AUTOINHIBITION EFFECTS OF THE $Sn(OH)_4$ FILM ON DROPPING MERCURY ELECTRODE

Maria Valnice BOLDRIN ZANONI*
Nelson Ramos STRADIOTTO**

■ ABSTRACT: The polarographic behaviour of Sn(II)/3 mol.dm^{-3} $NaClO_4$ oxidation offers a classic case of autoinhibition process. The adverse effects such as maxima, erratic drop behaviour and nonlinear calibrated curves are associated with the presence of $Sn(OH)_4$ film on the dropping mercury electrode. Some procedures have shown that analytically undesirable behaviour due to such phenomena may be simply eliminated by using short controlled drop times ($0,5 < tg < 2,0s$); appropriate range of pH ($0,5 < pH < 2,0$) and small concentrations of Sn(II) (8.10^{-5} to 8.10^{-4} mol.dm^{-3}). Also, it is discussed the influence of surface active materials.

■ KEYWORDS: Tin(II); autoinhibition phenomena; polarographic oxidation.

Introduction

A common phenomenon which can prevent obtaining useful concentration dependent response in electroanalysis is observed when the products of an electrode reaction are adsorbed on the electrode.

This case is noticed for tin determination in aqueous solution when certain complexing agents are not present in the supporting electrolyte.[1, 2] The polarographic behaviour of tin(II) oxidation has been investigate previously in perchlorate medium[3] and it offters a classic case of adsorption of the product of charge transfer.[4, 5] This system give only a two electron anodic wave, which $Sn(OH)_4$ formed is responsible for an inhibiting film at the surface of the dropping mercury electrode. Such inhibition phenomenon affects electrode response adversely in several ways and waves of these types may be grossly distorted preventing meaningful current measurements.

* Departamento de Química Analítica – Instituto de Química – UNESP – Araraquara – SP.
** Departamento de Química – Faculdade de Filosofia, Ciências e Letras – USP – 14049 – Ribeirão Preto – SP.

So, it is the aim of the present paper to investigate some factors controlling the extent and the rate of film formation of $Sn(OH)_4$ on the mercury electrode with a view to minimize or eliminate these effects.

Experimental

$Sn(ClO_4)_2.3H_2O$ was prepared from tin oxide by the literature procedure[6] and its concentration in solution was determined by back-titration with EDTA.[7] The $NaClO_4$ was used as supporting electrolyte. The mercury used as working electrode was purified as usual method.[8]

Polarograms were recorded with Polarecord E506 (Metrohm) with mechanically controlled dropping mercury electrode (EA 1022) and an apparatus Electroscan TM 30 (Beckman) with natural drop time upper 3s and m= 1.70 $mg^{2/3}.s^{-1/2}$. All measurements were taken on freshly prepared solutions of $Sn(ClO_4)_2$ containing 3M $NaClO_4$ previously dearated.[2] Two Ag/AgCl electrodes in 3M NaCl (model EA 852) were used as auxiliary and reference electrodes. The polarographic measurements were done on a cell model EA 875/20 (Metrohm). The pH measurements were done with a glass electrode (EA 121) connected to a pHmeter (E 500 Methohm).

Results and discussion

Under the usual conditions employed for polarographic measurements, only one anodic wave was observed for tin(II) oxidation, with the features of an adsorption wave,[4,5] (Figure 1). In fact, at pH = 3.0, concentrations lower than 6.10^{-4} mol dm^{-3} and natural drop of the dropping mercury electrode (DME), the polarograms are markedly affected by broad maximum on the limit plateau and erratic drop behaviour. If we take in account the previous results, this behaviour can be attributed to the presence of a film of reaction product on the electrode surface, according to:

$$Sn^{+2} + 4\,H_2O \rightleftarrows Sn(OH)_4 + 4H^+ + 2e- \qquad (1)$$

Essentially, the film is due to the adsorption of insoluble species $Sn(OH)_4/SnO_2.xH_2O$, which disturb the electrochemical reaction by inhibition effect. Accordingly, the extend of inhibition of a given electrode reaction during the life of a drop is related to the extend of coverage of the electrode surface through film formation. The kinetics of film formation on a mercury drop have been derived,[9] which assumes that the time required to cover the surface is inversely proportional to the concentration of the surface active species and rate of growth of the mercury drop surface. Moreover, another parameter can disturb the coverage of the electrode surface: the pH changes, when it can modifies the structure of the film or the addition of surfactants, which can disturb the adsorption equilibrium, by competitive effect.

A typical polarographic response involving the presence of surface-active substances is shown in the Figure 1y, when 0.03% gelatin is enough to reduce the adsorption effects. However, the irreversible characteristics of the wave shows that this procedure is ineffective to prevent total formation of the insoluble film at pH = 3.00. However, increasing the addition of gelatin, or utilizing triton x-100 the wave shows the same shape, although it causes depressions on the polarograms. Besides, it cause severe changes in the conditions present at the electrode-solution interface,[10] such as displacement of adsorbed ions and solvent molecules, changes in the dielectric constant and a different geometrical positioning of the reducible species at the electrode surface, and consequently a film of surface-active agents must be avoided always it is possible.

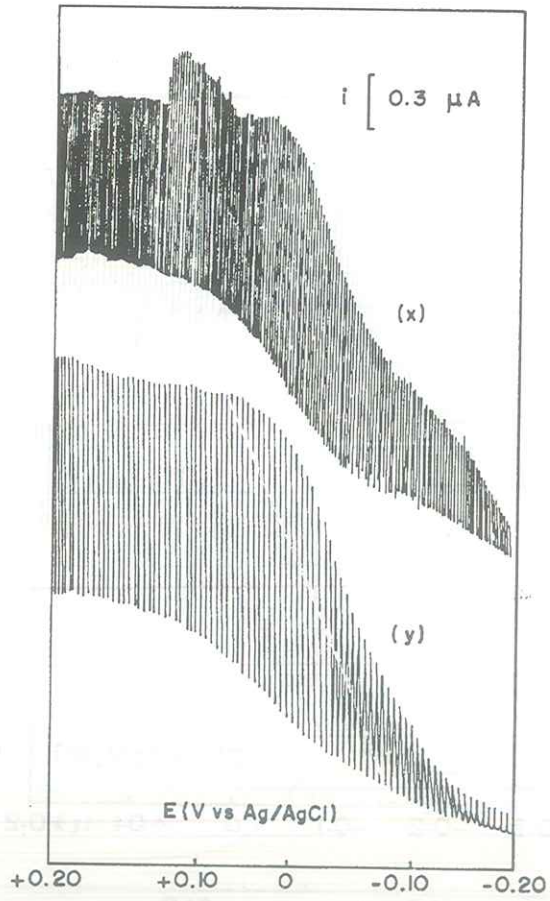

FIGURE 1 – Influence of addition of surfactants in polarograms of $6x10^{-4}$ mol.dm^{-3} Sn(II)/3 M $NaClO_4$ at pH = 3.00: (x) without gelatin (y) with 0.03% gelatin.

The influence of the pH in the polarographic parameters of tin(II) oxidation can be seen in the Figure 2. A comparison of the curves recorded at natural drop time and 6.10^{-4} mol.dm^{-3} tin(II) concentration showed that the shape of the polarogram is markedly improved as the pH decreased. Moreover, the electrodic process showed great variations of polarographic reversibility and pronounced shif of the $E_{1/2}$ towards anodic potential.[3] Several studies[11] about chemistry of tin(IV) have shown the occurrence of the $Sn(OH)_3^+$ and $Sn(OH)_4$ hidroxo-complexes formation at the range < 0 pH < 2.0 at concentration lower than 10^{-3} mol.dm^{-3}. However, $Sn(OH)_3$ species could be competitive on the system at pH values lower than 1.0. So, this behaviour could be indicative that increasing the proton concentration there is a reduction of the $Sn(OH)_4$ species, which autoinhibition property is responsible by irregularities observed on the polarogram. Nevertheless, the anodic waves correspondent to tin(II) in this region of pH is not too-well defined because the oxidation process occurs at very positive potentials where the wave is obscured by the wave due to the mercury oxidation/supporting electrolyte.

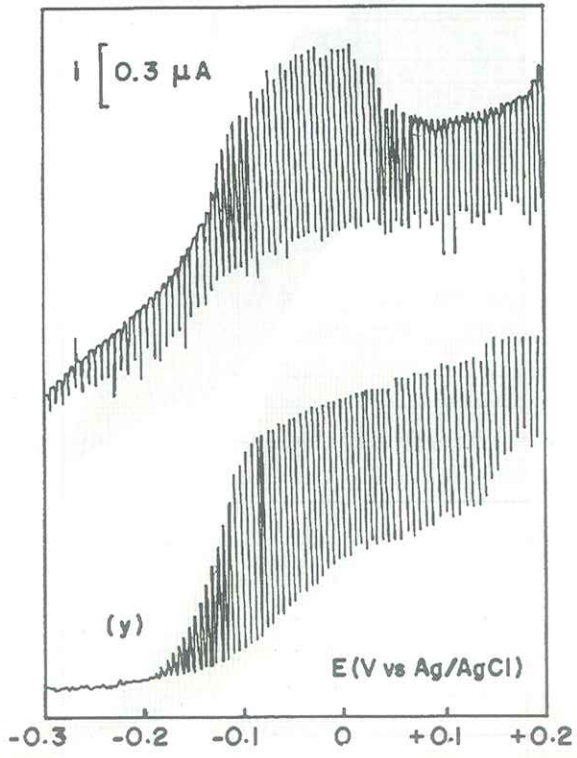

FIGURE 2 – Influence of pH in polarograms of 6.10^{-4} mol.dm^{-3} Sn(II)/3M $NaClO_4$: (x) = pH = 2.00 (y) = pH = 1.00.

A comparison of conventional and rapid polarograms of $6.0.10^{-4}$ mol.dm^{-3} Sn(II)/3M $NaClO_4$ at pH = 1.50 is shown in the Figure 3, which illustrate the advantage of short drop times for this system. The erratic behaviour verified at natural drop time is completely attenuated at drop times less than 2s. Hence, these conditions have been showed enough to overcome the most of the problems arising from films formation on the DME in the investigated system, without resorting to the use of gelatin or higher concentration of acids. This behaviour may be explained qualitatively in the following way: from the instant of the formation of a new drop the specie diffuses to the drop surface and the product of the charge transfer adsorbs on it. So, how higher the concentration of surface active material, the shorter is the time required to cover the drop. However, for small concentrations how higher drop time more material can be adsorbed on the expanding drop surface and can produce a considerable disturb of the electrode reaction. In other words, the rate of covering increase compared to the rate of growth of the mercury drop surface and consequently intensify the adsorption effects on the resulting wave. However, it was established that shortest drop time (t < 0.4s) have demonstrated to result in slight decrease in the current

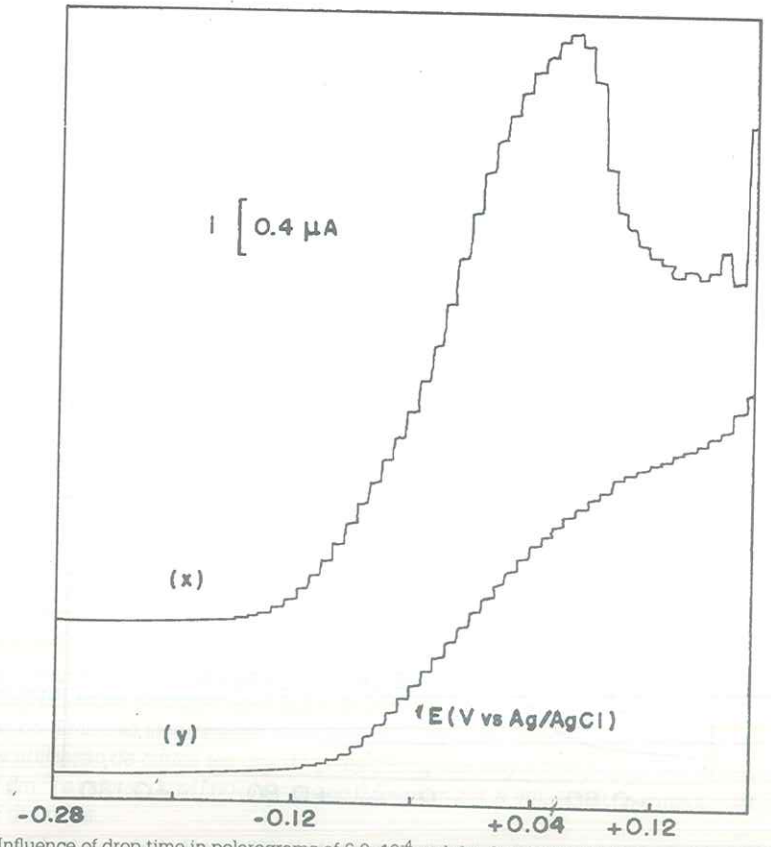

FIGURE 3 – Influence of drop time in polarograms of $6.0x10^{-4}$ mol.dm-3 Sn(II)/3M $NaClO_4$ at pH = 1.50: (x) = drop time 3s (y) drop time 0.4s

limit of the polarograms, and therefore it must be avoided because of sensitivity problems.

The last autoinhibition effect on the dropping mercury electrode was seen for sufficiently high concentrations of tin(II). Although, the improved polarographic behaviour of tin(II) under DC_T conditions has been attributed to the decreasing of the extent of surface coverage at rapid dropping time, the wave recorded for the system, at tin(II) concentration upper than $6.0x10^{-4}$ mol.dm^{-3} and pH = 1.50, presents anodic limiting current poorly defined and fluctuations of the current in all length. In addition, at concentration upper than 2.10^{-3} mol.dm^{-3} two waves were observed, whose total limiting current is slightly constant with tin(II) concentration up to this level, Figure 4. The analysis of the wave shape permited us to note that the irregular behaviour occurs always in the region up to -40 mV towards anodic potentials. These results can be interpreted as the formation of a consistent "adsorption" layer when the concentration is larger than the saturation value, which would be sufficient to cover completely the surface with a compact film. Regular build up and break down of this film would be responsible for the resulting periodic fluctuations in the current of this wave. Although the waves at pH = 0.50 seems to rise at very positive potentials, the

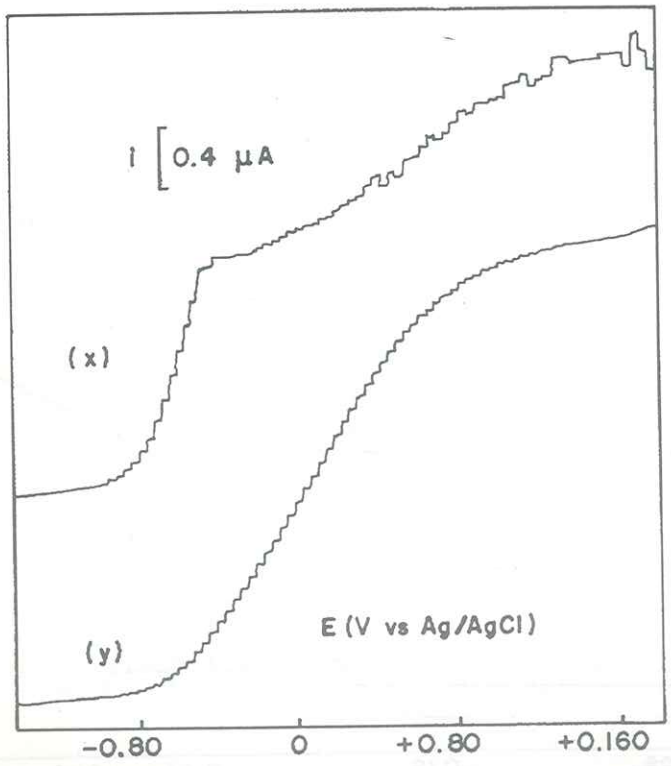

FIGURE 4 – Influence of concentration in polarograms of Sn(II)/3M $NaClO_4$ at pH= 1.50, tg = 1s: (x) = [SnII] = 8.10^{-3} mol.dm^{-3} (y) = SnII = $6x10^{-4}$ mol.dm^{-3}.

polarograms recorded at the same above conditions did not showed splitting of the wave or other anomalies, what is indicative that in this range of pH there is a lower contribution of the autoinhibition process.

Conclusion

Based on the experimental evidence of the electrode process discussed above, it is possible to suggest some procedures to eliminate the influence of the autoinhibition of the $Sn(OH)_4$ film in the tin(II) oxidation on the mercury dropping electrode.

Concerning the ideal range of pH, it can be established that the wave became better defined in the range 0.5 < pH < 2.0. For the Sn(II)/Sn(IV) system inhibited by adsorption on the surface of DME the improved polarographic behaviour can be obtained under rapid conditions 0.5s < tg < 2.0s. In addition, it is possible to suggest the concentration range of 8.10^{-5} to 8.10^{-4} mol.dm^{-3} as the optimum conditions for the system. By the way, the presence of surfactants can improve the shape of the wave, too. Hence, the polarograms under these circunstances can be analyzed precisely and became useful for electroanalytical purpose.

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BOLDRIN ZANONI , M. V. et al. Efeitos da auto-inibição do filme de $Sn(OH)_4$ sobre eletrodo gotejador de Mercúrio. *Ecl. Quím.*, São Paulo, p. 105-112, v. 17, 1992.

■ *RESUMO: O comportamento polarográfico da oxidação do sistema Sn(II)/3 M $NaClO_4$ tem mostrado características típicas de um processo de auto-inibição eletródica. A presença de máximos polarográficos, tempo de gotejamento irregular e curvas de calibração não-lineares têm sido atribuídas à presença do filme $Sn(OH)_4$ sobre o eletrodo gotejador de mercúrio. Alguns fatores que controlam a extensão e velocidade do filme são investigados visando minimizar estes efeitos analiticamente indesejáveis. É proposta a utilização de curtos tempos de gotejamento (0,5 < tg < 2,0); baixas concentrações (8.10^{-5} – 8.10^{-4} mol.dm^{-3}) e valores de pH no intervalo de 0,5 < pH < 2,0. A influência de surfactantes no processo também é discutida.*

■ *UNITERMOS: Estanho (II); fenômenos de auto-inibição; oxidação polarográfica.*

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