

Electroanalysis of Ag^+ , Hg^{2+} and Fe^{3+} by Voltammetry at an Iodine - Coated Platinum Electrode

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ABSTRACT. Voltammetric investigations on iodine-coated platinum electrodes revealed their remarkable inertness towards molecular adsorption, which means suppression of surface processes, interferences and generally the current background in voltammetric measurements. In the present work, iodine-coated platinum electrodes were prepared by potentiostatic adsorption of iodine at 0.20 V from 1 mM KI solution in 1.0 M HClO_4 . The passive potential window (the working potential range) in 1.0 M HClO_4 was approximately from -0.20 to 0.9 V. Electroanalysis of Ag^+ , Hg^{2+} and Fe^{3+} by cyclic voltammetry showed the existence of a linear relationship between the peak current on the E-i curves and the bulk concentration of the ions.

Iodine-coated platinum electrodes exhibit a remarkable inertness towards molecular adsorption (Ross and Hubbard 1975, Wieckowski *et al.* 1984, Hubbard *et al.* 1983). This inertness of iodine-coated platinum electrodes has been taken as a basis for the preparation of platinum (Zurawski *et al.* 1987) and rhodium (Hourani and Wieckowski 1988) single crystal electrodes at atmospheric pressure. Moreover, on the contrary to bare platinum or mercury electrodes, the iodine-coated platinum

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electrode is also insensitive to oxygen in aqueous solutions (Wieckowski *et al.* 1984). These electrodes, however, are responsive to oxidation and reduction of ions such as NO_2^- for instance (Cox and Kulesza 1984)

The simplicity with which iodine-coated platinum electrodes are prepared and their durability make them good candidates to replace the costly, laborious mercury electrodes for the analysis of ions. These electrodes might be used as detectors in HPLC and flow-injection systems.

In the present work, utilization of iodine-coated platinum electrodes in electroanalytical voltammetric measurements is demonstrated.

Experimental

Cell, Materials and Electrodes

A 362 potentiostat (Princeton Applied Research) along with a Philips x-y recorder was used for electronic control and data acquisition. A conventional, three-electrode cell equipped with a multiple-inlet system for admission of supporting electrolyte and for purging and blanketing the solution with oxygen-free nitrogen. The reference electrode was a $\text{Ag}/\text{AgCl}/1.0\text{ M Cl}^-$ and all the potentials reported in this paper are referenced to this electrode. The working electrode was a 2-mm diameter platinum rod (99.99% pure, Johnson Matthey), where only the tip of this rod was exposed to the solution through a hanging meniscus arrangement (Dickertmann *et al.* 1976)

All the reagents used were highly pure certified analytical reagent grade (A.R.) chemicals and were used as received from the suppliers without further purification. The working and auxiliary electrodes were made of platinum (Johnson Matthey, 99.99% purity). The used gases were c.p. grade products supplied by the National Gas Company and coupled with oxosorb cartridges (Supelco) for removal of residual traces of oxygen. All solutions were made from the above-mentioned reagents dissolved in triply distilled water where the second distillation was carried out from basic potassium permanganate solution.

Experimental Procedures

Initially the platinum electrode was cleaned in a freshly prepared chromic acid solution. The electrode was conditioned by cycling the potential between the hydrogen- and oxygen-evolution limits (ca. -0.2 and 1.3 V) until the regular voltammogram of the clean polycrystalline platinum electrode was reproduced. Potentiostatic iodination of platinum electrode was carried out at the double layer region (0.20 V) by admission of 1 mM KI solution into the working electrode compartment. After the electrode was allowed to equilibrate with the solution for

two minutes, iodide solution was drained from the working electrode compartment, and the electrode was rinsed extensively with iodide-free 1 M HClO_4 solution. The electrode potential was scanned between the hydrogen evolution limit and the threshold potential for iodine oxidation (ca. 0.9 V). The absence of any faradiac current in the scanned potential window is indicative of the electrode-protection provided by iodine (Fig. 1: The dotted-line) (Ross and Hubbard 1975, Wiecowski *et al.* 1984, Hubbard *et al.* 1983).

Cyclic voltammograms were recorded for the iodine-coated platinum electrode in 1 M HClO_4 solutions which contained different concentrations of Ag^+ and Hg^{2+} . Cyclic voltammetry measurements were also recorded for Fe^{3+} in 0.5 M H_2SO_4 solution.

Results and Discussion

Fig. 1 shows a representative voltammogram of iodine-coated platinum electrode and 1.0 mM Ag^+ in 1 M HClO_4 solution (the dashed line), along with the cyclic voltammogram of iodine-coated platinum electrode in 1 M HClO_4 (the dotted line) superimposed on the voltammogram of polycrystalline platinum electrode in 1 M HClO_4 solution (the full line). The absence of any redox activity for the iodine-coated platinum electrode in 1 M HClO_4 solution between hydrogen evolution limit (-0.2 V) and the threshold of iodine oxidation (ca. 0.9 V) (Fig. 1: the dotted line) indicates almost total suppression of surface processes. This suppression of the background is attributed to the presence of iodine adlattice (Hubbard *et al.* 1983, Zurawski *et al.* 1987).

The iodine adlattice on platinum is extremely stable; it is not desorbed by rinsing the electrode with water, 1.0 M HClO_4 solution or even chromic acid solution. Under ambient conditions, iodine can be removed from the surface by excessive cyclization of the electrode potential between hydrogen and oxygen evolution limits (-0.2 and -0.9 V) or through thermal desorption of iodine from the surface by annealing the electrode in hydrogen flame or resistive heating. Iodine-coated electrode is stable as far as the potential of the electrode was maintained under the threshold potential for oxidation of adsorbed iodine (≈ 0.9 V). No deterioration was observed in the iodine monolayer during experimentation for 24 hours. In spite of the simplicity of preparation of the iodine-coated electrode, we have started our daily experiments with a freshly prepared electrode.

The major advantage of using the iodine-coated electrode is due to the absence of molecular adsorption on the electrode. On the other hand, simple charge-transfer reactions may occur at the iodine-coated electrode. Differences in peak potentials, however, are expected because of the difference in their standard electrode potentials, E° 's for the different electrochemical reactions. The value of the peak potential provides the means for speciation while the peak current provides the

means for quantitation.

The cyclic voltammogram for iodine-coated platinum electrode in 1 M HClO_4 with 1 mM Ag^+ solution (Fig. 1: the dashed line) shows distinct peaks for oxidation and reduction of silver ions superimposed on negligible background. The voltammogram shows a cathodic peak for reduction of Ag^+ centered at 0.33 V and an anodic peak, for stripping of silver, centered at 0.43 V. Anodic peak currents (*i.e.* silver-stripping peak currents) were measured and plotted against the concentration of silver in the bulk solution (Fig. 2). The relationship between the anodic peak current (i_p) and the concentration of silver in the bulk is linear with a correlation coefficient of 0.9944. This result indicates that iodine-coated electrodes can be used for analysis of monovalent cations which deposit on the iodine-coated platinum electrodes upon reduction.

Applicability of the iodine-coated platinum electrode to analysis of divalent cations was demonstrated by analysis of mercuric ions. Fig. 3 shows a voltammogram of the iodine-coated platinum electrode recorded in 1 M HClO_4 plus 1.0 mM Hg^{2+} solution (the dot-dash line). The voltammogram shows two cathodic peaks and two anodic peaks associated with the $\text{Hg}^{2+}/\text{Hg}_2^{2+}$ and $\text{Hg}_2^{2+}/\text{Hg}$ couples. Based on peak sharpness criterion, we have chosen the first anodic peak, centered at 0.18 V (Fig. 3: the dot-dash line) as a signal for the concentration of Hg^{2+} in the solution. Peak currents were measured and plotted against the concentration of Hg^{2+} in the solution (Fig. 4). Statistical analysis of the data showed that the relationship between i_p and the concentration of Hg^{2+} is linear with a correlation coefficient of 0.9981.

Furthermore, applicability of the iodine-coated platinum electrodes in analysis of trivalent cations was verified by electroanalysis of Fe^{3+} . Fig. 5 shows the *i*-E curve for iodine-coated electrode traced in 0.5 M H_2SO_4 solution containing variable concentration of Fe^{3+} . Cathodic peak currents were extracted from the voltammograms and plotted against the concentration of Fe^{3+} (Fig. 6). Analysis of the data indicates that the relationship between i_p and the concentration of Fe^{3+} is linear with a correlation coefficient of 0.9928. The plot evidently does not pass through the origin most likely because of the uncertainty in determining the background level.

This behavior is not inclusive of positive ions but negative ions also show similar behavior. Nitrite ion, for instance, showed an improved voltammetric behavior on iodine-coated platinum electrode (Cox and Kulesza 1984). Determination of nitrite on iodine-coated electrodes, in a hydrodynamic system, is now being investigated in our laboratory and will be published separately.

Conclusions

In the present work, utilization of iodine-coated platinum electrodes in electroanalysis of ions has been explored. Iodine-coated electrodes with their extraordinary inertness towards molecular adsorption and inhibition of surface processes, may prove themselves as competitive electrodes for analysis of ions. Voltammetric measurements of the iodine-coated electrodes in 1.0 M HClO_4 containing variable concentration of Ag^+ and Hg^{2+} showed a linear relationship between the peak current (i_p) and concentration of these ions. Voltammetry in solutions containing variable concentration of Fe^{3+} also showed a linear relationship between peak current (i_p) and concentration of Fe^{3+} . Analysis of these ions using the iodine-coated electrodes may find wide applications in cyclic voltammetric analysis, as well as electrochemical detectors for HPLC, and flow-injection systems. *In vivo* investigations may also benefit from the extraordinary inertness of the electrode toward molecular adsorption to overcome the complications that might be introduced by the matrix complexity.

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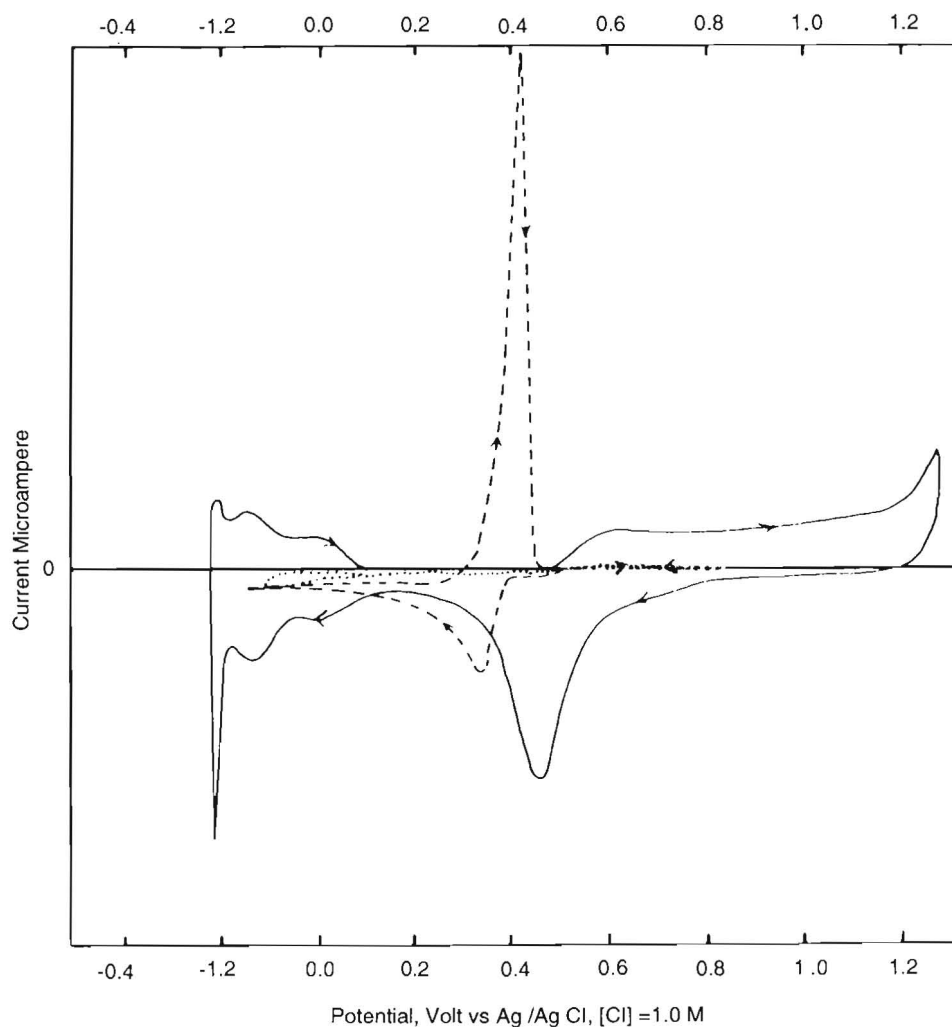


Fig. 1. Cyclic voltammograms for polycrystalline platinum electrode. (—) Bare electrode in 1.0 M HClO_4 traced, scan rate = 50 mV/s; sensitivity = 10 $\mu\text{A}/\text{cm}$. (.....) iodine-coated electrode in 1.0 M HClO_4 (scan rate = 50 mV/s, sensitivity = 10 $\mu\text{A}/\text{cm}$) and; (----) for iodine-coated platinum electrode traced in 1.0 M HClO_4 + 1 mM Ag^+ (scan rate = 20 mV/s, sensitivity = 20 $\mu\text{A}/\text{cm}$)

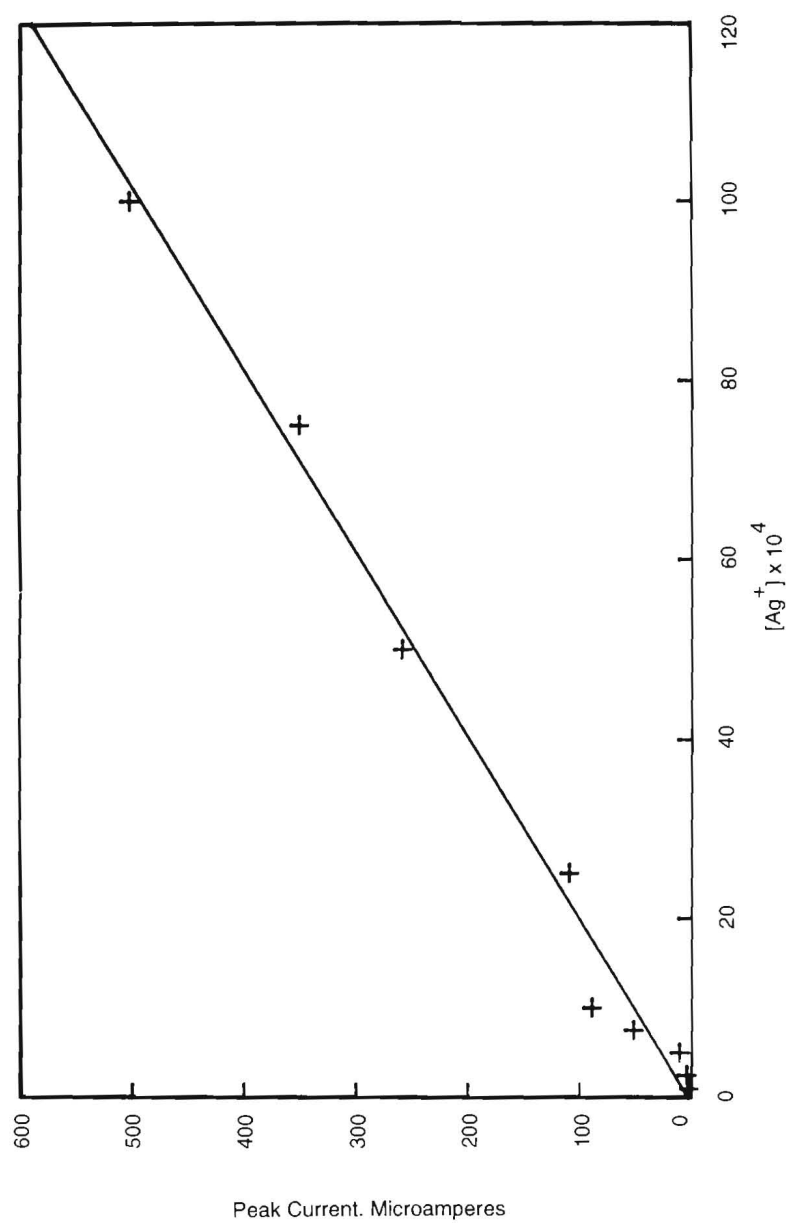


Fig. 2. A plot of peak current (i_p) for silver-stripping from iodine-coated platinum electrode in 1.0 M $HClO_4$ containing silver ions vs. the concentration of Ag^+ in the solution.

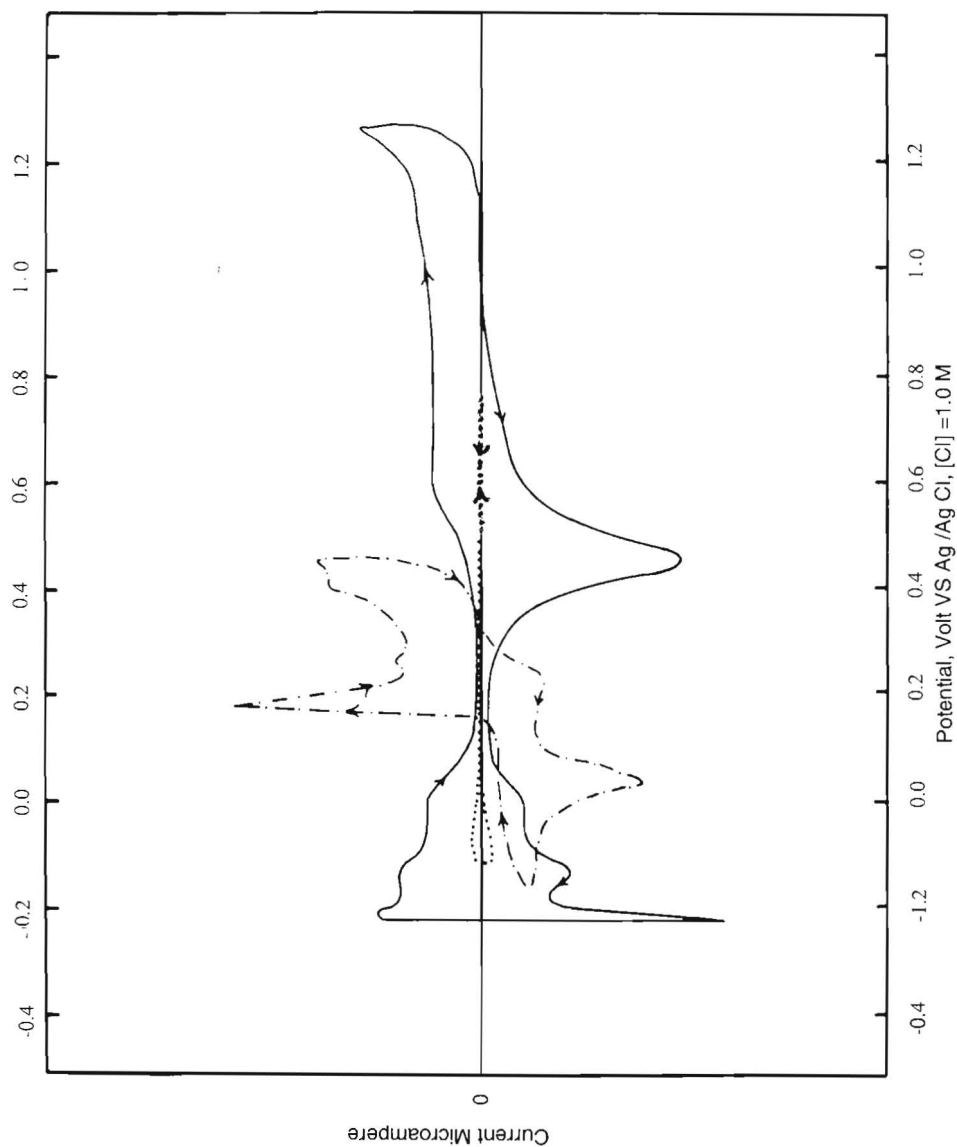


Fig. 3. Cyclic voltammogram for polycrystalline platinum electrode. (—) Bare platinum electrode in 1.0 M HClO_4 (scan rate = 50 mV/s, sensitivity = 10 $\mu\text{A}/\text{cm}$); (.....) iodine-coated platinum electrode in 1.0 M HClO_4 (scan rate = 50 mV/s, sensitivity = 10 $\mu\text{A}/\text{cm}$); and (- · - · -) for iodine-coated platinum electrode in 1.0 M HClO_4 + 1 mM Hg^{2+} solution (scan rate = 20 mV/s, sensitivity = 10 $\mu\text{A}/\text{cm}$).

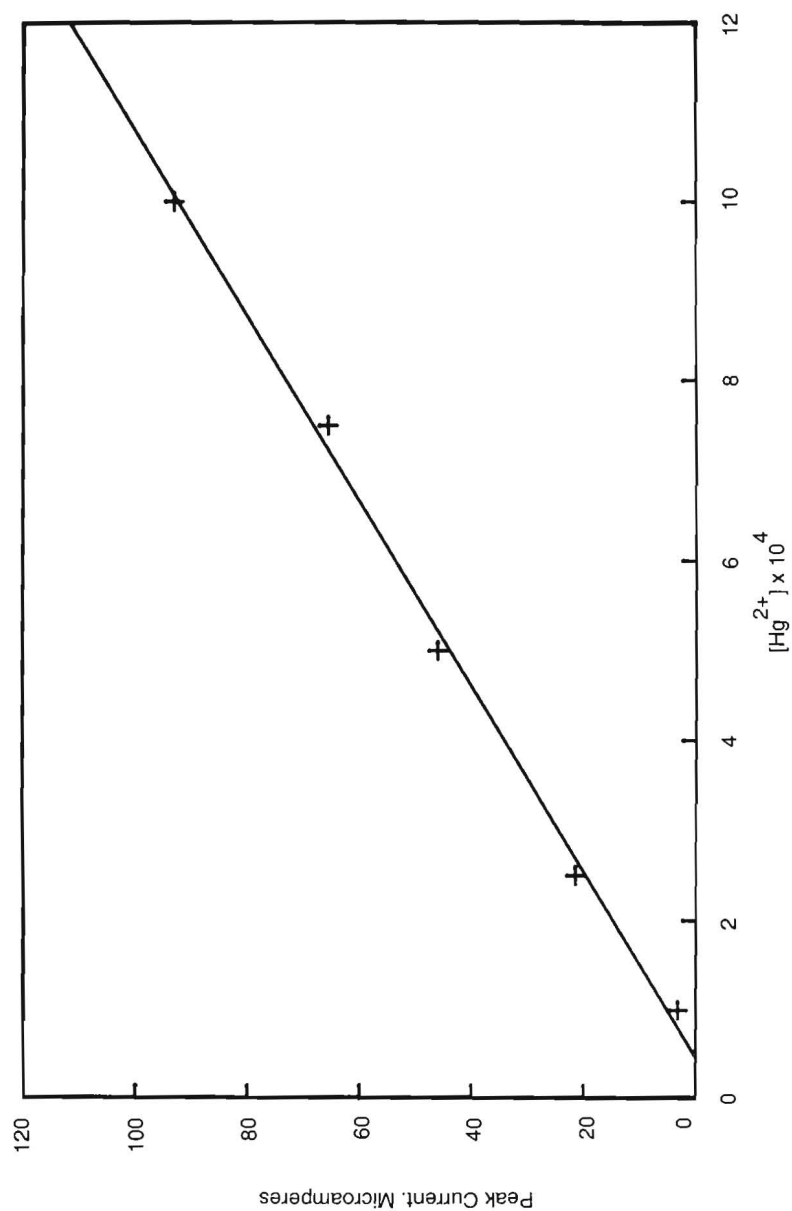


Fig. 4. A plot of peak current (i_p) for stripping of mercury from iodine-coated platinum electrode in 1.0 M $HClO_4$ containing mercury ions vs. the concentration of Hg^{2+} in the solution.

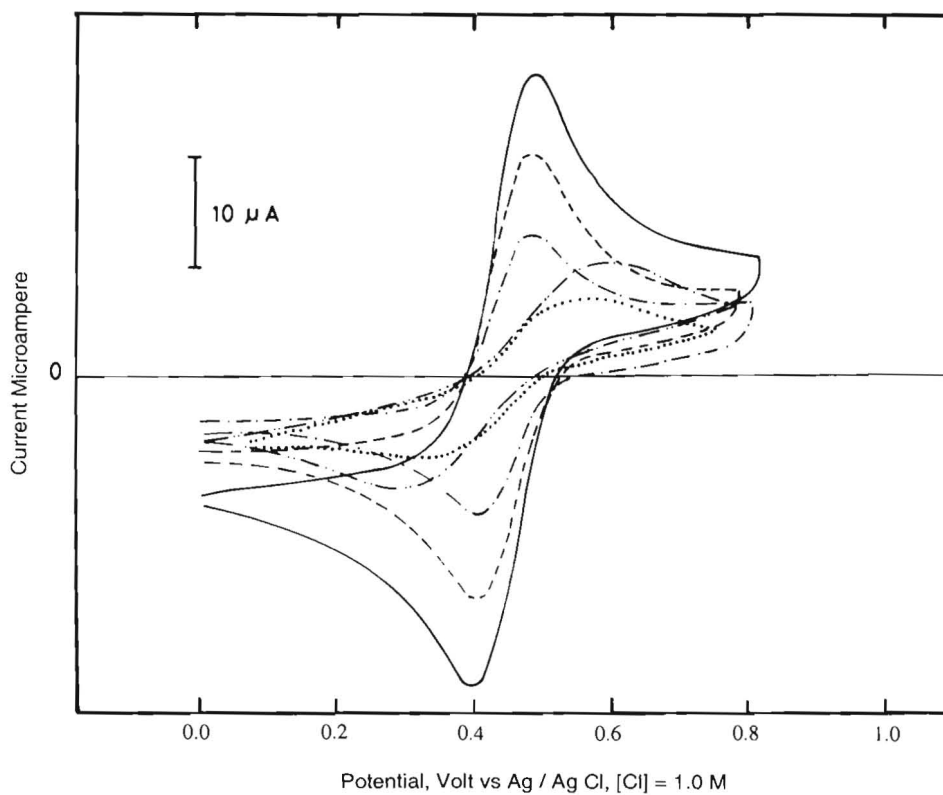


Fig. 5. Cyclic voltammogram of iodine-coated platinum electrode in H_2SO_4 solution containing variable concentration of Fe^{3+} . (—) 4 mM Fe^{3+} ; (----) 3 mM Fe^{3+} ; (- - - -) 2 mM; (- · - · - · -) 1.5 mM; and (.....) 1 mM of Fe^{3+} solution.

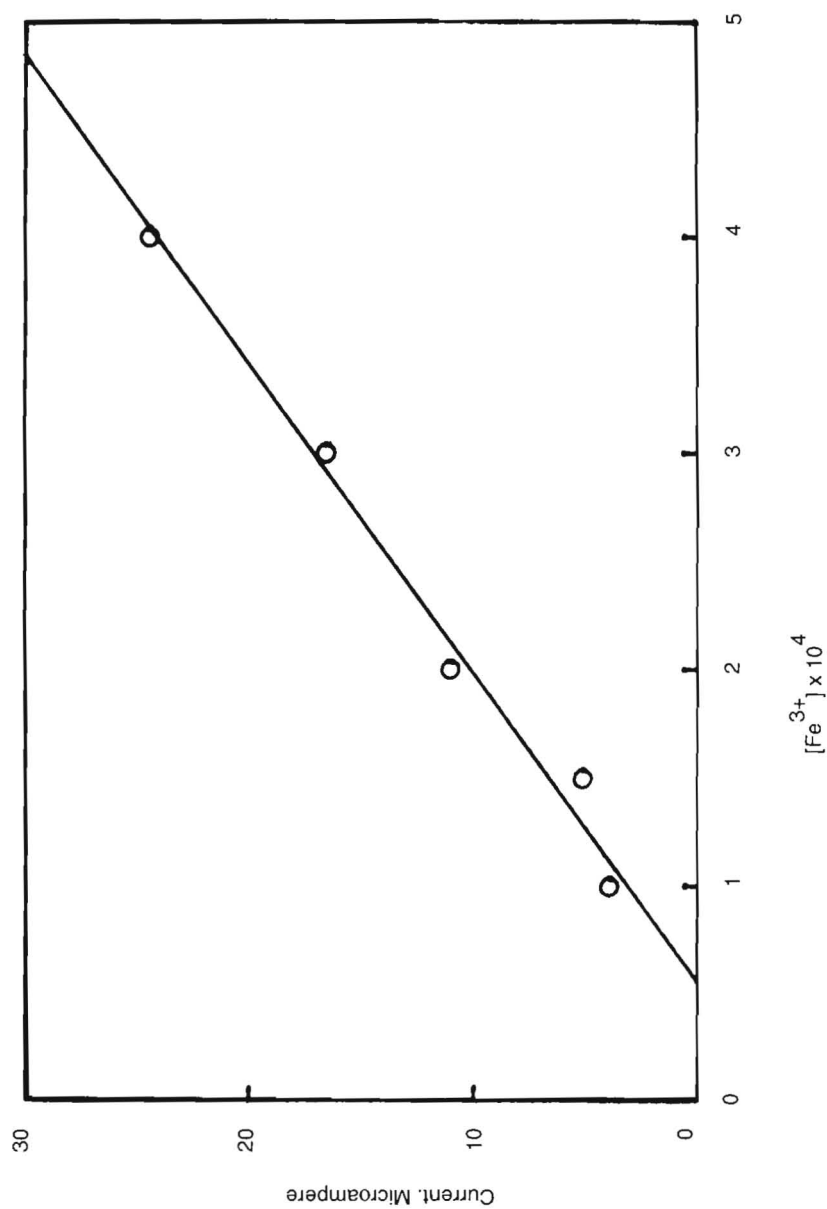


Fig. 6. A plot of cathodic peak current (i_p) for reduction of Fe^{3+} on iodine-coated platinum electrode in 1.0 M H_2SO_4 vs. the concentration of Fe^{3+} in the solution.

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التحليل الكهروكيميائي ل Ag^+ و Hg^{2+} و Fe^{3+} بالفولتامترية على أقطاب ألبلاتين المغطاة باليود

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لقد دلت الإختبارات الفولتامترية أن قطب البلاتين المغطى بطبقة من اليود يتمتع بخصمولية عالية تجاه الإمتزاز الجزيئي ، الأمر الذي يعني إستئصال العمليات السطحية ، والتفاعلات الدخيلة ، وبشكل عام تقليل مستوى الخلفية في القياسات الفولتامترية .

وفي البحث الحالي قمنا بتحضير أقطاب البلاتين المغطى باليود بغمس قطب البلاتين الذي يخلو سطحه من الشوائب - كما يؤكد ذلك منحني الجهد - تيار - في محلول 1 مللي مول/ لتر KI عند جهد ثابت مقداره 0.2 فولت . ثم قمنا بدراسة خصائص هذا القطب حيث اتضح خموله الكيميائي على الفولتاموغرام بغية أي نشاط كهروكيميائي عند مسح الجهد الكهربائي في المنطقة الواقعة بين - 0.2 و 0.9 فولت في محلول 1 مول/ لتر حامض البير كلوريك .

وهذا النطاق المذكور يمثل في الحقيقة نطاق الجهد الذي يجب أن لا تتجاوزه عند إستخدام هذا القطب (نطاق جهد العمل) . ثم قمنا بدراسة إمكانية تحليل أيونات الفضة والزنبق و الحديدك بإستخدام تقنية الفولتامتية الحلقية

على قطب البلاتين الموشى بطبقة من اليود ، فكانت نتيجة التجارب إيجابية حيث دلت النتائج على وجود علاقة خطية بين تراكيز الأيونات السالفة الذكر وتيار ذروة إنتزاع المعدن على الفولتاموغرام .