Separation of Ytterbium and Lutetium with Solutions of (2-Ethylhexyl)phosphonic Acid Mono-2-ethylhexyl Ester in Hydrocarbons from Nitric Acid Solutions and Its Simulation

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Abstract—Recovery of lutetium and ytterbium with solutions of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester in isopar-M and *m*-nitrobenzotrifluoride (F3), as well as with solutions of bis(2,4,4-trimethylpentyl)phosphinic acid in isopar M was investigated. Using the equilibrium shift method, it was shown that ytterbium and lutetium are recovered by the cation exchange mechanism in the form of the $Ln[HA_2]_3$ adduct up to 3 M HNO_3, and with a further increase in the concentration of nitric acid in an aqueous solution, the separation mechanism changes to a solvate one. The separation factors β(Lu/Yb) in the studied separation systems are 1.4–1.6. The obtained data can be used for subsequent calculations of the extraction cascade for the separation of lutetium and ytterbium. Mathematical processing of experimental data was carried out to derive separation constants.

Keywords: lutetium, ytterbium, liquid extraction, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, bis(2,4,4-trimethylpentyl)phosphinic acid, extraction separation, mathematical modeling

INTRODUCTION

Lutetium-177 (^{177}Lu) is a therapeutic radioisotope, which is widely used for medical purposes due to optimal nuclear-physical parameters: a convenient half-life ($T_{1/2} = 6.7$ days); acceptable energy of β-particles (maximum energy 0.5 MeV), which allows destroying small tumors and metastases 1–3 mm in size without affecting healthy tissues; soft γ-radiation emission with energy sufficient to visualize and track drug migration in the patient's body ($E_γ = 113$ keV (6.4%) and 208 keV (11%)) [1, 2]. The decay product of ^{177}Lu is the stable isotope ^{177}Hf. In addition, ^{177}Lu has chemical properties suitable for protein labeling (e.g., dotatate peptide [3]) with bifunctional chelating agents [4].

The main method for producing a high specific activity ^{177}Lu preparation is neutron irradiation of the starting material containing ^{176}Yb [5]. Irradiation of an ytterbium target highly enriched in the 176 isotope is advantageous since in this case, due to the β–decay of the ^{177}Yb, a monoisotopic product, ^{177}Lu, is formed. Thus, the problem of obtaining an isotopically pure target product is reduced to its separation from the target material by chemical methods.

The separation of Lu from Yb is a difficult task, since both elements are lanthanides and are similar in their physicochemical properties. Therewith, even a small amount of impurities of stable isotopes of lutetium at a level of several tenths of a mass fraction can lead to a significant decrease in the specific activity of ^{177}Lu. Taking into account the rather short half-life of ^{177}Lu, the separation should be carried out using highly selective methods: extraction or chromatography [6]. Chromatographic separation is usually employed to produce chemically pure individual elements, but such a process is unproductive: concentration to prepare fractions up to 1 g/L is difficult to enhance productivity [7].

The problems of separating elements with similar chemical properties are also solved by the extraction method, in particular, when separating REE and transplutonium elements. In industry, organophosphorus acids such as P507 (2-ethhexylphosphonic acid mono-2-ethylhexyl ester) [8], Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) [9, 10], INET-3 (2,3-dimethylbutyl)(2,4,4'-trimethylpentyl)phosphinic acid [11], HDEHP (di-(2-ethylhexyl)phosphoric acid) [12] have recently been utilized for these purposes. It is also known that the separation of Yb/Lu by blends of extractants Cyanex 272, P507, and HDEHP exhibits a synergistic effect [9, 13].

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (P507) is a promising extractant in the REE production, since systems based thereof have higher separation factors of lanthanides [14].

The task of the extraction method is to separate ^{177}Lu as fast as possible because of the short half-life, from the main mass of ytterbium, ensuring the most convenient subsequent handling of the recovered lutetium. This work is aimed at assessing the possibility of using the organophosphorus extractants P507 and Cyanex-272 for the separation of pure lutetium.

EXPERIMENTAL

Nitric acid and ytterbium and lutetium oxides of chemically pure grade, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (P507) manufactured by Luoyang Zhongda Chemical Co. with a purity of at least 99%, bis-(2,4,4- trimethylpentyl)phosphinic acid (Cyanex-272) from Cytec Solvay Group (content of the main substance 90.6%), isopar-M (Exxon Mobil), and *m*-nitrobenzotrifluoride (F3) with a chemical purity of 99% were employed in the study.

The solution was evaporated to dryness. After cooling, the resulting mixed salt was dissolved in 1 M HNO_3, transferred into a 25-mL volumetric flask, and made up to the mark with distilled water. As a result, standard solutions of 20 g/L Lu and 200 g/L Yb were obtained. Working solutions were prepared by diluting the standard. Working concentrations varied from 0.05 to 200 g/L. The concentrations of standard solutions were monitored by inductively coupled plasma atomic emission spectrometry (ISP-OES) on a Prodigy Plus spectrometer. The following characteristic wavelengths of radiation of Yb and Lu atoms were chosen: ytterbium,

289.138 and 369.419 nm; lutetium, 291.139 and 302.054 nm.

Extraction tests were carried out in test tubes with a volume of 15 mL. The phases were in contact for 5 min. Reextraction of Lu and Yb from the organic phase was carried out with 5 M HNO_3 solutions. Before taking the back extract for analysis, the samples were centrifuged to completely separate the aqueous and organic phases. Then the concentrations of ytterbium and lutetium in the back extracts were determined.

Solutions of Yb and Lu metals were prepared according to the standard procedure: metal oxides (99.99%) weighed on a Mettler Toledo ML303T/A00 analytical balance (accuracy class II), were dissolved in concentrated 8 M nitric acid at heating without boiling. The solution was evaporated to dryness. After cooling, the resulting mixed salt was dissolved in 1 M HNO_3, transferred into a 25-mL volumetric flask, and made up to the mark with distilled water. As a result, standard solutions of 20 g/L Lu and 200 g/L Yb were prepared. Working solutions were produced by diluting the standard. Working concentrations varied from 0.05 to 200 g/L. The concentrations of standard solutions were monitored by inductively coupled plasma atomic emission spectrometry (ISP-OES) on a Prodigy Plus spectrometer. The following characteristic wavelengths of radiation of Yb and Lu atoms were chosen: ytterbium 289.138 and 369.419 nm; lutetium 291.139 and 302.054 nm.

Extraction tests were carried out in 15 mL test tubes with a volume. The phases were in contact for 5 min. Reextraction of Lu and Yb from the organic phase was carried out with 5 M HNO_3 solutions. Before taking the back extract for analysis, the samples were centrifuged to completely separate the aqueous and organic phases. Then the ytterbium and lutetium concentrations in the back extracts were determined.

RESULTS AND DISCUSSION

The separation of REE from nitric acid media with solutions of organophosphorus acids can be represented as the reaction equation

$$Ln^{3+}_{(aq)} + nNO_3^{-}_{(aq)} + m(HA)_{2(o)}$$
$$= [Ln(NO_3)_nA_{3-n}(HA)_{(2m+n-3)}]_{(o)} + (3-n)H^+_{(aq)}, \quad (1)$$
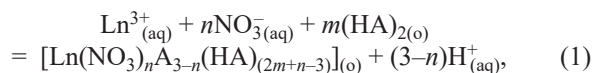
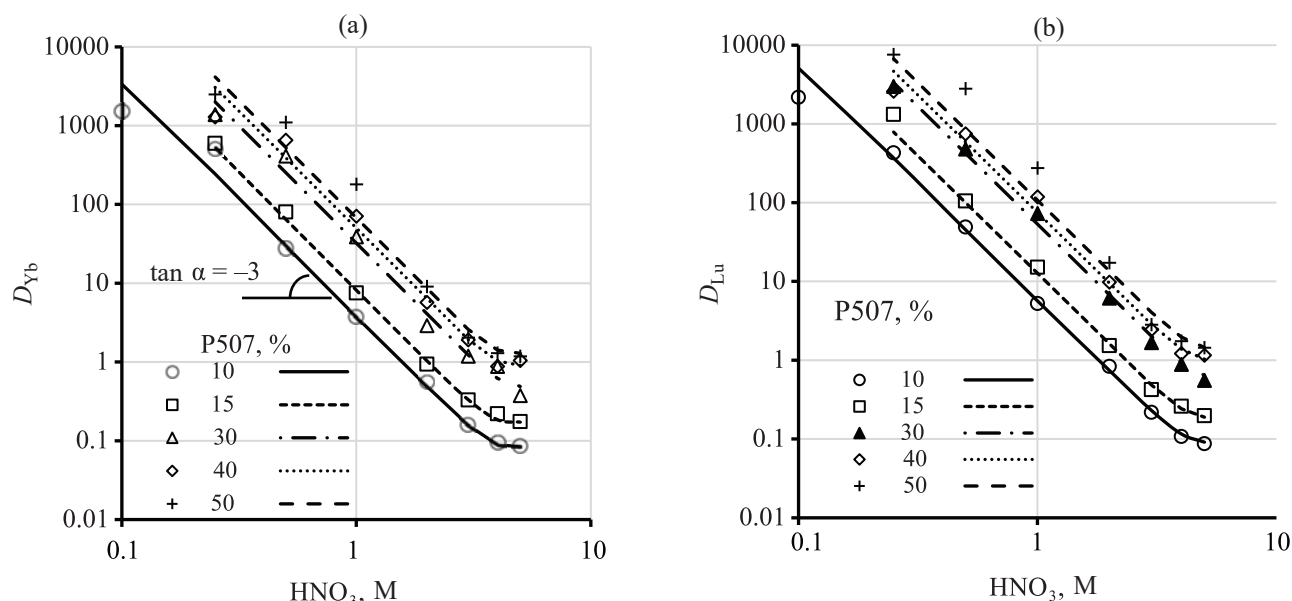where Ln^{3+} is REE cation, and HA is an organophosphorus

Fig. 1. Effect of equilibrium HNO_3 concentration on distribution coefficients of (a) Yb and (b) Lu at extraction with P507 solution in isopar M. Initial REE concentration 0.2–0.4 g/L. (Point) experiment, (line) calculation.

acid molecule. Most authors believe that the extractant is present in the organic phase as a dimer $(HA)_2$ [15], since the dimerization constants of P507 and Cyanex-272 are very high (log $K = 20$ and 4.2, respectively [16]).

In the separation of rare earth elements with P507 solutions in the range of HNO_3 concentrations not higher than 4 M, a linear relationship between the logarithms of Yb and Lu distribution coefficients and the logarithm of the HNO_3 concentration is observed with a slope close to –3 (Fig. 1), which allows the reaction equation to be applied:

$$Ln^{3+}_{(aq)} + 3(HA)_{2(o)} = Ln(HA_2)_{3(o)} + 3H^+_{(aq)};$$
$$m = 3, n = 0. \qquad (2)$$
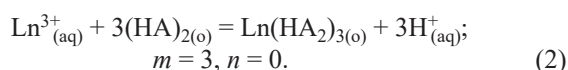
The equilibrium constant of this reaction is:

$$K_H = \frac{\left[\overline{Ln(HA_2)_3}\right][H^+]^3}{[Ln^{3+}]\left[\overline{(HA_2)}\right]^3}. \qquad (3)$$

In this case, the distribution coefficient should be inversely proportional to the concentration of the proton in the cube and directly proportional to the concentration of the dimer of the extractant, also to the third power:

$$D = K_H \frac{\left[\overline{(HA_2)}\right]^3}{[H^+]^3}. \qquad (4)$$

The deviation from the linearity (Fig. 1) at a concentration of 4 M HNO_3 and higher may be due to the transition to extraction by the solvate (donor-acceptor) mechanism, which occurs, for example, in the extraction of REE with HDEHP solutions from acidic media [17, 18]. It is assumed that from 1 to 3 extractant molecules take part in the formation of the solvate [19], however, in view of the insignificance of this reaction contribution to the overall extraction mechanism and the lack of data at higher HNO_3 concentrations, the value of m was taken equal to 1, as in [4].

$$Ln^{3+}_{(aq)} + 3NO^-_{3(aq)} + (HA)_{2(o)} = H_2[Ln(NO_3)_3A_2]_{(o)};$$
$$m = 1, n = 3. \qquad (5)$$
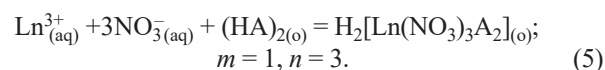
Thus, the deviation from the linear relationship between the REE distribution coefficients and the HNO_3 concentration in logarithmic coordinates in the region of its high concentrations (above 3 M) can be described using the equilibrium constant:

$$K_S = \frac{\left[\overline{H_2[Ln(HA_2)_3A_2]}\right]}{[Ln^{3+}]\left[NO^-_3\right]^3\left[\overline{(HA_2)}\right]^3}. \qquad (6)$$

The high values of the ytterbium and lutetium distribution coefficients during extraction with P507 solutions in isopar M complicate the REE re-extraction, which brings about the need to use solutions with a high HNO_3 concentration at this stage of the process and
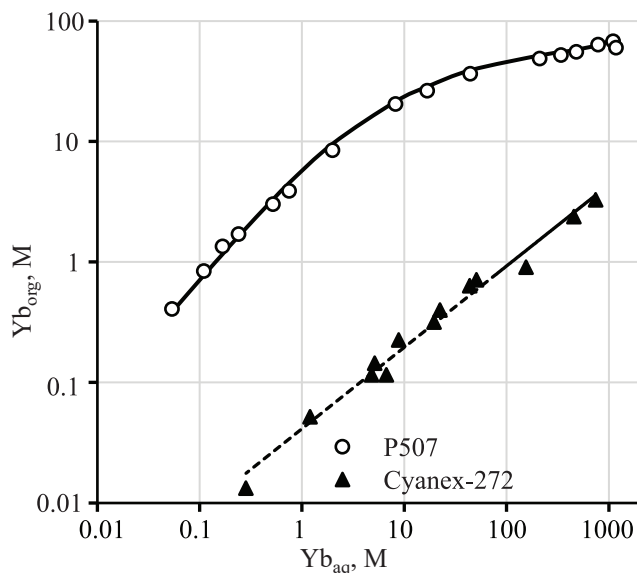
Fig. 2. Extraction isotherm of Yb in 15% P507 solutions and Cyanex-272 in isopar M from 1 M HNO_3.

complicates further handling of the products. Reduction of the P507 concentration can be considered as an alternative variant, however, it leads to a decrease in the productivity of the process, since the saturation of the extractant decreases. At a P507 concentration of 15% (0.45 M), the maximum saturation of the extract with ytterbium tends to 0.075 M (Fig. 2), which corresponds to the molar ratio of REE : P507 = 1 : 6 in the organic

phase and to Eq. (2), as well as indirectly confirms the participation of P507 dimer molecules in the formation of compounds with REE.

It is known that the use of heavy fluorinated diluents, for example, F3, also leads to a decrease in the REE distribution coefficients; therefore, it was of interest to study the effect of this diluent on the REE extraction with P507 solutions. The nature of the relationship between the REE distribution coefficients and the HNO_3 concentration in the extraction of Yb and Lu with P507 solutions in F3 does not depend on the nature of the diluent (Fig. 3), however, the influence of the solvation mechanism starts to manifest itself somewhat earlier (from 3 M HNO_3) than in the case of extraction with P507 solutions in isopar M.

The curve of the distribution coefficients of ytterbium and lutetium vs. the P507 concentration in isopar-M constructed in logarithmic coordinates (Fig. 4) have a linear form with a slope close to 2, and not to 3, which may be a consequence of an increase in the degree of association of extractant molecules with a growth in its concentration. This fact leads to a decrease in the REE extraction constants with a rise in the P507 concentration (Table 1). The concentration equilibrium constants of Eq. (5) turned out to be the same for isopar M and F3, therewith for lutetium they turned out to be lower than for ytterbium.
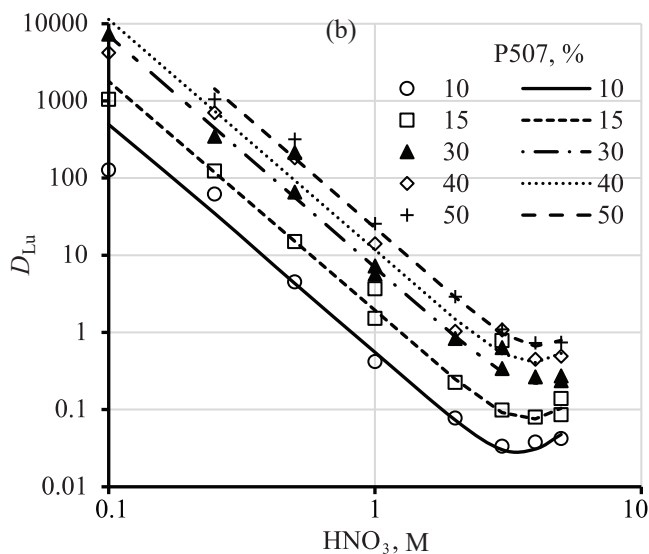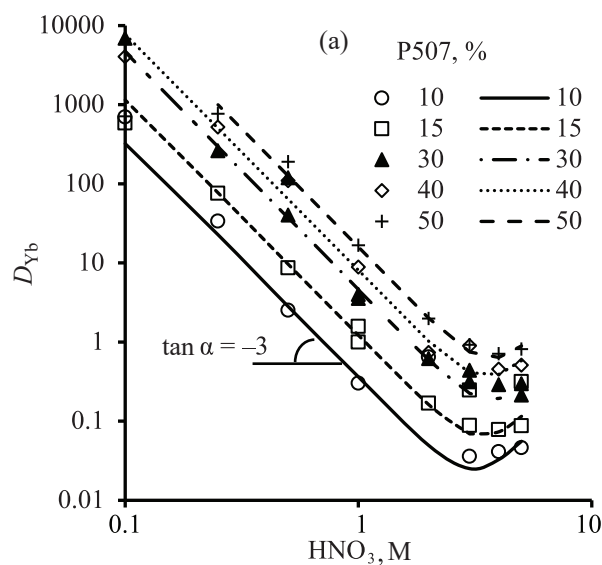

Fig. 3. Effect of equilibrium HNO_3 concentration on distribution coefficients of (a) Yb and (b) Lu at extraction with P507 solution in F3 (initial REE concentration 0.2–0.4 g/L).
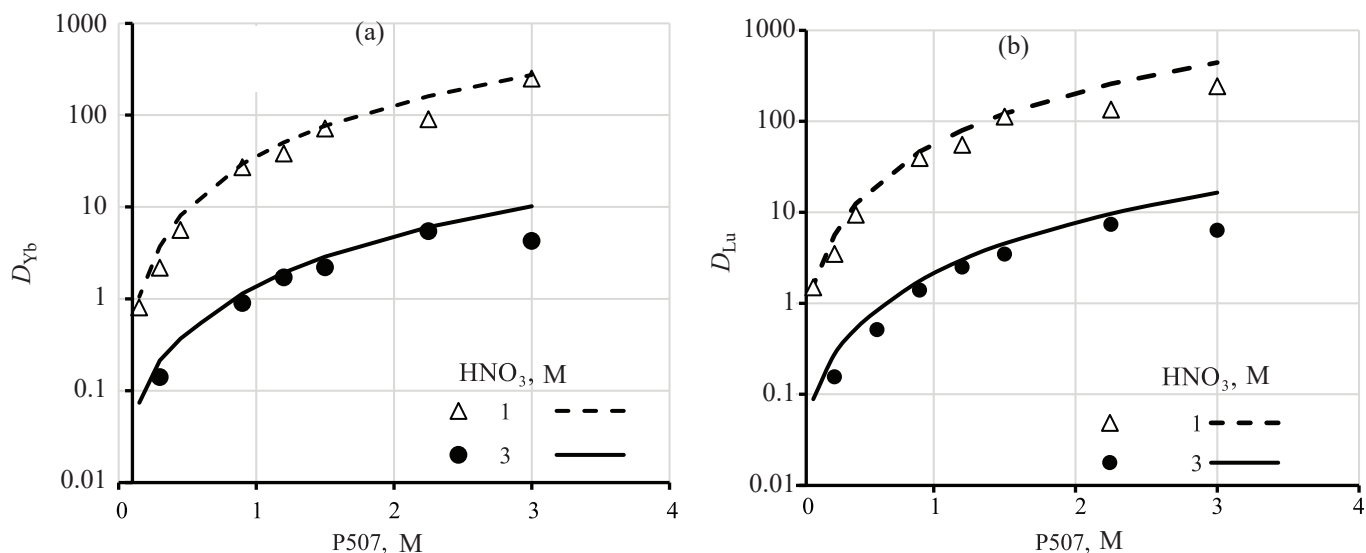
Fig. 4. Effect of P507 concentration in isopar M (0.15, 0.3, 0.45, 0.9, 1.2, 1.5, 2.25, 3 M) on distribution coefficients of (a) Yb and (b) Lu at their extraction from HNO_3 solution of varios concentrations (initial REE concentration 0.2 g/L).

Table 1. The equilibrium constants of reactions (2) (K_H) and (5) (K_S) for P507 solutions in light and heavy diluents

P507 concentration, %	P507 concentration, M	K_H P507 in isopar M		K_H P507 in F-3		K_S (does not depend on diluent)	
		Yb	Lu	Yb	Lu	Yb	Lu
5	0.15	2750	4100				
10	0.30	1214	1839	113	173	0.0028	0.0023
15	0.45	763	1147	112	170	0.0038	0.0032
20	0.60	550	850				
30	0.90	363	606	53	80	0.0042	0.0038
40	1.20	236	357	38	56	0.0070	0.0059
50	1.50	161	260	38	55	0.0083	0.0065
75	2.25	120	190				
100	3.00	84	136				

Table 2. Parameters of Eq. (7) for Yb and Lu during their extraction with P507 solutions in isopar-M or F3

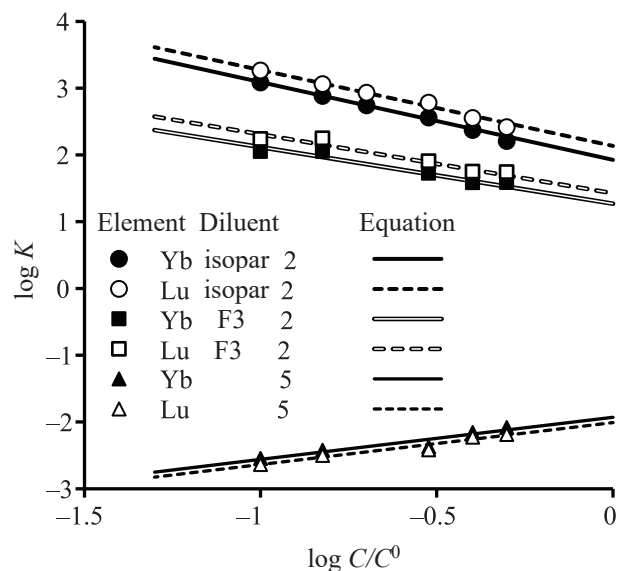| Reaction equation	Parameter	P507				Cyanex-272	
		isopar M		F3		in isopar M	
		Yb	Lu	Yb	Lu	Yb	Lu
(2)	$\log K^0$	1.95	2.13	1.27	1.43	−1.22	−0.87
	a	−1.16	−1.14	−0.85	−0.88	1.26	1.23
(5)	$\log K^0$	−1.93	−2.01	−1.93	−2.01	−3.3	−3.3
	a	0.630	0.627	0.630	0.627	−	−
(8)	$\log K^0$					−1.82	−1.75
	a					−0.89	−0.90
(9)	$\log K^0$					−1.8	−1.8
	a					−	−

Fig. 5. Logarithms of the Yb and Lu extraction constants according to Eqs. (2) and (5) vs. the logarithm of the P507 concentration in various diluents.

To take into account this effect caused by the influence of the diluent, the equation can be used:

$$\log K = \log K^0 + a \log C_{HA}^0, \tag{7}$$

where C_{HA} is P507 concentration, C_{HA}^0 is undiluted

extractant concentration, $\log K^0$ is equilibrium constant of reaction (2) or (5) for undiluted P507. Similar relationships were used in [14], where the effect of the P507 concentration on the logarithms of the REE extraction constants from chloride media was described by the BC_{HA}^y term.

Figure 5 shows the linear relationship between the logarithms of the equilibrium constants (2) and (5) and the logarithm of the relative P507 concentration. The values of the slope coefficients a and the values of the parameters $\log K^0$ calculated by the least squares method are presented in Table 2. Unfortunately, the derived $\log K^0$ values were found to be different for these two diluents, which did not allow reducing the number of parameters used.

The almost parallel behavior of the curves of the REE distribution coefficients vs. the P507 concentration and the HNO_3 concentration indicates that the separation factors of Yb and Lu will slightly rise with a decrease in the extractant concentration remaining in the range of 1.4–1.6 (the separation factors were derived as the ratio of the experimentally found distribution coefficients from solutions containing Yb and Lu in different proportions). With an increase in the HNO_3 concentration in an aqueous solution, the solvate mechanism of REE extraction begins to play an increasingly important role resulting in a decrease in separation factors.
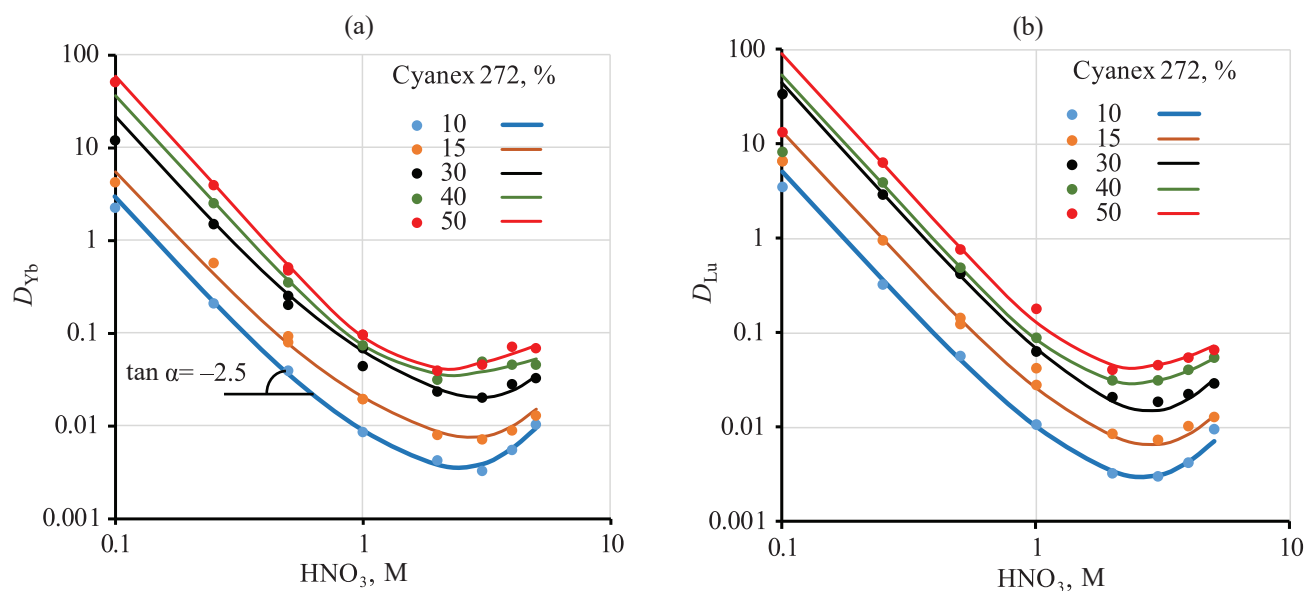

Fig. 6. (Color online) Effect of HNO_3 concentration on the distribution coefficients of (a) Yb and (b) Lu during extraction with Cyanex-272 solutions in isopar-M (initial REE concentration 0.2–0.4 g/L. (Points) experiment; (lines) calculation.
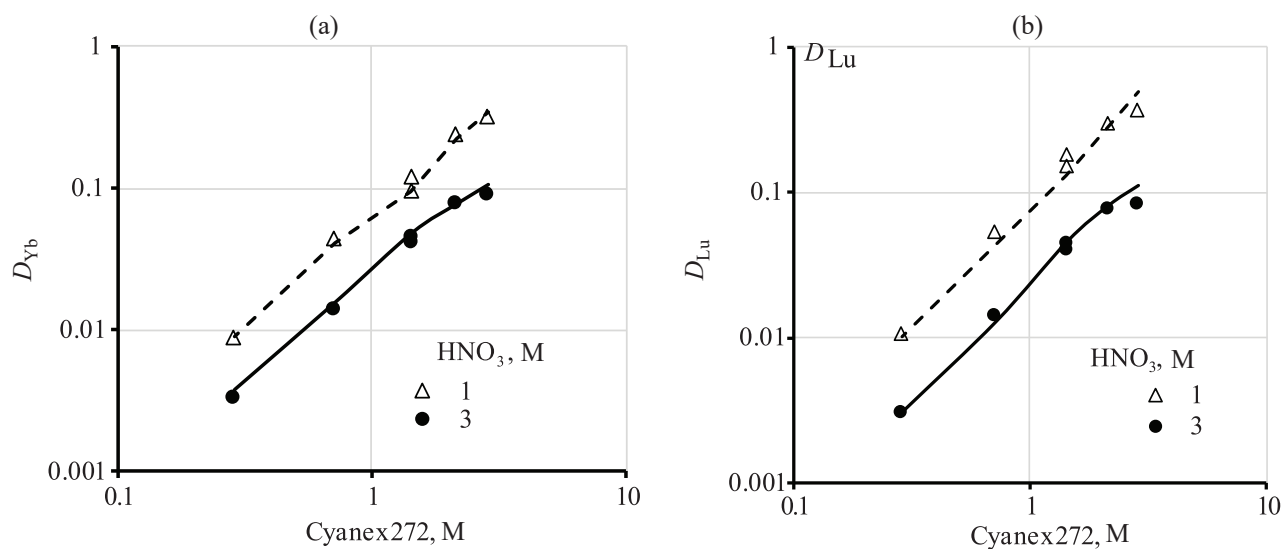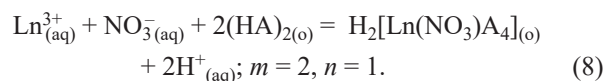
Fig. 7. Effect of Cyanex-272 concentration in isopar M on the distribution coefficients of (a) Yb and (b) Lu during their extraction from HNO$_3$ solutions of various concentrations (initial REE concentration 0.2–0.4 g/L. (Points) experiment; (lines) calculation.

It is known that the use of bis-(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex-272) as an extractant instead of P507 leads to a decrease in the REE distribution coefficients by approximately 2 orders of magnitude while maintaining high values of the separation factors [20, 21]. Therefore, it was of interest to study the regularities of Yb and Lu extraction with solutions of Cyanex-272 in isopar M.

In contrast to the system with P507, the functions of the logarithms of the Yb and Lu distribution coefficients vs. the logarithm of the HNO$_3$ concentration at a concentration of less than 1 M in this system have a slope of about –2.5 (Fig. 6), which results in the need to apply for simulation of the REE extraction in this region not only Eq. (2), but also Eq. (8) derived from Eq. (1) at $m = 2$ and $n = 1$:

$$Ln^{3+}_{(aq)} + NO^-_{3\,(aq)} + 2(HA)_{2(o)} = H_2[Ln(NO_3)_2A_4]_{(o)}$$
$$+ 2H^+_{(aq)}; \; m = 2, n = 1. \qquad (8)$$

With increasing the acid concentration in the aqueous phase above 3 M, the REE extraction brings about an increase in the distribution coefficients, which can be due to a gradual transition to the solvate mechanism of extraction. At the same time, with an increase in the concentration of Cyanex-272, the slope of the ascending section of the function of the distribution coefficient vs. the HNO$_3$ concentration diminishes (Fig. 6), which can

be described by Eqs. (5) and (9) derived from Eq. (1) at $m = 1$ and $n = 2$:

$$Ln^{3+}_{(aq)} + 2\,NO^-_{3\,(aq)} + (HA)_{2(o)}$$
$$= H[Ln(NO_3)_2A_2]_{(o)} + H^+_{(aq)}; \; m = 1, n = 2. \qquad (9)$$
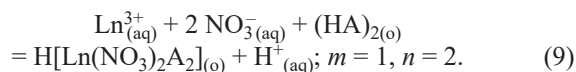
The slope of the function of REE distribution coefficient vs. the Cyanex-272 concentration in isopar M at 1 and 3 M HNO$_3$ concentrations (Fig. 7) is close to 1.6, which corresponds to the cumulative proceeding of reactions (2), (5), (8), and (9).

The slope coefficients a and the parameters log K^0 of Eq. (7) presented in Table 1 evidence that the values of the parameters a of Eq. (7) practically do not differ for Yb and Lu, which notices that the separation factors of these elements are independent of the extractant concentration. The equilibrium constants of Eqs. (5) and (9) for Yb and Lu coincide and practically do not depend on the extractant concentration, which confirms the decrease in the separation factors of these elements at HNO$_3$ concentrations above 2 M. At a lower concentration, the separation factors of the Yb/Lu pair increase and reach 1.4–1.6, which makes it possible to consider this extractant as an alternative to P507. At the same time, the low saturation of Cyanex-272 (Fig. 2) necessitates the use of Cyanex-272 only in a mixture with other extractants.

The average error in calculating the distribution coefficients according to the model does not exceed 7–8 rel %.

CONCLUSIONS

Extraction systems for the separation of lutetium and ytterbium based on acidic organophosphorus extractants P507 and Cyanex-272 from nitric acid solutions have been studied. In the course of the experiments, results were found both with the use of a light diluent (Isopar M) and a heavy diluent F3. The separation factors of lutetium and ytterbium in the studied extraction systems are 1.4–1.6. The obtained experimental data on the extraction of lutetium and ytterbium with P507 were used to construct a mathematical model that makes it possible to predict the behavior of Yb and Lu in the extraction cascade. A special report will be devoted to testing technological regimes for the lutetium and ytterbium separation.

CONFLICT OF INTERESTS

The authors declare no conflict of interest.

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