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Short Communications

The Polarographic Reduction of Platinum(II) Complexes in Dimethylformamide

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The anomalous polarographic reduction of platinum(II) complexes has so far been studied only in aqueous media.[1] It was considered important to extend these studies to other solvent systems and dimethylformamide (DMF) was chosen, because in this solvent the reduction can be studied in the absence of hydrolysis, which strongly affects the polarograms in aqueous solution.[2] Moreover, catalytic hydrogen evolution [1] should be less pronounced in this aprotic medium and the interaction between DMF and platinum(II) complexes is weak.[3]

In Fig. 1 are shown the polarograms of *cis*-$Pt(NH_3)_2Cl_2$, *trans*-$Pt(NH_3)_2Cl_2$, and

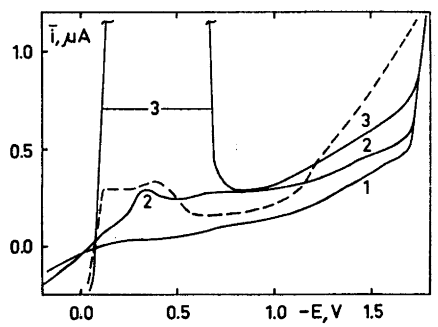

Fig. 1. Polarograms of platinum(II) complexes in 0.1 M $NaClO_4$ in DMF, $t = 25.0$°C: (1) residual current in 0.1 M $NaClO_4$, (2) 10^{-3} M *trans*-$Pt(NH_3)_2Cl_2$, (3) 10^{-3} M K_2PtCl_4, and dashed 10^{-3} M *cis*-$Pt(NH_3)_2Cl_2$.

$PtCl_4^{2-}$ in DMF. The polarogram of *cis*-$Pt(NH_3)_2Cl_2$ (Fig. 2) has the same shape as in aqueous solution, but the current never reaches a diffusion controlled level. When the dependence of the current on the height of mercury, $\bar{i} = \text{const} \cdot h^x$, was measured, it was found that the exponent x had a value of 0.14 in the potential range -0.15 to -0.30 V, but at the potential of the small maximum at -0.4 V, the value of x was 1.0. The temperature coefficient of the current between 25 and 55°C had a value of 2.4 %/deg. in the former potential range and a value of 1.3 %/deg. at -0.4 V. The variation of drop time with potential (Fig. 2, uppermost curves) showed that the electrocapillary maximum of mercury (ECM) in 0.1 M $NaClO_4$ in DMF is situated at about -0.3 V and that on the positive side of the ECM, the drop time in the presence of *cis*-$Pt(NH_3)_2Cl_2$ is lowered, indicating adsorption of the depolarizer.

The current varied linearly with the concentration of *cis*-$Pt(NH_3)_2Cl_2$ in the concentration range 0.4–2.5 mM.

In view of these experimental facts, it is concluded that the reduction of *cis*-$Pt(NH_3)_2Cl_2$ is kinetically controlled at potentials more positive than the ECM, probably as the result of a slow electron transfer between the adsorbed complex and the electrode. At potentials more negative than the ECM, the rate of adsorption decreases and the current at -0.4 V is subject to control by adsorption.[4] At more negative potentials, desorption occurs and the current drops.

The reduction of *trans*-$Pt(NH_3)_2Cl_2$ (Fig. 1, curve 2) proceeds as in aqueous solution without the appearance of a definite minimum. No indication of adsorption of this complex could be found.

The reduction of $PtCl_4^{2-}$ (Fig. 1, curve 3) starts directly from an anodic wave, which is probably caused by oxidation of mercury in the presence of the complex. A large maximum then follows and the current

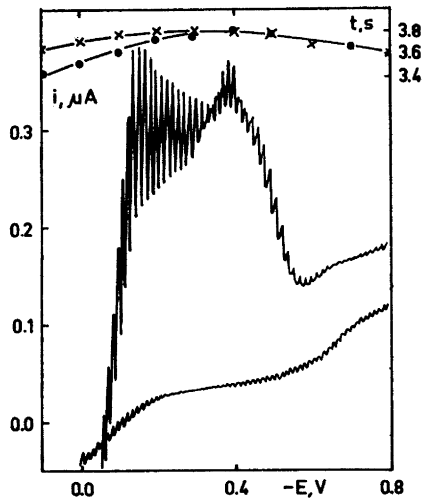

Fig. 2. Polarogram of (1) 0.1 M $NaClO_4$, (2) 0.1 M $NaClO_4 + 10^{-3}$ M *cis*-$Pt(NH_3)_2Cl_2$ in DMF solution at 25.0°C. Uppermost curves: variation of drop time with potential for solution (1), ×, and for solution (2), ●.

drops to a minimum at −0.7 to −0.8 V. In contrast to the situation in aqueous solution, no diffusion-controlled limiting current region was found on the polarograms in DMF.

In the region of the minimum, from −0.8 to −1.5 V, the magnitude of the current was independent of the head of mercury and thus kinetically controlled. This conclusion is further supported by the observation that the temperature coefficient of the current at the minimum was 6.5 %/deg.[4] The current at the minimum was practically independent of the concentration of K_2PtCl_4 in the range studied, 0.4−2.0 mM.

In conclusion, the results of the polarographic measurements in DMF solutions are in agreement with the explanation given for the reduction of these platinum (II) complexes in aqueous solutions.[1]

Experimental. The polarograms were measured using a Radiometer PO 4 polarograph and the previously described [5] potentiostatic equipment with a potentiometer (program unit FPP-1, Fiskars Electronic) driven by a synchronous motor as the source of the slow potential sweep.

Potassium tetrachloroplatinate(II) from Engelhard was used without further purification. *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ was purchased from K&K Laboratories Inc. Sodium perchlorate, *puriss.* grade, from Fluka AG, was dried at 100°C under vacuum before use.

Dimethylformamide, "Baker's analyzed" grade, was dried with molecular sieve 4A, distilled under reduced pressure in a current of nitrogen through a 70-cm vac. jacketed column packed with Berl saddles and stored with molecular sieve 4A under nitrogen.

The dropping mercury electrode had the characteristics $m = 2.02$ mg Hg/s, $t = 3.82$ s, measured with the electrode shortcircuited to the reference electrode, which was a silver-silver chloride electrode in DMF prepared according to the directions given by Kumar and Pantony [6] and connected to the cell through a salt bridge. All the potential values reported are referred to this electrode.

The counter electrode used in the potentiostatic system was a platinum wire helix separated from the cathode compartment by a sintered glass disc.

1. Sundholm, G. *Soc. Sci. Fennica, Commentationes Phy. Math.* **34** (1968) 39.
2. Sundholm, G. *Suomen Kemistilehti* **B 41** (1968) 306.
3. Langford, C. H. and Gray, H. B. *Ligand Substitution Processes*, W. A. Benjamin, Inc., New York 1965, p. 40.
4. Vlcek, A. A. *Progr. Inorg. Chem.* **5** (1963) 211.
5. Sundholm, G. *Electrochim. Acta* **13** (1968) 2111.
6. Kumar, G. P. and Pantony, D. A. *Polarography 1964*, Macmillan, London 1966, Vol. 2, p. 1061.

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