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CORROSION BEHAVIOUR OF TIN ELECTRODE IN CITRIC ACID, MALIC ACID AND GLUTAMIC ACID

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SUMMARY

Corrosion behaviour of tin in citric acid, malic acid and glutamic acid at pH 2 and pH 6 in the concentration range of 10^{-1} M- 10^{-4} M was investigated. Corrosion potentials were shifted to more negative values with the increasing of citric acid and malic acid concentrations and corrosion rates were increased both at pH 2 and pH 6 Corrosion potentials in glutamic acid at pH 6 were shifted to noble values with increasing of concentration and this was attributed to the film formation. But no regular change between glutamic acid concentration and corrosion rate was observed at pH 2. Order of increasing of corrosion rate of acids were as follows.

Citric acid > malic acid > glutamic acid

Corrosion rate of tin was increased by the addition of nitrate or nitrite. But accelerating effect of nitrate and nitrite was pronounced at pH 2. Also accelerating effect of nitrite was found to be greater than nitrate.

INTRODUCTION

The corrosion resistance of tin plate depends upon the interrelationships of the characteristic of can and the product packed therein. Tin may behave as cathode or anode with respect to steel depending upon the nature of corrosive medium. It is generally believed that the protection offered by tin to steel at the interior surface of tin plated food cans is a sacrifical one. Contrary to its position in the electrochemical series of element which would require tin to be cathodic to iron, the metal becomes the anode in the local electrolytic cell that are set up when tin plate is in contact with the liquid medium of food product. The observed change in polarity is accepted to be related with complexing ability of different organic acids. Corrosion of cans by tomato juice is known to be stimulated mainly by citric acid, malic acid and glutamic acid (Takeuchi, 1978).

It is well known that nitrite and nitrate are accelerators for the corrosion of tin in organic acid (Board, Holland, 1969; Luft, 1973; Britton, 1973). Thus it was deemed desirable to investigate the corrosion behaviour of tin in citric acid, malic acid and glutamic acid in a wide range of concentration and pH values. The accelerating effect of nitrates and nitrites on dissolution of tin plated can of acid products has been investigated through canned model experiments by solution analysis (Yaron and Samuel, 1976).

Systematic investigation correlating the increasing corrosive effect of nitrate and nitrite in citric acid, malic acid and glutamic acid needed to be studied by electrochemical technique. This study was thought to be essential to help in understanding the corrosion mechanism of food system.

EXPERIMENTAL METHODS

Solutions of citric acid, malic acid and glutamic acid were prepared using double distilled water. The pH of solutions were adjusted by adding small increments of sodium hydroxide or perchloric acid and checked with pH-meter. All chemicals used were of Merck quality, nitrite and nitrate were introduced in the form of KNO_2 and $NaNO_3$. Polarization experiments were carried out in electrolytic cell that was provided with an inlet and outlet to permit deaeration by passing nitrogen gas through the test solution before each measurement. A platinum counter electrode and saturated calomel electrode as reference electrode were used. Tin electrode was prepared from pure tin rods. A constant predermined area of 86.5 mm^2 was exposed to the test solution. Potentiodynamic polarization curve were obtained using Tacusel PRG-5 polarographic analyzer.

RESULTS AND DISCUSSION

Cathodic polarization curves in deareated citric acid, malic acid and glutamic acid solutions obtained when tin electrode was polarized from corrosion potential in cathodic direction at a scan rate of 2 mV / sec did not exhibit normal Tafel line. But shoulder region just negative to the corrosion potential was observed. This shoulder did not occur when tin electrode was precathodized for 5 minutes at -900 mV.

The shoulder which was observed just negative to the corrosion potentials appearently represents the reducible form of tin oxide which was reduced when tin electrode was precathodized for 5 minutes at -900 mV (S.C.E.). Same situation was observed by Henry Leidheiser and A. Rauch (Leidheiser, et. al., 1981) in polarization of tin electrode in deaerated 0.33 M citric acid solutions.

Cathodic polarization curve in deaerated 10^{-1} M citric acid at pH 6 is shown in Figure (1) by curve (a). Cathodic polarization curve in 10^{-1} M citric acid at pH 6 obtained when tin electrode was precathodized for 5 minutes at -900 mV is shown in Figure (1) by curve (b). In (Fig. 2), (Fig. 3) and (Fig. 4) cathodic polarization curves in citric acid at pH 6 in concentration range of 10^{-1} M-10^{-4} M cathodic polarization curve in malic acid at pH 6 in concentration range of 10^{-1} M-10^{-4} M and cathodic polarization curves of glutamic acid at pH 6 in concentration region of 10^{-1} M-10^{-4} M are given respectively. Cathodic polarization curves in citric acid, malic acid and glutamic acid in the concentration range of 10^{-1} M-10^{-4} M at pH 2 are shown in (Fig. 5), (Fig. 6) and (Fig. 7) respectively.

Corrosion currents were obtained by extrapolating the cathodic polarization (Tafel line) to the predetermined steady state open circuit potential. The summary of the results obtained in citric acid, malic acid and glutamic acid at pH 6 and pH 2 are listed in Table 1 and Table 2 respectively. Corrosion currents in all acid solutions at pH 6 and pH 2

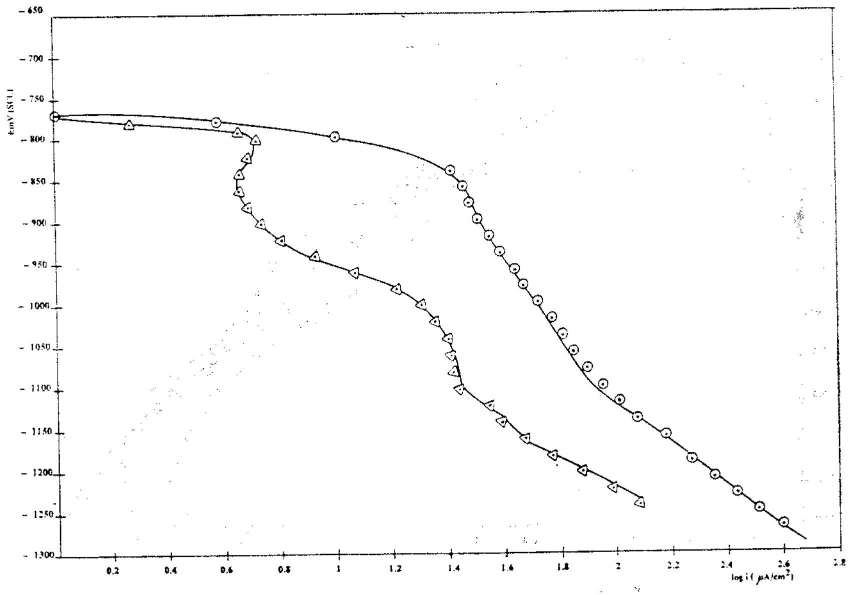


Figure 1. Cathodic polarization curves of tin in deaerated 10^{-1} M citric acid solutions at pH 6.

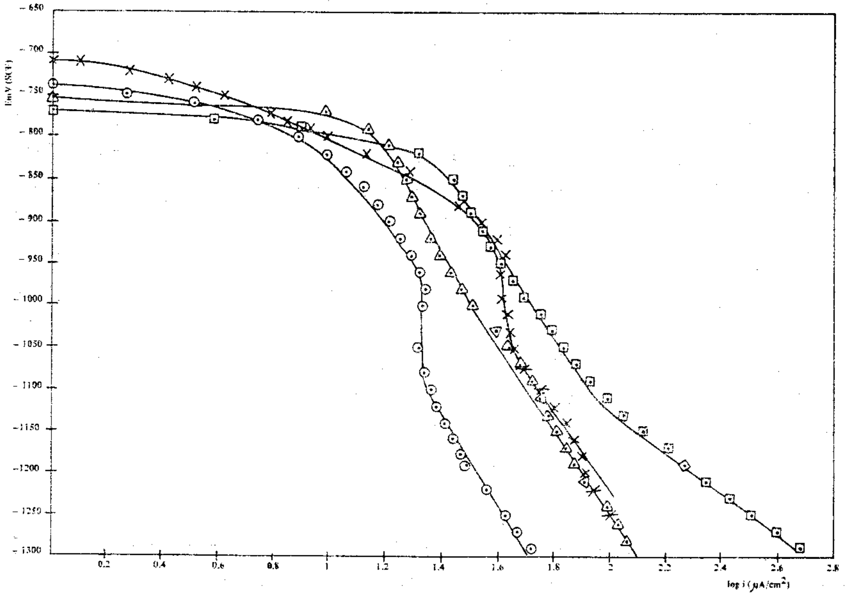


Figure 2. Cathodic polarization curve of tin in deaerated citric acid solutions at pH 6.
□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

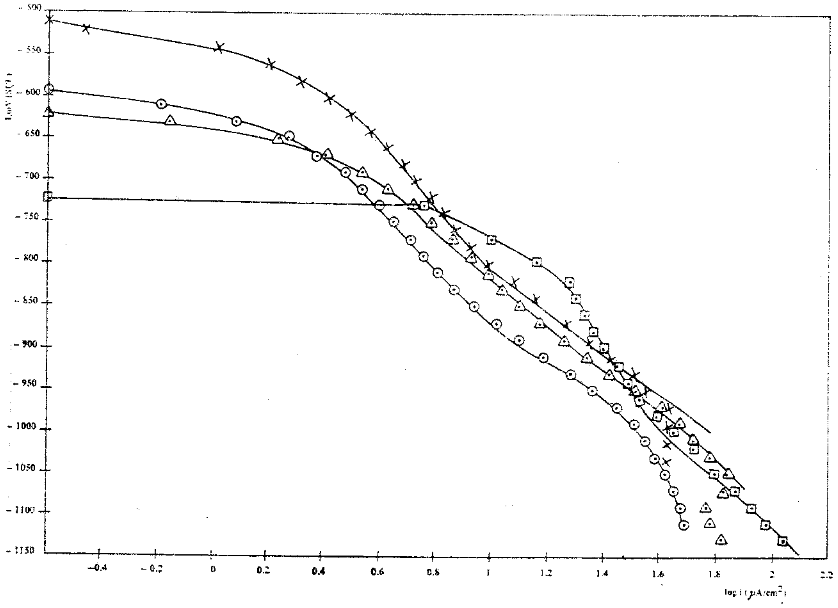


Figure 3. Cathodic polarization curve of tin in deaerated malic acid solutions at pH 6.
□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

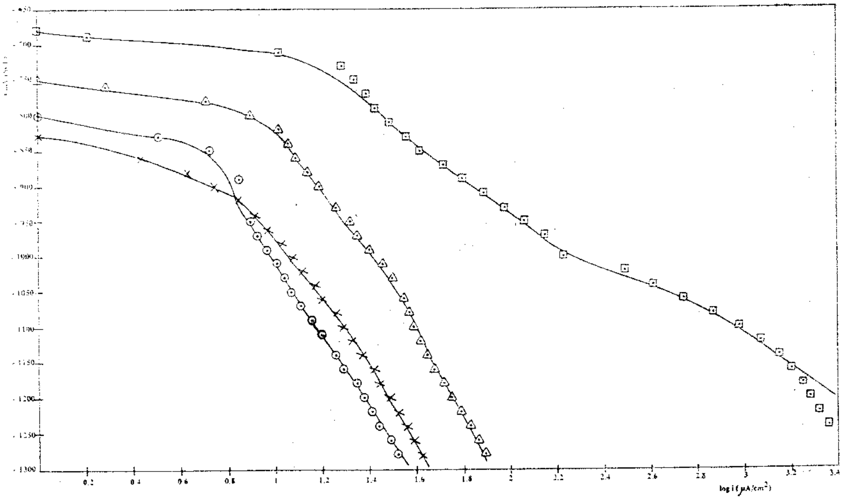


Figure 4. Cathodic polarization curve of tin in deaerated glutamic acid solutions at pH 6.
□ 10^{-1}M △ 10^{-2}M ○ 10^{-3}M × 10^{-4}M

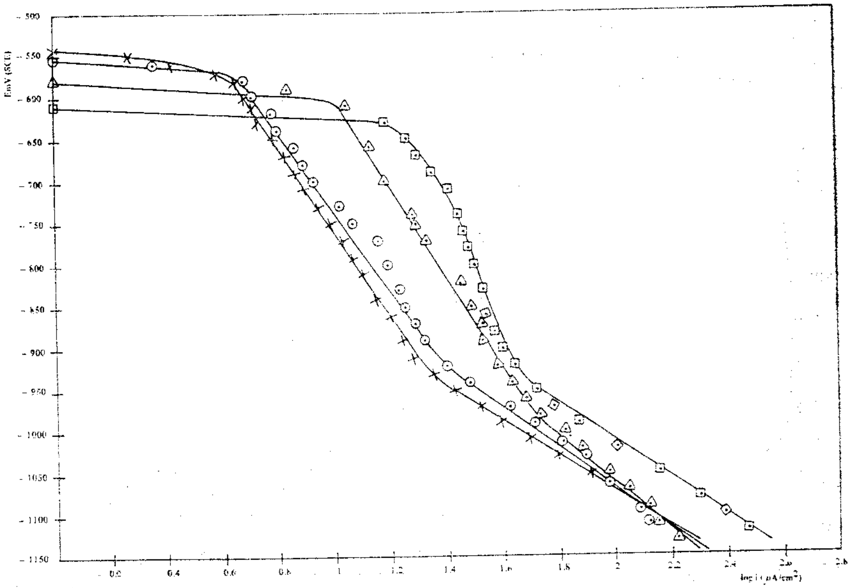


Figure 5. Cathodic polarization curve of tin in deaerated citric acid solutions at pH 2.
□ 10^{-1}M △ 10^{-2}M ○ 10^{-3}M × 10^{-4}M

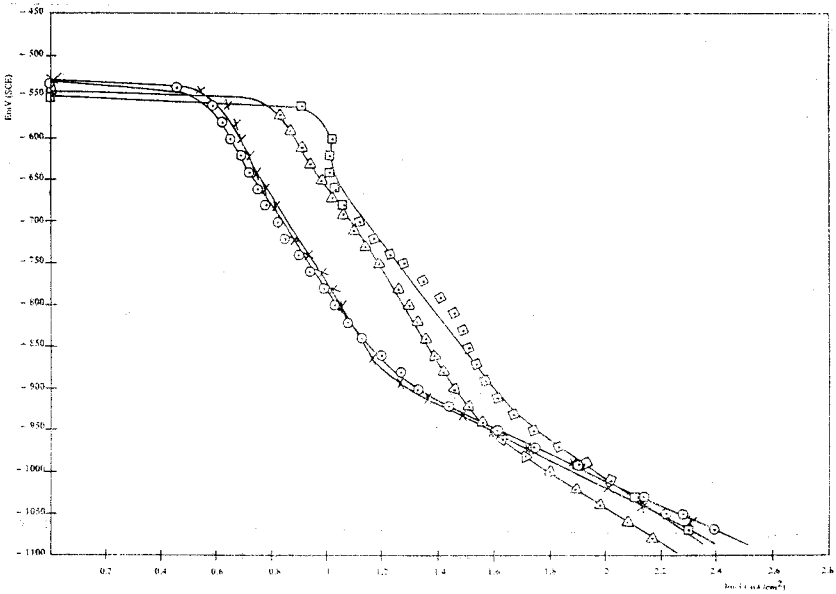


Figure 6. Cathodic polarization curve of tin in deaerated malic acid solutions at pH 2.
□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

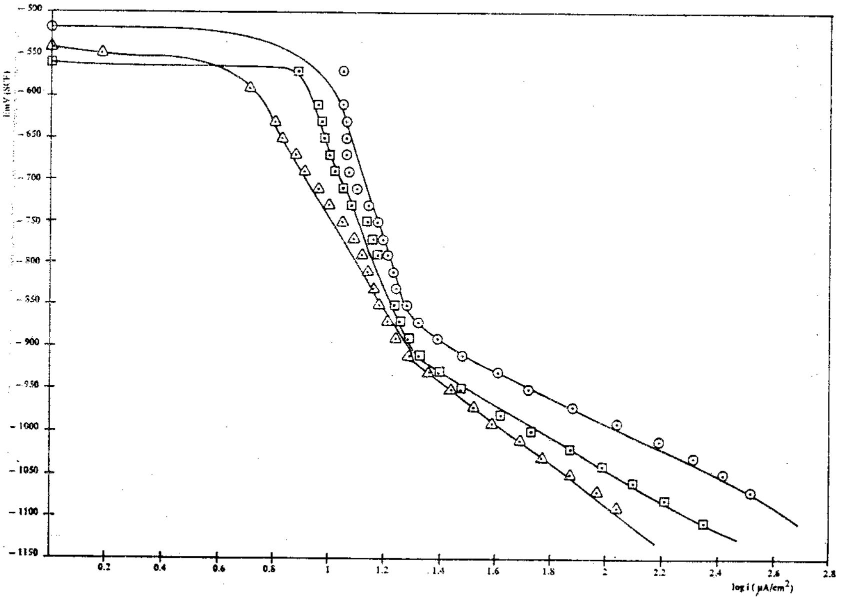


Figure 7. Cathodic polarization curves of tin in deaerated glutamic acid solutions at pH 2.
□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

Table 1. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid at pH 6.

Acid	Concentration (M)	Ecorr (mV)	Icorr (μA / cm^2)
Citric Acid	10^{-1}	-770	18.62
	10^{-2}	-755	13.80
	10^{-3}	-740	6.76
	10^{-4}	-695	1.99
Malic Acid	10^{-1}	-725	14.12
	10^{-2}	-620	3.71
	10^{-3}	-595	1.51
	10^{-4}	-510	1.32
Glutamic Acid	10^{-1}	-680	10.96
	10^{-2}	-750	6.61
	10^{-3}	-800	4.17
	10^{-4}	-830	4.16

Table 2. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid at pH 2.

Acid	Concentration (M)	Ecorr (mV)	Icorr (μA / cm^2)
Citric Acid	10^{-1}	-610	20.42
	10^{-2}	-585	10.00
	10^{-3}	-555	4.79
	10^{-4}	-545	3.80
Malic Acid	10^{-1}	-550	12.59
	10^{-2}	-545	6.02
	10^{-3}	-530	4.78
	10^{-4}	-525	3.89
Glutamic Acid	10^{-1}	-560	7.76
	10^{-2}	-545	4.26
	10^{-3}	-520	9.33
	10^{-4}	-510	not able to be computed

containing 10^{-3} M nitrate were obtained by polarization resistance method by taking value of $\beta=26$ mV. In the same way corrosion currents in all acid solutions at pH 6 and pH 2 containing 10^{-3} M nitrite were obtained by polarization resistance method taking value of $\beta=26$ mV. Attempts were made to obtain typical Tafel line by cathodic polarization in acid solutions containing nitrate or nitrite by precathodization period of 5 minutes at -900 mV. But there was no success. The curves had the shape of cathodic passivity curve described previously by Clarke and Bernie (Clarke and Bernie, 1967), The tentative interpretation of this behaviour is that at potential up to approximately 200 mV negative of the corrosion potential the surface of tin is partially covered with a tin oxide resulting from the oxidizing character of nitrate and nitrite.

Corrosion currents in acid solutions at pH 6 and pH 2 containing 10^{-3} M nitrate or nitrite are given in Table (3), Table (4), Table (5),

Table 3. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid Solutions Containing 10^{-3} M $NaNO_3$ at pH 6.

Acid	Concentration (M)	Error (mV)	Icorr (μA / cm^2)
Citric Acid	10^{-1}	-760	19.07
	10^{-2}	-750	13.6
	10^{-3}	-760	5.2
	10^{-4}	-685	2.23
Malic Acid	10^{-1}	-760	16.40
	10^{-2}	-770	5.77
	10^{-3}	-745	3.28
	10^{-4}	-735	3.58
Glutamic Acid	10^{-1}	-780	8.84
	10^{-2}	-840	10.00
	10^{-3}	-820	3.50
	10^{-4}	-825	6.00

Table 4. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid Solutions Containing 10^{-3} M $NaNO_3$ at pH 2.

Acid	Concentration (M)	Ecorr (mV)	Icorr (μA / cm^2)
Citric Acid	10^{-1}	-600	35.36
	10^{-2}	-575	24.96
	10^{-3}	-550	20.8
	10^{-4}	-510	8.91
Malic Acid	10^{-1}	-530	60.00
	10^{-2}	-515	46.43
	10^{-3}	-495	31.20
	10^{-4}	-470	23.26
Glutamic Acid	10^{-1}	-510	82.20
	10^{-2}	-450	68.25
	10^{-3}	-430	40.86
	10^{-4}	-425	35.75

Table 5. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid Solutions Containing 10^{-3} M KNO_2 at pH 6.

Acid	Concentration (M)	Ecorr (mV)	Icorr (μA / cm^2)
Citric Acid	10^{-1}	-770	10.00
	10^{-2}	-750	12.29
	10^{-3}	-740	5.72
	10^{-4}	-650	1.25
Malic Acid	10^{-1}	-760	19.76
	10^{-2}	-785	6.42
	10^{-3}	-825	5.20
	10^{-4}	-820	3.80
Glutamic Acid	10^{-1}	-850	5.81
	10^{-2}	-820	6.12
	10^{-3}	-790	4.04
	10^{-4}	-810	5.2

Table (6) respectively. Typical linear current potential curves for these solutions are given in (Fig. 8) and (Fig. 9) respectively.

Table 6. Corrosion Potentials and Corrosion Currents for Tin in Citric Acid, Malic Acid and Glutamic Acid Solutions Containing 10^{-3} M KNO_2 at pH 2.

Acid	Concentration (M)	Ecorr (mV)	Icorr (μA / cm²)
Citric Acid	10^{-1}	-555	60.66
	10^{-2}	-525	91.00
	10^{-3}	-490	83.20
	10^{-4}	-480	80.00
Malic Acid	10^{-1}	-530	75.83
	10^{-2}	-510	52.00
	10^{-3}	-490	32.12
	10^{-4}	-475	17.79
Glutamic Acid	10^{-1}	-530	110.5
	10^{-2}	-480	64.00
	10^{-3}	-460	72.22
	10^{-4}	-430	50.14

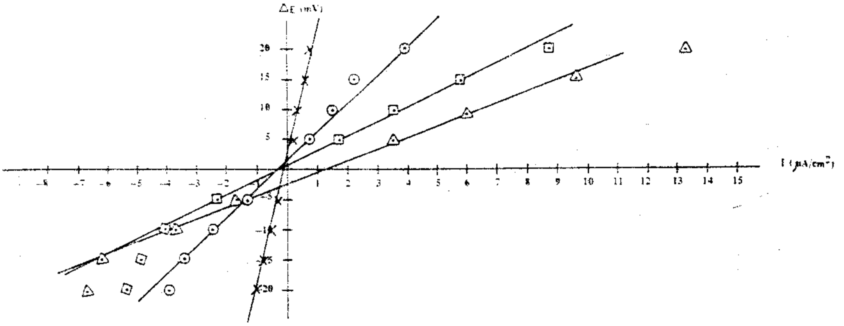


Figure 8. Linear polarization curves in deaerated citric acid solutions containing 10^{-3}M nitrite at pH 6.

□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

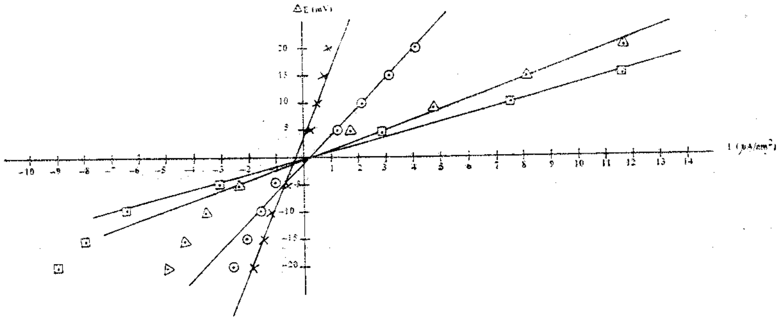


Figure 9. Linear polarization curves in deaerated citric acid solutions containing 10^{-3} M nitrate at pH 6.

□10^{-1}M △10^{-2}M ○10^{-3}M ×10^{-4}M

Plots of corrosion potentials as a function of the logarithm of acid concentrations are shown in (Fig. 10), (Gig. 11), (Fig. 12) for citric acid, malic acid and glutamic acid respectively. At pH 6 and pH 2 linear relationship holds between corrosion potentials and logarithm of the acid concentrations. Except foı glutamic acid at pH 6 corrosion potentials are shifted towards more negative values with the increasing of acid concentrations. For glutamic acid at pH 6 change of corrosion potential towards more positive values signifies the film foımation (Evans, 1968). This film formation is probably resulted from the hydıolysis of glutamic acid-tin complex near the neutral solutions (Shrier, 1977). Shifting towards more negative values in corrosion potential with increasing acid

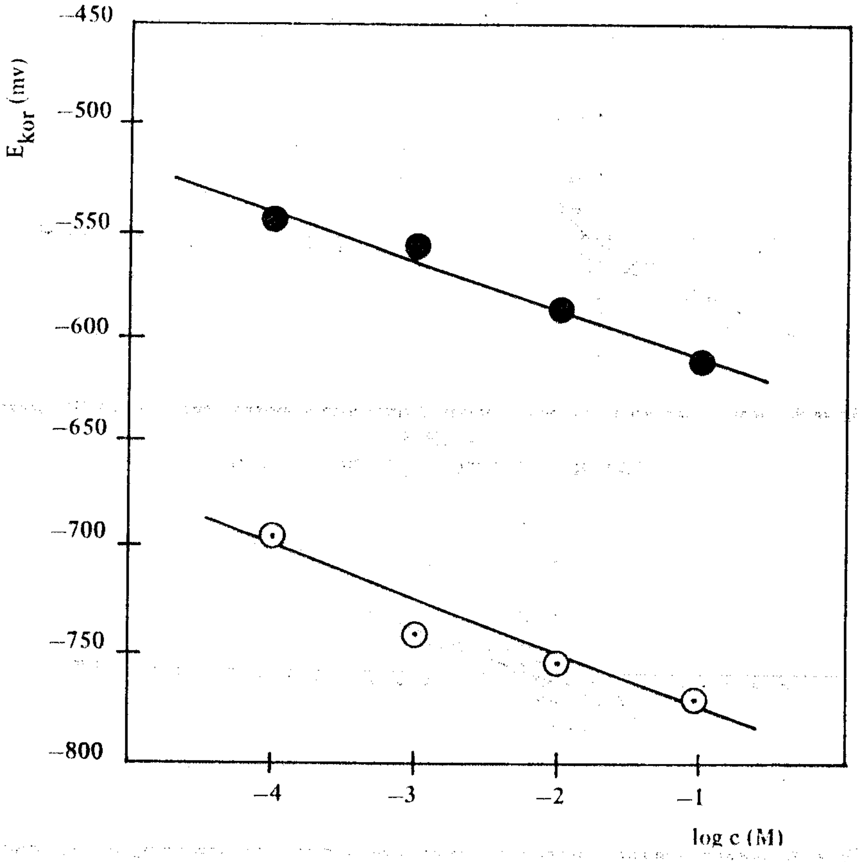


Figure 10. The variation of corrosion potentials with the logarithm of citric acid concentrations.
●pH2 ○pH 6

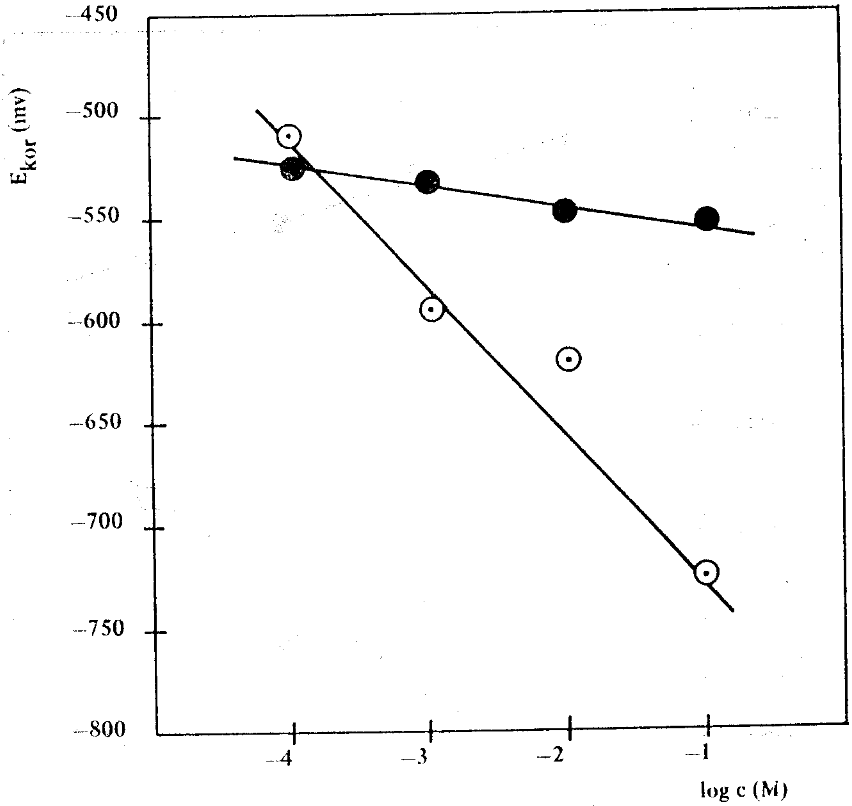


Figure 11. The variation of corrosion potentials with the logarithm of malic acid concentr t ons.
●pH2 ○pH 6

concentration at pH 6 and pH 2 in citric acid and malic acid accompanied by simultaneous increase in the corrosion rate of tin. All these results suggest that the corrosion of tin in these solutions is anodically controlled (Gouda, et., el., 1981).

In glutamic acid at pH 2 there was not regular increase in corrosion currents with increasing of acid concentration. This disagreement may be due to competition between the film formation and complex formation effect of glutamic acid.

Citric acid has the following structure and might act as tetradentate ligand towards Sn^{2+} ion.

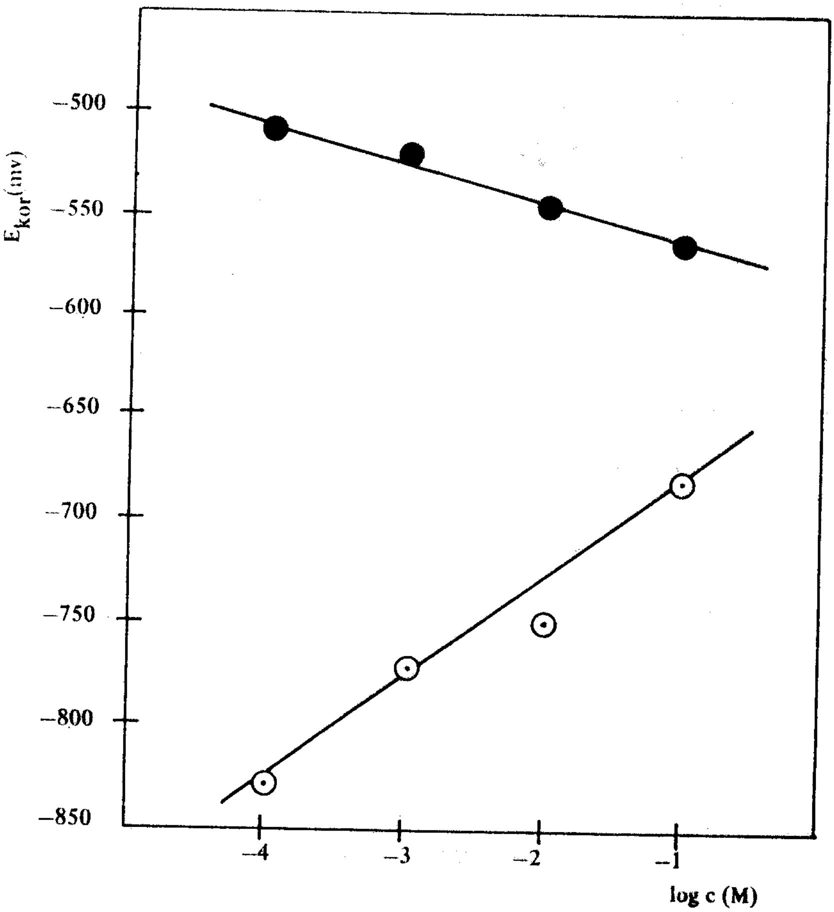
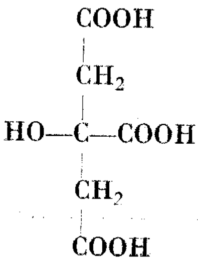


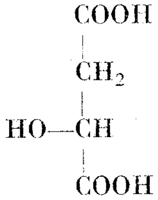
Figure 12. The variation of corrosion potentials with the logarithm of glutamic acid concentrations.

●pH 2 ○pH 6



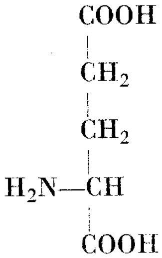
$$\begin{array}{c} COOH \\ | \\ CH_2 \\ | \\ HO-C-COOH \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

While malic acid has the following structure which acts as tridentate ligand (Smith, 1961). It has been suggested that tin Sn^{2+} is four-coordinated in certain chelates and p^3d hybrid orbitals are involved in bonding (Smith, 1961).



$$\begin{array}{r@{}l} & COOH \\ & | \\ & CH_2 \\ & | \\ HO— & CH \\ & | \\ & COOH \end{array}$$

Thus citric acid forms 1:1 chelates while malic acid forms $Sn(H_2O)$ L type complexes. That is three of the four sites around the central metal ion are occupied by malic acid fourth side by water. Certainly citric acid forms more stable complex. On the other hand glutamic acid acts as tridentate ligand towards Sn^{2+} and has the following structure.



$$\begin{array}{r@{}l} & COOH \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ H_2N— & CH \\ & | \\ & COOH \end{array}$$

Difference between malic acid and glutamic acid is that two electron rich groups are separated by two $-CH_2$ group this might cause the tin-glutamic acid complex to be less stable than tin-malic acid complex. In addition amine groups has inhibition action for many metals (Hluchan, et al. 1988). Corrosion rate of tin in three acid solution in 10^{-1} M concentration is as follows

citric acid $>$ malic acid $>$ glutamic acid

This order is parallel of stability order to tin-acid complex. As it is seen from Table (1), Table (3) and Table (5) increase in corrosion rate by the addition of nitrite or nitrate in citric acid, malic acid, glutamic acid at pH 6 is not as much to be considered. These results are consistent with the corrosion rate of tin plated can in organic acid containing nitrite or nitrate at pH 6 which the corrosion rates were determined by solution analysis (Farrow et al., 1970).

But addition of 10^{-3} M nitrate or nitrite to the different concentration of citric acid, malic acid and glutamic acid at pH 2 incerases corrosion rate of tin very much as it is seen in Table (2), Table (4) and Table (6). Acceleration effect of nitrate or nitrite in organic acid for the corrosion of tin may be due to electron accepting effect of nitrite or nitrate when tin dissolves. In this way, nitrite or nitrate increases the rate of cathodic reaction, thus corrosion rate.

Electron accepting reactions of nitrate or nitrite are the followings and occur in acidic solutions.

$$NO_3^- + 3H^+ + 2e^- \rightleftarrows HNO_2 + H_2O$$

$$NO_3^- + 4H^+ + 3e^- \rightleftarrows NO + 2H_2O$$

$$HNO_2 + H^+ + e^- \rightleftarrows NO + H_2O$$

$$NO_3^- + 10H^+ + 8e^- \rightleftarrows NH_4^+ + H_2O$$

Reduction of nitrate to nitrite is slow and is the rate determining step. But reduction of nitrite to ammonia is very rapid. That is why corrosion rate is higher in nitrite containing solutions.

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