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Use of di-(2-ethylhexyl)-orthophosphoric acid for the extraction of lanthanum, neodymium, samarium and yttrium from nitric acid solutions

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Abstract: The process of separating rare-earth elements into individual components is considered the most important problem in rare-earth technology because of the similarity in their physical and chemical properties. Currently in the world dialkyl phosphate compounds are widely used as effective extractors for rare earths. However, most extraction processes have been studied from hydrochloric acid or perchlorate solutions. In Russia, tributyl phosphate has long been used to extract rare earths from nitric acid solutions, but the distribution coefficients of the elements are not high, and the process must be repeated multiple times. In this study di-(2-ethylhexyl)-orthophosphoric acid was used for the extraction of lanthanum, neodymium, samarium, and yttrium from nitric acid solutions. When the concentration of nitric acid increased, distribution coefficient of elements gradually decreased to minimum (in the range of 1 to 5M) then increased backward. However, when the concentration was too high ($C > 5M$), nitric acid was extracted to the organic phase due to the properties of the phosphoryl group. Moreover, the study of dependence of solvation number of neodymium on the concentrations of nitric acid shows that rare earths in the organic phase can be extracted as $Re(HA_2)_3$ ($C < 1M$) or $Re(NO_3)_3 \cdot 3HA$ ($C > 5M$).

Keywords: *Extraction; rare-earth elements (REE); di-(2-ethylhexyl)-orthophosphoric acid (D2EHPA); distribution coefficient; solvation number.*

I. INTRODUCTION

Rare-earth elements (REE) are a group of 17 metals, including scandium (Sc), yttrium (Y) and lanthanides. Currently industries require highly purified REE. However, since REE has extremely similar physical and chemical properties, separating them apart is considered the most challenging part. The patterns of extraction of REE have been studied in detail using di-(2-ethylhexyl)-orthophosphoric (D2EHPA) [1,2], 1,5-bis[di(p-tolyl)phosphoryl]-3-oxapentane [3], bis(2-ethylhexyl)diglycolamic acid [4], organophosphorus ligands, diamides and N-heterocycles [5], diphosphine dioxides and their mixtures with chlorinated cobalt dicarbollide [6], (2-ethylhexyl)phosphonic acid 2-ethylhexyl monoester [7], tributyl phosphate isomers with trialkylmethylammonium nitrate [8], various organic acids [9], (diphenyl-phosphinylmethyl) phenylphosphinic acid [10], universal solvent extractants (Unex) [11], bidentate neutral

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organophosphorus extractants [12], dibutyl phosphoric (DBPA) [13], di(2-ethyl-hexyl) phosphoric acid in hexane [14], diamyl phosphoric (DAPA) [15] and bis-(diphenylphosphinylmethyl)-phosphinic acid [16] as extractants of different types. This is because these extractants have satisfactory characteristics for separating mixtures of lanthanides into individual components. In most works, extraction was studied from hydrochloric acid or perchlorate solutions of low or moderate concentrations.

In Russia, tributyl phosphate (TBP) has been used for decades as extractant from nitric acid solutions. However, distribution coefficients of elements in organic phase are not too high and the process must be repeated several times. Since the extraction (of REE by using TBP) from nitric acid solutions is better than from chloride and phosphate medium, the purpose of this work is to study the patterns of extraction of several REE (La, Nd, Sm, Y) by using D2EHPA from nitric acid solutions in a wide range of nitric acid concentrations (from 0,01 to 20M). From the obtained results, a conclusion is drawn about the dependence of distribution coefficient and solvation number on concentration of nitric acid.

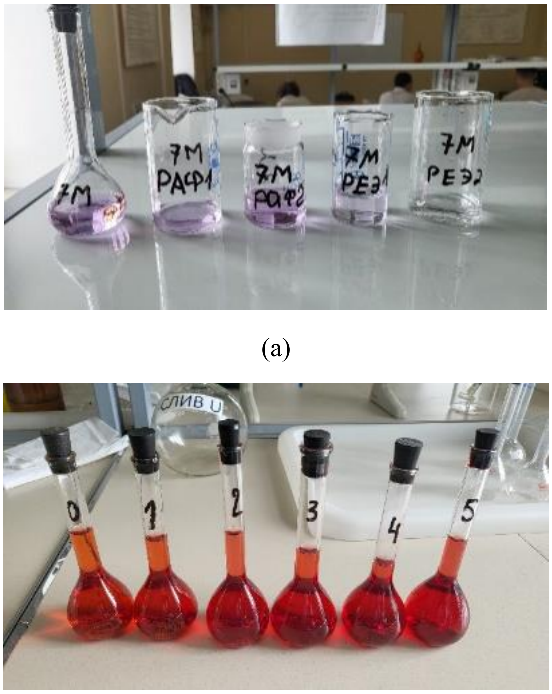
II. THE MAIN PART OF THE REPORT

A. Research subjects and methodology

REE samples available at laboratories of TPU include La_2O_3, $Nd(NO_3)\cdot 6H_2O$, $Sm(NO_3)\cdot 6H_2O$ and Y_2O_3 with >99 % purity. Nitric acid solutions with different concentrations were prepared by dilution from the concentrated solution (C = 20 M). The amount of sample was taken so that after being dissolved in 50 ml of nitric acid a 0.5 M solution of REE was obtained. The extraction process is carried out by taking 10 ml of the above solution and mixing it with 10 ml of D2EHPA mixed with benzene in the ratio 7:3. The phase mixing time was 5 min, which is several times longer than the time to reach equilibrium in the system [14], on a laboratory shaker. The temperature in the laboratory was stable in the range of 25±2 °C. After centrifugation of the phases, the REE distribution coefficient was determined as the ratio of the activities of the aqueous and organic phases.

After the shaking phase, the solution was moved to separatory funnel. As a result, the first extract and raffinate were obtained. The raffinate was then added another 10ml of mixed D2EHPA for second extraction. 2 solutions of extract were analyzed by spectrophotometry method with the help of calibration curve (fig. 1).

B. Results



(a)

(b)

Fig. 1. Example experiment with Nd

(a) – Solutions after 2 times of extraction at concentration of HNO_3 7M

(b) – Prepared samples with arsenazo-III for spectrophotometry

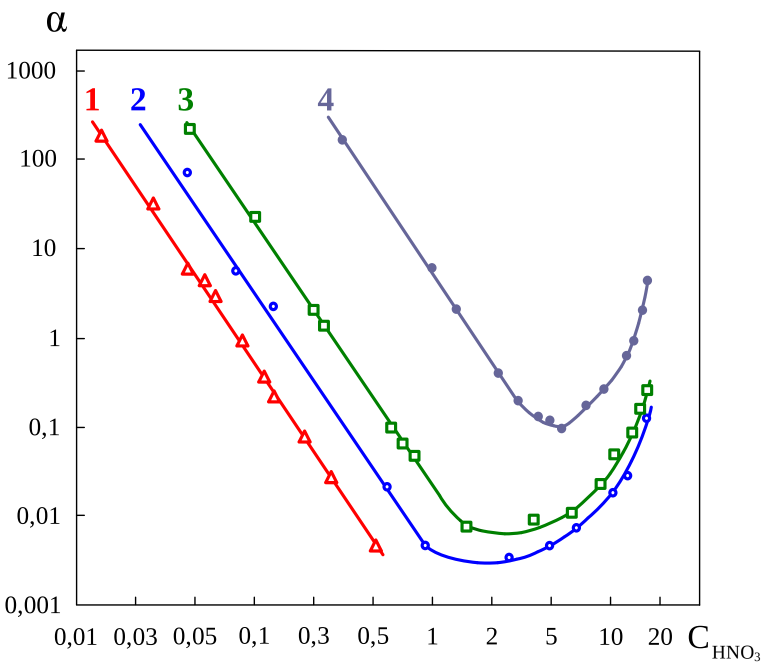
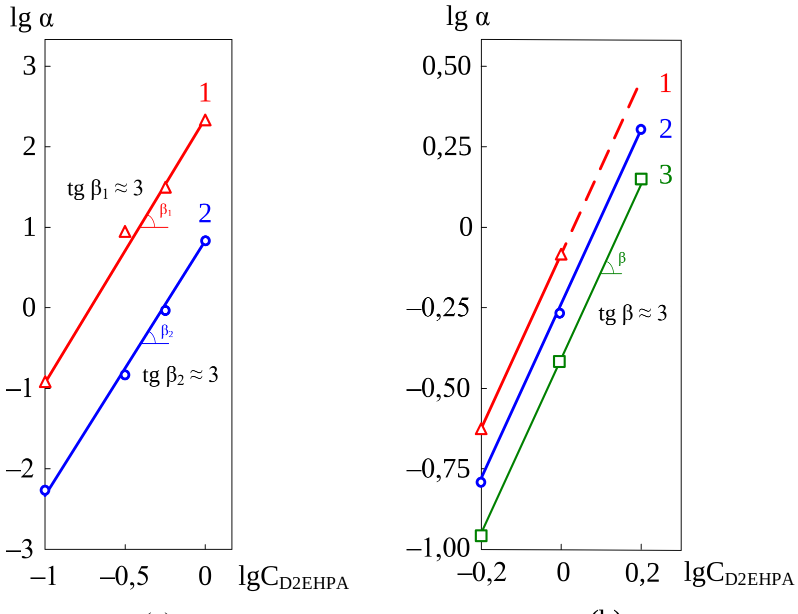


Fig. 2. Dependence of distribution coefficients of some REE on concentrations of HNO_3

1 – La, 2 – Nd, 3 – Sm, 4 – Y



(a)

(b)

Fig. 3. Determination of solvation numbers during extraction Nd

(a) – at low and moderate concentrations of HNO_3 (1 – 0,5M; 2 – 1,5M)

(b) – at high concentrations of HNO_3 (1 – 9,5M; 2 – 9,0M; 3 – 8,5M)

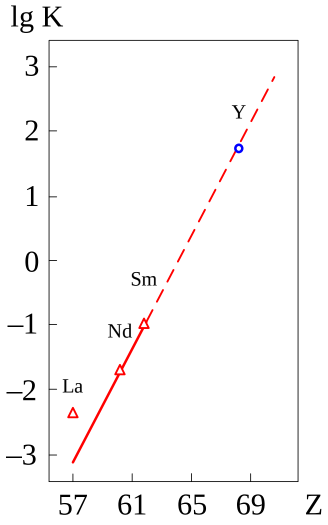


Fig. 4. Dependence of logarithm extraction constants on atomic number Z

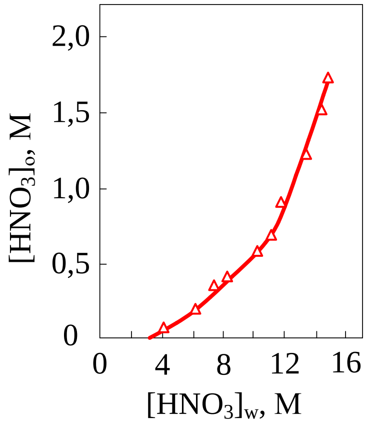


Fig. 5. Isotherm of nitric acid extraction with solution of D2EHPA in benzene

C. Discussion

Fig. 2 shows the dependence of the distribution coefficients (α) of the indicator amounts of La, Nd, Sm and Y on the concentration of nitric acid in the aqueous phase. An obtained characteristic feature of the dependences is the presence of a minimum (in the nitric acid concentration range of 1 to 5M): the distribution coefficients first decrease with increasing acidity, reach a certain minimum value, and then increase again.

For the above elements, the distribution coefficient on the left side of the dependence (in the region of the rectilinear section) is inversely proportional to the concentration of hydrogen ions in the aqueous phase. Fig. 3 shows that the tangent of the slope of the straight sections of the curves is equal to –3. The same dependence was established for the distribution coefficient of Y during extraction from nitric acid solutions with dibutyl- and diamylphosphoric acids [16,17].

The solvation number in the organic phase during the extraction of Nd from aqueous solutions of nitric acid of low and moderate concentrations was determined by diluting the organic phase with an inert diluent (benzene) (fig. 3a). It is equal to 3, as in the extraction of Nd and other REE by using D2EHPA from hydrochloric acid solutions [14]. From fig. 3b the dependence of the neodymium's distribution coefficient on the concentration of the extractant in logarithmic coordinates is rectilinear, the slope is 3. Therefore, in the region of high concentrations of nitric acid, a solvate of the $Re(NO_3)_3 \cdot 3HA$ type is extracted into the organic phase. This compound is identical to the compound extracted with tributyl phosphate from neutral solutions.

The equation for the extraction of REE from concentrated solutions of nitric acid (C > 5M) can be represented as:

$$Re^{3+}_w + 3NO^-_{3_w} + 3HA_o = [Re(NO_3)_3 \cdot 3HA]_o \quad (1)$$

This scheme assumes that D2EHPA is a monomerized extractant. The dimeric molecules of the extractant present in neutral diluents are destroyed during the extraction of significant amounts of nitric acid.

In the region of moderately concentrated aqueous solutions (C = 1-5M), in which nitric acid begins to be extracted in appreciable amounts and both dimeric and monomeric molecules of the extractant are present in the organic phase, the solvate is formed stepwise and extraction can be described by the equation (where x changes from 0 to 3):

$$\begin{aligned} & Re^{3+}_w + xNO^-_{3_w} + 3HA_o + (3\text{-}i)(HA)_{2_o} \\ & = Re(HA_2)_{3\text{-}x}(NO_3)_x(HA)_{x_o} + (3\text{-}x)H^+_w \quad (2) \end{aligned}$$

The data obtained indicate that the mechanism of REE extraction by using D2EHPA depends significantly on the acidity of the equilibrium aqueous phase. In the region of low concentrations of hydrogen ions, extraction is carried out according to the mechanism characteristic of acidic extractants. In the region of high concentrations of hydrogen ions, the extraction properties of D2EHPA are determined by the oxygen donor properties of the phosphoryl group, as is the case in extraction with neutral organophosphorus compounds.

Considering the dimerization of the extractant in benzene, the equation for the extraction of REE in the region of low and moderate concentrations of nitric acid (C < 1M), corresponding to the straight sections of the straight lines in fig. 1 can be represented as:

$$Re^{3+}_w + 3(HA)_{2_o} = Re(HA_2)_{3_o} + 3H^+_w \quad (3)$$

The equilibrium constant (extraction constant) of reaction (1) will be:

$$K = \frac{[Re(HA_2)_3]_o \cdot [H^+]^3_w}{[Re^{3+}]_w \cdot [(HA)_2]^3_o} \quad (4)$$

From which we get:

$$lgK = lg\frac{[Re(HA_2)_3]_o}{[Re^{3+}]_w} + 3lg[H^+]_w - 3lg[(HA)_2]_o$$

(5)

$$\Rightarrow lg\alpha = lgK + 3lg[(HA)_2]_o + 3pH \quad (6)$$

From (6) we can conclude that α is a function of the equilibrium pH and concentration of the extractant. Using equation (6), the extraction constants for La, Nd, Sm, and Y were calculated. Fig. 4 shows the dependence of the REE extraction constants on the element atomic number Z. This dependence can be represented as a straight line described by the equation:

$$lgK = 0{,}42 \cdot Z - 26{,}95 \quad (7)$$

Significant deviations are observed only for La. Apparently, this is due to minor impurities of mono-(2-ethylhexyl)-orthophosphoric acid in the extractant, which significantly increases the distribution coefficients of La.

A comparison of the Y extraction constants of D2EHPA in benzene (K = 1.59) and DAPA in benzene (K = 2.45) [17] shows that alkyl phosphoric acids with a linear chain of alkyl radicals have a noticeably higher extraction ability than branched chain acids. An increase in distribution coefficients in the region of high concentrations of nitric acid is characteristic of REE (see fig. 2). This phenomenon can be explained by a change in the extraction mechanism. In the region of high concentrations of acids, the dissociation of D2EHPA is suppressed to a large extent, thus the process of REE extraction according to reaction (3) is suppressed. Under these conditions, D2EHPA apparently behaves like neutral organophosphorus extractants, which means extraction proceeds due to the donor properties of the oxygen of the phosphoryl group P=O. To confirm this, an isotherm of the extraction of nitric acid with D2EHPA in benzene in ratio of 7:3 was obtained. It can be seen from fig. 5 that in the range of low concentrations (C < 4M), nitric acid is practically not extracted; with an increase in the acid concentration in the aqueous phase, its extractability noticeably increases. The extraction of nitric acid proceeds due to the donor properties of the oxygen of the phosphoryl group, as in the extraction of neutral organophosphorus compounds, assuming that of the participation of oxygens of alkyl radicals or the OH^- group is unlikely.

III. CONCLUSION

Despite the wide variety of extractants used in rare earths extraction processes, organic acids remain the extractants most widely used in extraction processes for the isolation of rare-earth elements, their separation and concentration. D2EHPA has undoubted advantages over organophosphorus neutral extractants, for example tributyl phosphate, since it provides the possibility of extraction not only from nitrate, but also from sulfate solutions. The latter circumstance is very important for the processing of sulfuric acid productive solutions of rare-earth elements formed during their sulfuric acid leaching from ores. However, the use of D2EHPA for the processing of nitrate solutions is also very promising, since it is carried out at a significantly lower concentration of D2EHPA compared to TBP.

Regularities in the extraction of La, Nd, Sm, and Y with D2EHPA from nitric acid solutions were studied. Distribution coefficient was determined with the minimum in the medium region of concentrations of nitric acid (C_M = 1-5 M). The determination of the solvation number of Nd led to the conclusion about composition of compounds extracted into the organic phase: in the region of low and moderate concentrations of nitric acid (C < 5M), REE are extracted in the form of $Re(HA_2)_3$ complexes, and in the region of high concentrations (C > 5M), in the form of solvates $Re(NO_3)_3 \cdot 3HA$.

The values of solvate numbers of compounds formed during Nd extraction at low and high acidity of the medium were also determined. The dependence of the logarithm of the extraction constant on the Ln atomic number was studied and it was shown that with increasing atomic number, lgK increases. This confirms the fact that heavy REE are extracted better than light ones. When studying the dependence of the change in the concentration of HNO_3 in the organic phase on its concentration in the aqueous phase (extraction isotherm), it was shown that with an increase in the concentration of HNO_3 in the aqueous phase in the range of 4-16 M, it begins to be extracted and has a competing effect on the extraction of rare-earth elements. This circumstance must be taken into account when extracting rare-earth elements from solutions with high acidity.

It has been shown that, depending on the acidity of the aqueous phase, D2EHPA can be extracted both by the mechanism typical for acidic extractants ($C < 1M$) and by the mechanism characteristic of neutral organophosphorus compounds ($C > 5M$) due to the properties of phosphoryl group.

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