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MECHANISM OF THE ELECTROCHEMICAL REDUCTION OF HALIDE COMPLEXES OF PLATINUM AT A DROPPING MERCURY ELECTRODE

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The electrolytic reduction of $PtCl_4^{2-}$ on a dropping mercury electrode was first studied by Laitinen and Onstott[1]. They found that reduction of $PtCl_4^{2-}$ begins at potentials more positive than the zero-charge potential of the electrode and that at these potentials the normal limiting diffusion current of $PtCl_4^{2-}$ is consistent with the Ilkovič equation.

On passing to potentials more negative than that of zero charge of mercury, the rate of reduction of $PtCl_4^{2-}$ sharply decreases and the current decreases to a minimum and then increases to the value of the limiting diffusion current. An increase in the concentration of the supporting electrolyte causes a small increase of the current at the minimum and a narrowing of the range of potentials at which the current decreases, but the decrease of the current was observed even in 4*N* potassium chloride. The authors explained the decrease of the current at potentials approaching that of zero charge of the electrode by desorption of $PtCl_4^{2-}$ from the mercury surface, and the increase of the current after the minimum by a not quite clear hypothesis of reduction of $PtCl_4^{2-}$ without previous adsorption. The reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ has been studied in greater detail by Frumkin and Florianovich[2]. The shape of the polarisation curve in the reduction of $PtCl_6^{2-}$ was the same as in the reduction of $PtCl_4^{2-}$, but while in the reduction of $PtCl_6^{2-}$ at various supporting-electrolyte concentrations the minimum current always reached half of the limiting current, in the reduction of $PtCl_4^{2-}$ the minimum current reached 5–10% of the limiting current, even at high concentrations of the supporting electrolyte. The authors believe that the retardation of the reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$, like the retardation of the reduction of $S_2O_8^{2-}$, [2,3] is due to a sharp decrease of the concentration of the anions in the double layer of the electrolyte, caused by the electrostatic repulsion of the anions by the negatively charged electrode surface. They believe that the union of the anion with the electron is the slowest step in the process. However, their theory of reduction of $S_2O_8^{2-}$ does not explain the retardation of the reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ in concentrated solutions of supporting electrolyte. It has been suggested that these phenomena can be explained by a considerable specific adsorption of $PtCl_4^{2-}$ and $PtCl_6^{2-}$, which causes a sharp change in the concentration of the anion on the surface with increasing negative electrode potential, even at a high total concentration of the electrolyte, and hence the retardation in concentrated solutions of supporting electrolyte.

Kivalo and Laitinen[4,5] suggested that the reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ is not electrochemical, but a purely chemical reaction of $PtCl_4^{2-}$ with mercury in the bulk of the solution. Frumkin and Nikolaeva-Fedorovich[6,7] investigated the effect of organic and inorganic cations on the reduction of $PtCl_4^{2-}$ and showed that the theory of Kivalo and Laitinen is incorrect.

According to Gierst[8,9], the mechanism of the electrolytic reduction of $PtCl_4^{2-}$ corresponding to the descending branch of the current–voltage curve is different from that corresponding to the ascending branch. In the case of the descending branch the reaction rate is determined by the formation of an ion pair in the bulk of the solution according to the reaction $PtCl_4^{2-} + M^+ \rightleftharpoons MPtCl_4^-$, and in the case of the ascending branch by the rate of the electron transfer. It has been shown[16] that it is improbable that the formation of an ion pair is the rate-determining stage.

In the present work the mechanism of the electrolytic reduction of halide complexes of platinum at a dropping mercury electrode has been investigated. Part of this work has been published earlier[7,10].

EXPERIMENTAL

The cell for the determination of polarisation curves has been described earlier[11]. The anode consisted of a platinum foil. The constants of the two capillaries with circular cross sections used in this work were as follows: flow rates $m_1 = 1.4$ mg sec^{-1}, $m_2 = 1.2$ mg sec^{-1}; the drop times τ_1 and τ_2, determined in 10^{-1} *N* KCl at the zero-charge potential of mercury, were 5.2 and 5.8 sec respectively. All the potentials quoted in this work are referred to the normal calomel electrode, which was used as the reference electrode. The potentials were determined by the usual compensation method, accurate to 2–5 mV. The current was measured with an M-21 mirror galvanometer with the maximum sensitivity 1×10^{-9} A mm^{-1}. All the determinations were carried out in a nitrogen atmosphere, which was freed from traces of oxygen by being passed first over ignited calcium chloride and activated charcoal and then through a furnace at 220° containing finely divided reduced copper deposited on kieselguhr. The copper catalyst was periodically reduced with hydrogen. The experiments were carried out at 20° ± 2°. All the reagents were carefully purified: potassium chloride, sodium sulphate, caesium chloride, sodium chloride, and barium chloride were twice recrystallised from twice-distilled water; potassium chloride and sodium sulphate were also ignited. K_2PtCl_6 was prepared by the reaction between potassium chloride and H_2PtCl_6, which was obtained by dissolving pure platinum in aqua regia. K_2PtBr_4 and K_2PtBr_6 were a gift from S.S.Batsanov and K_2PtCl_4 from N.N.Zheligovskaya. Water used in the experiments was twice distilled, and mercury was purified chemically and then twice distilled *in vacuo*. The solutions of tetramethyl-, tetraethyl-, and tetrabutyl-ammonium sulphates were prepared according to the published method[14]. Tetra-n-pentyl and tetra-n-hexyl ammonium bromides were a gift from Professor Bertsch, the director of the Institute of Organic Chemistry of the Berlin Academy of Sciences, whom we thank.

All the polarisation curves for the reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ have been corrected for charging currents, which were measured in 10^{-4} *N* sodium sulphate containing the electrolytes used in the investigation of the reduction of their anions. The polarisation curves obtained at the dropping mercury electrode were usually complicated by the presence of polarographic maxima. Only the parts of the curves not distorted by the maxima are shown in the figures. The electrolytic reduction of halide complexes is complicated by hydrolysis[2] and exchange reactions in the bulk of the solution[12]. Therefore all the experiments were carried out under identical conditions.

Electrolytic Reduction of $PtCl_4^{2-}$ and $PtBr_4^{2-}$

It has been shown earlier that polarisation curves for the reduction of $PtCl_4^{2-}$ reflect a retardation of the reaction at some potentials (Fig.1). Potassium chloride increases the rate of reduction in the region of decreasing current, but potassium chloride added in concentrations lower than 10^{-3} N has practically no effect on the electrolytic reduction of $PtCl_4^{2-}$ (Fig.1).[2] In these solutions the limiting current increases with increasing total concentration of the electrolyte, due to the disappearance of the migration effect. The effect of the supporting-electrolyte cation increases with increase in its charge. Thus 10^{-1} N Ba^{2+} accelerates the reaction more than K^+ at the same concentration, and 10^{-3} N La^{3+} is still more effective. The effect of the cations increases also with their size, as was found earlier in the case of the reduction of $S_2O_8^{2-}$ [15]. It is seen from Fig.1 in ref.7 that the reduction of $PtCl_4^{2-}$ is accelerated by cations in the order $Na^+ < K^+ < Cs^+$, but even in the presence of 1 N caesium chloride some retardation of the reaction still occurs.

Tetramethylammonium and tetraethylammonium cations (Fig.2 in ref.7) increase the reaction rate over the entire range of their adsorption potentials and are more effective than inorganic cations. The effect of additives on the rate of reduction of $PtCl_4^{2-}$ is the same as that observed in the cases of other anions, *e.g.* $S_2O_8^{2-}$, $[Fe(CN)_6]^{3-}$, $[Hg(CN)_4]^{2-}$.[13] The different sensitivity of the reduction of the anions to the effect of the additives may be due to the different geometry of the anions[7]. Planar anions, such as $PtCl_4^{2-}$, which can come close to the electrode, are not very sensitive to the additives. The reduction of these anions is retarded even in concentrated solutions of supporting electrolyte. Non-planar anions, *e.g.* tetrahedral $S_2O_8^{2-}$ and $[Hg(CN)_4]^{2-}$,[13] or octahedral $[Fe(CN)_6]^{3-}$, are very sensitive to the additives. This difference is very pronounced in the effect of large organic cations, *e.g.* the tetrabutylammonium cation, on the reduction of the anions[7]. $[(C_4H_9)_4N]^+$ accelerates the electrolytic reduction of $PtCl_4^{2-}$ only at potentials more negative than -1.2 V (Fig.3 in ref.7) up to the desorption potential. Up to a potential of -1.2 V, the positive charge of the tetrabutylammonium cation is relatively distant from the electrode surface and is ineffective, since planar $PtCl_4^{2-}$ comes close to the electrode. In this range of potentials the reduction of $PtCl_4^{2-}$ is retarded by $[(C_4H_9)_4N]^+$ due to the inhibition of the accelerating effect of inorganic cations which are displaced from the surface of the electrode by the organic cation. This is proved by the increase of the relative retardation of the reduction with increasing concentration of the tetrabutylammonium cation (Fig.3 in ref.7), with increasing concentration of the inorganic cation of supporting electrolyte (Fig.4 in ref.7) and with increasing radius of the supporting-electrolyte cation (Fig.2).

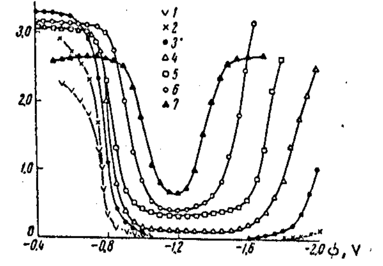

Fig.1. Polarisation curves for reduction of 10^{-4} N K_2PtCl_4 in the presence of added potassium chloride:
1) 0; 2) 10^{-4}; 3) 10^{-3}; 4) 5×10^{-3}; 5) 10^{-2}; 6) 10^{-1}; 7) 1 N.

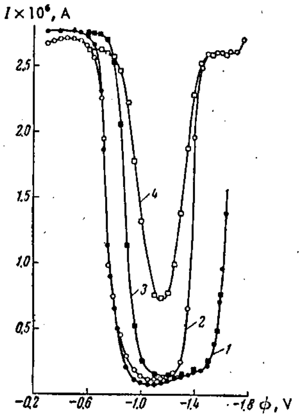

Fig.2. Polarisation curves for the reduction of 10^{-3} N K_2PtCl_4 in the presence of additives:
1) 10^{-1} N NaCl + 10^{-4} N $[(C_4H_9)_4N]_2SO_4$;
2) 10^{-1} N CsCl + 10^{-4} N $[(C_4H_9)_4N]_2SO_4$;
3) 10^{-1} N NaCl; 4) 10^{-1} N CsCl.

Thus, when Na^+ is replaced by a large monovalent cation such as Cs^+ (Fig.2), the relative retardation of the reduction of $PtCl_4^{2-}$ by the addition of an equal amount of $[(C_4H_9)_4N]^+$ becomes greater. When a large amount of the organic cation, *e.g.* 10^{-3} N $[(C_4H_9)_4N]_2SO_4$, is added, causing complete desorption of inorganic cations from the electrode surface, the difference between the rates of reduction in the presence of added Cs^+ and Na^+ disappears. Reduction of the concentration of $[(C_4H_9)_4N]^+$ at the same concentration of either Cs^+ or Na^+ reveals the different effects of Cs^+ and Na^+. Thus, simultaneous action of inorganic and organic cations of different size is determined by the concentration ratio of the additives. The increase of the reaction rate at potentials more negative than -1.2 V may be due to a deformation of the $[(C_4H_9)_4N]^+$ cation at the electrode[7].

The hypothesis that the effect of the supporting-electrolyte cations on the electrolytic reduction of anions depends on the geometry of the anions is corroborated by the results of an investigation of the reduction of $PtBr_4^{2-}$, which, like $PtCl_4^{2-}$, is planar. As in the reduction of $PtCl_4^{2-}$, the polarisation curve for the reduction of $PtBr_4^{2-}$ shows a drop in current, which becomes smaller when foreign cations are added (Fig.3). The shape of the current–voltage curve for the solution of 10^{-3} N K_2PtBr_4 + 10^{-3} N $[(C_4H_9)_4N]_2SO_4$ is the same as that for the solution of $PtCl_4^{2-}$ containing the same amount of $[(C_4H_9)_4N]^+$: the reduction is retarded up to the potential -1.2 V, after which the reduction rate sharply increases. After the desorption potential of $[(C_4H_9)_4N]^+$ has been reached, addition of $[(C_4H_9)_4N]^+$ does not affect the

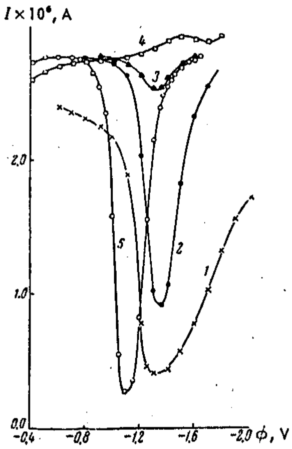

Fig. 3. Polarisation curves of reduction of: 1) 10^{-3} N K_2PtBr_4; and with added potassium bromide: 2) 10^{-2} N; 3) 10^{-1} N; 4) 5×10^{-1} N; 5) 10^{-1} N KBr + 10^{-3} N $[(C_4H_9)_4N]_2SO_4$.

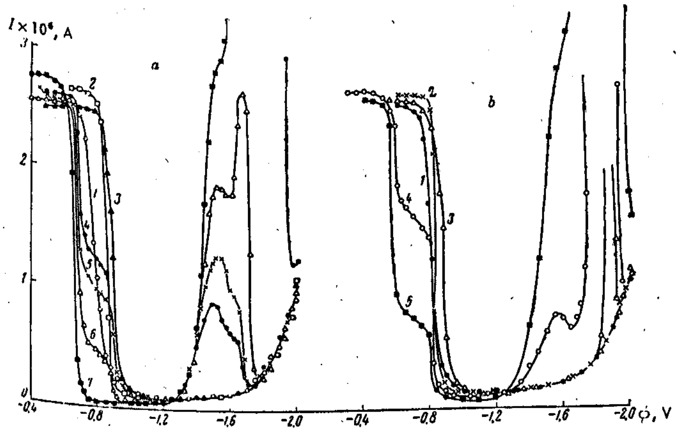

Fig. 4. Polarisation curves for the reduction of 10^{-3} N K_2PtCl_4 in the presence of additives:
a) $[(C_5H_{11})_4N]Br$: 1) 0; 2) 2×10^{-5}; 3) 4×10^{-5}; 4) 6×10^{-5}; 5) 7×10^{-5}; 6) 10^{-4}; 7) 10^{-3} N; b) $[(C_6H_{13})_4N]Br$: 1) 0;

curve. As in the reduction of $PtCl_4^{2-}$, a catalytic wave of hydrogen evolution is observed in the current–voltage curves in the presence of $[(C_4H_9)_4N]^+$.

The effect of tetrapentylammonium and tetrahexylammonium cations (Fig. 4, a and b) on the reduction of $PtCl_4^{2-}$ at potentials more negative than -1.2 V is the same as that of $[(C_4H_9)_4N]^+$ but at more positive potentials a number of new phenomena are observed. Thus, with increasing concentration of $[(C_5H_{11})_4N]Br$ and $[(C_6H_{13})_4N]Br$, added to 10^{-3} N K_2PtCl_4 solution, the descending branch of the curve is at first displaced to the right, which corresponds to acceleration of the reaction, and then to the left, which corresponds to retardation. In the presence of these cations, particularly $[(C_6H_{13})_4N]^+$, in the region of the descending branch the rate of reduction only slightly depends on the potential. Since data on the dependence of the capacity on the potential in the presence of $[(C_5H_{11})_4N]Br$ and $[(C_6H_{13})_4N]Br$ are not available, we cannot explain these phenomena. The effect of the simultaneous action of inorganic cations and $[(C_5H_{11})_4N]^+$ or $[(C_6H_{13})_4N]^+$ on the electrolytic reduction of $PtCl_4^{2-}$ is the same as that of $[(C_4H_9)_4N]^+$ and the corresponding amounts of the inorganic cations (Fig. 5).

Electrolytic Reduction of $PtCl_6^{2-}$

It has been shown that the current at the minimum of the current–voltage curve for the reduction of $PtCl_6^{2-}$ in the presence of foreign electrolyte at a concentration equal to, or greater than 10^{-3} N always reaches half of the value of the limiting current, while in the reduction of $PtCl_4^{2-}$ the current at the minimum is very much smaller than the limiting current. It has been postulated[5,10], that the reduction of $PtCl_6^{2-}$ takes place in two stages:

$$[PtCl_6]^{2-} + 2\bar{e} \rightarrow [PtCl_4]^{2-} + 2Cl^-, \tag{1}$$

$$[PtCl_4]^{2-} + 2\bar{e} \rightarrow Pt + 4Cl^-. \tag{2}$$

The observed retardation of the reduction is due to the retardation of both stages. The retardation of the reduction of $PtCl_4^{2-}$ (the second stage) can be investigated separately, which facilitates the investigation of the reduction of $PtCl_6^{2-}$. Since the reduction of $PtCl_4^{2-}$ is little affected by the concentration of the supporting electrolyte when its concentration is smaller than 10^{-3} N, the concentrations of the additives should be kept very small. In the investigation of the reduction of the $PtCl_6^{2-}$ anion (10^{-4} N), potassium chloride at concentrations smaller than 10^{-3} N strongly accelerates the reduction of $PtCl_6^{2-}$ (Fig. 6), while at higher concentrations, $e.g.$ on passing from 10^{-2} to 1 N, the increase in the rate is negligible. The different sensitivity of the reaction to the concentration of the supporting electrolyte may

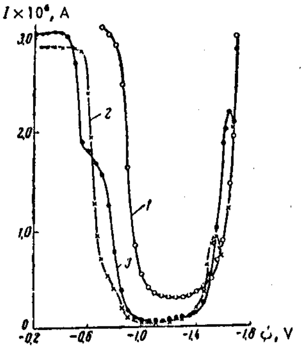

Fig. 5. Polarisation curves for the reduction of 10^{-3} N K_2PtCl_4 in the presence of additives:
1) 10^{-1} N Na_2SO_4; 2) 10^{-1} N Na_2SO_4 + 10^{-4} N $[(C_5H_{11})_4N]$ Br;
3) 10^{-1} N Na_2SO_4 + 5×10^{-5} N $[(C_6H_{13})_4N]$ Br.

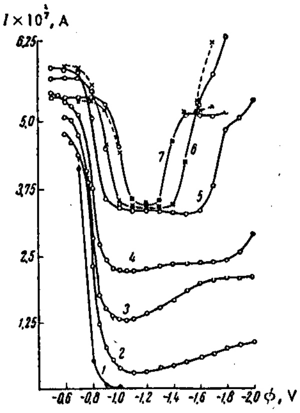

Fig. 6. Polarisation curves for the reduction of 10^{-4} N K_2PtCl_6 in the presence of KCl: 1) 0; 2) 10^{-4}; 3) 5×10^{-4}; 4) 9×10^{-4}; 5) 10^{-2}; 6) 10^{-1}; 7) 1 N; [broken lines: 6) polarisation curve for 10^{-4} N K_2PtCl_4 + 10^{-1} N KCl; 7) polarisation curve for 10^{-4} N K_2PtCl_4 + 1 N KCl].

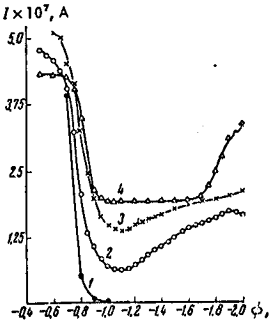

Fig. 7. Polarisation curves for the reduction of $10^{-4}N$ K_2PtCl_6: 1) without additives; 2) in the presence of $5 \times 10^{-4}N$ NaCl; 3) $5 \times 10^{-4}N$ KCl; 4) $5 \times 10^{-4}N$ CsCl.

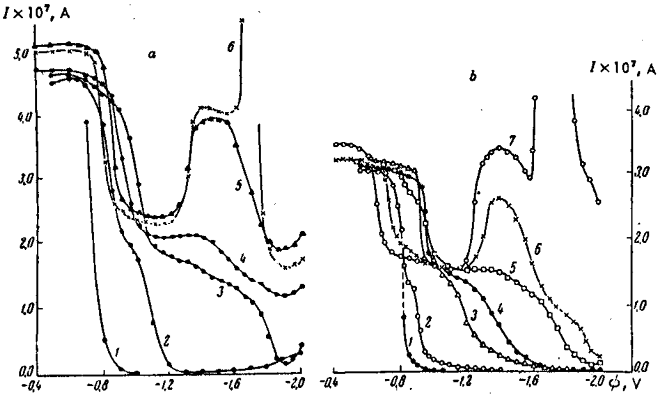

Fig. 8. Polarisation curves for the reduction of 10^{-4} N K_2PtCl_6 in the presence of additives:
a) $[(C_4H_9)_4N]_2SO_4$: 1) 0; 2) 10^{-5}; 3) 5×10^{-5}; 4) 10^{-4}; 5) 5×10^{-4}; 6) $10^{-3}N$;
b) $[(C_5H_{11})_4N]Br$: 1) 0; 2) 10^{-5}; 3) 2×10^{-5}; 4) 2.5×10^{-5}; 5) 4×10^{-5}; 6) 7×10^{-5}; 7) $10^{-3}N$.

be due to the geometry of the anions: octahedral $PtCl_6^{2-}$, reduced in the first stage, is more sensitive to the additives than the planar $PtCl_4^{2-}$. Therefore at concentrations of the supporting electrolyte lower than 10^{-3} N, where probably there is no retardation of the first stage in the reduction of $PtCl_6^{2-}$, small amounts of potassium chloride cause a large increase of the current. At higher concentrations of the supporting electrolyte the rate of reduction of $PtCl_6^{2-}$ is determined by the rate of reduction of $PtCl_4^{2-}$, for which the dependence of the current at the minimum on the concentration of the supporting electrolyte is negligible over a wide range of concentrations. This explanation is confirmed by a comparison of electrolytic reduction curves at any given potential, *e.g.* at the potential of the minimum. The curves for 10^{-4} N K_2PtCl_6 + 10^{-1} N KCl and 10^{-4} N K_2PtCl_4 + 10^{-1} N KCl (Fig. 6, curve *6*), 10^{-4} N K_2PtCl_6 + 1 N KCl and 10^{-4} N K_2PtCl_4 + 1 N KCl (Fig. 6, curve *7*), and for 10^{-3} N K_2PtCl_6 + 10^{-1} N KCl and 10^{-3} N K_2PtCl_4 + $10^{-1}N$ KCl are the same within experimental error.

The rate of the first stage in the reduction of $PtCl_6^{2-}$ strongly depends on the charge of the supporting-electrolyte cation and on its radius. Thus with 10^{-4} N La^{3+} there is no retardation, while in the reduction of $PtCl_4^{2-}$ the retardation remains even when the concentration of La^{3+} is 10^{-3} N. With 5×10^{-4} N CsCl (Fig. 7) there is almost no retardation of the first stage, while the reduction of $PtCl_4^{2-}$ is retarded even in 1 N CsCl. The reaction rate increases with increasing radius of the supporting-electrolyte cation in the order $Na^+ < K^+ < Cs^+$ (Fig. 7).

$[(CH_3)_4N]^+$ and $[(C_2H_5)_4N]^+$ accelerate the electrolytic reduction of $PtCl_6^{2-}$ and $PtCl_4^{2-}$;[7] the cation with the longer carbon chain is more effective. The retardation of the first stage in the reduction of $PtCl_6^{2-}$ is removed by the addition of 5×10^{-4} N $[(CH_3)_4N]_2SO_4$, while the reduction of $PtCl_4^{2-}$ is still retarded in the presence of 10^{-1} N $[(CH_3)_4N]_2SO_4$. Addition of dilute $[(C_4H_9)_4N]_2SO_4$ (up to 10^{-4} N), in contrast to its effect on the reduction of $PtCl_4^{2-}$ (Fig. 3, ref. 7), accelerates the first stage of the reduction of $PtCl_6^{2-}$ (Fig. 8) over the entire range of adsorption potentials of the organic cation. At higher concentrations of the cation, when the retardation of the first stage in the reduction of $PtCl_6^{2-}$ is removed and the reaction rate is determined by the second stage, the shapes of the curves are similar to those observed in the reduction of $PtCl_4^{2-}$ in the presence of the organic cation at the same concentrations. The curve for the solutions with added 10^{-3} N $[(C_4H_9)_4N]_2SO_4$ is situated below that corresponding to added 5×10^{-4} N $[(C_4H_9)_4N]_2SO_4$, which reflects the increase in the relative retardation of the reduction of $PtCl_4^{2-}$ with increasing concentration of $[(C_4H_9)_4N]_2SO_4$. The same relationship between the rate of reduction of $PtCl_6^{2-}$ and the concentration of the organic cation has been observed for $[(C_5H_{11})_4N]Br$ (Fig. 8*b*).

Thus, the experimental data confirm the hypothesis that the reduction of $PtCl_6^{2-}$ takes place in two stages, with $PtCl_4^{2-}$ as the intermediate. The reduction of $PtBr_6^{2-}$ is also retarded at strongly negative potentials, and the retardation decreases with increasing concentration of the supporting electrolyte. However, polarisation curves for the reduction of $PtBr_6^{2-}$ in electrolyte solutions are complicated by chemical reactions in the bulk of the solution[12].

We thank academician A.N. Frumkin for his advice and interest in this work.

SUMMARY

1. The effect of various electrolytes on the reduction of halide complexes of platinum at a dropping mercury electrode has been investigated and it has been shown that the retardation of the reaction observed at potentials more negative than the zero-charge potential of mercury may be explained as due to repulsion of anions from the negatively charged electrode surface causing a decrease of their concentration in the double layer.
2. Investigation of the rate of reduction as a function of the concentration of the supporting electrolyte and the charge and radius of its cation, together with the observed difference in the effects of surface-active organic cations on the reduction of $PtCl_6^{2-}$, $PtCl_4^{2-}$, and $PtBr_4^{2-}$, showed that the varying sensitivity of the reduction to the additives may be due to the geometry of the anions.
3. The data for the dependence of the rates of reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ on the composition of the solution show that the reduction of $PtCl_6^{2-}$ takes place in two stages, *via* $PtCl_4^{2-}$ as the intermediate.

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ADSORPTION OF TETRA-ALKYLAMMONIUM CATIONS ON MERCURY

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Many organic substances are adsorbed at the metal-solution boundary. Early work on the electrocapillary phenomena revealed that the extent of adsorption of neutral organic substances depends on the potential difference between the electrode and the solution and that at high surface charges the organic molecules are desorbed[1,2]. A quantitative theory of the effect of the electric field on the adsorption of neutral molecules was developed by Frumkin[3], who showed that when allowance is made for the force of attraction among the adsorbed molecules, the degree of surface coverage θ and the concentration of the surface-active substance c are related by the following expression:

$$Bc = \frac{\theta}{1-\theta} e^{-2a\theta}, \tag{1}$$

where a and B are constants at constant electrode potential; a is a measure of the mutual attraction of the adsorbed molecules. When $a = 0$, Eqn. (1) reduces to the Langmuir isotherm. If the adsorbed substance has a high molecular weight, $a > 0$ and the adsorption isotherm is S-shaped. When the interaction among the adsorbed species is very strong, there may be an abrupt change in the degree of coverage as the concentration of the adsorbed substance increases.

It was shown later[5] that differential-capacity measurements constitute a more sensitive method for the study of adsorption of organic substances than electrocapillary measurements. Up to the present much work has been done on the structure of the adsorption layer and also on the kinetics of the adsorption of organic substances on the electrode surface[4-13]. When the adsorption of surface-active organic molecules and ions is not complicated by the formation of multilayers or micellar films, differential-capacity curves may be satisfactorily interpreted on the basis of Frumkin's theory[3], at least for the adsorption of saturated aliphatic compounds. The theory was further developed by Hansen *et al.*[4] who applied it to establish the relation between differential capacity and polarisation and adsorption.

In the present work the differential-capacity method was applied to the adsorption of tetramethylammonium, tetrabutylammonium, and tetraethylammonium cations on a mercury electrode.

EXPERIMENTAL

The differential-capacity measurements were made by means of the previously described impedance bridge[14] on a pendant mercury drop electrode. The auxiliary electrode was a platinum cylinder symmetrically surrounding the mercury drop and the reference electrode was a normal calomel half-cell. All values of the potentials quoted are in volts with respect to the normal calomel electrode. The temperature was 25° ± 0.1°.

The sulphates of the organic cations were prepared as follows. The initial tetra-alkylammonium iodide or