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Liquid Extraction of Some Rare Earth Elements with Aminomethylphosphine Oxides

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Abstract—Methods were developed of the solvent extraction from aqueous solutions of hydrochloric, nitric, and perchloric acids of the triply charged ions of rare earth elements including samarium, lutetium, dysprosium, neodymium, and ytterbium, using as reagents the lipophilic aminomethylphosphine oxides containing two or four dialkylphosphinyl groups, and toluene, chloroform, and methylene chloride as the organic media. The study of the effect of concentration of mineral acids on the degree of metal extraction showed that the highest extraction efficiency of lanthanides is achieved with bis(dihexylphosphinylmethyl)octylamine (**I**) from perchloric media: extraction degree 80%, whereas extraction from the solutions in two other acids did not exceed 30%. It was shown that the highest selectivity was reached at the extraction of scandium in all the extraction systems. A possible mechanism of extraction is discussed.

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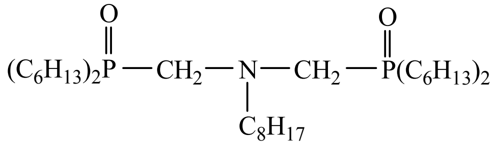
Solvent extraction processes have been successfully used and do not yet have an adequate alternative in the industry of rare and scattered metals for the separation of compounds of the elements with similar properties, as well as for extraction, concentration, and separation of many other elements from the hydrometallurgical technological solutions [1]. Among the efficient and selective reagents used for these purposes an important place belongs to the neutral organophosphorus compounds (tributyl phosphate, tributyl- and trioctylphosphine oxides, etc.) [2], as well as to higher tertiary amines (trioctylamine, dilaurylamine, etc.) [3]. In recent years data has appeared in the literature on the possibility of effective use in the extraction technology of alkali, alkaline earth [4] and noble metals [5], as well as scandium and some other trace elements [6, 7] of α-aminoalkylphosphoryl compounds that belong to the class of substances combining the structural features of the above two types of extraction reagents, the neutral organic phosphorus derivatives and amines. This combination of functional groups provides high efficiency and selectivity of these extractants in hydrometallurgical technologies of extraction and separation of metals [8], they are highly effective as a membrane transporter substrates of acidic nature [9] and the components of ion-selective electrodes [10]. However, together with the performance and prospects of use in addressing these challenges, the aminophosphonates, which were mainly used in the above cited studies, have one major drawback: a relatively low thermal and hydrolytic stability due to the presence in the molecules of labile ester bonds P–O–C that becomes a serious obstacle to the realization of technological processes of solvent extraction of metals, which as a rule is carried out in the industry from acidic aqueous media.

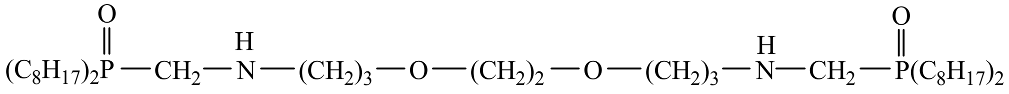
The lipophilic aminomethylphosphine oxides (APO) with long chain substituents at the phosphorus and nitrogen atoms, which do not possess labile bonds, are devoid of this drawback. They are characterized by the hydrophilic–lipophilic characteristics appropriate for optimal interphase distribution. These compounds showed high efficiency and selectivity in the process of solvent extraction of substrates of different nature [11–13]. The study of the influence of structure on the efficiency and selectivity of the aminomethylphosphine oxide in the liquid [11–13] and membrane [7] extraction of ions of rare and dispersed metals allowed us to establish that the best performance showed the lipophilic polydentate complexing agents bis(dialkylphosphinylmethyl)alkylamines.

This paper presents the results of investigations on the solvent extraction from acidic aqueous media of triply charged cations of the lanthanide series samarium, lutetium, dysprosium, neodymium, and ytterbium with bis(dihexylphosphinylmethyl)octylamine (**I**) and two polyester azapodands with two (**II**) and four (**III**) terminal *N*-dialkylphosphinylmethyl groups.



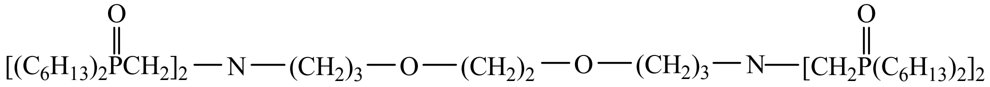
$$(C_6H_{13})_2\overset{O}{\overset{\|}{P}}-CH_2-\underset{C_8H_{17}}{\underset{|}{N}}-CH_2-\overset{O}{\overset{\|}{P}}(C_6H_{13})_2$$

I



$$(C_8H_{17})_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{H}{N}-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-\overset{H}{N}-CH_2-\overset{O}{\overset{\|}{P}}(C_8H_{17})_2$$

II



$$[(C_6H_{13})_2\overset{O}{\overset{\|}{P}}CH_2]_2-N-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-N-[CH_2\overset{O}{\overset{\|}{P}}(C_6H_{13})_2]_2$$

III

The current experience in the extraction of rare earth elements with organophosphorus extractants suggests a promising use of the compounds like phosphinic acids derivatives [14], aminoalkylphosphonates [15, 16], and phosphorylated polyester podands [17]. Bisphosphinylamines before our studies were not used in the lanthanide extraction technology.

As noted above, the process of extraction of metals is performed as a rule from the acidic aqueous phase produced at the acid treatment of mining raw materials, so it can be complicated by the co-extraction of the mineral acid. In this regard, the data on the conditions of extraction of selected mineral acids are important for the understanding of the mechanism of the process under study, since the degree of acid transfer should be taken into account. Most often, in the industrial extraction processes hydrochloric, nitric, and perchloric acid are used. We have studied the extraction of these acids with solutions of oxide **I** of the concentration 0.05 M using as a diluent either toluene, chloroform, or methylene chloride. Based on experimental data for all three interphase systems, we have built the extraction isotherm with the reagent **I**. Figure 1 shows as an example the isotherms of extraction of acids in toluene. Virtually the same type of extraction isotherms were obtained for the other two diluents.

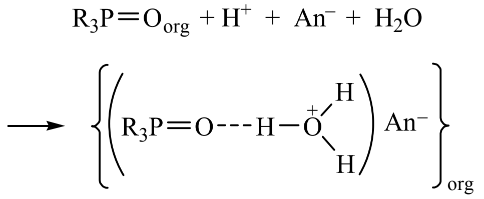
The weak extractability of hydrochloric acid attracts an attention: the amount of HCl in the organic phase increases monotonically and reaches maximum at the acid concentration in the aqueous phase above 5 M, with the formation of the solvate of 1:1 composition with the extractant. Given the fact that the most basic functional group in the molecule of the reagent is the amino group, we can assume that hydrochloric acid is extracted in the form of ionic associate consisting of the reagent molecule protonated at the nitrogen atom and chloride anion. Such a mechanism occurs in the extraction of HCl with the nitrogen-containing reagents, the higher amines and aminophosphonates [3, 18]. The reason for the weak extractability of hydrochloric acid is the high hydration energy of the chloride ion.

At a low acid concentration in the aqueous phase the perchloric acid exhibits the best extractability. The extraction isotherm reaches its limit at a concentration of $HClO_4$ in the organic phase close to 0.05 M, which corresponds to the total binding of the reagent to form ion associate of 1:1 composition. According to [3] perchloric and hydrochloric acids are extracted by similar mechanisms, but due to low hydration energy of the perchlorate ion the perhloric acid is transferred into organic phase much more effectively than hydrochloric acid. Consequently, it is reasonable to study the extraction of metals from perchloric media only at a low pH of the aqueous phase.

The behavior of nitric acid in the studied two-phase system differs markedly from that of perchloric and hydrochloric acids. In the high acidity region nitric acid is extracted better than hydrochloric and perchloric acids, and the isotherm for the reagent does not reach the limit at the concentration in the organic phase 0.05 M and increases monotonically. Probably, at low concentrations of nitric acid the 1:1 solvate is formed, and with increasing the medium acidity a solvate of more complex composition is formed.

According to the experimental data, at low acidity (0.9 M) extractability decreases in the series $HClO_4$ > HNO_3 > HCl, in accordance with the energy of hydration of the anions: the $-\Delta G^{*}_{hydr}$ for chloride, nitrate and perhlorate ions are 330, 288 and 209 J mol^{-1}, respectively [19].

It is known [2, 18] that the strong inorganic acids are extracted by neutral organophosphorus compounds in line with hydrate–solvate mechanism.



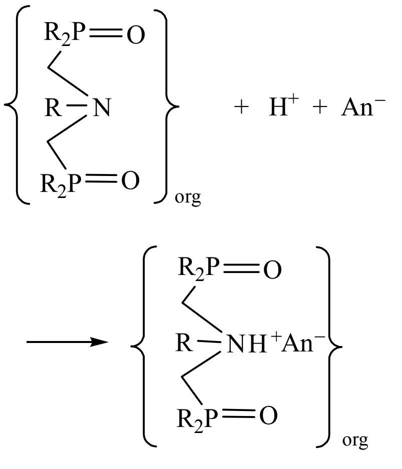
$An^- = Cl^-, Br^-, I^-, ClO_4^-$.

The extraction of nitric acid by the same reagents proceeds by a solvate mechanism, with the formation of the H-complex of undissociated molecule of nitric acid with the oxygen atom of the phosphoryl group.

$$R_3P{=}O_{org} + HNO_3 \longrightarrow \left\{R_3P{=}O\text{---}H{-}NO_2\right\}_{org}$$

As for the highly basic extractants, like higher aliphatic amines, the extraction of these acids proceeds through the formation of ion associates of the protonated amine and the anion of the corresponding acid [3].

Note that, as stated earlier [20], the basicity center of the aminophosphoryl compounds is just the nitrogen atom, rather than the phosphoryl oxygen. Therefore, the H-complexes resulting at the interaction of phosphine oxide **I** with strong acids are extracted the most likely along the solvation scheme in the form of ionic associates.



$An^- = Cl^-, NO_3^-, ClO_4^-$.

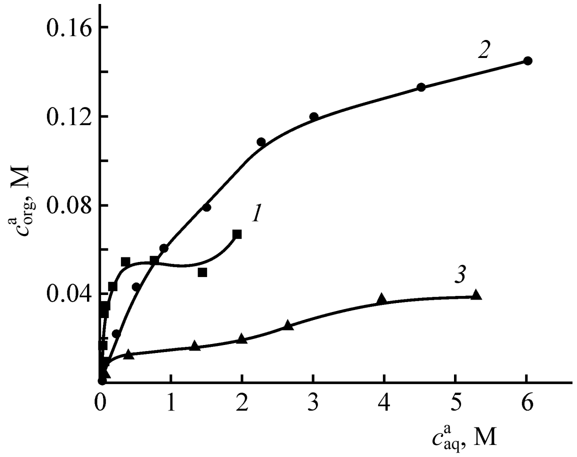
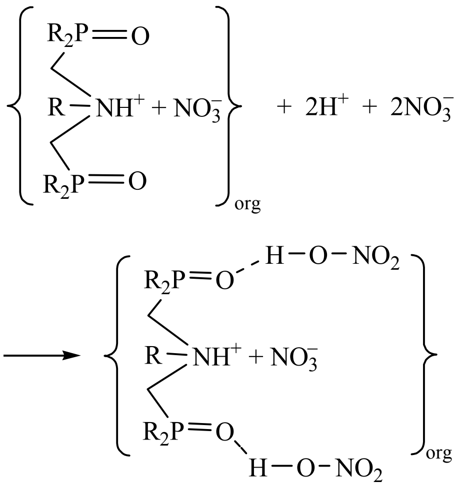


Fig. 1. Isotherms of extraction of acids with reagent **I** in toluene. (*1*) $HClO_4$, (*2*) HNO_3, and (*3*) HCl.

Binding the subseuent molecules of hydrochloric or perchloric acid by phosphoryl groups by the hydrate-solvate mechanism is apparently more difficult due to the Coulomb repulsion arising at the protonation of nearby ammonium and two oxonium centers. At the same time, the formation of H-complexes with a second and third molecules of nitric acid is possible.



The obtained data are important for the understanding of the patterns of the metal ions extraction by the studied agent because they contain the information on the form in which the agent exists in the organic phase at varied acidity of the aqueous phase. At the extraction from hydrochloric acid media in a wide range of acidity, the organic phase will contain the nonprotonated aminomethylphosphine oxide in a mixture with its hydrochloride. At low (up to 1 M) concentrations of perchloric acid the reagent **I** exists in the organic phase probably as a mixture of protonated and nonprotonated forms. The most complicated is the situation with nitric acid: the reagent may be present in the organic phase in four forms, including neutral one, with protonated nitrogen, and as two solvates of 1:2 and 1:3 composition.

The reagent **I** we used has a much lower basicity ($pK < 2$) [9] compared with the higher aliphatic amines, and therefore we can assume that the degree of protonation of its nitrogen center is lower than in the case of aliphatic amines and monophosphorylamines. For this reason, this reagent, as well as the other bisphosphorylated amines, may be very promising in the extraction processes of metals, due to a less significant effect of competing extraction of acids.

The hydrochloric acid solutions are used in hydrometallurgy of rare earth elements relatively seldom, so we investigated the effect of concentration of hydrochloric acid in the aqueous phase on the degree of extraction of only two elements, samarium and lutetium, belonging respectively to the cerium and yttrium lanthanide subgroups. For the extraction we used 0.025 M solution of oxide **I** in toluene, methylene chloride, and chloroform at 1:1 ratio by volume of the aqueous and organic phases. An example below shows the degree of extraction of these metals with the reagent **I** in toluene depending on the concentration of hydrochloric acid in the aqueous phase. Almost a similar dependence we found for chloroform and methylene chloride.

c_{HCl}, M	0.21	0.22	0.65	1.1	1.5	2	3	4.6	4.8	6
E_{Sm}, %	19	18	11	17	15	19	20.5	32	20	11
E_{Lu}, %	2.9	3.3	4.8	2.9	6.1	7.8	0	5.4	6.4	2.8

Analyzing the dependence, we can say that the degree of extraction of lanthanides in all the investigated two-phase systems is relatively low, and do not exceed 30% for samarium and 20% for lutetium. The better extractability of Sm(III) in comparison with Lu(III) occurs over the entire range of acidity, that is consistent with the published data on the extractability of the ions of rare earth elements with higher aliphatic amines from hydrochloric acid media [21].

The application of aqueous nitric acid medium is more important for the hydrometallurgical lanthanide extraction and purification processes. Therefore we investigated the influence of nitric acid concentration in the aqueous phase on the degree of extraction of ions Sm(III), Lu(III), Dy(III), Yb(III), and Nd(III) with 0.025 M solution of reagent **I** in toluene, chloroform, and methylene chloride (Table 1). As seen, the degree of extraction of metals from nitric acid media is as low, as from the hydrochloric acid. The unusual behavior of Sm(III) extraction with the toluene solution of the reagent **I** attracts the attention, for the degree of extraction at high concentrations increases to 60%, while for other metals the value is less than 10%. To understand this phenomenon more research is necessary.

It should be noted that for all the studied cations at low concentrations of HNO_3 a decrease is observed in the degree of extraction with increasing acid concentration. The series of extractability of the lanthanides at the low and high acidity of the aqueous phase differ: in weakly acidic media (0.25 M) the sequence of decreasing extractability is reflected by the series Sm > Lu > Nd > Yb, whereas in strongly acidic media the sequence is as follows: Sm > Nd ~ Yb > Lu. There is no clear correspondence with ionic radii of the investigated elements (*r*, Å): 0.964, 0.995, 0.858, 0.848, respectively [22].

Using the values of extraction from nitric acid media, we calculated the partition coefficients relative to scandium(III), which, as noted above, was almost completely recovered by the reagent **I** used in these experiments. The results are shown in Table 2. It should be noted that when toluene or chloroform are used as diluents, a high separation of the test components is achieved, with the highest selectivity on the scandium. Particular attention merits the high selectivity in the scandium–lutetium pair in a wide range of concentrations of nitric acid in the aqueous phase.

The most widespread in the technology of extraction of rare and trace elements was the use of

Table 1. Dependence of the degree of extraction of Sm, Lu, Nd and Yb with reagent **I** on the HNO_3 concentration[a]

$c(HNO_3)$, M	Yb	Nd	Sm	Lu	Sm	Lu	Sm	Lu
	toluene				chloroform		metylene chloride	
0	0	10.6	34	25.9	21	25	24	34
0.06	0.9	0.4	23	16	–	–	–	–
0.1	1.4	0.9	14.8	0	17.5	0	31	12
0.2	2.8	2.1	13.8	0	24	0	28	20
0.3	2.9	2.4	17	0.8	–	–	–	–
0.43	–	–	–	–	19.4	1.7	22	29
0.6	2	2.9	18.5	3	–	–	–	–
1.1	5.5	5	20.5	4.8	23	6.1	30	29
1.8	2.8	7	32.4	1.8	24	0	20	11
3	2.5	7	26.6	0	30	0	8.8	15.2
4.3	3	7	29.0	0	10.4	0	33	14.9
4.9	3.5	–	39	8.9	23	0	12.5	3.5
6.1	4	–	59	0	19.8	0	26	5.9

[a] $c_{Sm} = 0.0031$, $c_{Lu} = 0.0028$, $c_{Nd} = 0.005$, $c_{Yb} = 0.005$ M; $c_{\mathbf{I}} = 0.025$ M, phase ratio 1:1.

aqueous perchlorate media, because the relatively low hydration energy of perchlorate ion provides greater efficiency of extraction complexes and ion associates with the weakly hydrated perchlorate ion, in comparison with similar compounds containing the nitrate and chloride ions.

We have studied the effect of perchloric acid and sodium perchlorate concentration on the degree of extraction of ions Sm(III), Lu(III), Dy(III), Yb(III), and Nd(III). For the extraction processes from perchlorate medium an increase in the degree of the metal extraction with increasing acid concentration in the aqueous phase is typical. This effect is significantly higher than that achieved in the hydrochloride and nitrate aqueous solutions. As an example, Fig. 2 shows the dependence of degree of lanthanide ions extraction on the concentration of perchloric acid at the extraction with the toluene solution of the reagent **I**. Similar relationships were obtained using two other dilutents, chloroform and methylene chloride.

As mentioned above, the degree of extraction from perchloric acid solutions was significantly higher (80%) than from hydrochloric and nitric acid (10–30%). A series of extractability of metals at the acid concentration 0.25–0.5 M is Nd > Sm > Dy > Yb> Lu that corresponds to a sequence of decreasing ionic radii of lanthanides (*r*, Å): 0.995, 0.964, 0.908, 0.858, 0.848, respectively. This is consistent with the published data [2] on the increase in the degree of extraction with increasing ionic radius at the extraction of rare earth elements by neutral organophosphorus compounds: The increase in the degree of extraction of elements of the cerium subgroup placed before europium and then the decrease to lutetium.

In the system we studied we observed an increase in the degree of extraction of ions with increasing concentration of perchloric acid. It is noteworthy that at low pH better extraction of lutetium occurs compared to samarium, and at the concentration 0.15 M begins better extraction of samarium. The reason for this, as discussed below, may be the change in the mechanism of extraction of lanthanides in this region of acidity.

We calculated the metal partition coefficients at the extraction of scandium with the reagent **I** from perchlorate media. As an example, Table 3 shows the dependence of partition coefficients on the perchloric

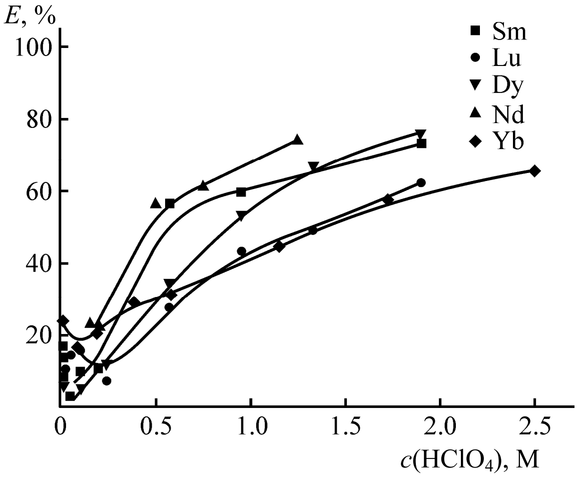


Fig. 2. Dependence of the degree of extraction of Sm, Lu, Dy, Yb, and Nb with reagent **I** (c = 0.025 M) on the HCl concentration. c_{Sm} = 0.0032, c_{Lu} = 0.0028, c_{Nd} = 0.0062, c_{Yb} = 0.0057 M; diluent toluene, phase ratio 1:1.

acid concentration. As seen, the highest separation factors for all the studied metals were obtained with toluene as a diluent.

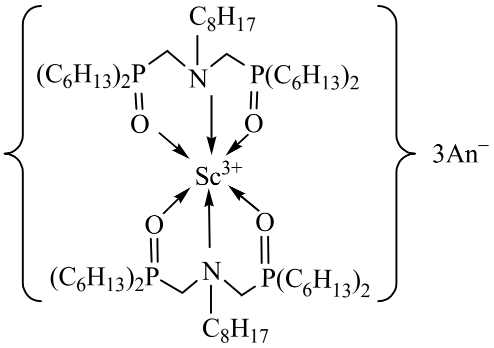
In order to assess the contribution of competing co-extraction of the used acid by aminophosphinyl reagents, we have studied processes of extraction with the reagent **I** of the ions Lu(III), Dy(III), Nd(III), and Yb(III) from aqueous solutions of sodium perchlorate, while the concentration of hydrogen ions in aqueous phase was kept constant (0.01 M). As follows from the data in Fig. 3, in the absence of competitive protonation of the reagent in the extraction system the degree of extraction of dysprosium increases significantly (~90%) even at low concentrations of the perchlorate ion. A similar character of changes in dependence in the processes of extraction from perchlorate aqueous media was found for other metals.

Table 2. Partition coefficients[a] at the extraction with 0.025 M solution of reagent **I** in toluene and chloroform from solution in HNO_3 ($V_{\mathrm{aq}}/V_{\mathrm{org}}$ = 1)

$c(HNO_3)$, M	$K^{\mathrm{Sc/Sm}}_{\mathrm{partit}}$	$K^{\mathrm{Sc/Lu}}_{\mathrm{partit}}$	$K^{\mathrm{Sc/Sm}}_{\mathrm{partit}}$	$K^{\mathrm{Sc/Lu}}_{\mathrm{partit}}$
	toluene		chloroform	
0	1.16	1.70	0.485	0.398
0.123	36.0	387	0.323	$>10^4$
0.184	77.7	$>10^4$	0.228	$>10^4$
0.430	34.2	$>10^4$	0.894	12.2
1.12	4.53	43.9	1.88	8.81
1.80	0.895	$>10^4$	1.24	$>10^4$
3.04	1.22	$>10^4$	0.718	$>10^4$
4.26	0.766	$>10^4$	2.26	$>10^4$

[a] $K = D_{\mathrm{Sc}}/D_{\mathrm{M}}$, M = Sm(III), Lu(III).

According to earlier results [11], the reagent **I** can be regarded as neutral tridentante ligand which forms complex **A** with the scandium ion of 1:2 composition.



A

It can be assumed that the extraction of scandium from perchlorate solution proceeds in accordance with Eq. (1) suggesting that the extractable compound is an ionic associate consisting of the scandium atom bound to form a chelate ring with two molecules of reagent and three anion species.

$$Sc^{3+} + 2[\mathrm{APO}]_{\mathrm{org}} + 3ClO_4^- \rightarrow \{[\mathrm{ScAPO}_2]^{3+}\cdot 3(ClO_4)^-\}_{\mathrm{org}}. \quad (1)$$

We attempted to study composition of the extracted complex of samarium(III) with phosphine oxide **I** and to find its stoichiometry using the method of equilibrium shift, which consists in the construction of bilogarithmic dependence of the distribution coefficient of the reactant concentration in the organic phase. The solvation number, according to Eq. (2) is equal to the slope of the dependence of log D vs. log c_{R}, where D is the distribution coefficient, c_{R} is the concentration of the reagent in the organic phase.

$$\log D = \mathrm{const} + q \log c_{\mathrm{R}}. \quad (2)$$

However, the fact should be taken into account that the increasing concentration of the extractant is often accompanied by changes in the slope of the dependence in these coordinates. Therefore, the coefficient q as a rule is determined at low concentrations of extractant, which, however, does not guarantee obtaining

Table 3. Partition coefficients[a] at the extraction with 0.025 M solution of reagent **I** in toluene, chloroform, and metylene chloride ($V_{aq}/V_{org} = 1$)

$c(HClO_4)$, M	$K_{Sc/Lu}$	$K_{Sc/Dy}$	$K_{Sc/Sm}$	$K_{Sc/Lu}$	$K_{Sc/Dy}$	$K_{Sc/Sm}$	$K_{Sc/Lu}$	$K_{Sc/Dy}$	$K_{Sc/Sm}$
	toluene			chloroform			metylene chloride		
0.005	214	>10^4	1040	1.11	43.4	2.00	21.6	101	388
0.01	34.1	>10^4	539	2.54	>10^2	3.80	32.8	>10^4	25.2
0.02	535	100	9.84	4.10	>10^2	4.52	22.7	664	66.4
0.05	903	>10^4	2160	2.12	587	4.50	26.5	538	29.0
0.1	>10^4	610	>10^4	4.14	>10^4	3.48	33.9	84.6	20.3
0.2	3140	180	992	6.61	8.97	7.77	79.7	88.2	15.9
0.572	6550	470	1910	13.6	7.14	3.33	>10^4	>10^4	59.9
0.953	255	304	134	10.4	7.12	3.70	27.2	23.6	34.1
1.91	71.8	111	216	15.5	9.40	5.98	>10^4	>10^4	18.7

[a] $K = D_{Sc}/D_M$, M = Sm(III), Lu(III), Dy(III).

true solvation numbers for the region of high concentrations of the extractant [23].

Unfortunately, in this case the bilogarithmic plot obtained is not linear indicating the formation of several compounds in the two-phase extracting system, and their stoichiometry cannot be determined adequately. The attempted use of an alternative method based on constructing the extraction isotherm, that is, a dependence of the metal content in the organic phase on the concentration in the aqueous phase at a constant concentration of the reagent, also was not successful. It turned out that in some cases with increasing concentrations of metal ions in the two-phase system a third phase is formed as a fine dispersion.

Establishing the mechanism of extraction processes is not a simple task even for simple monodentate ligands such as tertiary phosphine oxides and tertiary aliphatic amines, and hitherto it remains an incompletely solved problem. As for the complexes of rare earth elements with polydentate ligands, the problem is complicated due to the fact that these metals can form complexes with coordination number greater than 6.

In this connection, we have to note that it is impossible to draw any conclusions about the mechanism of extraction on the basis of the data on the effect of acidity of the aqueous phase on the degree of extraction of rare earth elements, since in our case the studied reagent contains three donor centers of different nature: two phosphine oxide and one amino groups.

The interpretation of our results should be based on the assumption that only electrically neutral particles can transfer in the organic phase, and that the extractant, being highly lipophilic, has no noticeable effect on the processes occurring in the aqueous phase. We can therefore assume that the formed metal complex with the tridentate ligand **I** occupying six

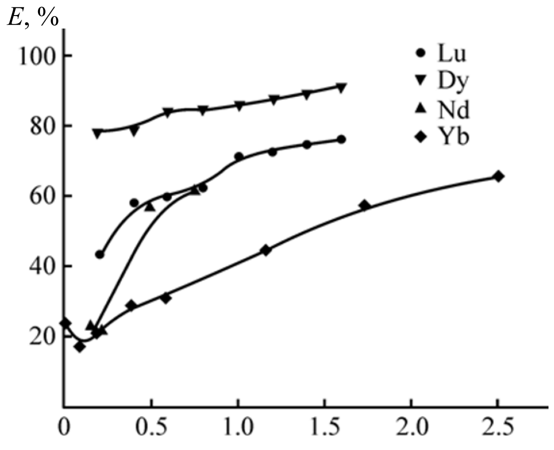
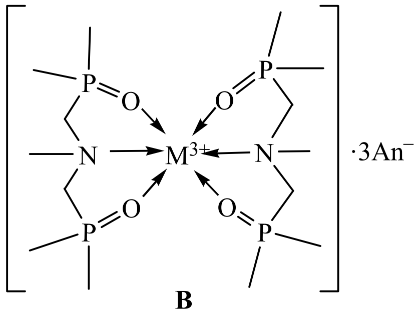


Fig. 3. Dependence of the degree of extraction of Lu, Dy, Nd and Yb with reagent **I** on the concentration of $NaClO_4$. $c_{Lu} = 0.0046$, $c_{Dy} = 0.0051$, $c_{Nd} = 0.0062$, $c_{Yb} = 0.0057$ M; diluent toluene, $c_I = 0.025$ M, phase ratio 1:1.

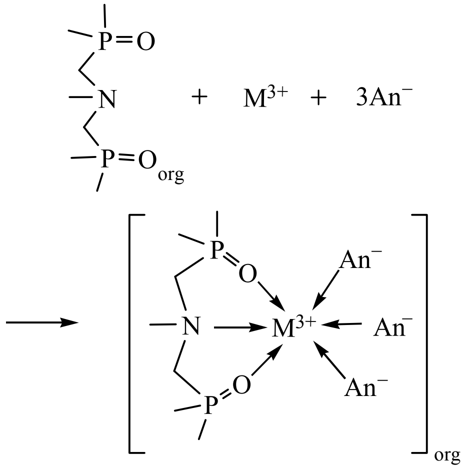
coordination sites passes in the organic phase as an ion associate **B** with three anions of acid.



B

$An^- = NO_3^-, Cl^-, ClO_4^-$.

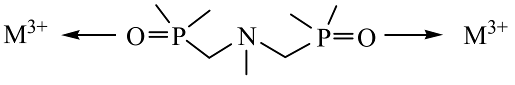
However, there is also a probability of formation of a mixed-ligand complex **C** of 1:1 metal–ligand **I** composition, in which the donor nitrogen and oxygen atoms of the reagent occupy three coordination sites and the acid anions occupy another three sites.



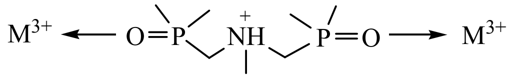
C

In addition, it is not possible to exclude the formation of ionic associates by the protonated extractant $[HAPO]^+$ and anionic complex particles formed by the ion of the extracted metal and anions of mineral acid, for example, $\{[HAPO]^+·[M^{3+} An_4]^-\}$.

A probability should be taken into account of the coordination with the formation of bi- or polynuclear complexes with the neutral or protonated reagent acting as a bridging ligand, **D** and **E**.



D



E

Based on the foregoing, we can assume that with increasing acid concentration in the aqueous phase the studied systems will undergo the changes leading essentially to the gradual replacement of the extraction reagent in the inner coordination sphere of metal ions by anions of inorganic acid. In this case, the formation of complexes of **B** type occurs at low acid concentrations, when the fraction of free agent in the organic phase is high. Such a mechanism is most probable at the extraction from the perchlorate media because of the weak complexing properties of this anion.

In the region of higher concentrations of acid, the formation of complexes of **C** type is more likely, since in this region the concentration of neutral reagent in the organic phase and acid anion in the aqueous phase is quite high. The probability of this mechanism is high in the cases of perchloric and hydrochloric acids. In the latter case, this is due to weak competition of the acid co-extraction and its higher ability of the complex formation compared with the nitrate and perchlorate media.

The extraction of metal ions along the outer-sphere mechanism **D**, when the composition of the extracted species includes the protonated ion of the ligand, should occur at high concentrations of inorganic acids, when the concentrations of H^+ in water phase is high and the proportion of free (non-protonated) reagent in organic phase is low.

The investigation of extraction properties of azapodands **II** and **III** has been carried out only on a low number of extraction systems because of their relatively difficult synthetic accessibility. The dependence of the degree of extraction of lutetium(III) with the reagents **II** and **III** on the perchloric acid concentration in the aqueous phase using 0.025 M solutions of these compounds in toluene, chloroform, and methylene chloride revealed their qualitative similarity, the variation of diluents also did not change the overall picture of the degree of dependence of the metal extraction on the concentration of perchloric acid. For this reason, this paper describes only the results of experiments shown in Fig. 4. It is seen that the degree of extraction of lutetium is maximum at the minimum concentration of perchloric acid (~0.01 M), and then a decrease occurs and further monotonic increase of extraction up to 2 M, which agrees well with the data on the extraction of perchloric acid with the solutions of reagent **I** in the same solvents. In general, there is a similarity of the obtained dependences of the Lu(III) extraction degree on the concentration for all three chemicals investigated in this paper.

We can assume that the extraction of lanthanides proceeds by a similar mechanism, but the limitations of the experimental results do not allow to judge reliably about the nature of the extracted azapodand complexes. The relatively difficult synthetic accessibility of new azapodands **II** and **III** also does not lead to optimistic prediction of their application: on this way multistage synthetic processes exist unsuitable technologically. It should also be emphasized that the use of aqueous hydrochloric and nitric acid media in the potential hydrometallurgical processes of lanthanide extraction with the aminophosphinyl extractants cannot be regarded as reasonable, since the degree of extraction of metals in these extraction systems is low. However, it can be stated that the bisphosphorylated amine **I** can be used in liquid extraction technology for the group extraction and concentration of lanthanides from solutions in perchloric acid with a number of organic diluents. In this case, as discussed previously [11], it shows a high selectivity on scandium, and in some cases on pairs of rare-earth ions.

EXPERIMENTAL

We used as solvents toluene (analytical grade), chloroform (reagent grade), methylene chloride (reagent grade). The solutions of the reagents in organic solvents were prepared using precise weighing. The rare earth elements nitrates and chlorides were of reagent and analytical grade. The metal perchlorates were prepared by precipitation of the element hydroxide from the corresponding metal nitrate solution with 25% solution of ammonia by adding it to pH 9, followed by dissolving the precipitate in the studied concentrated acid. The exact concentration of metal in the obtained solution was determined by complexometric titration. In an Erlenmeyer flask was placed 2 ml of metal salt, 2 ml of acetic acid–acetate buffer, pH 6.04, xylenol orange indicator (2–3 drops), and 50 ml of distilled water, and the mixture was titrated with Trilon B with concentration of 0.005 M (0.01 N) [24].

To create the desired acidity, in the solution was added hydrochloric, perchloric, or nitric acid of reagent grade, working solutions were prepared in double-distilled water. The acid–base titration of mineral acids was carried out using a 10 ml burette, the pH changes were recorded with a laboratory pH-ionomer 150MI by measuring the potential of glass electrode relative to a silver chloride electrode. We used the following equipment: an installation for the mechanical shaking AVU 6c, a centrifuge OP 8UHL4.2, an ionomer pH 150MI (Russia), an X-ray spectrometer X-Ray 3070E Rigaku (Japan). The degree of extraction was calculated from the data obtained by measuring the concentration of metals in aqueous and organic phases by X-ray fluorescence spectroscopy using the method described in [11].

The extraction of inorganic acids was carried out using solutions of aminomethylphosphine oxide in chloroform, methylene chloride, and toluene (0.05 M). We used glass tubes and the installation for the mechanical shaking, the shaking continued for 30 min. Phase separation was carried out by five-minute centrifugation at 2000 rpm. An aliquot of 2 ml was placed in a glass cell, 20 ml of water–isopropanol was added in a ratio of 1:3 by volume. Acid concentration in the organic phase was determined by potentiometric titration with 0.03 M solution of alkali in a water–isopropanol solvent mixture, titration curves were built in integral and differential forms. From the calculated equivalent volume of alkali was determined the equilibrium concentration of acid in the organic phase. On the basis of the data on the acid concentration in both phases the extraction isotherms were built.

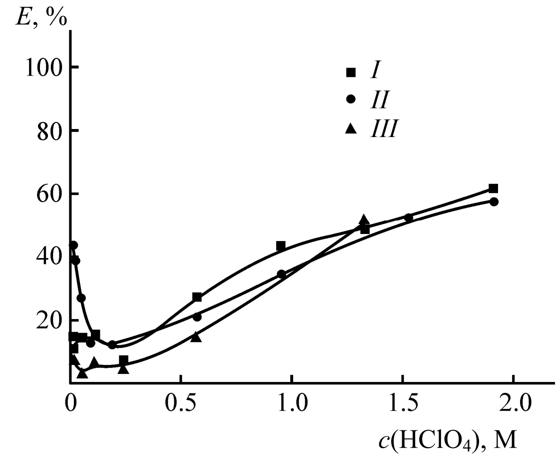


Fig. 4. Dependence of the degree of extraction of Lu with reagents **I–III** on the concentration of $HClO_4$. c_{Lu} = 0.0028 M, $c_{reagent}$ = 0.025 M, diluent toluene, water–organic phase ratio 1:1.

The extraction of metal ions was carried out at 1:1 by volume ratio of phases (2 ml) in glass tubes, mixing was carried out mechanically, the phase contact duration 30 min, then the aqueous and organic phase samples were centrifuged for 5 min.

Synthesis of aminomethylphosphine oxides was carried out according to three-component Kabachnik–Fields reaction. Method for the synthesis and characterization of the reagent **I** is given in [9]. Methods of synthesis and characterization of di- and tetraphosphinylpodands will be presented in one of the future publications.

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