{LnA}_3) \cdot (\text{NR}_x\text{H}_{4-x}\text{A})_s$ , which increases the extraction of metal into the organic phase;

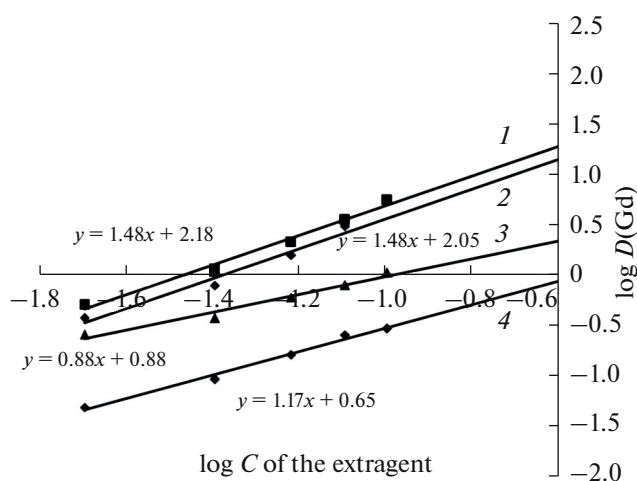
–the formation of associates of lanthanide organic salts with amine chlorides  $(\text{LnA}_3) \cdot (\text{NR}_x\text{H}_{4-x}\text{NO}_3)_s$ , which decreases the effect of salting out lanthanide salts into the aqueous phase.

Furthermore, self-association always takes place in systems with amine salts. In the presence of excess extractant, the most likely solvate type is  $(\text{LnA}_3) \cdot (\text{NR}_x\text{H}_{4-x}\text{A})_s$ . In this case, Eqs. (1) and (2) can be converted to the form



where  $s$  is the solvate number.

Conventional heterogeneous equilibrium constant for reaction (3), which excludes the activity coefficient



**Fig. 3.** Distribution factor of gadolinium nitrate as a function of extractant concentration in the range 0–0.1 mol/L. (1) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of trioctylammonium; (2) 0–0.1 mol/L dioctylammonium caprate; (3) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of dioctylammonium; (4) 0–0.1 mol/L trioctylammonium caprate.

of the ions and compounds in the aqueous and organic phase, may be written as

$$K_{ex} = \frac{[\text{LnA}_3(\text{NR}_x\text{H}_{(4-x)}\text{A})^s]_{(o)}[\text{R}_x\text{H}_{(4-x)}\text{NO}_3]_{(o)}^3}{[\text{Ln}^{+3}]_{(aq)}[\text{NO}_3^-]_{(aq)}^3[\text{R}_x\text{NH}_{(4-x)}\text{A}]_{(o)}^{(3+s)}} \quad (4)$$

For the case of a large excess of the extractant, in the absence of salting-out agents in the aqueous phase (nitrates of the other metals), the dependences of the distribution coefficients of the metals ( $D_{\text{Ln}}$ ) on the binary extractant concentrations (5) and (6) can be easily obtained as follows:

$$D_{\text{Ln}} = K_{ex}[\text{R}_x\text{NH}_{(4-x)}\text{A}]_{(o)}^{\frac{3+s}{4}}, \quad (5)$$

$$\log D_{\text{Ln}} = \frac{3+s}{4} \log[\text{R}_x\text{NH}_{(4-x)}\text{A}]_{(o)} + \log K_{ex} \quad (6)$$

The experimental logarithmic dependences of the distribution coefficients of gadolinium nitrate on the concentrations of various extractants are presented in Fig. 3. Solvate numbers were calculated from Eq. (6) for the range of extractant concentrations of 0–0.1 mol/L at an initial concentration of  $\text{Gd}(\text{NO}_3)_3$  in the aqueous phase of 0.0028 mol/L. In all cases, the extracted gadolinium compounds are solvated by excess extractant. Thus, for systems with di-(2-ethylhexyl) phosphate of trioctylamine and dioctylamine caprate an organic salt is solvated with three molecules of extractant, while monosolvate formation is typical for systems with di-(2-ethylhexyl) phosphate of dioctylamine and trioctylamine caprate. The case of excess amine nitrate in the organic phase compared with the stoichiometry of an inorganic salt extraction and salting-out the metal (excluding solvation process and at

high extractant excess) can be described by Eqs. (7) and (8) as follows:

$$D_{\text{Ln}} = K_{ex}[\text{R}_x\text{NH}_{(4-x)}\text{A}]_{(o)}^{(3+s)} \times [\text{NO}_3^-]_{(aq)}^3[\text{R}_x\text{NH}_{(4-x)}\text{NO}_3]_{(o)}^3, \quad (7)$$

$$\log D_{\text{Ln}} = (3+s) \log(K_{ex} + [\text{R}_x\text{NH}_{(4-x)}\text{A}]_{(o)}) + 3(\log[\text{NO}_3^-]_{(aq)} - [\text{R}_x\text{NH}_{(4-x)}\text{NO}_3]_{(o)}). \quad (8)$$

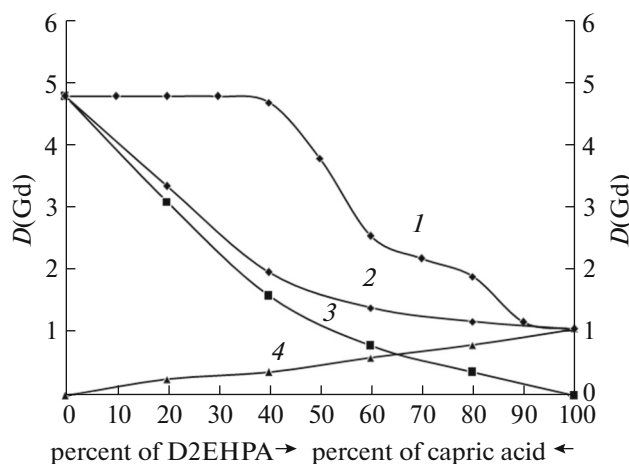
If mutual solvation and the self-association of the organic phase components are independent processes, the coefficient value for linearized logarithmic dependences (Fig. 2, the lines 1 and 2) should be equal to 3. For caprates of secondary and tertiary amines, the slope coefficient of the lines is about 1 and 2, respectively. The observed differences are likely due to the self-association of amine nitrates in the organic phase.

In the case of mixed binary extractants ( $\text{NR}_x\text{H}_{4-x}\text{B}$ ,  $\text{NR}_x\text{H}_{4-x}\text{A}$ ), the formation of more complex solvates, the development of synergistic effects, and the change in the solubility of extracted compounds can be expected.

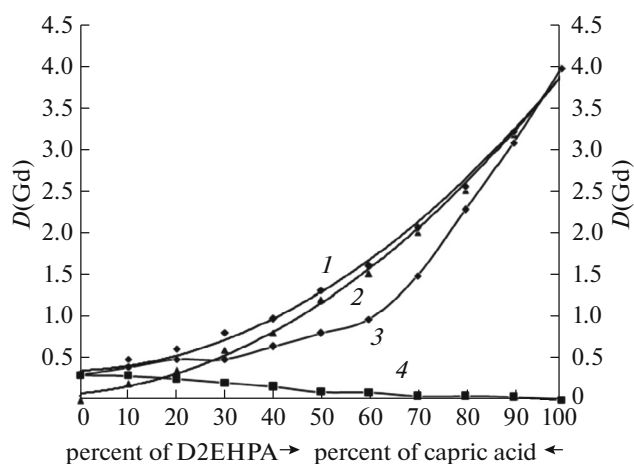
In the case of secondary amines, the extraction of lanthanide nitrates with carboxylates and di-(2-ethylhexyl) phosphates was found to be more efficient (Fig. 4, curves 3 and 4). For mixtures of binary extractants, the values of lanthanide ion distribution coefficients are much higher than the sum of the distribution coefficients for individual extractants at the same concentration (Fig. 4, curves 1 and 2). Both initial extractants and the reaction products can be solvated by amine carboxylates. Thus, the explanation of the synergistic effect can be based on the assumption that, in the organic phase, extraction products are better solvated by secondary amine carboxylate than the initial extractants.

Carboxylates of tertiary amines are less effective in the extraction of lanthanide nitrates if compared with carboxylates of secondary amines (Fig. 5). The distribution coefficients for amine carboxylate ( $\text{R}_3\text{NHB}$ ) (Fig. 5, curve 4) are significantly lower than those for di-(2-ethylhexyl) phosphate ( $\text{R}_3\text{NHA}$ ) (Fig. 5, curve 3). When extracting  $\text{Gd}(\text{NO}_3)_3$  with the mixtures of binary extractants,  $D$  values are lower than the sum of the distribution coefficients for individual extractants at the same concentration (Fig. 5, curves 1 and 2). This can be explained by the inefficient solvation of extraction products by tertiary amine carboxylates in the organic phase.

For extractants containing carboxylates and di-(2-ethylhexyl) phosphates of secondary and tertiary amines, when extracting lanthanide nitrates, an increase in the distribution coefficients with an increase in the atomic number of the metal is observed (table). For all types of extractants studied in this paper, the dependence of  $\log(D_{\text{Ln}})$  on the lanthanide atomic number is nonmonotonous. There are several sharp bends typical of cation-exchange extraction in



**Fig. 4.** Synergistic effect for the system of di-(2-ethylhexyl) caprate of dioctylammonium in toluene- $\text{Gd}(\text{NO}_3)_3$ ; ( $C_{\text{Cd}(\text{NO}_3)_3} = 0.002 \text{ mol/L}$ ): (1) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of dioctylammonium; 0–0.1 mol/L dioctylammonium caprate; (constant concentration of dioctylamine–0.1 mol/L); (2) the sum of  $D_{\text{Ln}}$  values for the curves 3 and 4; (3) 0–0.1 mol/L dioctylammonium caprate; (4) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of dioctylammonium.



**Fig. 5.** Synergistic effect for the system of di-(2-ethylhexyl)caprate dioctylammonium in toluene- $\text{Gd}(\text{NO}_3)_3$  ( $C_{\text{Cd}(\text{NO}_3)_3} = 0.002 \text{ mol/L}$ ): (1) sum of  $D_{\text{Ln}}$  values for the curves 3 and 4; (2) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of trioctylammonium; (3) 0–0.1 mol/L di-(2-ethylhexyl)phosphate of trioctylammonium; 0–0.1 mol/L trioctylammonium caprate; (constant concentration of trioctylamine – 0.1 mol/L); (4) 0–0.1 mol/L trioctylammonium caprate.

the curve, which is representative of the so-called double–double effect.

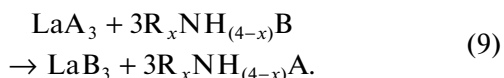
Thus, for all of the above types of extractant mixtures, a significant decrease in extraction selectivity compared with binary extractants based only on di-(2-

ethylhexyl) phosphate is observed. At the same time, the solubility of extracted compounds increases and gel formation is reduced. Taking this fact into account, it can be concluded that the balance (9) in the organic phase is shifted predominantly to the right, i.e., to the

Separation coefficients ( $\beta_{\text{Ln}/\text{La}}$ ) and distribution coefficients ( $\log D$ ) as a function of the atomic number of the element  $\Sigma[\text{Ln}^{3+}] = 2 \times 10^{-3} \text{ mol/L}$

Element	$\text{R}_2\text{NH}_2\text{A}$ , 0.1 mol/L		$\text{R}_2\text{NH}_2\text{A}$ , 0.1 mol/L + $\text{R}_2\text{NH}_2\text{B}$ , 0.3 mol/L		$\text{R}_3\text{NHA}$ , 0.1 mol/L + $\text{R}_3\text{NHB}$ , 0.3 mol/L		$\text{R}_2\text{NH}_2\text{A}$ , 0.1 mol/L + $\text{R}_2\text{NH}_2\text{B}$ , 0.1 mol/L		$\text{R}_2\text{NH}_2\text{B}$ , 0.1 mol/L	
	$\log D$	$\beta_{\text{Ln}/\text{La}}$	$\log D$	$\beta_{\text{Ln}/\text{La}}$	$\log D$	$\beta_{\text{Ln}/\text{La}}$	$\log D$	$\beta_{\text{Ln}/\text{La}}$	$\log D$	$\beta_{\text{Ln}/\text{La}}$
La	-0.92	1	0.08	1	-0.16	1	-0.65	1	-0.35	1
Ce	-1.00	0.8	0.60	3.3	0.18	2.2	-0.57	1.2	-0.14	1.6
Nd	-0.71	1.6	0.97	7.8	0.64	6.4	-0.19	2.9	-0.11	1.7
Sm	-0.34	3.8	1.31	17.1	1.01	15.1	0.34	9.6	0.17	3.3
Eu	-0.06	7.3	1.36	19.2	1.11	18.7	0.55	15.9	0.23	3.8
Gd	0.00	8.4	1.39	20.2	1.09	18.1	0.57	16.4	0.26	4.1
Tb	0.50	26.4	1.40	20.7	1.28	27.7	0.61	18.1	0.41	5.7
Dy	0.82	54.8	1.52	27.3	1.34	32.2	0.66	20.4	0.44	6.2
Ho	0.91	68.0	1.56	30.3	1.41	37.4	0.67	20.7	0.50	7.2
Er	1.47	249	1.66	37.4	1.53	49.2	0.76	25.3	0.57	8.3
Tm	2.20	1328	1.88	62.6	1.75	82.5	0.89	34.3	0.70	11.4
Yb	2.40	2090	2.00	92.7	1.97	136.0	1.19	68.2	0.84	15.5
Lu	2.64	3623	2.21	132.9	2.23	247.0	1.37	104.1	0.94	19.4

formation of more stable lanthanide carboxylates solvated by an excess of the binary extractants as follows:



### CONCLUSIONS

The extraction of lanthanide salts by mixed extractants based on di-(2-ethylhexyl) phosphates and carboxylates of organic amines was found to obey the regularities of the binary extraction as follow:

—isotherms of salt distribution are linear in the initial section, i.e., the area of low concentration of metals in the organic phase;

—only an insignificant change in pH value of the aqueous phase is observed when extracting by di-(2-ethylhexyl) phosphates and carboxylates of tertiary and secondary amines and their mixtures.

The pH value is close to those of the initial solutions, with the difference being less than 0.5. When extracting Gd (NO<sub>3</sub>)<sub>3</sub> by the mixtures of the binary extractants, a synergistic effect is observed that is positive for R<sub>2</sub>NH<sub>2</sub>A–R<sub>2</sub>NH<sub>2</sub>B and negative for R<sub>3</sub>NHB–R<sub>3</sub>NHA systems.

For all of the examined types of extractant mixtures, a significant decrease in the extraction selectivity compared with binary extractants based on di-(2-ethylhexyl) phosphates is observed. At the same time, the solubility of the extracted compounds increases and gel formation is reduced. For all types of extractants studied, high separation coefficients of lanthanide pairs were observed. For mixtures of binary extractants, the selectivity of the extraction separation of lanthanides is determined by binary extractant with higher values of distribution factor for lanthanide salts.

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