

Influence of the Adsorption on the Oxidation of Oxalic Acid on a Gold Electrode in Acid Media

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Summary. The influence of an adsorption process on the oxidation of oxalic acid on a gold electrode has been analysed. To disclose this influence, different supporting electrolytes have been used with different adsorption of the anion (SO_4^{2-} , NO_3^- and ClO_4^-). Moreover, it has been studied the modifications produced in the oxidation process by the presence of some species in solution with a strong adsorption (halides), but at low concentration levels.

Keywords. Adsorption; Gold electrode; Oxalic acid oxidation.

Der Einfluß der Adsorption auf die Oxidation von Oxalsäure an der Goldelektrode in saurem Medium

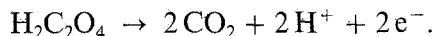
Zusammenfassung. Um den Einfluß der Adsorption auf die Oxidation von Oxalsäure an der Goldelektrode in saurem Medium zu untersuchen, wurden Support-Elektrolyten mit verschiedener Anionenadsorption verwendet (SO_4^{2-} , NO_3^- und ClO_4^-). Außerdem wurden Modifikationen des Oxidationsprozesses in der Gegenwart von stark adsorbierten Spezies, diese allerdings in geringen Konzentrationen, untersucht (Halogenide).

Introduction

The electrocatalytic activity of gold polycrystalline electrodes has been widely studied in oxidation processes of organic compounds of low molecular weight [1–3]. The mechanisms proposed for this kind of processes include in general adsorption steps of the reactant itself or that of some reaction intermediate, an adsorption that can be modified by the presence of some substances not electroactive but able to be adsorbed. This kind of species can even modify the oxidation process of the electrode surface [4].

The electro-oxidation of oxalic acid has been the object of a great number of investigations to analyze the general oxidation mechanisms of organic compounds [5, 6 and references therein]. The oxidation of this acid has been studied on different electrodes and the influence of some experimental variables, such as concentration, *pH*, potential or solvent, on the reaction mechanism has been analyzed; with these studies it has been concluded that the previous adsorption of the reactant plays an important role in the oxidation process [7, 8]. It is for this reason that the oxalic acid is very suitable to study how an oxidation process can be modified by the adsorption of other species in solution.

The oxalic acid is oxidized on a polycrystalline gold electrode in acid medium ($0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) at potentials previous to the oxides formation through a two electrons irreversible process, CO_2 being the oxidation product:



The process is diffusion controlled with a Tafel slope of 60 mV/decade . In the voltammetric curve an anodic current is observed in the negative scan as a consequence of inhibition caused by the surface oxidation of the electrode.

The aim of this work is to study the influence of the adsorption of the species present in solution on the oxidation process, the influence of both, species with weak adsorption but present at high concentrations (supporting electrolyte) and that of substances with high adsorption but at low concentrations, even at contamination levels (halides).

Experimental

The voltammograms were recorded with a Belpot 105 potentiostat with iR compensation, together with an X-Y Philips PM 8133 recorder and a Belpot 305 signal generator.

The stationary working electrode was a polycrystalline gold sphere (99.998%), obtained by melting a wire of 1 mm of diameter. The counter electrode was a gold spiral of the same quality. All measurements were referred to an MSE. The temperature was kept constant at $18 \pm 0.2^\circ\text{C}$.

Oxalic acid used in the solutions was from Baker p.a. quality and sulphuric, nitric and perchloric acids from Merck suprapur. In all cases the oxalic acid concentration was $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ and that of the acids 0.5 mol dm^{-3} . Solutions containing Cl^- , Br^- and I^- were prepared from their corresponding sodium salts from Merck suprapur. The water was purified using a Millipore-Milli Q system and its purity was controlled by means of the voltammetric curve of a gold electrode in H_2SO_4 solutions 0.5 mol dm^{-3} . All solutions were carefully deoxygenated and were maintained in a nitrogen overpressure during the measurements.

Typical voltammograms were recorded from -0.3 to 1.0 V using in general a potential sweep of 50 mV s^{-1} , obtaining a good reproducibility when the curve was recorded after holding the potential at -0.3 V during 15 s .

Results and Discussion

Influence of the Supporting Electrolyte

The voltammogram obtained for the oxidation of oxalic acid in HClO_4 and HNO_3 media is similar to that recorded in H_2SO_4 medium, although it presents some modifications (Fig. 1). Thus, the oxidation process is more favoured in these media than in H_2SO_4 , starting at more positive potentials: E_p (in H_2SO_4) = 435 mV , E_p (in HNO_3) = 394 mV , E_p (in HClO_4) = 379 mV . Moreover, the current density of the oxidation peak is higher than that observed in H_2SO_4 medium.

On the other hand, the $i-t$ curves obtained at different potentials using a RDE show the inhibition processes also observed in H_2SO_4 medium, self inhibition and inhibition due to oxides, although this second type of inhibition becomes apparent at more positive potentials than in H_2SO_4 . Moreover, in both cases, HClO_4 and HNO_3 , the current density observed in the voltammograms is always positive. In the cathodic scan two oxidation peaks are observed as a consequence of the reduction process of the surface oxides and that of the oxalic acid accumulated near the electrode.

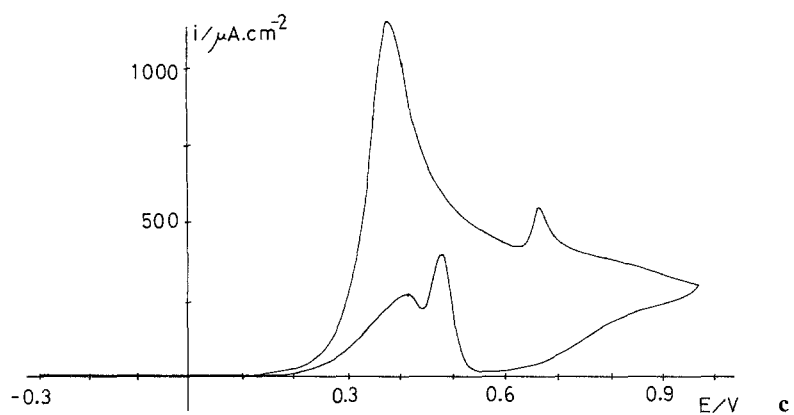
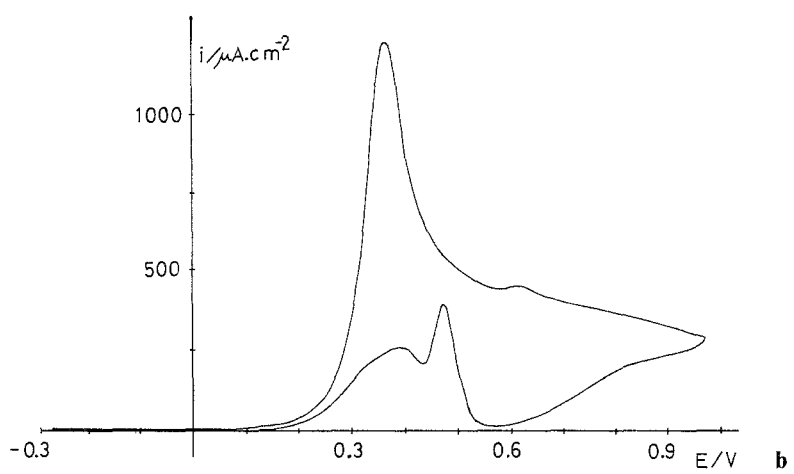
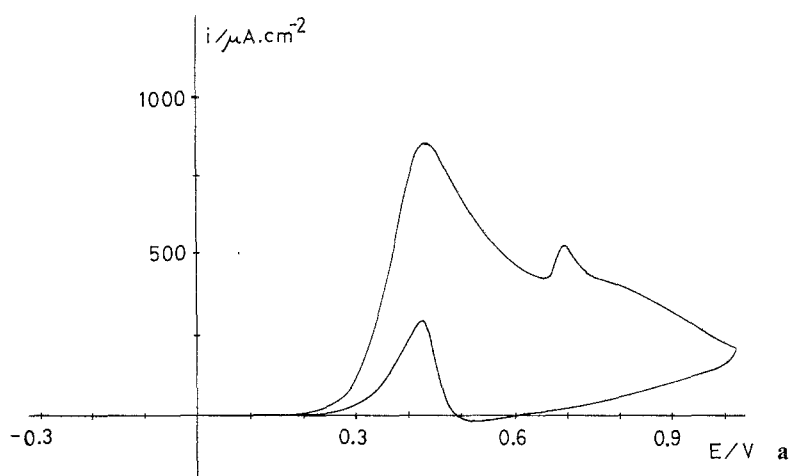


Fig. 1 a-c. Voltammograms corresponding to the oxidation of oxalic acid in a solution $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ and 0.5 mol dm^{-3} of: (a) H_2SO_4 , (b) HClO_4 , (c) HNO_3 ; $\nu = 50 \text{ mV s}^{-1}$

The Tafel slopes calculated in both cases are of 60 mV/decade, coincident with the value obtained in H_2SO_4 medium. When all the results obtained for this oxidation process in the three different media are compared it can be seen that, although the general behaviour is similar, the peak intensities are not; they follow the relation:

$$i_p (\text{in HClO}_4) > i_p (\text{in HNO}_3) > i_p (\text{in H}_2\text{SO}_4).$$

With this result and the E_p values mentioned before it can be concluded that the process is favoured with decreasing anion adsorption on the gold electrode ($\text{ClO}_4^- < \text{NO}_3^- < \text{SO}_4^{2-}$). This fact is in agreement with the proposal of an adsorption step of the oxalic acid previous to the oxidation process [5, 6].

Influence of the Chloride Adsorption on the Oxidation Process

In view of the influence of the adsorption of the supporting electrolyte on the oxidation process, it would be interesting to study this process when the solution also contains a species with a strong adsorption and moreover, to analyze if that modification introduced is different depending on the media. To carry out this study the species selected is the chloride anion at concentrations lower than those where its reaction with the gold electrode can be detected; this reaction is described in the literature in H_2SO_4 medium ($[\text{Cl}^-] < 4 \cdot 10^{-5} \text{ mol dm}^{-3}$) [9–12]. Thus, a previous study of the gold electrode in HClO_4 and HNO_3 in presence of Cl^- ions has been made, and from a given concentration value the reaction has found to be parallel to that described in H_2SO_4 medium (Fig. 2).

The presence of Cl^- in the solution is shown clearly from $3 \cdot 10^{-6} \text{ mol dm}^{-3}$ on, and in general, little amounts of Cl^- shift the acid oxalic oxidation to more positive potentials while the shape and peak intensity are maintained. By increasing the chloride concentration the deformation of the voltammogram is more evident, in such a way that from $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ the decrease of i_p is pronounced and the oxidation process mainly takes place on the oxidized electrode surface (Fig. 3).

The presence of Cl^- in the solution promotes a great dependence of the voltammetric response on the experimental conditions (concentration, initial potential, holding time at these potentials). Thus, if the scan starts at negative potentials (greater than -0.3 V) the current density is increased with the holding time (Fig. 4), while if the scan begins at positive potentials the shape of the voltammogram does not depend on this holding time but the peak intensity is appreciably lower than the original. This response is in agreement with a higher adsorption of chloride ions at positive potentials, a process that is fast at these potential values.

On the other hand, although the peak intensity does not vary up to concentrations at which the voltammogram is clearly modified, the current density at the foot of the peak decreases gradually with the Cl^- concentration, in such a way that the Tafel slope increases (Table 1).

After this description of the general behaviour of the process, the influence of Cl^- ions can be analyzed in detail for the different media considered. The i_p , E_p (Fig. 5) and Tafel slope values corresponding to the oxidation of oxalic acid vary

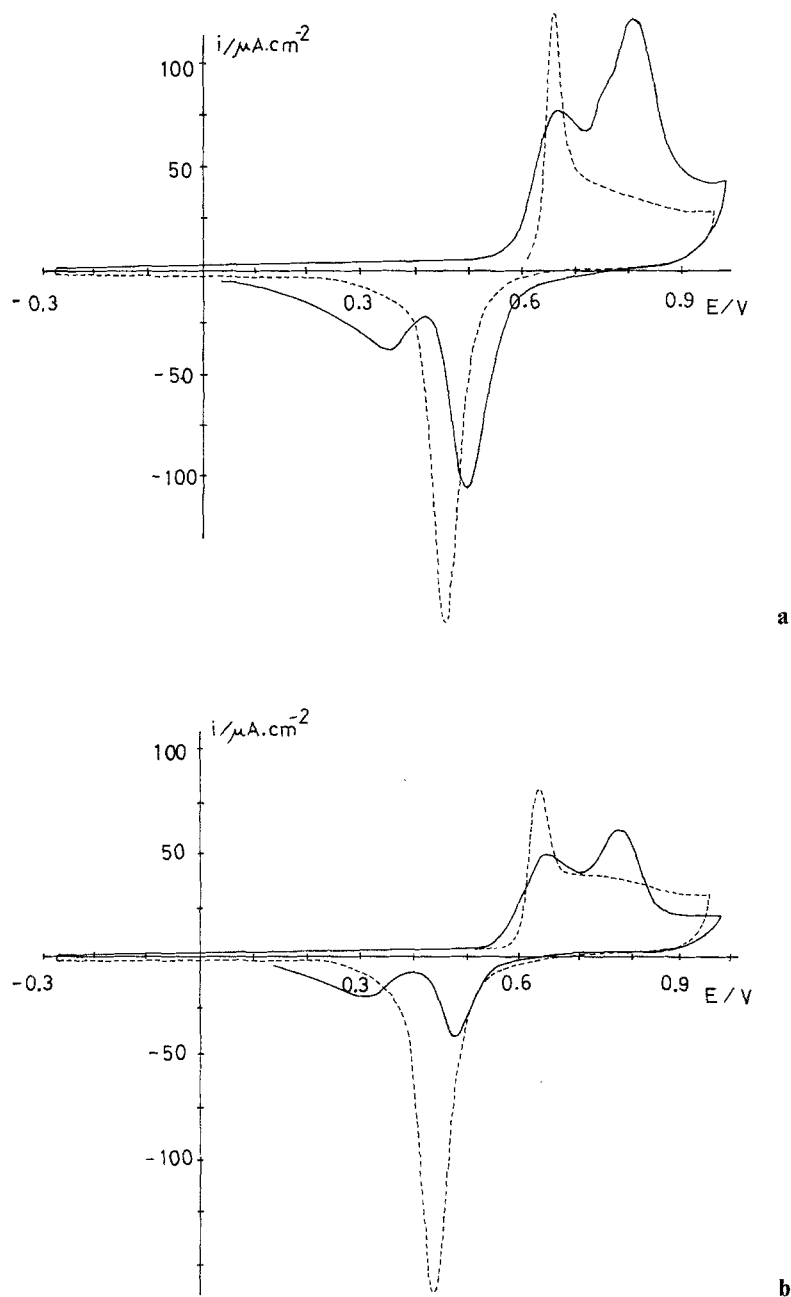


Fig. 2 a, b. Voltammogram of a gold electrode in presence of $10^{-4} \text{ mol dm}^{-3} \text{ NaCl}$ in 0.5 mol dm^{-3} of: (a) HNO_3 , (b) HClO_4 ; $\nu = 50 \text{ mV s}^{-1}$

practically in the same way by adding Cl^- ions: the peak potential is shifted to more positive values, the peak intensity decreases and the Tafel slope increases, but the relation is the same observed without chloride ions:

$$i_p(\text{H}_2\text{SO}_4) < i_p(\text{HNO}_3) < i_p(\text{HClO}_4),$$

$$E_p(\text{HClO}_4) < E_p(\text{HNO}_3) < E_p(\text{H}_2\text{SO}_4).$$

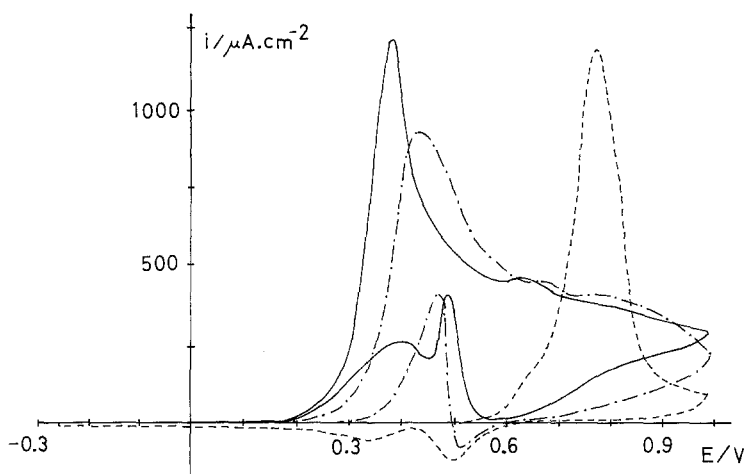


Fig. 3. Voltammogram corresponding to the oxidation of oxalic acid $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ in HClO_4 0.5 mol dm^{-3} with different NaCl concentrations: (—) 0, (---) $3.0 \cdot 10^{-5}$ and (-·-) $6.9 \cdot 10^{-4} \text{ mol dm}^{-3}$, $v = 50 \text{ mV s}^{-1}$

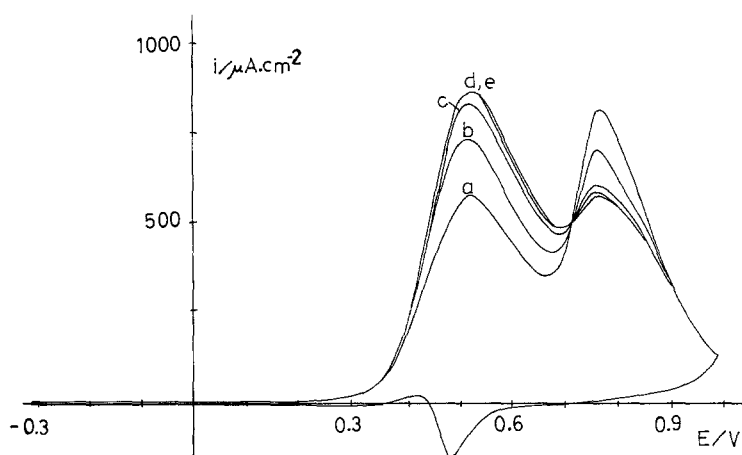


Fig. 4. Cyclic voltammetry of oxalic acid $4 \cdot 10^{-3} \text{ mol dm}^{-3}$, NaCl $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ and H_2SO_4 0.5 mol dm^{-3} showing the effect of different potential holds at -0.3 : (a) 0, (b) 5, (c) 10, (d) 45, and (e) 90 s; $v = 50 \text{ mV s}^{-1}$

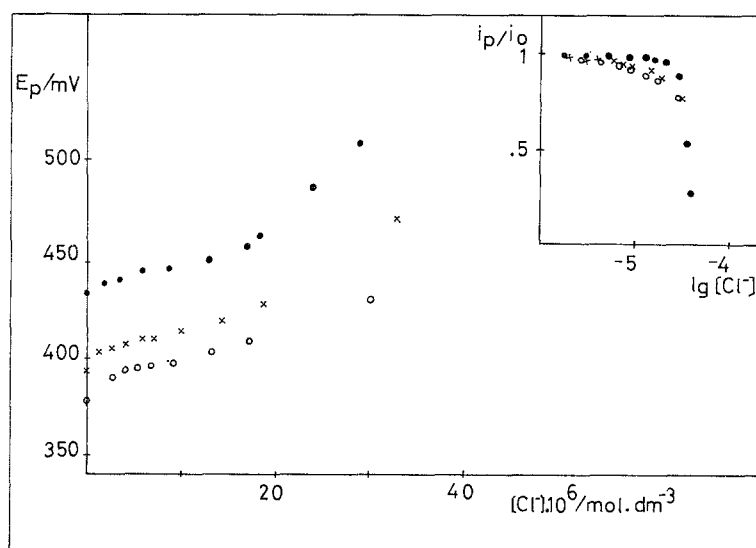
This fact can be again justified by the different adsorption of the ions ClO_4^- , NO_3^- and SO_4^{2-} on the gold electrode ($\text{ClO}_4^- < \text{NO}_3^- < \text{SO}_4^{2-}$). However, the shape of the voltammograms is more sensitive to the chloride ions in H_2SO_4 medium than in HNO_3 or HClO_4 , in such a way that in the latter media the original shape of the voltammograms is maintained up to higher chloride concentrations.

Influence of the Br^- and I^- Ions on the Oxidation of Oxalic Acid in H_2SO_4 Medium

Since chloride, bromide, and iodide ions have a strong specific adsorption on the gold electrode they will modify any electrode process. To establish how the different adsorption of these ions affects the oxidation of the oxalic acid, the experimental

Table 1. Tafel slopes for the oxidation of oxalic acid in H_2SO_4 , HNO_3 and HClO_4 in presence of chloride ions

H_2SO_4		HNO_3		HClO_4	
$[\text{Cl}^-]$	Tafel slope	$[\text{Cl}^-]$	Tafel slope	$[\text{Cl}^-]$	Tafel slope
0	60	0	60	0	60
$1.08 \cdot 10^{-6}$	62	$1.46 \cdot 10^{-6}$	62	$2.68 \cdot 10^{-6}$	63
$4.32 \cdot 10^{-6}$	66	$2.92 \cdot 10^{-6}$	64	$5.35 \cdot 10^{-6}$	67
$1.08 \cdot 10^{-5}$	73	$4.38 \cdot 10^{-6}$	67	$9.32 \cdot 10^{-6}$	76
$2.16 \cdot 10^{-5}$	81	$7.27 \cdot 10^{-6}$	73	$1.33 \cdot 10^{-5}$	82
$4.32 \cdot 10^{-5}$	93	$1.02 \cdot 10^{-5}$	77	$1.72 \cdot 10^{-5}$	87
		$1.14 \cdot 10^{-5}$	88		

**Fig. 5.** Variation of the peak magnitudes (E_p , i_p/i_0) with the chloride concentrations for the oxalic acid oxidation in 0.5 mol dm^{-3} : (●) H_2SO_4 , (×) HNO_3 , and (○) HClO_4 . i_0 : peak intensity in absence of Cl^-

results have been quantified in H_2SO_4 (because of its general use in this kind of experiments).

The presence of Br^- and I^- can be detected in the voltammogram of the oxalic acid oxidation even at very low concentrations: $7 \cdot 10^{-7} \text{ mol dm}^{-3}$ for Br^- and $5 \cdot 10^{-7} \text{ mol dm}^{-3}$ for I^- . In general, the behaviour obtained with both halides is the same observed in the case of Cl^- : a decrease in the current density of the oxidation peak and a shift of the process to more positive potentials until concentration values at which the oxidation process only takes place on the oxidized electrode surface (Fig. 6).

To analyze the influence of the different halides, the value of the peak magnitudes (E_p , i_p) and Tafel slopes have been compared (Fig. 7, Table 2). From

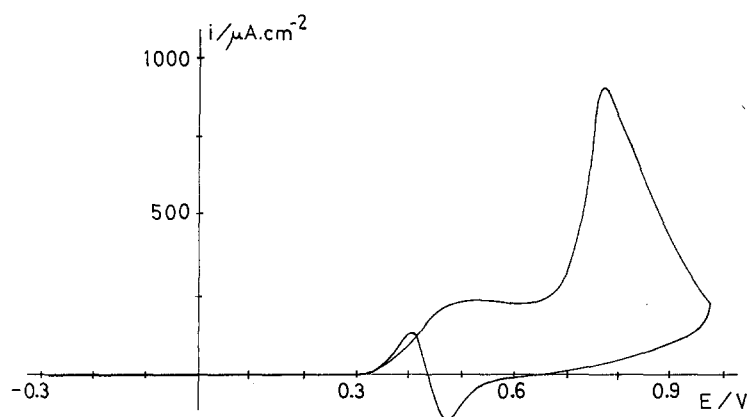


Fig. 6. Cyclic voltammogram of oxalic acid $4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $1.16 \cdot 10^{-5} \text{ mol dm}^{-3}$ NaBr and $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; $v = 50 \text{ mV s}^{-1}$

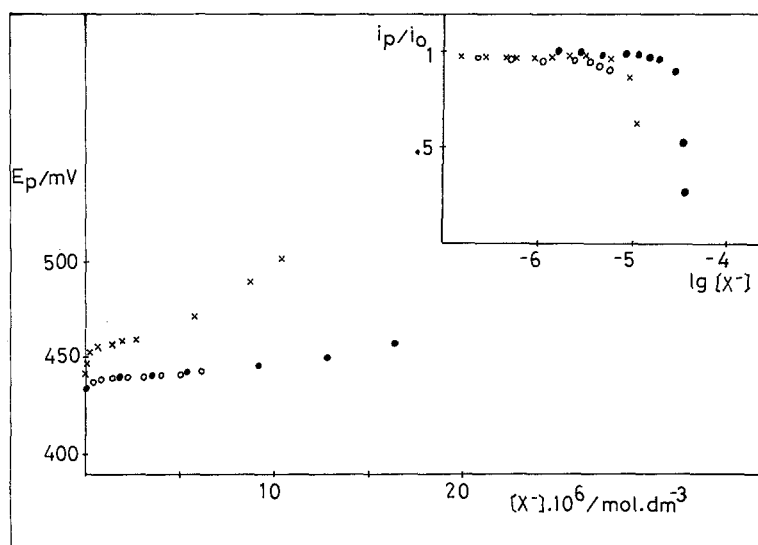


Fig. 7. Variation of the peak magnitudes for the oxalic acid oxidation in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ with different halide concentrations: (●) $\text{X}^- = \text{Cl}^-$, (×) $\text{X}^- = \text{Br}^-$, and (○) $\text{X}^- = \text{I}^-$

Table 2. Tafel slopes for the oxidation of oxalic acid in H_2SO_4 in presence of halide ions

$[\text{Cl}^-]$	Tafel slope	$[\text{Br}^-]$	Tafel slope	$[\text{I}^-]$	Tafel slope
0	60	0	60	0	60
$1.08 \cdot 10^{-6}$	62	$1.60 \cdot 10^{-7}$	60.5	$2.47 \cdot 10^{-7}$	61
$4.32 \cdot 10^{-6}$	66	$4.81 \cdot 10^{-7}$	65	$5.35 \cdot 10^{-7}$	63
$1.08 \cdot 10^{-5}$	73	$6.40 \cdot 10^{-7}$	68	$9.10 \cdot 10^{-7}$	63
$2.16 \cdot 10^{-5}$	81	$7.99 \cdot 10^{-7}$	72	$1.35 \cdot 10^{-6}$	65
$4.32 \cdot 10^{-5}$	93	$1.12 \cdot 10^{-6}$	78	$2.20 \cdot 10^{-6}$	70
		$1.59 \cdot 10^{-6}$	84	$3.19 \cdot 10^{-6}$	77
				$4.19 \cdot 10^{-6}$	83

these data it can be concluded that the oxidation process of the oxalic acid is more inhibited by bromides and iodides than by chlorides. By comparing bromides and iodides, it can be seen that, at the same concentration value, the change in the Tafel slope is more important when Br^- is used. Concerning the peak potential, it is shifted to more positive potentials as the bromide concentration increases, while it is practically unaffected in the case of iodide. Thus, it seems that the oxidation of oxalic acid is less affected by the presence of iodides than by bromides. When the scan rates are lower than the usual (or making potential holds of different length at positive potentials), the voltammogram recorded in presence of iodides is also strongly modified which may suggest that the rate of adsorption is in this case relatively slow. However, at these low scan rates the influence of the bromide ion on the oxidation process is again more pronounced.

Conclusions

With the experimental results obtained in this study it can be concluded that a previous adsorption process modifies the oxidation of oxalic acid on a gold electrode in acid media. Concerning the influence of the supporting electrolyte, the modifications observed are the expected, taking into account the different adsorption of the ions involved in the process. In the halides case, it has been observed that bromides and iodides interfere the oxidation process more than chlorides, in agreement with their different adsorption in the gold electrode. However, when iodides and bromides are compared the results are surprising. It is known that I^- ions have a stronger adsorption than Br^- on a gold electrode, but the oxidation process of oxalic acid is more inhibited by bromides than by iodides, even at low scan rates. Thus, at these experimental conditions, the influence of halides in the oxidation process is rather unusual and it seems that the adsorption of the halide ions is also modified by the presence of oxalic acid adsorbed on the electrode surface.

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