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Effect of some polymeric materials on the corrosion behaviour of tin in succinic acid solution

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Abstract

The anodic behaviour and corrosion of tin in various concentrations (0.05–0.7M) of succinic acid were studied using cyclic voltammetry. The potentiodynamic anodic polarization curves exhibit active/passive transition. The active dissolution of tin involves one anodic peak. The cathodic curve exhibits one cathodic peak corresponding to the reduction of the passive layer. The ratio of the anodic charge/cathodic charge is more than unity indicating that the passive layer is very thin and the dissolution products are mainly soluble species. Additions of some polyethylene glycols to the succinic acid solution decrease the anodic peak current and shift the peak potential in the negative direction. These changes depend on the concentration and molecular weight of the polyethylene glycol added. The effect of the inhibitors decreases in the following order: $(PEG)_{6000} > (PEG)_{4000} > (PEG)_{1200}$. The inhibition efficiency decreases with increase in temperature, suggesting physical adsorption.

1. Introduction

Tin is widely used as a protective coating for steel in the manufacture of tin plate and the corrosion behaviour and passivation of tin in carboxylic acids have been intensively studied [1–12]. In most cases the anodic polarization of tin in these acids exhibits active/passive behaviour. Commonly observed oxidation states of soluble oxidation products of tin are the thermodynamically soluble Sn(II) and Sn(IV) species. Passivation results from film formation on the metal surface by a solution-precipitation mechanism. In the active/dissolution region tin dissolves as Sn(II) which is immediately oxidized to more stable Sn(IV) [8, 13] according to the following equations:

$$Sn = Sn(II) + 2e^-$$

$$Sn(II) = Sn(IV) + 2e^-$$

It is known that tin undergoes hydrolysis in acidic medium [14, 15].

$$Sn(IV) + 4H_2O = Sn(OH)_4 + 4H^+$$

$Sn(OH)_4$ is highly insoluble and precipitates giving rise to a passive film on the electrode surface. The stability of the film increases upon dehydration [16].

$$Sn(OH)_4 = SnO_2 \cdot xH_2O + (2 - x)\ H_2O$$

Precipitation of SnO_2 on the surface blocks the dissolution active sites and causes inactivation of a part of the surface with respect to the corrosive medium. When the surface is entirely covered with SnO_2 film, the anodic current density falls to a very small value.

Very little work is available on the influence of polymers on the corrosion behaviour of tin in these organic acid media [17].

The present work was undertaken to study the corrosion behaviour of tin in succinic acid solution. The effects of acid concentration, temperature, scan rate and the presence of polyethylene glycols as additive polymers (different in molecular weights equal 1200, 4000 and 6000) on cyclic voltammograms were investigated. Polyethylene glycols are water-soluble, waxy solids used extensively in the cosmetic and toiletry industry. They are also used in cleaners to dissolve oil and grease as well as thicken products. Because of their effectiveness, polyethylene glycols are often used in caustic spray-oven cleaners, yet are also found in many personal care products [18].

2. Experimental

The experiments were carried out in aerated succinic acid solutions without or with various concentrations of three polyethylene glycols $[HOCH_2(CH_2OCH_2)_nCH_2OH]$ as corrosion inhibitors.

All solutions were prepared from analytical grade chemicals and doubly distilled water.

The working electrode was a tin rod (99.99%; Koch light laboratories, Colnbrook, Bucks, England) with an apparent exposed area of 1 cm^2. Prior to each experiment, surface pretreatment of the working electrode was performed by mechanical polishing (using polishing machine model Poliment I, Buehler Polisher) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The polished electrode was then degreased with acetone and washed with running doubly distilled water. The counter electrode was platinum wire. The potentials were recorded relative to a saturated calomel electrode (SCE). To avoid contamination with Cl^- ions, the reference electrode was connected to the working electrode through a bridge filled with the solution under test.

The potentiodynamic polarization (E/i) curves were recorded by changing the electrode potential automatically from −2.0 to 2.0 at the desired scan rate. A potentiostat/galvanostat (EG&G model 273 A) and a personal computer were used. M 352 corrosion software from EG/G Princeton applied research was used to the technique mentioned above. Each run was carried out in aerated solution at 298 K ± 1 K.

3. Results and discussion

Figure 1 shows cyclic voltammograms of the tin electrode in succinic acid solutions of different concentrations (0.05 M, pH 2.78–0.7 M, pH 2.65) at 298 K. The potential was swept from −2.0 V up to 3.0 V(SCE) and then reversed in the same solution with the same scan rate 30 mV s^{-1}. It is clear that this change in pH of solution has no significant effect on the tin corrosion behaviour. On the positive going sweep, the cathodic current density corresponding to hydrogen evolution reaction decreases gradually and changes its sign at zero current potential. The anodic excursion part exhibits active/passive transition. The active dissolution potential region involves one anodic contribution (peak A). In the active dissolution region, tin dissolves as Sn(II) which is subsequently oxidized to Sn(IV) [2]. Beyond the peak potential E_{pA} of peak A, the active dissolution current falls rapidly as a result of passivation. It seems that passivation is due to precipitation of a porous film of $Sn(OH)_4$ and or SnO_2 on the electrode surface. The value of the passive current density i_{pass} is limited by chemical dissolution of the film, the chemical film dissolution is counterbalanced by film formation. The rate of these two processes is approximately equal at steady state of so as the film thickness remains constant. The current i_{pass} starts to increase rapidly as a result of oxygen evolution. An increase in acid concentration enhances the passive current and shifts the oxygen evolution potential negatively. The cathodic sweep exhibits one small peak C, which is due to the reduction of the anodically formed passive film. Figure 1 reveals that the amount of electricity consumed during the anodic sweep is much higher than that used during the cathodic sweep suggesting that most of the tin dissolves into solution and/or the reduction of the passive film is incomplete. It is seen that the peak current density (i_{PA}) and i_{pass} increase while the corresponding peak potential (E_{PA}) shifts positively with increasing succinic acid concentration, The linear dependence of i_{PA} on log C_{acid} is shown in Figure 2. The acceleration effect of the acid

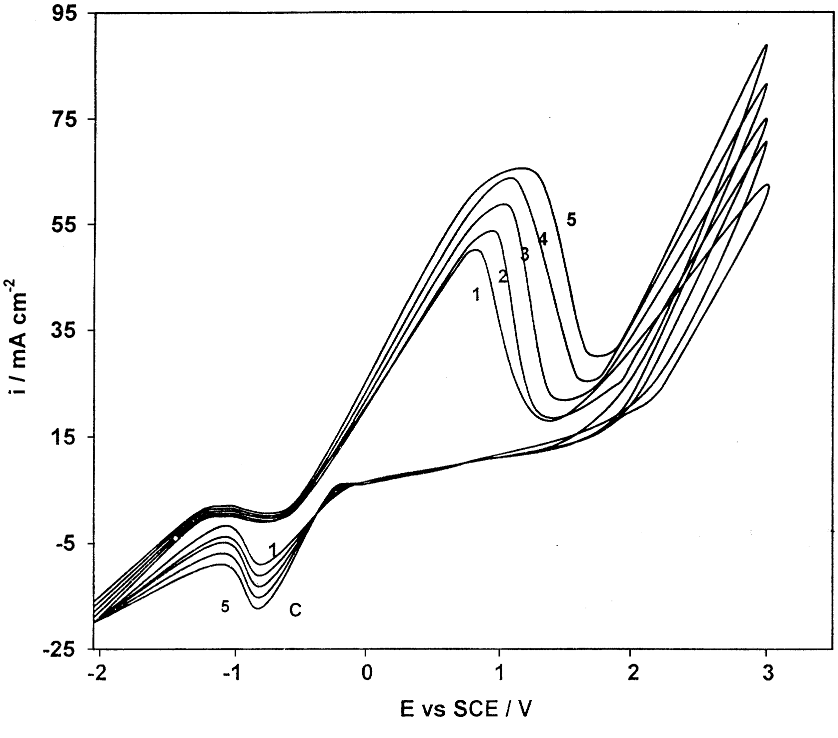

Fig. 1. Cyclic voltammograms of tin electrode in succinic acid solutions of different concentrations at 298 K and scan rate of 30 mV s^{-1}. (1) 0.05 M (2) 0.1 M (3) 0.3 M (4) 0.5 M (5) 0.7 M succinic acid.

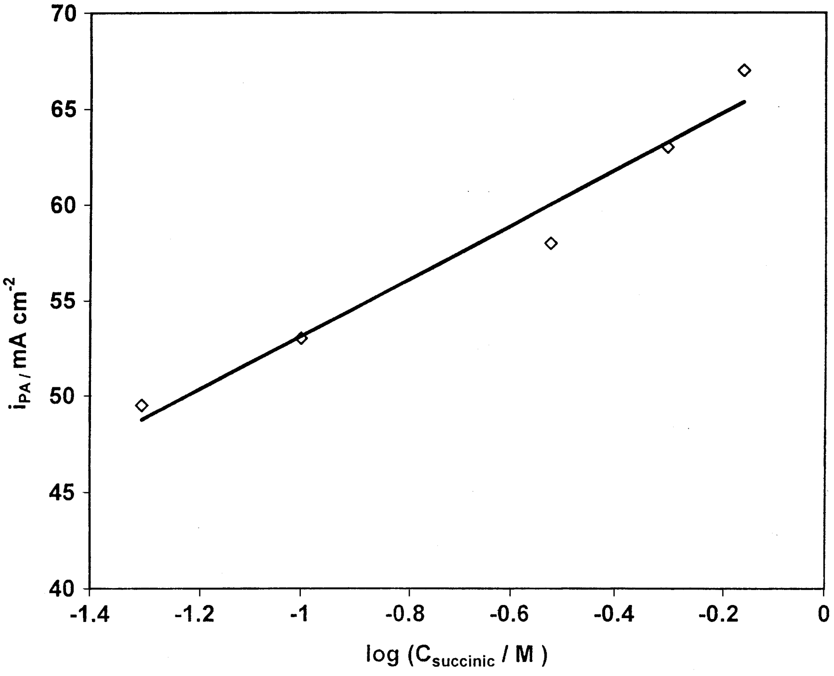

Fig. 2. Relation between i_{PA} vs log $C_{\text{succinic acid}}$ for a tin electrode at 298 K and scan rate of 30 mV s^{-1}.

may be due to adsorption of succinate ions (L^{-2}) at active surface sites followed by desorption of the formed soluble species SnL as follows:

$$\mathrm{Sn} + \mathrm{L}^{-2}_{(\mathrm{ads.})} \rightarrow \mathrm{SnL}_{(\mathrm{ads.})} + 2\mathrm{e}^{-}$$

$$\mathrm{SnL}_{2(\mathrm{ads.})} \rightarrow \mathrm{SnL}_{2(\mathrm{aqu.})}$$

A similar explanation was given for the active dissolution of tin in maleic acid [19], isobutyric acid [20] and citric acid [21].

The effect of scan rate (ν) (5–50 mV s^{-1}) on the potentiodynamic polarization curves of tin in 0.5 M succinic acid is shown in Figure 3. An increase in ν, shifts E_{pA} positively and increases i_{PA} and i_{PC}. Plot of i_{PA} against $\nu^{1/2}$ is shown in Figure 4. A linear relation is

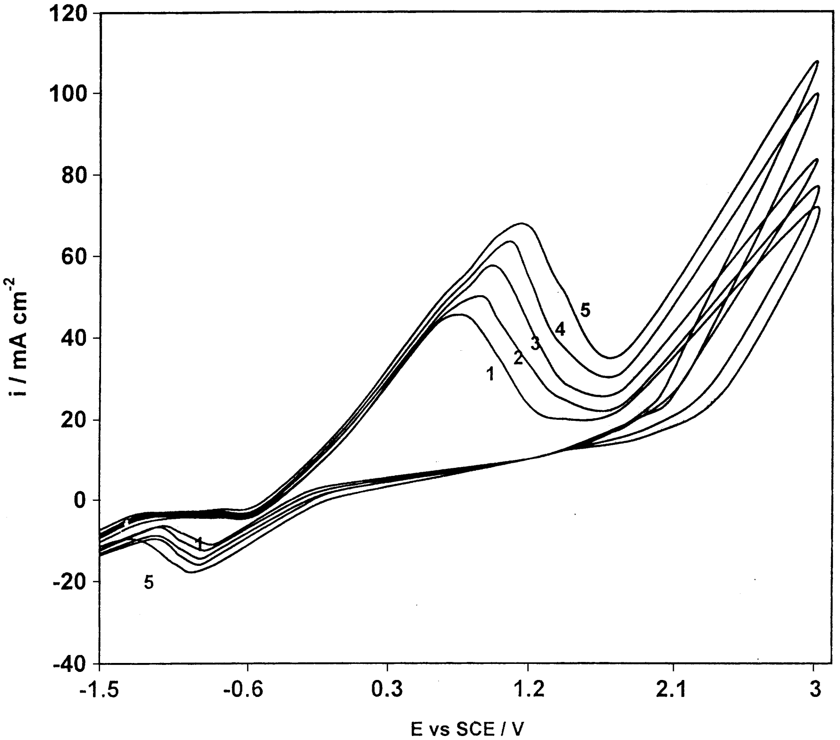

Fig. 3. Cyclic voltammograms of tin electrode in 0.5 M succinic acid at 298 K and at different scan rates. Curves (1) 5 (2)10 (3)20 (4) 30 (5) 50 mV s^{-1}.

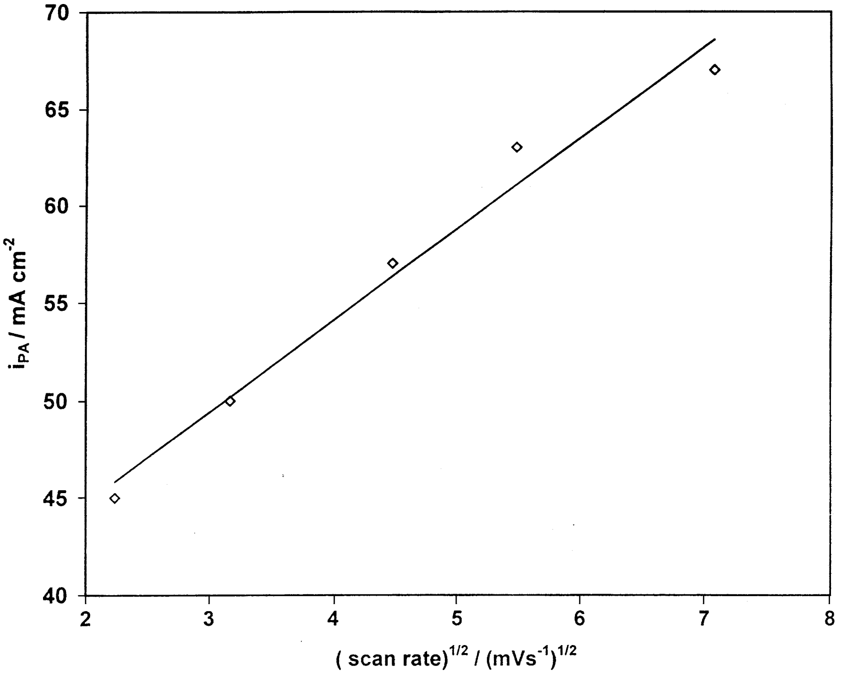

Fig. 4. Relation between i_{PA} vs $v^{1/2}$ for tin electrode in 0.5 M succinic acid at 298 K.

obtained but the line does not pass through the origin. These results imply that the active dissolution of tin is at least partly diffusion controlled [1].

Figure 5 shows the influence of solution temperature (298–338 °K) on the potentiodynamic response of tin in 0.5 M succinic acid with a sweep rate 30 mV s^{-1}. Increase in temperature results in an increase in both anodic and cathodic current density (i_{PA} and i_{PC}), and shifts E_{PA} positively while E_{PC} shifts negatively. The values of log i_{PA} for various temperatures were plotted as a function of $1/T$ (K) (Arrhenius plot) and are shown in Figure 6; a linear relation is obtained. The apparent activation energy E° for peak A was calculated from the slope of this Arrhenius plot. The data furnish an apparent activation energy E° of 6.32 kJ mol^{-1}.

Figure 7 shows cyclic voltammogrames for tin in 0.5 M succinic acid at 298 °K at a scan rate of 30 mV s^{-1}

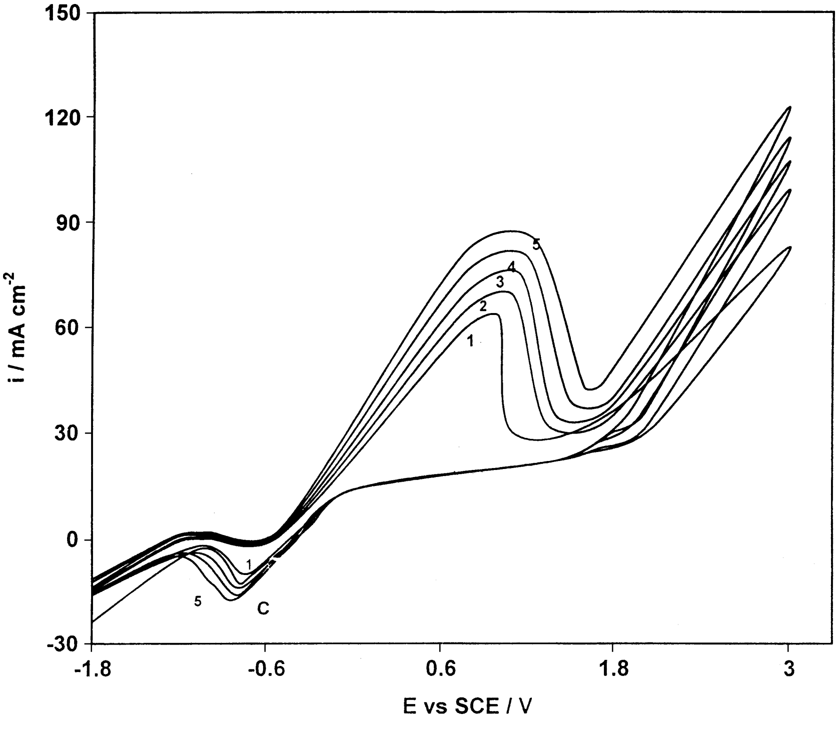

Fig. 5. Cyclic voltammograms of tin electrode in 0.5 M succinic acid at scan rate 30 mV s^{-1} and at different temperatures. Curves (1) 298 (2) 308 (3) 318 (4) 328 (5) 338 K.

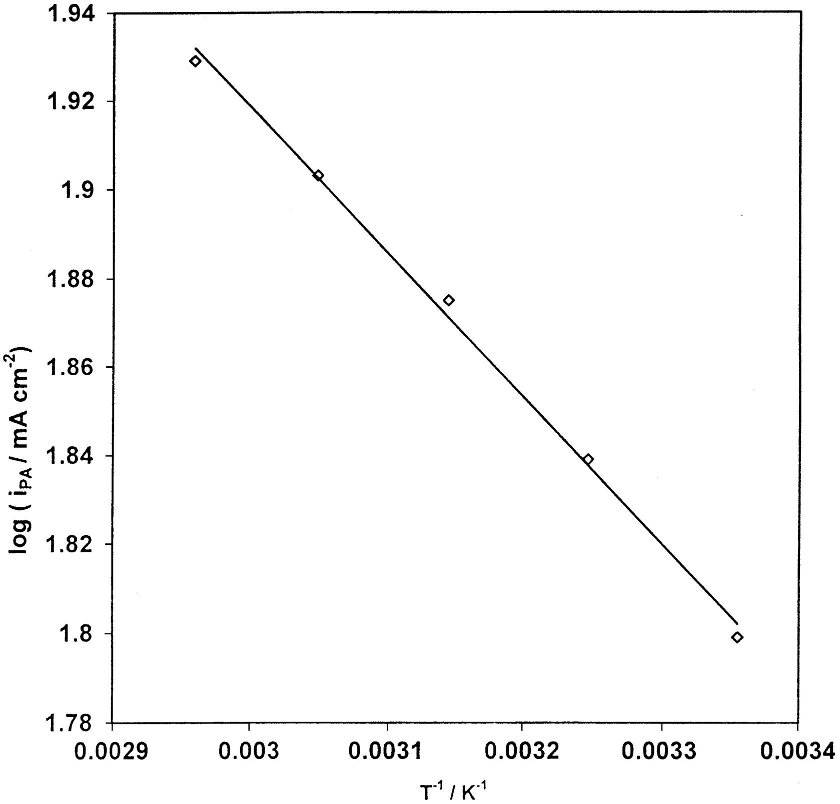

Fig. 6. Relation between log i_{PA} vs $1/T$ for tin electrode in 0.5 M succinic acid at scan rate of 30 mV s^{-1}.

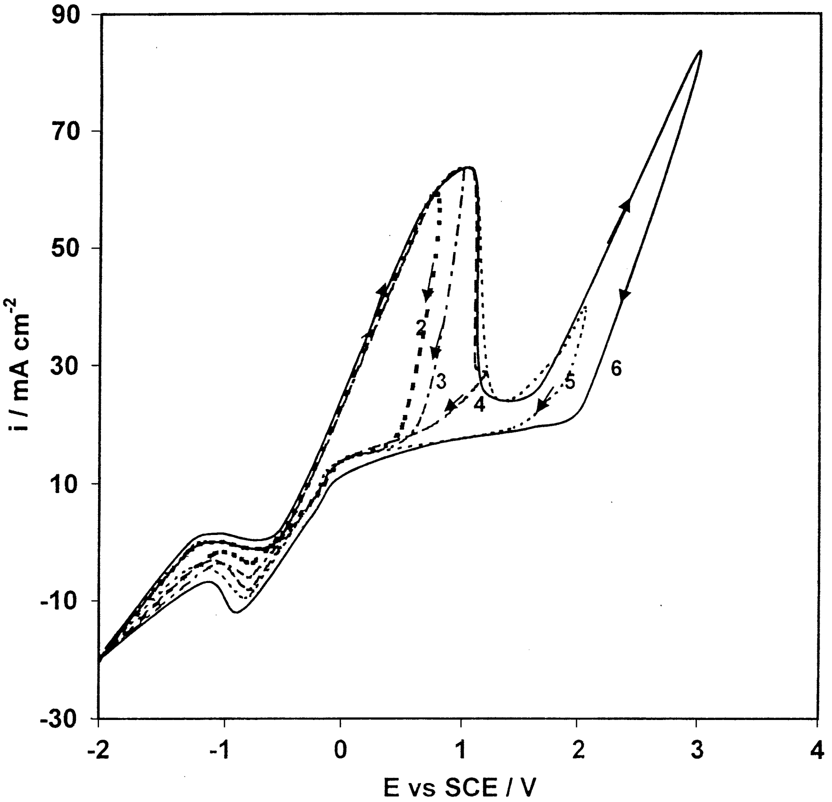

Fig. 7. Influence of increasing potential limit on cyclic voltammograms of tin in 0.5 M succinic acid at scan rate 30 mV s^{-1}. (1) 0.00 (2) 0.75 (3)1.00 (4)1.20 (5) 2.00 (6) 3.00 V.

starting at −2.0 V (SCE) and reversed at progressive increases of the anodic potential limit. When the anodic potentials is reversed at zero V (on the ascending side of peak A), the reverse sweep retraces itself and does not show a cathodic peak, indicating that the anodic surface is free from passive film. When the anodic potential is reversed at 0.75 V, the reverse sweep shows a cathodic peak C. The size of the cathodic peak C increases with increasing reverse anodic potential limit. The appearance of this cathodic peak C is related to the reduction of the passive film on the electrode surface.

Figure 8 shows typical voltammograms of tin in 0.5 M succinic acid pH = 2.69) at a scan rate of 30 mV s^{-1} between −2.0 V and +3.0 V under the influence of repetitive cycling. The amount of charge consumed through peak A and peak C decreases as the number of cycles increases. This result may be due to incomplete reduction of the passive film during the cathodic sweep. In such a case, a certain quantity of the passive film remains unreduced on the electrode surface although hydrogen evolution was observed before the end of the cathodic sweep. The presence of this unreduced passive film on the electrode surface decreases the active dissolution of tin in the following anodic cycles.

The effect of adding increasing concentrations of three polyethylene glycols of different molecular weights, $(PEG)_{1200}$, $(PEG)_{4000}$ and $(PEG)_{6000}$ on the anodic polarization curves of tin in 0.5 M (pH = 2.64) succinic acid solution at 298 K was investigated. The pH of 0.5 M succinic acid was unaffected by the addition of the different polyethylene glycols. Figure 9 (as an example) shows the influence of progressive additions of $(PEG)_{4000}$ on the anodic polarization curve. It is clear that the presence of the polymers in the succinic acid solution inhibits anodic dissolution. An increase in the polymer concentration causes a decrease in the current density of peak A and shifts the corresponding peak potential negatively.

Scanning electron micrographs of a tin surface potentiodynamically polarized from −2.0 to 3.0 V at scan rate 30 mV s^{-1} in the absence and presence of $(PEG)_{6000}$ are shown in Figure 10. In the absence of $(PEG)_{6000}$ the surface is covered with corrosion product (Figure 10a) and in the presence of $(PEG)_{6000}$ the density of corrosion product decreases (Figure 10b).

The inhibition efficiencies (P%) of these inhibitors were calculated using the equation:

$$P\% = i^0_{PA} - i_{PA}/i^0_{PA}$$

where $i^0{}_{PA}$ and i_{PA} are the anodic current densities in the absence and presence of polyethylene glycol, respectively.

Figure 11 illustrates of the inhibition efficiency P% vs the logarithm of the polyethylene glycol concentration at 298 K. The plots show S-shaped adsorption isotherms. The inhibition efficiency increases with polymer concentration. The polymers function as inhibitors adsorption on the metal surface via ethylene oxide groups, which block the active dissolution sites on the surface available for the formation of tin succinate complexes [22]. The inhibition efficiency of the inhibitors increases in the following order:$(PEG)_{1200} < (PEG)_{4000} < (PEG)_{6000}$, with increasing molecular wight [22]. This is due to the increase in the number of ethylene oxide groups attached in the molecule [23].

Figure 12 displays the influence of temperature on the anodic polarization curves of tin in 0.5 M succinic acid solution at a scan rate 30 mV s^{-1} in the presence of 10^{-5} M $(PEG)_{4000}$. Increase in temperature increases peak current density of peak A and shifts the corresponding peak potential positively. The inhibition efficiency decreases with increase in temperature. This is due to desorption process at higher temperature

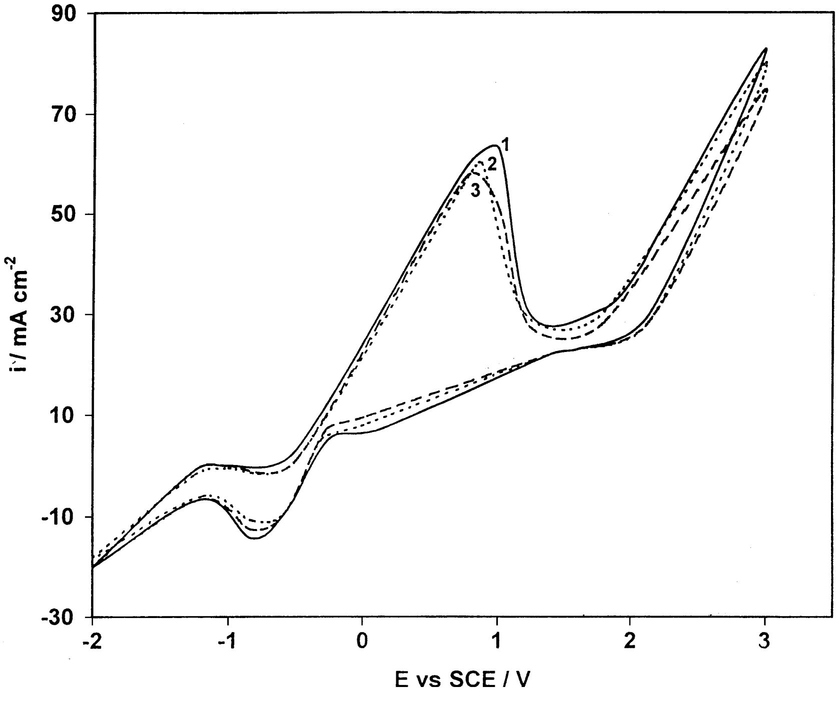

Fig. 8. Typical voltammograms of tin in 0.5 M succinic acid at scan rate of 30 mV s^{-1} between −2.0 V and +3.0 V under influence of repetitive cycling.

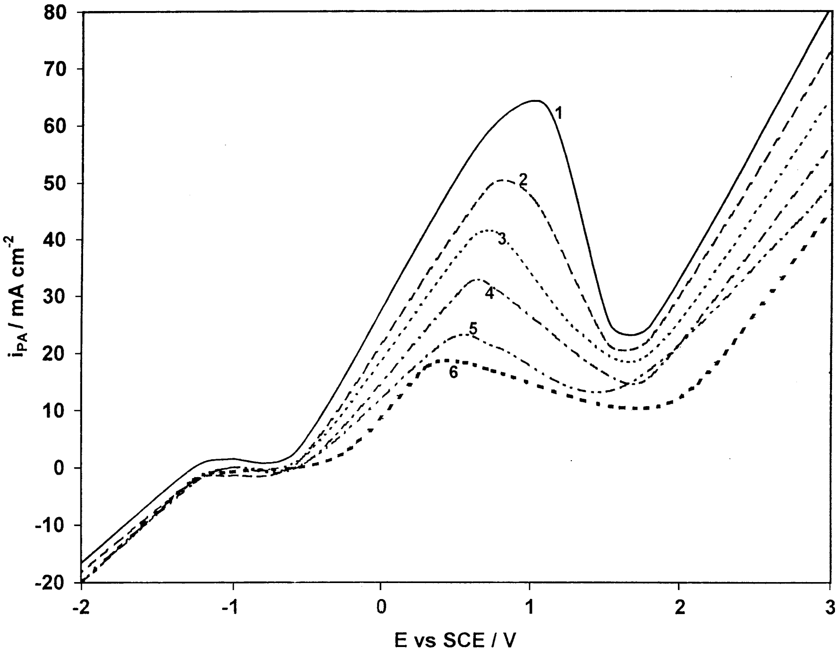

Fig. 9. Cyclic voltammograms of a tin electrode in 0.5 M succinic acid in presence of various concentrations of polyethylene glycol $(PEG)_{4000}$ (M.wt = 4000) at 298 K at scan rate 30 mV s^{-1}. (1) 0.00 M (2) 1×10^{-5} M (3) 5×10^{-5} (4) 1×10^{-4} (5) 5×10^{-4} (6) 1×10^{-3} M $(PEG)_{4000}$.

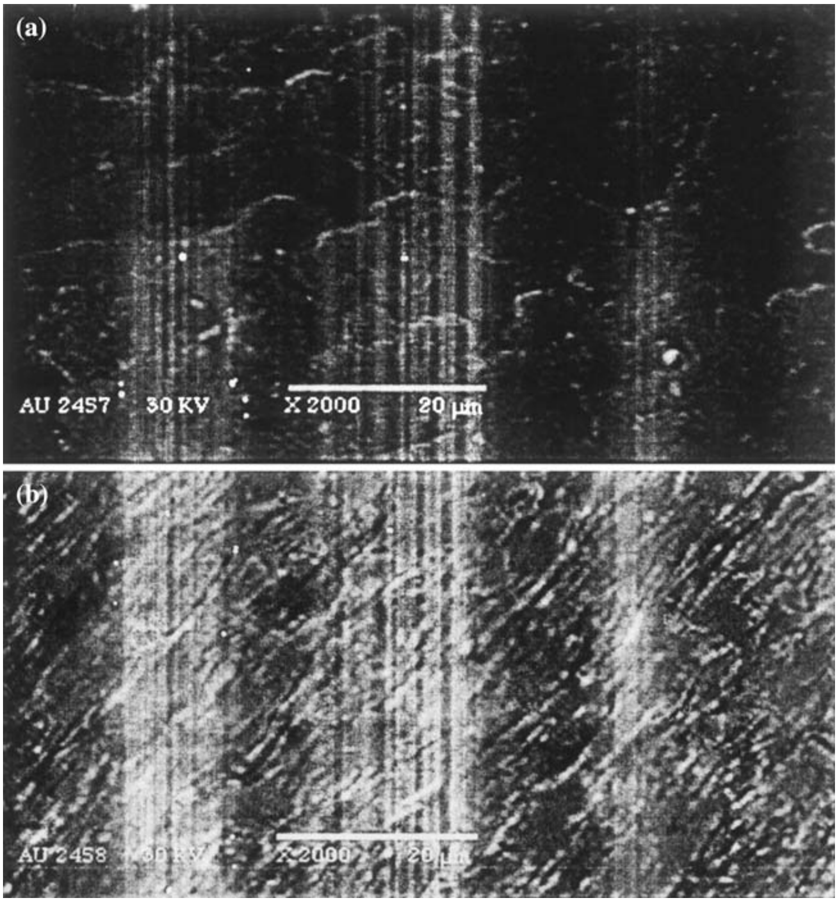

Fig. 10. SEM of tin electrode in (a) 0.5 M succinic acid (b) 0.5 M succinic acid + 1×10^{-3} M polyethylene glycol (M.wt = 6000).

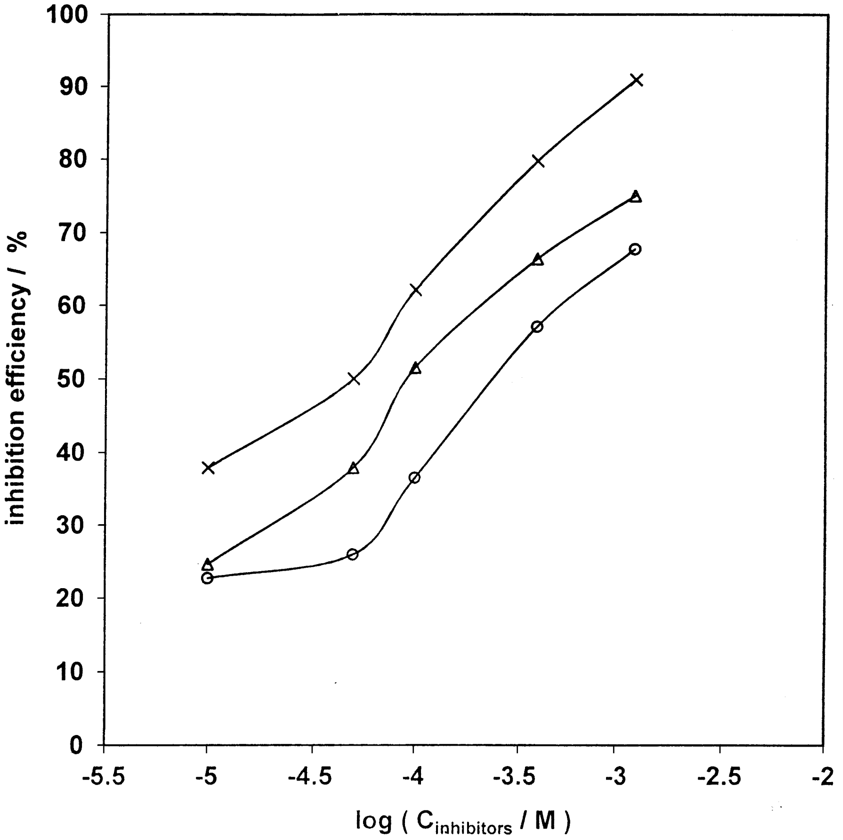

Fig. 11. Plot of the inhibition efficiency (*P*%) vs the logarithmic concentration of the polyethylene glycol O $(PEG)_{1200}$,Δ $(PEG)_{4000}$,×$(PEG)_{6000}$.

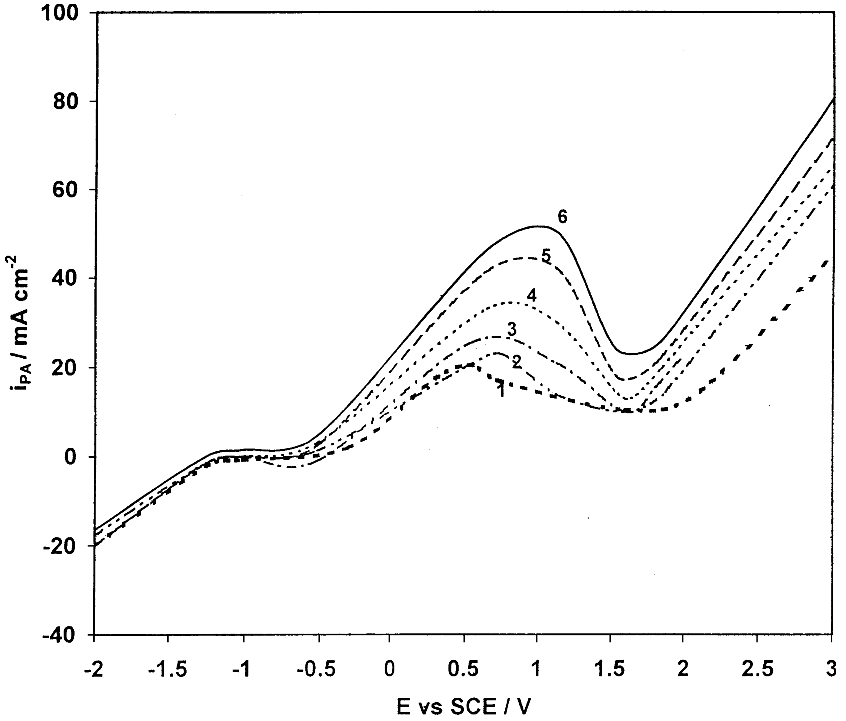

Fig. 12. Cyclic voltammograms of tin electrode in (0.5 M succinic$+1\times10^{-3}$M $(PEG)_{4000}$) at scan rate 30 mV s^{-1} and at different temperatures.

suggesting physical adsorption of the inhibitors on the sample surface.

4. Conclusion

1. The potentiodynamic polarization curves exhibit one anodic peak and one cathodic peak.
2. The active dissolution of tin is at least partly diffusion controll.
3. Increase in temperature leads to an increase in both anodic and cathodic current densities (i_{PA}, and i_{Pc}).
4. The ratio of anodic charge/cathodic charge is more than unity, indicating that the passive layer is very thin.
5. The amount of charge consumed through peak A and peak C decreases as the number of cycles increases.
6. The presence of polyetheylene glycols (PEG) in the succinic acid solution inhibits the anodic dissolution of tin.
7. The inhibition efficiency of the inhibitors increases in the following order: $(PEG)_{1200} < (PEG)_{4000} < (PEG)_{6000}$.

References

1. B.F. Giannetti, P.T. Sumodjo and T. Rabockai, *J. Appl. Electrochem.* **20** (1990) 672.
2. F. Assaf, A. El-Sayed and S.S. Abd El-Rehim, *Bull. Electrochem. (India)* **7** (1991) 207.
3. A. El-Sayed, F. Assaf and S.S. Abd El-Rehim, *Hung. J. Indus. Chem.* **19** (1991) 207.
4. C. Chan, K. Khoo, Y. Chua and S. Guruswamy, *Br. Corros. J.* **28** (1993).
5. B.F. Giannetti, P.T.A. Sumodjo, T. Rabockai and A.M. Souza, *Electro. Chim. Acta* **37** (1992) 143.
6. B.F. Giannetti and T. Rabockai, *Anals. Brasil. Quim.* **43** (1994) 1.
7. S.A.M. Refaey, *J. Appl. Electrochem.* **26** (1996) 503.
8. C.M.V. Almeida, B.F. Giannetti and T. Rabockai, *J. Appl. Electrochem.* **29** (1999) 123.
9. M.S.S. Morad and A.A.A. Hermas, *J. Chem. Technol. Biotechnol.* **76** (2001) 401.
10. S.S. Abd El-Rehim, H.H. Hassan and N.F. Mohamed, *Corros. Sci.* **46** (2004) 1071.
11. E.E. Foad El-Sherbini, Affinidad. IQS, 61(511) (2004) in press.
12. S.S. AbdEl Rehim, S.M. Sayyah and M.M. El-Deeb, *Mater. Chem. Phys.* **9887** (2003) 8.
13. K. Ogura, *Electrochim. Acta* **25** (1980) 335.
14. A.E. Smith, *Analist* **98** (1973) 209.
15. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., (Inter-Science, John Wiley, New York, 1972), pp. 320.
16. J. Kragten, *Atlas of Metal Legend Equilibrium in Aqueous Solutions* (Ellis Horwood, Chester, 1978), pp. 623.
17. S.M. Sayyah, S.S. Abdel Rehim and M.M. El-Deeb, *Intern. J. Polymeric. Mater.* **49** (2001) 59.
18. P. Lagasse and L. Goldmann (Eds.), Columbia Encyclopedia, 6th ed., (Gale publishing Group, New York 2001).
19. S.S. AbdEl Rehim, H.H. Hassan and N.F. Mohamed, *Corros. Sci.* **46** (2004) 1071.
20. E.E. Foad El-Sherbini, *Electroanal. Chem.* **584** (2005) 167.
21. S.S. AbdEl Rehim, S.M. Sayyah and M.M. El Deep, *Mater. Chem. Phys.* **80** (2003) 696.
22. E.E. Foad El-Sherbini, S.M. Abd El-Wahab and M.A. Deyab, *J. Mater. Chem. Phys.* **82** (2003) 631.
23. E.E. Foad El-Sherbini, S.M. Abd El-Wahab and M.A. Deyab, *J. Mater. Chem. Phys.* **89** (2005) 183.