ARTICLES

The Study of the $PtCl_6^{2-}$ Concentration with Reversed Micelles as a Function of the Acid−Salt Content of the Feed

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It is shown that the acidity and the electrolyte concentration of the feed can control the solubilizing capacity and size of the micelles in extraction systems, which may be used to improve the $PtCl_6^{2-}$ concentration. The increase in HCl concentration increases the recovery but decreases the concentration, because of the formation of large micelles of a high solubilizing capacity. The addition of Na_2SO_4 to the acid solutions improves the concentration and recovery, the size and the capacity of the micelles being decreased. An increased concentration of H^+ and Cl^- ions and a decreased concentration of Na^+ and SO_4^{2-} ions in micelles relative to their concentration in the feed was established. The micellar pseudophase composition points to the formation in the micelles of a double electric layer (DEL) capable of exchanging its counterions for $PtCl_6^{2-}$. Impregnation into reversed micelles of an anionic oil-soluble surfactant (bis(2-ethylhexyl)sodium sulfosuccinate (AOT)) compensates the surface charge of the micelle and depresses the extraction.

Introduction

The large specific surface area of reversed micelles suggests their potential use in separation and concentration processes. In liquid extraction, the formation of reversed micelles is described by many investigators as the phenomenon accompanying the extraction of metals. Possible aggregation of tributyl phosphate (TBPh) at high acid and salt contents of the organic phase was shown.[1,2] The composition of the TBPh micelles and location of $FeCl_4^-$ and ClO_4^- anions (in the surface layer and in the micelle core, respectively) was studied by IR spectroscopy.[3] The size and the shape of the forming micelles in the extraction of nickel and cobalt with bis(2-ethylhexyl)-phosphoric acid were determined.[4,5] In the extractive recovery of alkali-earth elements, lanthanides and zirconium, with the same extractant in the presence of aliphatic alcohols, the formation of complex vesicular structures was observed.[6] The

formation of micelles in the extraction system with potassium alkylphenolate was described.[7] The association of the Kelex-100 extractant in the extraction of chloride complexes of rhodium(III) was studied by different methods.[8] Sometimes surfactants are used in the extraction systems instead of the conventional extractants. The possibility of effective separation of Cu(II) and Fe(III) with micelles of bis(2-ethylhexyl)sodium sulfosuccinate (AOT) was shown.[9,10] A 3-fold concentration of Ni(II) with microemulsions of sodium dodecyl sulfate was achieved.[11] A 5-fold concentration of Al(III) and Ga(III) from acid media was obtained with the phenol formaldehyde oligomer "Yarresine B" as the surfactant.[12] By employing the peculiarities of the supramolecular structural transformations in micellar solutions of the ethoxylated surfactant, Neonol APh_9-4, a method for the concentration of metals was developed[13] which combines the advantages of both the extractive and sorptive concentration and shows improved characteristics compared with the known methods of extractive concentration (the absolute concentration

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coefficient of halogenide metal complexes of as high as 1.5×10^3 could be achieved in one stage). The aim of this work was to study the effect of feed composition on the $PtCl_6^{2-}$ concentration efficiency with micelles of an ethoxylated surfactant.

Experimental Section

Reagents. For the formation of reversed micelles in the organic phase, ethoxylated nonylphenol with an average degree of ethoxylation of 4, Neonol APh_9-4, was used. The reagent is produced by Diagnostikum (Belgorod, Russia) and is the analogue of Triton N-42. The hydrophilic−lipophilic balance was equal to 9.1 ± 0.3. The content of the ethoxylated homologues was equal to 99.9%; the content of the homologue with the degree of ethoxylation of 4 was 30%. The compensation for the micellar surface charge created by protonated Neonol APh_9-4 species was achieved with an oil-soluble surfactant, AOT, produced by Serva. The surfactants were used as received. Reagent-grade purity *n*-decane was used as the organic solvent for the surfactants. Prior to use *n*-decane was kept for a prolonged time over Al_2O_3 and twice distilled. The starting Neonol APh_9-4 concentration in the solution was equal to 10 mass % in all cases. The desolubilization of the aqueous pseudophase was performed with the reagent-grade purity chloroform. The inorganic reagents (HNO_3, HCl, HBr, $NaCl$, Na_2SO_4, $BaCl_2$, $AgNO_3$, $Na_2B_4O_7$, and $SnCl_2$) were at least of reagent-grade purity. Twice-distilled water was used for the preparation of aqueous solutions. The solutions of Pt(IV) were prepared by dissolving metallic platinum (99.9%) in a mixture of HNO_3 and HCl (1:3) by the known procedure.[14]

Equipment. The potentiometric titration was performed with an I-135 ionometer (Analitpribor, Tbilisi, Georgia). The photocolorimetric determination of platinum(IV) was performed on a KFK-2MP colorimeter (ZOMZ, Zagorsk, Russia). The hydrodynamic radius of the micelles was determined by photon correlation spectroscopy (PCS). The PCS spectrometer was designed and constructed at the Institute of Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia). The 13 mW and 630 nm wavelength LG-69 He−Ne laser was used as the source of laser radiation. The pulse collection and processing was performed with a 60-channel digital correlator coupled to a minicomputer.

General Procedures. The extraction and determination of the micellar pseudophase composition was performed as follows. The volume ratio of the aqueous feed and the organic phase was equal to 5 in all cases. The phases contacted for 30 min under the conditions of "soft" stirring achieved with a propeller mixer. The aqueous phase was the continuous phase. For the back-extraction (desolubilization) of the aqueous pseudophase the extract was transferred into a conical vessel with walls covered with polyethylene and diluted with chloroform in the volume ratio of 2:1.[13] One to several days were required for the complete disengagement of the solubilized aqueous pseudophase. The disengaged phase was separated from the organic phase with a pipet and analyzed. The H^+ and Cl^- ion concentrations were determined by the potentiometric titration with solutions of sodium tetraborate and silver nitrate, respectively.[15] The SO_4^{2-} ion content was determined by the titration with barium chloride in a water−acetone medium in the presence of thorin and methylene blue as indicators.[16] The Na^+ ion concentration was calculated using the electroneutrality principle. The $PtCl_6^{2-}$ and $PtBr_6^{2-}$ ions were determined in the feed (in the chloride and sulfate media) photometrically using the known tin dichloride procedure.[17]

The hydrodynamic radius of the micelles was determined by the PCS method. The programs were based on the solution of the inverse problem of the correlation spectroscopy by the regularization method of Tikhonov.[18] The effective hydrodynamic radii of the micelles were calculated from the diffusion coefficients for spherical particles of equal size (fitting of experimental values of the autocorrelation function of one exponent). The measurement of the hydrodynamic radius was performed at an angle of 30° and sampling times of 20 or 40 μs; the collection time was several minutes. No angular dependence of the hydrodynamic radius was found in the studied systems at angles from 15° to 90°. For each system the hydrodynamic radius was determined as the average value of 10 measurements. The autocorrelation functions satisfying the criteria of ref 19 were used. The measurement error was 10%. Prior to the measurements, the micellar solutions were dedusted by filtering in a closed box through a glass filter with a pore diameter of 5.1 μm. The aqueous solutions of the ions being determined and the working (standard) solutions were filtered through a membrane filter with a pore size of 0.12 μm.

Results and Discussion

Effect of the Feed Composition on the Solubilizing Capacity and the Micelle Size. The overall concentration coefficient of $PtCl_6^{2-}$ (K) depends on the extent of recovery in the stages of extraction (R_{ex}) and back-extraction (R_{bex}) and the volume ratios of the contacting phases:[20]

$$K = R_{ex} \times \frac{V_w}{V_o} \times R_{bex} \times \frac{V_o}{V_s} \tag{1}$$

where V is the volume and the subscripts w, o, and s refer to the feed, organic phase, and solubilized aqueous pseudophase, respectively. From eq 1 it follows that to increase the absolute concentration coefficients it is necessary to decrease the solubilizing capacity of the micellar solution (V_s/V_o), but the changes of the conditions and the feed composition must not decrease the recovery of the metal (R_{ex}).

Acidic chloride and sulfate−chloride media are most widely used in platinum metal chemistry, industry, and analysis.[21,22] As follows from the experimental data shown in Figure 1a, the increase in the HCl concentration increases and the increase in the Na_2SO_4 concentration decreases the solubilizing capacity. The changes of the hydrodynamic radius of micelles proceed analogously (Figure 1b).

From Figure 1b it follows that with the reduced solubilizing capacity of the micellar solution there is a decrease of the micellar size. At the Na_2SO_4 concentrations from 1 to 4 mol/L this decrease in size is insignificant while the overall solubilizing capacity of the micelles decreases by several times. This may be because not only the size but also the shape of the micelles might be changed. Strongly elongated micelles may have a large hydrodynamic radius at a small solubilizing capacity. The use of the geometrical approach[23] to the solubilization allows quite substantiated suggestions to be made concerning the structural transformations in micellar solutions. At high HCl concentrations spheroid-like micelles with a high solubilizing capacity are formed.[23] With increasing salt electrolyte concentration there takes place partial dehydration of the micelles and the transformation of their shape through the successive formation of spheroids, spheroidocylinders, and prolate ellipsoids. Numerical estimates within a "uniform" solubilization model indicate that at high Na_2SO_4 concentrations, formation of micelles with the shape of prolate ellipsoids is possible whose half axis radius is

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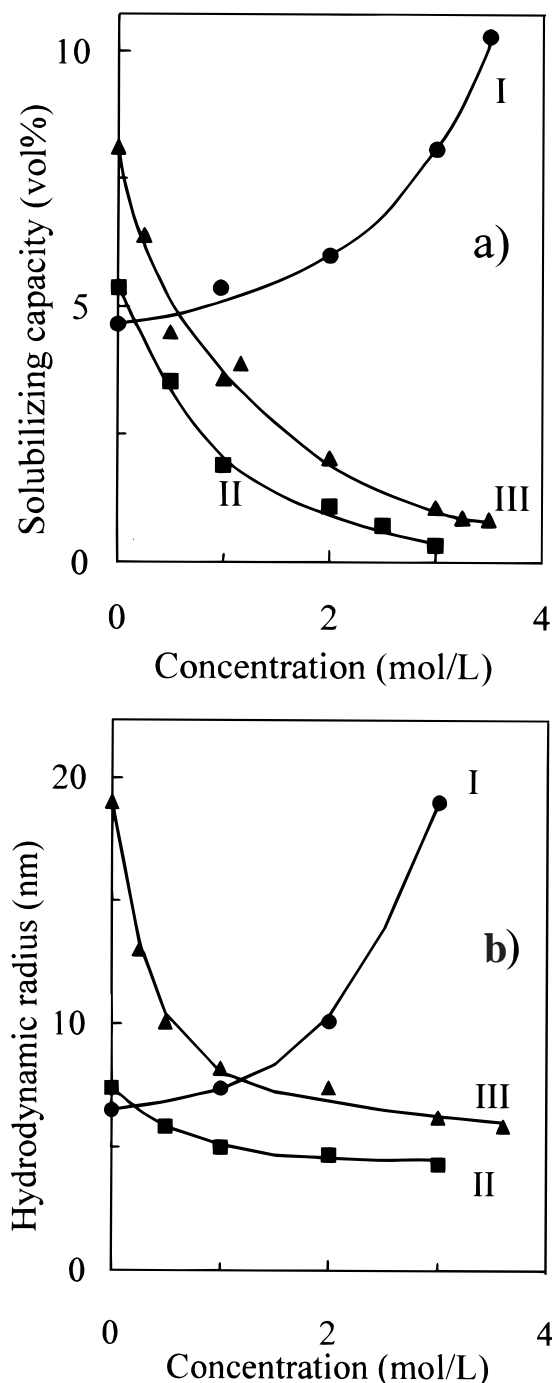
Figure 1. Solubilizing capacity (a) and hydrodynamic radius of micelles (b) as a function of the concentration of HCl (I) and Na$_2$SO$_4$ (II, III) in the feed. For the systems II and III the solution acidity is constant and equal to 1 and 3 mol/L HCl, respectively.

shorter than the length of the surfactant molecule (2.8 nm). From this it follows that the strongly dehydrated ethoxyl groups of the surfactant molecules either "shrink", changing their orientation relative the surface layer, or penetrate each other. Calculations with "nonuniform" solubilization models also indicate the existence of spherical micelles containing the electrolyte in their cores and no solution in the surface layer.

Thus, to achieve high values of absolute concentration coefficients of metals it is necessary to create a considerable concentration of salts with strong dehydrating properties. The high concentrations of acids lead to the opposite effect. The changes in the micelle size are analogous to the changes in the solubilizing capacity, but in the micellar solution, there takes

place complex structural rearrangements as a result of which different shapes of micelles are formed. A more detailed study of the micellar shapes in the extraction systems will be undertaken in a separate work in the future. Now consider the effect of the acidity and the salt content on the composition of the micelles and the interaction of the anionic complexes of platinum(IV) with reversed micelles.

Composition of the Micellar Aqueous Pseudophase. Earlier, when the extraction solubilization was studied,[21] it was shown that the micellar aqueous pseudophase composition insignificantly differs from that of the equilibrium aqueous phase. However, the study was made with simple one-component solutions as models. The situation becomes more complex when acids and salts are present simultaneously.

The composition of the micellar aqueous pseudophase was determined as a function of the feed composition in the same systems as were used in the determination of the solubilizing capacity and the hydrodynamic radius of micelles. As follows from the data shown in Table 1, the peculiarities of the changes of the compositions of the organic phase and the micellar aqueous pseudophase with the increasing concentration of Na$_2$SO$_4$ are significantly different from each other. The H$^+$ and Cl$^-$ ion concentrations of the organic phase systematically decrease by almost 1 order of magnitude, whereas the concentration of H$^+$ ions in the aqueous phase is approximately constant for 1 mol/L HCl and increases for 3 mol/L HCl. The Cl$^-$ concentration increases independent of the acid concentration in the feed. The Na$^+$ and SO$_4^{2-}$ ion concentrations in the organic phase go through a maximum, whereas in the aqueous pseudophase they increase continuously. These differences are because the organic phase volume remains constant while that of the aqueous pseudophase decreases by almost 1 order of magnitude.

Consider in more detail the changes in the ion concentrations of the micellar aqueous pseudophase as compared with the aqueous feed phase. As follows from the values of the relative concentration shown in Table 2, higher concentrations in the aqueous pseudophase as compared with the feed were found for the Cl$^-$ and H$^+$ ions (for the system with 3 mol/L HCl). The Na$^+$ and SO$_4^{2-}$ ion concentration in the micelles is considerably lower than in the aqueous phase in equilibrium with the micelles. In media of a higher acidity, more of these ions may get into micelles. The differences discussed above may be due to the increase of the solubilizing capacity of the micelles with the growing feed acidity. At low water concentration in the micelles, as a result of the competition for H$_2$O, it is more difficult for the ions with a high hydration energy (Na$^+$ and SO$_4^{2-}$) to get into the micelles.

The process of the formation of the electrolyte composition of the micelles can be represented as follows. In accordance with the commonly accepted conceptions,[24] the polar portion of the reversed micelle has an ordered structure consisting of a surface layer and a core. In acid media, there takes place a specific interaction of hydrogen ions with the oxygen of the ethoxyl group of the surfactant molecule (protonation[25]). As a result, the surface layer of the micelles becomes positive. To compensate for this positive charge, the corresponding amount of counterions goes over from the feed to the micelles. In media containing only HCl, it is the Cl$^-$ ions that act as the counterions. In acid−salt media, the formation of a mixed (from Cl$^-$ and SO$_4^{2-}$) layer of counterions is possible, and then the aqueous core of the micelle is formed. The final distribution of ions between the phases is determined by the equality of the chemical potentials, the interfacial tension, and the osmotic pressure.[26,27]

TABLE 1: Composition of the Organic Phase and Aqueous Pseudophase of Reversed Micelles as a Function of Feed Composition

no.	acid and salt concentration of the feed (mol/L)		concentration of water and ions in the extract (mol/L)					concentration of ions in the micellar aqueous pseudophase (mol/L)			
	HCl	Na_2SO_4	H_2O	H^+	Cl^-	Na^+	SO_4^{2-}	H^+	Cl^-	Na^+	SO_4^{2-}
1	1.0	–	3.00	0.060	0.063	–	–	1.12	1.17	–	–
2	1.0	0.5	1.96	0.037	0.036	0.027	0.014	1.05	1.02	0.74	0.39
3	1.0	1.0	1.06	0.022	0.020	0.020	0.011	1.15	1.04	1.06	0.58
4	1.0	2.0	0.60	0.011	0.014	0.019	0.008	1.05	1.27	1.60	0.69
5	1.0	2.5	0.44	0.009	0.012	0.015	0.006	1.12	1.45	1.77	0.72
6	1.0	3.0	0.19	0.003	0.006	0.009	0.003	0.90	1.79	2.69	0.90
7	3.0	–	4.51	0.233	0.234	–	–	2.87	2.88	–	–
8	3.0	0.25	3.56	0.181	0.195	0.048	0.017	2.83	3.04	0.73	0.26
9	3.0	0.5	2.31	0.133	0.126	0.033	0.020	3.20	3.04	0.81	0.49
10	3.0	1.0	1.99	0.133	0.118	0.049	0.032	3.71	3.29	1.35	0.89
11	3.0	2.0	1.13	0.087	0.074	0.051	0.032	4.24	3.61	2.63	1.63
12	3.0	3.0	0.59	0.046	0.042	0.036	0.020	4.31	3.91	3.42	1.91
13	3.0	3.25	0.48	0.036	0.038	0.036	0.017	4.19	4.33	4.14	2.00
14	3.0	3.5	0.47	0.036	0.037	0.037	0.018	4.33	4.44	4.41	2.15
15	3.0	3.55	0.40	0.030	0.031	0.033	0.016	4.21	4.34	4.73	2.30

TABLE 2: Relative Concentrations of Ions in the Micellar Aqueous Pseudophase

no.[a]	$[H^+]_s/[H^+]_w$	$[Na^+]_s/[Na^+]_w$	$[Cl^-]_s/[Cl^-]_w$	$[SO_4^{2-}]_s/[SO_4^{2-}]_w$	$[PtCl_6^{2-}]_s/[PtCl_6^{2-}]_w$	$K_{PtCl_6^{2-}}{}^{b}$
1	1.12	–	1.17	–	4.7	4.4
2	1.05	0.74	1.02	0.77	10.5	9.8
3	1.15	0.53	1.04	0.58	21.2	19.6
4	1.05	0.40	1.27	0.34	64.8	56.8
5	1.12	0.35	1.45	0.29	147.0	119.0
6	0.9	0.45	1.79	0.30	379.8	301.8
7	0.96	–	0.96	–	9.9	8.7
8	0.94	1.46	1.01	1.04	–	–
9	1.07	0.81	1.01	0.97	–	–
10	1.24	0.67	1.10	0.88	25.1	21.3
11	1.41	0.66	1.20	0.82	83.6	62.3
12	1.44	0.57	1.30	0.64	259.6	167.1
13	1.40	0.64	1.44	0.62	–	–
14	1.44	0.63	1.48	0.61	507.1	273.6
15	1.40	0.66	1.45	0.64	833.2	380.4

[a] The number of systems are as in Table 1. [b] Calculated values at $K_{bex} = 1$.

At present it is difficult to determine the detailed distribution of ions in the micelle between its surface layer and core. It can only be suggested that a larger portion of the H^+ ions is contained in the surface layer and that a larger portion of the Na^+ ions is present in the micelle core. Note also that the concentrations given in Tables 1 and 2 are the averaged values over the whole volume of the micelle, and the actual concentration of H^+ and counterions in the surface layer and the Na^+ concentration in the micelle core must be higher. Assuming the Na^+ concentration in the micelle core to be the same as in the feed allows simple estimates to be made. For example, for the system shown in Table 1 (no. 15), the volume fraction of the surface layer is about 40% and the recalculated concentration of the H^+ ions increases to approximately 11 mol/L.

In conclusion, we emphasize the important observation that the counterion concentration of double electric layer (DEL) (Cl^- and SO_4^{2-}) increases with increasing concentration of Na_2SO_4 in the feed. This increase is more pronounced in the medium with a higher acidity. This appears to be because the micelles have a higher surface charge in the extraction systems with 3 mol/L HCl. The sharp decrease in the water content of micelles (see Table 1) indicates also that the hydration conditions of ions in micelles may also be changed compared with the hydration in the aqueous feed phase. Although the difference of the overall concentrations of all ions in the micelle and in the feed is insignificant, it should be remembered that a substantial portion of the water molecules in micelles is bound to the polar groups of the surfactant molecules and the concentration of these groups recalculated for the volume of the polar portion of the micelle

may be quite considerable. For example, at the surfactant concentration in the organic phase equal to 0.25 mol/L, the polar group concentration recalculated for the solubilized volume is approximately 5 and 25 mol/L at a 6% and 1% content of the aqueous pseudophase, respectively. It should also be taken into account that each polar group contains five oxygen atoms capable of hydration. As a result, the degree of hydration of ions in the micelle (especially of the counterions of the double layer) may differ strongly from the ion hydration in the aqueous phase.

Extraction of $PtCl_6^{2-}$ with Reversed Micelles from Acid Chloride and Sulfate-Chloride Media. In Figure 2, the distribution ratios of $PtCl_6^{2-}$ are shown as a function of the salt concentration of the feed in the extraction from acid chloride and sulfate−chloride media. For a qualitative treatment of the observed regularities we make use of the simple scheme describing the extraction of anionic complexes of metals from acid media with an oxygen-containing extractant.[28] All physicochemical interactions between the ions are assumed to take place only in the micelles. Therefore, in the equations given below, we shall consider the concentrations of the complexes "protonated surfactant − counterion" (marked by the horizontal line) in the aqueous micellar pseudophase and not in the whole volume of the organic phase. Accordingly, the distribution ratio of $PtCl_6^{2-}$ between the aqueous micellar phase and the feed (D_s) will be used instead of the "traditional" distribution ratio given in Figure 2. In the presence of acid, the protonation of the polar groups of the ethoxylated surfactant molecules takes place:
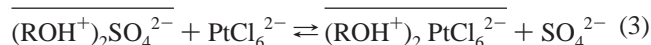
PtCl₆²⁻ Concentration with Reversed Micelles

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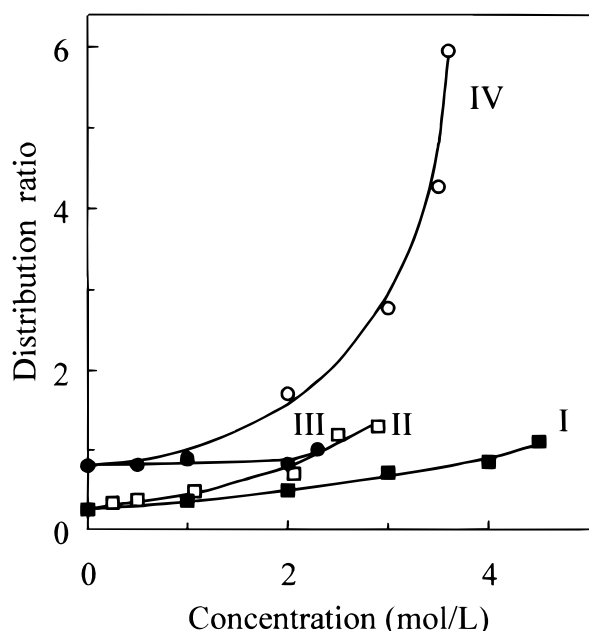
Figure 2. The distribution ratio of $PtCl_6^{2-}$ as a function of the concentration of NaCl (I, III) and Na_2SO_4 (II, IV) in the feed at a constant concentration of HCl. I, II: 1 mol/L; III, IV: 3 mol/L. The initial concentration of platinum $C^o_{Pt} = 5 \times 10^{-4}$ mol/L.

$$\overline{RO} + HCl \rightleftharpoons \overline{ROH^+Cl^-}$$
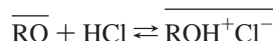
The study of the ionic composition of micelles indicated that with increasing Na_2SO_4 concentration of the feed the Cl⁻ ions of the surface layer may be partially exchanged for the sulfate ions:

$$2\,\overline{ROH^+Cl^-} + SO_4^{2-} \rightleftharpoons \overline{(ROH^+)_2SO_4^{2-}} + 2\,Cl^-$$
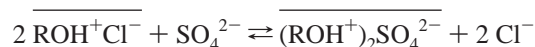
As a result, the conditions for the anionic exchange of the DEL counterions for a complex anion of platinum are created:

$$2\,\overline{ROH^+Cl^-} + PtCl_6^{2-} \rightleftharpoons \overline{(ROH^+)_2\,PtCl_6^{2-}} + 2\,Cl^- \quad (2)$$

$$\overline{(ROH^+)_2SO_4^{2-}} + PtCl_6^{2-} \rightleftharpoons \overline{(ROH^+)_2\,PtCl_6^{2-}} + SO_4^{2-} \quad (3)$$

In the general case, the distribution ratio of $PtCl_6^{2-}$ depends on the contributions to the ion exchange of each of the species:

$$D_s = \frac{\overline{[PtCl_6^{2-}]_s}}{[PtCl_6^{2-}]_w} =$$

$$\frac{\overline{[(ROH^+)_2\,PtCl_6^{2-}]_{Cl}} + \overline{[(ROH^+)_2\,PtCl_6^{2-}]_{SO_4}}}{[PtCl_6^{2-}]} =$$

$$K_1 \frac{\overline{[ROH^+Cl^-]}^2}{[Cl^-]^2} + K_2 \frac{\overline{[(ROH^+)_2\,SO_4^{2-}]}}{[SO_4^{2-}]} \quad (4)$$

where K_1 and K_2 are the concentration constants of reactions 2 and 3, respectively. From eq 4 it follows that the efficiency of the $PtCl_6^{2-}$ recovery depends on the ratio of two components: the "concentration" component, which is equal to the ratio of concentrations of the bound anion and the anion in the feed, and the "energetic" component, which depends on the conditions and the state of exchanging ions in micelles. From the data in

Table 2 it follows that the relative concentration of Cl⁻ ions increases by approximately 1.5–1.8 times, and the relative concentration of the sulfate ions decreases by about 1.5–3.3 times for systems containing 3 and 1 mol/L HCl, respectively. At the same time, the distribution ratio of $PtCl_6^{2-}$ between the micellar pseudophase and the feed increases by almost 2 orders of magnitude for each system. It is therefore rather difficult to explain such a drastic increase in D_s as being due only to the "concentration" component. It is therefore evident that changes in the state of the exchanging ions and the interaction conditions in micelles take place, which results in the growth of the exchange constants.

In the discussion of the composition of the micelles, a substantial decrease in the water content of micelles with the increasing concentration of Na_2SO_4 was noted, and the conclusion was made that partial dehydration of SO_4^{2-} and Cl⁻ in the surface layer of micelles takes place. The exchange of these ions for $PtCl_6^{2-}$ ions from the feed gives an excess of energy because the energy of hydration of the sulfate and chloride ions in the feed is higher than that of $PtCl_6^{2-}$ (the enthalpy of hydration of $PtCl_6^{2-}$ is −602 kJ/mol,[29] whereas the same values for SO_4^{2-} and 2 Cl⁻ are −1017 and −703 kJ/mol,[30] respectively). Because the dependence of the K_1 and K_2 constants on the difference of energy between the exchanging ions is exponential, even small changes in the energy state of the ions in the micelle may lead to a considerable increase of the $PtCl_6^{2-}$ distribution ratio (D_s). The order in which the Neonol APh₉-4 micelles extract the anionic complexes of platinum(IV) from sulfate−chloride media[28] ($PtI_6^2 > PtBr_6^2 > PtCl_6^{2-}$), which is opposite to the energies of their hydration[29] (−561, −584, and −602 kJ/mol, respectively), serves as a further evidence for the "hydration" mechanism.

Note that the values of the relative distribution ratios of anionic complexes of platinum(IV) estimated from the difference of their energies of hydration considerably exceed those obtained experimentally.[28] This appears to indicate that only a partial rather than complete dehydration of the complex ions takes place in the micelles.

Extraction of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ from Acid Sulfate-Chloride Media under Conditions of Compensated Surface Charge of the Micelles. To study the effect of the micellar surface charge, the extraction of the complex $PtCl_6^{2-}$ and $PtBr_6^{2-}$ anions was studied under conditions of compensated surface charge with the acid−salt composition of the feed remaining unchanged. The charge of the micelle was reduced by the addition to the organic phase of an oil-soluble surfactant, AOT. The feed contained 3 mol/L HCl and 3.55 mol/L Na_2SO_4. As follows from the experimental data given in Figure 3, the distribution ratios of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ decrease with increasing AOT concentration of the organic phase. It appears that AOT presence in the organic phase leads to the formation of mixed micelles having a lower overall surface charge of DEL. As a result, the concentration of the counterions in micelles capable of the exchange decreases, which leads to the corresponding decrease in the distribution ratios. It appears that the constancy of the acid−salt composition of the aqueous feed phase also ensures the invariance of the hydration of the exchanging anions.

Peculiarities of the $PtCl_6^{2-}$ Concentration with Reversed Micelles. By changing the acid−salt content of the feed, it is possible to influence the metal concentration at both the extraction and the back-extraction stages. Consider, for example, systems containing 1 and 3 mol/L HCl in the presence of 3 mol/L Na_2SO_4. In the first system, the lower content of the acid

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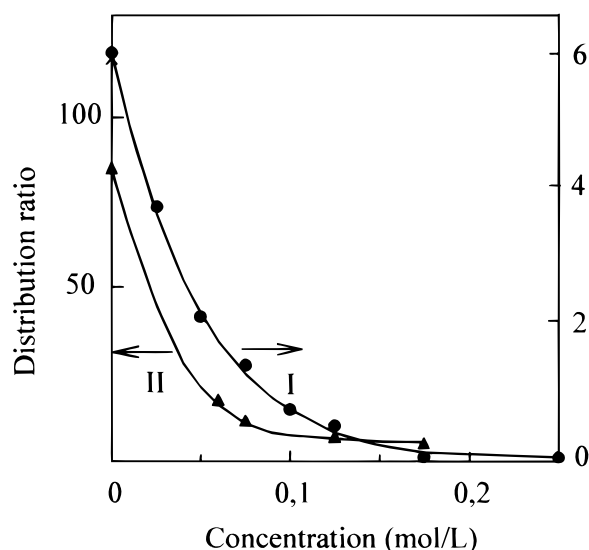
Figure 3. Variation of the distribution ratio of $PtCl_6^{2-}$ (I) and $PtBr_6^{2-}$ (II) under conditions of the surface charge compensation by AOT molecules. The composition of the feed: 3 mol/L HCl + 3.55 mol/L Na_2SO_4. The initial concentration of platinum $C^o_{Pt} = 6 \times 10^{-4}$ mol/L.

reduces the $PtCl_6^{2-}$ extraction (18% compared to 35%) and concentration in the stage of extraction. But the reduced solubilizing capacity of the micellation agent (0.3% compared to 1%) helps to increase the concentration in the stage of back-extraction. Substituting these values into eq 1 and assuming R_{bex} = 1 gives the overall concentration of $PtCl_6^{2-}$ of approximately 300 for 1 mol/L HCl and 170 for 3 mol/L. Further increase of the Na_2SO_4 concentration for 3 mol/L HCl increases the recovery in the stage of extraction by two times (with a small decrease in the solubilizing capacity to 0.7%). Accordingly, the concentration increases to 380 (see Table 2).

For micelles, the concentration is achieved due to the microcomponent being transferred from the large volume of the feed to the small volume of the micellar aqueous pseudophase. The study of the pseudophase composition (Tables 1 and 2) indicated that the background electrolyte concentration changes insignificantly, whereas the $PtCl_6^{2-}$ concentration changes by 2 orders of magnitude relative to the matrix. Because of this fact, in the present variant of micellar concentration, it is impossible to separate or replace the matrix. Therefore, in our view, the micellar concentration of metals represents a special kind of concentration where only the concentration of the microcomponent is changed.

Conclusion

Changing the composition of the aqueous feed phase makes it possible to change parameters of the reversed micelles as "nanoreactors" extracting the $PtCl_6^{2-}$ from the aqueous feed phase and "nanoreservoirs" allowing the concentration and separation of the metal from the organic phase. The increase in the HCl concentration helps to improve the recovery but decreases the concentration. The addition of Na_2SO_4 to the feed increases both the recovery and concentration. Such a behavior is determined by complex structural rearrangements taking place in the reversed micellar systems. Along with the changes of the micellar size and shapes, the chemical interaction of the surfactant with the components of the aqueous phase leads to the formation in the micelles of a double electric layer and a qualitative and quantitative change of the electrolyte content as compared with the feed. The experimentally found regularities

can help to more effectively approach the problem of micellar concentration of $PtCl_6^{2-}$.

The "pseudophase" approach[31] used in this work is one in which all micelles are treated as a separate phase dispersed in an organic solvent. Such an approach seems promising because it allows one to reveal the details of the interactions taking place in the micelles. In particular, the study of the ionic composition and water content of micelles suggested an anion-exchange mechanism of $PtCl_6^{2-}$ extraction with a partial dehydration of the ions.

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