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Corrosion behaviour of Tin in citric acid solutions and effect of some inorganic and organic compounds

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ABSTRACT

The electrochemical Behaviour and corrosion of tin in various concentrations of citric acid solutions (0.1 to 1.0M) has been studied by using cyclic voltametric technique under different experimental conditions. The potentiodynamic anodic polarization curves exhibit active/passive transition. The active dissolution of tin involves one anodic peak. During the active region, tin dissolves as Sn(II), which is oxidized to Sn(IV) to yield either Sn(OH)₄ or SnO₂ on the anode surface. The active dissolution of tin enhances with increasing acid concentration, temperature and scan rate. The cathodic curve exhibits one cathodic peak corresponding to the reduction of passive layer. Addition of Cl⁻, Br⁻ or I⁻ ions to the citric acid solution enhances the anodic dissolution of tin. The aggressiveness of the halide ions towards the stability of the passive film decreases in the order Cl⁻>Br⁻>I⁻. Addition of some polyethylene glycols to citric acid solution decreases the current density of the anodic peak and shifts its peak potential towards the negative direction. These changes depend on the concentration and molecular weight of the polyethylene glycol added.

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KEYWORDS

Corrosion;
Tin;
Citric acid;
Halide ions;
Polyethylene glycol.

INTRODUCTION

Tin, an amphoteric metal, reacts in both acid and alkaline but is relatively resistant to neutral media. Used as an electrodeposited coating on steel, copper or nickel, it presents very large surface arrears to corrosive environments. Potential pH diagrams^[1,2] shows it favourably corrodes in acid and alkaline, the behaviour of tin changes from passivity to corrosion at pH 5-4, which is in the acid rain range.

High purity tin dissolves only slightly in acids free from air or other oxidizing agents due to the high over

potential of hydrogen and thus, corrosion is controlled by the oxygen supply rate. However, in large concentration oxidants may practically stop corrosion and bring about passivation. Corrosion increases if tin is in contact with a metal with a low hydrogen over potential and accelerates if small quantities of metallic impurities, such as those commercial grades tin are present^[3,4].

Literature shows that electrochemical behaviour and corrosion of tin in the presence of carboxylic acid and the so-called fruit acid has been the subject of considerable interest^[5-16].

Uniform corrosion of tin is observed in pure citric

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acid revealing a surface that shows anisotropic reflection of polarized light.

There is a general agreement in the literature that high corrosion resistance of tin in citric acid solution is due to the presence of a thin stable passive film that forms on the metal surface. Several authors report that the corrosion accelerate when the surface is exposed to aqueous solution containing aggressive anions such as halides^[17-19].

Only very little work is available on the influence of polyethylene glycol as additive polymers on the electrochemical behaviour of tin in carboxylic acid media. These compounds (PEG) are water soluble, waxy solid that are used extensively in the cosmetic and toiletry in industry. Yet are also found in many personal care products^[20,21].

The present work was undertaken to study the corrosion behaviour of tin in citric acid solution. The effect of acid concentration, temperature, scan rate and presence of some halide ions and polyethylene glycols as additive polymers different in molecular weight equal 1200, 4000 and 6000 were investigated by means of cyclic voltammograms.

EXPERIMENTAL

The working electrode employed in the present work was made of spec pure tin (99.99, Johnson Matthey Chemical Ltd). The investigated material was cut as cylindrical rod, welded with Cu-Wire for electrical connection and mounted into glass tubes of appropriate diameter using araldite offer on active flat disc shaped surface of (0.785cm²) geometric area for the electrode, to contact the test solution. Prior to each experimental, the surface pretreatment of the working electrode was performed by mechanical polishing (using a polishing machine model POLIMENT I, BUEHLER POLISHER) of the electrode surface with successive grades of energy papers down to 12000 grit up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrolytic cell.

The experiments were performed in a 100ml volume cell at 25°C±1, using Pt wire and SCE as auxiliary and reference electrodes respectively. The SCE was connected via a Luggin capillary, the tip of which was very

close to the surface of the working electrode to minimize the IR drop. All potential given in this paper are referred to this reference electrode.

The experiments were carried out in 1.0M citric acid (C₆H₈O₇) solution devoid of and containing different concentrations of NaCl, NaBr, NaI and polyethylene glycol. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used. Each run was carried out, using water thermostat, pH values of solutions were measured and by using an ORION RESEARCH digital ion analyzer (model 501).

The potentiodynamic current/potential curves were recorded by changing the electrode potential automatically from -2000mV to +2000mV with scanning rate of 30mV s⁻¹.

A Potentiostated Galvanostat (EG and G model 273) and a personal computer were used. M352 corrosion software from EG and G Princeton Applied Research was used for the potentiodynamic polarization. Some experiments were repeated at least three times and the results were reproducible.

RESULTS AND DISCUSSION

The cyclic voltammogram of tin electrode in various concentrations (0.1-1.0M) of citric acid solutions (C₆H₈O₇) between -2000mV and +2000mV (Vs. SCE) by scan rate of 30mV s⁻¹ is shown in Figure 1. On the forward scan the cathodic current density corresponding to the hydrogen evolution decreases gradually and changes its sign at potential -0.750mV and shows active/passive transition. The active dissolution potential involves a net anodic contribution. This is followed by a passive region. Beyond the potential (E_p) the active dissolution current density falls rapidly to a very small value (I_{pass}) denoting the most of permanent passivation. This region extends up to +2000mV with almost constant current density I_{pass} and oxygen evolution was not observed up to +2000 mV, indicating the poor electro conductance of the passive film. It seems that the passive film increase, the over potential for oxygen evolution^[23]. Passive film formation and thickening were mainly caused by ionic conductance^[13].

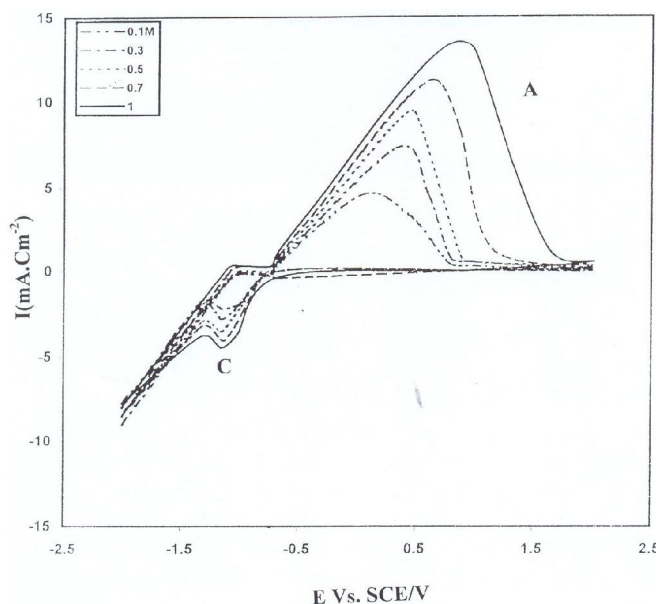
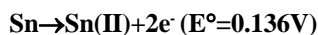
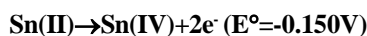


Figure 1 : Cyclic voltammograms of tin electrode at various concentrations of citric acid at 25°C between -2000mV and +2000mV at scan rate 30mVS⁻¹

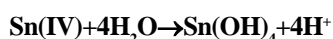
The reverse scan exhibits one small cathodic peak (C), the appearance of the cathodic peak is due to the reduction of the passive film. In the active dissolution region, tin dissolves as Sn(II):



Where E° is the standard oxidation potential^[24]. This reaction is followed by the formation of Sn(IV) species according to



Since the equilibrium potentials corresponding to the above oxidation reaction are very close^[25]. It is known that tin undergoes hydrolysis in acidic media^[25].



Since the hydroxide is highly insoluble, it precipitates on the anode surface giving rise to a passivating film. The most stable species under anodic polarization, however, is the hydrated oxide $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ^[26,27]



For this dehydration reaction DG is -42Kj.mol⁻¹ and is therefore highly irrev^[25].

It can safely be assumed that dehydration to $\text{SnO}_2 \cdot \text{H}_2\text{O}$ is also irreversible. Therefore one can conclude that the passivity is due to the presence of a film of Sn(OH)_4 and/or $\text{SnO}_2 \cdot \text{XH}_2\text{O}$ on the anode surface.

Inspection of the data of Figure 1 reveals that the amount of electricity consumed during the anodic

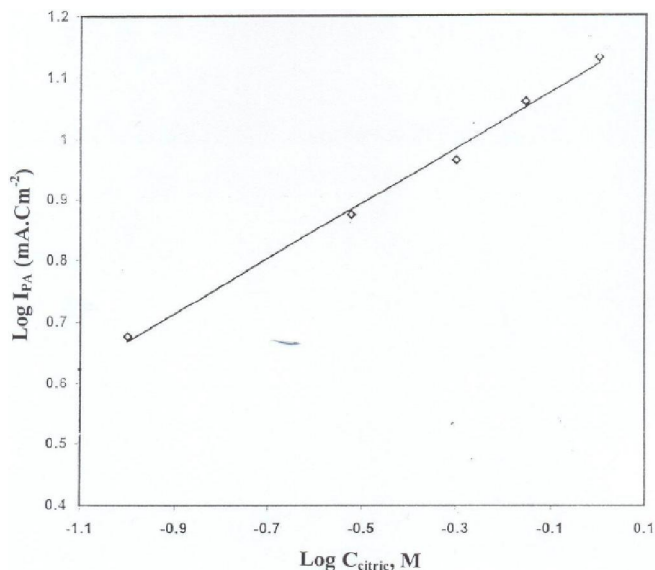


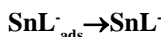
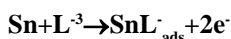
Figure 2 : The relation between peak current density (I_{PA}) and $\log C_{\text{citric}}$

sweep is much higher than the amount used during the cathodic sweep suggesting that the tin dissolves into the solution and the passive film must be quite thin.

It seems that the peak current (I_{PA}) of peak A increases while its corresponding peak potential (E_{PA}) shifts towards more positive values with increasing of the citric acid concentration. The relationship between $\log I_{PA}$ Vs $\log C_{\text{acid}}$ is shown in Figure 2 and this relation obeys the following equation

$$I_{PA} = 0.62 + 0.95 \log C_{\text{acid}}$$

These results may be due to the decrease in the formation and precipitation of the passive oxide film, the acceleration effect of acid can be due to adsorption of citrate ion L^{-3} at active sites on the electrode surface followed by desorption of the formed soluble SnL species as following



Therefore, the anodic current peak (I_{PA}) is indicative of the two processes; the dissolution of tin and formation of soluble $\text{SnL}^{-1}_{\text{aq}}$ and precipitation of tin oxides on the electrode surface, precipitation of tin oxides on the anodic surface blocks the active surface sites and causes inactivation of a part of the surface with respect to the corrosive media.

When the surface is completely covered with the passive film, the anodic current density falls to a small

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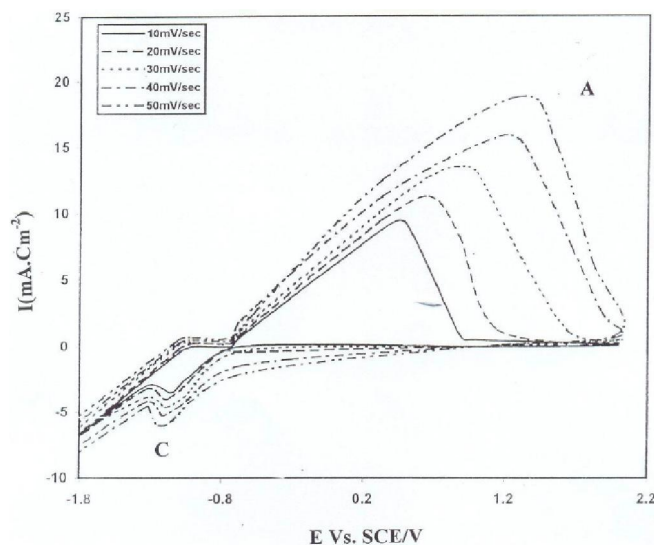


Figure 3 : Cyclic voltammograms for tin in 1.0M citric acid at 25°C at different scan rates (v)

value I_{pass} . Some authors report similar mechanism for dissolution of tin anode in citric^[10-16], maleic^[13] and isobutyric acid^[15].

The effect of potential scan rate (v) on the cyclic voltammogram of tin electrode in 1.0M citric acid is shown in Figure 3. It is observed that the peak potentials of anodic peaks shift to more positive direction while those of their conjugated cathodic peak shift to more negative direction. Consequently, the separation between anodic and cathodic peaks enhances with the increasing scan rate. These results are consistent with the irreversible nature of the oxidation/reduction processes. Moreover, the peak current densities of anodic and cathodic peaks increase with increase in scan rate.

Plot of I_{PA} against $v^{1/2}$ is shown in Figure 4. A linear relation is obtained but the line passes through the origin. The $v^{1/2}$ dependence observed can be interpreted on the basis of Delhay model^[28].

$$I_{\text{PA}} = abZ^{1/2}CD^{1/2}v^{1/2}$$

Where a and b are constant, D and C are diffusion coefficient and concentration of reaction species and Z is the number of exchanged electrons. This result suggests that the dissolution of tin is under diffusion control by mass transport in the solution. As predicted by this equation, the peak current density goes to zero as sweep rate goes to zero. Figure 5 represents the dependence of the peak potential EPA of peak A on $\log v$. A linear relationship is observed with a slope of 1.19mV decade⁻¹. This observation is considered with irreversible formation of a passivating film on the electrode surface^[29].

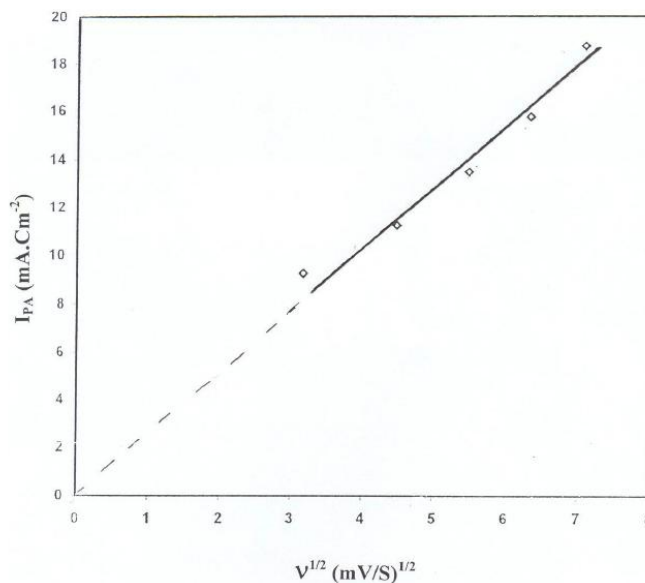


Figure 4 : The relation between the peak current densities (I_{PA}) against the square root of the scan rate ($v^{1/2}$)

Figure 6 shows the influence of solution temperature (25–65°C) on the potentiodynamic response of tin in 1.0M citric acid with a sweep rate of 30mVS⁻¹. The data obtained shows the general features of the cyclic voltammograms remain spatially unaffected by changing the temperature. It is observed that the current density flowing along the whole range of the cyclic voltammograms increases with rising temperature. The height of peak A shifts in positive direction while the peak potential of peak C shifts towards the more negative direction. The values of $\log I_{\text{PA}}$ various temperatures were plotted as a function of $1/T(^{\circ}\text{K})$ (Arrhenius plot) and are shown in Figure 7. The data reveal that the increase in temperature accelerates the rate of transportation and diffusion of the reactant and product species^[30-31] and hence increases the corrosion reaction. The apparent activation energy E_a , for electrochemical process associated with peak A was calculated from the slope of Arrhenius plot. The data furnish an apparent activation energy value $E_a = 19.96\text{Kj.mol}^{-1}$. The relation between the anodic and cathodic behaviour of tin in citric acid can be established by the increasing of the anodic limiting potential in steps. Figure 8 represents the cyclic voltammograms of tin electrode in 1.0M citric acid at 25°C. The measurements starts at -2000mV and reversed at various anodic potential limiting with scan rate 30 mVS⁻¹. It is found that when the anodic potential is reversed at -0.33V (on the ascending side of peak A) the reverse potential sweeps returns itself

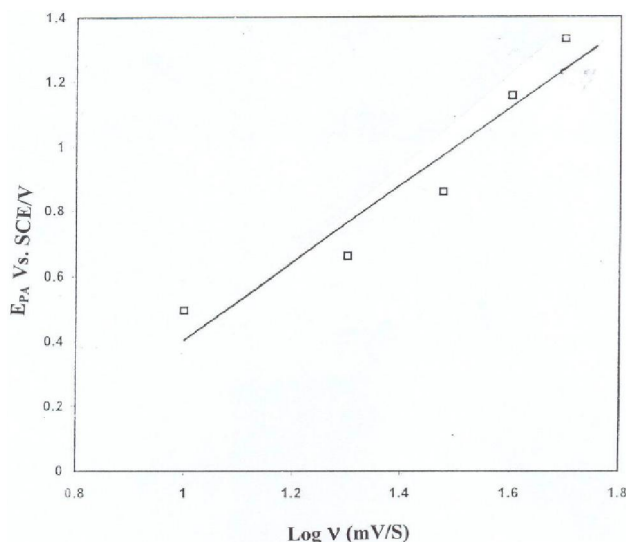


Figure 5 : The relation between the anodic peak potential (E_{PA}) against the square root of the scan rate ($\log v$)

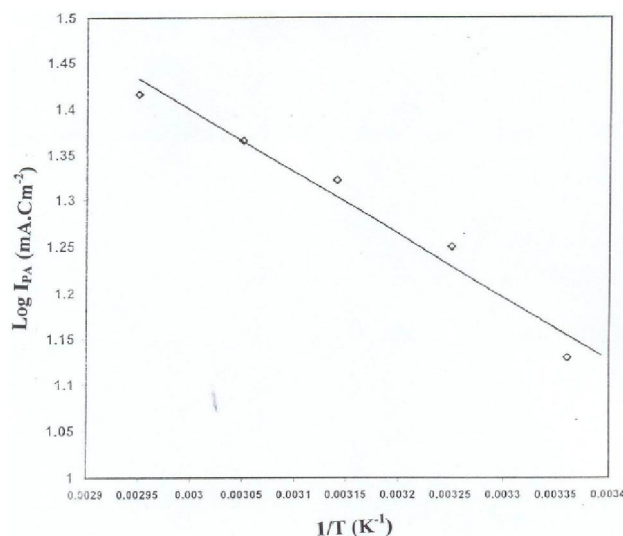


Figure 7 : The relation between the peak current densities (I_{PA}) against temperature

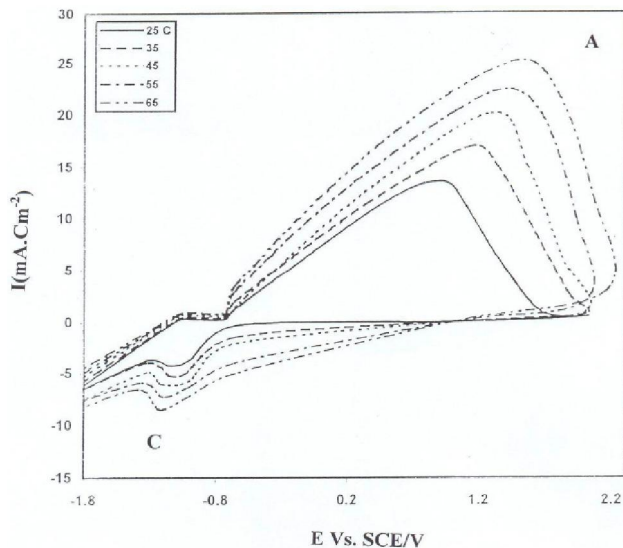


Figure 6 : Influence of temperature (20-65°C) on cyclic voltammograms of tin electrode in 1.0M citric acid at scan rate 30 mV S^{-1}

and does not show any cathodic peak, indicating that the anode surface is free from any passive film. When the anodic potential is reversed at 1.0V (on the descending side of peak A), the reverse sweep shows the cathodic peak C suggesting that the precipitation of the passive film on the electrode surface cause the observed drop in the dissolution current beyond the anodic peak potential. When the anodic potential limits are reversed with the passive regions, the reverse sweep yields the cathodic peak C. A stepwise increase in the anodic potential limit enhances the peak current of peak C and shifts its peak potential to more negative values. Figure

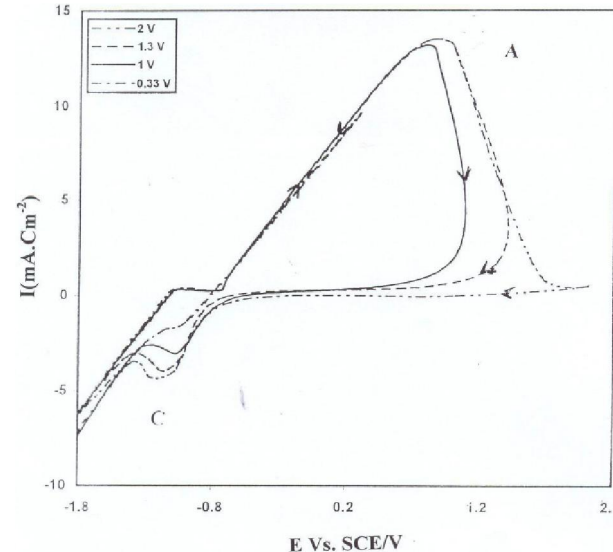


Figure 8 : Influence of increasing stepwise potential on cyclic voltammograms of tin electrode in 1.0M citric acid at scan rate 30mV S^{-1}

9 represents typical cyclic voltammograms of tin in 1.0M citric acid at 25°C and 30mV S^{-1} under the influence of successive cycling between -2000mV and +2000mV (SCE) without withdrawing the electrode or changing the solution. The data reveal that the amount of change consumed through peak A (QA) and peak C (QC) increases with repetitive cycling. The activation may be related to progressive increase in surface area of presumably as a result of increasing surface roughness^[21]. The data reveal that the ratio QA/QC (as represented by the area of each peak) is greater than unity (QA/QC \approx 4). It can be seen that the peak potential differ-

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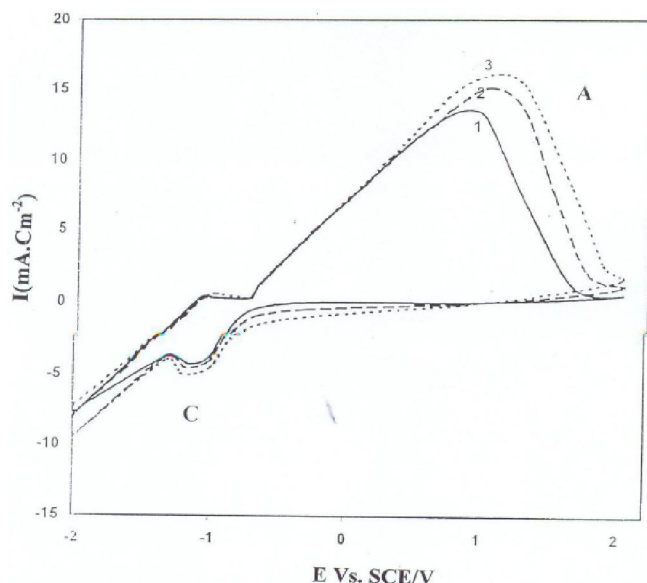


Figure 9 : Influence of successive cycling on cyclic voltammograms (3 cycles) of tin electrode in 1.0M citric acid at scan rate 30mVS^{-1}

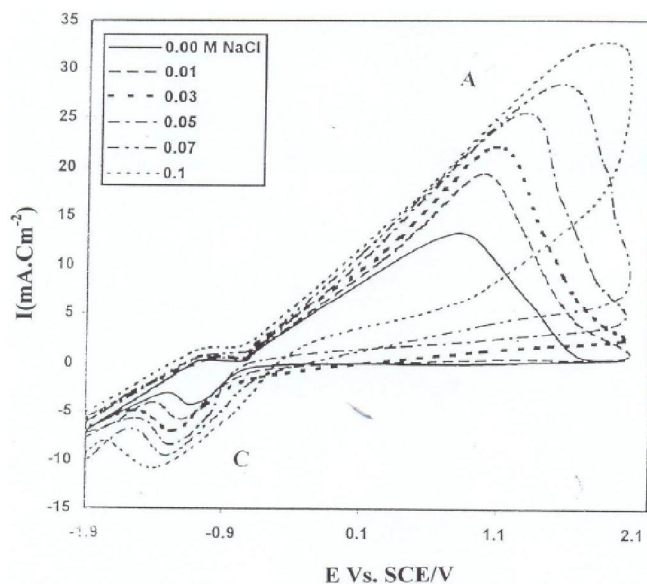


Figure 10 : Cyclic voltammograms of tin electrode in 1.0M in presence of various concentrations of NaCl (0.01 to 0.1M) between potential -2000mV and +2000mV at scan rate 30mVS^{-1} . The peak potential difference DE (i.e. $E_{\text{PA}} - E_{\text{PC}}$) is almost 1.1V confirming the irreversible nature of the processes. Furthermore, the peak potential difference DE enhances with increasing number of cycles such as phenomenon may also be due to effect of changes in the surface roughness^[32]. The effect of addition increasing amounts of NaCl, NaBr and NaI on the anodic behaviour of tin in 1.0M citric acid are given in Figure 10-12. The measurements were carried out between -2000mV and +2000mV with a sweep rate of 30mVS^{-1} . Inspection

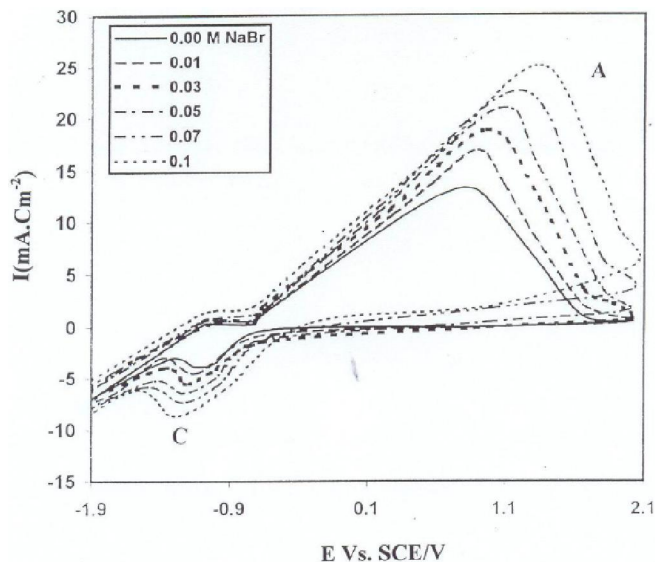


Figure 11 : Cyclic voltammograms of tin electrode in 1.0M in presence of various concentrations of NaBr (0.01 to 0.1M) between potential -2000mV and +2000mV at scan rate 30mVS^{-1}

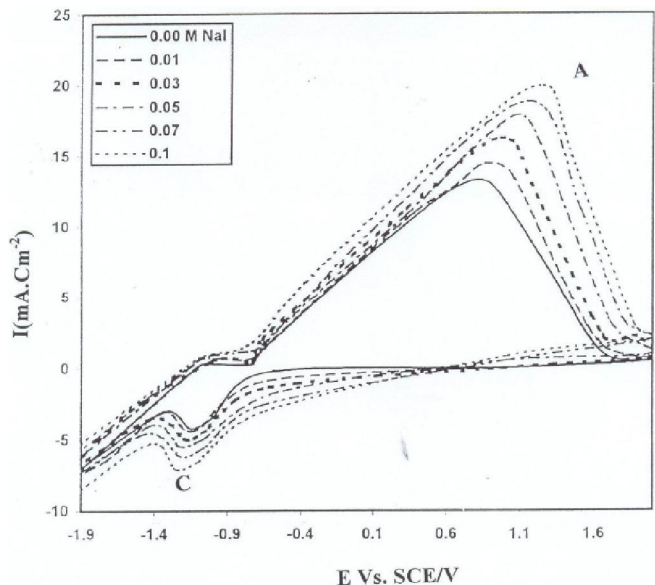


Figure 12 : Cyclic voltammograms of tin in 1.0M citric acid in presence of various concentrations of NaI (0.01 to 0.1M) between potential -2000mV to +2000mV at scan rate 30mVS^{-1} . The relationship between the peak current density I_{PA} of peak A Vs $\log C_x$ ($X = \text{Cl}^-, \text{Br}^-$ and I^-) in 1.0M citric acid is shown in Figure 13, a linear relationship is observed. The data

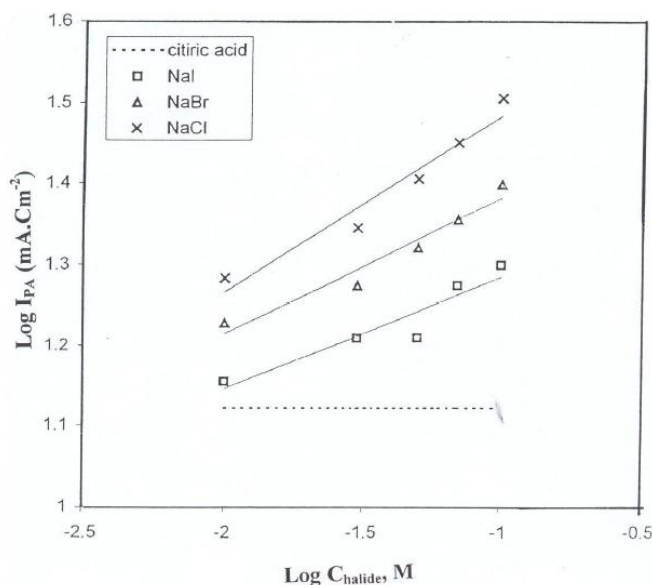


Figure 13 : The relation between log peak current densities (I_{PA}) and $\log C_{halide}$

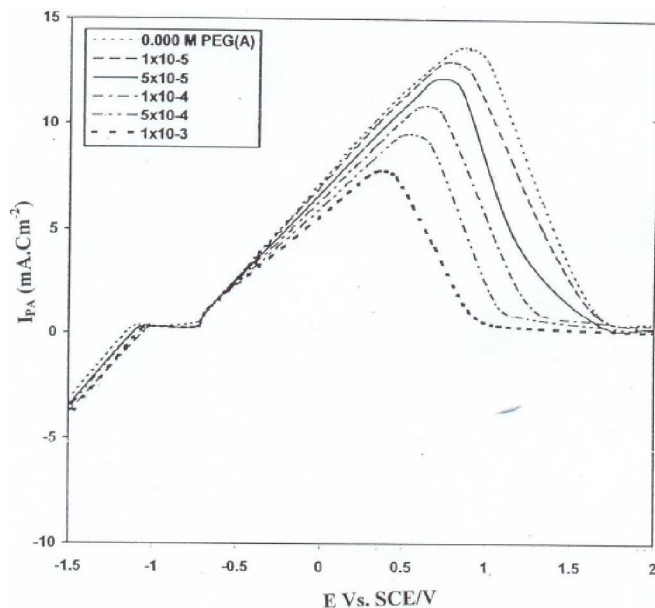


Figure 14 : The potentiodynamic polarization curves of tin electrode in citric acid and in presence of polyethylene glycol for $(PEG)_A$

show that the accelerating effect of the halide anion increases with an increase in its concentration. Moreover, the accelerating effect of these anion decreases in the order: $Cl^- > Br^- > I^-$.

It seems probable that these anions are effective through an adsorption process^[33]. These anions might be adsorbed in competition with citrate anions on the electrode surface, and in that manner have a net effect of increasing anodic dissolution. It is possible that the adsorbed halide ions reduce the free energy of the system and impedes the passage of ion-atoms of metal

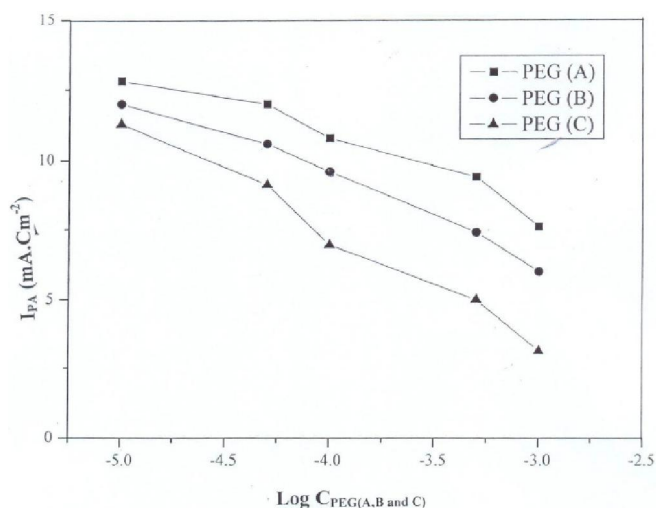


Fig. 15 : The relation between $\log C_{poly}$ against I_{PA}

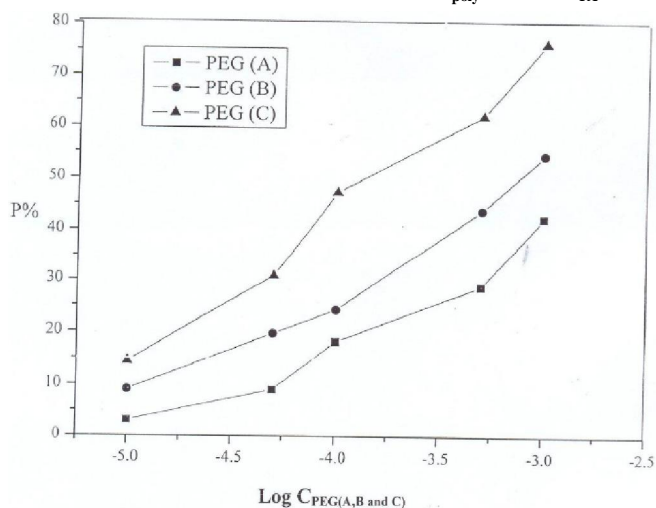


Figure 16 : The relation between the inhibition efficiency ($P\%$) and $\log C_{inh}$

from the lattice into the solution. Because of the high rate of metal dissolution with halide ions, the halide ions do not stay adsorbed but form a soluble species, which their reactions lead to accelerate dissolution. The effect of various concentrations of polyethylene glycol samples $[HOCH_2(CH_2OCH_2)_nCH_2OH]$ which have different molecular weights $[(PEG)_A=1200, (PEG)_B=4000 \text{ and } (PEG)_C=6000]$ on the corrosion behaviour of tin in citric acid solution was investigated at $25^\circ C$ by using potentiodynamic polarization technique. The potentiodynamic polarization curves for tin in citric acid and in presence of polyethylene glycol for $(PEG)_A$ are given in Figure 14 (similar results were obtained for $(PEG)_B$ and $(PEG)_C$). It is clear that the presence of various concentrations of the polymers in citric acid solution has a great effect on potentiodynamic polarization curves. Inspection of the

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data reveals that, the anodic peak current density I_{PA} decreases with the increases of polyethylene glycol concentrations. This may suggest that these polymers inhibit the acid dissolution of tin by adsorption at the tin/acid solution interface. The adsorption takes place via ion pair and ion exchange mechanism by their ethylene oxide groups^[34]. Inhibition of the adsorbed polymers can be explained by blocking the active sites available for dissolution reactions^[35]. Figure 15 presents the relationship between $\log C_{poly}$ Vs I_{PA} . It is clear that the corrosion of tin decreases with increasing the polymer concentration. Moreover the corrosion of tin decreases considerably with increasing molecular weight of polymer i.e. the corrosion decrease in the order: $(PEG)_A > (PEG)_B > (PEG)_C$.

This may be due to the different in the number of ethylene oxide groups, where the number of ethylene oxide groups increases with increasing molecular weight of polymer and this causes an increase in the bulk of the groups attached to the absorption sites^[36,37] and hence reduces the rate of corrosion. The inhibition efficiency of PEG on the corrosion of tin, the electrochemical parameters (I_{corr} and E_{corr}) associated with polarization curve (Figure 14) have been simultaneously determined. The data show clearly that the addition of the inhibitors decreases the corrosion current density (I_{corr}) and shifts the corrosion potential E_{corr} to more positive value. Since the corrosion rate is directly related to I_{corr} , the inhibition efficiency (P%) is calculated by the following equation:

$$P\% = \frac{I_{corr}^{\circ} - I_{corr}}{I_{corr}^{\circ}} \times 100$$

Where I_{corr}° is corrosion current in absence of inhibitor and I_{corr} is corrosion current in presence of inhibitor. The relation between the inhibition efficiency (P%) and $\log C_{inh}$ is given in Figure 16. The plots have S-shaped adsorption isotherms. These data confirm the assumption that the presence of these glycols inhibits the corrosion of tin in 1.0M citric acid solution via adsorption process. In all cases the inhibition efficiency increases when the concentration of the inhibitors increases^[14,38]. The inhibition efficiency of these inhibition decreases in the order: $(PEG)_C > (PEG)_B > (PEG)_A$.

CONCLUSIONS

The active anodic dissolution of tin increases with increasing acid concentration, temperature and scan rate.

The ratio of anodic charge QA consumed within peak A to the cathodic charge QC consumed within its conjugated peak C (as represented by the area of each peak) is greater than unity. It is probable that the dissolution products formed during the anodic sweep have tended to diffuse into the bulk of the solution before being reduced on the negative-going sweep.

Addition of Cl⁻, Br⁻ and I⁻ ions to the citric acid solution enhances the anodic dissolution of tin.

The potentiodynamic polarization curve for tin in citric acid in the presence of polyethylene glycol $(PEG)_A$, $(PEG)_B$ and $(PEG)_C$ indicates that these polymers inhibit the acid dissolution of tin by adsorption at the tin/acid solution interface.

The inhibition of these compounds increases with their concentration as well as their molecular weight and therefore, the corrosion decrease in the order: $(PEG)_A > (PEG)_B > (PEG)_C$.

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