ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 1997–2004. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.R. Garifzyanov, S.V. Leont'ev, N.V. Davletshina, A.V. Voloshin, R.A. Cherkasov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 11, pp. 1796–1804.

Synthesis, Transport, and Ionophore Properties of α,ω-Biphosphorylated Azapodands: VIII.[1] Solvent Extraction of the Metal Ions with *N*,*N*'-Bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane

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Received January 14, 2013

Abstract—Liquid extraction from the aqueous solutions of perchloric acid with neutral azapodand extractant *N*,*N*'-bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane has been highly efficient in the cases of uranyl ions and some metals of groups II and III. To estimate the synergic effect of organophosphorus extractants, the neutral extractant was applied in the mixture with an acidic component, bis(pentadecyl)phosphoric acid. The synergic effect has exclusively been observed in the extraction of zinc and cadmium ions.

DOI: 10.1134/S1070363213110054

Podands form a wide class of acyclic supramolecular hosts with pendant binding sites. Previously, we have demonstrated that α,ω-diphosphorylated azapodands can serve as effective membrane extractants of mineral acids [1], the alkali and alkaline earth metal ions [2], Sc(III) and Nd(III) ions (via passive membrane transport), and Sr(II) and Ba(II) ions (via active membrane transport) [3]. Solvent extraction of different metal ions, although used in industrial extraction, concentration and separation of the hydrometallurgy resources, has remained unexplored with respect to phosphorylated azapodands as liquid extractant.

We herein fill this gap by reporting the features of solvent extraction of selected metal ions from aqueous perchloric or hydrochloric acid solutions. *N*,*N*'-Bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane (**I**) is a well known aminophosphoryl extractant, effecttive and selective membrane carrier of the metal ions [2, 3]. Furthermore, we have investigated the possibility of using azapodand **I** as a component of synergic extraction composition with acidic extractant, bis(pentadecyl)phosphoric acid (**II**).

The use of synergic extractants in liquid extraction, concentration, and separation processes is a remarkable trend in modern laboratory and industrial technology. The commonly used phosphorus-containing synergic extraction reagents are mixtures of acidic and neutral phosphorus acids esters: tributyl phosphate or trioctylphosphine oxide, phosphorus mono- and dithioacids, and diorganylphosphates of the Cyanex group [4, 5]. The pronounced synergic effect of phosphorus-containing multicomponent extractants has inspired researchers to develop new efficient metal ions extraction technologies basing on such mixtures [6–8].

We studied solvent extraction of a series of metal ions ($c_M^{n+} = 2\times10^{-3}$ mol/L) from aqueous medium with toluene solution of **I** at varied pH of the aqueous phase adjusted with perchloric acid. Preliminary experiments revealed that the highest extraction degree of metal ions was reached in perchlorate media. Noteworthily, perchlorate media are widely applied in industrial hydrometallurgical extraction as well. Perchlorate ion is more hydrophobic as compared with other inorganic anions, thus, providing sufficiently high degree of metal ions transfer to the organic phase.

The data on extraction degree of metal ions of the groups I–II and other selected doubly charged cations at different concentrations of perchloric acid in aqueous phase is collected in Table 1 (values) and in Fig. 1 (plots). It is clear that the extraction degree was

[1] For communication VII, see [1].

Table 1. Degree of extraction of singly and doubly charged metal ions from perchlorate media with **I**, as function of the aqueous phase acidity

pH [c($HClO_4$)]	Li(I)	Co(II)	Ca(II)	Ba(II)	Ni(II)	Mg(II)	Sr(II)	Mn(II)	Cd(II)	Zn(II)
(7.41)	0	0	0	0	0	0	0	0	0	0
(3.63)	0	0	0	0	0	0	0	0	0	0
0.55	16.8	23.4	11.1	25.3	34.5	10.0	20.6	20.7	26.0	31.5
0.80	6.3	9.9	0	9.5	13.0	0	6.8	10.6	9.6	5.7
1.50	7.7	12.6	0	12.2	16.2	0.13	7.6	12.3	13.8	9.2
2.00	3.4	6.5	0	1.1	10.3	0	1.3	5.6	8.0	2.8
3.50	9.7	18.7	7.4	17.9	21.2	3.6	13.7	14.7	65.3	32.6
5.40	7.8	78.3	21.8	47.5	96	1.8	21.1	68.9	100	94.9
5.70	7.0	80.1	24.9	53.2	96	2.0	23.5	69.5	100	94.8
6.00	8.1	96.4	49.5	76.8	99	6.6	44.6	92.9	100	99.4
7.30	11.6	95.4	–	76.6	98	7.9	45.3	90.3	100	98.5

not monotonous with pH. At pH < 0.5 the extraction efficiency somewhat increased with pH, but as pH was increasing from 0.5 to about 2, the extraction degree reduced down. In the pH range below 2, the extraction efficiency of the ions followed the series Mg(II) < Ca(II) < Li(I) < Sr(II) ≈ Mn(II) < Co(II) < Ba(II) ≈ Cd(II) < Zn(II) < Ni(II). A further decrease of pH at pH > 2 caused monotonous increase in the metals extraction degree, except for Mg(II) and Li(I); the extraction efficiency leveled off at pH 5.3. Noteworthily, the extraction degree at weakly acidic media increased in a different order, Mg(II) < Li(I) << Sr(II) < Ca(II) < Ba(II) < Mn(II) < Co(II) < Ni(II) ≈ Zn(II) < Cd(II); for the four letter cations the extraction was practically quantitative.

Study of the triply charged lanthanide ions and UO_2^{2+} revealed a different trend (Table 2, Fig. 2): in the cases of all the studied lanthanide ions the extraction efficiency gradually increased with pH to reach about 20% at pH 2–3, and then grew abruptly, leading to practically quantitative extraction at pH of 4.7. In the whole pH range below 4.7, the uranyl ion extraction degree was much higher than that of the lanthanide ions, thus demonstrating remarkable selectivity of the azapodand **I** towards UO_2^{2+}.

In the case of group III metals, except for Sc(III), (Table 3, Fig. 3) a similar trend was observed: gradual increase of the extraction degree at pH < 2–3 (reaching 20–40% depending on the cation), and subsequent abrupt increase to about 90% at pH 5.4. At highest pH of the aqueous phase the solutions of triply charged metal ions became turbid, and the extraction process was poorly controlled. In the case of Sc(III) ions, much higher extraction efficiency was observed over the whole pH range, thus, azapodand **I** was extremely selective towards that cation; the same was characteristic of other aminophosphoryl carriers [9].

Obviously, the azapodand **I** is very promising for development of novel effective extractants for the group extraction of scandium and uranyl ions, and (to a lesser extend) of lanthanide ions.

In order to finding for an acid component of potential synergic mixture of the metal ions extractants, we studied the extraction properties of bis(pentadecyl)phosphoric acid **II** solution in toluene. The acid **II** is a long-chain analog of Cyanex 272 {bis(2,4,4-trimethylpentyl)phosphoric acid [10]}; the latter is widely used in industrial extraction. In general, dialkylphosphoric acids are relatively cheap and commercially available, thus they are widely applied in the practice of metal ions separation and concentration [11–13].

In the experiments involving **II**, we used aqueous solutions of hydrochloric acid as releasing medium. With increasing acidity, the extracted complex structure was supposed to change: instead of the dialkyl-

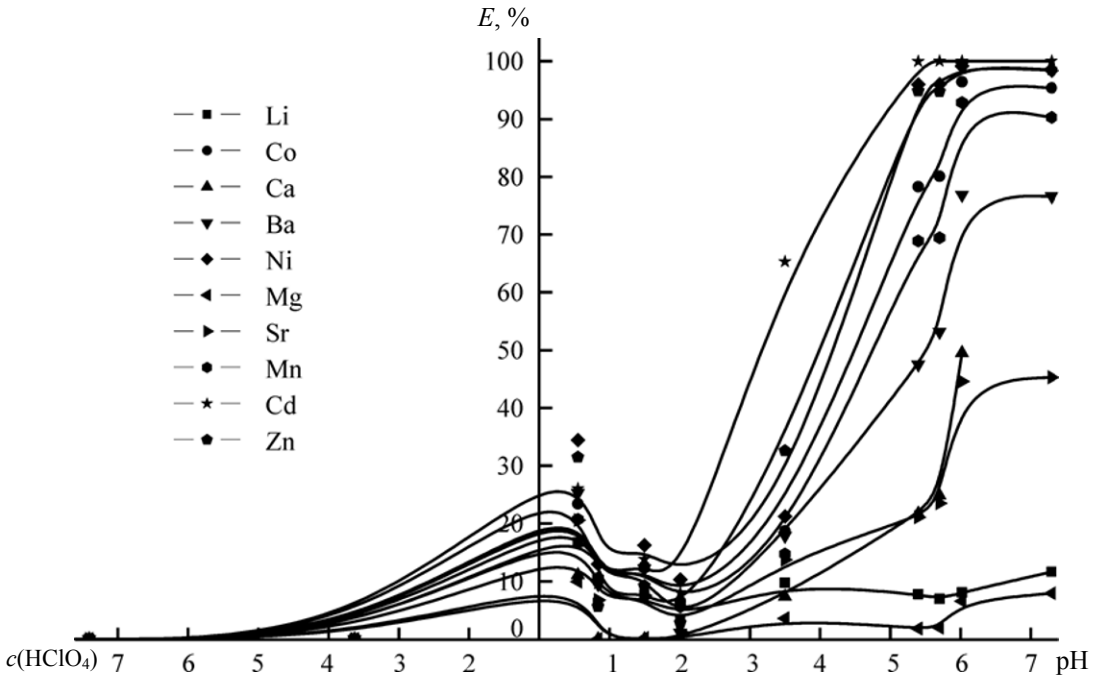

Fig. 1. Degree of extraction of singly and doubly charged metal ions from perchlorate media with **I**, as function of the aqueous phase acidity.

phosphate anion, the mineral acid anion acted as the complex counterion. In such case, using of more hydrophilic chloride anion was beneficial over more hydrophobic perchlorate anion.

From the plots in Fig. 4, the extraction degree of singly and doubly charged ions depended weakly on pH: at pH < 3.5, the extraction level did not exceed 13%. The only exception was Zn(II), revealing about 95% extraction at pH 3.3. Unfortunately, at higher pH the extraction of most of the ions was not possible: white clotted mass appeared throughout the whole sample, obviously, due to the formation of metal complexes with the ligand, sparingly soluble in toluene.

The efficiency of the extraction of triply charged large lanthanide cations followed the series Lu(III) < Gd(III) < Sm(III) < Nd(III) < Ce(III) < La(III) at lower

Table 2. Degree of extraction of lanthanide and UO_2^{2+} ions from perchlorate media with **I**, as function of the aqueous phase acidity

pH [c(HClO$_4$)]	La(III)	Ce(III)	Gd(III)	Lu(III)	Nd(III)	Sm(III)	UO_2(II)
(8.91)	2.6	2.1	1.7	1.7	2.3	2.1	48.5
(5.89)	6.3	6.0	6.3	6.3	6.4	6.8	39.0
(3.16)	5.9	5.0	5.1	5.1	5.8	5.3	33.7
0.60	20.0	19.2	17.6	15.3	18.0	17.0	80.5
1.40	23.8	21.6	19.4	18.3	19.7	16.7	93.4
1.80	22.8	20.6	17.9	15.8	19.4	15.9	96.3
3.25	23.7	24.1	21.3	31.3	22.4	21.1	97.0
3.90	76.5	88.2	78.2	68.2	90	89.4	99.95
4.65	97.5	99.1	98.2	96.9	99.3	99.3	99.7
5.20	89.3	91.5	73.0	83.0	87.8	82	99.6

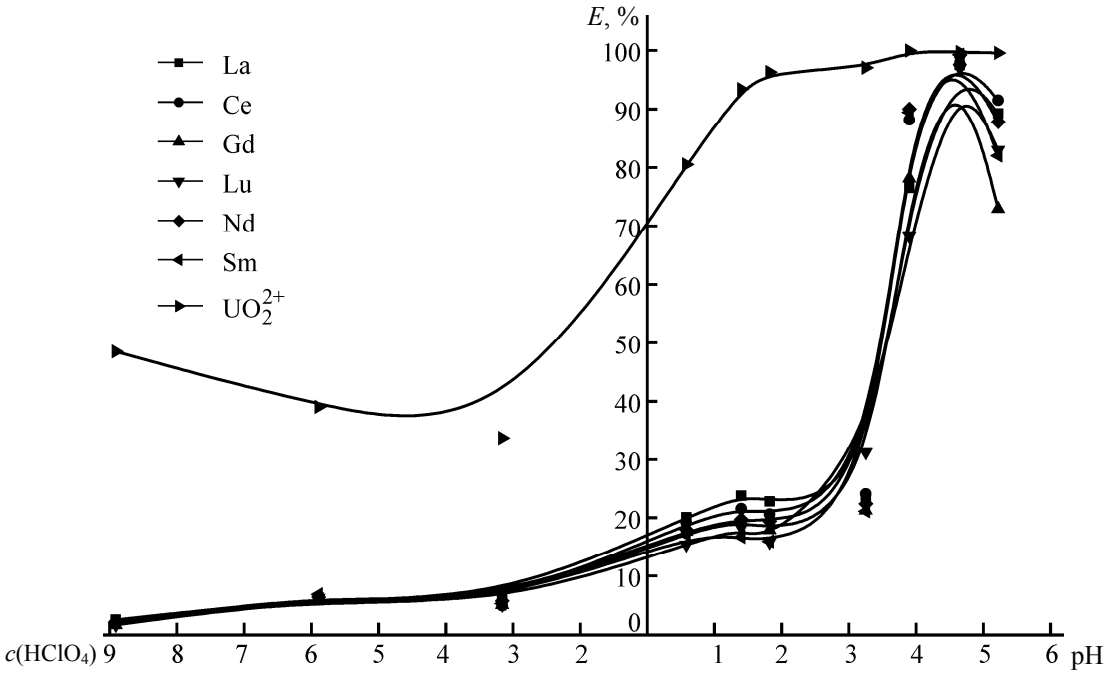

Fig. 2. Degree of extraction of lanthanide and UO_2^{2+} ions from perchlorate media with **I**, as function of the aqueous phase acidity.

pH of releasing aqueous hydrochloric acid medium. That row was consistent with the results of liquid extraction with bis(2-ethylhexyl)phosphoric acid reported in [6]. The extraction of triply charged metal ions (Table 4, Fig. 5) was efficient over fairly wide range of pH (0.5–5.2); the extraction of lutetium and uranyl ions was quantitative, in the cases of gadolinium and samarium the extraction degree reached 60–65%, being 50–56% in the cases of neodymium and cerium, and less than 39% in the case of lanthanum.

Table 3. Degree of extraction of group III elements and Fe(III) ions from perchlorate media with **I**, as function of the aqueous phase acidity

pH [c($HClO_4$)]	In	Ga	Al	Y	Fe	Sc
(13.2)	0	0	0	0	0	47.37
(9.1)	0	0	0	0	0	41.30
(6.3)	0	0	0	0	0	44.33
0.6	18.6	19.2	10.6	16.1	23.1	69.6
1.0	34.1	37.4	21.5	23	40.8	77.7
1.5	30.5	33.9	18.2	19	37.7	74.6
3.3	39.8	36.2	16.4	19.7	57.7	93.9
5.4	94.5	92.3	89.1	85.9	92.3	99.7

Thus, we conclude that the acid extractant **II** exhibited a pronounced selectivity towards triply charged, zinc, and uranyl cations being almost inert to alkali, alkaline earth, and other doubly charged cations.

In order to increase the extraction efficiency and selectivity, especially towards singly and doubly charged cations, we investigated the extraction of metal ions with a mixture of phosphoric acid **II** and neutral azapodand **I** in the ratio of 2 : 1 from aqueous hydrochloric acid solutions.

As followed from the results in Fig. 6 and Table 5, satisfactory degree of extraction was only obtained in the cases of Cd(II) and Zn(II), at the highest concentrations of hydrochloric acid in the aqueous phase; other cations were not extracted at pH < 2.3. The increase of pH was accompanied by a slight increase of Co(II), Mn(II), and Ni(II) recovery (up to 35–50%), degree of extraction of other metals was below 10%. Under similar conditions, recovery of cadmium and zinc ions was again the most complete: 99% of Cd(II) and 88% of Zn(II). Thus, the use of mixture of **I** and **II** did not reveal any pronounced synergic efficiency increase in the extraction of singly and doubly charged ions.

The studied mixture, however, was highly efficient in extraction of uranyl and lutetium ions, reaching almost quantitative recovery over wide range of acidity

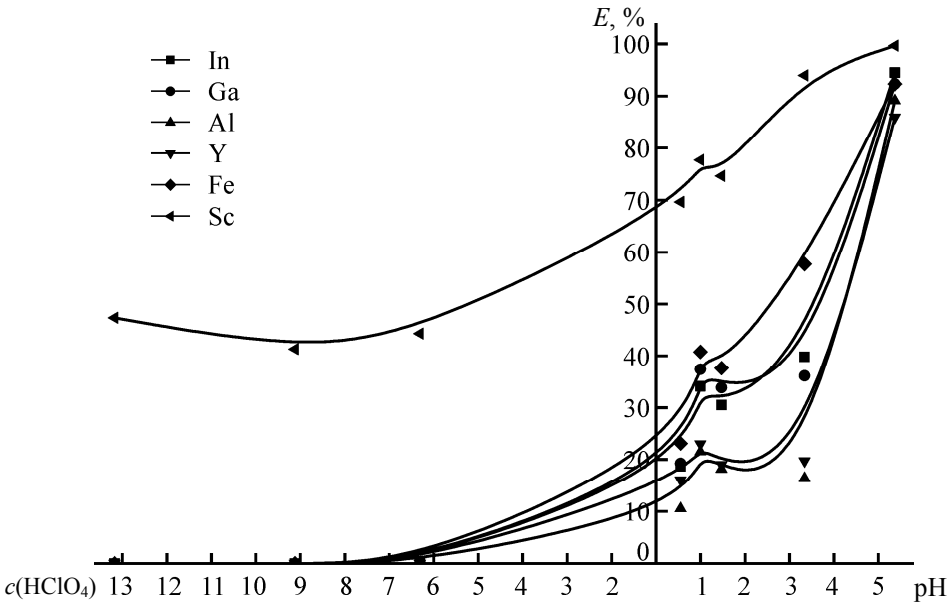

Fig. 3. Degree of extraction of group III elements and Fe(III) ions from perchlorate media with **I**, as function of the aqueous phase acidity.

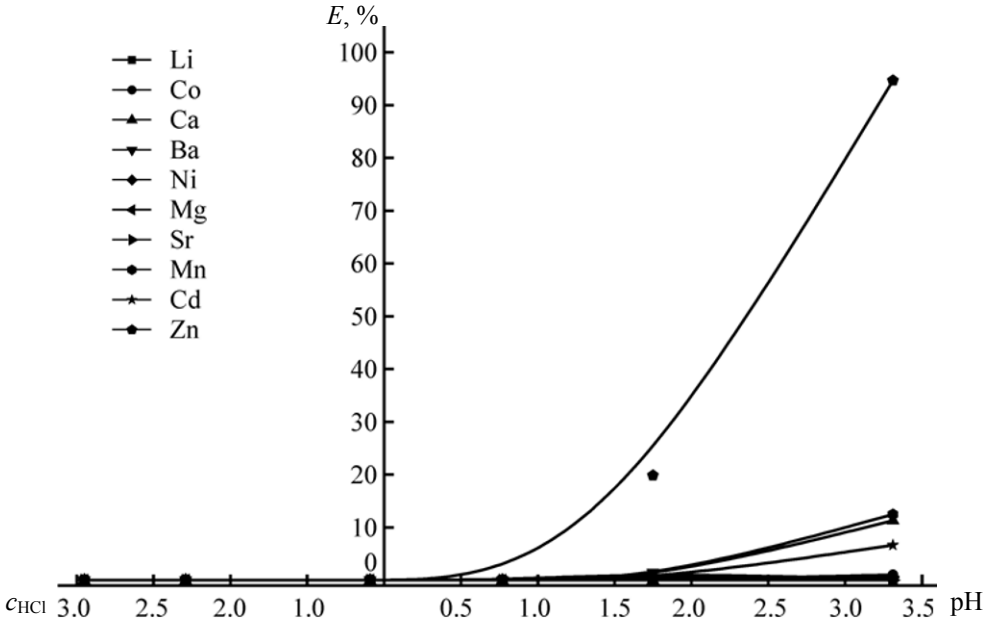

Fig. 4. Degree of extraction of singly and doubly charged metal ions from aqueous hydrochloric acid media with **II**, as function of the aqueous phase acidity.

(Table 6). Some of the triply charged cations were recovered efficiently in weakly acidic medium: at pH of 5.1, the extraction degree reached 85.3% of In(III) and 98.4% of Y(III). The ions of Ga(III), Fe(III) and Al(III) were extracted with lesser efficiency at the same pH (38–42%); the degree of extraction was slightly lower than those in the case of azapodand **I** alone (Table 2). Sc(III) ions were extracted quantitatively over the whole range of the studied pH.

The synergic effect in the extraction with a binary mixture of reagents was quantified by calculating the coefficients of synergy $K_s = E_{mix}/\Sigma E_i$, with E_{mix} being degree of extraction with a mixture of **I** and **II**,

Table 4. Degree of extraction of lanthanide and UO_2^{2+} ions from aqueous hydrochloric acid media with **II**, as function of the aqueous phase acidity

pH (c_{HCl})	La(III)	Ce(III)	Gd(III)	Lu(III)	Nd(III)	Sm(III)	UO_2(II)
(3.6)	11.8	9.2	6.8	7.5	7.8	6.8	24.7
(2.5)	6.1	5.7	2.5	6.6	4.6	2.7	18.0
(1.2)	4	4.5	0.63	3.8	2.6	1.4	64.2
0.65	10.6	9.8	10.9	84	7.5	9.5	98.3
1.4	9.3	15.1	55.7	99.9	21.2	45.9	99.3
2.1	17.1	40.1	74.7	99.98	47.4	70.3	99.4
5.0	33.4	41.4	44.9	94.8	35.0	40.5	82.6
5.2	39.2	56.1	64.6	99	48.8	59.5	97.7

Table 5. Degree of extraction of singly and doubly charged metals with 2:1 mixture of extractants **II** and **I** as function of the aqueous phase acidity

pH (c_{HCl})	Li(I)	Co(II)	Ca(II)	Ba(II)	Ni(II)	Mg(II)	Sr(II)	Mn(II)	Cd(II)	Zn(II)
(4.0)	0	0	0	0	0	0	0	0	41.8	36.7
(2.4)	0	0	0	0	0	0	0	0	39.1	35.5
(1.1)	0	0	0	0	0	0	0	0	36.2	18.1
0.9	0	0	0	0	0	0	0	0	1.9	0
2.4	0	0	0	0	0	0	0	0	0	0
3.46	4.0	4.6	0	0	3.2	1.0	4.4	5.9	32.8	29.1
5.3	0.3	39.1	10.4	3.5	22.2	2.3	2.2	34.3	98.0	88.2
7.3	5.7	55.9	11.0	1.1	36.8	8.2	0	39.0	98.6	85.8

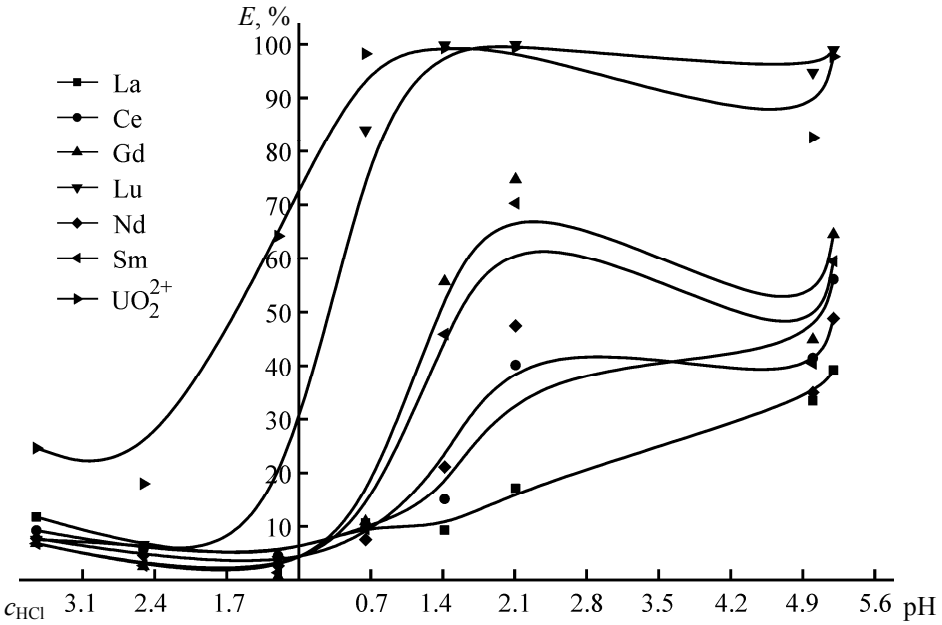

Fig. 5. Degree of extraction of lanthanide and UO_2^{2+} ions from aqueous hydrochloric acid media with **II**, as function of the aqueous phase acidity.

E_i being that for each component **I** and **II** acting separately. In the cases of lithium ions and most of doubly charged ions the values of K_s revealed little difference from no synergic effect, whereas in the cases of zinc and cadmium at c_{HCl} = 2.95 mol/L the synergy coefficients were of 2.3 (Zn) and 11.5 (Cd).

Efficiency of lanthanides extraction with the extractants mixture decreased in the series Lu(III) > UO_2(II) > Gd(III) > Sm(III) > Nd(III) > Ce(III) > La(III), corresponding to decreasing ionic radii. The series was practically the same in the cases of individual extractants; K_s did not exceed 0.7, which indicated no synergy.

To conclude, we observed high extraction efficiency of some doubly and, in particular, triply charged cations with neutral (**I**) and acidic (**II**) organophosphorus extractants. The synergic effect was proved in the extraction of zinc and cadmium ions.

EXPERIMENTAL

Extraction of metal ions was carried out at the phases volume ratio of 1 : 1 (2 mL of each), in glass tubes under mechanical stirring, the phases contact time was of 30 min. The reagent concentration in the diluent was of 0.025 mol/L.

Concentration of metals was measured using mass spectrometer equipped with a radio-frequency electromagnetic generator for exciting inductively coupled argon plasma, a controller of argon flow rate, and a hardware processor of the spectrometer output capable of correction for the background. The following parameters were used for the metals analysis with ELAN DRCII mass spectrometer: flows, plasma forming 15 L/min, supporting 1.2 L/min, spraying 0.95 L/min; input power 1150 W, the sprayer cross-stream, material PEEK, sapphire tips; the pump rotor speed 24 rpm, the spectral resolution 0.8 atomic mass unit for ^{7}Li, 0.5 for ^{55}Mn, 0.7 atomic mass unit for other elements. Concentration limits of detection of metal ions were from 0.1 to 1×10^{-5} mg/L. Average sensitivity was of 1×10^{-3} mg/L.

Table 6. Degree of extraction of singly and doubly charged metal ions with 2:1 mixture of **II** and **I**, as function of the aqueous phase acidity

pH	La(III)	Ce(III)	Gd(III)	Lu(III)	Nd(III)	Sm(III)	UO_2(II)
2.9	0	0	57.1	99.1	0	21.2	94.5
5.0	0.97	4.8	81	99.98	7.8	47.3	99.9
5.5	0.69	4.4	81	99.8	6.8	47.3	99.4

The degree of extraction E, % was determined from the concentration of the metal in the aqueous phase as $E = c_m^{rec}/(c_m^{rec} + c_m^{rel})\times100\%$, with c_m^{rec}, concentration of the metal in the receiving phase; c_m^{rel}, concentration of the metal in the releasing phase.

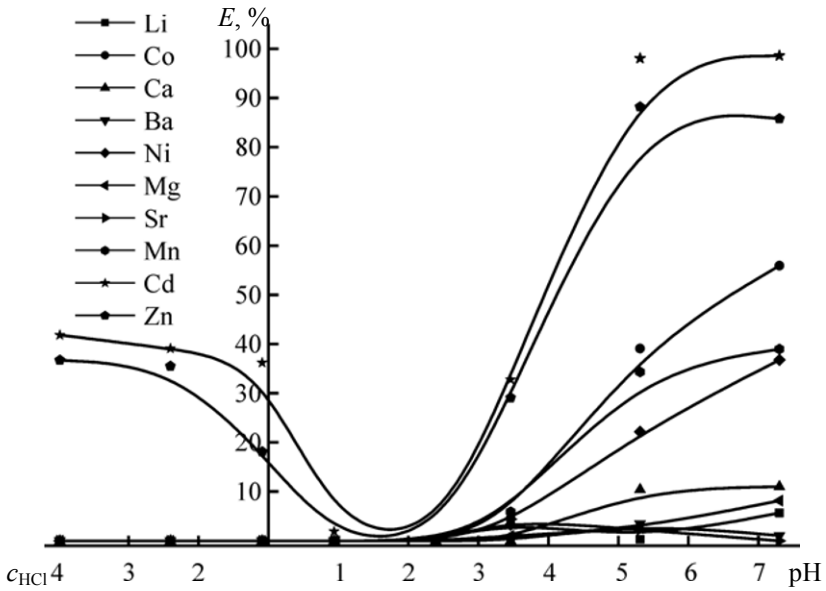

Fig. 6. Degree of extraction of singly and doubly charged metal ions with 2:1 mixture of **II** and **I**, as function of the aqueous phase acidity.

Preparation and characterization of **I** and **II** were performed as described in [15] and [16], respectively.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-00536).

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