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Synthesis, Transport, and Ionophore Properties of α,ω-Bisphosphorylated Azapodands: IX[1]. Extraction of Metal Ions with Quasiliquid Emulsions on the Basis of *N,N'*-Bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane and Acidic Components

A. R. Garifzyanov, S. V. Leont'eva, N. V. Davletshina, R. R. Davletshin, and R. A. Cherkasov

Kazan Federal University, ul. Kremlevskaya 18, Kazan, Tatarstan, 420008 Russia
e-mail: rafael.cherkasov@ksu.ru

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Abstract—Processes of extraction of ions of the I–IV group metals from acidic water solutions with paraffin quasiliquid emulsions containing neutral phosphorylazapodand, bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane **I,** and acidic components, bispentadecylphosphoric **II** and hexadecylsulfonic acid **III** is studied. High effectiveness of extraction of metal ions with these extraction compositions is established. It significantly exceeds the effectiveness of liquid extraction in the same systems, especially of ions of the II group metals. The extraction of three-charged ions proceeds more effectively by the mixture of organophosphorus reagents **I** and **II**, than with the composition consisting of azapodand **I** and organosulfur acid **III**.

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Recently we established the possibility to use a synergetic extractant consisting of neutral phosphoryl-azapodand, *N,N'*-bis(dioctylphosphorylmehyl)-1,8-diamino-3,6-dioxaoctane **I,** and acidic component, bispentadecylphosphoric acid **II**, for the extraction of metal ions of the I–III groups.

It was shown that each of these organophosphorus reagents as well as their mixture exhibit sufficiently high effectiveness in the extraction of ions of the III group metals. They possess high selectivity for Sc(II) and UO_2(II) ions. Besides, their mixture shows expressed synergism in the liquid extraction of Zn(II) and Cd(II) ions from acidic water solutions [1]. Note that using synergetic mixtures of neutral and acidic organophosphorus extractants in the experimental and industrial technologies of isolation, separation, and concentration of metals from mining raw materials seems to be the clearly traced trend in the development of extraction methods [2, 3].

The method of concentration most widely used in practice is liquid extraction. Its significant fault is comparatively low value of concentration coefficients (≤50) what is caused by complication of quantitative separation of extract at high values of ratio of volumes of water and organic phases [4]. One of the ways of overcoming this obstacle in the development of concentration methods is the extraction with solid and low-melting extractants [5–7]. Besides, in the last years one more innovational method of extraction of substrates of various nature was developed occupying the intermediate position between the extraction and sorption, i.e., extraction with quasiliquid emulsions. It is based on the use of solution of transporting reagent in paraffin emulsified in water solution of extracted substrate (metal ion) [8, 9]. Using this method permits achieving high (up to 10^4) values of concentration coefficient giving the possibility of successful solving problems connected with isolation of metal ions from strongly diluted water solutions with the concentration of target components below 10^{-4} M [10]. Due to that the described method is promising for the concentration of microelements in the analytical techniques, in the development of waste-free technologies in hydrometallurgy, solving ecological problems like

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

Table 1. Dependence of the degree of extraction of two-charged metal ions on the pH of water phase in the course of combined extraction with quasiliquid emulsion of the solution of azapodand **I** and the acid **II** in paraffin

pH	Ba	Pb	Sr	Co	Ni	Cu	Cd
3.74	0	1.76	0	1.34	0	14.11	2.17
4.66	63.74	95.03	62.96	92.3	89.42	87.07	88.2
5.68	18.13	97.04	18.65	81.41	77.7	91.75	96.96
6.43	33.51	98.88	24.27	90.23	83.22	96.08	98.7

Table 2. Dependence of the degree of extraction of three-charged metal ions and UO_2(II) on the pH of water phase in the course of combined extraction with quasiliquid emulsion of the solution of azapodand **I** and the acid **II** in paraffin

pH	In	Ga	UO_2	Sc	Y	Ce
3.74	98.04	91.65	97.45	95.66	98.28	99.37
4.66	99.98	98.22	99.97	99.34	99.98	99.98
5.68	99.97	95.27	99.96	98.82	99.98	99.98

purification of waste water from highly toxic and radioactive components, etc.

Continuing our previous studies connected with the development of a method of concentration and extraction of metal ions with organophosphorus extractants of various structure we have recently reported the results of investigation of processes of extraction of the ions of the II and III group metals with quasiliquid emulsions from the acidic water solutions. The solution of acid **II** in paraffin with the 40% concentration was used as a carrier [11]. Here we report on the new results of investigation of the processes of extraction of metal ions of the I–IV groups with quasiliquid emulsions. Now we have used various combinations of neutral organophosphorus extractant **I** and the acids of different nature, the lipophilic phosphorus acid **II**, and sulfur-containing acidic reagent, hexadecylsulfonic acid (as sodium salt) **III.** Mixtures of the above-mentioned extractants were dissolved in paraffin and used as paraffin emulsion in the acidic water solution of the extracted metal ions. We considered it interesting to compare the results of investigation of processes of extraction with quasiliquid emulsions and liquid extraction of ions of the same metals in the two-phase water: organic diluent system with the mixture of reagents **I** and **II**. We reported on the latter process recently [1].

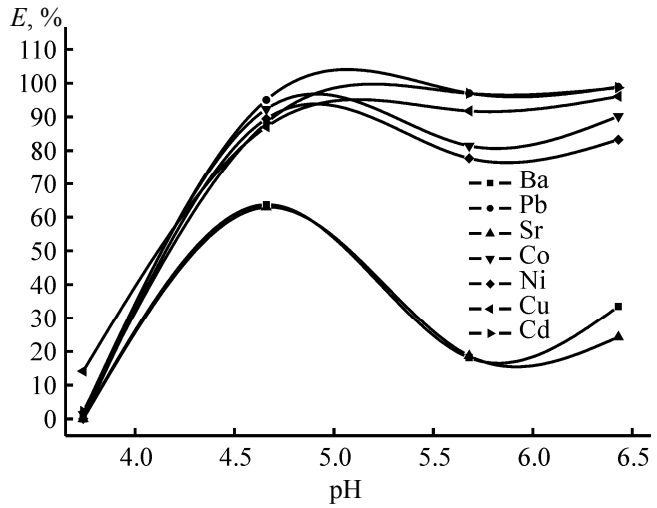

Fig. 1. Dependence of the degree of extraction of double-charged metal ions on pH of the water phase. Composition of emulsion: 19.5% of azapodand **I**, 40.5% (with respect to organic phase) of the acid **II**, 40% (with respect to organic phase) of paraffin; V of water in the emulsion per 1.5 g of organic phase] 4 mL; $V_{\text{water phase}}$ 15 mL; m_{em} 0.1 g; c_{m} 100 μg/L.

Dependences of degree of metal ions extraction on the acidity of the initial phase in the pH range 3.5–6.5 with paraffin emulsion containing azapodand **I** and lipophylic organophosphorus acid **II** are presented in Tables 1, 2 and in Figs. 1, 2. In the pH range below 3 the filtrate after removing the emulsion remains turbid which makes its analysis impossible. Comparing the results obtained in the investigation of extraction with quasiliquid emulsions of metal ions from the acidic water solutions with the data [1] where the processes of liquid extraction of the same metals are reported, it is possible to note the significant increase in the degree of extraction in the concentration of metals with paraffin emulsions. Thus, in the course of liquid extraction Ba(II) and Sr(II) practically do not go over from water to the organic phase (maximum 3.5 and 4.4% respectively), but while using of the extraction with quasiliquid emulsions the degree of extraction of these metals increases to 63%.

In the acidity range of water phase under study the quantitative extraction of rare and scattered elements as well as uranyl ion takes place (Fig. 2, Table 2). The degree of extraction of Ce(III) and Ga(III) ions using the extraction with quasiliquid emulsion increases to 98–99% as compared to 4.8 and 38% respectively obtained in the course of liquid extraction of these

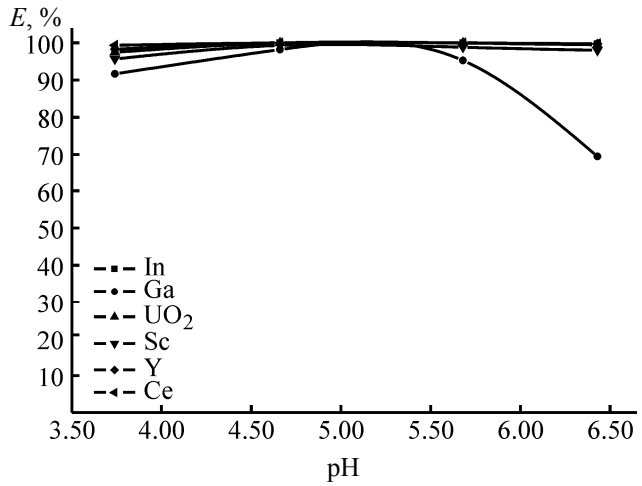

Fig. 2. Dependence of the degree of extraction of triple-charged metal ions and $U(II)O_2$ on pH of the water phase. Composition of emulsion: 19.5% of azapodand **I**, 40.5% (with respect to organic phase) of the acid **II**, 40% (with respect to organic phase) of paraffin: V of water in the emulsion per 1.5 g of organic phase 4 mL; $V_{\text{water phase}}$ 15 mL; m_{em} 0.1 g; c_{m} 100 μg/L.

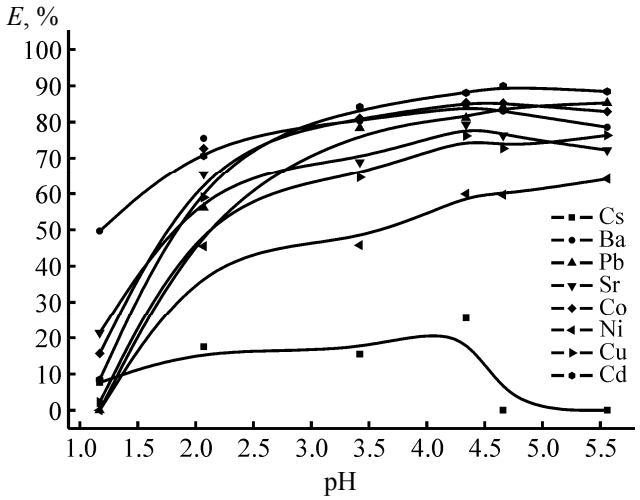

Fig. 3. Dependence of the degree of extraction of single- and double-charged metal ions on the pH of the water phase. Composition of emulsion: 26.5% (with respect to organic phase) of azapodand **I**, 33.5% of sodium hexadecyl-sulfonate **III**, 40% (with respect to organic phase) of paraffin: V of water in the in the emulsion per 1 g of organic phase 4 mL, $V_{\text{water phase}}$ 15 mL; m_{em} 0.1 g; c_{m} 100 μg/L.

ions. The concentration of In(III), UO_2(II), Sc(III), and Y(III) in the processes of their extraction with quasiliquid emulsion proceeds quantitatively in all the pH range.

In the experiments where the extraction with quasiliquid emulsions took place we have used artificial mixtures of ions of rare, scattered, and potentially radioactive metals prepared from the native water of Volga. Quantitative extraction of Cu(II), Cd(II), Pb(II), Sc(III), Y(III), In(III), Ce(III), and UO_2(II) was achieved. But the concentration of such potentially radioactive elements as cesium, strontium, and barium in the processes of extraction with quasiliquid emulsions with the participation of a mixture of organophosphorus reagents **I** and **II** is not effective because the extraction degree is low.

With the purpose of achievement of increase in extracting ability of extraction reagents under study in paraffin emulsions in relation to Cs(I) ions a mixture of azapodand **I** and sodium hexadecylsulfonate **III** was used. It can be noted that in the pH range under study degree of extraction of Cs(I) ions reaches 22% (Figs. 3, 4, Tables 3, 4). The pH range where quantitative extraction of two-charged metal ions is observed broadens significantly at the extraction with quasiliquid emulsions. At the same time this extraction system occurred to be moderately effective for the extraction of three-charged metal ions. At the exclusion of Sc(III) and Ce(III) ions in strongly acidic media (see Table 4 and Fig. 4) the degree of extraction of the majority of metals of the III group does not exceed 80–85% in the pH range 2–5. Selectivity of extractive action in the series of metal ions under study also does not appear noticeably. In this connection note that the combination of azapodand **I** and bispentadecyl phosphate **II** much more effectively extracts three-charged ions in the range of moderate acidity (pH 3.5–5.5, see Table 2 and Fig. 2). Nevertheless it may be stated that the extractive system consisting of azapodand **I**, sodium hexadecylsulfonate **III**, and paraffin is quite promising for the process of group concentration of three-charged metal ions by the extraction with quasiliquid emulsions from strongly acidic water media (pH 1–1.5, Table 4). As in all the cases mixtures of extractants chosen by us show high indexes of concentration of metal ions involved in the investigations, we considered it unsuitable to evaluate the synergetic effect of mixtures of reagents under study.

Hence, paraffin emulsions containing a mixture of neutral (phosphorylazapodand) and acidic extraction reagents exhibit the expressed ability to the extraction of ions of rare earth elements, scandium, barium, strontium, and cesium from nature waters. It may open

Table 3. Dependence of degree of extraction of one- and two-charged metal ions on the pH of water phase at the combined extraction with quasiliquid emulsion of the solution of azapodand **I** and sodium hexadecylsulfonate **III**

pH	Cs	Ba	Pb	Sr	Co	Ni	Cu	Cd
1.17	7.64	49.67	0	21.35	15.65	0	2.25	8.45
2.07	17.5	75.51	56.13	65.52	72.64	45.48	58.98	70.61
3.42	15.48	80.3	78.36	68.92	81.06	45.78	64.59	84.16
4.34	25.5	84.52	81.16	79.32	85.38	59.93	76.2	88.09
4.66	0	82.99	84.13	76.27	85.24	59.67	72.72	89.93
5.56	0	78.55	85.28	72.27	82.87	64.11	76.33	88.43

Table 4. Dependence of degree of extraction of three-charged metal ions and UO_2(II) on the pH of water phase at the combined extraction with quasiliquid emulsion of the solution of azapodand **I** and sodium hexadecylsulfonate **III**

pH	In	Ga	UO_2	Sc	Y	Ce
1.17	89.97	78.25	93.54	97.13	91.33	90.23
2.07	83.14	78.11	81.06	57.75	80.39	80.09
3.42	69.95	82.46	81.73	33.64	76.64	84.5
4.34	53.69	80.34	74.19	31,31	75.66	83.39
4.66	70.63	86.43	81.61	51.34	77.76	86.69
5.56	53.66	82.39	70.32	37.11	67.33	74.99

prospects of use of new methods and reagents described in this article while solving the problems of protecting environment, and also while planning technologies of extraction, concentration, and separation of metal ions from natural mixtures.

EXPERIMENTAL

Weighing was carried out on an Ohlaus SPS 2001F, Scout Pro, and Acculab sortorius group Vicon scales. For shaking test tubes laboratory shaker AVU 6s was used (shaking acceleration 1.5 m/s^2). Titration was performed on a pH-150MI ionometer. Mass spectra were obtained on an ELAN-DRC II mass spectrometer with the inductively bound plasma.

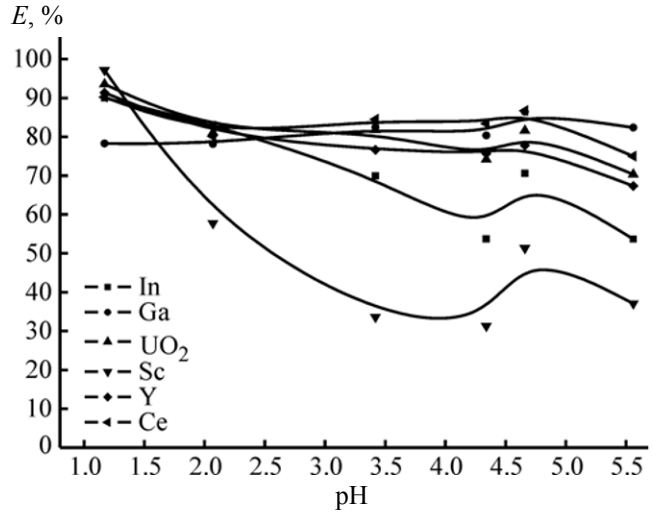

Fig. 4. Dependence of the degree of extraction of triple-charged metal ions and UO_2^{2+} on the pH of the water phase. Composition of emulsion: 26.5% (with respect to organic phase) of azapodand **I**, 33.5% of sodium hexadecylsulfonate **III**, 40% (with respect to organic phase) of paraffin: V of water in the emulsion per 1 g of organic phase 4 mL, $V_{\text{water phase}}$ 15 mL; m_{em} 0.1 g; c_{m} 100 μg/L.

Solutions containing In(III), Y(III), Ca(III), Sc(III), Sr(II), UO_2(II), Sc(I), Ba(II), and Ce(III) were prepared from the corresponding nitrates and chlorides of "chemically pure" and "pure for analysis" grades using accurately weighed samples. State standard samples of metal ions for preparing solutions of Co(II), Cu(II), Ni(II), Pb(II), and Cd(II) were also used.

For preparing emulsions paraffin of "pure" grade was used, TU 6-09-3637-74. Emulsions were obtained by heating a mixture consisting of water, paraffin, extraction reagent, and surfactant to the temperature exceeding the melting point of paraffin (70–80°C) and cooling to room temperature under the intense stirring. For obtaining necessary size of particles in the emulsion in the course of its preparation a concentrated water solutions of ammonia was added dropwise to the water-paraffin-reagent mixture. The size of particles was controlled with a microscope.

The obtained emulsion was transferred in water solution of target component under study and stirred for 30 min. After that the organic phase was filtered off by means of MFAS-OS-2 membrane filters. The content of extractant in the organic phase depending on its nature was no more than 40–60%.

Method of the synthesis and characteristics of *N,N'*-bis(dioctylphosphorylmethyl)-1,8-diamino-3,6-dioxaoctane are presented in [12]. Bispentadecylphosphoric acid and hexadecylsulfonic acid were prepared according to [13].

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