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CORROSION BEHAVIOUR OF TIN IN CARBOXYLIC ACID SOLUTIONS CONTAINING NO_2^-, NO_3^- AND Cl^- ANIONS AT DIFFERENT pH VALUES

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The corrosion behaviour of pure tin in deaerated solutions of oxalic, tartaric and citric acids in the presence and absence of NO_2^-, NO_3^- and Cl^- anions were studied by means of potential-time measurements, corrosion rate and galvanostatic technique at the pH range 2.5 - 6.5 for 0.1 M of the three tested acids. At pH 4.5 there is a maximum negative potential for oxalic acid and at pH 5.5 for tartaric and citric acids. From pH 2.5 to 4.5, the corrosion mechanism is anodically controlled by the reaction of Sn^{+2} ion with the anion of the tested acids. At pH 5.5 the corrosion of tin is reduced which may be due to the formation of a film on the tin electrode resulting from the hydrolysis of tin complex species. The potential of the tin electrode in the three tested acid solutions tends to be shifted to the less negative values in the presence of additives NO_2, NO_3 and Cl anions at pH 4.5.

Key words: Corrosion, Tin, Carboxylic acids, NO_2^-, NO_3^- and Cl^- additives.

Introduction

It was suggested [1] that anions can contribute both to the destruction of oxide films on metals and to the passivation process in which the oxide film is stabilized. Mao and Hoare [2] studied the anodic dissolution in solutions containing both Cl^- and NO_3^- anions, and they found that Cl^- ions produce localized dissolution of the passive film formed in the presence of NO_3 ions. Willey [3] showed that increasing the pH of the medium from 3 to 5 is accompanied by an increase of the corrosion action of organic acids on tin.

The aim of this present paper was to study the effect of NO_2^-, NO_3^- and Cl^- ions on corrosion behaviour of tin in solutions of oxalic, tartaric and citric acids. Some of the acids commonly present in canned foods, possibly, have an important bearing on the corrosion of tin coating [4]. The steady-state galvanostatic technique was used in the study. It was found that vibration increases the corrosion of tin [5].

Experimental

The electrodes used (one centimeter long and 0.7 cm in diameter) were in the form of spectroscopically pure tin rods (99.99%, Johanson and Matthey, London). Electrode surface was prepared as previously described [6].

The potential of the tin electrodes, immersed in 0.1 M of the test solutions, was followed as function of time by means of a manual potentiometer (WAP 0.1% Type P 30, England) versus a saturated calomel electrode (SCE).

Measurements were carried out until a steady state potential value was reached at 30°C at different pH values from 2.5 to 6.5.

Solutions of oxalic, tartaric and citric acids (0.1 M) were prepared from the Analar reagents and doubly distilled water and were deaerated by passing O_2^- free nitrogen through the solutions for at least 5 hr before the electrode was introduced into the cell.

In order to test the effect of NO_2^-, NO_3^- and Cl^- ions on the corrosion behaviour of tin in the carboxylic acid solutions, increments of concentrated solutions of $NaNO_2$, KCl and KNO_3, respectively, ranging from 10^{-4} to 10^{-1} M, were added to the tested acid solutions. The pH values were adjusted to 4.5 by addition of a NaOH solution.

The details of the cell used in the present investigation were described earlier [7]. The cathodic polarisation curves were obtained using a simple galvanostatic technique in the absence (blank) and in the presence of NO_2^-, NO_3^- and Cl^- at 30°C. Potentials were measured using a platinum counter electrode and an SCE as reference. The tin electrodes were cathodically polarised using a constant device (Type Leybold-Germany) using a saturated calomel electrode with a fin Luggin capillary tube position close to the electrode surface in order to minimize ohmic potential drop. Several runs were taken for each set of experiments.

Results and Discussion

Potential-time measurements. The open circuit potentials of tin in 0.1 M oxalic, tartaric and citric acid solutions of pH 2.5 - 6.5 were followed as a function of time till the steady state values were attained as shown in Fig. 1-3.

It is clear from Fig. 1-3 that the corrosion potential of tin shifts to the negative direction as the pH values changed from

2.5 to 4.5 and then shifted to noble direction when the pH changed from 5.5 to 6.5 in the case of oxalic acid solution. Similar results were also obtained for citric and tartaric acid, where the potential shifts to the negative direction as the pH changed from 2.5 to 5.5 and then shifted to less negative values when the pH increases to 6.5. It is clear that there is an initial negative fall in the potential after a few minutes of immersion depending on the pH values.

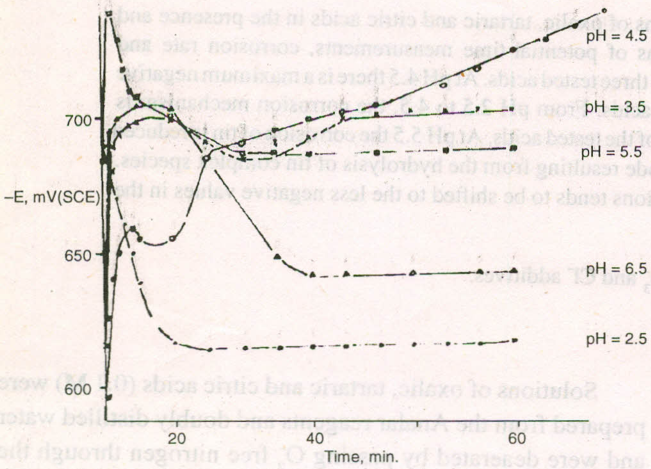

Fig. 1. Relation between potential and time for tin in 0.1M oxalic acid solution at different pH values.

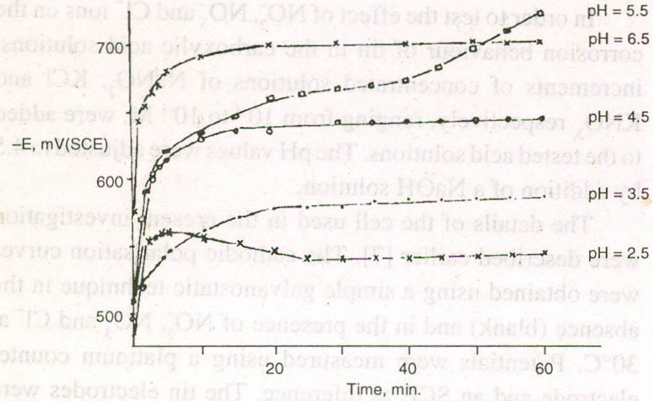

Fig. 2. Relation between potential and time for tin in 0.1M citric acid solution at different pH values.

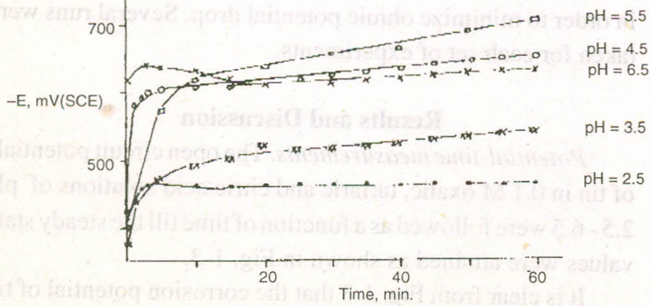

Fig. 3. Relation between potential and time for tin in 0.1M tartaric acid solution at different pH values.

This behaviour may be due to the formation of tin complexes with the tested acid anions as ligands; the following formula:

$$\begin{array}{ll} \mathrm{Sn}^{+} \xrightarrow{\hspace{3cm}} & \mathrm{Sn}^{++} + 2\,\bar{e} \\ & \ \downarrow\uparrow \\ & \mathrm{Sn}^{+2}\,(L) \end{array} \qquad L = \text{complexing ligand}$$

will diminish the concentration of Sn^{++} leading to a decrease in the tin potential. Change of pH from 5.5 to 6.5 leads to a change in the corrosion behaviour of tin, the potential values of which may be attributed to the pre-immersion oxide film on tin electrode, is healed to a decrease in the anodic area. Inhibition increases at high pH values.

Concentrations of complex species and free metal ions were determined by using double-beam optical atomic absorption spectrometers of Perkin - Elmer Model 303.

The steady-state corrosion potentials of tin, E_{corr} attained after one hour of immersion in the solutions of three tested acids in the absence and presence of NO_2^-, NO_3^- and Cl^- ions in the concentration range of 10^{-4}-10^{-1} M are given in Table 2.

From Table 1, it is clear that at pH 6.5 there is a decrease in the complex species of metal ions. Thus, reduce of the potential of electrode (Table 2) is due to the decrease of Sn^{++} ion concentration.

From the data in Table 2, E_{corr} for tin in solutions of pure acids decreases in the order: oxalic >citric >tartaric acid, which follow the same sequence of stability constants of tin chelates [8]. The relatively high negative values of E_{corr} in oxalic solution (Table 2) is attributed to the higher stability of $Sn(OX)_2$ complex species compared to those of citric or tartaric (Table 1). The results obtained in the presence of Cl ion from 10^{-4} to 10^{-1} M indicate that E_{corr} in all acids examined is

TABLE 1. CONCENTRATION OF FREE AND COMPLEXED TIN SPECIES IN OXALIC, CITRIC AND TARTARIC ACID SOLUTIONS.

Acid concentration	pH	Free tin (mole/l)	Tin complex $Sn\ (complex)_2$ mole/l
0.1 M Oxalic	2.5	4.06×10^{-13}	1.62×10^{-7}
	4.5	1.45×10	3.59×10^{-7}
	6.5	3.80×10^{-18}	5.98×10^{-8}
0.1 M Citric	2.5	6.08×10^{-13}	1.53×10^{-7}
	4.5	4.99×10^{-14}	5.78×10^{-8}
	6.5	3.60×10^{-14}	4.88×10^{-8}
0.1 M Tartaric	2.5	3.45×10^{-10}	8.03×10^{-8}
	4.5	3.32×10^{-11}	1.09×10^{-7}
	6.5	5.07×10^{-12}	4.72×10^{-8}

shifted to less negative direction for each acid. This may be attributed to the attack of oxide film by Cl^- which will depress the potential of tin followed by film repair via precipitation of the insoluble complex species Sn(OH)Cl (in which the Cl^- forms very sparingly soluble basic salts of the type Sn (Cl) OH). There are also displacement reactions between SnL and Cl.

$$Sn_2L + 2\,Cl^- \longrightarrow Sn_2Cl + 2\,L^-$$

At lower concentration of Cl^- ion (10^{-4}M), it has a dissolution action on the oxide film formed on tin [2].

The effect of NO_3^- ions on the corrosion potential of tin in the carboxylic acids examined, is approxi. similar to that of Cl^- (nitrate is not normally an inhibitor for tin in citric acid). The mere shift of corrosion potential to a more positive value does not necessarily indicate inhibition because a relative increase in the cathodic half reaction could produce the same effect and would in fact be associated with an increase in corrosion thus nitrate usually aggravates detinning in canned foods.

The inhibitive action of nitrate ions can be ascribed on its ability to penetrate the oxide layer and oxidatively maintain the inner barrier layer [9]. The partially aggressive character of NO_3^- ions was assumed to be related to a possible reduction of nitrate ions [10]. Gouda *et al.* [11] found that nitrite ions behave bifunctionally promoting corrosion at high dilution and stifling it in moderately concentrated solutions by forming a stable precipitate.

The function of NO_2^- anion as inhibitor is to block the pores in the oxide film. Accordingly, the passive potential is most probably due to the high resistance [12] in the pores of oxide film (anodic area) which leads to a very low current density at the cathodes.

TABLE 2. CORROSION POTENTIAL OF TIN IN DEAERATED 0.1 M CARBOXYLIC ACID SOLUTIONS IN THE PRESENCE OF Cl^-, NO_3^- AND NO_2^- AT PH 4.5.

Anion	Concentration mole/l	Oxalic -E, mV(SCE)	Citric -E, mV(SCE)	Tartaric -E, mV(SCE)
Cl^-	0	740	685	625
	1×10^{-4}	735	640	575
	1×10^{-3}	726	635	572
	1×10^{-2}	723	630	568
	1×10^{-1}	710	628	565
NO_3^-	1×10^{-4}	735	685	620
	1×10^{-3}	732	678	616
	1×10^{-2}	730	678	616
	1×10^{-1}	720	665	613
NO_2^-	1×10^{-4}	717	645	632
	1×10^{-3}	698	641	620
	1×10^{-2}	674	640	613
	1×10^{-1}	665	639	610

In the presence of tartaric acid solution, results obtained for both the NO_2^- and NO_3^- ions reveal the remarkable low influence of either nitrate or nitrite ions (within the concentration range 10^{-4}-10^{-1} M); this may be attributed to the presence of a compact barrier oxide layer and/or strongly adsorbed tartrate ions [13].

From the relation between steady-state potential values and pH of the tested acid solutions (Fig.4), the slopes were found to be -50, - 48, -45 mV for oxalic, citric and tartaric acids, respectively, in the pH range 2.5 - 4.5 which is in agreement with the results of Willey [14]. The decrease in the (b) values seems to be related to the decrease in aggressiveness of the acids (i. e. a decrease in its corrosive function).

Polarization technique. Galvanostatic cathodic polarization of tin was measured in different acid solutions. Fig 5 shows the results of polarization for tin in oxalic acid, as an example, in the absence of additives at different pH values. The corrosion current was obtained by extrapolating the cathodic Tafel line to the predetermined steadystate open circuit potential. Table 3 represents the results. From these results, it was found that corrosion current increases with the increasing pH values to 4.5, then decreases at higher pH values. The decrease in i_{corr} at pH 6.5 may be due to film formation on the electrode surface in near neutral solutions which may result from the hydrolysis of tin complex [13]. At

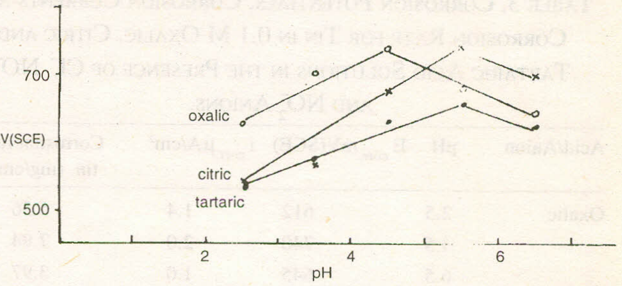

Fig. 4. Relation between potential and pH for tin in oxalic, tartaric and citric acid solutions.

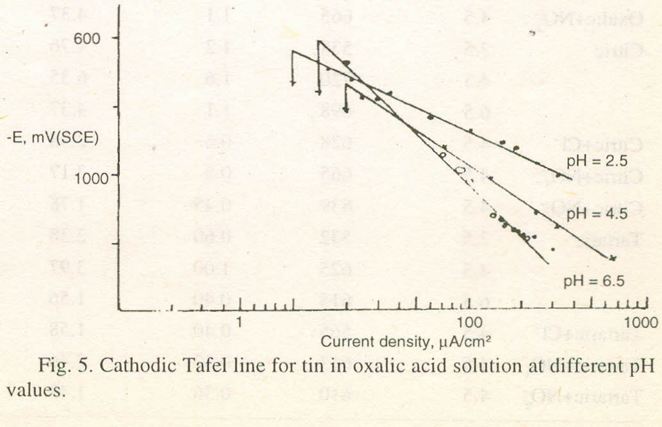

Fig. 5. Cathodic Tafel line for tin in oxalic acid solution at different pH values.

pH 2.5 - 4.5 the corrosion mechanism is mainly under anodic control as discussed before.

Rate of corrosion measurements. The corrosion rate of tin metal in 0.1 M oxalic, citric and tartaric acid in the presence and absence of Cl,$^-$ NO_3^- and NO_2^- were calculated from the polarization results. The corrosion current $i_{corr.}$ measurement can be converted to the rate of corrosion data. To determine the rate of corrosion, based on corrosion current measurement, the following equation can be used:

$$i_{corr.} = 0.96 \times (W) \quad ....(1)$$

where $i_{Corr.}$ is the corrosion current, ($\mu A/cm^2$) and W is the corrosion rate in $mg/cm^2/hr$ which can be calculated over a period of hours [15].

The results are present in Table 3. The corrosion rate increases from pH 2.5 to 4.5 then decreases again. In the presence of NO_2^-, NO_3^- and Cl^- ions, the corrosion rate decreases which may be due to the pre-immersion oxide film on tin electrode, is healed and this leads to a decrease in the anodic areas and consequently to a decrease in the corrosion rate. The corrosion rate of tin in the presence of Cl^-, NO_2^- and NO_3^- anions indicate that all anions reduce the corrosion rate in the order $NO_2^- > Cl^- > NO_3^-$.

The higher corrosion rate for tin in the oxalic acid solution compared to those obtained in the citric and tartaric acids at the same pH values can be attributed to the higher porosity of oxide film formed in the oxalic acid [16]. Goulding [14] found that in the presence of tartrate and citrate in near neutral solutions, a compact oxide layer (barrier type) is formed while the presence of oxalate allows some anodic dissolution resulting in the formation of porous oxide layers. On the other hand, higher stability of the formed soluble oxalate complexes may lead to an increase in the corrosion rate. Decrease in the corrosion rate with increase in the pH of solutions suggest that the corrosion process is controlled by H^+ ions discharge (cathodic control).

TABLE 3. CORROSION POTENTIALS, CORROSION CURRENTS AND CORROSION RATE FOR TIN IN 0.1 M OXALIC, CITRIC AND TARTARIC ACID SOLUTIONS IN THE PRESENCE OF Cl^-, NO_3^- AND NO_2^- ANIONS.

Acid/Anion	pH	$-E_{corr.}$ mV(SCE)	$i_{corr.}$ $\mu A/cm^2$	Corrosion rate of tin ($mg/cm^2/hr$)
Oxalic	2.5	612	1.4	5.56
	4.5	740	2.0	7.94
	6.5	645	1.0	3.97
Oxalic+Cl^-	4.5	710	1.2	4.76
Oxalic+NO_3^-	4.4	720	1.6	6.35
Oxalic+NO_2^-	4.5	665	1.1	4.37
Citric	2.5	538	1.2	4.76
	4.5	720	1.6	6.35
	6.5	698	1.1	4.37
Citric+Cl^-	4.5	628	0.6	2.38
Citric+NO_3^-	4.5	665	0.8	3.17
Citric+NO_2^-	4.5	639	0.45	1.78
Tartaric	2.5	532	0.60	2.38
	4.5	625	1.00	3.97
	6.5	615	0.40	1.56
Tartaric+Cl^-	4.5	565	0.40	1.58
Tartaric+NO_3^-	4.5	613	0.62	2.46
Tartaric+NO_2^-	4.5	610	0.36	1.43

From Fig. 6, values of $di_{corr.}$ / d pH are 0.34, 20 and 0.17 for oxalic, citric and tartaric acid respectively.

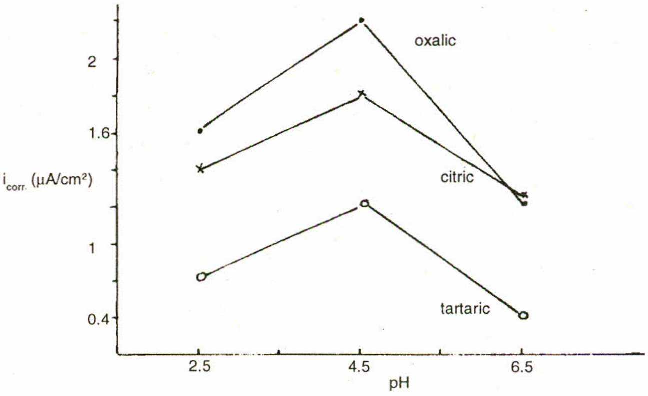

Fig. 6. Relation between d $i_{corr.}$ /d pH for tin in oxalic, citric and tartaric acid solutions.

Conclusion

The corrosion mechanism is anodically controlled by the reaction of Sn^{++} with anion of the tested acids. At pH 4.5 there is a maximum negative potential; the potential of the tin electrode in all tested acid solutions shifted to less negative direction in the presence of chloride, nitrate and nitrite at pH 4.5.

References

1. D. M. Brasher, Br. Corros. J., **4,** 122 (1969).
2. K. Mao and J. P. Hoare, Corros. Sci., **13,** 799 (1973).
3. A. R. Willey, Br. Corros. J., **7,** 29 (1972).
4. S. C. Britton, *Tin Versus Corrosion,* I. T. R. I. Pub. No. 510, September (1975), pp. 35.
5. S. M. Abd El-Wahaab and G.K. Gomma, Communication de La Des Science De L'Universite D'Ankara, **31,** 183 (1985).
6. G. K. Gomma, J. Indian Chem. Soc., **70,** 31 (1993).
7. G. K. Gomma, J. Indian Chem. Soc., **70,** 130 (1993).
8. J. Inczedy, *Analytical Applications of Complex Equilibria* (Horwood, Chichester, 1976).
9. S. T. Hirozawa, International Conference on Corrosion

Inhibitors, Dallas, Paper No.15 (1983).

10. A. M. Mckissick, A. A. Adams and R. T. Foley, J. Electrochem. Soc., **117,** 1459 (1970).
11. V.G. Gouda, M. G. Akhedr and A. M. Shams El-Din, Corros. Sci., **7,** 221 (1967).
12. M. Cohen, Corrosion, **9,** 732 (1943).
13. L. L. Shrier, *Corrosion* (Butter Worth, London, 1977), Vol. I, Ch. 4, pp. 143.
14. R. M. Hudson and T. J. Warning, Corros. Sci., **17,** 577 (1977).
15. J.W. Diggle and M. Dekker, *Oxides and Oxide Films* (INC., New York, 1973), pp. 174, 176, 188,199, 226.
16. J. W. Diggle, T. C. Downic and C. W. Goulding, Chem. Rev., **65,** 365 (1969).