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**STUDY OF THE REACTION OF Pt(IV) ON MERCURY ELECTRODE
IN THE PRESENCE OF DIMETHYLGLYOXIME*****Marija Georgieva**Institute of Chemistry, Faculty of Science, St. Cyril & Methodius University,
Skopje, REPUBLIC OF MACEDONIA**Abstract**

The adsorptive behavior of Pt(IV) ions in the presence of dimethylglyoxime (DMG) has been investigated using adsorptive stripping voltammetric method. It was found that the bis-dimethylglyoximate platinum(IV) complex is adsorbed strongly between pH 4 and 5. The peak current is linearly proportional to the Pt(IV) concentration in the solution and various experimental parameters affecting the stripping response, indicating the concentration of the electrolyte, the accumulation time and the addition of surfactants, were studied to obtain a highly linear response. From the results a general scheme for the reaction process was given.

Keywords: Platinum, Adsorptive stripping voltammetry, Dimethylglyoxime, Determination

Introduction

The ability of the platinum group metals (PGM) to form many species in a given oxidation state, their tendency to the formation of polynuclear complexes make determination very difficult. Complete dissolution of the PGM, quantitative conversion into suitable complexes and their preconcentration before final detection are critical steps in almost all analytical procedure [1].

Many electrochemical active complexes of PGM can be adsorbed on the mercury electrode surface to cause a catalytic hydrogen current. Mostly based on this principle, several electro-analytical methods for the trace determination of PGM have been reported in the last few years [2-5].

In our previous investigations dimethylglyoxime (DMG) and other oximes [6-7] were used for the adsorptive preconcentration of palladium on the stationary mercury electrode. The present study is examined the utility of adsorptive stripping voltammetric procedure for platinum (IV), based on the reduction of the adsorbed platinum-dimethylglyoximate complex (Pt-DMG) in acidic media.

Experimental

All reagents were of analytical reagent grade. Deionized water was additionally purified using the Milli-Q system. Acetate buffer of pH 4.6 was used as a supporting electrolyte. This was prepared by mixing the appropriate amounts of 0.1 M acetic acid and 0.1 M sodium acetate. A stock solution of 0.1 M DMG (butane-2,3 dione dioxime, Merck) was prepared by dissolution of the pure substance in absolute ethanol. A platinum standard stock solution (1.00 mg/ml) was prepared by dissolving platinum wire (99.99%) in aqua regia. The residue was then dissolved in a few drops of 1 M HCl and the solution obtained was diluted to 50 ml with 0.1 M HCl. The platinum(IV) solution was standardized gravimetrically (precipitation with DMG). Working standards were prepared by serial dilution with 0.1 M HCl. A combined glass electrode and a pH meter were used for the pH measurement.

Voltammetric measurement were performed with an EG&G PAR model 264A stripping voltammeter in connection to the EG&G 303 stationary mercury electrode (SMDE). An Ag/AgCl electrode filled with a saturated KCl solution was used as a reference electrode and a platinum wire as an auxiliary. The voltammograms were recorded on an Omnigraphic 100 X-Y recorder

* Editorial note: Recognized by Greece as FYROM.

Model RE 00 89. Measurements were made by applying a differential pulse (DPP) mode with scan rate of 10 mV/s in the negative (cathodic) direction.

Results and Discussion

The linear dependence of the metal-ligand current signal upon the metal concentration, inspired us to explore the feasibility of using various experimental parameters affecting the stripping response of the complex, such as the concentration of the electrolyte, the accumulation time and the addition of surfactants.

The voltammetric peak potential (A) and peak height (B) (Fig.1) is influenced by the concentration of the supporting electrolyte, i.e., ionic strength. When the concentration of the acetate buffer was increased from 0.01 M to 0.1 M peak potential shifted approximately 70 mV in a cathodic direction. The height of the peak in the observed concentration range was doubled.

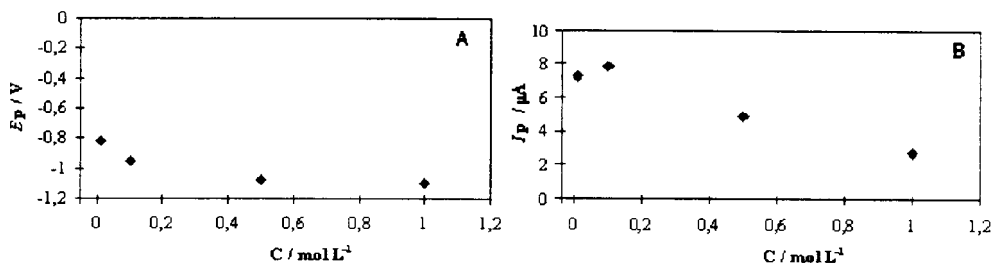


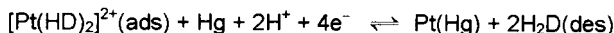
Figure 1. Dependence of the peak potential (A) and peak current (B) on the concentration of the supporting electrolyte (pH 4.6); 1×10^{-4} M DMG, 15 μ g Pt/L, deposition time 2 min at -0.4 V, electrode area: 0.028 cm².

The height of the peak in the observed concentration range was doubled. But, at still higher ionic strength it declines and begins to decrease when the concentration of the supporting electrolyte is increased to 0.5 M. This fact can be explained by the changes in the composition of the double layer and/or with thinning of the adsorption of platinum chelate at higher buffer concentration.

The extent of preconcentration depends on the length of time over which the adsorption is allowed to proceed. Such time-dependent profile reflects the enhancement of the surface concentration of the Pt-DMG complex. Short accumulation times are sufficient for obtaining a substantial signal enhancement, and a well-defined response. In consequence of, a 60 s accumulation yielded about 7-fold enhancement of the peak, to that obtained without preconcentration, respectively.

The presence of the nonionic surfactant Triton X-100 has a severe effect on the peak height. Its effect becomes more pronounced as the potential of zero charge (pzc) is approached. The peak height was completely suppressed with addition of 1 mg/L Triton X-100. The influence of the iodide ions on the platinum peak height is related to their specific adsorption on the mercury electrode [5].

The mechanism of the electrode process is difficult to define in detail, but the properties reported provide some evidence about the reduction of platinum(IV) in the presence of DMG. We propose that the platinum chelate is reduced to a low oxidation state. The reduction is described by the following overall reaction:



Conclusion

The results of our investigations showed that platinum(IV) is reduced from its adsorbed state. The reduction process is totally irreversible, only in the presence of DMG ligand. The surface concentration of Pt-DMG complex which is adsorbed depends on the concentration of this species in the bulk of solution according to dynamic equilibria between different platinum species.

The optimization of the differential-pulse operation indicated that a scan rate of 10 mV/s and a pulse height of 25 mV were the most favorable for the adsorptive stripping voltammetric measurements of this metal.

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