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Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik

Liquid Extraction of Noble Metal Ions with Bis(α-aminophosphonates)

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Abstract—Extraction of Au(III), Pt(IV), and Pd(II) ions from hydrochloric acid media with solutions of two bis(aminophosphonates), such as *N,N*-bis(dipentoxyphosphorylmethyl)octylamine and *N,N'*-bis[[(dioctyloxyphosphoryl)methyl]butylamine], in chloroform and xylene was investigated. Both these extractants proved to be highly effective for Au(III) ions in a wide acidity range, which allows these ions to be separated from other noble metal ions with a high degree of selectivity. At the same time, Pt(IV) and Pd(II) ions cannot be separated from one another with the extractants studied. The selectivity of their separation from Fe(III), Cu(II), Co(II), and Ni(II) metal ions is, too, not high. The reasons for these results lie in the specific structural features of the extractants, which predetermine the extraction mechanism.

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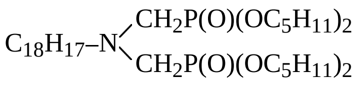
We previously showed that α-aminophosphoryl compounds and podands containing terminal α-aminoalkylphosphoryl groups exhibit complex-forming properties that can be used for developing new types of extractants [1, 2] and membrane carriers for metal ions [3] and organic and inorganic acids [3,4], components of ion-selective electrodes [5], and other new advanced technology products. In [6] we found that bis(2-ethylhexyl) *N*-butyl-*N*-octylaminomethylphosphonate (**I**) effectively extracts ions of noble metals, such as Au(III), Pt(IV), and Pd(II), into the organic phase from weakly acidic aqueous media. Therewith, noble metals were highly selectively separated from their concomitant Fe(III), Cu(II), Co(II), and Ni(II) ions.

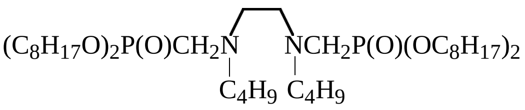
Monofunctional aminophosphonate **I**, while being effective for group extraction of noble metal ions, proved to be unsuitable for solving one more important problem, i.e. separation of these metals from one another. We suggested that one of the ways to attack this problem is to introduce additional functional groups in the phosphorylated amine and thus alter the coordination properties of the carrier and enhance its selectivity.

In the present work we studied the extractive ability of bisphosphonates, such as *N,N*-bis(dipentoxyphosphorylmethyl)octylamine (**II**) and *N,N'*-bis[[(dioctyloxyphosphoryl)methyl]butylamine] (**III**), toward Au(II), Pt(IV), and Pd(II) ions. The compounds studied are difunctional aminophosphonates in which two phosphorylmethyl groups reside on one (**II**) or two (**III**) basic amine centers.



$C_{18}H_{17}{-}N(CH_2P(O)(OC_5H_{11})_2)_2$

II



$(C_8H_{17}O)_2P(O)CH_2N(C_4H_9)\ \ N(C_4H_9)CH_2P(O)(OC_8H_{17})_2$

III

We proposed that these two extractants differ from each other and from their "monofunctional" analog **I** in the electronic and steric characteristics of potential coordination centers, primarily nitrogen atoms. In this connection we can note that there are scarce data on the extraction of noble metal ions with bisphosphorylated amines and diamines. In particular, Medved' *et al.* [7] showed that Au(III) ions can be extracted from hydrochloric acid media with ethylenediaminodialkylphosphonic acids with subsequent reextraction with ammonia and nitric acid.

As we previously established [8], α-aminophosphonates are 4-5 orders of magnitude less basic than

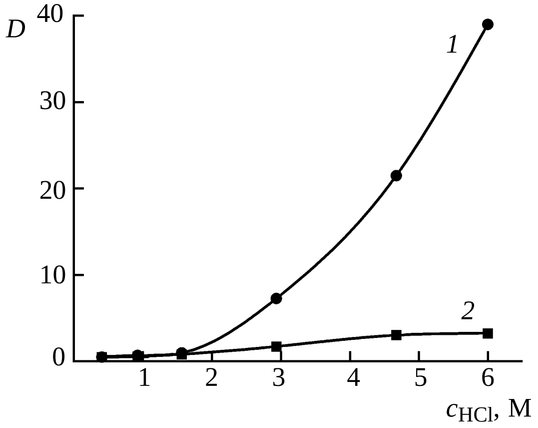


Fig. 1. Dependence of the distribution coefficient of (*1*) Pt(IV) and (*2*) Pd(II) on the concentration of HCl in the aqueous phase on the extraction with 0.15 M solutions with aminodiphosphonate **II** in xylene.

their precursors, nonphosphorylated amines, and the pK_a of their conjugate acids vary in the range 4–6. It is evident that such a decrease of the acidity of the amine, produced by its phosphorylation, is caused by a strong electron-acceptor effect of the phosphoryl group. Introduction of the second phosphoryl group further decreases the basicity, and diphosphorylated amine **II** cannot be titrated with strong acids in water–2-propanol media. Thus the pK_a of the conjugate acid can be estimated to be lower than 1. That means that in water this compound exhibits very weak basic properties.

We investigated dependence of the degree of extraction of noble metals with 0.15 M solutions of bisphosphonate **II** in xylene on the acidity of the aqueous phase. Figure 1 presents data for platinum and palladium, which show that the degree of extraction increases with increasing concentration of hydrochloric acid.

In this respect extractant **II** strongly differs from monofunctional α-aminophosphonate **I** that characteristically extracts less platinum and palladium as the concentration of HCl increases [1]. Furthermore, reagent **II**, by contrast to its monophosphorylated analog **I**, better extracts platinum than palladium over a wide acidity range. With **II**, the extraction of palladium and platinum probably proceeds by the outer-sphere mechanism, because the low basicity and high steric congestion of the nitrogen atom in the diphosphorylated amine excludes the intra-sphere mechanism. In this case, the increase of the distribution coefficients of metals with increasing acidity is caused by the accumulation of the protonated form of extractant **II**, that takes place only at high HCl concentrations. This effect distinguishes the diphosphorylated amine from such common reagents as higher aliphatic amines and α-aminophosphonates. The metal : diphosphonate **II** molar ratio in the extracted complex was established by the equilibrium shift method by analogy with [6]. It occurred to be 1 : 2 both for Pt(IV) and for Pd(II).

Since in hydrochloric acid media these ions exist in the aqueous phase as strong chloride complexes ($PdCl_4^{2-}$ and $PtCl_6^{2-}$), we can suggest that their extraction with the aminophosphonate (AP) in hand occurs by the outer-sphere mechanism according to the following equations.

$$PdCl_4^{2-} + 2AP_{org} + 2H^+ = \{[PdCl_4^{2-}]\cdot[APH^+]_2\}_{org},$$

$$PdCl_6^{2-} + 2AP_{org} + 2H^+ = \{[PdCl_6^{2-}]\cdot[APH^+]_2\}_{org}.$$

The resulting dependences lead us to conclude bisphosphonate **II** is suitable for extractive separation of gold from platinum or palladium from weakly acidic media, i.e. at $c_{HCl} < 0.2$ M.

At HCl concentrations below 2 M, the distribution coefficients of Pt(IV) and Pd(II) are not high and close to each other (Fig. 1). In strongly acidic media (c_{HCl} 6 M), Pt(IV) is extracted quantitatively, the distribution coefficient reaching 40 (vide supra). At the same time, the distribution coefficient of Pd(II) under these conditions is not so high but still appreciable (3.22), and, therefore, Pt(IV) and Pd(II) are extremely difficult to separate using this reagent.

c_{HCl}, M	0.4	0.9	1.5	3	4.5	5.6
D_{Pt}	0.5	0.8	1	7.25	21.5	39
D_{Pd}	0.48	0.58	0.84	1.74	3.04	3.22

To find out whether noble metals can be separated from concomitant elements with extractant **II**, we studied extraction of Fe(III), Cu(II), Co(II), and Ni(II) under conditions of quantitative extraction of platinum at c_{HCl} 6 M. It was found that these metal ions all are fairly extracted with a solution of diphosphonate **II** in xylene, the distribution coefficient being 3.2 for Fe(III), 0.25 for Cu(II), 1.3 for Co(II), and 0.16 for Ni(II). These data show that extractant **II** can only be used for quantitative extraction of gold from weakly acidic media.

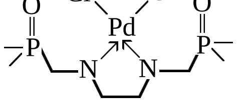
In the above-described examples we used secondary amine **II** whose two phosphoryl groups are located at the same basic center, the nitrogen atom. We considered it important to study the extractive ability of diphosphorylated diamine **III** in which both basic centers, the nitrogen atoms, bear phosphorus-containing groups. In this case, along with the basicity factor of the amine centers, we expected chelation of metal ions to take forth.

Preliminary experiments showed that, irrespective of the concentration of HCl in the aqueous phase, in this case, too, gold was extracted quantitatively, which prevented assessment of the distribution coefficient from the residual concentration of this metal in the aqueous phase. Therefore, with diphosphorylated diamine **III**, we only studied extraction of platinum and palladium. Similarly to the other extractants of the aminophosphoryl series, viz. compounds **I** and **II**, compound **III** is practically insoluble in water and readily soluble in organic solvents. For this reason, the losses of the extractant on metal extraction are minimal. The dependences of the distribution coefficients (*D*) of platinum on the extraction with 0.075 M solutions of compound **III** in xylene and chloroform are shown in Fig. 2.

As follows from Fig. 2, reagent **III** is close to monofunctional phosphonates in extractive properties. Unlike bisphosphorylated amine **II**, bis(aminophosphonate) **III** exhibits a higher extractive ability from weakly acidic media, which is evidently connected with its higher basicity compared with the basicity of monofunctional analogs. In weakly acidic media, Pd(II) is extracted quantitatively, and the distribution coefficient sharply decreases with increasing c_{HCl} (see table). This fact agrees with the results in [1], according to which the mechanism of Pd(II) extraction changes from intra- to outer-sphere as the concentration of acid in the aqueous phase increases. This circumstance together with the competing effect of chloride ions explains the observed effect of the acidity of the aqueous phase.

At the same time, the extraction of Pt(IV), that occurs by the outer-sphere mechanism over a wide c_{HCl} range, is characterized by a slight decrease of the distribution coefficient with increasing c_{HCl} both in xylene and in chloroform (see table).

To determine the composition of the extracted complex, we made use of the isomolar series method [1, 6]. It was thus shown that the complex has a 1:2 metal:ligand ratio. This excludes the possibility of formation of a 1:1 chelate complex between Pd(II) and diamine **III** in the organic phase.



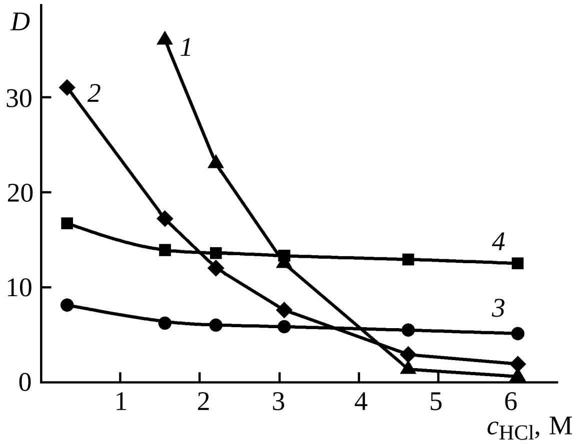


Fig. 2. Dependence of the distribution coefficient of (*1, 2*) Pd(II) and (*3, 4*) Pt(IV) on the concentration of HCl in the aqueous phase on the extraction with 0.075 M solutions of diaminodiphosphonate **III** in (*1, 3*) xylene and (*2, 4*) chloroform.

Our present data provide further evidence for the previous conclusion that the extraction of palladium with diphosphorylated diamine **III** proceeds analogously to the extraction with monofunctional α-aminophosphonates, including reagent **I** [1, 6].

All attempts to find practically feasible methods for reextraction of palladium from its complexes with diamine **III** failed, since inorganic acids, available and common industrial reextractants, proved ineffective in this case. It should be admitted that compounds **II** and **III** are unlikely to find practical application as extractants for palladium and platinum. The possible reason for such an inefficiency of difunctional aminophosphonates **II** and **III** lies in specific features of their their complex-forming ability. Geminal diphosphorylated diamine **II**, because of the strong electron-acceptor effect of the two phosphoryl groups bound with the basic center, the tertiary nitrogen atom,

Effect of the concentration of hydrochloric acid in the aqueous phase on the distribution coefficient of platinum and palladium on the extraction with solutions of diaminodiphosphonate **III** in xylene and chloroform

Solvent	c_{HCl}, M					
	0.33	1.56	2.20	3.06	4.62	6
	D_{Pt}					
Chloroform	16.7	13.9	13.6	13.3	12.9	12.5
Xylene	8.1	6.2	6.0	5.83	5.48	5.12
	D_{Pd}					
Chloroform	31	17	14.5	12	2.89	1.92
Xylene	–	36	23	12.5	1.35	0.58

proves to be too weak base to exhibit selectivity toward definite ions. By contrast, diaminodiphosphonate **III** possesses two pronounced basic amine centers and thus is capable of strongly binding extracted ions, which complicates or even prevents reextraction of the latter. At the same time, the high extractive ability of these types of α-aminiophosphonates toward gold ions makes us to expect that research in this field may lead to creation of highly effective reagents for selective extraction of gold ions from various industrial objects.

EXPERIMENTAL

The extractive properties were studied as described in [6]. The extractants were synthesized as described in [3].

***N,N*-Bis(dipentoxyphosphorylmethyl)octylamine II** was prepared in 80% yield as a viscous light yellow liquid which was purified by column chromatography (eluent acetone–chloroform, 1:4). Completion of the reaction was established by the amount of the evolved water. The purity was controlled by TLC (Silufol UV-254 plates, eluent acetone–chloroform, 1:4), R_f 0.75 (development in iodine vapor with subsequent treatment with water); n_D^{20} 1.4490; δ_P 24 ppm.

***N,N'*-Bis[[(dioctyloxyphosphoryl)methyl]butylamine] (III)** was purified analogously, yield 75%, R_f 0.56, n_D^{20} 1.4458; δ_P 24 ppm.

ACKNOWLEDGMENTS

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