Pitting Corrosion Currents of Tin in Relation to the Concentration of the Inhibitive and Corrosive Anions under Natural Corrosion Conditions

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The changes in the pitting corrosion current density with time for tin electrode concerning the concentrations of both the passiviting oxalate and the aggressive chloride anions were followed using a simple electrolytic cell. The experimental data show that, at the moment of addition of the aggressive Cl^- anions to the passivating oxalate anions solution, instantaneous high currents are observed. After that, the values of these currents were decreased to lower values until steady state was attained. These currents were dependent on the concentration of both the oxalate and Cl^- anions. At a constant concentration of oxalate anions, the pitting corrosion current density varied with the concentration of Cl^- anions according to the relation: $\log I_{pit} = a_1 + b_1 \log C_{Cl^-}$. It also varies with the oxalate anions concentration at a constant Cl^- ions concentration according to the relation: $\log I_{pit} = a_2 - b_2 \log C_{oxalate}$. The constants a_1, a_2, b_1 and b_2 were experimentally determined for all systems studied.

1. INTRODUCTION

Breakdown of passivity of metals by aggressive anions occurs locally rather than generally. Micro anodes of active metal are surrounded by large cathodic areas of passive metal. There is a difference in potential between the anodic and cathodic areas of such a passive - active cell amounting in some cases to be about 0.5 V or more. High current densities at the anode surface due to high rates of metal penetration accompanied by cathodic protection of the metal area immediately surrounding the anode. This fixes the position of anode and results in pitting corrosion [1]. Comparatively, little work on the measurements of such currents has been published with the exception of some experiments on currents resulting from deferential aeration [2-4].

However, Britton and Evans [5] and Streicher [6] proposed a procedure for the evaluation of the penetration power of various anions through the passiviting films. This was done by maintaining a constant potential difference between two similar electrodes immersed in an inhibiting solution and measuring the resulting current when a corrosive anion was added to the solution. Although useful information was gained from this technique, the results obtained cannot be applied directly to actual working conditions.

Shams El-Din et al [7] have been devised a simple model cell which provided a direct evidence for the flow of electric currents under free corrosion conditions leading to pitting corrosion. The obtained information regards the dependence of such currents on the type and concentration of both the corrosive and inhibiting agents. The principle of this method is based on the presence of two similar electrodes in a two compartment cell filled with a solution of the inhibiting agent of such a concentration as to stifle corrosion [8]. The two electrodes are short–circuited through a low resistance micrometer. When a steady-state is attained, no current flows through the electrical circuit. An aggressive anion is then introduced into one of the cell compartments, to initiate pitting corrosion. Local corrosion currents are flowed through the micrometer. This is followed as a function of time until steady-state current values are obtained. The feasibility of this procedure was examined by using Zn [7, 9, 10], Fe [11, 12] and Sn [13] as test metals and the results were satisfactory and informative.

However, the aqueous corrosion of tin is a vitally important subject that encompasses many different industrial commercial and environmental interests. The most widely use of tin is its coating of steel in canning industry. As a consequence of this usage, tin coating comes in contact with an innumerable variety of environments. Thin tin coating is used in solders, marine equipment, roofing, gasoline tanks, and exhaust pipes. Because of its utility especially in food containers, the researches of tin corrosion in aqueous solutions containing organic acids and their salts have become increasingly important. Few reports have been published on the pitting corrosion of Sn in different aqueous solutions [13-25]. The phenomenon of black spots [14] developing on the surface of Sn particles must be looked upon as an indication of localized attack. This disproves the claim that, the metal is immune towards pitting corrosion [26]. As will be study in the present investigation, the same model cell was used to investigate the localized corrosion and to determine the variation of pitting corrosion currents of tin in sodium oxalate solutions in presence of NaCl. Also, scanning electron microscope technique, SEM, was used to confirm the presence of such type of attack.

2. EXPERIMENTAL PART

Spectroscopically pure Sn rods (Johnson – Matthey, England) were used as working electrodes. They were axially embedded in Araldite holder to offer an active flat disc shaped surface of an equal apparent area of 0.28 cm². Before each run, the electrodes were polished successively with different grades of wet emery papers of decreasing grain sizes down to 600 meshes. The polished electrodes were rinsed with acetone and finally washed with running bi-distilled water.

The electrolytic cell used was the same as described previously [7, 9, 10] and shown diagrammatically in Fig 1. It consists of a 250 ml Pyrex glass cell (A) containing 100 ml of inhibiting

solution and one of Sn electrode. The second electrode was enclosed in a glass tube (B) ending in fine porosity, fritted centered glass (G_4). The cell has a double wall jacket through which, water at the adjusted temperature was circulated. A magnetic stirrer with a constant speed rate was used to dissolve the added salt. The two Sn electrodes were short-circuited through a calibrated, low resistance micrometer. Since the two electrodes have an equal surface area and the composition of the electrolyte in the cell compartments was the same, no current flowed when connecting the two electrodes through the micrometer. In a few experiments, however, small currents were noticed, apparently resulting from slight uncontrollable differences in the surface conditions. These currents were noticed to decay within a few minutes. When this condition was established a weighed amount of the aggressive salt, sodium chloride, was added to the test solution of the main compartment (A) and the flowing current was recorded as a function of time until a steady-state value was established. Since the electrode is initially in the passive state [7, 9, 10] the conditions are suitable for the initiation and propagation of pitting corrosion after addition of the aggressive anion.
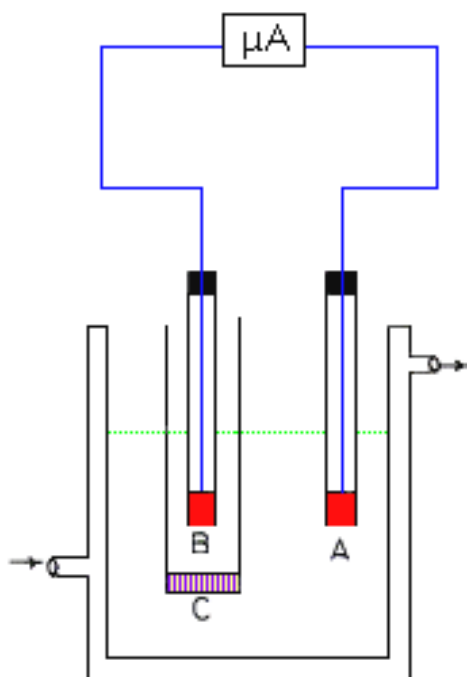
Figure 1. Diagrammatic representation of the cell used for measuring pitting corrosion currents. A and B are two identical electrodes while C is fritted centered glass disk G_4.

Two sets of experiments were conducted. In one set, the effect of concentration of the aggressive agent, Cl^- anions, on the magnitude of the pitting corrosion current was examined. Each experiment was carried out with freshly prepared electrodes and with new portions of solution. In other set of the experiments, the effect of concentration of the inhibiting anion on the corrosion current at constant concentration of the aggressive anion was studied. This was done by adding the same amount

of the aggressive Cl⁻ anions to different concentration of the inhibiting oxalate anions and recording the corrosion current.

The pH of the test solution was adjusted by drop-wise addition of NaOH solution. Digital solution Analyzer (Cole-Parmer Instrument Co, U.S.A) was used to measure the pH of the solution. All chemicals were of analytical-grade qualities. Solutions were prepared by using doubly distilled water. Measurements were carried out at a constant temperature, 25±0.1ºC, except those related to the effect of temperature. The cell temperature was controlled by using an Ultra-thermostat (Cole Parmer Instrument Co, U.S.A). Scanning electron microscopy of the tested electrode was carried out using Jeol Scanning Microscope, JSM – T100 (Japan).

3. RESULTS AND DISCUSSION

The curves of Fig 2 show the variation in the pitting corrosion current density, I, of Sn with time in minutes, in solutions of 0.01M sodium oxalate to which different amounts of NaCl were added to give a known concentration of the aggressive Cl⁻ anions, in each addition. Similar curves were also obtained using different concentrations of sodium oxalate (0.005, 0.01, 0.05 and 0.1M, not shown here).
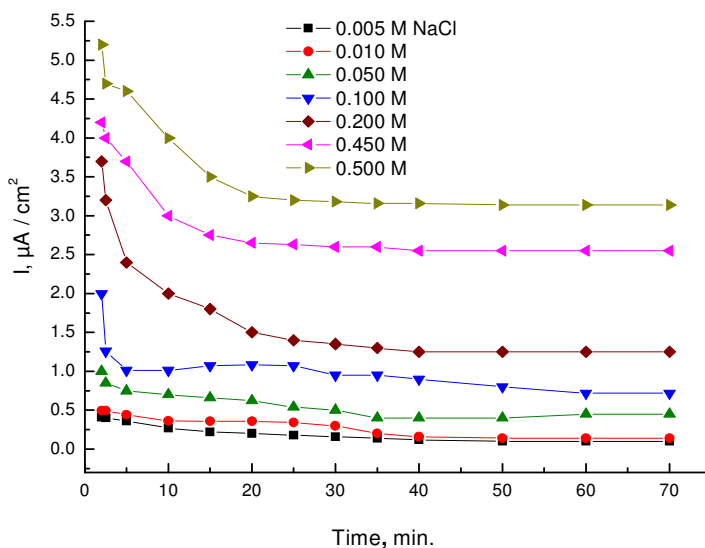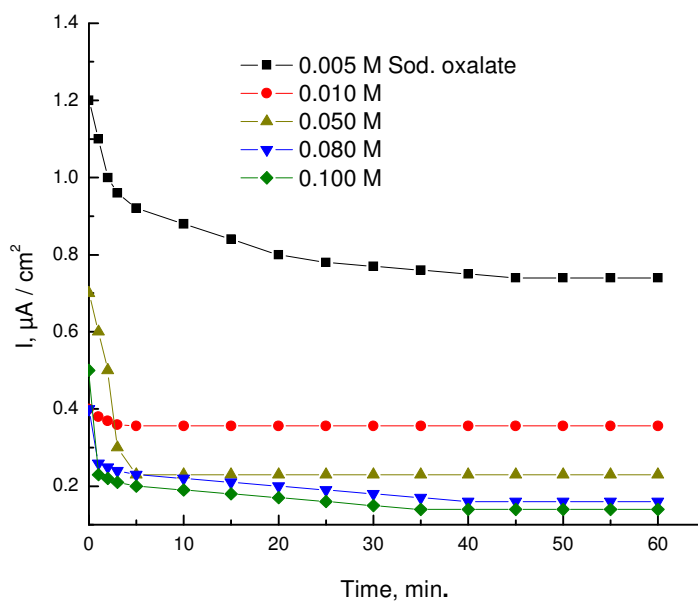

Figure 2. Variation of the pitting corrosion current density with time, in solution of 0.01M sodium oxalate containing different concentrations of NaCl, at 25ºC.

The curves of Fig 3 show the change in the pitting corrosion current density of Sn with time recorded, in solutions of varying concentrations of sodium oxalate to which a constant amount of NaCl were added to give a constant concentration of Cl⁻ anions, 0.1M, in each case .

It is noteworthy to see from Fig 2 and similar ones that, the Cl⁻ anions when present in a very small concentration which can be tolerated by the oxalate ions, no current flow occurs between Sn

electrodes in the cell. However, as the amount of Cl⁻ anions is further increased and at the moment of its addition an instaneous high current is measured. This current quickly decreases to steady state value, which is dependent on the concentration of Cl⁻ anions (where $i_a = i_c = i_{pit}$). The existence of such high currents upon introducing the aggressive anion is an indication of the occurrence of an electrochemical reaction on the electrode surface [13]. This behavior is in agree with data reported by Abd El Wahab et al [13] and in variance with that recorded with normally pitting metals like Zn [7, 9,10] and Fe [11,12]. With these two last metals, the flowing current after an induction period rises steadily to attain a constant value which increases with the increase in the concentration of the aggressive anion [7, 9, 10]. On the other hand, Abd El-Haleem et al [12] studied the variation of pitting corrosion current for steel in Na_2WO_4 in presence of Cl⁻, Br⁻ and I⁻ anions. They found that, in presence of very small additions of the attacking agent, the induction periods were too short to be detected. At relatively higher concentrations of halide anions, larger pitting corrosion currents were firstly appeared and then after passing through a maximum, they decayed to steady state values. They suggested that, the primary attack of the aggressive anions leads to the reduction of the passivator with formation of the corresponding soluble halogen-W-Complexes [7, 27]. The latter offers no protection to the electrode surface.


Figure 3. Variation of the pitting corrosion current density with time, in solution of 0.1M NaCl containing different concentrations of sodium oxalate, at 25ºC.

However, the data of Figs 2 & 3 could indicate that, the primary attack of Cl⁻ anions may causes the flow of initially high currents, which is soon stifled either by the action of the inhibiting oxalate anions or as a result of the limited solubility of the produced Sn oxy-salt [13]. However, the fact that the current does not decay to zero, but reaches to steady-state value indicates that the action of the Cl⁻ anion is not completely eliminated. When the electrode was left for long times, in the solution under examination, visible pits were seen to develop on its surface.

The steady-state pitting corrosion current density value is dependent on the ambient concentrations of both the inhibiting and corrosive agents. The constancy in the pitting corrosion current value denotes that, a state of equilibrium is attained and the number of formed pits on the metal surface remains constant and the dissolution occurs only from the bottom of the pits which propagate vertically with constant dimension [7]. Therefore, the detected increase of the steady-state corrosion current upon increasing the aggressive anion concentration denotes an increase in the number of pits, i.e., an increase in the anodic area [7].
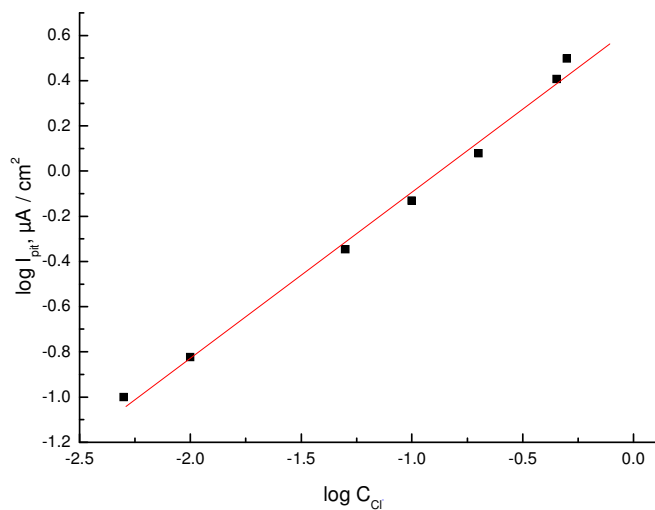
Figure 4. Variation of the logarithm of the steady-state pitting current density, I_{pit}, with logarithm of the concentration of Cl^- anion, C_{Cl^-}.
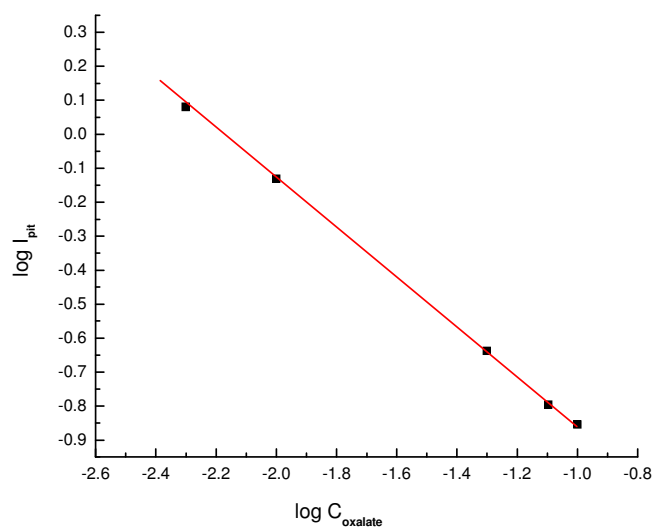
Figure 5. Variation of the logarithm of the steady-state pitting current density, I_{pit}, with logarithm of the concentration of oxalate anions, $C_{oxalate}$.

As is seen from the curves of Figs 2 and similar ones, i.e., in solutions of constant oxalate anions concentration, increasing the Cl^- anion concentration is associated with a corresponding increase in the magnitude of steady-state pitting corrosion current density flowing between the passive electrode and that undergoing corrosion. The relation between the two variables on a double logarithmic scale is shown graphically in Fig 4, and can be represented as:

$$\log I_{pit} = a_1 + b_1 \log C_{Cl^-} \qquad (1)$$

where a_1 and b_1 are constants which depend on the metal under test and the type and concentration of electrolyte [7, 9-13].

On the other hand, when keeping the concentration of the aggressive Cl^- anions constant, and varying that of the oxalate anions, Fig 3, and similar ones, the steady-state pitting corrosion current density is inversely proportional with the oxalate anion concentration in the medium. The relation between the two variables on a double logarithmic scale is shown graphically in Fig 5, and can be represented as:

$$\log I_{pit} = a_2 - b_2 \log C_{oxalate} \qquad (2)$$

where a_2 and b_2 are constants, which depend on the metal under test and both the aggressive and passivating agents [7, 9-13]. Table 1 shows the values of the constants a_1, b_1, a_2 and b_2 as obtained from the experimental data. The minus sign of b_2 values indicates a negative slope as exhibited by equation 2 above. The significance of relation 1 and 2 and their implication for studying pitting corrosion was derived theoretically by Shams El Din and Abd El Haleem on the basis of competitive adsorption of the two opposing agents on the electrode surface. [7]

**Table 1.** Values of the constants a_1, b_1, a_2, b_2, α_1 and α_2

System	Concentration	a_1	b_1	a_2	b_2	α_1	α_2
Oxalate+Cl^-	1×10^{-2} M oxalate	0.53	0.92	----	-----	0.46	-----
	5×10^{-2} M oxalate	0.32	0.92	----	------	0.46	-----
	10×10^{-2} M oxalate	0.15	0.92	----	-----	0.46	-----
	1×10^{-1} M Cl^- + x M oxalate.	-----	------	1.6	0.74	-------	0.37

Fig.6 shows scanning electron micrograph of the tin electrode after immersion in a solution containing in 0.01M sodium oxalate and 0.1M NaCl for a period of 60 minutes. It is clear that, the presence of Cl^- anions causes the formation of well defined pits, which are randomly distributed in the passive film.

The curves of Fig 7 show the variation of pitting corrosion current density recorded with time in solutions of 0.01M oxalate anion at different temperatures (range from15 to 55 ºC) to which Cl⁻ anions were added to give a constant concentration, 0.1M. From this figure, the steady state pitting corrosion density can be drawn against temperature as shown in figure 8.
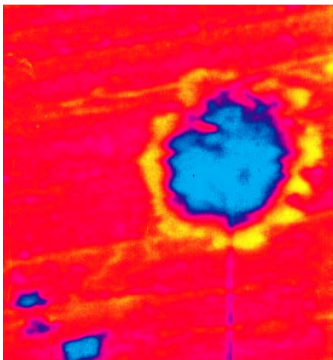

Figure 6. Scanning electron micrograph of the Sn electrode After immersion in solution of 0.01M sodium oxalate containing 0.1M Cl⁻ anion at 25 ºC.
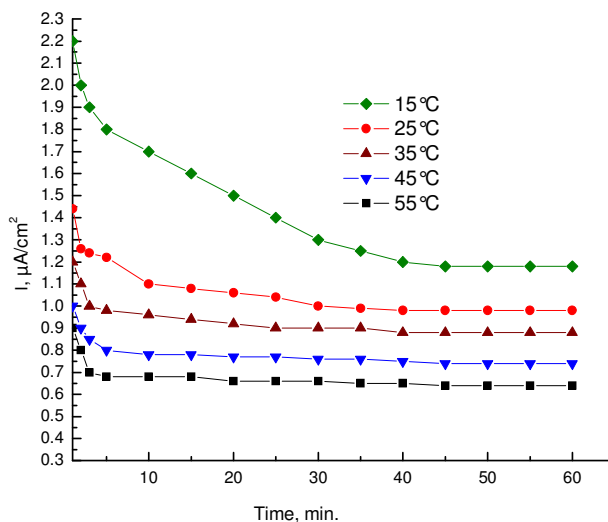

Figure 7. Effect of temperature on the pitting corrosion current density in solution of 0.01M sodium oxalate containing 0.1M NaCl.

It is clearly shown that, as the temperature is increased, the steady state pitting corrosion current density is decreased. This behavior could be attributed to the decrease in the corrosive tendency of Cl⁻ anions towards the passive tin electrode as the temperature is increased. The decrease in the reactivity of Cl⁻ anions with higher temperatures could be attributed to the decrease in Cl⁻ anions ability to penetrate through the passive layer on Sn metal surface due to formation of Sn oxy-chloride salt [13], which sustains the existence of the passive film.
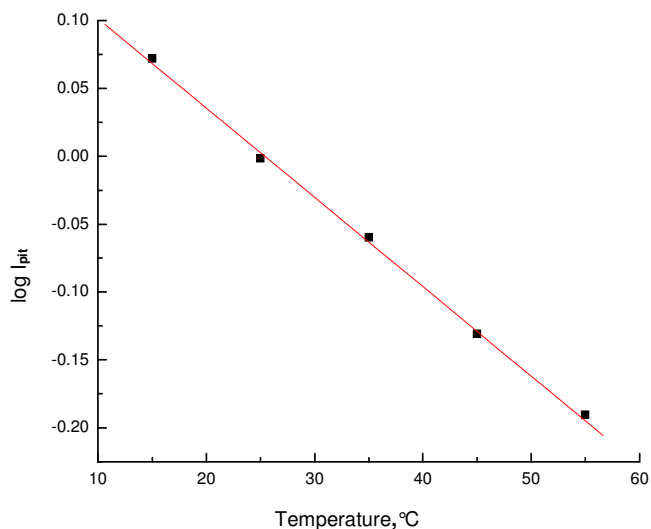
Figure 8. Variation of the logarithm of the steady-state pitting corrosion current density, log I_{pit}, with solution temperature.
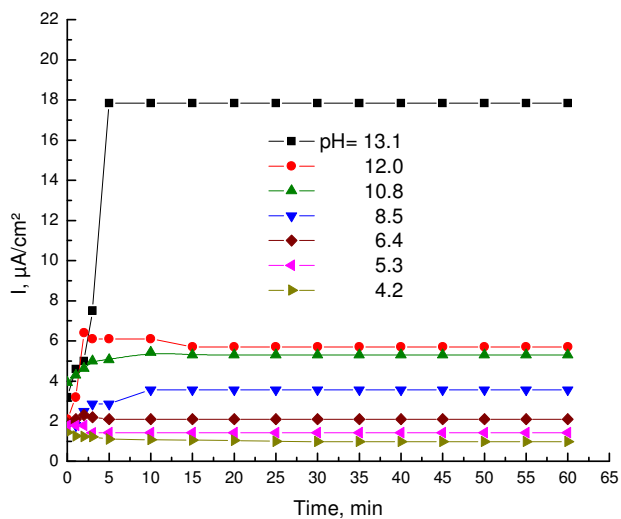
Figure 9. Variation of the pitting corrosion current density with time in solutions of 0.01M sodium oxalate containing 0.1 M NaCl at different pH values, at 25°C

The curves of Fig 9 show the variation of pitting corrosion current density recorded with time in solutions of 0.01M oxalate anions at different pH values, to which Cl^- anions were added to give a constant concentration, 0.1M. The data of this figure show that, as the pH of the solution is increased the steady-state pitting corrosion current density is increased. This indicates that, the corrosive action of Cl^- anion increases as the pH of the solution is increased. Such behavior could be attributed to the decrease in the thickness of the formed passive layer with increasing pH of the solution [10].

One of the pitting corrosion theories indicates that, the presence of the aggressive anions destruct the oxide film of the passive metal by increasing its permeability and penetrates it through

pores or cracks. The second one involves adsorption of the aggressive anions on the metal surface in competition with the inhibitor species. Further, the role of the inhibiting anion, when present in a sufficiently high concentration is to keep a state of permanent passivity by supplying material for repair the defective sites on the passive metal [28]. The increase of the inhibitor concentration above the threshold to stifle corrosion would make the influence of corrosion products of secondary effect [8]. This increase of the inhibitor concentration, however, would affect the kinetics of the cathodic reaction through influencing the potential drop from the metal bulk to the plane of closest approach to the surface of the metal, i. e., the potential of the inner Helmholtz plane [7, 11]. The occurrence of competitive adsorption between the counteracting aggressive and inhibiting anions, as is generally the case, affects in addition to the ψ potential, the energies and rates of the opposing reactions as well as the stability and properties of the inhibiting film.

However, the present data indicates that, when the metal is immersed in a solution of an inhibiting anion of sufficient concentration, a state of passivity occurs with no current flows [7, 10, 11], i.e., $i_a = i_c = 0$. On the addition of sufficient amount to the aggressive anions to the inhibiting solution (compartment A, Fig 1), it competes with inhibitor for some of the active sites depending on its concentration. This leads to destruction of the passive layer on the metal surface giving pitting corrosion currents [7, 10]. These currents attain a steady–state value depending on the concentration of the aggressive and inhibiting anion. As it is known that, the logarithm of the pitting corrosion current, I_{pit}, varies with that of the molar concentration of the aggressive, C_{agg}, or the inhibiting agents, $C_{inhibit}$, in solution can be ascribed by the following two relations. [7, 9-12].

For the aggressive anions:

$$\ln I_{pit} = \text{const}_1 + (\alpha_1 n_1 / z_1) \ln C_{agg} - (\alpha_1 n_1 F / RT) E_{corr} \qquad (3)$$

For the inhibiting anions:

$$\ln I_{pit} = \text{const}_2 - (\alpha_2 n_2 / z_2) \ln C_{inhibit} - (\alpha_2 n_2 F / RT) E_{corr} \qquad (4)$$

where α is the transfer coefficient, n the number of electrons involved in the reaction and E_{corr} is the corrosion potential and 1 and 2 refer to the anodic and cathodic reactions, respectively. Z_1 and Z_2 are the charges carried by the aggressive and inhibiting anions, respectively. From the arrangement of the experiments under consideration, that the major part of the working electrode is a cathodic area and it is short circuited to the counter electrode which is totally a cathodic area. So, the anodic area is much too small to affect the potential of the couple [10, 11] and hence E_{corr} is considered to be practically independent on the concentration of the aggressive anion and the anodic area is considered as constant.

According to equation 3, the slope of the log I_{pit} – log C_{agg} plots should correspond to the value of the term $\alpha_1 n_1 / z_1$, where α_1 is the transfer coefficient of the anodic reaction, n_1 is the number of electrons involved by the oxidation reaction and z_1 is the valency of the aggressive anion. However, from the value of b_1, the values of α_1 are calculated. The corrosion reaction is taken as $Sn = Sn^{+2} + 2 e^-$. Therefore, when n_1 is set equal to 2 and z_1 equal to 1 (for the case of Cl^-) values of α_1 so calculated as shown in Table1. These values indicate an average value of 0.5 for Cl^- anions. The magnitude of

the transfer coefficient depends on the nature of the electrode reaction as well as the concentration of the supporting electrolyte [7]. For electrode reactions governed by transfer across a single energy barrier, values ranging between 0.3 and 0.7 are commonly given [7].

The term, a_1, i.e, the value of the log I_{pit} at C_{Cl^-} = 1M, is a measure of the corrosive action of the particular aggressive agent, Cl^- anions. The value depends on the concentration of the inhibiting anion used. As expected the value of a_1 decreased with an increase in the concentration of the inhibiting anion. This indicates that the corrosive action of Cl^- anions as pitting corrosion agent decreases with increasing oxalate anion concentrations.

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