Back extraction of platinum metals from liquid membranes in an electric field

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Abstract

A new method for back extraction of platinum metals from the salts of tertiary amines and quaternary onium bases in the organic phase is proposed. This method allows the back extraction of platinum metals into diluted solutions of mineral acids over one stage. The method involves the passing of direct current through a system in which the extract containing a platinum metal is a liquid membrane. This method allows a practically complete back extraction of the anions $PtCl_6^{2-}$, $RuNOCl_5^{2-}$ and $Ru_2OCl_{10}^{4-}$ (the latter passes into the aqueous phase without breaking the dimer anion). It was found that when $PtCl_6^{2-}$, $PdCl_4^{2-}$ and $Ru_2OCl_{10}^{4-}$ are in a liquid membrane based on Oct_3NHCl in 1.2-dichloroethane, under the action of an electric field all these anions are transferred into aqueous 1 M HCl ($E > 85\%$). To provide maximum back extraction of platinum metal anions, it is necessary to use small concentrations of extractants in 1.2-dichloroethane (0.1 M for Oct_3NHCl and 0.03–0.04 M both for Oct_4NCl and Ph_4PCl) over the period of the back extraction. Cyclic voltametry has demonstrated the determining role of chloroions in current transport through the interface of phases I and II.

Notation and symbols

Oct_3NHCl	*n*-trioctylammonium chloride
Oct_4NCl	tetraoctylammonium chloride
Ph_4PCl	tetraphenylphosphonium chloride
E	back extraction degree (%)
i	current density (A m^{-2})
j	the amount of anion flow through the phase interface II (mol m^2 s)
l_m	thickness of a membrane (m)
V_m	volume of a liquid membrane (m^3) concentration (mol × 10^3 m^{-3})
η	metal yield by current (%)
U	voltage (V)

1. Introduction

The salts of tertiary amines [1–11] and quaternary onium bases [2, 7–9, 12–15] allow the extraction of platinum metals from an aqueous phase with a high coefficient of distribution. These extractants can be used for effective partition of the platinum metals, as well as their separation from the base metals [2, 7–9, 13, 16].

Certain difficulties accompanying the further transport of platinum metals from the organic phase into aqueous solutions (appropriate for further recycling) are serious handicaps to the practical application of extractants [7–9, 16–22]. The difficulties in the back extraction of platinum metal from the amine salt-based

extractants are related to the implantation [1, 2, 8, 9]. Under the conditions suppressing the implantation reaction (i.e., necessary pH of the aqueous phase, aprotone solvent), the concentrated HCl extracts platinum and rhodium completely [2, 8, 10].

The formation of multinuclei complexes [17, 21] in the organic phase also complicates the back extraction of platinum metals. Moreover, their formation is more typical for the salts of quaternary onium bases than for the salts of tertiary amines [21]. Due to an increase in the hydrophility of the organic phase, the multinuclei complexes break up and the back extraction of platinum metals is enhanced [17, 18, 21].

The association of compounds, forming in the organic phase [19, 20], adversely affects the back extraction of platinum metals. This process depends on the nature of the organic reagent (an amine salt or a quaternary onium base), the solvent and the concentration of complexes in the organic phase. The deterioration of the back extraction process as the time of extract storage increases is also determined by the polymerization and solvation of complexes in the organic phase [21]. In such cases, in the process of back extraction of platinum metals it is recommended to introduce hydrophilic additives in the organic phase (organic acids are preferable) [7, 16, 18, 21].

It has been shown [23] that the reason for the inefficiency of 1 M HCl solution as a back extractant of $PdCl_4^{2-}$ from extracts based on Oct_3NHCl in toluene is the formation of a mixed monolayer at the phase

interface, in which, as the concentration of $(Oct_3NH)_2$-$PdCl_4$ increases, chloroions are displaced by the $PdCl_4^{2-}$ anions in the organic phase.

The authors [24, 25] illustrate the extraction of palladium electrochemically from the complexes of quaternary onium bases in different diluents with added ethanol by placing the cathode in the organic phase. We have found that during electrochemical extraction, when the cathode is directly in the organic phase containing $(Oct_3NH)_2PtCl_6$ in 1.2-dichloroethane, $PtCl_6^{2-}$ is transferred from the organic phase into the aqueous phase even at small currents ($i = 2$ A m^{-2}). But due to the cathode processes, involving Oct_3NH^+ and 1.2-dichloroethane, a new organic compound appears, in which an organic anion exists as a counter ion. Adsorption of this compound was found while studying the process of back extraction by the drop volume method [26].

To resolve the problem of the back extraction of platinum metals, a new method is proposed, which involves the passing of direct current through System A in which the extract containing a platinum metal serves as a liquid membrane.

2. Experimental details

The experiments were carried out in a five-chambered Teflon dialyser (A) with two platinum electrodes and rigid cation-exchange membranes (MK-40) that separated the near-electrode chambers (**a**, **f**) from the chambers **b**, **d** with hydrochloric acid, where II is the liquid membrane/back extraction solution interface, as shown in Figure 1.

A liquid membrane of thickness $l_m = 4 \times 10^{-3}$ m and volume $V_m = 3 \times 10^{-6}$ m^3 was bordered on two sides (I and II) by cellophane films. The presence of this film made the processes of electrochemical extraction and back extraction specific [27, 28]. The observed area of contact of the liquid membrane (**c**) with the aqueous phase (**d**) was 7.1×10^{-4} m^2. The process was carried out galvanostatically.

Solutions of *n*-trioctylammonium chloride (Oct$_3$-NHCl, 95% of Oct$_3$N) and tetraoctylammonium chloride (Oct$_4$NCl, 98% of main substance) in 1.2-dichloroethane were used as extractants. It should be stressed that the application of an electric field imposes specific demands on organic solvents (e.g., necessary electric conductivity of the membrane, exclusion of such phenomena as electrical breakdown [28], transfer of the

solvent into the aqueous phase etc.). 1.2-dichloroethane satisfies most of these criteria. 1.2-Dichloroethane is also a polar solvent, which reduces the association of compounds in the organic phase [9]. This ensures high distribution coefficients in the extraction of platinum metals. 1.2-Dichloroethane was purified by the method described in [29] using fractions with $t_{boil} = 83.4$–83.5 °C. Previous to extraction, *n*-trioctylamine was transformed into hydrochloric salt Oct$_3$NHCl by reaction with 2 M HCl.

Platinum(IV) and ruthenium(IV) were used as corresponding compounds of $H_2[PtCl_6]6H_2O$ and $K_4[Ru_2OCl_{10}]H_2O$. The extracts were prepared by shaking the solutions of platinum metals in 1 M HCl ($C_{Pt} = 0.02$ M, $C_{Ru} = 0.01$ M if not specified) together with Oct$_3$NHCl solutions (0.5–0.05 M) and Oct$_4$NCl solutions (0.1–0.02 M) in 1.2-dichloroethane. $K_4[Ru_2OCl_{10}]\cdot H_2O$ salt was synthesized following the method described in [30]. Since the hydrolysis processes are rather fast in weak-acid solutions containing the $Ru_2OCl_{10}^{4-}$ anion [31], ruthenium was extracted from the newly prepared solutions. The concentration of metal in the aqueous phase was defined by spectrophotometric methods [32, 33]. During simultaneous back extraction of platinum, palladium and ruthenium the concentration of each metal in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry [34].

3. Results and discussion

When direct current passes through System A, platinum and ruthenium, as corresponding $PtCl_6^{2-}$ and $Ru_2OCl_{10}^{4-}$ anions, are transferred to the solution in chamber **d** (Figure 1). This is confirmed by the analysis results and by the electronic absorption spectra in aqueous solutions. Moreover, the two-nuclei complex does not break up during the back extraction of $Ru_2OCl_{10}^{4-}$.

Figure 2 shows that the proposed method allows the extraction of platinum(IV) and ruthenium(IV) from organic solutions based on Oct$_3$NHCl (runs 1 and 2), on Oct$_4$NCl (runs 4 and 5) and on Rh$_4$PCl (run 3) with high degrees of back extraction (E). But E greatly depends on the concentration of extractant at the stage of extraction: the higher C_{extr}, the lower the degree of platinum metal back extraction from the liquid membrane with other conditions being equal. In view of the definite demands, the dependence $E = f(C_{extr})$ allows the
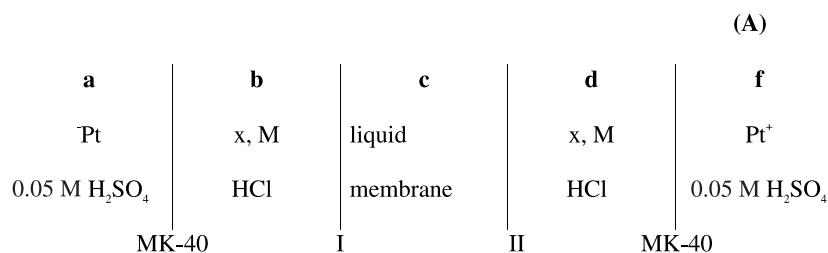
(A)

a	b	c	d	f
Pt	x, M	liquid	x, M	Pt$^+$
0.05 M H$_2$SO$_4$	HCl	membrane	HCl	0.05 M H$_2$SO$_4$
	MK-40	I	II	MK-40

Fig. 1. Scheme of an electrochemical compartment for the back extraction process (details in text).
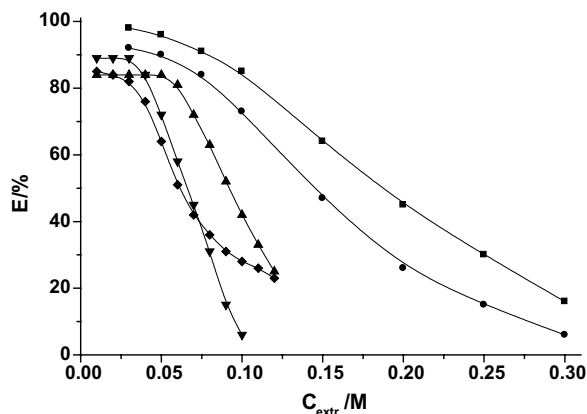
Fig. 2. Degree of back extraction ($i = 42$ A m^{-2}) against extractant concentration ($\blacklozenge$) Pt ($t = 1800$ s); ($\bullet$) Ru ($t = 1200$ s); ($\blacktriangle$) Ru ($t = 2400$ s); ($\blacktriangledown$) Ru ($t = 1800$ s). (1, 2) Oct$_3$NHCl; (3) Ph$_4$PCl; (4, 5) Oct$_4$NCl. Key: ($\blacksquare$) 1, ($\bullet$) 2, ($\blacktriangle$) 3, ($\blacktriangledown$) 4 and ($\blacklozenge$) 5.

Fig. 4. Rate of ruthenium flow ($C_{Ru} = 0.01$ M; $i = 42$ A m^{-2}) against time of the process. Key: ($\blacksquare$) (Oct$_3$NH)$_2$RuNOCl$_5$; ($\bullet$) 0.1 M Oct$_3$NHCl; ($\blacktriangle$) 0.03 M Oct$_4$NCl; ($\blacktriangledown$) 0.03 M Ph$_4$PCl).

selection of the most appropriate extractant from the salts of tertiary amines or quaternary onium bases. Due to the efficient extractability of the salts of quaternary onium bases [35], during the extraction one can use solutions of Oct$_4$NCl or Ph$_4$PCl, which are 2–4 times less concentrated than Oct$_3$NHCl. Therefore, to extract PtCl$_6^{2-}$ and Ru$_2$OCl$_{10}^{4-}$, respectively, 0.04 M and 0.03 M Oct$_4$NCl, and 0.1 M Oct$_3$NCl and 0.03 M Ph$_4$PCl solutions in 1.2-dichloroethane were used in further experiments.

As the current passing through System A increases, the rates of PtCl$_6^{2-}$ and Ru$_2$OCl$_{10}^{4-}$ anion flows decrease (Figures 3 and 4). Moreover, the form of the curves $j = f(t)$ under the experimental conditions depends on the nature and concentration of the extractant. The decrease in j and small current values ($\eta < 40\%$) are related to the presence of a supporting electrolyte in the system (1 M HCl of chamber **b** and a free extractant of chamber **c**); its chloroions suppress the migratory flow of platinum metal anions through phase interface II (Figure 1). Furthermore, the longer the experiment, the more current is transferred by chloroions. This assumption is confirmed by a series of experiments. Thus, the higher
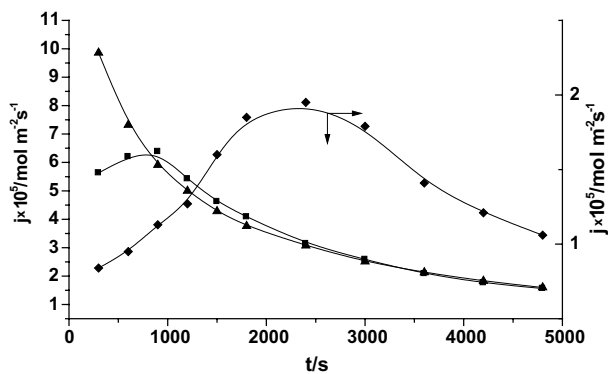
the concentration of the extractant at the stage of extraction, the lower the values of j (Figure 3, runs 1, 2) and less significant are the values of the current for platinum (η is about 3%). The largest values of j (at least, at the beginning of the process) were registered during the electrochemical back extraction of platinum(IV) and ruthenium(IV) from the liquid membranes containing the solutions of *a priori* precipitated solid individual compounds of platinum metals in 1.2-dichloroethane, for example, (Oct$_3$NH)$_2$RuNOCl$_5$ (Figure 4, run 1) [36].

An increase in current density passing through System A results in an increase in j for all cases under discussion (Figure 5).

The acidity of the aqueous phase has been found to influence the electrochemical back extraction of platinum metals at the stage of liquid extraction. This influence is determined by the nature of the complex metal anion and the extractant (Figure 6). A significant decrease in the degree of platinum back extraction takes place only if Oct$_3$NHCl is used as an extractant when extracted from solutions with $C_{HCl} < 0.1$ M (Figure 6,

Fig. 3. Rate of platinum flow ($C_{Pt} = 0.02$ M; $i = 42$ A m^{-2}) against time of the process. Key: ($\blacksquare$) 0.1 M Oct$_3$NHCl; ($\blacklozenge$) 0.3 M Oct$_3$NHCl; ($\blacktriangle$) 0.04 M Oct$_4$NCl).
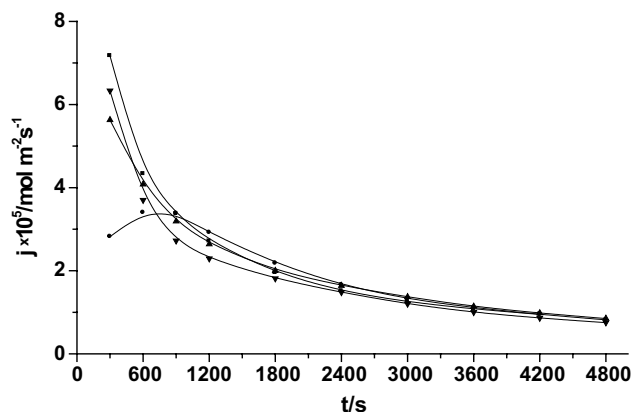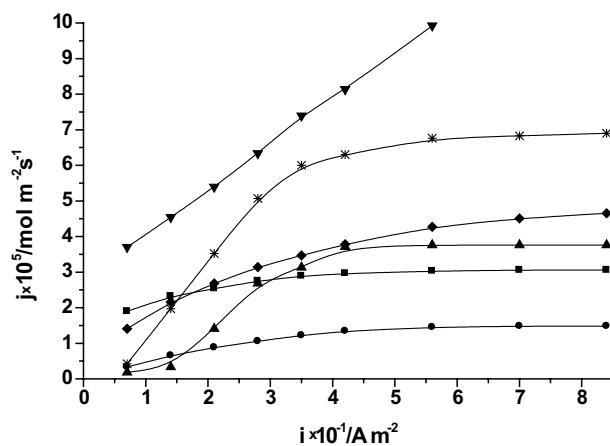

Fig. 5. Dependence of anion flow rate (1, 2, 3 for Ru (0.01 M); 4 for (Oct$_3$NH)$_2$RuNOCl$_5$ (0.03 M); 5, 6 for Pt (0.02 M) on current density (1, 5 for Oct$_4$NCl; ; 2 for Ph$_4$PCl; 3, 6 for Oct$_3$NHCl). Key: ($\blacksquare$) 1, ($\bullet$) 2, ($\blacktriangle$) 3, ($\blacktriangledown$) 4, ($\blacklozenge$) 5 and ($*$) 6.
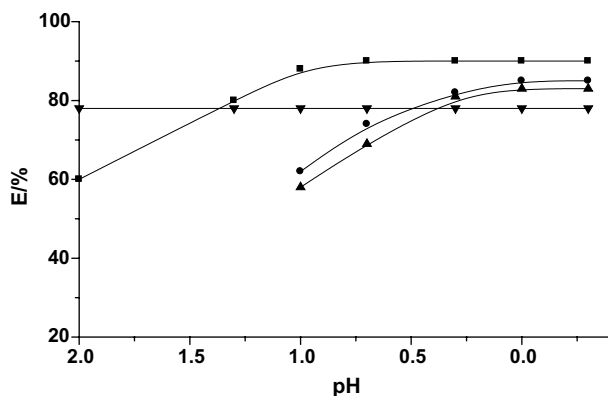
Fig. 6. Back extraction degree ($i = 42$ A m^{-2}; $t = 1800$ s): 1, 4 for Pt; 2, 3 for Ru) against HCl concentration (1, 2 for Oct$_3$NHCl; 3, 4 for Oct$_4$NCl). Key: (■) 1, (●) 2, (▲) 3 and (▼) 4.

Fig. 7. Back extraction degree (■) and the value of ruthenium flow (▲) against the concentration of (Oct$_3$NH)$_2$RuNOCl$_5$ in chamber **c** ($i = 42$ A m^{-2}; $t = 1200$ s).

run 1). This is associated with the apparent implementation reaction characteristic of tertiary amines under such conditions [1, 2, 8, 9]. The degree of back extraction for ruthenium decreases when extracted from solutions with $C_{HCl} < 0.5$ M by both extractants (Figure 6, runs 2, 3). This dependence is explained by the hydrolysis of Ru$_2$OCl$_{10}^{4-}$ anions taking place under such conditions [31].

The concentration of platinum metals in the liquid membrane increases with thickening of chamber **c** of System A; the degree of back extraction for both metals decreases at a rate of $l_m > 6 \times 10^{-3}$ m. The calculations reveal that the reason for the above phenomenon is an insufficient (to sustain high values of E) current passing through the system. However, experimental attempts to prove the above have failed because the increase in current density or time, at a considerable thickness of the membrane, results in membrane heating and electric breakdown of the system [28]. To study the influence of platinum metal concentration in the liquid membrane on the qualitative characteristics (E, j) of its electrochemical back extraction into chamber **d**, (Oct$_3$NH)$_2$ RuNOCl$_5$ solutions produced by diluting the corresponding sample in 1.2-dichloroethane were used (Figure 7). The rate of ruthenium anion flow through phase interface II increases proportionally to the metal concentration in the liquid membrane, ranging within 0.5–4.5 M, and the degree of back extraction reaches 80% (Figure 7).

The extractability of the salts of quaternary phosphonium bases, if compared to ruthenium(IV), is higher in hydrochloric solutions than the extractability of tertiary amines and neutral phosphorous-organic compounds [35]. When ruthenium(IV) is extracted from a newly prepared solution containing mostly Ru$_2$OCl$_{10}^{4-}$, the degree of extraction by 0.03 M Ph$_4$PCl solution in 1.2-dichloroethane is about 99.1%; there is practically no back transport of ruthenium into 1 M HCl (the degree of back extraction is about 3%).

The method of electrochemical back extraction assures a reasonably high degree of ruthenium back extraction from 0.02–0.05 M Ph$_4$PCl-based extracts.
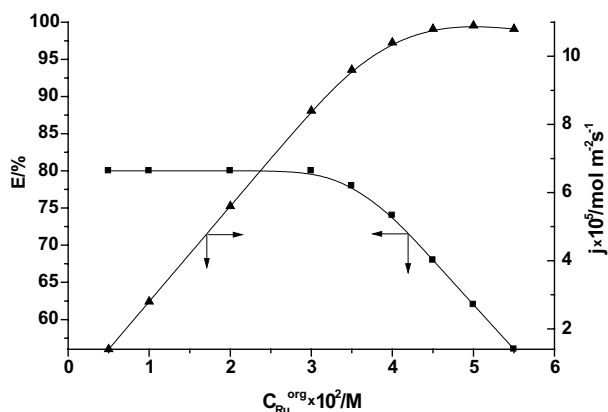
The character of the dependence on the extractant concentration (Figure 2, run 3), on the current conductance time (Figure 4, run 4) and its density (Figure 5, run 2) is similar to the curves obtained for Oct$_4$NCl (Figures 2, 3 and 4). When solutions of Ph$_4$PCl $\geqslant$ 0.05 M are used as extractants, the degree of ruthenium back extraction (Figure 2, run 3) is 10–40% more than for the same solutions of Oct$_4$NCl (Figure 2, runs 3, 4). However, in electrochemical processes Ph$_4$P$^+$ cations more easily go to the aqueous phase than the cations of Oct$_4$N$^+$ [37].

Several platinum metals can exist together in industrial solutions [2, 7, 12]; and the Oct$_3$NHCl solution in 1.2-dichloroethane extracts them all simultaneously. As the direct current passes through the liquid membrane containing Oct$_3$NHCl with PtCl$_6^{2-}$, PdCl$_4^{2-}$ and Ru$_2$OCl$_{10}^{4-}$ anions, these anions (about 90%) are transferred to the 1 M HCl solution in chamber **d** (Figures 8 and 9).

The electrochemical properties of the liquid membranes on the base of tertiary amines and quaternary ammonium bases were investigated in [(C$_8$H$_{17}$)$_3$NH]$_2$-PtCl$_6$ and [(C$_8$H$_{17}$)$_4$N]PtCl$_6$ compounds. The salts of
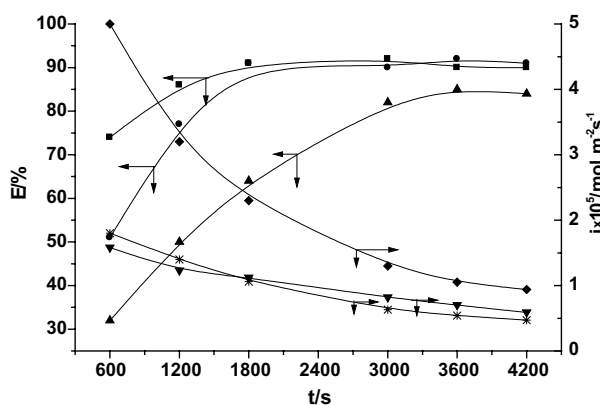

Fig. 8. Back extraction degree (E) and the flow rate (j) of platinum metals against time of the process ($i = 42$ A m^{-2}; $C_{Pt} = 0.01$ M; $C_{Pd} = 0.007$ M; $C_{Ru} = 0.005$ M). (■) Pt, (●) Ru, (▲) Pd, (◆) Pt, (*) Ru, (▼) Pd.
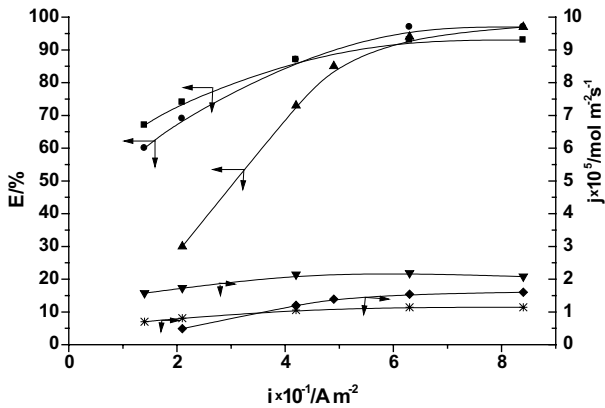
Fig. 9. Back extraction degree (E) and the flow rate (j) of platinum metals against current density ($C_{Pt} = 0.01$ M; $C_{Pd} = 0.007$ M; $C_{Ru} = 0.005$ M). (■) Pt, (●) Ru, (▲) Pd, (♦) Pd, (∗) Ru, (▼) Pt.

Fig. 11. Cyclic voltammetry of System B. Sweep rate 6 V s^{-1}. C_{HCl} in chambers **b** and **d**: (♦) 1.0 M; (○) 0.1 M; (×) 0.01 M. Liquid membrane 1×10^{-4} M solution [(C$_8$H$_{17}$)$_4$N]PtCl$_6$.

platinum were precipitated as solid substances and identified with reference to the results of element analysis and electronic absorption spectra.

To obtain the voltametric characteristics, cyclic voltametry was applied [38]. A 5×10^{-4} M solution of [(C$_8$H$_{17}$)$_3$NH]$_2$PtCl$_6$ (Figure 10) or 1×10^{-4} M solution of [(C$_8$H$_{17}$)$_4$N]PtCl$_6$ (Figure 11) in 1.2-dichloroethane served as liquid membranes in the symmetrical system B, with the concentration of HCl in chambers **b** and **d** varying between 0.01–1.0 M (Figure 12).

The initial segments of the voltametric curves (Figure 10) are determined by the electrical conductivity of
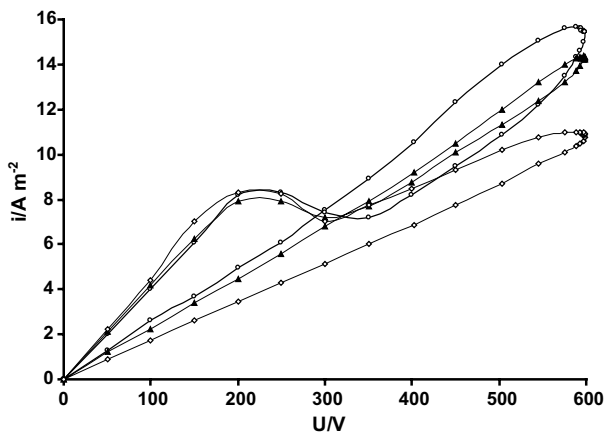

Fig. 10. Cyclic voltammetry of System B. Sweep rate 6 V s^{-1}. C_{HCl} in chambers **b** and **d**: (○) 1.0 M; (▲) 0.1 M; (◇) 0.01 M. Liquid membrane 5×10^{-4} M solution [(C$_8$H$_{17}$)$_3$NH]$_2$PtCl$_6$.

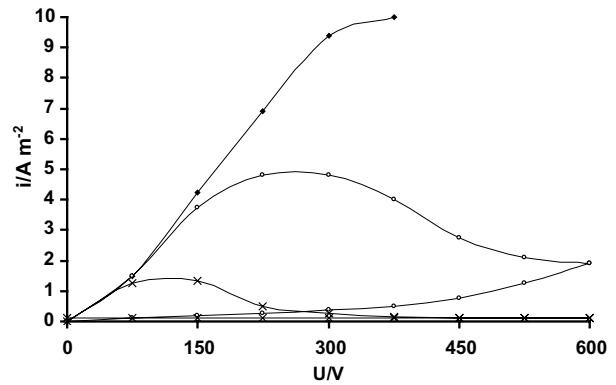[(C$_8$H$_{17}$)$_3$NH]$_2$PtCl$_6$ salt in 1.2-dichloroethane and do not depend on the HCl concentration in System B chambers (Figure 12). As soon as the current density reaches 82 A m^{-2}, virtually all platinum is transferred to the aqueous phase of chamber **d**. Along with the back extraction of PtCl$_6^{2-}$, a partial deprotonization of (C$_8$H$_{17}$)$_3$NH$^+$ occurs [39]. If the concentration of HCl in chambers **b** and **d** of System B is low (0.01 M, Figure 10, run 3), a drop in system conductivity is related to the transfer of (C$_8$H$_{17}$)$_3$NH$^+$ to the aqueous phase of chamber **b** (Figure 12). As the concentration of HCl increases (1.0 M, Figure 10, run 1), the conductivity, which is determined by the protonization of (C$_8$H$_{17}$)$_3$N and the formation of (C$_8$H$_{17}$)$_3$NHCl salt, increases.

The voltametric characteristics of the liquid membrane with [(C$_8$H$_{17}$)$_4$N]PtCl$_6$ (Figure 11) are slightly different. These differences are mostly related to the extractant behaviour in the electrochemical back extraction. The initial segments of the voltametric curves (Figure 11), which are determined by the transport of PtCl$_6^{2-}$ anions from the organic phase to the aqueous solution of chamber **d** (Figure 12), nearly match up. This is confirmed by an experimental fact concerning the independence of the degree of platinum metal back extraction on the concentration of HCl in chambers **b** and **d** (Figure 12). The increase in system conductivity is caused by current transport by chloroions. Moreover, these segments of the voltametric curves are determined by the concentration of HCl in chamber **b**: the higher the HCl concentration, the higher the time and the value of the corresponding segment. After 1.0 M KCl solution is added to 0.01 M HCl solution in chamber **b** (Figure 11,
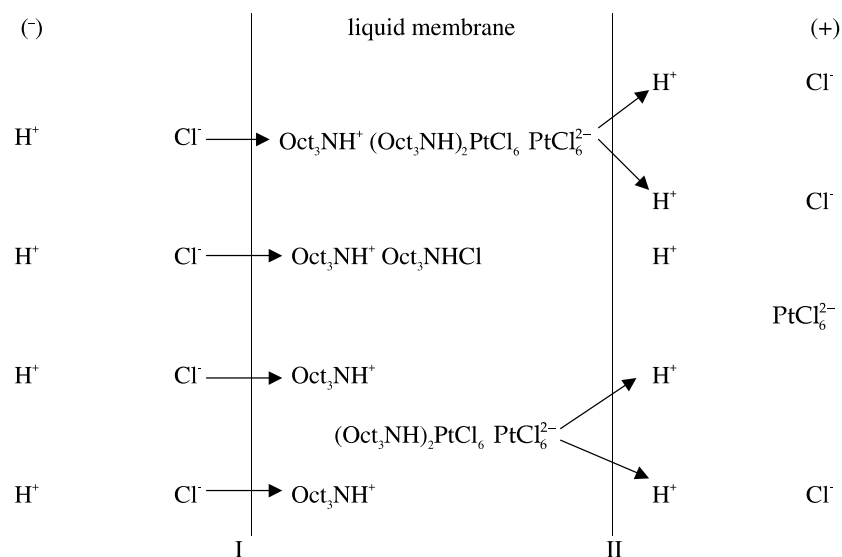

Fig. 12. Scheme of an electrochemical compartment for voltametric measurements (details in text).

| (⁻) | | liquid membrane | | | (+) |

$$\text{H}^+ \quad \text{Cl}^- \longrightarrow \text{Oct}_3\text{NH}^+ \ (\text{Oct}_3\text{NH})_2\text{PtCl}_6 \ \text{PtCl}_6^{2-} \nearrow^{\text{H}^+ \quad \text{Cl}^-}_{\searrow \text{H}^+ \quad \text{Cl}^-}$$

$$\text{H}^+ \quad \text{Cl}^- \longrightarrow \text{Oct}_3\text{NH}^+ \ \text{Oct}_3\text{NHCl} \qquad \text{H}^+$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{PtCl}_6^{2-}$$

$$\text{H}^+ \quad \text{Cl}^- \longrightarrow \text{Oct}_3\text{NH}^+$$

$$\qquad\qquad (\text{Oct}_3\text{NH})_2\text{PtCl}_6 \ \text{PtCl}_6^{2-} \nearrow^{\text{H}^+}_{\searrow \text{H}^+}$$

$$\text{H}^+ \quad \text{Cl}^- \longrightarrow \text{Oct}_3\text{NH}^+ \qquad\qquad \text{H}^+ \quad \text{Cl}^-$$

I   II

Fig. 13. Scheme of electrochemical back extraction of PtCl_6^{2-} anions from the extracts on the base of Oct_3NHCl in 1.2-dichloroethane.

run 3), the new voltametric curve is identical to curve 1 (Figure 11), which also confirms the conclusion on the determining role of chloroions in the transport of the current after completion of PtCl_6^{2-} anion back extraction.

A peculiarity of the salts of quaternary onium bases is their relatively high solubility in water determined by their high polarity [8, 9]. Therefore, the transfer of these salts to the aqueous phase is possible in electrochemical processes. The conductivity drop in System B, which greatly depends on the concentration of HCl (Figure 11), is associated with a decreased $[\text{C}_8\text{H}_{17}]_4\text{N}]\text{Cl}$ concentration in the membrane due to the transfer of $(\text{C}_8\text{H}_{17})_4\text{N}^+$ into chamber **b**: the higher the HCl concentration, the smaller this transfer. So, to prevent the escape of the salts of quaternary onium bases from the membrane phase, it is appropriate to use 1 M HCl as supporting electrolyte in the processes of platinum metal electrochemical back extraction.

In industrial systems, where the extract of platinum metals also containing water and a free extractant serves as a liquid membrane, a significant excess of free extractant can explain the comparatively small current values in the organic phase. The chloroions of this compound, which are constantly replenished due to the transport of chloroions from chamber **b** through phase interface I, suppress the migratory flow of platinum metal ions through the liquid membrane/chamber **d** phase interface (Systems A and B).

In light of the above, a scheme for platinum metal back extraction under the influence of direct current has been proposed (Figure 13).

4. Conclusion

The method proposed for the back extraction of platinum metals from organic phases by certain anion-exchange extragents falls into a new area of science and engineering, namely, membrane technology [40]. One of the most interesting techniques in this technology is the implementation of a power-dependent active transport of target components. In the current paper, the back extraction of platinum metals into the solution of diluted mineral acids is ensured by the imposition of a steady-state electric field on a system containing a liquid membrane. By varying the ratio of the current, the time and the concentration of the extractant (Oct_3NHCl, Oct_4NCl, Ph_4PCl) during the extraction, an almost complete extraction of small (0.01–0.02 M) amounts of platinum(IV) and ruthenium(IV) into aqueous solutions has been achieved. These solutions can be used for the extraction of platinum metal without additional processing. Based on the experimental data, a scheme for membrane back extraction of platinum metals under direct current has been proposed. This scheme not only explains the phenomena, but also suggests some ways to control the phenomena.

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