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Electrocatalytic Ethaneperoxoic Acid reduction at Gold Electrode

Omar A. Hazazi

Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University, P.O.Box : 6055
Makkah 21955, Saudi Arabia
E-mail: oahazazi@hotmail.com

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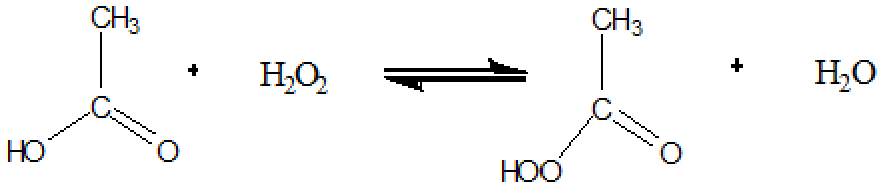
Electrocatalytic ethaneperoxoic acid (EPA) reduction at gold electrode in 0.5 M H_2SO_4 by ferric ions has been studied. Ferric ions acted as a mediator for EPA reduction where EPA is reduced via EC mechanism. The voltammetric behaviour of EPA has not been affected with the coexisting H_2O_2 or oxygen in naturally aerated EPA solutions. It has been found that ferric ions mediate EPA reduction but not H_2O_2. Interestingly while the EPA reduction peak is obtained at gold electrode in Fe^{3+} free H_2SO_4 is at around 0.2 V vs. Ag/AgCl, it is obtained at around 500 mV in the presence of ferric ions, i.e., it is around 300 mV positively shifted. The difference between the peak potential for EPA and H_2O_2 at gold electrode equals 0.5 and 0.9 V in the absence and presence of ferric ions, respectively. The large difference in the peak potentials in the presence of ferric ions, in addition to the well-defined reduction peak of EPA, has been utilized as a base for a selective analysis of EPA in the presence of H_2O_2 with acceptable sensitivity.

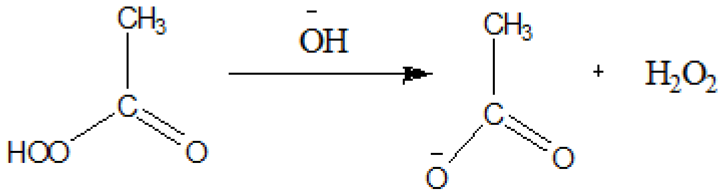
Keywords: Electrocatalysis, Electroanalysis, Ethaneperoxoic, H_2O_2.

1. INTRODUCTION

Ethaneperoxoic acid (EPA) is an eco-friendly disinfectant of a broad effect against microorganisms; it has diverse applications in for example milk and dairy products processing, wastewater treatment and pulp and paper process [1]. The electrochemical behaviour of EPA is obscured by the presence of unavoidable hydrogen peroxide. The coexistence of these two species is mainly due to the preparation of EPA from H_2O_2 through a reaction, which is of an equilibrium nature (Eq. 1), and due to the continuous decomposition of EPA to H_2O_2 (Eq. 2) [2-5]. Thus it has been reported that EPA may coexist with a large excess of H_2O_2 of about 100 times larger than that of EPA [6]. Peroxides analysis based mainly on their oxidizing properties; some of peroxides act as a strong oxidizing agent, and some of them may act as reducing agents in the presence of strong oxidizing agents comparatively. Thus all reported methods for the analysis of peroxides depends on their reactions with reducing agents [7-14]. The change during this reaction have been followed by several techniques such as spectrophotometry [15-18] and potentiometry [19-22]. In the potentiometric method the Ethaneperoxoic acid has been analysed in the presence of hydrogen peroxide with different ratios up to 500 fold of the Ethaneperoxoic acid [20].



(1)



(2)

The analysis has based on the large difference in the rates of oxidation of iodide by the different peroxides. Recently chromatographic methods based on the oxidation of sulphides by peroxides have been reported [23-29]. In all reported methods the stoichiometry of reactions on which the analysis is based on and the cross reaction which is reflected on the selectivity are the main challenges. Recently the electroanalysis of Ethaneperoxoic acid in the presence of hydrogen peroxide at bare and modified gold electrode have been reported [30-38].

In the present work the electrochemical behaviour of EPA and hydrogen peroxide in their coexistence in the presence of ferric ions as a mediator has been studied. The effect of oxygen has been also studied.

2. EXPERIMENTAL

Deionized water was used to prepare all solutions. The EPA stock solution was analyzed using the conventional method proposed by Greenspan and Mackellar [2] and compared with the Sully and William method [3]. Solutions of appropriate concentrations of the EPA and H_2O_2 were prepared from their stock solutions.

The polycrystalline gold electrode (1.6-mm diameter) was polished with aqueous slurries of successively finer alumina powder (down to 0.06 μm) and was sonicated for 10 min in water. The Au electrodes were then electropretreated in 0.05 M H_2SO_4 solution by repeating the potential scan in the potential range of – 0.2 to 1.5 V versus Ag/AgCl (NaCl sat.) at 100 mV s^{-1} for 10 min or until the CV characteristic for a clean Au electrode was obtained.

Cyclic voltammetric measurements were performed using a EG&G potentiostat (model 273A) operated with E-Chem 270 software. A porous glass separated the working electrode and the counter electrode (a platinum spiral wire). An Ag/AgCl (NaCl sat.) electrode was used as the reference electrode. Electrolyte solutions were, if necessary, deareated by bubbling N_2 gas for at least 20 min prior to electrochemical measurements.

3. RESULTS AND DISCUSSION

Fig. 1 shows CVs obtained at Au (1.6 mm) electrode in (a) N_2- and (b) naturally aerated 0.1M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ solution. In curves a and b the Fe^{2+} oxidation obtained at around 0.5 V is coupled by the reduction at around 0.45 V. The effect of oxygen on this redox couple is negligible as revealed from the constant peak current both in the presence (curve a) and absence (curve b) of oxygen. However, in the presence of oxygen (curve b), as expected at gold electrode in acid medium, an additional broad peak is obtained over the potential range 0~0.4 V. This peak corresponds to oxygen reduction to H_2O_2 and the further reduction to water (Eqs. 3 and 4), in agreement with literature [39-41]. However this peak is obscured by the overlapping with the hydrogen evolution. It is noteworthy to mention that Fe^{2+}/Fe^{3+} couple is not significantly affected by oxygen or by its reduction product (H_2O_2 in the present case). This might be attributed to the slow reaction of Fe^{3+} and H_2O_2 [42].

$$O_2 + 2H^+ + 2e = H_2O_2 \qquad (3)$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O \qquad (4)$$

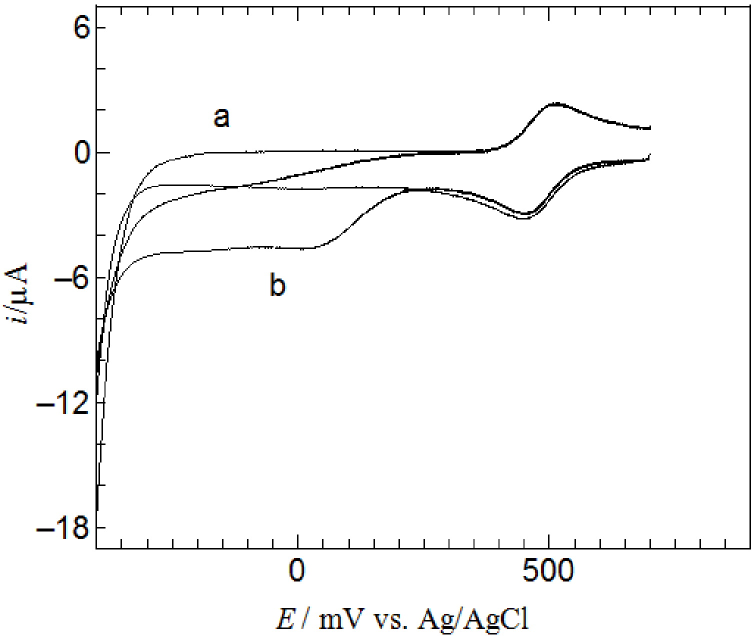


Figure 1. CVs obtained at Au (1.6 mm) electrode in (a) N_2- and (b) naturally aerated 0.1M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ solution.

Fig. 2 shows CVs obtained at Au electrode (1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and (b) 2.2 mM H_2O_2, (c) 4.4 mM H_2O_2, (d) 8.8 mM H_2O_2 and (e) 2.75 mM EPA + 9.65 mM H_2O_2. Inset shows the CV obtained at Au electrode in N_2-saturated 0.1 M

H_2SO_4 containing 2.75 mM EPA + 9.65 mM H_2O_2. As can be seen in the inset the the voltammetric curve has two peaks revealed at 0.13 and -0.23 V which corresponds to the reduction of EPA and H_2O_2, respectively in a quite agreement with literature [6, 20]. The two peaks are not well defined and the corresponding current for the two species could not be obtained without deconvolution. The difference in the peak potentials ($\Delta Ep = (Ep)_{EPA}-(Ep)_{H2O2}$, where $(Ep)_{EPA}$ and $(Ep)_{H2O2}$ are the peak potentail for EPA and H_2O_2 reduction, respectively) between the two peaks for the reduction of the two species equals 0.39 V. Curve b shows the well defined Fe^{2+}/Fe^{3+} couple which is centered at around 0.475 V. In curve c the currents of the Fe^{2+}/Fe^{3+} couple does not significantly changed upon increasing the concentration of H_2O_2. However a broad peak is obtained before the hydrogen evolution. This peak corresponds to the hydrogen peroxide reduction to water as explained above, revealed at -0.35 V, at Au electrode, consistently with the reported value [6].

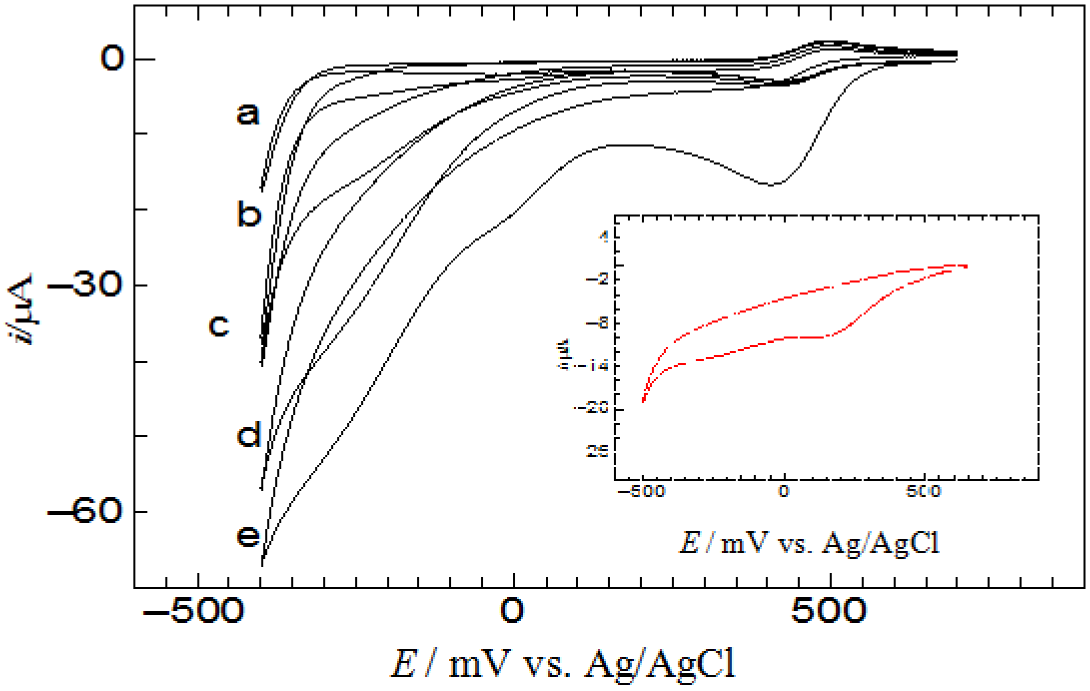


Figure 2. CVs obtained at Au electrode (1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and (b) 2.2 mM H_2O_2, (c) 4.4 mM H_2O_2, (d) 8.8 mM H_2O_2 and (e) 2.75 mM EPA + 9.65 mM H_2O_2. Inset is the CV obtained at Au electrode (1.6 mm) in N_2-saturated 0.1 M H_2SO_4 containing 2.75 mM EPA + 9.65 mM H_2O_2

In curve d which represents the CV obtained in 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and a mixture of 2.75 mM EPA + 9.65 mM H_2O_2 the reduction peak obtained at 0.5 V significantly increases. This peak is not revealed upon adding only hydrogen peroxide (curves b and c). This confirms the correspondence of this peak to the reduction of the added EPA. This increase could be explained on the basis that Fe^{3+} is electrochemically reduced to Fe^{2+} (Eq. 5) and in a following chemical step Fe^{2+} is oxidized back to Fe^{3+} by EPA (Eq. 6), i.e., EC mechanism [43, 44]. Thus the concentration of Fe^{3+} is increased and this is reflected on the increase of the reduction peak obtained at 0.5 V. In other word the reduction of EPA is mediated by Fe^{2+}/Fe^{3+} couple. The increase in the reduction peak is coupled by the decrease in the Fe^{2+} oxidation confirming the mediation of EPA by Fe^{2+}/Fe^{3+} couple. Interestingly the difference between the two reduction peaks for EPA and H_2O_2 is around 900 mV, a point that expresses the high selectivity of the present behavior as a basis for a selective simultaneous analysis of the two species in their coexistence.

$$Fe^{3+} + e = Fe^{2+} \qquad (5)$$

$$CH_3COOOH + Fe^{2+} + 2H^+ = CH_3COOH + H_2O + Fe^{3+} \qquad (6)$$

Fig. 3 shows CVs obtained at Au electrode (diameter = 1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and (b) 1.65 mM EPA + 5.97 mM H_2O_2, (c) 1.65 mM EPA + 7.79 mM H_2O_2 and (d) 1.65 mM EPA + 9.61 mM H_2O_2. Again two peaks are obtained for the reduction of EPA and H_2O_2 as explained above. Curves (b-d) is obtained in the presence of a constant concentration of EPA and different concentrations of H_2O_2.

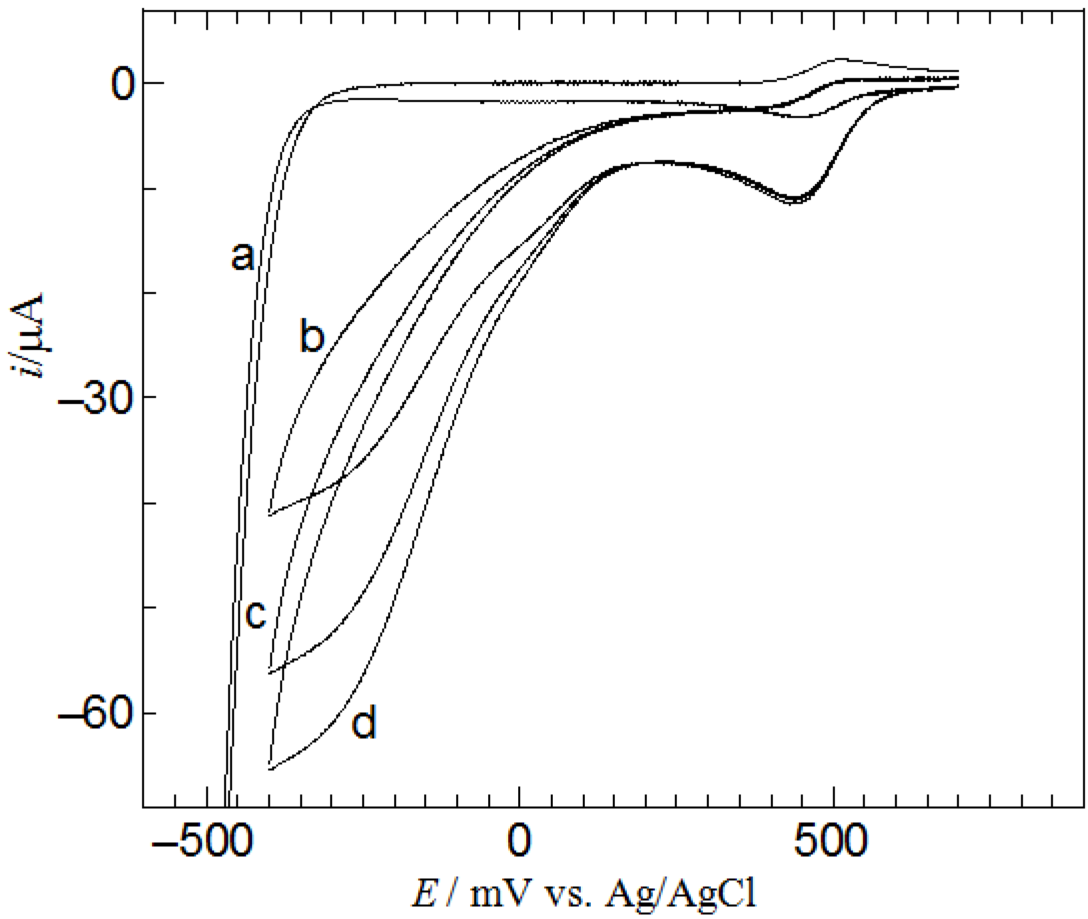


Figure 3. CVs obtained at Au electrode (1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and (b) 1.65 mM EPA + 5.97 mM H_2O_2, (c) c. 1.65 mM EPA + 7.79 mM H_2O_2 and (d) 1.65 mM EPA + 9.61 mM H_2O_2

One can see that the reduction peak at 0.45 V is constant while the reduction peak at around –0.4 V (for H_2O_2 electroreduction) increases upon increasing the concentration of H_2O_2, proving the correspondence of the former peak to EPA reduction and the latter one to H_2O_2 reduction. Again the constancy of the former peak upon increasing the concentration of H_2O_2 confirms the correspondence of this peak to EPA reduction. It also confirms the high selectivity of the present method for being used as a basis for simultaneous analysis of the two species in their coexistence. It is noteworthy to mention that the present method present high selectivity compared with that obtained at gold electrode in the absence of Fe3+ [45].

Fig. 4 shows CVs obtained at Au electrode (1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and different concentrations of EPA and H_2O_2: (b) 0.55 mM EPA + 0.17 mM H_2O_2, (c) 1.10 mM EPA + 0.34 mM H_2O_2, and (d) 1.65 mM EPA + 0.51 mM H_2O_2. Similar voltammetric curves were obtained in the presence of various concentrations of EPA and H_2O_2, and only limited curves are selected for the sake of simplicity.

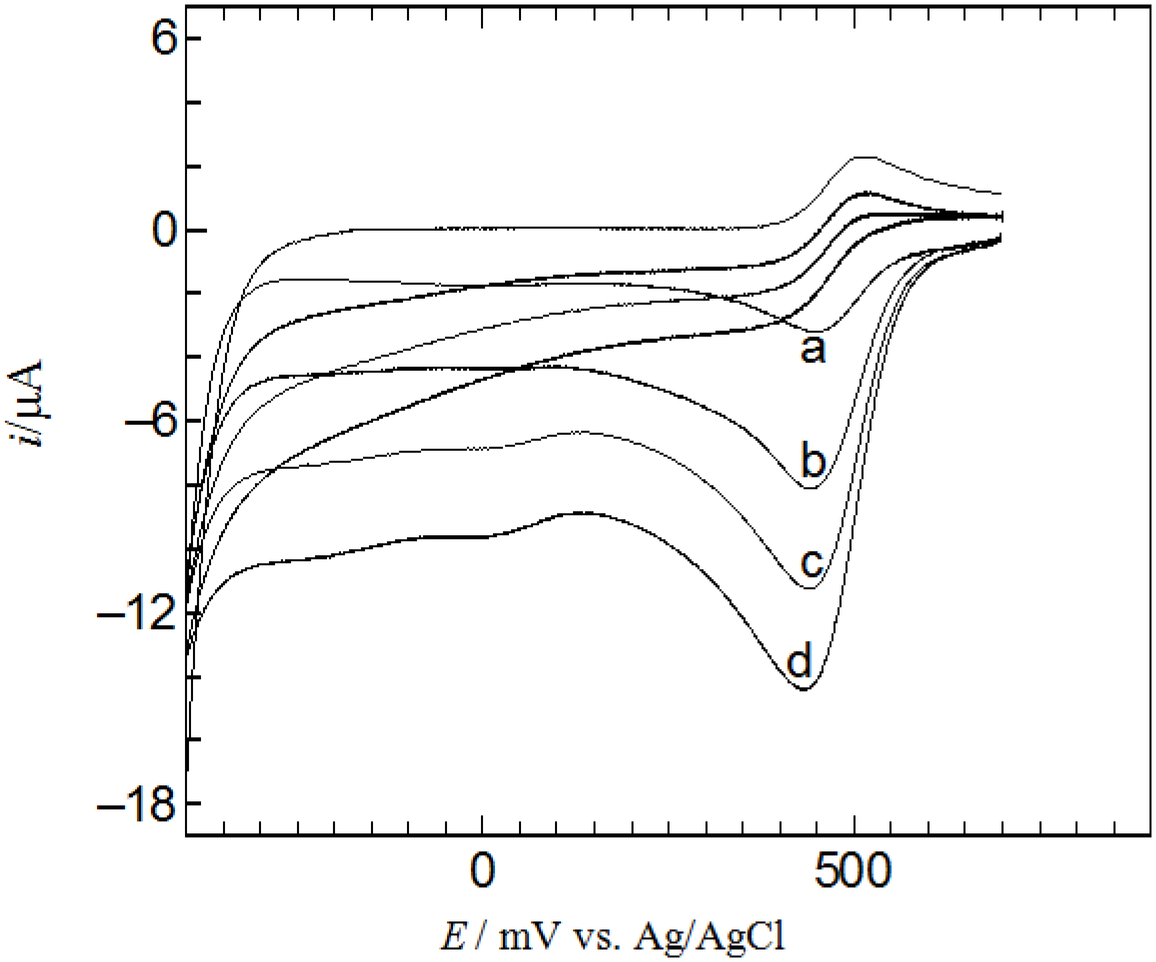


Figure 4. CVs obtained at Au electrode (1.6 mm) in (a) N_2-saturated 0.1 M H_2SO_4 containing 0.44 mM $Fe_2(SO_4)_3$ and (b) 0.55 mM EPA + 0.17 mM H_2O_2, (c) 1.10 mM EPA + 0.34 mM H_2O_2, and (d) 1.65 mM EPA + 0.51 mM H_2O_2

Inspection of this figure reveals the continuous increases of the peak of EPA reduction at around 0.45 V. From this figure the EPA current values were collected and plotted against the concentration of EPA and the data are shown in Fig. 5 in which a straight line passing through the origin with a correlation coefficient of 0.996 and a slope (sensitivity) of 6.35 μA/mM is obtained. This indicates the suitability of the present method for the analysis of EPA under the present conditions compared with the reported methods [45].

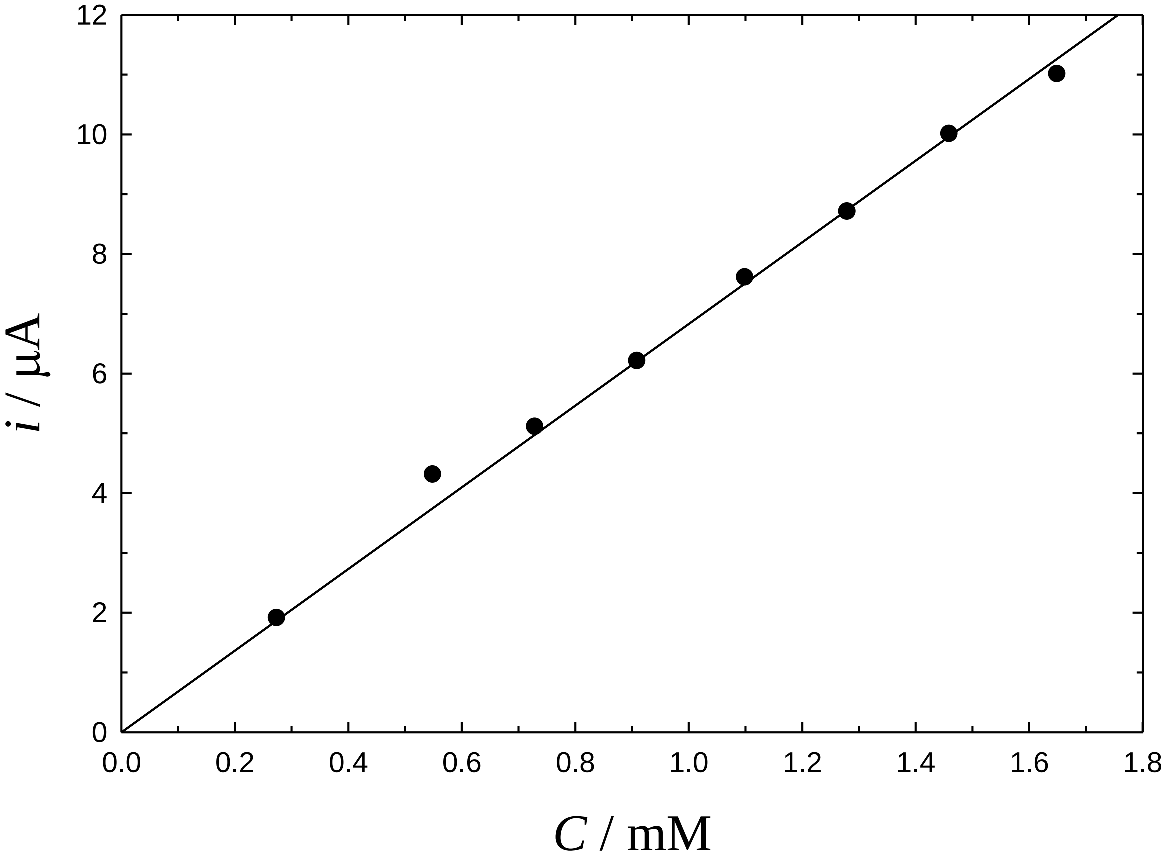


Figure 5. Calibration curve for Ethaneperoxoic acid. Data were taken from Fig. 4.

4. CONCLUSIONS

EPA electroreduction at polycrystalline gold electrode in 0.1 M H_2SO_4 is homogenously catalyzed by ferric ions. The reduction peak of EPA positively shifted by 300 mV in the presence of ferric ions. The positive shift in EPA reduction is reflected on the high selectivity of the present method for the analysis of EPA in the presence of the coexisting H_2O_2.

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