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Extraction of lanthanide ions from acidic and strongly acidic media by phosphine oxide derivatives using temperature-induced phase separation*

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A composite for the extraction of lanthanide ions from strongly acidic media by temperature-induced phase separation was designed based on the nonionic surfactant Triton X-100 and new phosphine oxide derivatives. The dependence of the efficiency and selectivity of micellar extraction on the length of the hydrophobic substituent at the P=O group is determined by both the influence of hydrophobic substituents on the electron-donor capacity of the P=O group and the solubility of phosphine oxides in aqueous and micellar phases. The nitric acid concentration was found to influence the efficiency of extraction of lanthanide ions by phosphine oxides with different structures. An increase in the concentration of nitric acid in an aqueous medium from 0.1 to 1 mol L^{-1} leads to a decrease in the degree of extraction by water-soluble derivatives and a substantial increase in the degree of extraction by phosphine oxides, which are soluble only in the micellar phase of Triton X-100.

Key words: micelles, phase separation, lanthanide ions, phosphine oxides, extraction.

In the world practice, various procedures are used for the concentration and isolation of actinides and lanthanides based on the precipitation, adsorption, extraction, or micellar ultrafiltration.[1—4] The experience of nuclear waste disposal shows that the liquid-liquid extraction with the use of neutral organophosphorus ligands is currently the most efficient technique for the separation, isolation, and concentration of radioactive elements. However, the efficient liquid-liquid extraction requires large volumes of organic solvents, due to which this process becomes environmentally dangerous and necessitates the additional concentration of metals in the organic phase. In this connection, the improvement of the available extraction processes and the development of new techniques are of great scientific interest and practical importance.

In the last decade, several procedures were developed for the concentration and extractions of actinides and lanthanides with the use of a wide range of organic reagents (phosphates, phosphonates, phosphine oxides, and phosphomethylated calixarenes).[4—12] The main requirements imposed on extractants are the efficiency, the selectivity, and the possibility of the quantitative extraction of metal ions in a wide range of nitric acid concentrations. Mono- and bidentate phosphine oxides are the most promising extractants for the nuclear waste reprocessing and fractionation. These compounds are characterized by high stability combined with unique complex-forming properties. They have attracted interest as extractants also because their extraction ability substantially changes depending on the molecular structure. In terms of the Lewis theory, the phosphoryl group of phosphine oxides is a base, whose strength depends on the electron density at the phosphorus atom, *i.e.*, on the nature of its substituents. The basicity of phosphine oxides and, consequently, the complex-forming ability of this series of compounds can be varied by changing the natrue of the substituents. For monodentate phosphine oxides, it was found that the efficiency of extraction increases with increasing donor properties of the oxygen atom, which depend on the length of the alkyl substituent.[13] In addition, the extraction of Ln^{III} ions from nitrate solutions by neutral phosphorus-containing compounds is influenced by the structure of the substituent.[14] In the isomeric $Bu_2R'PO$ series, the degree of extraction decreases with increasing steric effect with a change of R´ in the series $Bu^n > Bu^i > Bu^s > Bu^t$. The strong steric effect that hinders the coordination of metal ions is observed for R´ = *cyclo*-C_6H_{11}. The analysis of the complex formation

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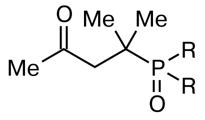
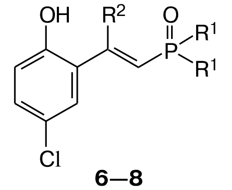
of lanthanides with the ligands $Me_3P{=}O$, $Me_2(MeO)P{=}O$, $Me(MeO)_2P{=}O$, and $(MeO)_3P{=}O$ showed[15] that the coordination to metal is much more strongly influenced by the steric effect than by a decrease in the basicity of the lone pair of the oxygen atom in the course of the successive replacement of the methyl substituents by methoxy groups.

However, in the case of organophosphorus compounds, this dependence was not always confirmed.[16] For example, the study of the extraction of Am^{III} and rare earth elements (REE) by bidentate organophosphorus reagents revealed the anomalous relationship between the extraction ability and the basicity of these compounds upon the replacement of the alkyl substituents by aryl groups and with increasing length of the alkylene bridge between phosphine oxide groups. It appeared that the replacement of alkyl substituents by aryl groups leads to an increase in the extraction ability of the compounds, which is inconsistent with the change in their basicity. An analogous dependence was found for a series of substituted *N*-phosphorylureas.[17] This phenomenon was first discovered by M. I. Kabachnik and K. B. Yatsimirskii[18] and was termed the anomalous aryl strengthening (AAS) effect. The AAS effect is attributed to the amphoteric nature of phenyl substituents, which can exhibit both electron-donating and -withdrawing properties depending on the nature of the complex-forming metal, the reagent, and the solvent. On the contrary, the AAS effect is not observed in the extraction by methylenebis(dibenzylphosphine) dioxide, in which the phenyl substituent is separated from the phosphorus atom by the methylene group. This fact is indicative of the π—π conjugation between the Ph substituent and the P=O group that occurs upon complex formation (a six-membered ring) and the electron density delocalization of the Ph group. In this case, the AAS effect is associated with the "aromatization" of the ring, *viz.*, the formation of a system of conjugated bonds, which argues in favor of the chemical (electronic) nature of this effect.[19]

Therefore, the data published in the literature provide evidence for a considerable influence of the structure of phosphine oxides on their extraction ability in the liquid-liquid extraction of actinide and lanthanide ions. However, the extension of a series of extractants by varying the structural features of phosphine oxides is to a great extent limited by the requirements for solubility of these compounds and their metal complexes in organic phases. In particular, the introduction of the 2-methyl-4-oxopent-2-yl moiety into phosphine oxides would lead not only to the better complex-forming ability of this series of compounds as a result of the formation of the second coordination site of metal ions but also to a substantial decrease in their lipophilicity. The extraction of rare earth elements by temperature-induced phase separation has been extensively developed in the last decades.[20—22] This method is unique in that it is environmentally friendly, simple, and rapid. In addition, a considerable advantage of this method is that compounds of different solubility (from hydrophilic to lipophilic) can be used as extractants. Hence, the aim of the present study was to investigate the extraction ability of new phosphine oxide derivatives **1—8** in micellar extraction of ions of the first (La), middle (Gd), and end (Lu) members of the lanthanide series.



1—5



6—8

R = Pr^n (**1**), Bu^n (**2**), n-C_5H_{11} (**3**), n-C_6H_{13} (**4**), Ph (**5**)

R^1 = Bu^n, R^2 = Ph (**6**),
R^1 = n-C_8H_{17}, R^2 = Ph (**7**),
R^1 = Ph, R^2 = Bu^n (**8**)

We chose phosphine oxides **1—8** as extractants with the goal of revealing the influence of the electronic and steric effects of substituents at the phosphorus atom, as well as of the solubility of phosphine oxide derivatives, on the efficiency and selectivity of micellar extraction of lanthanide ions.

Experimental

Phosphine oxides **1**, **2**, and **4—8** were synthesized according to known procedures.[22—25]

The ^{31}P-$\{^1H\}$ NMR spectrum was recorded on a Bruker CPX-100 instrument (36.48 MHz, ^{31}P) in $CDCl_3$ (25 °C) with H_3PO_4 as the external standard. The ^1H NMR spectrum was measured on a Bruker Avance-600 spectrometer (600 MHz, ^1H) in $CDCl_3$ (25 °C) with respect to the signals of the residual protons of the solvent. The IR spectrum was recorded in Nujol mulls on a Vector-22 Fourier-transform infrared spectrometer (Bruker). The mass spectrum was obtained on a TRACE MS Finnigan MAT instrument at the ionization energy of 70 eV and the ion source temperature of 200 °C. The heating of the vaporizer was programmed from 35 to 150 °C at a heating rate of 35 deg min^{-1}. The mass spectrometric data were processes with the use of the Xcalibur program.

Lanthanum(III), gadolinium(III), and terbium(III) nitrates (99.9%, Alfa Aesar) were used. The concentrations of Ln^{III} ions in the starting solutions were determined with Trilon B in the presence of the Thymol Blue and Xylenol Orange indicators.[26]

Phosphine oxide derivatives were dissolved in a 0.1 *M* Triton X-100 solution (TX-100). For all phosphine oxides, the initial solutions were prepared at concentrations in the range of 0.014—0.015 mol L^{-1}.

The micellar extraction was performed according to a procedure described in the study.[24] Solutions containing the nonionic surfactant Triton X-100 ($C_{TX\text{-}100}$ = 20 mmol L^{-1}), $Ln(NO_3)_3$ (C_{Ln} = 0.17 mmol L^{-1}), and chelating agents (phosphine oxide derivatives) at concentrations of 0.1—4 mmol L^{-1} were heated until they became turbid (to the so-called cloud point), resulting in the phase separation into a coacervate (heavier) phase and a phase containing a low surfactant concentration. The solutions were kept at this temperature for 15 min. In the presence of chelating agents, the cloud point for the TX-100 solution was 65±1 °C, which is close to the corresponding value for a TX-100 solution containing no additives. The pH value was varied by the addition of different amounts of nitric acid.

The phase separation was detected based on the appearance of the distinct interface. The ionic strength of the solutions was maintained constant ($I = 0.01$ mol L^{-1}). Then the solutions were cooled to 20 °C, which was not accompanied by the phase mixing. The aqueous phase was separated by decantation and analyzed for the lanthanide ion content by spectrophotometric technique in the presence of the Xylenol Orange indicator.[27] The degree of extraction (E) was calculated by the equation $E = 100 \cdot (A_0 - A_i)/A_0$, where A_0 is the absorbance of the starting lanthanide nitrate solution ($C = 1.7 \cdot 10^{-4}$ mol L^{-1}) and A_i is the absorbance of the solutions after extraction. These data were used for the calculation of the extraction constant (equilibrium (1)) by the graphical solution of Eqs (2) and (3).

$$m\mathrm{Ln}^{3+}{}_{(\mathrm{aq})} + n\mathrm{L}_{(\mathrm{aq})} = \mathrm{Ln}_m\mathrm{L}_{n(\mathrm{aq})}. \qquad (1)$$

According to equilibrium (1), the extraction constant (K_{ex}) and the logarithm of the extraction constant ($\log K_{\mathrm{ex}}$) were calculated by Eqs (2) and (3), respectively

$$K_{\mathrm{ex}} = [\mathrm{Ln}_m\mathrm{L}_n]/([\mathrm{L}]^n[\mathrm{Ln}^{3+}]^m), \qquad (2)$$

$$\log K_{\mathrm{ex}} = \log([\mathrm{Ln}_m\mathrm{L}_n]/[\mathrm{Ln}^{3+}]^m) - n\log[\mathrm{L}], \qquad (3)$$

where $[\mathrm{Ln}_m\mathrm{L}_n]/[\mathrm{Ln}^{3+}]^m = E/(1 - E)$ at $m = 1$, $[\mathrm{Ln}_m\mathrm{L}_n]$ is the concentration of the complex, $[\mathrm{Ln}^{3+}]$ is the equilibrium concentration of lanthanides in the aqueous phase, and [L] is the equilibrium concentration of the extractant.

All data reported in the present study are averaged results of at least two measurements.

(2-Methyl-4-oxopent-2-yl)dipentylphosphine oxide (3) was synthesized according to a known procedure.[22] The yield was 90%, transparent oil, b.p. 128 °C (0.055 Torr). Found (%): C, 66.63; H, 11.53; P, 10.74. $C_{16}H_{33}O_2P$. Calculated (%): C, 66.67; H, 13.03; P, 9.24. MS, m/z: 288 $[M]^{+\cdot}$, 273 $[M - CH_3]^+$, 245 $[M - C_2H_3O]^+$, 217 $[M - C_5H_{11}]^+$, 207 $[M - C_6H_9]^+$, 189 $[M - C_6H_{11}O]^+$, 175 $[C_9H_{19}OP]^+$, 147 $[C_7H_{16}OP]^+$, 134 $[C_6H_{15}OP]^+$, 99.0 $[C_6H_{11}O]^+$, 91, 83, 78, 55. IR, ν/cm^{-1}: 501, 526, 584, 642, 720, 783, 818, 861, 899, 942, 990, 1018, 1057, 1102, 1142, 1165, 1259, 1279, 1315, 1361, 1381, 1414, 1465, 1714, 2871, 2931, 2956. ^{1}H NMR, δ: 0.90 (br.t, 6 H, CH_3, $^3J_{\mathrm{HCCH}} = 7.3$ Hz); 1.29 (d, 6 H, CH_3, $^3J_{\mathrm{PCCH}} = 14.9$ Hz); 1.36 (m, 8 H, CH_2); 1.60 (m, 4 H, $PCCH_2$, A_2B_2 part of the $A_2B_2C_2D_2$ system); 1.72 (m, 4 H, PCH_2, C_2D_2 part of the $A_2B_2C_2D_2$ system); 2.18 (s, 3 H, CH_3); 2.69 (d, 2 H, CH_2, $^3J_{\mathrm{PCCH}} = 7.9$ Hz). ^{31}P-{^{1}H} NMR, δ: 52.24.

Results and Discussion

The extraction of metal ions by nonionic surfactants necessitates the use of a mediator capable of quantitatively binding hydrophilic cations and having affinity for the micellar phase.[28] Various chelating,[29,30] macrocyclic,[30] and cyclophane[31] ligands can serve as such mediators. Unlike the liquid-liquid extractions, ligands directly binding metal ions are called not extractants but chelating agents. We chose phosphine oxide derivatives **1**—**8** of different solubility as chelating agents. Thus, phosphine oxides **1** and **2** are soluble in water, whereas compounds **3**—**8** are soluble only in micellar solutions of Triton X-100 (TX-100).

The results of micellar extraction of lanthanum, gadolinium, and lutetium ions at a variable concentration of phosphine oxides **1**—**5** and pH 1 (corresponds to 0.1 M HNO_3) are presented in Figs 1—3. These data provide evidence that, first, a noticeable degree of extraction is observed even at low concentrations of the chelating agent, second, the structure of phosphine oxide has a substantial effect on the extraction ability in micellar extraction of

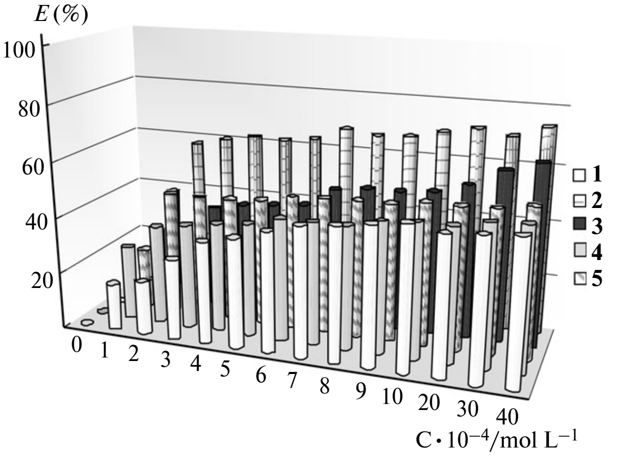


Fig. 1. Dependence of the degree of extraction of La$^{\mathrm{III}}$ ions on the concentration of phosphine oxides **1**—**5** in TX-100—phosphine oxide—Ln$^{\mathrm{III}}$ systems; $C_{\mathrm{Ln^{III}}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathrm{TX\text{-}100}} = 2 \cdot 10^{-2}$ mol L^{-1}, pH 1.

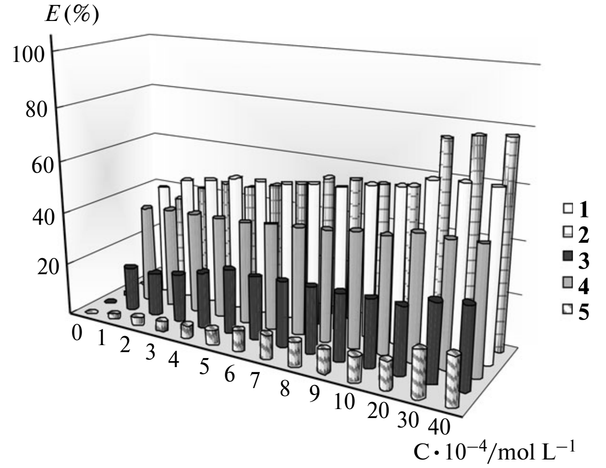


Fig. 2. Dependence of the degree of extraction of Gd$^{\mathrm{III}}$ ions on the concentration of phosphine oxides **1**—**5** in TX-100—phosphine oxide—Ln$^{\mathrm{III}}$ systems; $C_{\mathrm{Ln^{III}}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{\mathrm{TX\text{-}100}} = 2 \cdot 10^{-2}$ mol L^{-1}, pH 1.

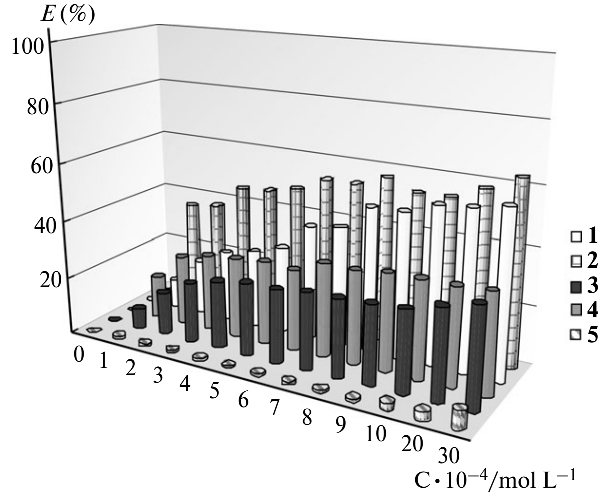


Fig. 3. Dependence of the degree of extraction of Lu^{III} ions on the concentration of phosphine oxides **1**—**5** in TX-100—phosphine oxide—Ln^{III} systems; $C_{Ln^{III}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{TX\text{-}100} = 2 \cdot 10^{-2}$ mol L^{-1}, pH 1.

lanthanides, and third, the common tendency is observed for lanthanum, gadolinium, and lutetium. Thus, water-soluble phosphine oxide **2** is the most efficient extractant for all the metals in the above-mentioned conditions.

Therefore, compound **2** was found to be the most efficient extractant in micellar extraction. However, this compound should be considered as the group extractant due to the low selectivity in the series La—Gd—Lu (Fig. 4). A universal dependence of the extraction ability on the length of the hydrophobic substituent at the P=O group was not revealed for all the metal ions under study, because the solubility of the ligand and the related complex depends not only on the electron-donating effect but also on the length of the hydrophobic substituent. Hence, it should be noted that the extraction of metal ions by water-soluble and lipophilic ligands occurs by different mechanisms. Thus, complexes of water-soluble ligands with lanthanide ions are formed in an aqueous phase, whereas lipophilic ligands coordinate metal ions in a polar layer of micelles. In addition, we found the conditions for the selective micellar extraction for the series La^{III}—Gd^{III}—Lu^{III} in 0.1 *M* HNO_3. Phosphine oxide **5** containing the phenyl substituent (see Fig. 4) is the most selective extractant in the lanthanum—gadolinium—lutetium series. Thus, the degree of micellar extraction of La^{III} ions by extractant **5** is approximately 4.5 times higher than the corresponding values for Gd^{III} and Lu^{III} ions. Phosphine oxide **3** is the second most selective extractant. The selectivity of the other phosphine oxides is low.

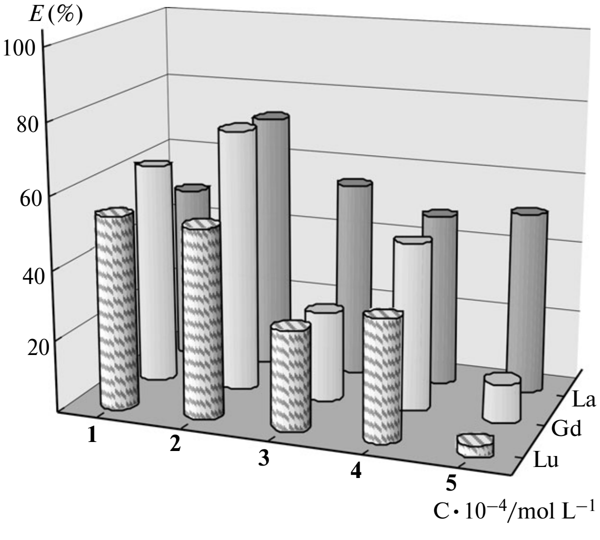


Fig. 4. Degrees of extraction of lanthanide ions by phosphine oxides **1**—**5** in TX-100—phosphine oxide—Ln^{III} systems; $C_{Ln^{III}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{TX\text{-}100} = 2 \cdot 10^{-2}$ mol L^{-1}, the concentration of phosphine oxides was $2 \cdot 10^{-3}$ mol L^{-1}, pH 1.

It should be noted that, as can be seen from Fig. 4, the presence of phenyl substituents at the phosphorus atom does not lead to an increase in the degree of extraction. Therefore, the AAS effect is absent in this series of phosphine oxides. Apparently, this can be attributed to the fact that the carbonyl oxygen atom in the phosphine oxides under consideration is distant from the P=O group (the absence of π—π conjugation) and the coordination to lanthanide ions cannot lead to the chelate ring formation.

It is known[32] that the protonation of phosphine oxides has a substantial effect on their extraction ability in acidic media. In this connection, we investigated the influence of the nitric acid concentration in the range from 0.1 to 1 mol L^{-1} on the extraction of lanthanide ions.

According to the published data, the dependence of the degree of liquid-liquid extraction of 4f and 5f ions by phosphine oxide derivatives has an extreme character[33] due to the counteraction of different forces. Thus, the more efficient salting-out effect leads to an increase in the degree of extraction with increasing nitric acid concentration, whereas the protonation results in a decrease in the degree of extraction. Even a more complex effect of counteracting forces would be expected in micellar extraction. It will suffice to mention the effect of nitric acid on the morphology of micellar aggregates, which, in turn, influences their solubilization capacity.[34] An important fact is that the oxyethyl chains of TX-100 are protonated, resulting in a decrease in their affinity for lanthanide complexes. It whould be expected that the influence of the nitric acid concentration will depend on the structure of phosphine oxide.

Let us consider phosphine oxides **6**—**8** containing a variable substituent at the P=O group. Earlier, we have used phosphine oxides **6**—**8** as chelating agents for the extraction of La, Gd, and Lu in 0.1 *M* nitric acid.[24] Since phosphine oxide derivatives **6**—**8** are insoluble in water, a comparison of the extraction data for these compounds

Table 1. Degrees of extraction of lanthanide ions (E (%)) in TX-100—Ln^{III}—phosphine oxide systems (**1—8**)* at different nitric acid concentrations

Phosphine oxide	REE	[HNO$_3$]/mol L^{-1}									
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1	La	49	46	35	22	26	68	50	22	36	43
	Gd	62	59	50	38	59	39	47	59	41	35
	Lu	54	46	39	58	60	59	77	57	59	39
2	La	72	72	11	26	49	56	62	5	68	67
	Gd	74	27	29	11	17	26	7	9	11	48
	Lu	53	54	66	70	70	82	71	66	41	34
3	La	55	46	0	0	44	69	42	5	76	99
	Gd	26	49	34	28	38	53	79	60	64	71
	Lu	28	5	5	17	19	37	42	8	21	31
4	La	48	36	0	30	34	41	56	0	59	75
	Gd	47	42	42	47	50	61	58	34	12	60
	Lu	34	74	71	40	41	78	77	45	48	72
5	La	51	67	35	29	25	13	4	3	3	2
	Gd	11	49	35	37	12	17	17	18	16	16
	Lu	5	26	24	19	14	13	13	1	4	10
6	La	71	76	62	63	82	89	87	86	83	89
	Gd	40	36	39	32	27	17	38	27	37	26
	Lu	5	30	13	25	37	19	48	29	29	29
7	La	86	14	7	75	84	79	50	20	0	0
	Gd	50	40	39	56	67	87	79	68	7	5
	Lu	21	39	48	65	62	60	56	60	59	51
8	La	82	73	20	45	34	10	0	5	31	31
	Gd	59	22	0	9	21	25	0	26	30	37
	Lu	58	38	24	26	12	11	2	20	37	31

* The concentration of phosphine oxides **1—8** was $2\cdot10^{-3}$ mol L^{-1}, $C_{\mathrm{Ln^{III}}} = 1.7\cdot10^{-4}$ mol L^{-1}, $C_{\text{TX-100}} = 2\cdot10^{-2}$ mol L^{-1}.

provides information on the influence of the acidity of the medium on the degree of extraction depending on the structure of the hydrophobic substituent in phosphine oxides.

As can be seen from Table 1, the degrees of extraction of La^{III}, Gd^{III}, and Lu^{III} ions by phosphine oxide **6** containing *n*-butyl substituents remain almost constant over the whole range of nitric acid concentrations. The selective extraction of lanthanum is retained at any acidity. For phosphine oxide **7** (see Table 1) containing *n*-octyl substituents, the extreme character is also observed; however, unlike phosphine oxide **6**, the extrema at 0.3 and 1 *M* HNO$_3$ are substantially deeper. For the lutetium ion, the degree of extraction increases with increasing nitric acid concentration until the limiting value is reached.

A radically different situation is observed for phosphine oxide **8** containing phenyl substituents. In this case, the degree of extraction monotonically decreases with increasing nitric acid concentration for all the metals under consideration.

It should also be noted that not only the character of the dependence is different but also the selectivity in the series La—Gd—Lu changes depending on the nitric acid concentration. As can be seen from Fig. 5, phosphine oxides **6** and **7** selectively extract lanthanum ions at 0.1 *M* HNO$_3$, whereas at 1 *M* HNO$_3$ compound **7** is the most efficient extractant for lutetium ions. The selectivity of phosphine oxide **6** with respect to lanthanum ions substantially increases with increasing nitric acid concentration from 0.1 to 1 mol L^{-1}. The replacement of alkyl substituents at the P=O group by phenyl substituents (compound **8**) results in the absence of the selectivity in strongly acidic media, and the degree of extraction is at most 37%.

As mentioned above, phosphine oxide derivatives containing propyl (**1**) or *n*-butyl substituents (**2**) are soluble in water, whereas phosphine oxides containing *n*-pentyl (**3**), *n*-hexyl (**4**), or phenyl substituents (**5**) are soluble only in a micellar solution of TX-100. It is interesting to find out how the solubility of phosphine oxide influences the degree of extraction at different nitric acid concentrations.

As can be seen from Fig. 6, *a*, the dependence of the degree of extraction of La^{III} and Lu^{III} ions by water-soluble phosphine oxides remains unchanged with a change in the acidity of the solutions under study. The efficiency of extraction changes in the same fashion, whereas the degree of extraction of gadolinium by less soluble phosphine oxide **2** is lower compared with that of phosphine oxide **1** (see Table 1).

For water-insoluble phosphine oxide derivatives **3** and **4**, the degrees of extraction change non-monotonically (see

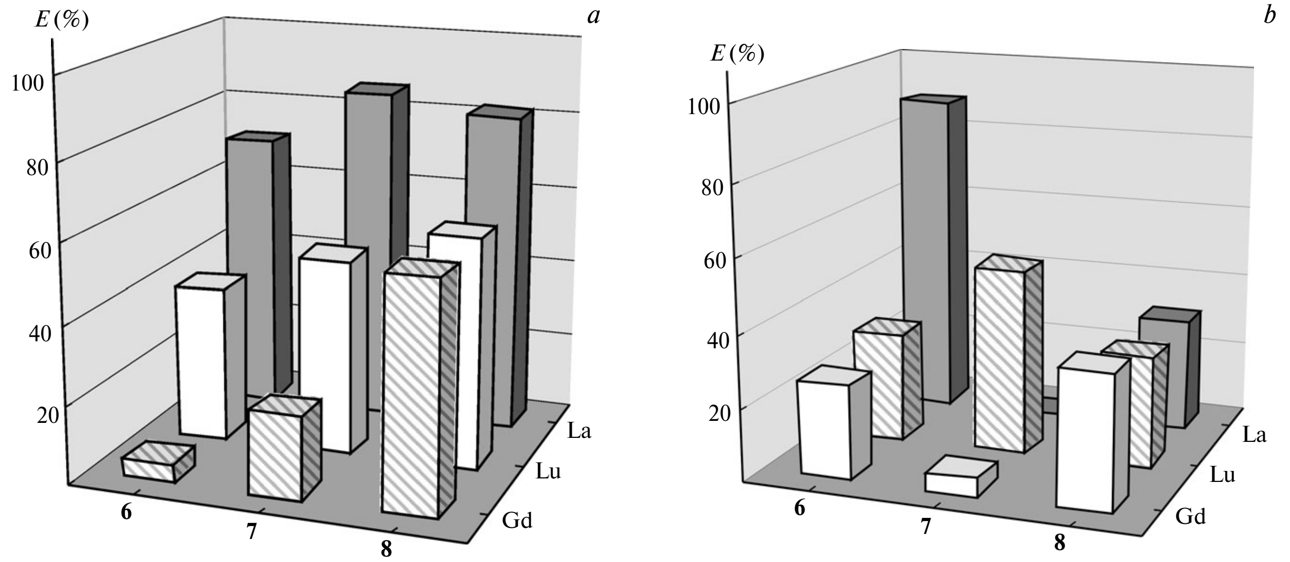


Fig. 5. Degrees of extraction of lanthanide ions by phosphine oxides **6—8** in TX-100—phosphine oxide—Ln^{III} systems in 0.1 *M* HNO_3 (*a*) and 1 *M* HNO_3 (*b*); the concentration of phosphine oxides was $2 \cdot 10^{-3}$ mol L^{-1}, $C_{Ln^{III}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{TX\text{-}100} = 2 \cdot 10^{-2}$ mol L^{-1}.

Fig. 6, *b* and Table 1), an increase in the length of the substituent at the phosphorus atom (from *n*-pentyl to *n*-hexyl) resulting in only a slight change in the efficiency of extraction of lanthanum, whereas the degree of extraction of lutetium being increased.

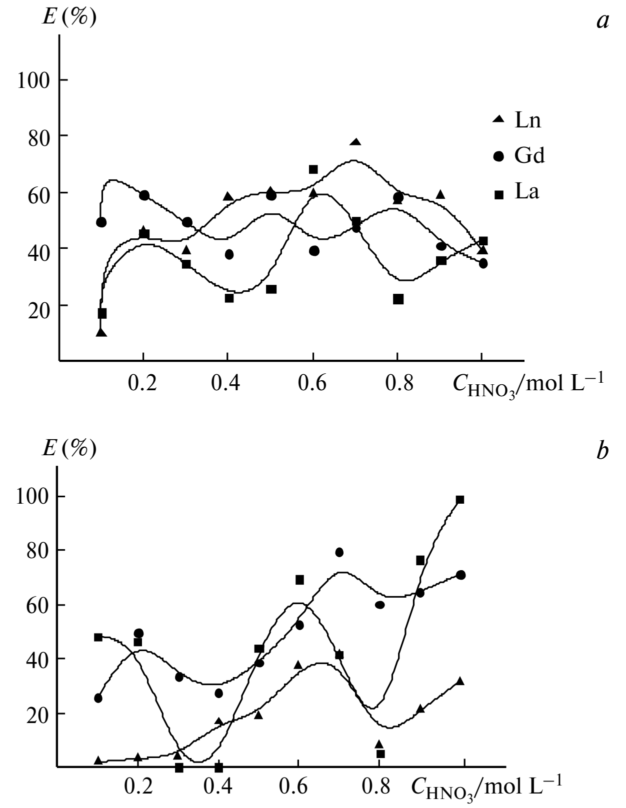


Fig. 6. Dependence of the degree of extraction of lanthanide ions by phosphine oxides **1** (*a*) and **3** (*b*) on the HNO_3 concentration in TX-100—phosphine oxide—Ln^{III} systems; the concentration of phosphine oxides was $2 \cdot 10^{-3}$ mol L^{-1}, $C_{Ln^{III}} = 1.7 \cdot 10^{-4}$ mol L^{-1}, $C_{TX\text{-}100} = 0.02$ mol L^{-1}.

In the case of the replacement of alkyl substituents by phenyl groups (compound **5**), the degrees of extraction of lanthanide ions decrease to 10% for La^{III} and Gd^{III} with increasing nitric acid concentration from 0.1 to 1 mol L^{-1}, whereas the degrees of extraction of Lu^{III} remain unchanged over the whole concentration range (see Table 1).

A comparison of the extraction ability of phosphine oxide derivatives **1—5** in 0.1 and 1 *M* HNO_3 shows (see Fig. 4 and Table 1) that the efficiency of extraction of lanthanide ions by water-soluble extractants decreases in strongly acidic media, whereas the extraction by phosphine oxides, which are soluble only in a micellar pseudophase of TX-100, substantially increases. However, this is not true for phenyl derivative **5**.

To conclude, the analysis of the above data shows that the extractant structure—extraction ability relationship is determined not only by the structure of phosphine oxides and their solubility but also by the nitric acid concentration. The influence of the nitric acid concentration on the degree of micellar extraction of lanthanide ions by phosphine oxide derivatives substantially differs from that observed in liquid-liquid extraction. It should be noted that the extraction behavior of phosphine oxide derivatives containing phenyl substituents at the P=O group is inconsistent with the anomalous aryl strengthening found for liquid-liquid extraction.

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