CHEMISTRY AND TECHNOLOGY OF RARE, TRACE, AND RADIOACTIVE ELEMENTS

Interphase Distribution of Lanthanide Nitrates in Aqueous Organic Two-Phase Systems with Amine and Organic Acid Salts

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Abstract—The extraction of lanthanide nitrates from 0.5 M $NaNO_3$ solutions in 1 : 1 : 1 ternary aqueous organic systems using mixtures of trioctylammonium dialkyl phosphate and dicyclohexylammonium caprylate as extractants was studied. The extractability of lanthanides was shown to increase in the series La < Pr < Nd, Sm, Eu < Gd < Tb < Dy < Ho < Er < Tm, in which the atomic number of the metal increases. The selectivity of extraction in the ternary system was observed during the extraction of heavy lanthanides.

Keywords: lanthanide nitrates, amines, organic acids, aqueous organic two-phase systems, interphase distribution, separation, extractability

INTRODUCTION

Rare-earth metals (REMs) are generally extracted and separated by extraction methods. Effective extractants of REMs are organophosphorus acids, for example, di-2-ethylhexylphosphoric acid (D2EHPA) [1, 2]. A disadvantage of the use of organic acids is the necessity of using relatively concentrated solutions of inorganic acids for re-extraction. An alternative are binary extractants, which, unlike cation-exchange extractants, allow easy re-extraction of metals from the organic phase in the absence of salting-out agents. These systems are characterized by insignificant influence of aqueous phase acidity on the interphase salt distribution and also by the possibility of obtaining large numbers of binary extractants with various properties by using combinations of various organic anions and cations [3–8].

The extraction separation of liquid mixtures using a combination of liquid extraction, liquid-liquid chromatography, and free liquid membrane techniques is being developed at the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences [9–28]. An important role in the development of these processes is played by the choice of extraction system. Unlike liquid extraction, in liquid–liquid extraction used mainly for separation and purification of biological products, environmentally safe multicomponent aqueous-organic two-phase systems are used. Earlier, we obtained data on the interphase distribution of lanthanide salts in ternary aqueous-organic systems with binary extractants based on

D2EHPA and trioctylmethylammonium [29] depending on the compositions of the aqueous and organic phases. The goal of this study was to investigate the 1 : 1 : 1 ternary systems including the hydrophilic (water) and hydrophobic (hexane) components, as well as isopropanol, which shows both hydrophilic and hydrophobic properties. For REM extraction, extractants of various compositions were added to the organic phase (hexane), including binary extractants based on amines and mixtures thereof.

EXPERIMENTAL

The starting solutions of lanthanum and gadolinium nitrates were prepared by dissolving the $La(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$ samples ("kh.ch." (reagent) grade) in distilled water. The starting solutions of Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm nitrates were prepared by dissolving the metal oxide samples ("kh.ch." (reagent) grade) in concentrated HNO_3 followed by repeated evaporation of solutions with water on a water bath to remove excess acid.

To prepare the binary extractants and mixtures of extractants, the following starting reagents were used: trioctylamine (Fluka), dicyclohexylamine (Fisher Biotech), di(2-ethylhexyl)phosphoric acid (Merck), Cyanex 272 (Cytec), and caprylic acid. The solvents used were hexane ("ch.d.a." (analytical) grade) and isopropanol ("kh.ch." (reagent) grade). The binary extractants based on ternary (R_3N) and secondary (R_2NH) amines were prepared by dissolving equimo-
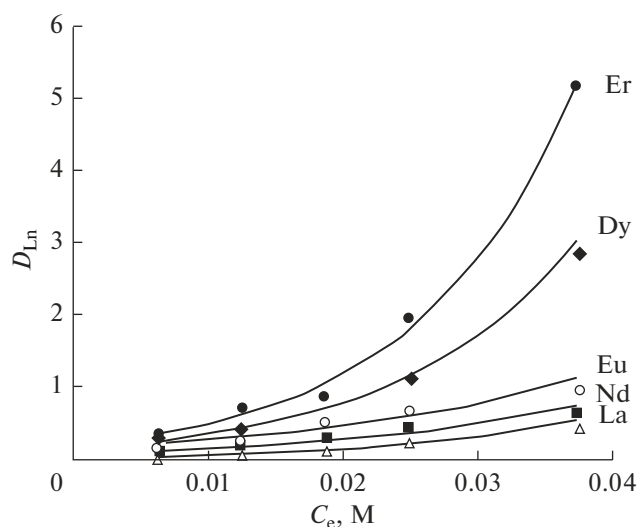
Fig. 1. Extraction of lanthanide nitrates in the 1 : 1 : 1 system depending on the concentration of trioctylammonium di(2-ethylhexyl) phosphate. The 1 : 1 : 1 system: $Ln(NO_3)_3$ in 0.5 M $NaNO_3$–R_3NHA solution in hexane–isopropanol. $C_{Ln(st)} = 0.018$ M; $V_{aq} : V_{org} = 5 : 4$.

lar amounts of trioctylamine or dicyclohexylamine and the corresponding organic acid (HA) in hexane.

The method for investigating the interphase distribution of REM nitrates in 1 : 1 : 1 multicomponent extraction systems was as follows. Aqueous solutions of REM nitrates in 0.5 M $NaNO_3$ and solutions with different concentrations of extractant (mixture of extractants) in hexane and isopropanol were taken in equal volumes.

The phases were mixed at 20°C in test tubes with ground-in stoppers for 15 min, which was enough for setting constant lanthanide distribution coefficients. As the introduction of the third component with hydrophilic and hydrophobic properties in 1 : 1 : 1 systems leads to the aqueous phase containing organic substances, which can contain water, the volumes of the upper (organic) and lower (water) phases were determined after separation.

The lanthanide concentration in the starting solutions and aqueous phases after extraction was determined by trilonometric titration with xylenol orange. The lanthanide concentration in organic phases was determined from the differences between the concentrations in the starting solution and aqueous phase after extraction including the changes in the volumes of the aqueous and organic phases. The lanthanide distribution coefficients in the multicomponent system were calculated by the equation

$$D = \frac{(C_{st} - C_{aq})V_{aq}/V_{org}}{C_{aq}},$$

where C_{st} and C_{aq} are the metal concentrations in the starting solution and aqueous phase after extraction, respectively; V_{aq} and V_{org} are the volumes of the aqueous and organic phases after extraction. In some cases, quantitative re-extraction of metals from the organic phase with a 0.5 M nitric acid solution followed by determination of the lanthanide content in re-extracts was performed.

RESULTS AND DISCUSSION

The distribution of REM nitrates from 0.5 M $NaNO_3$ solutions with trioctylammonium di(2-ethylhexyl) phosphate in a 1 : 1 : 1 system was studied at different concentrations of the binary extractant. According to Fig. 1, lanthanide extractability increases in the series La < Nd < Eu < Dy < Er, which corresponds to the increasing atomic number of the metals and correlates with their extractability in the starting extraction system with D2EHPA [2]. Note that at high lanthanide concentrations in the organic phase (over 0.01 M) in these systems, slightly soluble compounds LnA_3 form, as in extraction systems [7].

Carboxylic acids and their salts with organic amines were found to be effective solvating additives, which increase the solubility of lanthanide di(2-ethylhexyl) phosphates [3, 8]. Therefore, we studied various extraction mixtures of trioctylamine (TOA), dicyclohexylamine (DCHA), caprylic acid (CA), D2EHPA, and Cyanex 272 using the extraction of europium nitrate from 0.5 M $NaNO_3$ solutions in a 1 : 1 : 1 ternary system (Table 1). Precipitation was observed after extraction in all the systems except the system with a mixture of two binary extractants: trioctylammonium dialkylphosphate (R_3NHA) and dicyclohexylammonium caprylate ($R_2NH \cdot HA$) at a ratio of 2 : 1 (the total concentration of binary extractants was 0.33 M); europium was quantitatively extracted in the organic phase (Table 1).

The mixture of trioctylammonium dialkyl phosphate and dicyclohexylammonium caprylate was chosen as an extractant for use in the 1 : 1 : 1 ternary system. Figure 2 shows the data on the extraction of lanthanum, europium, and erbium nitrates from 0.5 M $NaNO_3$ solutions in a ternary system with a mixture of R_3NHA and $R_2NH \cdot HA$ (2 : 1) depending on the total concentration of the binary extractants.

The results showed that the metal distribution coefficients increase with the total concentration of binary extractants, and that the lanthanide extractability increases in the series La < Eu < Er. The calculated lanthanide separation coefficients in this system (Table 2) showed that the separation of metals improves with increasing concentration of binary extractants in the mixture.

Table 1. Compositions of the mixtures of extractants in a 1 : 1 : 1 system ($Eu(NO_3)_3$ in a 0.5 M solution of $NaNO_3$–mixture of extractants in hexane–isopropanol). $C_{Eu(st)} = 0.02$ M

| No.	Composition of the mixture of extractants in hexane
1	0.22 M TOA, 0.22 M D2EHPA, 0.22 M *Cyanex* 272
2	0.33 M TOA, 0.17 M D2EHPA, 0.17 M *Cyanex* 272
3	0.22 M TOA, 0.22 M D2EHPA, 0.22 M CA
4	0.22 M TOA, 0.17 M D2EHPA, 0.17 M CA
5	0.25 M TOA, 0.25 M DCHA, 0.25 M D2EHPA
6	0.22 M TOA, 0.11 M DCHA, 0.33 M D2EHPA
7*	0.22 M TOA, 0.11 M DCHA, 0.22 M D2EHPA, 0.11 M CA

* The system has no precipitates.

Table 2. Distribution and separation coefficients of REMs from 0.5 M $NaNO_3$ solutions in the 1 : 1 : 1 system with a mixture of R_3NHA and $R_2NH \times HA$ (2 : 1) at different initial concentrations of the total extractant ($C_{Ln(st)} = 0.018$ M; $V_{aq} : V_{org} = 5 : 4$)

C_e, M	D_{Ln}			$\beta_{Eu/La}$	$\beta_{Er/La}$	$\beta_{Er/Eu}$
	La	Eu	Er			
0.0187	0.44	0.625	0.93	1.42	2.11	1.49
0.025	0.83	1.00	1.46	1.20	1.76	1.46
0.0312	1.40	1.67	4.67	1.19	3.34	2.80
0.0375	2.11	2.84	7.75	3.46	3.67	2.73

It was of interest to study the effects of the R_3NHA to $R_2NH \cdot HA$ ratio in the mixture on the distribution of lanthanide nitrates. For this purpose, the extraction of lanthanum nitrate from the 0.5 M $NaNO_3$ solutions with isomolar mixtures of R_3NHA and $R_2NH \cdot HA$ in the 1 : 1 : 1 systems depending on the mole fraction of dicyclohexylammonium caprylate was studied (Fig. 3). According to the experimental data (Fig. 3), an increase in the proportion of the dicyclohexylammonium caprylate addition in the mixture of binary extractants leads to an increase in the lanthanum distribution coefficients; i.e., by varying the R_3NHA to $R_2NH \cdot HA$ ratio in the mixture, it is possible to regulate the interphase distribution of lanthanides. Earlier, a study of the extraction of lanthanum salts with trioctylammonium and dioctylammonium dialkylphosphates revealed lower extraction ability of the binary extractant based on secondary amine [7]. In this case, caprylate dicyclohexylammonium is a more efficient extractant. This may be due to the presence of bulky cyclic radicals in the dicyclohexylamine molecule and structural hindrances in the formation of the $R_2NH \cdot HA$ binary extractant compared to R3NHA, which leads to increased lanthanum distribution coefficients (Fig. 3).

Figure 4 presents data on the distribution of REM nitrates from the 0.5 M $NaNO_3$ solution in 1 : 1 : 1 systems in the presence of mixtures of R_3NHA and $R_2NH \cdot$ HA (2 : 1) depending on the serial number of lanthanide. It follows that the extractability of metals increases in the series La < Pr < Nd, Sm, Eu < Gd < Tb < Dy < Ho < Er < Tm in accordance with the
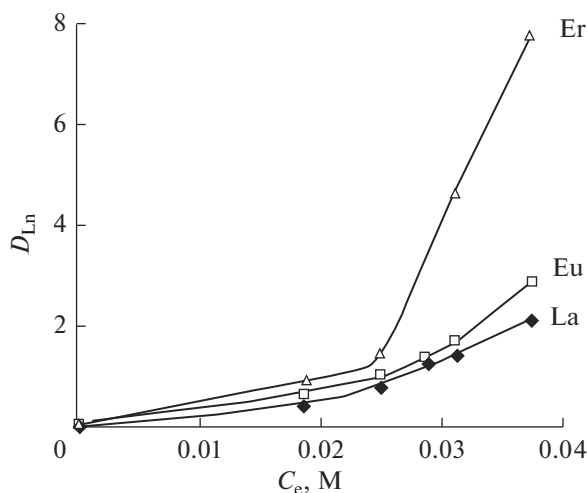
Fig. 2. Dependence of the extraction of lanthanide nitrates in the 1 : 1 : 1 system in the presence of mixtures of R_3NHA and $R_2NH \cdot$ HA depending on the total concentration of extractants. The 1 : 1 : 1 system: $Ln(NO_3)_3$ in 0.5 M $NaNO_3$–$R_3NHA + R_2NH \cdot HA$ (2 : 1) in hexane–isopropanol ($C_{Ln(st)} = 0.018$ M; $V_{aq} : V_{org} = 5 : 4$).
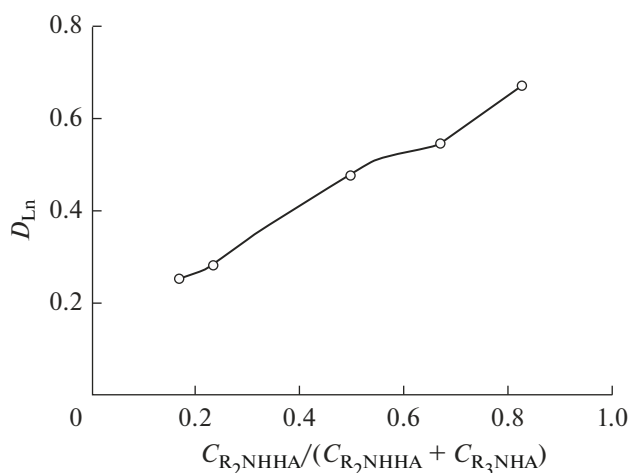
Fig. 3. Extraction of lanthanum nitrate from 0.5 M NaNO$_3$ solutions with isomolar mixtures of R$_3$NHA and R$_2$NH · HA in the 1 : 1 : 1 system depending on the mole fraction of dicyclohexylammonium caprylate (C_{R_2NHHA} + $C_{R_3NHA Ln(st)}$ = 0.018 M; V_{aq} : V_{org} = 5 : 4).

Fig. 4. (*1*) Distribution and (*2*) separation coefficients of lanthanides during extraction from 0.5 M NaNO$_3$ solutions in the 1 : 1 : 1 system in the presence of mixtures of R$_3$NHA and R$_2$NH · HA depending on the serial number of lanthanide. The 1 : 1 : 1 system: Ln(NO$_3$)$_3$ in 0.5 M NaNO$_3$−R$_3$NHA + R$_2$NH · HA (2 : 1) in hexane−isopropanol = 0.0375 M; $C_{Ln(st)}$ = 0.018 M; V_{aq} : V_{org} = 5 : 4.

increasing atomic number of lanthanides. This extractability series of REMs correlates with their extractability in the starting extraction system with D2EHPA [2]. The results (Fig. 4) showed that extraction selectivity in this case is observed mainly for extraction of heavy lanthanides (from dysprosium to thulium); this can be used, for example, for separating heavy lanthanides from light ones. The extractants have rather high capacity in this 1 : 1 : 1 multicomponent system. For example, during the extraction of erbium and thulium (Fig. 4), the ratio of the initial total concentration of binary extractants to the metal concentration in the organic phase is close to 2. The separation coefficients of lanthanides from the group of light metals differ slightly (curve *2*, Fig. 4); therefore, the extraction of nitrates of these metals in the 1 : 1 : 1 system using mixtures of R$_3$NHA and R$_2$NH · HA of different compositions was studied. According to the experimental data of Fig. 5, the lanthanide distribution coefficients significantly increase at increased mole fraction of R$_2$NH · HA in the mixture of binary extractants, but the extraction selectivity remains low. Thus, mixtures of binary extractants with mole fractions of dicyclohexylammonium caprylate of over 0.6 can be used for total extraction of REMs from nitrate solutions.

CONCLUSIONS

Data on the interphase distribution of lanthanide nitrates from 0.5 M NaNO$_3$ solutions in 1 : 1 : 1 ternary aqueous organic systems using trioctylammonium
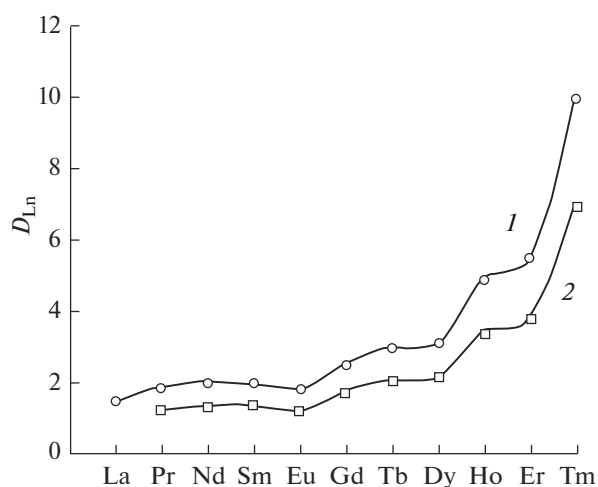
di(2-ethylhexyl) phosphate and mixtures of trioctylammonium di(2-ethylhexyl) phosphate with dicyclohexylammonium caprylate as extractants were obtained. In contrast to trioctylammonium dialkyl phosphate systems, in ternary aqueous organic systems with mixtures of binary extractants based on ter-
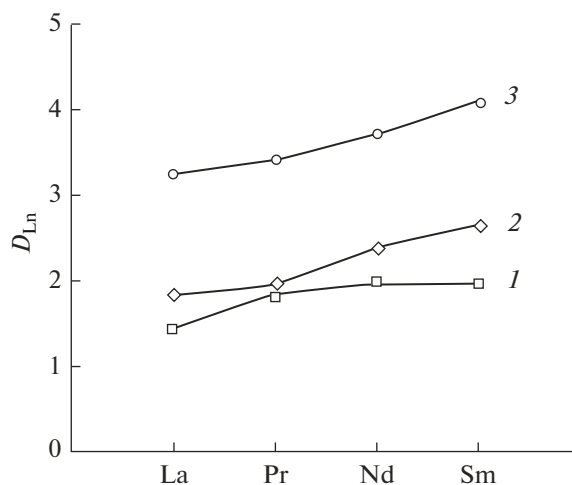

Fig. 5. Distribution coefficients of lanthanides during extraction from 0.5 M NaNO$_3$ solutions in the 1 : 1 : 1 system in the presence of mixtures of R$_3$NHA and R$_2$NH · HA depending on the serial number of lanthanide. The 1 : 1 : 1 system: Ln(NO$_3$)$_3$ in 0.5 M NaNO$_3$− R$_3$NHA + R$_2$NH · HA (2 : 1) in hexane−isopropanol (C_{R_2NHHA} + C_{R_3NHA} = 0.0375 M; $C_{Ln(st)}$ = 0.018 M; V_{aq} : V_{org} = 5 : 4). R$_3$NHA : R$_2$NH · HA = (*1*) 2 : 1; (*2*) 1 : 1; and (*3*) 1 : 2.

tiary and secondary amines, the solubility of extraction products is improved. The extractability of lanthanides in systems with mixtures of R_3NHA and $R_2NH \cdot HA$ increases in the series La < Pr < Nd, Sm, Eu < Gd < Tb < Dy < Ho < Er < Tm in accordance with the increasing atomic number of the metal and correlates with their extractability in the starting extraction system with D2EHPA. It was shown that the extraction and separation of REMs can be affected by varying the composition of the mixture of binary extractants and their total concentration. Extraction selectivity was observed mainly during the extraction of heavy lanthanides, which can be used, for example, for separating heavy lanthanides from light ones.

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