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Voltammetric characterization of Hg^{2+} ion behaviour in acid media on different electrodes

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Abstract: This article presents some aspects related to the cathodic discharge of the mercuric ion provided from $HgCl_2$ into an aqueous solution of 0.1 M H_2SO_4 on different types of electrodes: gold disc electrode (GDE), carbon paste electrode (CPE) and platinum-disk electrode (PDE). Using the rotating disk electrode technique applied on PDE it was established that the cathodic discharge mechanism for the mercuric ion is based on both process types: mass transport, achieved by diffusion and charge transfer, achieved by electron transfer from cathode to mercury ion.

Keywords: cyclic and linear voltammetry, rotating disk electrode technique, potential and current intensity peak.

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Introduction

Mercuric chloride is used as depolarizer in electric batteries and as a reactant in organic synthesis and analytical chemistry.[1,2] Being more soluble in water than $HgCl_2$ (calomel), with the solubility increasing with temperature, it dissolves in 100 mL: 3.6 g at 0°C, 7.4 g at 20 °C and 48 g at 100 °C.[3] According to European criteria it is a highly-toxic corrosive substance, dangerous for the environment.[4-10] Some examples of the high toxicity of this compound are listed below, thereby motivating the necessity of applying electrochemical methods, especially voltammetry, to detect the mercuric ion presence.

One of the ways of entering the body is the ingestion of mercuric chloride, which causes strong irritation of the lining of the gastrointestinal tract.

Clinical case for ingesting mercuric chloride reveals various symptoms. Thus a child of 19 months who ingested an unknown quantity of toxic powder had mouth blisters and ulcers accompanied by vomiting.[11] For adults, symptoms are more complex, a 35 year old woman who ingested a lethal dose, faced with vomiting, diarrhea, colicky abdominal pain, oropharyngeal pain, and ulceration and haemorrhages throughout the length of the gastrointestinal tract[12], while for another who ingested 30 mg Hg /kg was reported the presence of severe abdominal pain, nausea, vomiting and diarrhea.[13]

Effects of acute or prolonged exposure to mercuric chloride on thyroid gland have been the subject of some researches. Thus, studies on rats, receiving 7.4 mg Hg/kg/day as mercuric chloride by gavage, observed an increased release of iodine to the thyroid,[14] while in the case of rats after administration of 6 mg Hg/kg/day as mercuric chloride or mercury sulphide

for 10 days, decreased plasma concentrations of thyroid hormones (triiodothyronine and / or thyroxine) were found.[15]

In this study, the cathodic discharge of the mercuric ion provided from $HgCl_2$, into 0.1M H_2SO_4 aqueous solution was investigated by the voltammetric method [16-20] on different type of electrodes such as: GDE, CPE and PDE; the mercuric ion discharge mechanism was also investigated by applying the rotating disk electrode technique[21-23] in given experimental conditions.

Materials and equipments

Aqueous solutions of $HgCl_2$ in 0.1M H_2SO_4 were studied, by voltammetric measurements, carried out on the gold disc electrode (GDE), carbon paste electrode (CPE) and platinum-disk electrode (PDE), respectively.

The fresh solutions were prepared using analytical purity reagents and bidistilled water and the voltammograms were recorded after nitrogen bubbling in the solutions, in order to remove the dissolved oxygen from these. The linear and cyclic voltammograms were performed using the PGSTAT 302N potentiostat (Metrohm Autolab) and the rotating disk electrode technique was performed on the electrochemical combine VoltaLab 32 (Radiometer Analytical). The silver chloride electrode (SCE) was used as the reference electrode, while the platinum wire (in the VoltaLab 32 case) and plane (1x2 cm in the PGSTAT 302N case) electrodes were used as auxiliary electrodes at 25 °C temperature.

Results and discussions

In Figure 1 is shown a multiple cyclic voltammogram, obtained on GDE (Φ=2mm), from which it can be observed that at the first cyclization

the cathodic discharge peak (1) of the Hg^{2+} occurs at 45mV/-196 μA, corresponding to the reduction process according to the following equation:

$$Hg^{2+} + 2e = Hg \quad (1)$$

At the sweep return, the oxidation current peak of the previously formed Hg occurs (1') at 205 mV/24.4μA, both the distance between the two peaks as well as intensities of current, proving that it is a slow process, quasi-ireversible.[24] Further, as the second cyclization takes place the peaks movement (1) and also a decrease of the current intensity (145mV/-79.9μA) can be observed and explained by a second reduction process (2) that precedes this peak (237mV/-20.7μA) corresponding the reaction:

$$Hg^{2+} + 1e = Hg^{+} \quad (2)$$

At the last cyclization (15) the peak corresponding to the mercuric ion discharge appears at 105mV/-162μA already taking place a preconcentration of the Hg^{2+} through the return streak, when the last oxidation peak (15') has maximum intensity (229mV/88.3μA) as a consequence of the mercury discharged during the reduction.

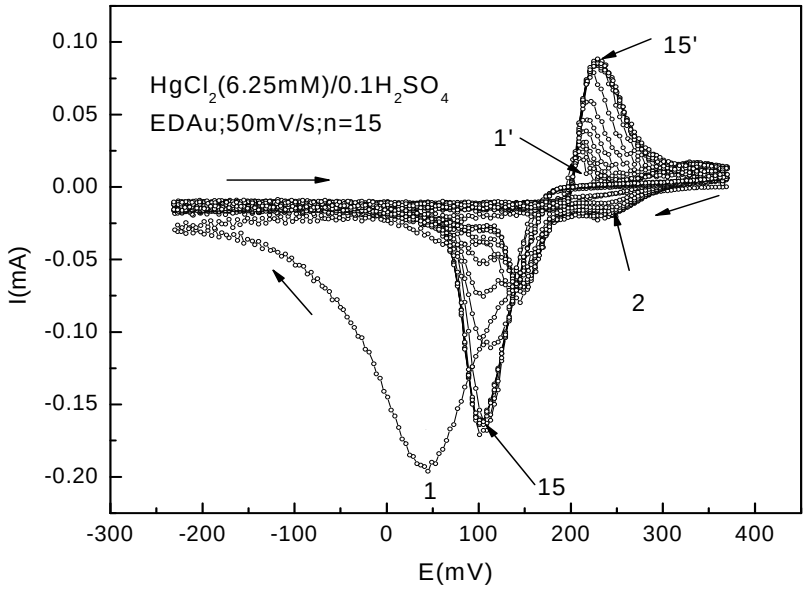

Figure 1. Multiple cyclic voltammogram in acid solution for the Hg^{2+} ion on gold disk electrode.

According to the data obtained in these experimental conditions it can be concluded that on the GDE a mercury preconcentration can take place and therefore the sensibility of the analytical method could be increased.

In Figure 2 is shown the cathodic linear voltammogram corresponding to the reduction of Hg^{2+} on the CPE (Φ=5mm) at different scanning rate. At low scanning rate (1 and 2) we can observe that the current peak corresponding to the mercuric ion discharge is preceded by another reduction peak which disappears at increasing scanning rate; therefore the second process (2) could not be pointed out.

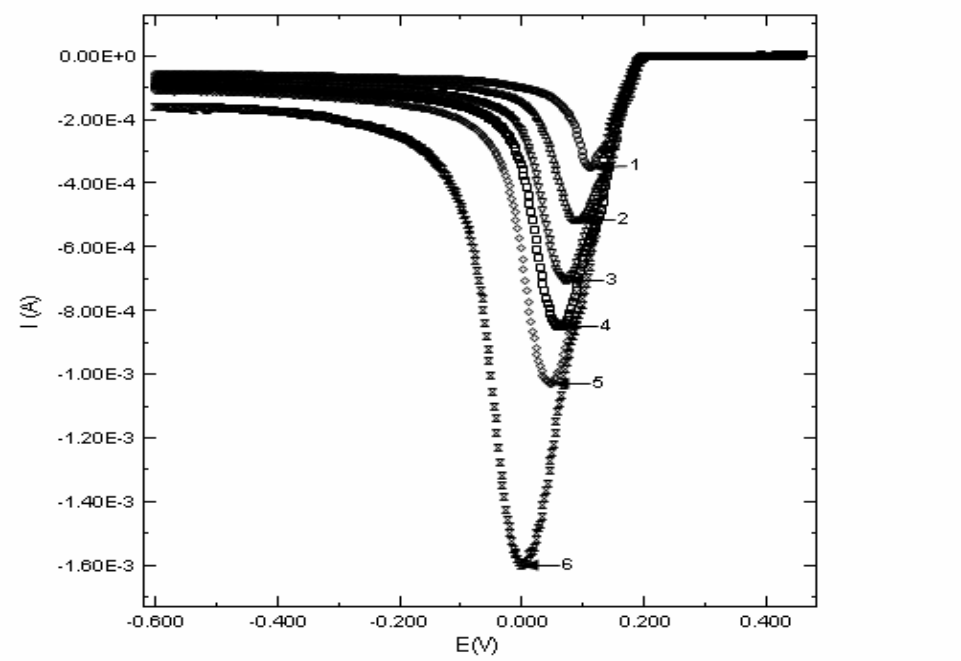

Figure 2. Linear voltammogram obtained at the Hg^{2+} reduction on carbon paste electrode in the acid medium at different scanning rate (1-10;2-20;3-30;4-40;5-50;6-100 mV/s).

According to the obtained data on CPE, the dependence on the scanning rate for mercuric ion discharge in acid media (0.1M H_2SO_4) at a concentration of 0.6 mM $HgCl_2$ was established as having the following form:

$$v_{red}(mol/s.mm^2) = 0.4495 + 41.6471*v(V/s) \text{ ; R= } 0.99934, \quad (3)$$

knowing that :

$$v_{red} = \frac{n}{S \cdot t} = \frac{j}{z \cdot F} \quad ; \quad j = \frac{I}{S} \tag{4}$$

where:

R is the linear correlation coefficient, **n** is the number of the involved moles in the cathodic process which correspond to z electrons, at **t** time, on the electrode surface **S**, at current density **j** current intensity I, **F** – Faraday constant (96485C/mol).

On the CPE at the scanning rate of 50 mV/s, in acid media, the dependence of the cathodic current peak on $HgCl_2$ concentration (mol/L) in the range of 0.006÷0.100M was obtained according to the following equation:

$$I(A) = -1.9657 \cdot 10^{-4} - 1.049 \cdot 10^{-2}\, c(mol/L); \; R = -0.9998 \tag{5}$$

In Figure 3 the mercuric ion behaviour in acid media on PDE (Φ=2mm) at different voltage scanning rate is presented.

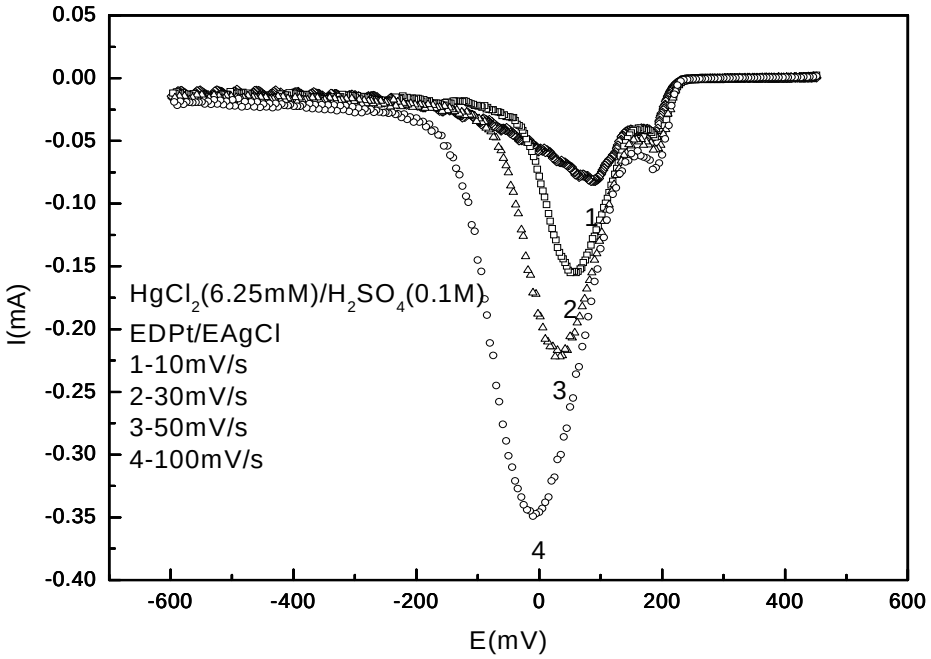

Figure 3. The linear voltammogram of Hg^{2+} at different scanning rate of platinum disk electrode in acid media.

On PDE the reduction process (2) can occur at higher scanning rate (3 and 4 from Figure 3) an increase of current intensity taking place (corresponding to the monoelectronic reduction process), depending on the

scanning rate. For the mercuric ion discharge (1) on PDE a linear relation between current intensity peak (I) and scanning rate (v) was established according to the following equation:

$$I(A) = -6.32 \cdot 10^{-5} - 2.92 \cdot 10^{-3} v(V/s); \quad R = -0.9958 \qquad (6)$$

By applying the technique of rotating disc electrode on PDE for the discharge of the mercuric ion in acid media the hydrodynamic curves were measured out and are presented in Figure 4.

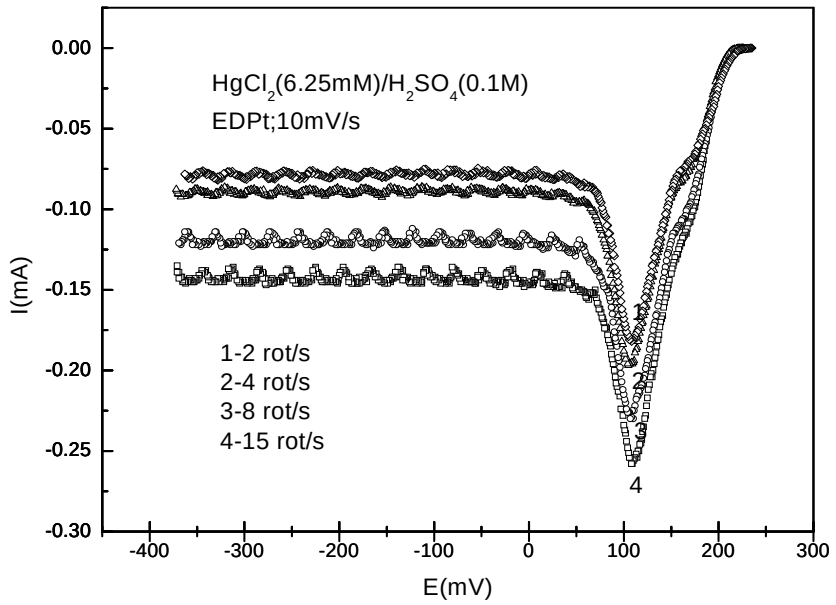

Figure 4. Hydrodynamic curves for the reduction of the Hg^{2+} ion, obtained by the rotating disc electrode technique on PDE.

The dependence of the limit cathodic current density recorded from the hydrodynamic curves on the square root of the angular velocity (ω) of RDPE is presented in Figure 5.

When the rate limiting step is the diffusion of the mercuric ions toward the platinum disc electrode surface, the Levich law should be confirmed, [24] meaning that the points from Figure 5 should be collinear. The equation which describes this dependence can be the proof that the mercuric ion discharge on PDE in acid media shows a complex mechanism due to

both charge transfer as well as the diffusion process of the Hg^{2+} ion from the solution to the electrode surface.

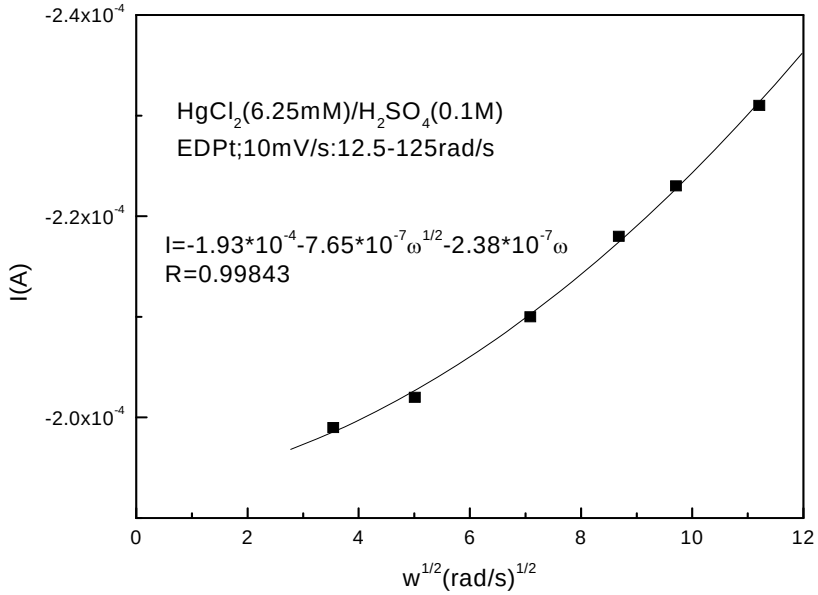

Figure 5. The dependence of the current peak corresponding to the reduction of the Hg^{2+} ion on the RDPE in acid media on the angular velocity ($\omega^{1/2}$).

Conclusions

The voltammetric studies on the behaviour of mercuric ion in 0.1 M H_2SO_4 leads to the following conclusions:

- the cathodic discharge processes of mercuric ion are slow and quasi-reversible on any of the three electrodes investigated;
- at low scanning rate (10mV/s) of the reduction potential on GDE and CPE, the monoelectronic transition process between the mercuric and the mercurous ions can be detected along with the mercuric ion discharge on the voltammogram;
- from all electrodes used, the CPE is the most sensitive, the equation describing the dependency between the cathodic peak intensity and the mercury concentration being established at the voltage scanning rate of 50 mV/s;
- on PDE the monoelectronic process is detected also at higher scanning rate (100 mV/s) with a sudden discharge of mercury, for which a

dependence relationship between peak current intensity and scanning rate was established;

- using the rotating disk electrode technique on EPD we proved that mercury discharge mechanism in given conditions is mixed, both diffusion and charge transfer at the electrode surface being decisive steps.

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