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Pitting Corrosion of Tin in Halogen Ions-Inhibition Using Organic Carboxylates

A. M. EL-KOT*, A. ABD EL-AAL and A. GHUZZA

Chemistry Department, Faculty of Science
Zagazig University, Zagazig, Egypt

A systematic study of the pitting corrosion on tin metal by halogen ions Cl^-, Br^- and I^- was carried out in sodium carbonate solutions. The strongest depassivating effect of Cl^- ions than Br^- and I^- ions was ascribed to the larger adsorbability of the Cl^- ion and thus its forming surface complex species by the overlapping of the chloride ion and the metal orbitals. Also the inhibition of the pitting corrosion of tin electrode using some organic carboxylates has been investigated. The inhibition of tin in 0.05 M Na_2CO_3 + 0.04 M NaCl increases in the order:

formate < acetate < succinate < tartrate < citrate.

INTRODUCTION

Since carbonate is a major constituent of natural water it is important to study its effect on the corrosion behaviour of tin. Although the anodic passivation of tin in alkaline solutions has been the subject of frequent investigations[1,2], it is well established that tin becomes passive at sufficiently anodic potential and very little work has been done on breakdown and pitting attack of the passive film. The formation and development of this type of attack on a metal surface can occur only in solutions containing the aggressive anions, Cl^-, Br^-, and I^-. Different authors seem also to disagree about the anodic behaviour of tin in the presence of Cl^- ions[3,4]. Hoar *et al.*[5] assumed that the initiation of pits might be due to the adsorption of aggressive anions on the surface of the oxide film followed by the penetration of ions through the film. The critical potential at which pitting is initiated is reported by several authors and found to depend on a number of factors including type and concentration of the attacking anions, type of metal used, presence and relative concentration of other anions and also on temperature[6]. However, Shams El-Din *et al*[7] have used four different techniques to prove the occurrence of pitting corrosion on tin surface by Cl^- ions. In the present study, systematic studies of the initiation of pitting corrosion on tin surface by halogen ions Cl^-, Br^- and I^- were carried out. The inhibition of the pitting corrosion using some alkali metal carboxylic acid salts was also investigated.

EXPERIMENTAL

The electrolytic cell was of pyrex glass with a thermostating jacket and has a capacity of 250 ml. Seven ground glass standard joints on top of the cell permitted the insertion of the working electrode, the counter electrode compartment, the reference electrode compartment, gas inlet and gas outlet, while the remaining two joints were used for insertion of a thermometer, and for filling the cell when needed. The working tin electrode was high purity 99.999% (Aldrich Chemical Company, Inc.). The metallic impurity analysis (ppm) is Si : 5, Fe : 3 and Mg : 0.7. It was fixed to pyrex glass tubings with araldite so that the total exposed surface area was 0.283 cm^2. Electrical contact was achieved through thick copper wire soldered to the end of the rods, not exposed to the solution. Before being used the electrode was abraded, successively, with 1-, 0-, 00-grade emery paper and then degreased with acetone. Silver/silver chloride electrodes were used as reference electrodes. All measurements were made under potentiostatic control using a wenking potentiostat (L.B. 75), and a wenking voltage scan generator (BSG 72) was used to provide a linearly increasing or decreasing control voltage input to the potentiostat. The current density-potential curves were recorded on X-Y recorder type (Linseis LY. 21 Cole Parmor Instrument U.S.A.). The electrolyte solutions were refluxed under prepurified nitrogen gas for six hrs prior to an experimental run. All experiments were carried out at room temperature (25 ± 0.5°C) using ultrathermostat model (1268-02).

RESULTS AND DISCUSSION

The potentiodynamic anodic polarization curves were carried out for Sn electrode in 5×10^{-1} M, 1×10^{-1} M, and 5×10^{-2} M Na_2CO_3 solution at a sweep rate of 10 mV/sec upon the addition of increasing concentrations of Cl^- ions (Fig. 1). In the absence of the aggressive agent, two oxidation peaks are recorded. The current then decreases to low values, which extend over a potential range of *ca.* 1.0 V. This corrosion current is used in the healing of defects in the oxide film brought about by chemical attack of the metal by the electrolyte. Finally, the current increases with the potential due to the transpassive region following by oxygen evolution on the passive electrode.

Addition of Cl^- ions up to a certain concentration which depend on the electrolyte bulk concentration has practically no effect on the dissolution of the passive state on the metal surface. The dissolution current density flowing along the first two anodic oxidation peaks is slightly decreased with the increase in the Cl^- content with the slight shift of the peak potential to the active direction, indicating that the presence of these ions inhibit the anodic dissolution of tin in sodium carbonate solution. The inhibitive function of Cl^- ions on the anodic dissolution of tin can be interpreted on the basis of specific adsorption of halogen ions, begining at the more negative potentials than those corresponding to anodic passivation. However, at a certain critical concentration the current flowing along the passive range, increases suddenly and markedly at some definite potentials denoting the destruction of the passivating oxide film and initiation of visible pits. The effect of increasing Cl^- ions content of the solution is to shift the critical pitting potential of the working electrode into active (negative) direction. Our findings are in agreement with many authors.[8,9]

The dependence of pitting corrosion potential of tin electrode on the concentration of Cl^- ion in different concentrations of Na_2CO_3 is shown in Fig. 2. Usually most of the investigations carried out on the pitting corrosion potentials reveal a straight line relationship between $E_{pitting}$ and $\log C_{agg}$[10,11] according to the equation:

$$E_{pitting} = a_1 - b_1 \log C_{agg} \qquad (1)$$

where a_1 and b_1 are constants. However, in the case under consideration such a relationship cannot be directly obtained. A plot of these variables gives rise to curves of sigmoidal nature in which equation (1) is obeyed only within a certain range of Cl^- ions concentration.[10] These sigmodial S-shaped curves are explained on basis of formation of passivatable, limiting active and continuously propagated pits depending on the range of Cl^- ion concentration. At lower Cl^- ion concentrations the critical pitting potential shifts slightly in the negative direction as the concentration of the halide ion is increased. One can conclude here that these Cl^- ions concentrations are not sufficient to destroy completely the passivating film on the metal surface, or that the pits formed are not completely active and may undergo repassivation. However, at higher concentrations of Cl^- ion, continuously propagated pits are formed.

Figure (3) shows the minimum concentration of Cl^- ions which affected the polarization characteristic of the tin electrode in 5×10^{-1}, 1×10^{-1} and 5×10^{-2} M Na_2CO_3. It represents the plot of the two variables on a double logarithmic scale. Linear relationships were obtained with a slope = 0.8, which satisfy the equation:

$$\log C_{CO_3^{--}} = k + n \log C_{agg} \qquad (2)$$

At low concentration of aggressive anions and high electrolyte concentration, there are some oscillations in E/I voltamogram of the potentiostatic polarization curves. These oscillations are attributed to alternated breakdown and repair of the passive film. Breakdown is caused by the aggressive Cl^- ions, while film repair is caused by O_2 and CO_3^{--} ions.

The relation between Log Δi (*i.e.* $i_{Cl^-} - i_0$) and $\log C_{Cl^-}$ in solutions of 5×10^{-1} and 1×10^{-1} MNa_2CO_3 is shown in Figure (4) according to the following equation :

$$\log \Delta i = a_2 + b_2 \log C_{Cl} \qquad (3)$$

where a and b are constants. i_{Cl^-} and i_0 are the current densities measured

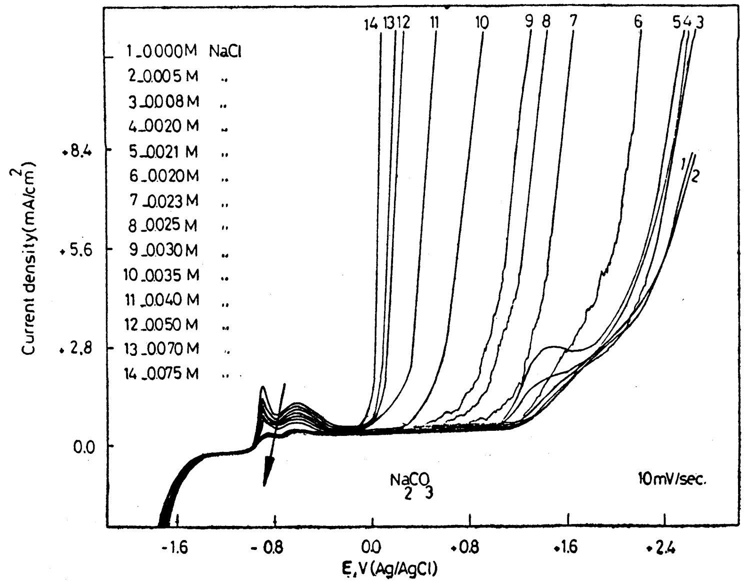

Fig. 1. The effect of Cl^- ion concentration in 0.1 M Na_2CO_3 on the anodic current-potential of tin electrode.

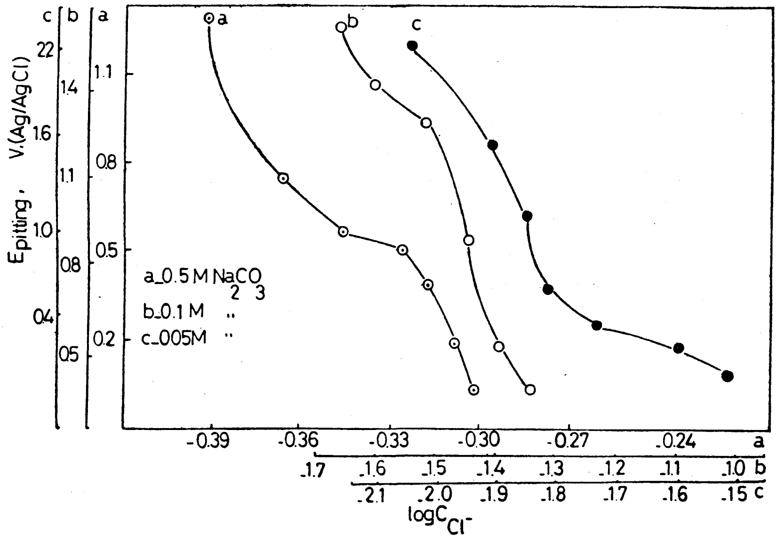

Fig. 2. The relation between the critical pitting corrosion potential, E pitting, and logarithm of the Cl^- ion concentration.

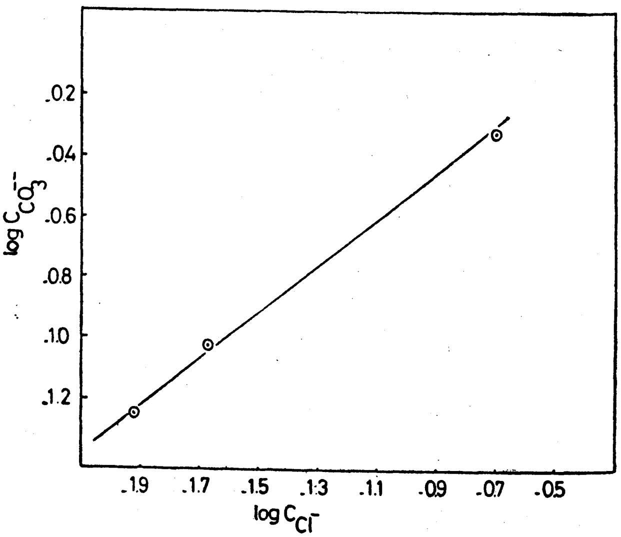

Fig. 3. The relation between log $C_{CO_3^{--}}$ versus logarithm of the minimum concentration of Cl^- ion.

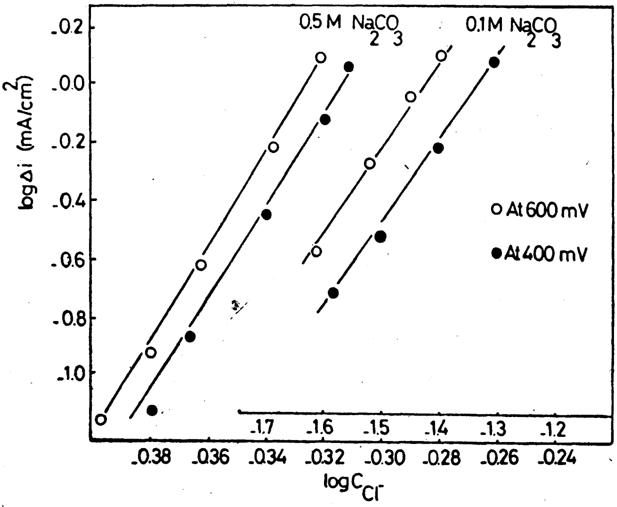

Fig. 4 The relation between log Δi(mA/cm^2) and log C of the Cl^-

in the presence and absence of Cl^- ion at one and the same electrode potential. It is seem that the relationships are independent of the potential at which current is measured.

Figure (5) illustrate the aggressive action of Br^- ions on the anodic passivity of tin in 1×10^{-1} MNa_2CO_3 where passivity breakdown and/or

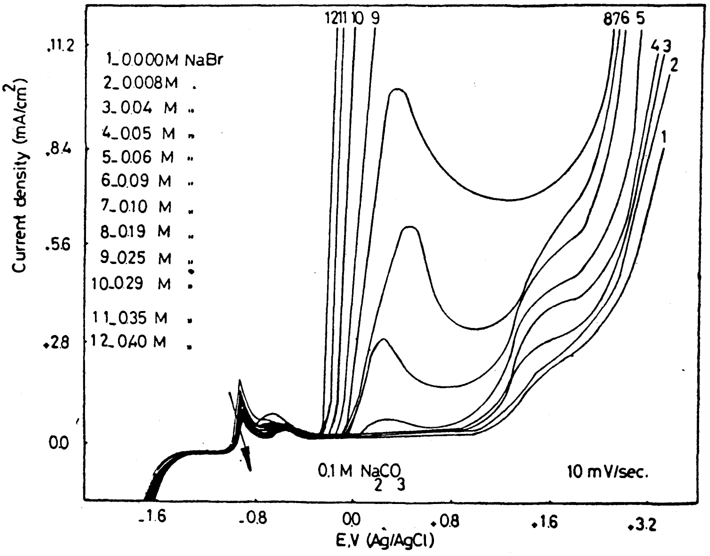

Fig. 5 The effect of Br^- ion concentration in 0.1 M Na_2CO_3 on the anodic current-potential of tin electrode

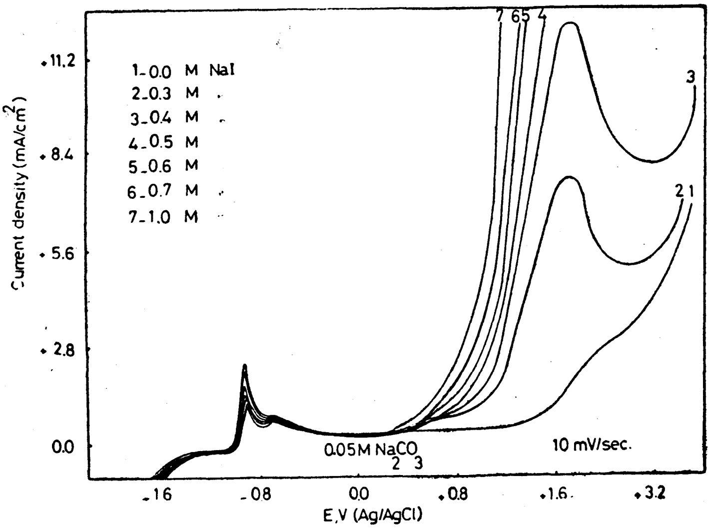

Fig. 6 The effect of I^- ion concentration in 0.05 M Na_2CO_3 on the anodic current-potential of tin electrode

general attack of the electrode surface occurred. However, Figure (6) shows that in the presence of I^- ions which is the least aggressive halide, pitting initiation occurs only at very high anodic potentials, near the oxygen evolution potential. The presence of I^- ions, on the other hand, causes a pronounced decrease in oxygen overvoltage which is probably ascribed to the catalytic effect of I^- ions on the oxygen evolution reaction.[12] At high I^- ions concentrations, I_2 liberated simultaneously with O_2. Vetter[13] has found that I_2 liberated at a number of electrodes required negligible overpotential.

The function of $E_{pitting}$ versus log C for the Cl^-, Br^- and I^- ions in 5×10^{-2} MNa_2CO_3 is shown in Fig. 7. These curves indicate that the

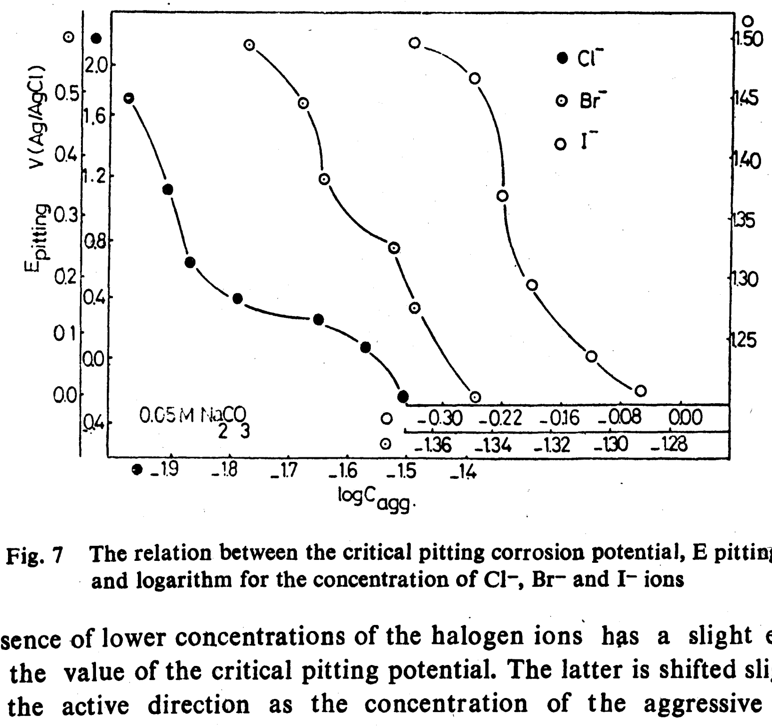

Fig. 7 The relation between the critical pitting corrosion potential, E pitting and logarithm for the concentration of Cl^-, Br^- and I^- ions

presence of lower concentrations of the halogen ions has a slight effect on the value of the critical pitting potential. The latter is shifted slightly in the active direction as the concentration of the aggressive ions is increased. The strongest depassivating effect of Cl^- ions than Br^- and I^- ions, that ascribed to the larger adsorbability of the Cl^- ion and thus its forming surface complex species by the overlapping of the Cl^- ion and the metal orbitals[14].

Inhibition of Pitting Corrosion of Tin Electrode Using Some Alkali Metal Carboxylic Acid Salts

The effect of addition of increasing concentration of the sodium salts of citrate, tartrate, succinate, acetate and formate, successively, on the potentiodynamic anodic polarization characteristic of the tin electrode is 5×10^{-2} M $Na_2CO_3 + 4\times10^{-2}$ M NaCl at scanning rate of 10 mV/sec. Inspection of the curves of these figures reveals that the presence of increasing concentration of these organic carboxylates causes a marked shift of the critical pitting potential into the noble (positive) direction. This effect denotes increased resistance for the pitting corrosion by these carboxylates.

The dependence of the critical pitting potential of the electrode, $E_{pitting}$, on the concentration of the carboxylic salts can be seen by the curves of Figure (8).

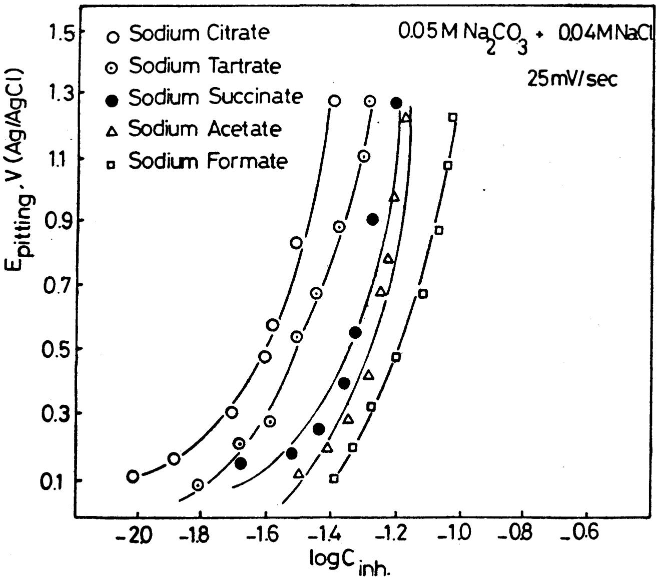

Fig. 8 The variation of the pitting corrosion potential, $E_{pitting}$ with logarithm of molar concentration of the inhibitors

Addition of carboxylic salts up to certain concentration which depends on the type of additive, causes the shift of the critical pitting potential in the noble direction and no visible pits could be detected on the surface of the metal in accordance with the following equation :

$$E_{pitting} = k_3 + b_3 \log C_{inh} \qquad (4)$$

where a_3 and b_3 are constants.

The concentration of the carboxylic salts required to cause the marked shift in potential into the noble direction (marked inhibition) increases in the order : formate < acetate < succinate < tartrate < citrate. This order reflects the increased tendency of these compounds to act as pitting corrosion inhibitors, *i.e.* formate is less effective while citrate is highly effective as pitting corrosion inhibitor. That may be ascribed to the alkyl-group in the carboxylic salt *i.e.* by increasing the alkyl-group the inhibiting effect will be increased. Therefore, the inhibiting effect of these salts can be explained on basis of two factors. First, in the competitive adsorption between the carboxylate anions $RCOO^-$ and/or the CO_3^{--} ions and Cl^- ions on the passive electrode surface. In this case the pitting corrosion potential shifted into the noble (positive) direction. This mechanism seems to be the most effective way to avoid pitting corrosion. Second, by the incorporation of the inhibitive molecules into the passive layer on the metal surface, forming an improved stability against the aggressive ions.

There are many studies of the mechanism of action of carboxylate as inhibitors. In general carboxylates, which may be represented by the formula $RCOO^-$, are most effective as inhibitors in neutral aqueous solutions, and it might be concluded that inhibition results from the bonding of the anion to the metal, or its oxide, covered surface by excess electrons on the O^{2--} ion. If this was so then it would be expected that the inhibitive properties of the different carboxylates would vary only in the degree of the nature of "R" which affected the electron density on the oxygen atom[15].

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