ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 1, pp. 9–16. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © L.N. Moskvin, S.A. Simanova, N.M. Yakimova, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 1, pp. 11–19.

New Capabilities in Extraction of Platinum Metal Chloride Complexes with Oxygen-Containing Extractants

L. N. Moskvin, S. A. Simanova, and N. M. Yakimova

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: moskvinln@yandex.ru

Received March 22, 2011

Abstract—The efficiency of extraction of platinum metal chloride complexes with oxygen-containing extractants can be increased in going from acid chloride solutions to mixed acid sulfate–chloride solutions.

DOI: 10.1134/S1070363212010021

In the initial stage of the development of extraction methods for the isolation of platinum metals attention was given mainly to extraction of their halide complexes with neutral oxygen-containing extractants [1]. Later on emphasis was transferred toward nitrogen- and sulfur-containing extractants [2, 3]. Taking into account the importance of reversibility of transitions between aqueous and organic phases for extraction methods, this tendency restricted their application for both analytical and technological purposes. The formation of stable complexes by platinum metals with sulfur- and nitrogen-containing extractant molecules makes the extraction process with such compounds (including chelating extractants with the same donor atoms) irreversible, so that platinum metals are transferred from aqueous solution into organic phase without a possibility for re-extraction. The potential for further improvement of extraction methods for isolation of platinum metals following traditional way of searching for new extractants was largely exhausted [4].

Loss of interest in oxygen-containing extractant was determined mainly by relatively low partition coefficients (K_D) [2]. Here, a negative factor was also wide dispersion of K_D values given by different authors. For instance, the dispersion of published data on the maximal K_D values for platinum metals in the most popular system HCl–tributyl phosphate [5] is as follows: Pd(II) 2.0–4.0, Ru(IV) 0.25–22.0, Pt(IV) 15.0–30.0, Ir(IV) 0.13–30, Os(IV) 6.0–2.5×10^3. The largest dispersion is observed for Os(IV), all data being assigned to $[OsCl_6]^{2-}$.

The goal of the present work was to analyze factors responsible for dispersion of K_D values and substantiate capabilities for improvement of the extraction efficiency of platinum metal chloride complexes with oxygen-containing extractants on the basis of the results of our previous studies [6–14]. While performing this study, specific attention was given to the synthesis of initial chloride complexes of each metal and development of procedures for their isolation from solution. To ensure maximal reliability in the determination of K_D, the concentration of platinum metals in both phases was monitored with the use of radioactive labels.

Figure 1 shows the results of the first step of our study as the dependences of refined K_D values of platinum metal chloride complexes in the system hydrochloric acid–tributyl phosphate. Comparison of the data in Fig. 1 with those given above shows that the only similarity is general trend for the maximal K_D value to increase in the series Pd(II) < Pt(IV) < Ir(IV) < Os(IV), whereas the maximal K_D values differ considerably. A quite satisfactory agreement is observed only for Pd(II), which may be expected taking into account lability of Pt(II) chloride complexes. On the whole, we can conclude that, despite the above refinement, the maximal K_D values for chloro complexes of all platinum metals are clearly insufficient for their isolation by extraction at both analytical and large-scale levels.

The partition coefficient K_D in the extraction of platinum metal compounds with oxygen-containing extractants may be increased in two ways. The first of

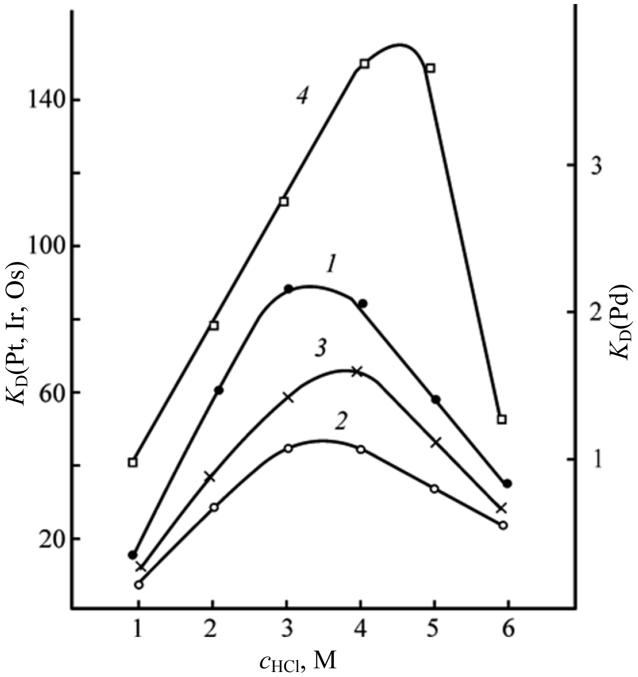

Fig. 1. Plots of partition coefficients of (*1*) $[PdCl_4]^{2-}$, (*2*) $[PtCl_6]^{2-}$, (*3*) $[IrCl_6]^{2-}$, and (*4*) $[OsCl_6]^{2-}$ in the extraction with tributyl phosphate from hydrochloric acid solutions versus concentration of the latter.

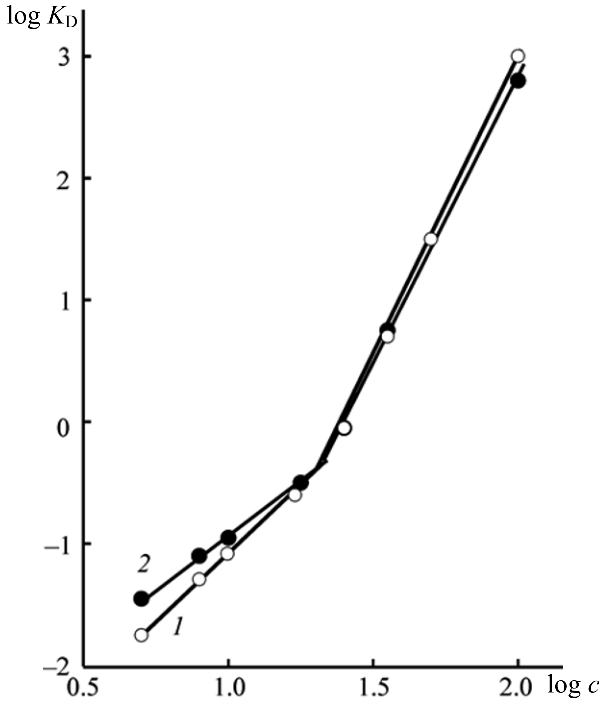

Fig. 2. Log plots of partition coefficients for (*1*) platinum(IV) and (*2*) palladium(II) chloride complexes in the system 2 M HCl–trioctylphosphine oxide in decan-1-ol versus molar concentration of trioctylphosphine oxide.

these is already noted traditional search for new extractants, and the second is optimization of the composition of aqueous solutions which are subjected to extraction. In particular, the use as extractant of a 0.05 M solution of tributylphosphine oxide in dichloroethane ensures a K_D value approaching 10^3 in the extraction of osmium(IV) as $[OsCl_6]^{2-}$ from aqueous solution [15].

The results of our studies on the use of trialkylphosphine oxides as extractants for platinum metals showed that K_D values can be increased considerably via appropriate selection of organic solvent and extraction with molten trialkylphosphine oxides [6]. In particular, among commonly used organic solvents, aliphatic alcohols ensure the maximal solubility of trioctylphosphine oxide. Therefore, in our studies we used decan-1-ol whose solubility in water is similar to the solubility of trioctylphosphine oxide, and the concentration of the latter in decan-1-ol at 20°C may reach 65 wt %.

As platinum metal compounds we selected chloro complexes of Pd(II) and Pt(IV). Figure 2 shows log dependences of their partition coefficients (log K_D) upon concentration of trioctylphosphine oxide in decan-1-ol at a constant composition of the aqueous phase (2 M hydrochloric acid). Two linear parts with different slopes are clearly distinguished in each dependence. At low trioctylphosphine oxide concentrations the slope is 2.0±0.2, and it changes to 5.0±0.2 in going to high concentrations. The bending point corresponds to 20% concentration of trioctylphosphine in decan-1-ol. Extrapolation of the second part toward higher trioctylphosphine oxide concentration gives a point reflecting extraction of Pd(II) and Pt(IV) complexes from solution having analogous composition with trioctylphosphine oxide melt at 60°C; this indicates similar solvation properties of trioctylphosphine oxide in melt and in solution in decan-1-ol.

Previously, dilute solutions of analogous extractants (left part of the plots shown in Fig. 2) were used for isolation of platinum metals [7]. Relatively small slope of the log K_D dependence upon logarithm of trioctylphosphine oxide concentration in the region of dilute solutions is likely to be the main factor responsible for reduced interest in such extractants. Sharp increase of the extraction ability in going to concentrated solutions of trioctylphosphine oxide in decan-1-ol indicates that the potential of such extraction systems was not discovered completely. This is confirmed by the dependences of K_D upon HCl concentration in the extraction of Pd(II) and Pt(IV) complexes with liquid trioctylphosphine oxide at 60°C and with its 50% solution in decan-1-ol (Fig. 3).

The observed dependences resemble those obtained previously for the traditional HCl–tributyl phosphate system [7]. On the other hand, despite similar general characters of these dependences indicating identical mechanisms of extraction processes with participation of trioctylphosphine oxide and tributyl phosphate, the K_D values in the extraction with a 50% solution of trioctylphosphine oxide in decan-1-ol and with liquid trioctylphosphine oxide are higher, respectively, by more than an order and two orders of magnitude, the compositions of the aqueous phase being comparable.

As concerns optimization of the composition of aqueous phase with a view to improve K_D in the extraction of platinum metals with oxygen-containing extractants, the most interesting were maxima on the curves for extraction of Pd(II) chloro complexes into both trioctylphosphine oxide and tributyl phosphate. These maxima are located in the region of low hydrochloric acid concentrations where Pd(II) exists mainly as singly charged anionic aquatrichloro complex $[Pd(H_2O)Cl_3]^-$. Transfer of palladium into both extractants in the form of singly charged anionic complex is well consistent with the results of our previous studies on electrodialysis of platinum(IV), iridium(IV), and palladium(II) chloride complexes through tributyl phosphate extraction membranes [8]. It was found that chloride complexes of platinum metals are transferred through tributyl phosphate membranes mostly as singly charged complex anions. This followed from the current efficiency for chloride complexes of all platinum metals isolated by electrodialysis; recalculation for doubly charged complexes $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[IrCl_6]^{2-}$ gave a current efficiency of higher than 100%, which is theoretically impossible.

The maxima on the curves for extraction of Pd(II) with tributyl phosphate and tributylphosphine oxide from dilute HCl solutions, where Pd(II) species are represented mainly by singly charged $[Pd(H_2O)Cl_3]^-$ ions, can be rationalized by comparing with predominant extraction of singly charged anionic complexes $[AuCl_4]^-$ and $[SbCl_6]^-$ from aqueous solution with oxygen-containing extractants [1]. It is more difficult to explain the transport of singly charged anionic chloride complexes of Pt(IV) and Ir(IV) through a tributyl phosphate membrane upon electrodialysis. The only hypothetical interpretation may be the transfer of the above species in the form $H[MCl_6]^-$ (where M = Pt or Ir), which may be assumed to exist in strongly acidic medium, i.e., when dissociation of the corresponding chlorometallic acid at the second step is partially or completely suppressed due to high concentration of H^+ ions. In this case, variation of proton concentration in solution changes the ratio of species occurring in dynamic equilibrium (1). This equilibrium is displaced to the right as the acidity increases.

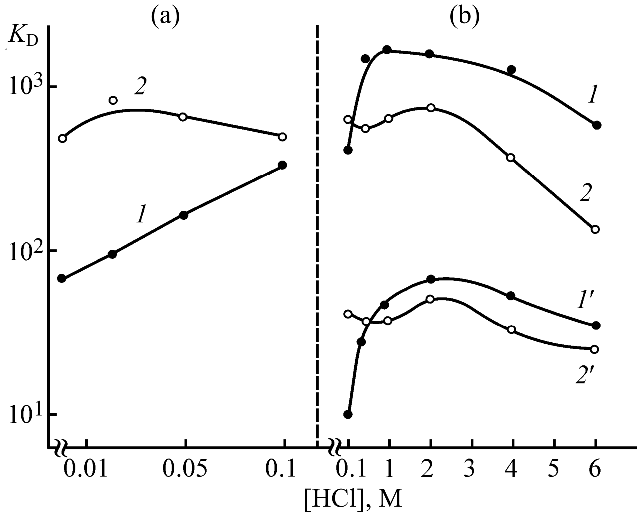

Fig. 3. Plots of partition coefficients for (*1*, *1'*) platinum(IV) and (*2*, *2'*) palladium(II) chloride complexes in the systems hydrochloric acid–liquid trioctylphosphine oxide (unprimed curve numbers) and hydrochloric acid–50% trioctylphosphine oxide in decan-1-ol (primed curve numbers). Range of HCl concentration, M: (a) 0.005–0.1 and (b) 0.1–0.6.

$$[MCl_n]^{2-} + 2H^+ \rightleftarrows H[MCl_n]^- + H^+ \rightleftarrows H_2[MCl_n]. \qquad (1)$$

Under the conditions ensuring the existence of platinum metal species as doubly charged tetra- or hexachlorometalate ions [16], their transition from aqueous phase into tributyl phosphate is unfavorable from the viewpoint of energy. This is confirmed by low K_D values for the extraction of Pt(IV) chloride complexes with tributyl phosphate (TBP) from dilute HCl solutions [2] with an acidity corresponding to the existence of $[PtCl_6]^{2-}$. Increase in the concentration of protons is accompanied by increase of the concentration of $H[MCl_n]^-$ and $H_2[MCl_6]$ species in the aqueous phase; the former tend to form an associate with solvated proton and transfer to organic phase (2).

$$[H^+{\cdot}H_2O_m{\cdot}TBF_n] + H[MCl_6]^- \rightleftarrows \{[H^+{\cdot}H_2O_m{\cdot}TBF_n]{\cdot}H[MCl_6]^-\}_{org}. \qquad (2)$$

Further rise in acidity shifts equilibrium toward formation of unextractable $H_2[MCl_n]$ species. This scheme rationalizes the dependences of K_D upon HCl concentration for extraction of platinum metals existing in solution as tetra- and hexachloride complexes. These dependences are characterized by maxima which may be assigned to $H[MCl_n]^-$. If the acidity is lower or higher than some optimal value, equilibria (1) and (2) are displaced toward poorly extractable $[MCl_4]^{2-}$ and $H_2[MCl_n]$ species. Provided that the proposed interpretation is valid, new capabilities appear for controlling the extraction conditions. Obviously, the increase in hydrogen chloride concentration in the aqueous phase with a view to displace the equilibrium toward formation of readily extractable $H[MCl_4]^-$ or $H[MCl_6]^-$ species is weakly effective because of simultaneous increase on the concentration of chloride ions which compete with anionic platinum metal complexes at the stage of formation of extractable associates with hydrated proton. The acidity required for displacement of equilibrium toward readily extractable $H[MCl_n]^-$ species may be achieved without raising chloride ion concentration via addition of another acid which does not affect the composition of inner coordination sphere of the complexes and is simultaneously less extractable into tributyl phosphate. Such an acid may be sulfuric acid. First, it is less extractable than HCl [2], and second, it does not induce decomposition of strong platinum metal chloride complexes [16].

Figure 4 shows plots of K_D for extraction of Pt(IV) and Pd(II) chloride complexes with tributyl phosphate versus overall concentration of protons at different concentration of chloride ions, where the acidity is controlled by variation of sulfuric acid concentration. The overall concentration of protons was calculated assuming that the degrees of dissociation of HCl and H_2SO_4 (at the first step) are equal to unity. It is seen that within the examined acidity range, partial replacement of HCl by H_2SO_4 increases the partition coefficient, i.e., decrease of HCl concentration in the mixture of acids is accompanied by increase of K_D. This is consistent with the assumed competing extraction of chloride ions. It should be noted that reduction of HCl concentration from 0.1 to 0.01 M does not affect K_D for Pt(IV) complexes to an appreciable extent, whereas analogous variation of HCl concentration becomes significant for extraction of Pd(II) complexes. Insignificant variation of HCl concentration in solution does not change the composition of the inner sphere of Pt(IV) complexes which retain six chloride ions therein. The effect of HCl concentration on the transport of Pd(II) complex into the organic phase is determined not only by competing extraction of chloride ions but also by formation of readily extractable $[Pd(H_2O)Cl_3]^-$ species at low chloride ion concentrations. The possibility for considerable improvement of the efficiency of extraction in going from hydrogen chloride solutions to acid sulfate–chloride solution, which was demonstrated for Pd(II) and Pt(IV) chloride complexes, also exists for analogous compounds of other platinum metals (Fig. 5) [17].

As in other cases, an important factor in the extraction of platinum metal chloride complexes with oxygen-containing extractants from mixed acid solutions is complete reversibility of the extraction process (Table 1). Linearity of the extraction isotherm over a wide range of metal concentration (up to 20 g/l) is also important. The observed increase in the efficiency of extraction of platinum metal chloride complexes in going from hydrogen chloride solutions to acid sulfate–chloride solution is general for all oxygen-containing extractants acting according to the hydrate–solvate extraction mechanism [1]. In the extraction of platinum(IV) and palladium(II) chloride complexes with higher alcohols the K_D value increases by 1.5–2 orders of magnitude in going from chloride to mixed chloride–sulfate solution, other conditions being comparable [12]. For instance, the K_D value for the extraction of Pt(IV) chloride complexes with heptan-1-ol attains 20, which is comparable with the maximal K_D value in the extraction from acid chloride solutions with tributyl phosphate.

Apart from high K_D values for platinum metal chloride complexes, the proposed extraction systems are interesting from the viewpoint of separation from impurities of base metals, such as Ni(II), Co(II), Cu(II), and Fe(III), which do not form chloride complexes with a comparable stability [11]. Unlike platinum metal complexes, partition coefficients of those metals considerably decrease in going from acid chloride to mixed chloride–sulfate solutions, so that platinum metals can be extracted with high selectivity. The maximal degree of separation of all platinum metals from associated impurities of nonferrous metals is observed at minimal chloride ion concentrations (0.01–0.1 M) and a moderate acidity ($[H^+]$ = 4–5 M). Under these conditions the difference in the partition coefficients of platinum and base metals reaches four orders of magnitude.

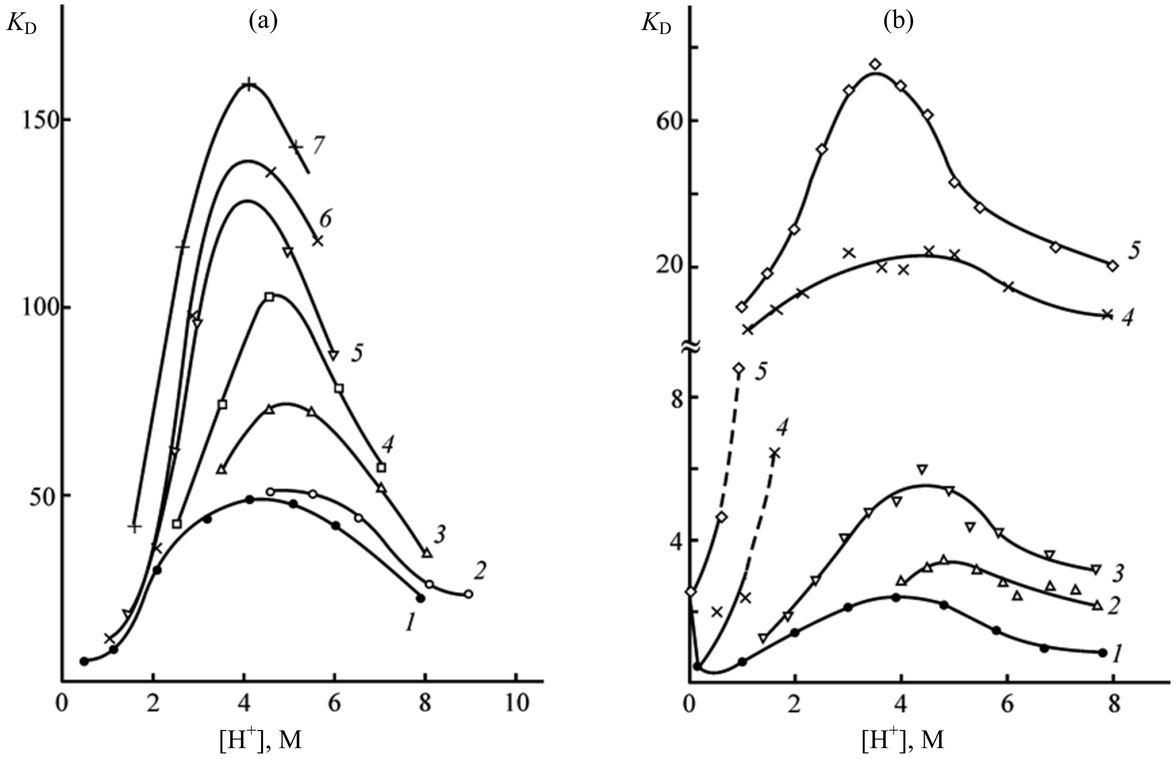

Fig. 4. Plots of partition coefficients of (a) platinum(IV) and (b) palladium(II) chloride complexes versus concentration of protons (M) for the extraction with tributyl phosphate from (*1*) acid chloride and (*2–7*) mixed chloride–sulfate solutions at HCl concentrations of (a): (*2*) 4, (*3*) 3, (*4*) 2, (*5*) 1, (*6*) 0.5, (*7*) 0.1 (0.01) M, [Pt] = 40 mg/l, and (b): (*2*) 3, (*3*) 1, (*4*) 0.1, (*5*) 0.01 M, [Pd] = 90 mg/l.

Due to high K_D values in combination with high selectivity, reversibility of the process, and linearity of the extraction isotherm extraction of platinum metal chloride complexes with tributyl phosphate from mixed acid chloride–sulfate solution attracts interest from both technological and analytical viewpoints. For analytical purposes, it becomes possible to pass from static extraction to extraction–chromatographic isolation of Pd(II) and Pt(IV) with simultaneous separation from associated impurities [10]. Optimal conditions for separation of platinum(IV) and palladium(II) can be found by calculating the selectivity coefficient K_s which is defined as the limiting value of the separation coefficient K_{sep}; the latter in turn is equal to the ratio of partition coefficients; i.e., in our case, $K_{sep}(Pt/Pd) = K_D(Pt)/K_D(Pd)$. The calculated limiting separation coefficients for different compositions of aqueous solutions are given in Table 2. These data show that the most favorable conditions for the separation of Pt(IV) from Pd(II) are attained at an HCl concentration of 1–2 M and H_2SO_4 concentration of 3–6 M. The optimal composition of aqueous phase for the separation of impurities of associated base metals by column extraction chromatography with tributyl phosphate as stationary phase is 0.01 M HCl–4 M H_2SO_4. The composition of mobile phase for separate elution of Pd(II) and Pt(IV) is the same as given above.

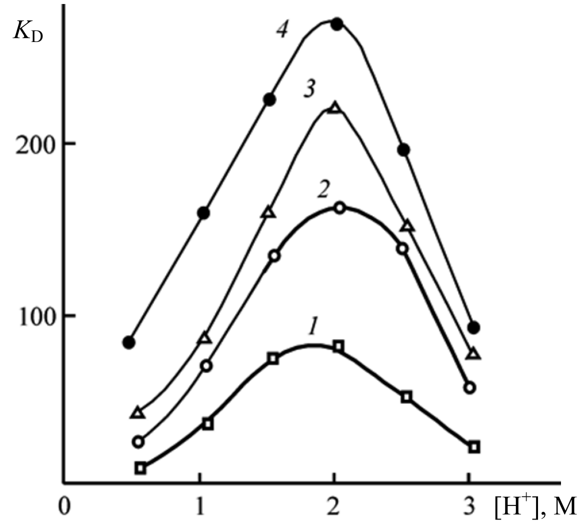

Fig. 5. Plots of partition coefficients of (*1*) $[PdCl_4]^{2-}$, (*2*) $[PtCl_6]^{2-}$, (*3*) $[IrCl_6]^{2-}$, and (*4*) $[OsCl_6]^{2-}$ versus concentration of protons in the system 0.01 M HCl + H_2SO_4–tributyl phosphate.

Table 1. Partition coefficients of platinum(IV) chloride complexes in extraction and re-extraction in the system acid chloride–sulfate solution–tributyl phosphate [9]

Composition of aqueous phase	K_D (extraction)	K_D (re-extraction)
0.1 M. HCl + 8 M. H_2SO_4	158	178
0.25 M. HCl + 8 M. H_2SO_4	144	132
0.5 M. HCl + 8 M. H_2SO_4	137	135
0.1 M. HCl + 5 M. H_2SO_4	109	115
0.25 M. HCl + 5 M. H_2SO_4	95	96
1.0 M. HCl + 5 M. H_2SO_4	92	82
2.0 M. HCl + 5 M. H_2SO_4	94	86

Table 2. Partition coefficients of platinum(IV) and palladium(II) chloride complexes in the system acid chloride–sulfate solution–tributyl phosphate at a constant H_2SO_4 concentration (4 M) and different HCl concentrations [10]

c_{H^+}, M	K_{sep}(Pt/Pd)			
	c_{HCl} 0.01 M	c_{HCl} = 0.1 M	c_{HCl} = 1.0 M	c_{HCl} = 2.0 M
1.0	1.11	3.33	10.0	–
2.0	2.38	6.90	17.9	–
3.0	1.95	7.15	19.5	18.2
4.0	2.15	6.92	19.8	21.0
5.0	2.91	5.96	19.3	20.3
6.0	2.88	5.58	18.6	20.3
7.0	2.28	5.18	14.4	18.4
8.0	1.43	4.29	9.4	12.5

Mutual contamination of platinum(IV) and palladium(II) fractions was no more than 0.1%, which corresponds to a mutual purification factor of 10^3. The upper limit of contamination of platinum and palladium with base metals was estimated by determination of ^{59}Fe in the corresponding fractions, which was added as radioactive label of the most extractable Fe(III) impurity. The purification factor was higher than 10^5.

The proposed procedure for the isolation of platinum(IV) and palladium(II) complexes by extraction chromatography via joint elution with a 0.01 M solution of HCl turned out to be readily adaptable to their determination by atomic absorption spectroscopy with electrothermal atomization [11]. On the other hand, separation of Pt(IV) and Pd(II) complexes by extraction chromatography using columns charged with tributyl phosphate made it possible to isolate pure chloride and aqua chloride platinum metal complexes, which is important from the viewpoint of interpretation of discrepant published data on the extraction of platinum metal chloride complexes with tributyl phosphate (see above).

Taking into account that the maximal dispersion of published data was observed for Os(IV) chloride complexes [5], the above procedure was applied to isolation of just Os(IV) complexes [13, 14]. The initial ratio of different Os(IV) species was controlled by the time of keeping initial $[OsCl_6]^{2-}$ compound in 0.05 and 6.0 M HCl solutions. The resulting solutions containing Os(IV) complexes were filtered through an extraction chromatographic column with tributyl phosphate as stationary phase. A fraction obtained by passing through the column the entire volume of the initial solution and washings (6 M HCl) contained Os(IV) species that are not extracted with tributyl phosphate, in particular $[Os(H_2O)_2Cl_4]$. Elution with 0.2 M HCl afforded $[OsCl_6]^{2-}$, and final elution with deionized water gave a fraction containing $[Os(H_2O)Cl_5]^-$. The isolated Os(IV) complexes were identified by their electron absorption spectra in the visible region, and these data confirmed once more that singly charged $[Os(H_2O)Cl_5]^-$ anion is the most extractable osmium compound.

By the preparative extraction chromatography we isolated pure Os(IV) complexes and prepared solutions for the determination of K_D for each complex. The duration of each operation was minimized so that to avoid appreciable variations in the composition of osmium complexes. Extraction of $[Os(H_2O)_2Cl_4]$ with tributyl phosphate from both acid chloride and mixed chloride–sulfate solutions was characterized by a K_D value of less than 0.1. The maximal K_D values for generally prevailing $[OsCl_6]^{2-}$ species in acid chloride solutions and chloride–sulfate solutions with the HCl concentration fixed at 1 M were 150 and 250, respecttively. Using K_D values for particular Os(IV) species [12] we estimated the contributions of each of them to the overall K_D value for their mixtures corresponding to real solutions. Taking into account that all experiments were performed with freshly prepared solutions, variation of the component ratio during the time necessary for extraction equilibration may be neglected. This assumption is quite appropriate for

6 M HCl solution selected as initial medium for extraction. Table 3 contains the experimental and calculated K_D values. The experimental values were determined for a series of specially prepared solutions with different concentration of pure osmium(IV) complexes isolated by extraction chromatography. The calculations were performed assuming additivity of contributions of K_D of particular complexes to the overall K_D value [12].

Following analogous procedure with the use of extraction chromatography we examined hydrochloric acid solutions of mixtures of Ir(IV) chloride complexes [13]. The $[IrCl_6]^{2-}$ complex was synthesized according to standard procedure [16], and its solutions in hydrochloric acid with different concentrations were prepared. These solutions were found to contain four complexes with sharply different extractabilities. Iridium(III) compounds and $[Ir(H_2O)_2Cl_4]$ were the least extractable species (first fraction). The second and third fractions contained $[IrCl_6]^{2-}$ and $[Ir(H_2O)Cl_5]^-$, respectively. In addition, a small amount of previously unknown doubly charged anionic Ir(IV) species was isolated; its extractability was intermediate between $[IrCl_6]^{2-}$ and $[Ir(H_2O)Cl_5]^-$. By analogy with ruthenium(IV) compounds [16], we presumed that these species have the composition $[Ir_2O_2Cl_8]^{2-}$. The relative concentrations of iridium complexes in different fractions are given in Table 4. The major form is hexachloroiridate(IV) $[IrCl_6]^{2-}$. As with osmium(IV) compounds, the maximal K_D values were observed for singly charged $[Ir(H_2O)Cl_5]^-$ complex.

While studying the compositions of iridium complexes in hydrogen chloride solutions saturated with gaseous chlorine for stabilization of Ir(IV) chloride complexes, we found one more factor affecting reproducibility in the determination of K_D for platinum metals; this factor should necessarily be taken into account in the development of extraction isolation methods. Preliminary saturation of the aqueous phase with chlorine under the conditions of extraction chromatography leads to sharp increase in the amount of chlorine transferred to the organic phase and appreciable reduction of partition coefficients of iridium complexes. Presumably, this effect is related to the shift of the equilibrium $Cl_2 + Cl^- \leftrightarrow Cl_3^-$ in the two-phase system aqueous solution–extractant toward the formation of relatively large singly charged Cl_3^- ion which is characterized by a small charge density. In keeping with the hydrate–solvate mechanism, such anions should be readily extracted into tributyl phosphate. Preferential extraction of a large amount of Cl_3^- during extraction chromatography leads to a sharp reduction of the extraction capacity of chromatographic column with respect to iridium(IV) chloride complexes, so that the efficiency of binding of Ir(IV) complexes from the eluent saturated with Cl_2 decreases. Insofar as chlorination of solutions may be used in extraction and extraction chromatographic processes for separation of various mixtures of platinum metals, the effect of co-extraction of Cl_3^- ion must also be taken into account in the isolation of other elements by extraction chromatography. As might be expected, co-extraction of chlorine under static extraction conditions exerts a considerably weaker effect, for it does not accumulate in the organic phase to a considerable extent.

Table 3. Fractions of different osmium(IV) complexes in the initial aqueous solution and their experimental (K_D^{exp}) and calculated (K_D^{calc}) partition coefficients in the system tributyl phosphate–6 M hydrochloric acid [12]

$[OsCl_6]^{2-}$	$[Os(H_2O)Cl_5]^-$	$[Os(H_2O)_2Cl_4]^0$	K_D^{exp}	K_D^{calc}
0.65	0.15	0.20	3.6	4.0
0.86	0.12	0.02	24	27
0.88	0.12	0.006	48	43
0.09	0.01	0.90	0.18	0.19

Table 4. Effect of hydrochloric acid concentration on the fraction of complex forms of Ir(IV) in hydrochloric acid solutions

[HCl], M	Freshly prepared solution			Solution stored for 35 days		
	1st fraction Ir(III) + $[Ir(H_2O)_2Cl_4]$	2nd fraction $[IrCl_6]^{2-}$	3rd fraction $[Ir(H_2O)Cl_5]^-$	1st fraction Ir(III) + $[Ir(H_2O)_2Cl_4]$	2nd fraction $[IrCl_6]^{2-}$	3rd fraction $[Ir(H_2O)Cl_5]^-$
0.1	–	93	6.0	–	92	8.6
1.0	–	95	5.0	–	90	9.5
3.0	1.8	94	3.3	0.8	96	2.5
6.0	2.8	95	2.3	2.0	95	1.7
8.0	4.2	96	0.6	2.6	97	0.2

Thus our results unambiguously indicate that the presence in solution of several forms of complexes characterized by different extractabilities and low rate of interconversion and the effect of co-extraction of chlorine are very important factors which should necessarily be taken into account while studying extraction processes with oxygen-containing extractants. It should also be kept in mind that spectro-photometric data given by many authors are clearly insufficient to prove the existence of platinum metals in solution in the form of a single complex. The positions of absorption maxima of their chloride and aqua chloride complexes in the visible region are very similar, which makes their direct spectrophotometric determination (at a relative concentration of up to 10% and more) almost impossible. For example, variation of the concentration of neutral osmium(IV) complex from 0.6 to 20% (Table 3) almost does not affect the electron absorption spectrum [14], whereas the overall partition coefficient changes by more than an order of magnitude.

From this point it becomes clear why different results were given by different authors for the extraction of platinum metals in the system hydrochloric acid–tributyl phosphate [5]. The given partition coefficients are actually average quantities for mixtures of different platinum metal complexes. All the above stated largely applies to all platinum metals, except for palladium whose chloride complexes are fairly labile; therefore, the data for palladium are characterized by the smallest dispersion.

The fact that published data on the extraction of platinum metal complexes with oxygen-containing extractants are related to the composition of the initial complexes is quite important. In this case, phase transfer processes are not accompanied by replacement of ligands in the inner sphere of complexes or their transformation into a single extractable form, as it generally occurs in the extraction of platinum metals with nitrogen- and sulfur-containing extractants. Therefore, reliable information on the forms of existence of platinum metal complexes in initial aqueous solution is necessary for studying their extraction with oxygen-containing extractants. The most efficient way of improving extractability of platinum metal complexes is the choice of appropriate conditions ensuring shift of the equilibrium in the aqueous phase toward formation of most extractable singly charged anionic species. It might be expected that the maximal efficiency in the isolation of platinum metal chloride complexes would be achieved by extraction with trialkylphosphine oxides from acidic mixed chloride–sulfate solution.

REFERENCES

1. Zolotov, Yu.A., Iofa, B.Z., and Chuchalin, L.G., *Ekstraktsiya galogenidnykh kompleksov metallov* (Extraction of Halide Metal Complexes), Moscow: Nauka, 1973.
2. Nikolaeva, Z.I. and Kartashova, N.A., *Ekstraktsiya neitral'nymi organicheskimi soedineniyami* (Extraction with Neutral Organic Compounds), Moscow: Atomizdat, 1976, vol. 1.
3. Gindin, L.M., *Ekstraktsionnye protsessy i ikh primenenie* (Extraction Processes and Their Applications), Moscow: Nauka, 1984.
4. Petrukhin, O.M., Myasoedova, G.V., and Malofeeva, G.I., *Analiticheskaya khimiya metallov platinovoi gruppy* (Analytical Chemistry of Platinum Metals), Zolotov, Yu.A., Varshal, G.M., and Ivanov, V.M., Eds., Moscow: URSS, 2003, p. 140.
5. Moskvin, L.N., Orlov, A.M., and Simanova, S.A.., *Zh. Prikl. Khim*., 1986, vol. 59, no. 10, p. 2285.
6. Grigor'ev, G.L., Mozzhukhin, A.V., Moskvin, L.N., and Orlov, A.M., *Dokl. Akad. Nauk SSSR*, 1987, vol. 292, no. 4, p. 884.
7. Moskvin, L.N., Grigor'ev, G.L., Krasnoperov, V.M., Orlov, A.M., and Simanova, S.A., *Dokl. Akad. Nauk SSSR*, 1981, vol. 257, no. 5, p. 1183.
8. Moskvin, L.N., Krasnoperov, V.M., and Chereshkevich, Yu.L., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1974, no. 2, p. 53.
9. Moskvin, L.N., Grigor'ev, G.L., and Krasnoperov, V.M., *Zh. Prikl. Khim*., 1983, vol. 56, no. 5, p. 1153.
10. Moskvin, L.N., Krasnoperov, V.M., and Grigor'ev, G.L., *Zh. Anal. Khim*., 1982, vol. 37, no. 5, p. 942.
11. Moskvin, L.N., Yakimova, N.M., and Alekseeva, I.A., *Zh. Anal. Khim*., 2005, vol. 60, no. 1, p. 41.
12. Moskvin, L.N., Grigor'ev, G.L., and Krasnoperov, V.M., *Zh. Neorg. Khim*., 1983, vol. 28, no. 12, p. 3119.
13. Moskvin, L.N., Grigor'ev, G.L., Krasnoperov, V.M., and Simanova, S.A., *Zh. Neorg. Khim*., 1985, vol. 30, no. 1, p. 170.
14. Moskvin, L.N. and Shmatko, A.G., *Zh. Neorg. Khim*., 1988, vol. 33, no. 12, p. 1229.
15. Bol'shakov, K.A., Sinitsyn, N.M., Bondar', N.M., and Shakhova, M.N., *Zh. Neorg. Khim*., 1975, vol. 20, no. 6, p. 1641.
16. Buslaeva, T.M. and Simanova, S.A., *Analiticheskaya khimiya metallov platinovoi gruppy* (Analytical Chemistry of Platinum Metals), Zolotov, Yu.A., Varshal, G.M., and Ivanov, V.M., Eds., Moscow: URSS, 2003, p. 16.
17. Moskvin, L.N., Grigor'ev, G.L., Krasnoperov, V.M., and Simanova, S.A., *Zh. Prikl. Khim*., 1980, vol. 53, no. 9, p. 1938.