

VOLTAMMETRIC BEHAVIOR OF ETHYLMERCURY USING PLATINUM AND GLASSY CARBON ELECTRODES

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abstract: There was studied the voltammetric behavior of ethylmercury with a three electrodes system with two different working electrodes-platinum and glassy carbon. Using Britton-Robinson buffers we analyzed the pH influence covering the 2.3-9.86 domain. There are discussed the influence of the adsorption phenomena and the chemical reaction interference for different values of working parameters.

keywords: voltammetric, determination, ethylmercury.

Introduction

Ethylmercury (chloride of) is an organomercury compound, a class of compounds with a large spectrum of application but they are also very well known for their toxicity. It's a certain fact that mercury is one of the most toxic elements from the periodical system, affecting human body especially, and all alive organisms in general. Exposure to mercury can lead to -SH groups binding, can block the sulfate transporter in intestines, kidneys, reduces glutathione availability, inhibits enzymes of glutathione metabolism, disrupts purine and pyrimidine metabolism, disrupts mitochondrial activities, especially in brain. It accumulates in amygdale, hippocampus, basal ganglia, cerebral cortex, etc. If inorganic mercury is highly toxic, the alkylate form is even more dangerous since it can be concentrated through the food chain as a consequence of its solubility in lipids [1].

The organomercury compounds have been, and still are used as pesticides (organomercury fungicides); primary data [2] derive from victims of contaminated fish (Japan-Minamata Disease) or grain (Iraq, Guatemala, Russia).

During 1980-1990 on the pharmaceutical market, appears a vaccine, B hepatic, which contains Thimerosal (having 49.6% ethylmercury), and who was given to the children, age 14 months [3]-[5]. In the earlier '90s appears the idea that Thimerosal could be the cause of children autism, a very serious disease, with a irreversible evolution [6]. That why, for a while, autism was also called as the mercury intoxication. Autism is not the only disease caused by the accidental or indirect ingestion of mercury; due to the fact that once inside of the human body affects especially the nervous cells and is interfering in the cardiovascular system, it may lead to the Alzheimer disease or to serious heart problems.

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Thimerosal (49.6% ethyl mercury) can also be found in some cosmetic products and in some drugs.

Due to the quite large applicability of the organomercury compounds, especially ethylmercury, it is justified this choose for an analytical study which may explain his behavior in different conditions.

In the literature, there are many references about the organomercury compounds studies made until now through different techniques, such as: AAS with its various designs [7,8], including the cold-vapor technique, AES [9,10], HPLC[11], LC [12,13], GC[14,15], ICP-MS [16].

Regarding the electrochemical techniques used for the determination of Hg in general, and of ethylmercury especially [17-24] we have to say that there is a big interest these days in use of polymer coated electrodes for inorganic and organic mercury determination [25,26].

Experimental

All chemicals used were of high purity or reagent grade provided by Merck, no further purification being need.

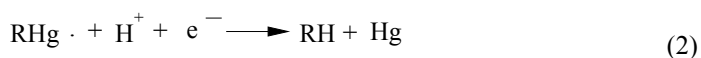
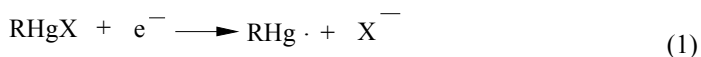
Water used for sample preparations and for glasses wash was triple distilled. All solutions used in the electrochemical measurements have been deoxygenated by purging purified argon stream into the solution from the electrochemical cell. for a 5 minutes period before each recording. The sweep rate was the same for all cases, 100mV/s. As working electrodes were used both Pt and glassy carbon who were polished after every recording with alumina powder.

Britton-Robinson buffer solution with a pH from 2.3 until 9.8 was used as indifferent electrolyte.

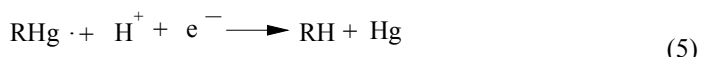
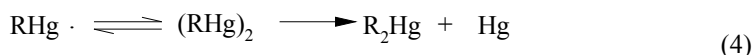
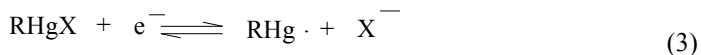
Electrochemical studies were carried out in a BAS, CV-50W, with a three electrodes electrochemical cell configuration where was used the Ag/AgCl electrode as the reference electrode, a wire of Pt as auxiliary electrode and a Pt millielectrode and a glassy carbon millielectrode as working electrodes.

Results and Discussion

In 1913 Kraus [2] discovered that by electrolyzing of an ammonia solution of alkylmercury chloride results a free radical RHg· which disproportionate to R₂Hg at room temperature. In the earlier '50s it was observed that for the reduction of an alkylmercury salt two polarographic waves were obtained attributed to the following irreversible processes:



The later studies [27] searched for the reversibility of these two steps, establishing that reaction (1) is a reversible process and reaction (2) is an irreversible process, reaction (1) being followed by a chemical reaction, dimerization of the alkylmercury free radical, and so the mechanism can be rewrite as:



The first polarographical studies based on the dropping mercury electrode, indicated that the free alkylmercury radicals are partly adsorbed on the working electrode surface, the adsorbed ones being those who are reduced in the second part of the mechanism (5); the unadsorbed radicals dimerize rapidly to the final dialkylmercury derivat [28].

Knowing these facts we tried to verify the mechanism using different working electrodes-Pt and glassy carbon- and to search for the ethylmercury behavior in different experimental conditions.

a) pH influence

Using as indifferent electrolyte Britton-Robinson buffer with pH values between 2.3 and 9.86, we recorded the cyclic voltammograms for the solutions of ethylmercury. The concentration of ethylmercury was equal to $2.5 \times 10^{-4} \text{ mole} \times \text{L}^{-1}$ in all samples.

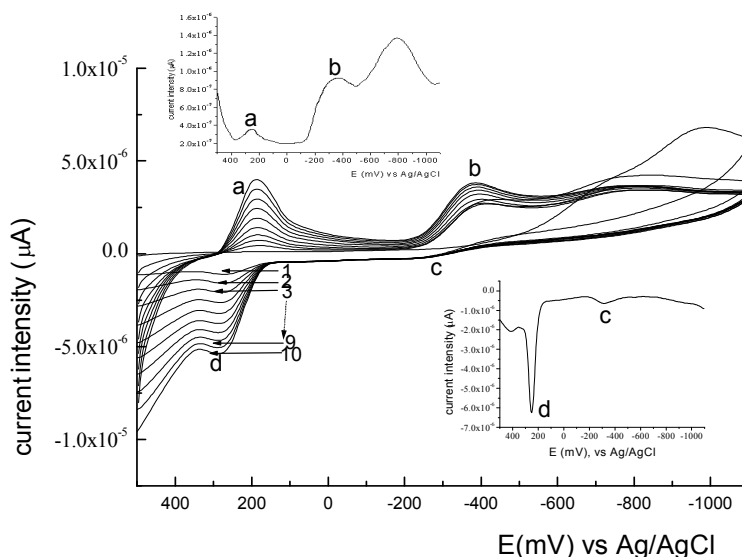


Fig. 1. Cyclic voltammograms recorded for ethylmercury in Britton-Robinson buffer (pH=7), $v=100\text{mV/s}$; - glassy carbon working electrode; the small icons represent the DPV curves recorded in the same conditions; 1-10-cycle number, a, b, c, d-CV and DPV peaks

As expected there are differences not only between the voltammograms recorded at different pH s values (acid, neutral and basic) but also between the voltammograms obtained at the same pH but using different working electrodes.

There are indicated the voltammograms at $pH=7$ recorded at a glassy carbon working electrode (Fig. 1) and at Pt working electrode (Fig. 2); for confirmation of the peaks identified by cyclic voltammetry we show in the small icons the differential pulse voltammograms recorded in same conditions for these systems.

As it can be seen, in the first case (fig.1), the voltammogram present 4 peaks, two reduction peaks at $E_{p1}=+0,102$ V vs Ag/AgCl, $E_{p2}=-0,450$ V vs Ag/AgCl and two oxidation peaks at $E_{p3}=+0,356$ V vs Ag/AgCl and $E_{p4}=-0,320$ V vs Ag/AgCl. The first reduction peak, E_{p1} , is very well defined, typical for the reversible processes, the second one E_{p2} is smaller than the first one, quite large which implies either a slow electronic transfer or an adsorption phenomena in the studied system.

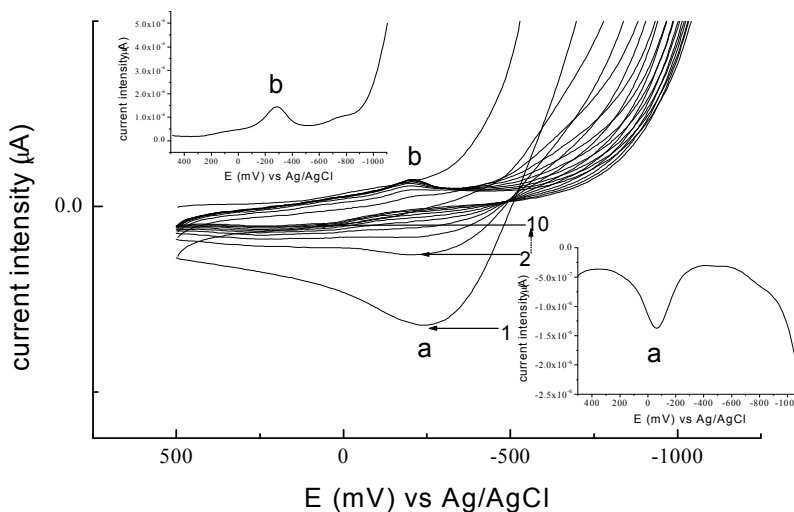
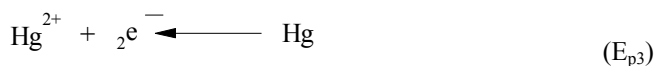
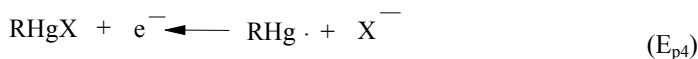
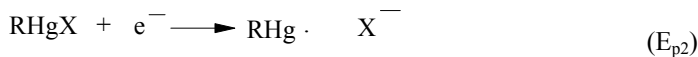
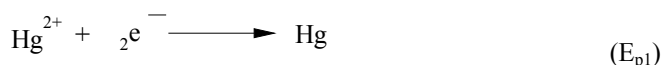


Fig. 2. Cyclic voltammograms recorded for ethylmercury in Britton-Robinson buffer ($pH=7$), $v=100$ mV/s; platinum working electrode; the small icons represent the DPV curves recorded in the same conditions; 1, 2,..., 10-cycle number; a, b-CV and DPV peaks

The first oxidation peak, E_{p3} , is also a typical reversible one and the second, E_{p4} being a very small and large, and as we saw in the later investigations appearing in a medium range of pH (6.52-7.19). We attributed these peaks, taking in count the order of appearance of the four peaks, as it follows:





The mercury atoms which are first oxidized (E_{p3}) and then reduced (E_{p1}) appear from the ethylmercury free radical dimerization (4), the free radicals resulting from the first electrochemical step (3) as the reduced form of the ethylmercury chloride; the mercury atoms involved in these reactions are adsorbed on the electrode surface forming a film, removed by polishing the electrode after each recording. We identify these peaks by recording the differential pulse voltammograms for the both electrochemical processes: reduction and oxidation.

It is very interesting the variation of these peaks in acidic and basic conditions. In acidic for the case of glassy carbon working electrode, for pH from 2.3 to pH 6.8 E_{p2} shift towards less positive values until $pH=4.67$ and than back to less negative ones; the peaks corresponding to Hg oxidation and Hg^{2+} reduction are increasing from pH 2.3 to pH 5.04 where they reach the maximum value for I_p decreasing than for the minimum value at pH 6.25 increasing again until $pH=7$.

In Pt working electrode case, the voltammogram (Fig. 2) presents one reduction peak with $E_{p2} = -0,209$ V vs Ag/AgCl, and one oxidation peak at $E_{p4} = -0,229$ V vs Ag/AgCl; the peaks corresponding to the processes for E_{p3} and E_{p1} from the earlier case do not appear due to the polarization of the electrode; in acidic conditions, E_{p2} has almost the same variation as for the glassy carbon electrode with the difference that the pH corresponding to the minimum value for E_{p2} is 6.25 and the oxidation peak disappear at $pH=4.67$ appearing again at $pH=7.00$. The peak defined by E_{p4} is practically inexistent at very low pH s values showing a better defined shape for a pH domain between 6.8 and 9.86.

As presented earlier there were recorded the differential pulse voltammograms for both systems and analyzed the response of peak current intensity at pulse amplitude change. As it can be seen in Fig. 3 in both cases we have a good linear relationship between I_p and ΔE .

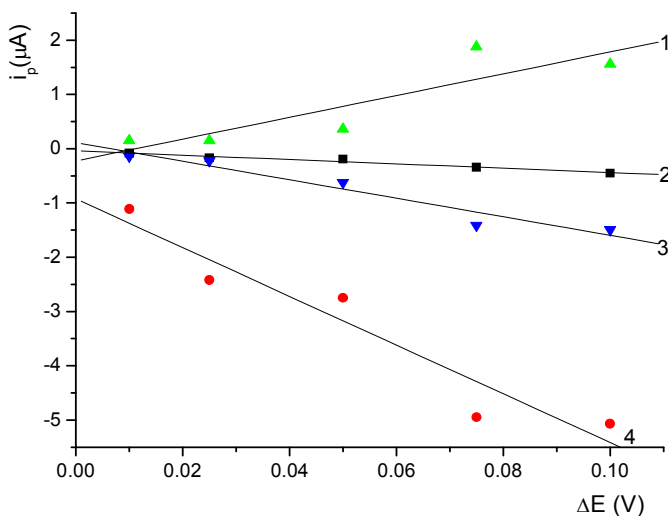


Fig. 3. $I_p=f(\Delta E)$ -glassy carbon electrode: 2- E_{p4} , 4- E_{p3} ; platinum electrode: 1- E_{p2} , 3- E_{p4}

In basic medium in case of glassy carbon electrode E_{p3} decreases while pH is growing, all peaks disappearing at $pH=9.86$; the fact that the peaks corresponding to the oxidation/reduction of Hg/Hg^{2+} disappear could only mean that at this pH value the second electrochemical step (not showing for this system) is becoming better underlined than the first one.

On the contrary, for case b, Pt working electrode, once the pH increase the peaks are becoming better defined, E_p shifting towards less positive (Fig. 4).

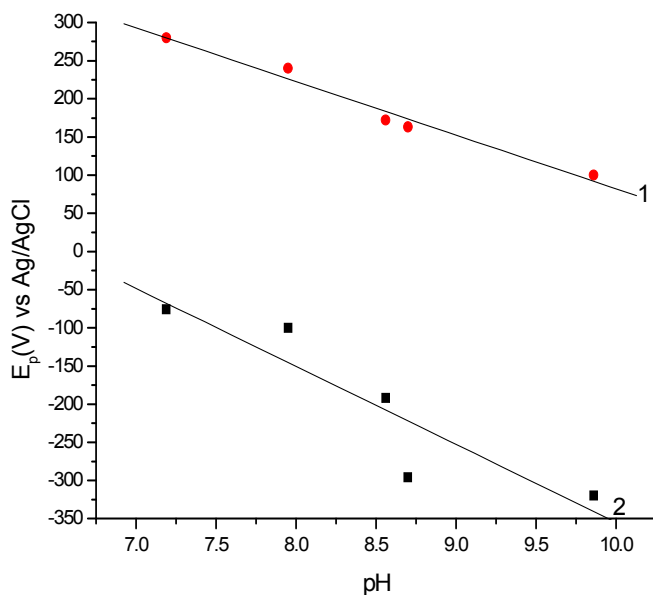


Fig. 4. $E_p=f(pH)$ for platinum electrode in basic medium: 1- E_{p1} ; 2- E_{p2}

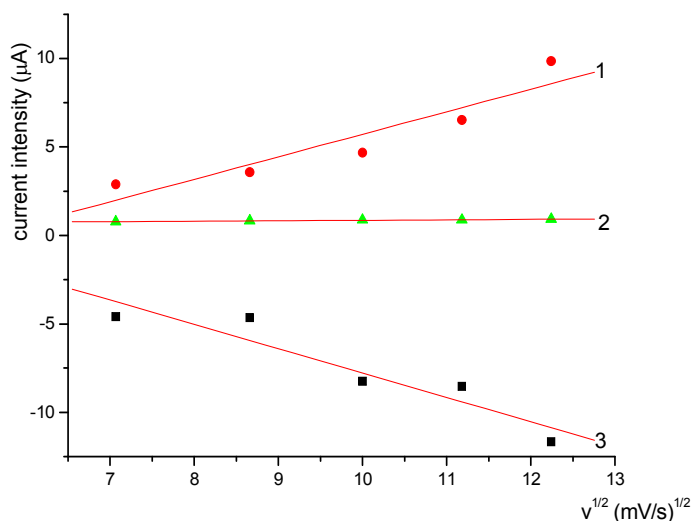


Fig. 5. $I_p=f(v^{1/2})$ at low sweep rate for the case of glassy carbon working electrode; 1- E_{p2} ; 2- E_{p1} ; 3- E_{p3}

b) $I_p=f(v^{1/2})$

By doing the $I_p=f(v^{1/2})$ representation (Fig. 5) we have a typical variation for the reversible electrode processes only in case of glassy working electrode at low sweep rate. For greater values an abnormal variation was observed which could be attributed to adsorption phenomena which occur at these levels and to the presence of the chemical reaction.

Conclusions

The electrochemical mechanism of ethylmercury in Britton-Robinson buffers at different pH values using as working electrodes both platinum and glassy carbon electrode was investigated.

In the imposed pH conditions use in this work only the first half of the mechanism with its variation in pH, sweep rate and nature of working electrode indicating the peaks corresponding to the reaction (3) (backward and forward) was demonstrated. Also in case of glassy carbon electrode, the peaks corresponding to the oxidation/reduction of the Hg/Hg²⁺ were identified.

As the extension of this study will be taken in consideration case of Hg working electrode in order to find the whole mechanism and to establish the amplitude of the adsorption phenomena and the rate of the competition between the chemical reaction and the second electrochemical process.

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