# Solvent Extraction of Some Trace Metals and Iron with *N*-Octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine

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**Abstract**—The processes were studied of the solvent extraction of the ions of triply-charged trace elements including scandium, indium, gallium, and yttrium, as well as iron, with *N*-octyl-*N*,*N*-bis(dihexylphosphinyl-methyl)amine solution in toluene, chloroform or methylene chloride from hydrochloric, nitric or perchloric acids aqueous solutions. The metals extraction dependence on the acid concentration showed that the best results were reached using perchloric acid. The calculation of partition coefficients of metals allowed us to reveal a high selectivity of the scandium extraction. The prospects of using the investigated bisphosphinylamine in the technology of extraction, concentration and separation of the trace metals ions was concluded.

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The solvent and membrane extractions are base of the concentration, separation and analysis of metals in natural and technological sources, providing a comprehensive processing of the mineral raw materials and secondary resources, as well as solution of important environmental problems [1-3]. In this context, it should be emphasized that the rapid development of the chemistry and technology of noble, rare-earth and non-ferrous metals is largely due to the development of the innovative extraction methods. Recently, much attention was given to extraction methods for extracting, separating and analyzing the trace metals [4-6]. A variety of extraction objects and the specificity of their extraction, concentration and separation is a need to find the new high-effective extractants suitable for extraction processes for each of the target substrates individually. Among the large set of organic reagents used to solve these problems, the prominent place belongs to the neutral organophosphorus compounds. In the extraction technology of rare and trace elements are used most frequently the organophosphorus compounds, including phosphates, phosphonates and phosphine oxides, in some cases containing various additional functional groups, which affect the coordination type of the extractant with the substrate [7, 8]. However, the arsenal of reagents used in the extraction technologies of the trace elements

does not practically involve such highly effective and selective liquid membrane metal carriers as aminophosphoryl compounds, although, as previously shown, they can be successfully used in the process of liquid membrane extraction of the alkali, alkaline-earth [9], noble [10, 11] and rare-earth metal ions. Recently, the study of the processes of the solvent and liquid membrane extraction of scandium and other rare-earth and trace elements was reported [12, 13]. A large number of aminophosphoryl compounds were found to be useful for the extraction of metal ions, in particular scandium(III). The best results were achieved using N-octyl-N,N-bis(dihexylphosphinylmethyl)amine  $Oct[HexP(O)CH_2]_2N$ . This work presents the results of studying the processes of solvent extraction of triply-charged ions of the trace elements indium, yttrium, scandium, and gallium with diphosphinylamine. In this series was included for comparison the ferric ion, which often accompanies these metals.

The solvent extraction of the metal ions is usually carried out from aqueous solutions of mineral acids such as hydrochloric, nitric, or perchloric. Therefore, the process of metals extraction may be accompanied by the mineral acid co-extraction. As shown previously [11], when studying the concentration dependence of the extraction degree of these acids with the selected reagent using toluene, chloroform or methylene

chloride as diluents, the extractability of perchloric acid at the starting concentration 0.2 M increases until a 1:1 solvate formation, and then remains unchanged up to a concentration of 4 M At the same time, the concentration of nitric acid in the organic phase increases continuously with increasing its content in the aqueous phase. The extraction isotherm of hydrochloric acid reaches the limit at the concentration in the aqueous phase equal to 6 M, with the formation of the 1:1 complex. These results suggest that at low concentrations of acids, the degree of the metals extraction will be the maximum, since effect of the competitive reactions of the extractant with the acid will be insignificant The acid extractability decreases in the following sequence:  $HClO_4 > HNO_3 > HCl$ , according to the orientation of the anion hydration energies: for perchlorate, nitrate and chloride anions they are 209, 288 and 330 J mol<sup>-1</sup>, respectively [14].

Hydrochloric acid is uncommonly used in the trace metals hydrometallurgy. Therefore, the effect of its concentration in the aqueous phase on the extractability with 0.025 M solution of N,N-bis(dihexyl-phosphinylmethyl)amine in toluene was studied only for Ga(III), Sc(III) and Fe(III) ions. Figure 1 shows the dependence of the ions extraction (*E*) on the hydrochloric acid concentration.

The extractability of scandium at the concentration of hydrochloric acid up to 0.5 M exceeds the efficiency of iron extraction, but with increasing acidity of the aqueous phase up to 2.5 M and higher the extractability of iron prevails. The reason for such dependence may be associated with a change in the extraction mechanism in the investigated range of acidity, and attention should be paid to the similarity of the curves character at the extraction of these metals with tributylphosphite and trioctylamine [7, 15]. It can be assumed that the complexation degree of these cations differing in their atomic radius is not identical in different acidity ranges. Under the selected conditions, gallium is not practically extracted with the examined agent in the whole range of acidity of the aqueous phase.

To evaluate the nature of iron(III) complexation with N,N-bis(dihexylphosphinylmethyl)amine at different concentrations of hydrochloric acid, the UV spectra of the organic phase were examined in the field near the maxima and minima of the iron extraction curves (Fig. 1), corresponding to different concentrations of the acid. Fe(III) chloride complexes are colored, and with the incorporation of chloride ion into



**Fig. 1.** Dependence of the extraction degree of Ga(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N toluene solution on the hydrochloric acid concentration.  $c_{\text{Fe}}$  10.28× 10<sup>-3</sup> M;  $c_{\text{Ga}}$  14×10<sup>-3</sup> M;  $c_{\text{Se}}$  0.5×10<sup>-3</sup> M; phases ratio 1:1.

the inner coordination sphere of the Fe(III) the charge transfer bands appear in the near-UV region. The solutions were prepared with a certain concentration of hydrochloric acid and the metal at a 1:1 ratio of the volumes of two phases. For comparison, Fig. 2 shows the absorption spectrum of the extract obtained by the Fe(III) extraction with the well studied extractant trioctylamine (Oct<sub>3</sub>N).

It can be seen that the spectra of the Fe(III) complexes with bisphosphinylamine and  $Oct_3N$  are almost the same, suggesting the similarity of the extraction mechanisms in a wide range of the acid concentrations. According to [15],  $Oct_3N$  extracts Fe(III) as an ionic associate I, formed by the protonated trioctylamine tetrachloride and iron.

$$\operatorname{Fe}_{\operatorname{aq}}^{3+} + 4\operatorname{Cl}_{\operatorname{aq}}^{-} + \operatorname{H}_{\operatorname{aq}}^{+} + (\operatorname{Oct}_{3}\operatorname{N})_{\operatorname{org}} \to [\operatorname{Oct}_{3}\operatorname{NH}^{+} \cdot \operatorname{Fe}\operatorname{Cl}_{4}^{-}]_{\operatorname{org}}.$$

Obviously, the process of Fe(III) extracting with aminobisphosphinyl extractant at high concentrations of hydrochloric acid can be expressed by the same equation, leading to the appearance of the extracting complex II.

As can be seen from Fig. 1, the curve of the extraction of Fe dependence on the HCl concentration is observed to decrease in the low concentration range, then at  $c_{\rm HCl} \sim 2.5$  M the extraction degree increases

almost to 100%. Comparing this relation with the absorption spectrum of the extracts, we can assume that at low acid concentrations the chloride-ion does not enter into the inner coordination sphere of the

iron. Probably, in this range the ionic associate **III** containing the iron complex with bisphosphinylamine and three chloride-ions [Eq. (1)] is transferred into the organic phase.



The further increase in the concentration of hydrochloric acid from 0.25 to 2.5 M causes the accumulation of chloride iron complexes in the aqueous phase. In the organic phase the free reagent fraction is reduced because of co-extraction of hydrochloric acid. The observed increase in the extraction degree in this range can be associated with the formation of mixed-ligand complex **IV**.



**Fig. 2.** The UV spectrum of Fe(III) complexes extracted with *N*-octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine.  $V_{org}/V_{aq} = 1$ , *c* 0.025 M, diluent toluene. (*I*)  $c_{HCI}$  0.33 M,  $c_{Fe}$  4.5×  $10^{-4}$  M; (*2*)  $c_{HCI}$  0.87 M,  $c_{Fe}$  4.5× $10^{-4}$  M; (*3*)  $c_{HCI}$  1.5 M,  $c_{Fe}$  2.3× $10^{-4}$  M; (*4*)  $c_{HCI}$  3.1 M,  $c_{Fe}$  0.9× $10^{-4}$  M; (*5*)  $c_{HCI}$  4.5 M,  $c_{Fe}$  0.9× $10^{-4}$  M; and (*6*)  $c_{HCI}$  4.5 M,  $c_{Fe}$  0.9× $10^{-4}$  M.



A maximum of the band in the UV spectrum, which arises due to the Fe $\rightarrow$ Cl charge transfer in the inner coordination sphere, corresponds to this state of the extracted complex. Further increase in the acid concentration leads to the transfer of the iron ion as a complex II into the organic phase.

The calculation of the metals partition coefficients (the ratio of their partition coefficients) with respect to the most effectively extracted element scandium shows a small value for the scandium/iron pair. The selectivity of the same scandium/gallium pair varies



**Fig. 3.** Dependence of the extraction degree of In(III), Ga(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N toluene solution on the nitric acid concentration.  $c_{\text{In}}$  5× 10<sup>-3</sup> M;  $c_{\text{Ga}}$  14×10<sup>-3</sup> M;  $c_{\text{Sc}}$  5×10<sup>-3</sup> M;  $c_{\text{Fe}}$  5×10<sup>-3</sup> M; phases ratio 1:1.

greatly at different acid concentrations and increases from 17 at  $c_{\rm HCl}$  0.4 M to 627 at 0.28 M with a further decrease to 37.8 at 1.12 M These results are well illustrated by the dependences shown in Fig. 1. However, as expected, the separation efficiency in hydrochloric acid is low.

Nitric acid medium is most frequently used in hydrometallurgical processes for obtaining and purification of the trace elements. We investigated the effect of nitric acid concentration on the extraction degree of In(III), Y(III), Ga(III), Sc(III) and Fe(III) with the reagent solutions in toluene, methylene chloride or chloroform. These relationships are shown in Figs. 3–5.

Nitric acid extraction systems are the most difficult to interpret, since in contrast to HCl, nitric acid itself is extracted into the organic phase by three types of extracting particles: ionic associate, formed as a result of bisphosphinylamine V protonation, and two solvates (H-comp-lexes) VI and VII, which are formed by the sequential binding of nitric acid with the phosphine oxide groups [11].

$$\{\operatorname{Oct}[\operatorname{Hex}_{2}P(O)CH_{2}]_{2}N\}_{\operatorname{org}} + \operatorname{H}_{aq}^{+} + \operatorname{NO}_{3aq}^{-} \\ \rightarrow \{\operatorname{Oct}[\operatorname{Hex}_{2}P(O)CH_{2}]_{2}NH^{+} \cdot \operatorname{NO}_{3}^{-}\}_{\operatorname{org}}, \\ V \\ V + \operatorname{HNO}_{3aq} \rightarrow (\{\operatorname{Oct}[\operatorname{Hex}_{2}P(O)CH_{2}]_{2}NH^{+} \cdots \operatorname{HNO}_{3}\} \cdot \operatorname{NO}_{3}^{-})_{\operatorname{org}},$$

VI



**Fig. 4.** Dependence of the extraction degree of In(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N methylene chloride solution on the nitric acid concentration.  $c_{\text{In}} \ 8.75 \times 10^{-3}$  M;  $c_{\text{Se}} \ 19.76 \times 10^{-3}$  M;  $c_{\text{Fe}} \ 16.04 \times 10^{-3}$  M, phases ratio 1:1.

$$VI + HNO_{3aq}$$
→ ({Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>NH<sup>+</sup>··2HNO<sub>3</sub>}·NO<sub>3</sub>)<sub>org</sub>.  
VII

In addition, it is well known that the nitrate ion can enter into the inner coordination sphere of the extracted metal ion [15].

Not monotonous change of the extraction of metals dependence on the nitric acid concentration indicates



Fig. 5. Dependence of the extraction degree of Y(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N chloroform solution on the nitric acid concentration.  $c_Y$  9.8×10<sup>-3</sup> M;  $c_{Sc}$  19.76×10<sup>-3</sup> M;  $c_{Fe}$  16.04×10<sup>-3</sup> M, phases ratio 1:1.

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**Fig. 6.** Dependence of the extraction degree of In(III), Y(III), Ga(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N toluene solution on the perchloric acid concentration.  $c_{\rm In}$  3.42×10<sup>-3</sup> M;  $c_{\rm Y}$  1.02×10<sup>-3</sup> M;  $c_{\rm Ga}$  8.25×10<sup>-3</sup> M;  $c_{\rm Sc}$  9.8×10<sup>-3</sup> M;  $c({\rm Fe})$  14.54×10<sup>-3</sup> M, phases ratio 1:1.

the complexity of the process occurrence at different pH values of the aqueous phase. This confirms the above assumption about the probable structure of the complexes extracted under these conditions. We can assume that in general the mechanism of extraction from nitric acid medium involves the formation of the complex particles with the same stoichiometry as for hydrochloric acid: at low acid concentrations the metal structures are probably formed  $[M^{3+}{Oct[Hex_2P(O) \cdot CH_2]_2N}_2]^{3+}\cdot 3NO_3^-$ ; in the media with moderate acidity (1–4 M) the mixed-ligand complexes  $[M^{3+}{Oct[Hex_2 \cdot P(O) \cdot CH_2]_2N}(NO_3^-)_3]$ , and in the strongly acidic media the more complex ionic associate  $(Oct[Hex_2P(O) \cdot CH_2]_2N \cdot 2HNO_3)^+ \cdot [M^{3+}(NO_3^-)_4]^-$ .

The strong influence of the diluent polarity should be noted: in the non-polar toluene the extractability increases at low acidity, and it falls at the higher acidity. In the more polar methylene chloride a smooth decrease in the extraction degree of scandium and the abrupt increase in the extraction degree of iron were observed with increasing nitric acid concentration in the aqueous phase. In chloroform, the extraction degree of these metals increases as acid concentration increases. The available data do not allow us to interpret confidently the nature of the solvate effects. One can only state the growth f the ion associates extractability using polar diluents. The extraction degree of the In(III), Y(III) and Ga(III) ions is much lower than that for Sc(III) and Fe(III). The efficiency of extraction from the aqueous nitric acid media is also lower than from hydrochloric acid. However, it is characteristic that, as in hydrochloric acid media, at the high acid concentrations the Fe(III) ion begins to be extracted better than Sc(III). The similarity of these two acidic media is found in the calculation of the metals partition coefficients relative to scandium: they are small in almost all used range of acidity in a scandium/iron pair and reach significant values (100– 300) in the range of moderate acidity for the three other studied elements, indium, gallium and yttrium, in all three diluents.

As shown earlier, the highest efficiency and selectivity of the liquid-liquid extraction with aminophosphinyl extractants can be achieved with use of perchloric acid aqueous solutions as a releasing phase [11]. The wide use of perchlorate aqueous media in the hydrometallurgical extraction processes is due to the fact that the perchlorate ion being the least hydrophilic inorganic anion provides a relatively high degree of the metal ions transfer into the organic phase. We studied the effect of perchloric acid concentration on the extraction degree of the studied triply-charged cations. The dependences obtained are shown in Figs 6–8.

The extractability sequence Sc > In > Fe > Y > Gain the range of low acidity does not coincide with a change in the ionic radii of extractable ions, which are (Å): 0.89, 0.94, 0.79, 1.04, 0.76 [16]. In the high acidity range the elements of a smaller radius are somewhat better extracted: Sc > Fe > Ga > Y >In. This tendency is characteristic for the metals extraction with neutral organophosphorus reagents [7].

These results demonstrate the similarity in the nature of the dependence between the degree of ions extraction and perchloric acid concentration in various diluents, suggesting the unity of the extraction mechanisms for all the used organic phases. The degree of scandium extraction in all cases is extremely high in toluene and methylene chloride in whole of acidity range of the aqueous phase. In chloroform it increases with the increasing concentration of perchloric acid. Noteworthy that in these conditions, in contrast to hydrochloric and nitric acid media, there is a very noticeable extraction degree for indium and which reaches 30–50%. For gallium. all the investigated metals the best extractability was observed in the less polar toluene as compared to methylene chloride and chloroform.



**Fig. 7.** Dependence of the extraction degree of In(III), Y(III), Ga(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N methylene chloride solution on the perchloric acid concentration.  $c_{In} \ 8.19 \times 10^{-3}$  M;  $c_{Y} \ 10.25 \times 10^{-3}$  M;  $c_{Ga} \ 8.25 \times 10^{-3}$  M;  $c_{Sc} \ 19.77 \times 10^{-3}$  M;  $c_{Fe} \ 14.54 \times 10^{-3}$  M, phases ratio 1:1.

Based on these experimental results, were calculated the partition coefficients of the metals in relation to the scandium in a wide range of perchloric acid concentrations in the aqueous phase for all the used diluents. The highest selectivity was observed for the scandium in a water-toluene system (Table 1) at  $c(\text{HClO}_4)$  0.05–0.1 M, reaching the highest values in the Sc(III)/Ga(III) pair. In the same concentration range of perchloric acid the higher selectivity relative to the scandium was revealed in methylene chloride. At high acid concentrations (~2 M) there is a selectivity growth in the Sc(III)/M(III) pairs for all the investigated cations (Table 2). In chloroform the selectivity (2-200) for all the Sc(III)/M(III) is relatively low, and only at high concentrations of perchloric acid (0.6-2 M) a moderate selectivity (200-600) was achieved.

The obtained results indicate a high efficiency of extraction with *N*-octyl-*N*,*N*-bis(dihexylphosphinyl-methyl)amine, which is suitable for the extraction of the studied trace elements ions from the aqueous nitric and perchloric acid media with an enhanced selectivity toward scandium. Taking into account the relative synthetic availability of this aminophosphine oxide reagent and its hydrolytic and thermal stability, it can be use in the processes of extraction, concentration and separation of the trace metal ions.



**Fig. 8.** Dependence of the extraction degree of In(III), Y(III), Ga(III), Sc(III) and Fe(III) with 0.025 M Oct[Hex<sub>2</sub>P(O)CH<sub>2</sub>]<sub>2</sub>N chloroform solution perchloric acid concentration.  $c_{\text{In}} 6.83 \times 10^{-3}$  M;  $c_{\text{Y}} 10.25 \times 10^{-3}$  M;  $c_{\text{Ga}} 8.25 \times 10^{-3}$  M;  $c_{\text{Sc}} 19.77 \times 10^{-3}$  M;  $c_{\text{Fe}} 14.54 \times 10^{-3}$  M, phases ratio 1:1.

## **EXPERIMENTAL**

The diluents, nitrates and chlorides of the investigated metals of chemical or analytical grade were used. The extractant solutions in the organic solvents were prepared using the accurately weighted

**Table 1.** Partition coefficients  $[K_{part} = D_{Met}/D_{Met}]$  of the metals at the extraction with 0.025 M solution of *N*-octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine in toluene  $(V_{ad}/V_{org} = 1)$ 

c(HClO <sub>4</sub> ), M	Sc(III)/Fe(III)	Sc(III)/ In(III)	Sc(III)/Y(III)	Sc(III)/Ga(III)
0.0049	22.7	232	3400	174
0.0107	110	12.5	150	950
0.0214	330	17.6	347	908
0.0488	77000	296	7230	194000
0.108	81300	4980	77000	116000
0.191	1260	259	2110	6310
0.243	337	331	2470	3300
0.954	183	1520	5150	1380
1.33	113	1220	1390	379
1.91	172	3850	2890	594

**Table 2.** Partition coefficients  $[K_{\text{part}} = D_{\text{Met}}/D_{\text{Met}}]$  of the metals at the extraction with 0.025 M solution of *N*-octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine methylene chloride  $(V_{\text{aq}}/V_{\text{org}} = 1)$ 

c(HClO <sub>4</sub> ), M	Sc(III)/ Fe(III)	Sc(III)/In(III)	Sc(III)/Y(III)	Sc(III)/Ga(III)
0.0049	4.92	16.8	69.6	437
0.0195	7.63	7.97	162	133
0.0488	40.1	12.0	122	375
0.0977	33.7	16.5	225	235
0.243	30.5	51.5	185	135
0.572	8770	208	91700	67600
0.954	11.4	95.4	200	57.0
1.52	17.7	411	676	154
1.91	3720	42200	64100	11500

samples of the compounds, the examined metal salts wereprepared by precipitating the metal hydroxides from the corresponding nitrates with 25% solution of ammonia to pH 9 followed by dissolving in the corresponding concentrated acid. The exact concentration of the metals in the obtained solutions was determined by the complexometric titration [17]. To produce the required acidity in aqueous solution was added hydrochloric, perchloric or nitric acid of chemically pure grade. The working solutions were prepared in distilled water.

The experimental studies were performed using an AVU 6c mechanical shaking devise, an OP 8UKhL4.2 centrifuge and a 3070E Rigaku X-ray fluorescence spectrometer (Japan). The extraction degree was determined by measuring the metals concentration in aqueous and organic phases by X-ray fluorescence spectroscopy using the method given in [11].

The extraction of the inorganic acid solution was carried out with *N*-octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine in chloroform, methylene chloride and toluene (0.05 M) using glass test tubes at the stirring for 30 min. The phase separation was carried out by a five-minute centrifugation at 2000 rpm. To a 2 ml aliquot in a glass cell was added 20 ml of water– isopropanol mixture (1:3). The acid concentration in the organic phase was determined by the potentiometric titration with 0.03 M alkali solution in a water–isopropanol mixture on the calculated equivalent amount of alkali. The titration curves were plotted in integral and differential forms, and on the basis of the acid concentration data in the both phases the extraction isotherms were plotted.

The metal ions extraction was performed at a 1:1 ratio of the phases, 2 ml each phase. in glass tubes. The mixing was carried out mechanically, after stirring for 30 min the samples of the aqueous and organic phases were acquired and centrifuged for 5 min.

The method for the synthesis and characterization of *N*-octyl-*N*,*N*-bis(dihexylphosphinylmethyl)amine is described in [18].

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