

METALLURGY OF LESS-COMMON AND NOBLE METALS

The Extraction of Noble Metals by Macrocyclic Compounds

T. M. Buslaeva^{a*}, E. A. Krylova^{a**}, E. V. Volchkova^{a***},
S. P. Gromov^{b****}, and N. I. Sidorenko^{a*****}

^a Lomonosov State Academy of Fine Chemical Technology, pr. Vernadskogo 86, Moscow, 119571 Russia

^b Center of Photochemistry, Russian Academy of Sciences, ul. Novatorov 7a, Moscow, 119421 Russia

*e-mail: buslaevatm@mail.ru

**e-mail: len-krylova@yandex.ru

***e-mail: volchkovaev@bk.ru

****e-mail: gromov@photonics.ru

*****e-mail: sidorenko80@mail.ru

Abstract—This is analytical article devoted to the extraction of noble metals by acyclic analogs of crown ethers (podands) covering the period from 1980 to 2007. Most attention is given to the extraction of noble metals by phosphoryl-containing podands from hydrochloric acid solutions. The efficiency of extraction depends mostly on the number and nature of donor centers in a reagent molecule. It is shown that the use of podands as noble metal extractants does not help to solve the problem of selective separation of noble metals from complex solutions.

DOI: 10.3103/S1067821208060059

INTRODUCTION

Noble metal extraction by various classes of extractants has been thoroughly studied, but interest in this problem remains due to the necessity of searching for efficient selective reagents. Despite a variety of conventional extractants (tributyl phosphate, trialkylphosphine oxides, dialkylsulfoxides, amines, alcohols, ketones, etc.), they do not allow one to solve the problem of selectivity.

Widespread interest in macrocyclic organic compounds emerged when Charles Pedersen published his works on the synthesis and applications of crown ethers in the 1960s [1–4]. The ability of macrocyclic compounds to form stable complexes with various metal ions and the recognition capabilities of these structures are their main advantages over simpler acyclic compounds. It is extraction by macrocyclic compounds that forms the basis for the technology of molecular recognition.

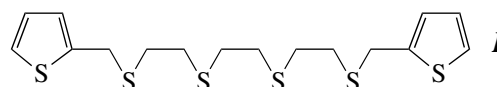
This review, prepared by us and devoted to the extraction of noble metals, consists of three parts: the first part is devoted to the extraction by acyclic analogs of crown ethers (podands), which are more readily available than the respective macrocyclic compounds; the second part is devoted to extraction by crown ethers containing O, S, and N donor authors; and the third part is devoted to extraction by calixarenes. This is the first part of the review.

EXTRACTION BY PODANDS

As mentioned above, podands are acyclic analogs of crown ethers which form pseudomacrocycles in the

course of complex formation. The high complex-formation ability of podands toward the ions of alkali, alkali earth [5–12], and rare-earth [13, 14] metals, as well as radioactive elements [15, 16] is known.

The following podand, which contains six donor sulfur atoms,



has been proposed for the extraction of noble metals Ag(I), Pd(II), and Au(III) from various acid solutions [17, 18].

It has been shown [17] that the solvent does not significantly affect the rate of establishing equilibrium (5 min) or the degree of extraction of α of Pd(II) from 1 M solutions of HClO₄ and HNO₃. In the extraction of Pd(II) from a 1 M solution of HCl, the maximum degree of extraction is reached when 1,2-dichloroethane is used as a solvent (Table 1).

Notably, the efficiency of Pd(II) extraction by 1×10^{-3} and 2.5×10^{-3} mol/l solutions of substance *I* in 1,2-dichloroethane or methyl isobutyl ketone is almost independent of the concentrations of HCl in the range 0.1–4.0 M, HClO₄ in the range 0.1–1 M, and HNO₃ in the range 0.25–3.50 M.

Podand *I* is capable of extracting Ag(I) from solutions containing 2×10^{-3} mol/l NaClO₄ and a 1 M solution of HClO₄, and $\alpha_{\text{Ag(I)}} > 99\%$ [17]. It has been found that under these conditions the ions of accompanying metals are not extracted (for Cu(II), Ni(II), and Co(II), $\alpha = 0$ –2%, which is close to the error of analysis).

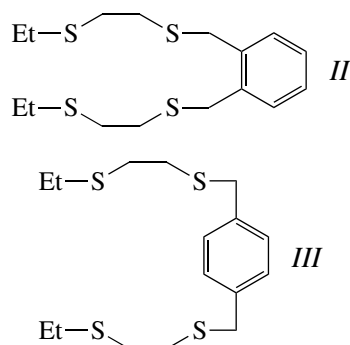
Table 1. Dependence of the degree of Pd(II) extraction (in %) on the solvent nature in extraction from 1 M solutions of acids by 2×10^{-3} mol/l solutions of podand *I* ($C_{\text{Pd}}^{\text{in}} = 9.4 \times 10^{-5}$ mol/l)

Aqueous phase	Solvent		
	1,2-dichloroethane	chloroform	methyl isobutyl ketone
HCl	>99	95	85
HClO ₄	>99	95	95
HNO ₃	30	30	28

The degree of Au(III) extraction from hydrochloric acid solutions (pH 1–4) using podand solution *I* in 1,2-dichloroethane is 98% [18]. In the case of nitric acid solutions, $\alpha_{\text{Au(III)}}$ decreases from 93 to 72% with an increase in the concentration of HNO₃ from 0.04 to 3 M.

Lachowicz and Krajewski [18] also noted the effect of a solvent on the extraction of Au(III) from 0.5 M HCl under conditions of extractant deficiency (10^{-5} mol/l): in the presence of 2×10^{-3} mol/l hydrazine sulfate, extraction is almost quantitative (up to 98%); however, in the absence of this compound, $\alpha = 15\%$. It is unclear from [18] what kind of an Au(I) complex is formed in the presence of a reducing agent. In our opinion, gold ions are likely to be reduced to elementary gold.

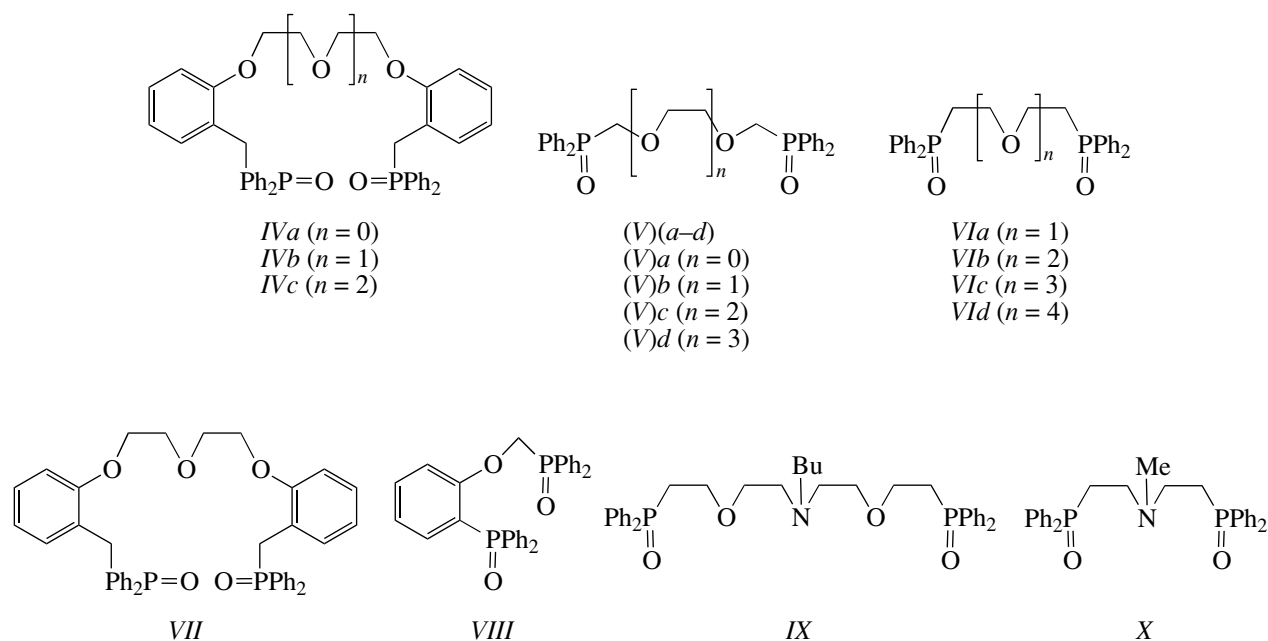
Solutions of sulfur-containing podands *II* and *III* in 1,2-dichloroethane were proposed for Pd(II) extraction from solutions containing picrate ions (pH 1–6) [19]:

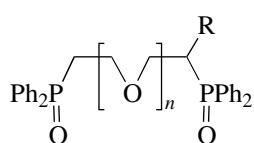
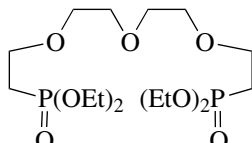
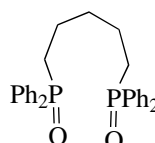
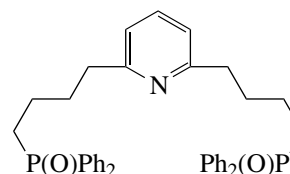
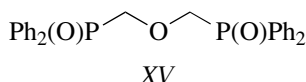
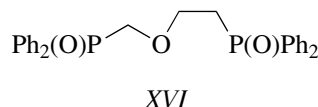
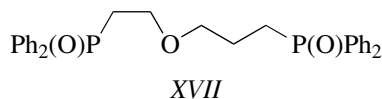
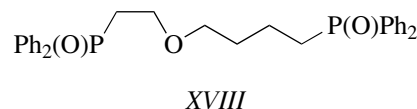


It was found that, as the pH of the initial aqueous solution increases from 1 to 3, the degree of palladium(II) extraction (the concentration of Pd(II) in the initial solution is $C_{\text{Pd}}^{\text{in}} = 5 \times 10^{-3}$ mol/l), which is 5×10^{-3} mol/l solutions of podands in 1,2-dichloroethane, first increases and then becomes constant and equal to 50% for *II* and >99% for *III*. According to [19], if the initial concentrations of extractants are <0.001 mol/l, the extractive ability of podand *II* is higher than that of podand *III*. If the concentration is >0.001 mol/l, then the reversed dependence is observed (Table 2).

Unfortunately, articles [17–19] do not discuss the reasons behind these patterns.

Major publications on the extraction of noble metals by podands refer to hydrochloric acid (chloride) solutions, because they find widespread use in refinement technology, analytical chemistry, and preparative chemistry. It should be underlined that, due to the presence of strong electron-donor end groups [20–23], podands are comparable with or better than macrocyclic compounds in their ability to form complexes [24]. Most widespread podands contain phosphoryl groups:



*XIa* ($n = 0$, $R = -(CH_2)_5CH_3$)*XIb* ($n = 1$, $R = H$)*XIc* ($n = 2$, $R = H$)*XId* ($n = 3$, $R = H$)*XIe* ($n = 4$, $R = H$)*XII**XIII**XIV**XV**XVI**XVII**XVIII*

In the study of the electron structure and complex-forming properties of phosphorylated podands, Vornek et al. [25] concluded that the main factors that determine the complex-forming ability are (i) the number and nature of donor centers in a molecule and the length of a polyethylene glycol chain, (ii) the structure of end groups of the ligand, (iii) the conformational rigidity of a podand, and (iv) the basicity of phosphoryl oxygen and the distance between the phosphoryl group and the first oxygen atom in the polyether chain [6].

For many years systematic studies into extraction by phosphoryl-containing podands have been carried out by Turanov et al. for various groups of elements: rare earth [13, 14, 26], radioactive [14, 15, 27–30], and noble [20–23, 31–35].

The efficiency of extracting platinum metals and gold by phosphoryl-containing podands is determined by the formation of a pseudomacrocycle with a hydroxonium ion and by its hydrophobicity as a condition for the transfer of the ionic associate formed to the organic phase. According to [36], podands are capable of forming a rather stable pseudomacrocycle with hydroxonium ion.

Table 2. Dependence of the degree of extraction of Pd(II) (in %) on the concentration of extractant (*II* and *III*) in 1,2-dichloroethane at pH 2.9 ($C_{Pd}^{in} = 5 \times 10^{-5}$ mol/l)

Initial extractant concentration	Extractant	
	<i>II</i>	<i>III</i>
1×10^{-4}	39	12
1×10^{-3}	44	45
1×10^{-2}	67	>99

Therefore, it is not surprising that the structure of extractant affects the degrees of Pd(II), Pt(IV), and Au(III) extraction [20, 21].

Thus, the maximum extraction of Pd(II) from 3.5 M HCl [20] and Pt(IV) from 4 M HCl [32] by reagents *IV*–*VII* is observed for ligands containing 5 donor atoms (compounds *IVb*, *Vc*, *VIc*, and *VII*). Let us consider data on the extraction of Pd(II) from a 3.5 M HCl solution by the 0.05 mol/l solutions of pentadentate and tridentate phosphoryl-containing podands in 1,2-dichloroethane:¹

Podand	<i>IVb</i>	<i>Vc</i>	<i>VIc</i>	<i>VII</i>	<i>Va</i>	<i>VIa</i>
$\alpha_{Pd(II)}, \%$	17	13	51	70	11	42

It is seen that podand *VII* is the most efficient of the considered compounds. This fact is explained by the fact that this reagent, which contains a benzene ring, has a greater rigidity than *VIc*, while the number of donor centers is the same [20, 32]. It was suggested [20, 32] that the structure of such podands is preferable for the formation of chelate structures, which include hydroxonium ions and the cationic part of the extracted ionic associates. Unfortunately, the use of ligand *VII* in extraction is limited by its low solubility in organic solvents, which is at most 0.03 mol/l in 1,2-dichloroethane.

Ether-group oxygen atoms are important in the coordination of metal atoms with podands. It was shown for the extraction of Pt(IV) by *XIII*, which is analogous to ligand *XIb* but has no ether-group oxygen atoms [32], that such a replacement leads to a considerable decrease in the extraction ability of an organic compound. If the extraction of Pt(IV) from 4 M HCl by

¹ Pentadentate podands contain three ether and two end oxygen atoms; tridentate podands contain one ether and two end oxygen atoms.

Table 3. The degree of Pt(IV) and Au(III) extraction (in %) from 4 M HCl by 0.01 mol/l solutions of various reagents in 1,2-dichloroethane

Ion	Podand				
	<i>XV</i>	<i>XVI</i>	<i>VIb</i>	<i>XVII</i>	<i>XVIII</i>
Pt(IV)	18	54	60	57	45
Au(III)	96	98	>99	97	85

an 0.01 mol/l solution of reagent *XIb* in 1,2-dichloroethane is 88%, than for compound *XIII*, it decreases to 42% other things being equal.

The effect of the length of a hydrocarbon chain between the end PO group and the ether-group oxygen atoms on the change in the efficiency of extraction was considered for the extraction of Pt(IV) and Au(III) by the solutions of podands *XV*, *XVI*, *VIb*, *XVII*, and *XVIII* in 1,2-dichloroethane [35] (see Table 3).

An increase in the degree of extraction of Pt(IV) and Au(III) in the series $XV < XVI < VIb$ was explained by Turanov et al. [35] by an increase in the conformational mobility of the reagent structure when methylene fragments are replaced by ethylene fragments and when the molecule simultaneously becomes more hydrophobic. It was assumed that these circumstances provide favorable conditions for the formation of pseudocyclic complexes of the protonated extractant. A further increase in the number of methylene groups leads to an increase in the hydrophobicity (reagents *XVII* and *XVIII*) but prevents the formation of a pseudocyclic structure of the protonated podand because of the large cycle size, which stipulates a decrease in the degree of extraction.

According to [32], the main factor that determines the extractive properties of phosphoryl-containing podands is the coordination ability of the phosphoryl group. Indeed, the replacement of phenyl groups in a molecule of ligand *XId* by more electron-accepting ethoxy groups (*XII*) leads to the suppression of Pt(IV) extraction: the degree of Pt(IV) extraction from 4 M HCl by 0.01 mol/l solutions of reagents in 1,2-dichloroethane is 95 and <1% for *XId* and *XII*, respectively [32].

It was found [21] that tridentate ligands (see below) possess the highest extraction ability toward Au(III)), but this dependence is not as explicit as in the case of Pd(II) extraction. For example, the degree of Au(III) extraction from 4 M HCl by 0.05 mol/l solutions of pentadentate and tridentate phosphoryl-containing podands in 1,2-dichloroethane is

Podand	<i>IVb</i>	<i>Vc</i>	<i>VIc</i>	<i>Va</i>	<i>VIa</i>	<i>VIII</i>
$\alpha_{Au(III)}, \%$	89	92	93	97	94	93

It was hypothesized [21] that the structures of the above-mentioned tridentate podands are the most favorable for the formation of a pseudomacrocycle with a hydroxonium ion in the course of complex anion $[AuCl_4]^-$ extraction into the organic phase.

The nature of the organic solvent substantially affects the distribution of Pd(II) between the phases [20, 35]. Thus, in Pd(II) extraction by 0.05 mol/l solutions of *VIa* in nitrobenzene, 1,2-dichloroethane, and methylene chloride, the degree of its extraction into the organic phase is 65, 42, and 15%, respectively [20]. In the case of Au(III) extraction by podands, the solvent nature does not play an important role: the value $\alpha_{Au(III)}$ in extraction by 0.01 mol/l solutions of reagent *VIa* is 72% in nitrobenzene, 71% in 1,2-dichloroethane, and 71% in CCl_4 [21]. The use of toluene and CCl_4 is limited by the solubility of podands in these solvents.

The degree of Pt(IV) extraction increases as the concentration of HCl increases in the aqueous phase, which is typical of the extraction of metal halide acids by extractants via the hydrate-solvate mechanism [37]. The dependence of the degree of extraction of the metal ion in Pd(II) and Au(III) extraction on the concentration of hydrochloric acid is pronounced [20, 21]. A decrease in the value of $\alpha_{Pd(II)}$ at $C_{HCl} > 5$ M and Au(III) at $C_{HCl} > 7$ M is due to the competitive action of HCl on the extractant.

The stoichiometric ratio metal: reagent in the complexes extracted by phosphoryl-containing podands was estimated by the method of equilibrium shift and saturation [20, 32, 35]. It was found that they are close to 1 in the extraction of one-charge complexes (Au and Ag) and they are 2 in the extraction of two-charge complexes (Pt and Pd). Note that the transfer of the complex anion to the organic phase without destruction was supported [28] by the presence of the band corresponding to $[PtCl_6]^{2-}$ in electron absorption spectra. However, such proof does not sound convincing, because the band at $\lambda = 456$ nm in the visible region is characterized by a very low intensity ($\epsilon = 54$). The hexachloroplatinate(IV) ion is identified by the band in the UV region at $\lambda = 262$ nm ($\epsilon = 22200$) [38].

The extraction of Pd(II) and the ions of elements accompanying Pd(II) from hydrochloric acid solutions by aza podands *IX* and *X* was studied in 1,2-dichloroethane [22, 23]. It was found that the replacement of the central ether-group oxygen atom in a phosphoryl-containing podand by a tertiary nitrogen atom leads to an increase in the extraction ability of the reagent toward platinum metal chloride complexes. Thus, aza podands *IX* and *X* lead to better extraction than ligands *VIc* and *VIa*, which have analogous structures. The extraction ability of the pentadentate ligand *IX* is higher than that of *X*, which is an aza podand with three donor atoms (Table 4).

Reagent *IX* is better at extracting many elements than ligand *X* [22]. This points to the participation of

the ether-group oxygen atoms of the aza podand molecule *IX* in the formation of a pseudomacrocyclic complex with the hydrated H^+ ion, which forms the cationic part of the extracted ionic associates. Its formation is supported by the fact that, when reagent *IX* is supported on the surface of an adsorbent, the degree of Pd(II) extraction noticeably decreases. It is likely that such a position of the aza podand molecule creates steric hindrances for the formation of a pseudomacrocyclic. Turanov et al. [22] underline that a nitrogen atom plays an important role in the formation of a complex with the hydrated H^+ ion. This is evidenced by the higher extraction ability of aza podand *IX* compared with its structural analog *VIc*.

Note that an increase in the concentration of HCl in an aqueous solution leads to a decrease in the degree of Pd(II) and Pt(IV) extraction, which is characteristic of platinum metal extraction by amines [39, 40]. The dependence of $\alpha_{Pd(II)}$ on C_{HCl} points to the considerable effect of the state of aza podands in the organic phase on the extraction of Pd(II) [22]. The protonation of the reagent with a decrease in the acidity of the aqueous phase leads to a transition from the coordination mechanism of extraction to the anion-exchange mechanism and is accompanied by a decrease in the degree of extraction. This fact is supported by the presence of a band at 400 nm in the electron absorption spectrum of a palladium-containing extract from a weakly acidic solution (pH 5.7) by aza podand *IX* [22], which points to a change in the inner coordination sphere of the initial Pd(II) complex due to interaction with the organic reagent. In extracts from solutions with a concentration of HCl greater than 0.01 M; absorption bands typical of the $[PdCl_4]^{2-}$ ions are observed at $\lambda = 476$ nm [38].

In extraction by aza podands, the degree of platinum metal ion extraction substantially affects the nature of the organic solvent: the extraction of chloride complexes increases with an increase in the solvent polarity [22,33]. Thus, in platinum extraction from 1 M HCl by a 0.01 mol/l solution of aza podand *IX* in nitrobenzene, 1,2-dichloroethane, chloroform, and toluene, the degree of extraction is >99, 99, 80, and 44%, respectively [28].

The effect of chloride ions on Pd(II) extraction was noted in [20, 22]. At a constant concentration of chloride ions, an increase in the acidity achieved by the addition of sulfuric acid to the aqueous phase (which, unlike HCl, does not affect the inner coordination sphere of the Pd(II) complex in extraction by the solutions of ligands *IV*–*VI*) leads to a noticeable increase in the degree of Pd(II) extraction compared to extraction from hydrochloric acid solutions without sulfuric acid additives [20]. The increase in the concentration of H^+ ions favors the formation of the protonated extractant and an increase in the degree of extraction; the increase in the concentration of the Cl^- ion in the aqueous phase

Table 4. The degree of extraction of Pd(II) and accompanying ions (in %) from 2 M HCl by the solutions of aza podands *IX*, *X*, and *XIVc* in 1,2-dichloroethane [22, 33]

Ligand	Pd(II)	Pt(IV)	Ag(I)	Cu(II)	Zn(II)
<i>IX</i>	95	>99	94	25	97
<i>X</i>	20	97	38	9	86
<i>XIV</i>	–	86	88	–	98

above a certain value leads to a decrease in the degree of extraction. In the case of aza podands *IX* and *X*, increasing the pH of the aqueous phase to 6 leads to an increase in the degree of Pd(II) extraction [22]. Then it decreases due to the formation of nonextractable Pd(II) complexes in the aqueous phase. An increase in the acidity of the aqueous solution by adding H_2SO_4 at a constant concentration of Cl^- ions leads to a decrease in α at a higher concentration of H^+ than in the case of extraction from HCl solutions.

The effect of aliphatic amines on the extraction of noble metals by pentadentate phosphoryl-containing podands from hydrochloric acid media [31, 34] has been studied. When extracting metal ions from 2 M HCl by an equimolar (0.025 mol/l) mixture of phosphoryl-containing podand *VIc* with various amines in 1,2-dichloroethane, a synergistic effect was observed. The synergistic coefficients (*S*) for various amines are shown in Table 5.

The synergistic effect is explained by the formation of the complexes of phosphoryl-containing podands with a protonated amine molecule, which is a cationic part of extracted associates, in the organic phase. If tri-octylamine is added to the system, *S* is less than 2 with rare exceptions in the case of metals Zn, Ga, Pd, Ag, In, Pt, Hg, and Bi (specific complexes were not mentioned). This is lower than for octylamine and dioctylamine. It was suggested [31, 34] that a protonated tri-octylamine–HCl molecule can create only one hydrogen bond with a PO group of the podand. In the case of dioctylamine and octylamine, the maximum number of hydrogen bonds increases to 2 and 3, respectively.

It was shown [34] that an increase in the concentration of amine and podand is favorable for the increase in the degree of Pd(II) extraction into the organic phase.

When considering the effect of podand structure on the extraction of chloride complexes in the presence of octylamine, an increase in the synergistic coefficient in the series *IVb* < *VIc* < *Vc* catches the eye. In [31], this is explained by the effect of the conformational mobility of the bridge between the polyether chain and the phosphoryl group. The highest value of *S* was found in Pd(II) extraction by the mixtures of podand *VIc* with octylamine.

Table 5. Synergistic coefficients in the extraction of various metal ions from 2 M HCl solutions by the equimolar (0.025 mol/l) mixtures of phosphoryl-containing podand *VId* with amines in 1,2-dichloroethane

Element	Trioctyl-amine	Dioctyl-amine	Octyl-amine	Isobutyl-amine	Diisobutyl-amine
Zn	1.93	4.57	3.01	1.20	2.54
Ga	1.35	1.35	1.80	1.07	1.00
Pd	1.20	1.20	68.5	1.20	1.00
Ag	1.37	1.32	1.49	1.00	1.23
Cd	2.20	7.60	5.86	1.00	2.55
In	1.04	1.68	1.68	1.20	1.00
Pt	2.45	1.30	6.40	1.08	1.20
Hg	1.56	3.90	3.98	1.03	2.05
Bi	1.77	3.16	4.32	1.00	1.27

The concentration of HCl in the aqueous phase affects the value of the synergistic effect in the system phosphoryl-containing podand–amine. In the case of Pd(II) extraction by a mixture containing octylamine, the distribution coefficient D_{Pd} decreases from 32 to 6 when the concentration of HCl increases from 0 to 7 M.

Accompanying element	Ag	Co	Cu	Ni	Pd	Pt	Zn
$\beta_{Au/Element}$	>100	>320	>320	>100	>100	>100	>1000

The highest selectivity is observed when the concentration of HCl is low (0.5–2.0 M), because, with an increase in C_{HCl} , chloride complexes of many metals transfer to the organic phase.

It has been also found [23] that the degree of Co(II) and Cu(II) extraction by aza podand *IX* from 2 M HCl is 9 and 25%, respectively. The degree of platinum and silver extraction remains higher than 95%.

CONCLUSIONS

Generalizing and analyzing the above data on the extraction of noble metals by podands makes it possible to draw the following conclusions:

(i) The number of publications devoted to extraction by podands is generally low. There have been very few of them in the last 5–10 years.

(ii) Since literature data on the extraction of noble metals by podands are scarce, we cannot judge the selectivity and potential of their use.

(iii) We cannot exclude that one of the reasons that podands have limited applicability as extractants is their poor solubility in the organic solvents that are widely used: kerosene, Escaid 100, Solvesso, etc.

However, this suggests rather than excludes the possibility and necessity of broadening the studies on

The dependence $\log D_{Pd}$ on C_{HCl} is almost linear. In the extraction by phosphoryl-containing podand without octylamine (other conditions being the same), this dependence passes through a maximum near $C_{HCl} = 5$ M ($D_{Pd} = 3$). This difference is associated with a change in the mechanism of extraction of palladium(II) chloride complexes by phosphoryl-containing podand from the anion-exchange mechanism (in the case of the mixture of podand and amine) to the hydrate–solvate mechanism.

As mentioned above, one important characteristic of extractants is their selectivity, that is, their ability to selectively interact with one or several components of the reaction mixture. The nature of donor atoms, the value of the electron density on them, and the compatibility of donor atoms with metal atoms play important roles in accordance to the principle of strong and weak acids and bases.

It was found [22] that the use of a solution of *Va* in 1,2-dichloroethane creates favorable conditions for the selective extraction of gold(III) in microamounts from hydrochloric acid solutions. Thus, the separation coefficients $\beta_{Au/E}$ in the course of Au(III) extraction from 0.5 M HCl by an 0.001 mol/l solution of podand *Va* in 1,2-dichloroethane are as follows:

extraction by podands containing oxygen and other (nitrogen and sulfur) donor atoms.

REFERENCES

1. Yakshin, V.V., *Koord. Khim.*, 2002, vol. 28, p. 742.
2. Shibutani, Y., Sakamoto, H., Hayano, K., and Shono, T., *Anal. Chim. Acta*, 1998, vol. 375, p. 81.
3. Marchand, A.P. and Chong, H.-S., *Tetrahedron*, 1999, vol. 55, p. 9697.
4. *Makrotsiklicheskie soedineniya v analiticheskoi khimii* (Macrocyclic Compounds in Analytical Chemistry), Moscow: Nauka, 1993.
5. Tsivadze, A.Yu., Levkin, A.V., Bondareva, S.V., et al., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 7, p. 1251.
6. Tsivadze, A.Yu., Levkin, A.V., and Bondareva, S.V., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 9, p. 2445.
7. Dmitrienko, S.G., Pletnev, I.V., Baulin, V.E., and Tsvetkov, E.N., *Zh. Anal. Khim.*, 1994, vol. 49, no. 8, p. 804.
8. Jeong, K.-S., Nam, J.W., and Cho, Y.L., *Bull. Korean Chem. Soc.*, 1995, vol. 16, no. 7, p. 571.
9. Pujo-Bouteille, A., Lamande, L., Lopez, L., and Cazaux, L., *Tetrahedron*, 1998, vol. 54, no. 15, p. 3817.
10. Nazarenko, A.Y., Baulin, V.E., Lamb, J.D., et al., *Solvent Extr. Ion Exch.*, 1999, vol. 17, no. 3, p. 495.
11. Xing, Y.J., Zhou, Z.X., Ma, L., and Lu, Z.W., *China Chem. Lett.*, 2000, vol. 11, no. 1, p. 17.

12. Reinoso-Garcia, M.M., Dijkman, A., Verboom, W., et al., *Eur. J. Org. Chem.*, 2005, no. 10, p. 2131.
13. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Zh. Neorg. Khim.*, 2006, vol. 51, no. 11, p. 735.
14. Turanov, A.N., Karandashev, V.K., and Bondarenko, N.A., *Radiokhimiya*, 2006, vol. 48, no. 2, p. 158.
15. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Radiokhimiya*, 2007, vol. 49, no. 3, p. 226.
16. Watanabe, M., Mirvaliev, R., Tachimori, S., et al., *Chem. Lett.*, 2002, no. 12, p. 1230.
17. Lachowicz, E. and Czapiuk, M., *Talanta*, 1990, vol. 37, no. 10, p. 1011.
18. Lachowicz, E. and Krajewski, A., *Anal. Chim. Acta*, 1986, vol. 188, p. 239.
19. Kenji Chayama and Eiichi Sekido, *Bull. Chem. Soc. Jpn.*, 1990, vol. 63, no. 8, p. 2420.
20. Turanov, A.N., Baulin, V.E., Solotnov, A.F., and Tsvetkov, E.N., *Zh. Neorg. Khim.*, 1995, vol. 40, no. 5, p. 866.
21. Turanov, A.N., Karandashev, V.K., Baulin, V.E., and Tsvetkov, E.N., *Zh. Neorg. Khim.*, 1955, vol. 40, no. 11, p. 1926.
22. Turanov, A.N., Bondarenko, N.A., Urinovich, E.M., and Tsvetkov, E.N., *Zh. Neorg. Khim.*, 1996, vol. 41, no. 11, p. 1891.
23. Turanov, A.N., Karandashev, V.K., Bondarenko, N.A., and Urinovich, E.M., *Zh. Neorg. Khim.*, 1996, vol. 41, no. 10, p. 1742.
24. Evreinov, V.I., Vostroknutova, Z.N., and Baulin, V.E., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 1, p. 67.
25. Vornek, A.A., Morosi, G., and Gamba, A., *Phys. Org. Chem.*, 1992, vol. 5, p. 109.
26. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Solvent Extr. Ion Exch.*, 1999, vol. 17, no. 6, p. 1423.
27. Turanov, A.N., Karandashev, V.K., Baulin, V.E., and Tsvetkov, E.N., *Radiokhimiya*, 1995, vol. 37, no. 2, p. 140.
28. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Radiokhimiya*, 1997, vol. 39, no. 5, p. 450.
29. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Radiokhimiya*, 1998, vol. 40, no. 1, p. 39.
30. Turanov, A.N., Karandashev, V.K., and Bondarenko, N.A., *Radiokhimiya*, 2006, vol. 48, no. 2, p. 175.
31. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Zh. Neorg. Khim.*, 1997, vol. 42, no. 9, p. 1570.
32. Turanov, A.N., Baulin, V.E., Kharitonov, A.V., and Tsvetkov, E.N., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 8, p. 1394.
33. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 2, p. 332.
34. Turanov, A.N., Belova, V.V., Zhidkova, T.I., et al., *Zh. Neorg. Khim.*, 2001, vol. 46, no. 9, p. 1573.
35. Turanov, A.N., Karandashev, V.K., and Baulin, V.E., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 10, p. 1734.
36. Yakshin, V.V., Vilkova, O.M., Tsarenko, N.A., and Seregina, O.N., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 11, p. 1885.
37. Zolotov, Yu.A., Iofa, B.Z., and Chuchalin, L.K., *Ekstraktsiya galogenidnykh kompleksov metallov* (Extraction of Halide Complexes of Metals), Moscow: Nauka, 1973.
38. Buslaeva, T.M. and Simanova, S.A., *Koord. Khim.*, 1999, vol. 25, no. 3, p. 165.
39. Gindin, L.M., *Ekstraktsionnye protsessy i ikh primeneniye* (Extraction Processes and Their Application), Moscow: Nauka, 1984.
40. Shmidt, V.S., *Ekstraktsiya aminami* (Extraction by Amines), Moscow: Atomizdat, 1980.