ЭКСТРАКЦИЯ НИТРАТОВ ЛАНТАНИДОВ ЛЕГКОЙ ГРУППЫ БИНАРНЫМ ЭКСТРАГЕНТОМ НА ОСНОВЕ ДИ-(2-ЭТИЛГЕКСИЛ)ФОСФОРНОЙ КИСЛОТЫ И ТРИОКТИЛАМИНА

С.Н. Калякин, М.А. Мулагалеева, В.И. Кузьмин, А.А. Кузьмина

Сергей Николаевич Калякин (ORCID 0000-0002-6072-441X)

Федеральный исследовательский центр "Красноярский научный центр Сибирского отделения РАН", Институт химии и химической технологии Сибирского отделения РАН - обособленное подразделение ФИЦ КНЦ СО РАН, Академгородок, 50, стр. 24, Красноярск, Российская Федерация, 660036
Кафедра органической и аналитической химии, Сибирский федеральный университет, просп. Свободный, 79, Красноярск, Российская Федерация, 660041
E-mail: snk@icct.ru

Марина Александровна Мулагалеева (ORCID 0000-0002-8930-6115)*, Владимир Иванович Кузьмин (ORCID 0000-0001-6473-3615), Анна Алексеевна Кузьмина (ORCID 0000-0002-6112-8230)

Федеральный исследовательский центр "Красноярский научный центр Сибирского отделения РАН", Институт химии и химической технологии Сибирского отделения РАН - обособленное подразделение ФИЦ КНЦ СО РАН, Академгородок, 50, стр. 24, Красноярск, Российская Федерация, 660036
E-mail: maral7508@mail.ru*, Kuzmin_vi@mail.ru, kuzmina@mail.com

В представленной статье был исследован процесс извлечения нитратов лантаноидов легкой группы из нейтральных водных растворов бинарным экстрагентом на основе ди-(2-этилгексил)фосфорной кислоты (НА), три-н-октиламина (NR₃) и сольватирующей добавки нитрата три-н-октиламина (NR₃HNO₃) в неполярном органическом разбавителе. На примере нитрата неодима показано, что данный экстрагент (NR₃HA+NR₃HNO₃) извлекает нитраты лантаноидов по законам бинарной экстракции. Катион и анион неорганической соли переходят в органическую фазу в стехиометрическом соотношении. Изотермы экстракции нитратов лантаноидов имеют S-образную форму, а во время экстракции наблюдается лишь незначительное изменение рН. На основании исследования спектров поглощения комплексов Nd в органической фазе установлено, что при низкой концентрации Nd образуется комплекс (NdA₃)•NR₃HNO₃, а при высокой концентрации Nd (при насыщении экстрагента) образуется соединение состава (NdA₂NO₃)•NR₃HNO₃. Введение высаливателей в водную или органическую фазу позволяет варьировать коэффициент распределения (D_Nd). С повышением концентрации нитрата натрия в водной фазе D_Nd увеличивается, а при повышении концентрации NR₃HNO₃(о), соответственно, уменьшается. Введение в органическую фазу высаливающего и сольватирующего агента NR₃HNO₃ исключает образование осадков в органической фазе при экстракции нитратов лантаноидов. Количественно процесс экстракции Nd в широком диапазоне концентраций Nd(NO₃)₃ и составов экстрагента можно описать на основе двух сопряженных уравнений бинарной экстракции и соответствующих концентрационных констант. Установлено, что предложенный экстрагент обеспечивает высокие коэффициенты разделения для неодима и других лантаноидов легкой группы.

Ключевые слова: бинарная экстракция, РЗЭ, ди-(2-этилгексил)фосфорная кислота, сольватирующие добавки, амин

EXTRACTION OF LIGHT GROUP LANTHANIDE NITRATES BY A BINARY EXTRACTANT BASED ON DI-(2-ETHYLHEXYL)PHOSPHORIC ACID AND TRIOCTYLAMINE

S.N. Kalyakin, M.A. Mulagaleeva, V.I. Kuzmin, A.A. Kuzmina

Sergey N. Kalyakin (ORCID 0000-0002-6072-441X)

Institute of Chemistry and Chemical Technology, Siberian Branch of the RAS (SB RAS), Federal Research Center «Krasnoyarsk Science Center SB RAS», Academgorodok, 50/24, Krasnoyarsk, 660036, Russia
Department of Organic and Analytical Chemistry, Siberian Federal University, 660041 Krasnoyarsk, Svobodny ave., 79, Russia
E-mail: snk@icct.ru

Marina A. Mulagaleeva (ORCID 0000-0002-8930-6115)*, Vladimir I. Kuzmin (ORCID 0000-0001-6473-3615), Anna A. Kuzmina (ORCID 0000-0002-6112-8230)

Institute of Chemistry and Chemical Technology, Siberian Branch of the RAS (SB RAS), Federal Research Center «Krasnoyarsk Science Center SB RAS», Academgorodok, 50/24, Krasnoyarsk, 660036, Russia
E-mail: maral7508@mail.ru*, Kuzmin_vi@mail.ru, kuzmina@mail.com

The process of extracting the light group lanthanide nitrates from neutral aqueous solutions with a binary extractant based on di-(2-ethylhexyl)phosphoric acid (HA), tri-n-octylamine (NR₃) and solvating additive of tri-n-octylamine nitrate in a non-polar organic diluent was investigated in this study. Using neodymium nitrate as an example, it was shown that this extractant (NR₃HA+NR₃HNO₃) extracts Ln(NO₃)₃ according to the laws of binary extraction. The cation and anion of the inorganic salt pass into the organic phase in a stoichiometric ratio. The extraction isotherms of lanthanide nitrates are S shape, and only slight variation of pH is observed during the extraction. Based on the study of the absorption spectra of Nd complexes in the organic phase, it was found that at low concentration the Nd form a complex (NdA₃)•NR₃HNO₃, and at a high concentration of Nd (when the extraction is saturated), a compound of the composition (NdA₂NO₃)•NR₃HNO₃ is formed. The introduction of salting-out agents in the aqueous phase or the organic phase makes it possible to vary the distribution coefficients (Dₙd). With an increase in the concentration of sodium nitrate in the aqueous phase, Dₙd increases, and with an increase in the concentration of NR₃HNO₃, it correspondingly decreases. The introduction of the salting-out and solvating agent NR₃HNO₃ into the organic phase eliminates the formation of precipitation in the organic phase during the extraction of lanthanide nitrates. Quantitatively, the Nd extraction process in a wide range of Nd(NO₃)₃ concentrations and extractant compositions can be described on the basis of two coupled binary extraction equations and the corresponding concentration constants. It has been established that the proposed extractant provides high separation factors for neodymium and other light group lanthanides.

Key words: binary extraction, REE, di-(2-ethylhexyl) phosphoric acid, solvating additives, amine

INTRODUCTION

Currently, the phosphorus-containing organic reagents are the most often used compounds in the separation of rare-earth metals (REM) by extraction methods [1-7]. However, for cation-exchange extractants of this type, the distribution coefficients of rare-earth metals (D_{Ln}) are usually very high. Therefore, it is necessary to use concentrated mineral acids for the stripping of metals from the organic phase. This leads to an increase in the consumption of reagents during the isolation and purification of individual REM [8]. Adding

anion-exchange extractant to cation-exchange extract-ants mixture allows changing the character of the pro-cess from cation exchange to the extraction of a neutral salt while creating new possibilities for stripping and reducing the consumption of the extractants [9, 10].

Binary extractants have several features. The interfacial transition of the cation and anion of the ex-tracted inorganic salt is stoichiometric and interde-pendent. The process of binary extraction of nitrates lanthanides obeys the following equation of the basic heterogeneous reaction (without taking into account additional solvation processes in the organic phase):
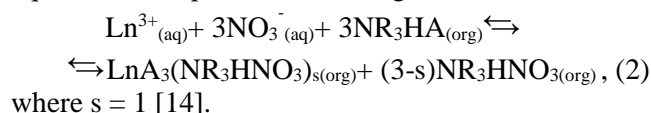
$$Ln^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3NR_3HA_{(org)} \rightleftharpoons$$
$$\rightleftharpoons LnA_{3(org)} + 3NR_3HNO_{3(org)}, \qquad (1)$$
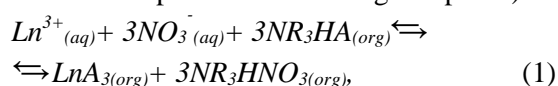
where $NR_3HA_{(org)}$ is a binary extractant such as the salt that formed by a di-(2-ethylhexyl)phosphoric acid and tri-n-octylamine [11].

At the same time, the stripping of salts of rare-earth metals can be carried out by water or with dilute solutions of mineral acids [12]. In accordance with equation (1), the addition of an excess of the inorganic salt of the anion-exchange extractant ($NR_3HNO_{3(org)}$) to the organic phase makes it possible to reduce the D_{Ln} value [13]. In this case, the salting-out effect from the organic phase due to the extraction product is mani-fested. When solvation processes occur, the solubility of REM extraction products in the organic phase is sig-nificantly increased. The solvation effect is a charac-teristic that is especially pronounced in the presence in amine nitrate. In addition, at high concentrations, amine nitrate themselves are capable of extracting metal nitrates by the mechanism of formation in the or-ganic phase of neutral solvates of nitrate rare-earth metals [12], changing the separation factors (β). There-fore, at investigation of binary extractants, it is neces-sary to study in detail the mechanisms of extraction of salts of lanthanides in a wide range of concentrations and compositions.

In the series of lanthanides of the light group (*La-Eu*), the strength of complex formation with phos-phorus-containing reagents increases with the increase of the atomic number of the element [11]. Chemical structure of the forming compounds is maintained. Therefore, the study of general laws of extraction in our work is carried out on the example of Nd, located in the middle of the light group lanthanides.

Our previous investigation of the process of extracting *Nd(NO₃)₃* from neutral aqueous solutions with a binary extractant we used 2-ethylhexylphosphonic acid-mono-2-ethylhexyl ester) *(EHEHPA)* and tri-n-octylamine *(NR₃)* in a non-polar organic diluent (tolu-ene) [14, 15]. The tri-n-octylammonium nitrate *(NR₃HNO₃)* was used as a solvating agent. For binary

extractants based on *EHEHPA*, extraction isotherms are linear in the initial segment (or S-shaped with the addition of *NR₃HNO₃*). At high concentrations, the slope decreases. The *Nd* concentration in the saturated extractant corresponds to the formation of the neutral *(NdA₃)·NR₃HNO₃* complex. Only slight variation of pH is observed during the extraction. It was found that in a wide range of concentrations the binary extraction equation corresponds to a heterogeneous reaction:

$$Ln^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3NR_3HA_{(org)} \rightleftharpoons$$
$$\rightleftharpoons LnA_3(NR_3HNO_3)_{s(org)} + (3-s)NR_3HNO_{3(org)}, \quad (2)$$

where s = 1 [14].

The selectivity of metal extraction is usually determined by the type of cation-exchange extractant contained within the binary extractant [16]. In addition, the value of the acid dissociation constant of the cation-exchange extractant determines the pH range of binary extraction. Therefore, when changing the type of cat-ion-exchange extractant, the extraction properties of the binary extractant must change significantly. Ac-cordingly, in this article we present materials describ-ing the main features of the binary extraction of nitrates of light lanthanides with extractants based on di-(2-ethylhexyl)phosphoric acid in the same sequence as in previous articles for extractants based on mono-2-ethylhexyl ether 2-ethylhexylphosphonic acid [14, 15].

The aim of the present study is to study the fea-tures of the extraction of *Nd(NO₃)₃* from neutral aque-ous solutions with a binary extractant based on di-(2-ethylhexyl)phosphoric acid (*HA, DEHPA*), tri-n-octyl-amine (*NR₃,TOA*) and a solvating additive of tri-n-octyla-mine nitrate (*NR₃HNO₃*) in a non-polar organic diluent.

MATERIALS AND METHODS

DEHPA (*P 204, TOPS 99, HDEHP*) – (CAS No. 298-07-7, 97 wt.%) and *TOA* – (CAS No. 1116-76-3, 98 wt.%) are sourced from Sigma-Aldrich and is used without further purification. Solutions of *La(III), Ce(III), Nd(III), Pr(III)* and *Sm(III)* are prepared by dissolving the corresponding REE oxide (99.9%) in concentrated nitric acid, they are then evaporated and diluted with distilled water.

NR₃HCl is obtained as a solid from a heptane solution of *NR₃* and an aqueous solution of *HCl* [17]. *NR₃HNO₃* is obtained as a solid from a heptane solution of *NR₃* and an aqueous solution of *HNO₃*.

The pH of the solutions and the other potenti-ometric measurements were carried out using a pH-me-ter "Expert-001" with combined electrode brand ESK-10601/7. Spectrophotometric measurements were per-formed using a Fiber Optic Spectrometer AvaSpec-ULS2048L. The element concentrations in the aqueous phase were analyzed by mass-spectrometry with in-ductive-coupled plasma using ICP-MS Agilent 7500A,

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in the aqueous and organic phases were analyzed using X-ray fluorescence spectrometer Spectroscan MAKS - GF-2E.

For the preparation of binary extractants (*R₃HA*) the exact weights of *DEHPA* and *NR₃HCl* (taken in the stoichiometric ratio) are dissolved in an organic solvent (80% of the total volume). The organic phase is washed once with a solution of ammonia (the ratio of the volumes of phases is 1:0.9) that has concentration equal to the concentration of the *DEHPA*. Upon the completion of the washing step, the organic phase is brought to the required volume. The extractant is treated 7 times with equal volumes of 0.001 mol/L *NH₃* solution until Cl⁻ is removed from the system and the pH of the aqueous phase changes from the neutral to basic. The extractant is subsequently washed three times with water. The exact contents of *DEHPA* and *NR₃HCl* in the initial reagents are determined by alkalimetric and argentometric titration methods. To prepare binary extractants with the addition of *NR₃HNO₃*, the calculated volumes of a solution with a known concentration of *NR₃HNO₃* and a binary extractant solution (*NR₃HA*) were mixed.

The extraction and phase separation of REE were carried out in a separating funnel for 5 min at a temperature of 25 °C, at an equal ratio of organic and aqueous phases. If the extraction equilibrium did not occur, then the extraction time was increased to 15 min. Single measurements were carried out in three parallels. Metal concentration in the organic phase was calculated calculated from the difference between the metal concentration in the aqueous phase before and after extraction or using stripping by aqueous solutions of *EDTA* tetrasodium salt with a concentration of 0.1 mol/L. The completeness of stripping was controlled using the methods of analysis given earlier.

The pH of the aqueous phase of the initial and aqueous phases after the equilibrium state was controlled, when carrying out extraction measurements. The absence of gel formation in the organic phase and the absence of a third phase in the extraction system were monitored.

RESULTS AND DISCUSSION

When *Nd(NO₃)₃* is extracted from neutral aqueous solutions by an organic phase containing a diluent and a binary extractant (*NR₃HA*) with a concentration of 0.1-0.3 mol/L, the maximum concentration of *Nd* in the organic phase is $3.8 \cdot 10^{-3}$ mol/L. At higher concentrations of *Nd* in the organic phase, the formation of a third gel phase is observed. When the *NR₃HNO₃* solvating additive is introduced in a ratio

with *NR₃HA* that exceeds 1:2, precipitation in the organic phase does not occur over the entire range of *Nd* content corresponding to the reaction stoichiometry (Eq. (1)).

The form of extraction isotherms (Fig. 1) describing extraction from neutral aqueous solutions of *Nd(NO₃)₃* by solutions of *NR₃HA+NR₃HNO₃* in an organic diluent qualitatively corresponds to the extraction of inorganic salts by the binary extraction mechanism (Eq. (1)):

- The extraction isotherms of *Nd(NO₃)₃* have an S shape. In the initial segment (in the region of a large excess of *NR₃HNO₃*), low D_{Nd} values are due to the salting out effect of amine nitrate;

- The pH of the aqueous phase during the extraction process varies only slightly. The initial 0.01 mol/L *Nd(NO₃)₃* solution has the pH 5.2. The pH value of aqueous phase at equilibrium point ranges between 4.2 and 4.3 (Fig. 1).
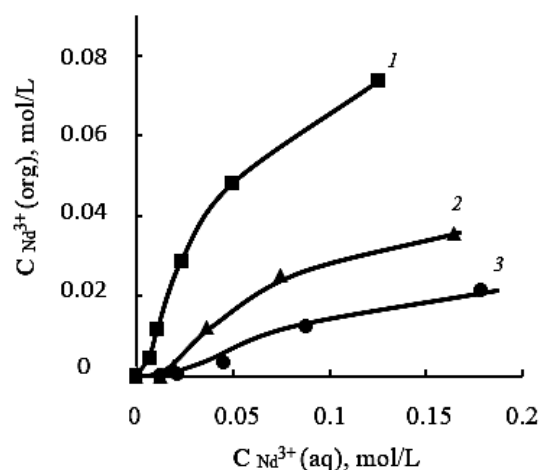
Fig. 1. The isotherms of *Nd(NO₃)₃* extraction by binary extractant containing c(*NR₃HNO₃*) = 0.1 mol/l and various concentrations of *NR₃HA*: 1 - c(*NR₃HA*) = 0.2 mol/l; 2 - c(*NR₃HA*) = 0.1 mol/l; 3 - c(*NR₃HA*) = 0.05 mol/l. Diluent is toluene. pH = 4.2-4.3. Points represent experimental data, while curves correspond to calculated, model data

Рис. 1. Изотерма экстракции *Nd(NO₃)₃* бинарным экстрагентом, содержащем c(*NR₃HNO₃*) = 0,1 моль/л и различные концентрации *NR₃HA*: 1 - c(*NR₃HA*) = 0,2 моль/л, 2 - c(*NR₃HA*) = 0,1 моль/л, 3 - c(*NR₃HA*) = 0,05 моль/л. Разбавитель толуол. pH = 4,2-4,3. Точки — экспериментальные данные, кривые — расчетные, модельные данные

Given the slight change in pH during the extraction, the interphase transition of the cation and anion (*Nd³⁺ and NO₃⁻*) occurs simultaneously in accordance with the principle of electroneutrality. The ratio between chemical species involved in this process is close to the stoichiometric. At high concentrations of *Nd* in the organic phase, the distribution coefficient

(D_{Nd}) decreases. The plateau of isotherm curve corresponds to the saturation range of the extractant. The maximum metal concentration in the organic phase ($^{max}C_{Nd_{org}}$) is estimated from the linear dependence that is typical for the saturation range of isotherm:

$$C_{Ndorg}^{-1} = kC_{Ndaq}^{-1} + {}^{max}C_{Ndorg}^{-1}. \qquad (3)$$

The ratio of the total extractant concentration $C_{NR_3HA_{org}}$ and $^{max}C_{Nd_{org}}$ ranges from 2.0 to 2.2 for the curve (1) and curve (3) of Fig. 1, respectively, which corresponds to the formation of metal compounds of the NdA_2NO_3 composition in the organic phase. Therefore, for the range of saturation isotherms, the extraction process can be described by the equation of a heterogeneous reaction:

$$Nd^{3+}_{(aq)} + 3NO_{3(aq)}^{-} + 2NR_3HA_{(org)} \rightleftarrows$$
$$\rightleftarrows NdA_2NO_{3(org)} + 2NR_3HNO_{3(org)}. \qquad (4)$$
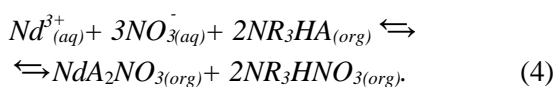
The type of Nd complexes formed in the organic phase was estimated based on a study of the absorbance spectra of Nd^{3+} in the 550-620 nm region, which corresponds to the "hypersensitive" electronic transition $^4I_{9/2} \rightarrow {}^{2,4}G_{7/2;5/2}$ (sensitive to the coordination environment of the metal). It is known that neutral complexes of $NdA_3(HA)_3$ with various anionic phosphorus-containing ligands (*DEHPA*, *EHEHPA*, etc.) are characterized by pseudo-octahedral coordination and identical absorbance spectra [18-20]. For the region of metal concentration in the organic phase corresponding to the middle (linear) segment of the extraction isotherms, the peak position on the Nd^{3+} absorbance spectra for the $Nd(NO_3)_3$-*HA*, $Nd(NO_3)_3$-NR_3HA and $Nd(NO_3)_3$-$(NR_3HA + NR_3HNO_3)$ extraction systems practically coincides (Fig. 2, spectra 2-4). What corresponds to the formation in these systems of complexes having the same structure of the internal coordination sphere – NdA_3.

For the $Nd(NO_3)_3$-NR_3HNO_3 extraction system, the absorbance spectrum of Nd^{3+} in the organic phase has a completely different form (Fig. 2, spectrum 1). This spectrum is very similar to the spectrum of the neutral complex $[Nd(NO_3)_3]TBP$. It should be noted that the extraction system $Nd(NO_3)_3$-NR_3HNO_3 has low D_{Nd}. To attain appreciable concentrations of Nd^{3+} in the organic phase, significant additives of 5 mol/L salting-out agent, NO_3^{-}, were introduced into the aqueous phase.

Taking into account the limiting ratio $C_{NR_3HA_{org}}/{}^{max}C_{Nd_{org}}$ found by Eq. (3), it can be assumed that in the extraction system, $Nd(NO_3)_3$-$(NR_3HA + NR_3HNO_3)$, the nitrate ion is likely to be involved in the coordination of the metal in the internal sphere of the extraction product (in accordance with Eq. (4)). Based on the obtained spectral data, the geo-

metric type of the complexes does not change. Therefore, for the specified extraction system, it is possible to expect high selectivity during the extraction of REM, which is typical for the initial cation-exchange extractant – *DEHPA*.
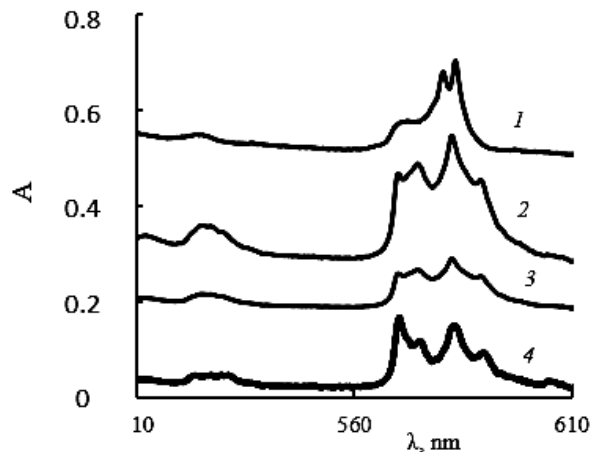

Fig. 2. Absorbance spectra of extracted neodymium complex: 1 – c(NR_3HNO_3) = 0.5 mol/L, c(Nd^{3+}) = 0.022 mol/L; 2 - c(NR_3HA) = 0.2 mol/L +c(NR_3HNO_3) = 0.2 mol/L, c(Nd^{3+}) = 0.044 mol/L; 3 - c(NR_3HA) = 0.2 mol/L, c(Nd^{3+}) = 0.0038 mol/L; 4 - c(*HA*) = 0.2 mol/L, c(Nd^{3+}) = 0.022 mol/L. The spectra are sequentially shifted by about 0.2. Diluent – toluene
Рис. 2. Спектры поглощения экстрагированного комплекса неодима: 1 – c(NR_3HNO_3) = 0,5 моль/л, c(Nd^{3+}) = 0,022 моль/л; 2 – c(NR_3HA) = 0,2 моль/л + c(NR_3HNO_3) = 0,2 моль/л, c(Nd^{3+}) = 0,044 моль/л; 3 – c(NR_3HA) = 0,2 моль/л, c(Nd^{3+}) = 0,0038 моль/л; 4 – c(*HA*) = 0,2 моль/л, c(Nd^{3+}) = 0,022 моль/л. Спектры последовательно сдвигаются примерно на 0,2. Разбавитель толуол
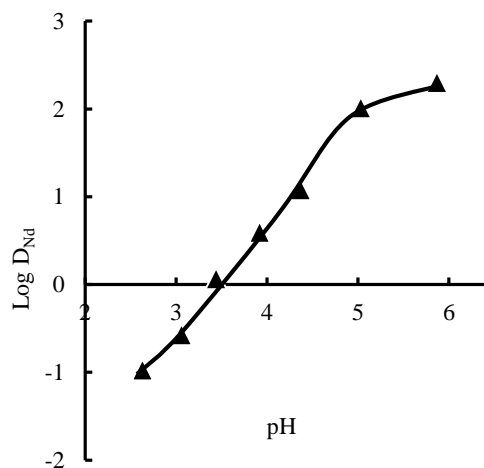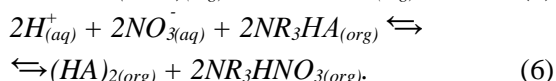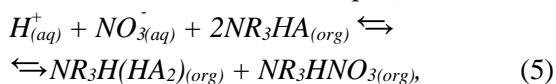

Fig. 3. Dependence between Log D_{Nd} and the equilibrium pH: Extractant - c(NR_3HA) = 0.2 mol/L, c(NR_3HNO_3) = 0.1 mol/L. Aqueous Phase: NaNO_3+ HNO_3, Sum c(NO_3^-)_(aq) = 0.1 mol/l, initial c(Nd(NO_3)_3)_(aq) = 0.001 mol/l
Рис. 3. Зависимость между Log D_{Nd} и равновесным pH: Экстрагент - c(NR_3HA) = 0,2 моль/л, c(NR_3HNO_3) = 0,1 моль/л. Водная фаза - NaNO_3+ HNO_3, сумма c(NO_3^-)_(aq) = 0,1 моль/л, исходная концентрация c(Nd(NO_3)_3)_(aq) = 0,001 моль/л

One of the features of the process of binary salt extraction (in accordance with Eq. (1)) should be a slight dependence on the pH of the aqueous phase. For the $Nd(NO_3)_3$- $(NR_3HA+NR_3HNO_3)$ extraction system, this pH range is rather narrow and close to neutral media 5-6 (Fig. 3).

In the region of lower pH values, competing extraction of mineral acid occurs (by the mechanism of binary extraction of acids) [9, 12] (Eqs. (5) and (6)):

$$H^+_{(aq)} + NO^-_{3(aq)} + 2NR_3HA_{(org)} \rightleftharpoons$$
$$\rightleftharpoons NR_3H(HA_2)_{(org)} + NR_3HNO_{3(org)}, \quad (5)$$
$$2H^+_{(aq)} + 2NO^-_{3(aq)} + 2NR_3HA_{(org)} \rightleftharpoons$$
$$\rightleftharpoons (HA)_{2(org)} + 2NR_3HNO_{3(org)}. \quad (6)$$

The pH region of the most abrupt change in D_{Nd} and competing nitric acid extraction is determined by the pKa value of $DEHPA$. The product $(NR_3H(HA_2))$ formed during reaction (5) can also be a binary extractant for $Nd(NO_3)_3$, and $(HA)_2$ - a cation-exchange extractant. Therefore, in the strongly acidic region, the extraction of lanthanide salts by binary extractants does not differ from ordinary cation-exchange extraction. It is necessary to note that we observe a decrease in D_{Nd} for this system when compared to $DEHPA$ without an amine [21]. This decrease in D_{Nd} take place due to a decrease in the equilibrium concentration of free $(HA)_2$ occurring through the formation of associates of $(HA)_2$ with amine nitrate salts.
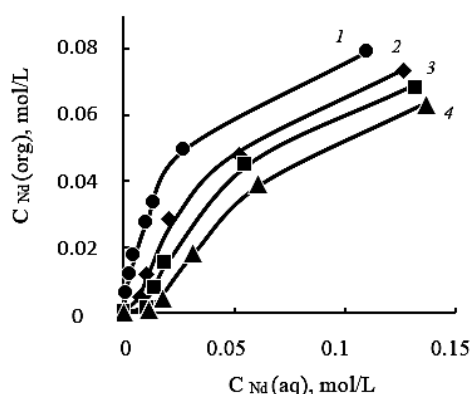
Fig. 4. The isotherms of $Nd(NO_3)_3$ extraction by binary extractant containing various concentrations of NR_3HNO_3. c(NR_3/HA) = 0.2 mol/l: 1 - c(NR_3HNO_3)$_{(org)}$ =0.1 mol/l with c($NaNO_3$)$_{(aq)}$ = 0.1 mol/l; 2 - c(NR_3HNO_3)$_{(org)}$ = 0.1 mol/l; 3 - c(NR_3HNO_3)$_{(org)}$ = 0.2 mol/l; 4 - c(NR_3HNO_3)$_{(org)}$ = 0.3 mol/l. Diluent is toluene. pH=4.2. Points represent experimental data, while curves correspond to calculated, model data

Рис. 4. Изотермы экстракции $Nd(NO_3)_3$ бинарным экстрагентом, содержащим различные концентрации NR_3HNO_3. c(NR_3/HA) = 0,2 моль/л: 1 - c(NR_3HNO_3)$_{(опр)}$ =0,1 моль/л + c($NaNO_3$)$_{(aq)}$ = 0,1 моль/л; 2 - c(NR_3HNO_3)$_{(опр)}$ = 0,1 моль/л; 3 - c(NR_3HNO_3)$_{(опр)}$ = 0,2 моль/л; 4 - c(NR_3HNO_3)$_{(опр)}$ = 0,3 моль/л. разбавитель – толуол. pH=4,2. Точки — экспериментальные данные, кривые — расчетные, модельные данные

In accordance with the binary extraction scheme Eq. (2), the introduction of the initial or final reaction products (salting-out agents) into the aqueous or organic phase should shift the chemical equilibrium.

The following effects are observed for the $Nd(NO_3)_3 – (NR_3HA+NR_3HNO_3)$ extraction system:
- a significant increase in D_{Nd} when conducting the anion of the same name (NO_3^-, sodium salt) into the aqueous phase (Fig. 4, curve (1));
- a decrease in D_{Nd} with an increase in the concentration of NR_3HNO_3 in the organic phase (at a constant pH of the aqueous phase 4.2) (Fig. 4, curves (2),(3),(4)).

With an equal concentration of salting-out agents in the aqueous and organic phases (Fig.4, curve (1)), their influence is leveled (as follows from Eq. (1)) and the corresponding extraction isotherms are linear in the low concentration range. With an excess of amine nitrate, the extraction isotherms are S-shaped. Based on the Eq. (1), it can be shown that in the limit a straight line drawn along the linear middle section of the S-shaped isotherm cuts off a segment on the concentration axis, in organic phase, equal to ¼ C of the salting-out agent.

Thus, for this extraction system, relatively small changes in the composition of the aqueous and organic phases (introduction of salting out additives, pH changes) allow D_{Nd} to be varied over a wide range.

For a quantitative description of the extraction system $Nd(NO_3)_3 – (NR_3HA+NR_3HNO_3)$, extraction equilibria can be considered for two limiting cases, namely 1) the initial sections of the extraction isotherm and 2) the saturation region, corresponding to Eqs. (2) and (4). In initial sections of the isotherms of the extractions, under conditions of a large excess of extractant, the Eq. (2) corresponds to the concentration constant $K_{ex(2)}$, Eq. (7). Based on Eq. (4), in the region of high concentrations of metals in the organic phase, the concentration constant $K_{ex(4)}$ can be expressed by Eq. (8). Accordingly, to describe the middle sections of the extraction isotherms, it is necessary to use the system of Eqs. (7) and (8).

$$K_{ex(2)} = \frac{[NdA_3(NR_3HNO_3)_{s(org)}] \cdot [NR_3HNO_{3(org)}]^{(3-s)}}{[Nd^{3+}_{(aq)}] \cdot [NO^-_{3(aq)}]^3 \cdot \gamma^4_\pm \cdot [NR_3HA_{(org)}]^3}, \quad (7)$$

$$K_{ex(4)} = \frac{[NdA_2NO_{3(org)}] \cdot [NR_3HNO_{3(org)}]^2}{[Nd^{3+}_{(aq)}] \cdot [NO^-_{3(aq)}]^3 \cdot \gamma^4_\pm \cdot [NR_3HA_{(org)}]^2}, \quad (8)$$

where $\gamma_\pm$ is the average ionic activity coefficient of $Nd(NO_3)_3$ in the aqueous phase [22], the coefficient (s) corresponds to the solvation number of NdA_3 by excess of $(NR_3HNO_3)_s$ in the organic phase.

The values of stoichiometric coefficients, solvation numbers, and constants are calculated on the ba-

sis of minimizing the difference between the experimental and calculated D_{Ln} for various concentration dependences (Figs. 1, 4). Within equations 7 and 8 the value of the solvation number *(s)* is 1 and the concentration constants of extraction $K_{ex(2)} = 3.36 \cdot 10^4$ (mol/L)$^{-4}$ and $K_{ex(4)} = 4.56 \cdot 10^4$ (mol/L)$^{-3}$. Additional interactions are possible in the organic phase, for example, self-association of amines salts and solvation of extraction products by an excessive amount of extractant. However, we set ourselves the task of finding the minimum set of parameters sufficient for a model quantitative description of the extraction system in a wide range of compositions and concentrations. Our experimental and calculated data are in good agreement as can be seen from Fig. 1, 4. The methodology used by us for calculating constants and parameters of extraction equilibriums is described in the article [23].
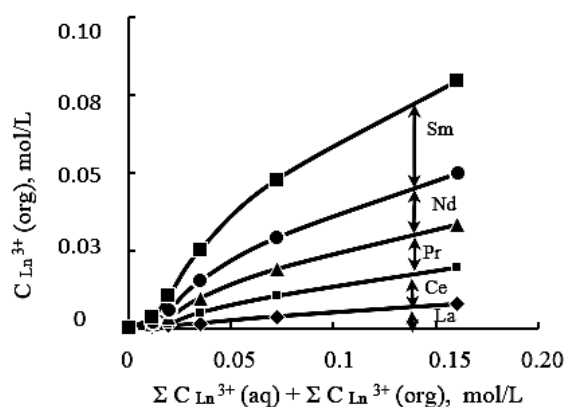
Fig. 5. Isotherm of light lanthanides joint extraction: c(NR_3HA)$_{(org)}$ = 0.2 mol/l + c(NR_3HNO_3)$_{(org)}$ = 0.3 mol/l. pH=5, O:A=1:1. Diluent is toluene. The initial concentrations of five metals in the aqueous phase are equal

Рис. 5. Изотерма совместной экстракции легких лантанидов: c(NR_3HA)$_{(opr)}$ = 0,2 моль/л + c(NR_3HNO_3)$_{(opr)}$ = 0,3 моль/л. pH=5, O:A=1:1. Разбавитель – толуол. Начальные концентрации пяти металлов в водной фазе равны

To assess the selectivity of the binary extractant based on *DEHPA* and *TOA* in the presence of a solvating additive of NR_3HNO_3, the isotherms of coextraction of rare-earth metals of the light group are obtained (Fig. 5). The initial concentrations of metals in the aqueous phase are equal. It is found that at low concentrations of REM, the selectivity of extraction is

higher than for a saturated extractant. In the average linear segment of the isotherms, the separation coefficients $\beta_{Nd/Pr}$ and $\beta_{Sm/Nd}$ are 1.32 and 5.5. In the saturation segment of the isotherms, $\beta_{Nd/Pr}$ and $\beta_{Sm/Nd}$ are 1.27 and 3.1. This can be explained by a change in the predominant form of REM compounds in the organic phase, in accordance with Eq. (2) at low and mid-concentrations, while Fig. 4 represents the behavior of the systems at high concentrations.

CONCLUSIONS

The process of extraction from neutral aqueous solutions of $Nd(NO_3)_3$ with a toluene solution of a binary extractant based on *DEHPA* and *TOA* in the presence of a solvating additive of *TOA* nitrate corresponds to the laws of binary extraction salts. The extraction isotherms are S-shaped, the change in the content of the salting-out agent − $NR_3HNO_{3(org)}$ allows D_{Ln} to be varied over a wide range of values. At low concentrations, the main form of metal compounds is $NdA_3(NR_3HNO_3)_{(org)}$, at high concentrations (when aches the plateau of the distribution isotherms), the main form is $NdA_2NO_{3(org)}$.

We show that in a wide range of $Nd(NO_3)_3$ concentrations and extractant compositions, the extraction process of *Nd* can be quantitatively described on the basis of the two coupled concentration constants.

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