

## Polarographic analysis of the reduction waves of Pt(II)–SATSC complex<sup>†</sup>

R PALANIAPPAN\* and AGNES PAUL

Department of Analytical Chemistry, University of Madras, Guindy Campus, Madras 600025, India

MS received 23 May 1988; revised 5 November 1988

**Abstract.** A polarographic study of the Pt(II)–salicylaldehyde thiosemicarbazone complex in sodium perchlorate as supporting electrolyte is described. In addition to the reduction wave of the complex, a catalytic hydrogen wave is also recorded. The characteristics of this catalytic hydrogen wave are studied under different experimental conditions such as varying acid/complex/supporting electrolyte/surfactant concentrations and also with mercury drop-time. Based on these, a probable mechanism for the electrode process has been postulated.

**Keywords.** Polarographic analysis; Pt(II)–salicylaldehyde thiosemicarbazone system; catalytic hydrogen wave.

### 1. Introduction

It is a well-known fact that transition metal ions in the presence of thio compounds exhibit catalytic hydrogen waves (Toropova and Anisimova 1969; Saxena and Chaturvedi 1971; Toropova *et al* 1971; Toropova and Budnikov 1975). In continuation of our earlier reports on salicylaldehyde thiosemicarbazone (SATSC) complexes of noble metals (Palaniappan and Agnes Paul 1987a, b, 1988), the present paper delineates studies on the polarographic investigation of Pt(II)–SATSC.

### 2. Experimental

Salicylaldehyde thiosemicarbazone (SATSC) was prepared by adopting the procedure of Sah and Daniels (1950) (m.p. 235°C). Stock solutions:

- (i) SATSC (0.1 M) in ethanol;
- (ii) Pt(II)Cl<sub>2</sub> (~ 0.05 M) (Arora Matthey) in 0.1 M HCl. The latter was standardised as per the literature methods (Beamish and Van Loon 1977).
- (iii) Supporting electrolyte: 0.2 M aqueous sodium perchlorate.
- (iv) 0.02% aqueous gelatin.

<sup>†</sup> Presented at the 12th Annual Symposium in Chemistry held at the Indian Institute of Technology, Madras in March 1987.

\* For correspondence

The current voltage curves were recorded on an Elico (India) model CL-25D automatic recording instrument. The d.m.e. had the following characteristics in 0.2 M NaClO<sub>4</sub>:

$$m = 2.56 \text{ mg/s} \quad t = 4.1 \text{ s} \quad h = 45 \text{ cm} \quad \text{and}$$

$$m^{2/3} \cdot t^{1/6} = 2.3694 \text{ mg}^{2/3} \text{ s}^{-1/2}.$$

An Elico pH-meter (model LI-120) was used for measuring pH (accuracy,  $\pm 0.01$  pH unit).

### 2.1 Preparation of Pt(SATSC)Cl<sub>2</sub>

[Pt(II)(SATSC)Cl<sub>2</sub>] was prepared by mixing equimolar (0.05 M) solutions of Pt(II) and SATSC, adjusting the pH to 3.5–4.0 and diluting the resultant solution 5-fold. The yellow amorphous product obtained, was repeatedly recrystallised from ethanol to a sharp m.p. 272°C. Elemental analysis data, Experimental: C, 21.0; Cl, 15.2; N, 10.0; S, 7.0 and Pt, 40.8; Theoretical: C, 20.8; Cl, 15.4; N, 9.1; S, 6.9 and Pt, 42.8%. The molar conductance of a 10<sup>-3</sup> M solution of the complex in nitrobenzene was 10.5 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> implying a neutral complex. The metal to SATSC ratio determined photometrically under polarographic conditions by Job's (1928) and mole-ratio (Yoe and Jones 1944) methods at  $\lambda_{\text{max}} = 388 \text{ nm}$  ( $\epsilon = 6.3 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), was 1:1.

## 3. Results and discussion

### 3.1 Polarogram of [Pt(II) (SATSC) Cl<sub>2</sub>] Complex

About 1 mM [Pt(II) (SATSC) Cl<sub>2</sub>] (96% alcoholic) solution in the presence of 0.2 M aqueous sodium perchlorate supporting electrolyte (resultant solution pH = 5.8) produced two waves, with  $E_{1/2} = -0.610$  and  $-1.320 \text{ V}$  respectively, vs. SCE (figure 1a).

**3.1a Characterization of 1st wave:** The first polarographic wave was well defined ( $E_{1/2}$  range  $-0.610$  to  $-0.630 \text{ V}$  in the pH range 2.0–5.0) and was found to be diffusion-controlled (constancy in  $id/h^{1/2}$  value) and irreversible (transfer coefficient value,  $\alpha$ , ranging from 0.34–0.61, and  $n = 2$  from controlled potential coulometry) in the pH range 3.0–4.5; linear graphs were observed in the Pt(II) concentrations ranging between 7.0–62.0 ppm. So these curves may be exploited analytically in the above said pH range (this aspect will be taken up at a later stage).

**3.1b Second wave:** The second wave was recorded as a single well-defined wave (pH 5.8) when the complex concentration was lower than  $4 \times 10^{-5} \text{ M}$ , but above this concentration the wave split into two well-defined waves. Gradual decrease of the complex concentration, merges the two waves once again into a single wave (figure 1b).

**3.1c Effect of H<sup>+</sup> (0.3 M HClO<sub>4</sub>):** In 0.3 M HClO<sub>4</sub>, [Pt(II) (SATSC) Cl<sub>2</sub>] solution reproduced the first wave ( $E_{1/2} = -0.610 \text{ V}$ ), but a second wave was recorded with

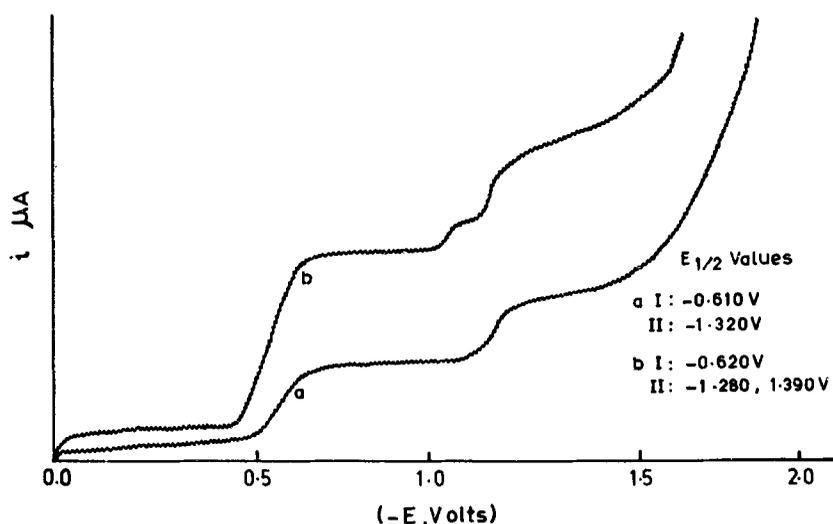


Figure 1. Polarogram of Pt(II)-SATSC in 0.2 M NaClO<sub>4</sub> complex concentrations: (a)  $4.5 \times 10^{-5}$  M, (b)  $1.03 \times 10^{-3}$  M.

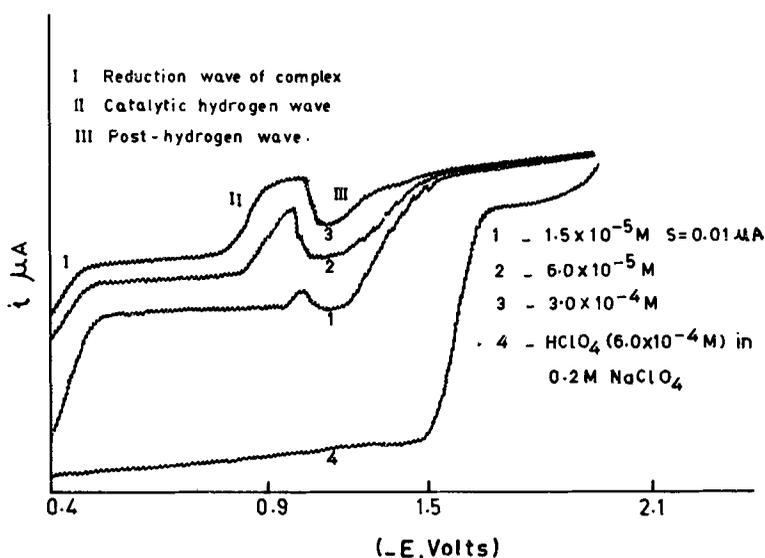


Figure 2. Influence of Pt(II)-SATSC concentration upon the shape of hydrogen waves of  $6.0 \times 10^{-4}$  HClO<sub>4</sub>.

$E_{1/2} = -0.920$  V. The catalytic nature of this wave was confirmed from (i) limiting dependence of current with respect to concentration, (ii) the relationship between  $i_c$  and  $h_{H_2}$  and (iii) increase in the limiting current value with increase in buffer concentration. Further, the slope value ( $-1.17$ ) from  $\log i_L$  vs pH plot (Gelb and Meites 1964) indicated the participation of one proton in the potential-determining step. Along with these waves, the post-hydrogen wave also appeared after the current minimum at  $-1.380$  V vs. SCE (figure 2) (third wave, III).

### 3.2 Characterization of post-hydrogen wave

The shape of the post-hydrogen wave varied with the concentrations of both acid and complex.

With solutions having almost equal concentrations of acid and complex or excess of complex concentration the polarogram recorded had two maxima-like waves. However, a well-defined hydrogen wave was observed when the acid concentration exceeded the complex concentration several-fold. Linear plots were observed in the height of the hydrogen wave with varying acid concentrations. Similar observations were made for the hydrogen wave in the absence of the complex in solution. However, there was a shift of this hydrogen wave towards more positive potential in the presence of the complex. The magnitude of the shift increased with increase of complex concentration (keeping the concentration of the acid constant) and decreased with increase of acid concentration (keeping the concentration of complex constant).

### 3.3 Characteristics of catalytic wave

Concentrations of acid and complex were found to have a profound influence on the shape of the catalytic wave.

The wave was peak-like in high acid concentrations, but transformed into a near well-defined polarogram when the concentration of the complex exceeded or equalled the concentration of the acid (figure 2). In both cases, after the limiting region of the wave, a decrease in the cell current leading to a current minimum between the catalytic and hydrogen wave was observed. The decrease in cell current value (formation of minimum) increased with increase of complex concentration. The catalytic current,  $i_c$ , of the catalytic wave showed limiting dependence (figure 3) (linearity observed with concentrations of complex solutions =  $0.2\text{--}2.6 \times 10^{-4}$  M) at a constant acid concentration ( $6.0 \times 10^{-4}$  M).

Splitting of the catalytic wave was also observed under the following conditions

- (i) When the concentration of acid exceeded that of the complex several-fold.
- (ii) By varying  $h_{\text{Hg}}$  from 25 to 60 cm (with a consequent change in the drop-time from 4.15 to 1.21 s).
- (iii) When the concentration of supporting electrolyte ( $\text{NaClO}_4$ ) was decreased from 0.2 M to 0.025 M.

Splitting of the catalytic wave under the above experimental conditions was considerably lessened by the addition of 0.02% gelatin (0.5 ml) which was eventually eliminated completely by the addition of excess gelatin ( $> 1.2$  ml) with a concomitant decrease in the height of the first wave (I) also.

- (iv) The splitting of the catalytic wave was highly dependent upon the time lapse after preparation of the complex solution. When the polarogram was recorded after 2 h, the splitting was completely eliminated. This may be indicative of the fact that the catalytic reduction of hydrogen is favoured predominantly by one particular structural form of the complex species in the solution with catalytic ability slightly higher than that of the other forms.

The relationship  $i = \text{const.}t^x$  calculated from the limiting current values gives  $x$  close to 1/5 for the hydrogen wave, both in the presence of the Pt-complex and

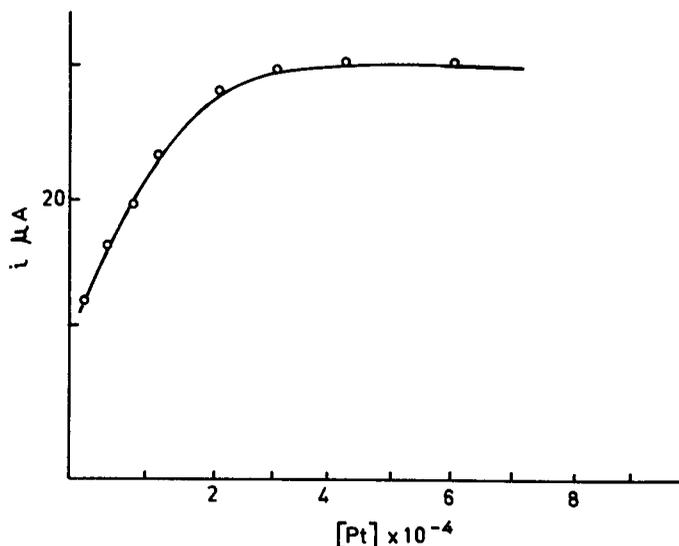


Figure 3. Dependence of height of catalytic hydrogen wave of  $6.0 \times 10^{-4}$  M  $\text{HClO}_4$  upon complex concentration.

without the catalyst. The value of  $x$  close to  $2/3$  obtained for the catalytic wave indicates kinetic limitation of the limiting current.

Two or more transient species in solution are converted into the predominant species when equilibrium is attained with time, which may be primarily responsible for giving rise to a single wave.

From the electrocapillary curves a slight dip around a potential of  $-1.380$  V (even though the drop-time is less) was observed.

### Conclusions

The assumption of catalytic properties in Pt(II)–SATSC leads to a relatively simple explanation of current minimum on the catalytic hydrogen wave. The minimum observed in the case investigated is characterized by a sudden and initially very rapid decrease of the current.

In cases known so far, the current minimum may appear owing to any one of the following phenomenon:

- (a) adsorption of surface active substance (may be due to the reduction product of first wave) leading to change in the characteristics of the d.m.e.
- (b) Change in complex structure in the electrical double layer under the influence of applied potential inhibiting the catalytic activity of the complex.

It may be that slight changes in the square planar structure of the reduced product in the presence of relatively large ligands makes the participation of the central metal atom in the catalytic process impossible. The additional assumption, that the change in reduced product structure takes place at potentials more positive than the desorption potential of a planar reduced species, enables us to explain the absence of a minimum on the wave in neutral solutions.

The splitting of the catalytic wave under the above experimental conditions is evidence that the complex has more than one catalytically active form and that chemical equilibrium is reached only after two hours when a single species predominates to give a single maximum.

### References

- Beamish F E and Van Loon J C 1977 *Analysis of noble metals* (New York: Academic Press)  
Gelb R I and Meites L 1964 *J. Phys. Chem.* **68** 2599  
Job P 1928 *Ann. Chim.* **9** 113  
Palaniappan R and Agnes Paul 1987a *Indian J. Chem.* **A26** 625  
Palaniappan R and Agnes Paul 1987b *Indian J. Chem.* **A26** 1071  
Palaniappan R and Agnes Paul 1988 *Electroanal. Chem. Interfacial Electrochem.* (in press)  
Sah P T and Daniels T C 1950 *Recl. Trav. Chim. Pays-Bas* **69** 1545  
Saxena R S and Chaturvedi G S 1971 *Indian J. Chem.* **9** 1402  
Toropova V F and Anisimova L A 1969 *Elektrokhimiya* **4** 1495  
Toropova V F, Anisimova L A and Gnedenkova C A 1971 *Zh. Obshch. Khim.* **41** 971  
Toropova V F and Budnikov G K 1975 *Elektrokhimiya* **11** 393  
Yoe J H and Jones A L 1944 *Ind. Eng. Chem., Anal. Ed.* **16** 111