Inhibiting Effects of Group 6 Oxo-Anions on the Pitting Corrosion of Tin in Citrate-Chloride Solution

Fawzi Hassan Assaf

Chemistry Department, Faculty of Science, South Valley University, Quena, Egypt

(Received May 17, 1999)

The effect of chloride ions on both anodic dissolution and pitting corrosion of tin metal in the aerated equimolar solutions 0.1 M (1 M = 1 mol dm^{-3}) citrate-chlorid–oxo-anions (CrO_4^{2-}, WO_4^{2-}, and MoO_4^{2-}) has been investigated. Different techniques were used, such as potentiodynamic, potentiostatic polarization, electrochemical impedance spectroscopy techniques. These were complemented by surface examination using scanning electron microscopy. Lower current values in the presence of equimolar (0.1 M) citrate-oxo-anions with addition of Cl^- in various concentrations were observed, compared with those obtained in the oxo-anion free solutions. Thus, these oxo-anions might create a certain impediment or barrier to the attack of the aggressive Cl^- on the metal surface. However, the addition of the studied anions at lower concentrations (10^{-3} and 10^{-2} M) in 0.1 mol dm^{-3} citrate-chloride, enhanced the active metal dissolution and passivity break down of tin. Retardation to a considerable extent was observed, however, at higher concentrations (5×10^{-2} and 10^{-1} M). All measurements using the different techniques, under the same conditions, confirmed that the order of reduced aggressiveness of Cl^- was CrO_4^{2-} > WO_4^{2-} > MoO_4^{2-}. This indicates that CrO_4^{2-} remains the best inhibitor to prevent the pitting corrosion, probably through its ability to repair defects in the oxide film.

Tin is widely used as an interior protective coating of steel in canned food.[1] Studies[2—7] show that considerable efforts have been made to study the corrosion of tin metal and its inhibition against the aggressive effect of ions which are naturally present in food and water. On the other hand, little attention has been paid to the corrosion behavior of tin in the so-called fruit acids.[8—10]

Reports showed that oxo-anions of group 6 are good anodic inhibitors. They are known to be passivating ions for iron,[11] stainless steel,[12,13] aluminium,[14—16] and zinc.[17,18] Moreover, they have the ability to suppress halide ions aggressivity.[12,15,18] Chromates, one of this group, are widely used as passivating oxidants and also as corrosion inhibitors. Health, economic and environmental considerations have led to a search for non-toxic alternatives to chromates. There have been many efforts to use molybdates and tungstates as possible replacements of chromates. Less attention has been paid to the inhibition effect of these alternative anions on the electrochemical behavior and corrosion of tin in aqueous solutions of those anions themselves.[19,20] It is hoped that anodizing tin and tin plate by forming thick amorphous anodic oxides which can resist Cl^- ions attack would solve many problems concerning the pitting corrosion of tin plate used in the canning industry. It is well known that citrate/Cl^- mixed ions commonly coexist in canned food.

However, few studies have been found on the effect of such anions as additives to the corrosive solutions. For this reason the present article is devoted to the effects of CrO_4^{2-}, WO_4^{2-}, and MoO_4^{2-} as corrosion inhibitors for tin metal in citrate solutions in the absence and presence of Cl^- ions. Potentiodynamic, potentiostatic and electrochemical impedance spectroscopy (EIS) measurements techniques were used in this study. The morphology of the electrode surface was investigated using a scanning electron microscope (SEM).

Experimental

Tin anode disks with an apparent exposed area of 0.28 cm^2 were prepared from extra pure tin rods, 99.999% (Aldrich). Each electrode was polished with successive grade emery papers, degreased with acetone and washed in running doubly distilled water. The counter electrode was a platinum sheet. The reference electrode was a saturated calomel electrode (SCE) and all potentials refer to the SCE. The electrolytic cell has been described elsewhere.[21] AR grade sodium citrate tribasic and sodium chloride were used for preparing solutions. Reagent grades (Fluka) Na_2CrO_4, $Na_2WO_4\cdot 2H_2O$, and $Na_2MoO_4\cdot 2H_2O$ were used as inhibitors.

Potentiodynamic and potentiostatic polarization studies were made using a corrosion system (parc EG&G). In the potentiodynamic experiments, the potential of the working electrode was varied (from $E_{corr.}$ up to +1600 mV vs. SCE) automatically by a software program (Model 352) through a potentiostat/galvanostat (Model 273A). The sweep rate was 1 mV s^{-1}. Potentiostatic current–time transients were conducted by imposing a constant potential on the tin anode and the variation of current was recorded automatically as a function of time. Some representative anodes were washed with doubly distilled water and examined using a scanning electron microscope (JEOL Model JSM 5300), after the imposition of a potential at +1000 mV vs. SCE (potentiostatic) for 10 min in either the absence or the presence of Cl^- ions and the investigated additives.

The EIS measurements were carried out in a frequency range of 10 kHz to 20 MHz and at −200 mV vs. SCE. An amplitude of 5 mV peak to peak was used for the a.c. signal. Details of the experimental procedures have been described elsewhere.[22] Each experiment was performed using freshly prepared solution and newly polished electrodes. Measurements were conducted at 25±0.5 °C. The solutions were not deaerated. Most of the experiments were repeated at least twice; the reproducibility was found to be satisfactory.

Results and Discussion

1. Effect of Aggressive Ion Concentrations in the Absence of Oxo-Anions: Figure 1 represents the potentiodynamic anodic polarization curves of tin in aerated 0.1 mol dm^{-3} citrate solutions in the absence and the presence of different concentrations of Cl^- ion (0.05—0.5 M). From these curves, it can be seen that the anodic behavior of tin in chloride ion-free citrate solution, exhibits active-passive transition. The peak potential, E_p, occurred at ca. −525 mV (vs. SCE), which is comparable with the equilibrium potential of the system $SnO/Sn(OH)_4$ (−614 mV) at the given pH of the solution (pH = 7.8). The positive shift may be attributed to an overpotential associating with the oxide/hydroxide formation or the change of pH at vicinity of the electrode surface.[5] According to the literature[3,8,10,23] most of the Sn^{2+} ions in the citrate solutions exist in the form of different soluble chelate Sn^{2+}-citrate[24] complexed species, while a small fraction of Sn^{2+} ions are in the form of $Sn(OH)_2$. Smith[25] has pointed out that all of these species undergo hydrolysis to form a thin layer of either $Sn(OH)_2$ and/or SnO on the metal surface.

The influence of Cl^- addition was revealed by a shift of the peak potential to more positive values and the curves exhibited high current values. This indicates the accelerating effect of Cl^- ion in both active and passive regions. The localized corrosion of Cl^- ions (pitting attack) was characterized for all examined concentrations. The pitting potentials for the various chloride ion concentrations are displayed in Fig. 5, which shows that pitting potentials are shifted towards more negative values with increasing the concentration of Cl^- ions.[26] The attack occurred at the early stage of the passive region; Fig. 1 (at Cl^- concentration > 0.2 M) indicates that pitting could attack any small defect in the oxide film.[27]

Fig. 1. Potentiodynamic anodic polarization curves for tin electrode in 0.1 mol dm^{-3} citrate in the presence of various Cl^- ion concentrations 1: 0 M; 2: 0.05 M; 3: 0.1 M; 4: 0.2 M; 5: 0.5 M.

Beyond the pitting attack (current oscillation) in the presence of higher concentrations of Cl^- ion (0.2 and 0.5 M), the anodic polarization curves showed a steady state current value. This steady state current value following the current oscillation may be associated with the formation of tin chloride oxide which blocks the active sites and prevents further attack by Cl^-. The same view was reported for tin in NaOH solutions containing Cl^- ions.[28] Covered pits with loosely white precipitate were observed by the naked eye on the electrode surface at the end of the experiment in the presence of such concentration of Cl^- ions.

The SEM micrographs (Figs. 6a and 6b) showed pits on the electrode surface in 0.1 mol dm^{-3} citrate–0.1 mol dm^{-3} NaCl solution (Fig. 6b), while in free 0.1 mol dm^{-3} Cl^- citrate solution, the pits were not observed under the conditions mentioned in the experimental section.

2. Effect of the Aggressive Ion in the Presence of 0.1 mol dm^{-3} of Oxo-Anions: The effects of various Cl^- concentrations on the potentiodynamic anodic polarization behavior of tin in aerated 0.1 mol dm^{-3} citrate solutions containing 0.1 mol dm^{-3} $CrO_4{}^{2-}$, $WO_4{}^{2-}$, and $MoO_4{}^{2-}$ are shown in Figs. 2, 3, and 4, respectively. The anodic po-

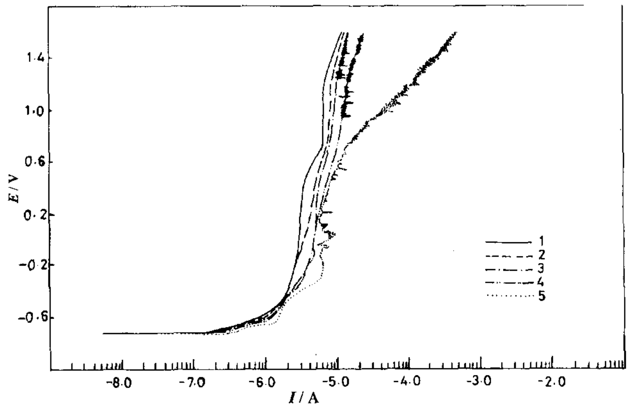

Fig. 2. Potentiodynamic anodic polarization curves for tin electrode in 0.1 mol dm^{-3} citrate+0.1 mol dm^{-3} $CrO_4{}^{2-}$ anion in the presence of various Cl^- ion concentrations 1: 0 M; 2: 0.05 M; 3: 0.1 M; 4: 0.2 M; 5: 0.5 M.

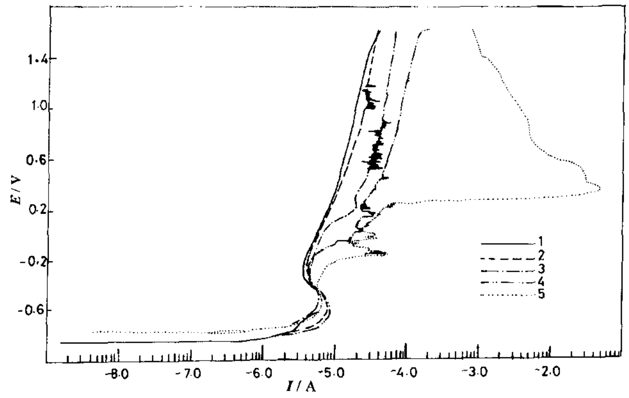

Fig. 3. Potentiodynamic anodic polarization curves for tin electrode in 0.1 mol dm^{-3} citrate+0.1 mol dm^{-3} $WO_4{}^{2-}$ anion in the presence of various Cl^- ion concentrations 1: 0 M; 2: 0.05 M; 3: 0.1 M; 4: 0.2 M; 5: 0.5 M.

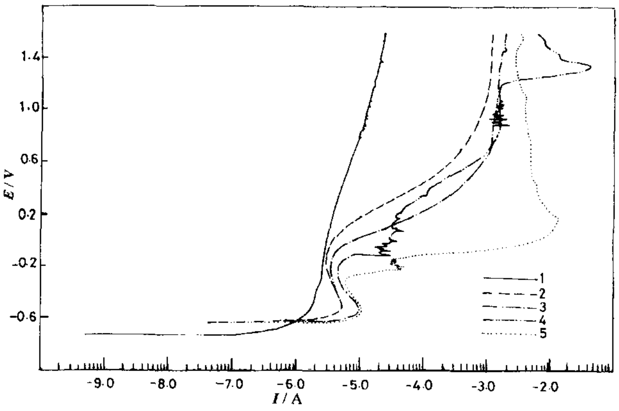

Fig. 4. Potentiodynamic anodic polarization curves for tin electrode in 0.1 mol dm^{-3} citrate + 0.1 mol dm^{-3} MoO_4^{2-} anion in the presence of various Cl^- ion concentrations 1: 0 M; 2: 0.05 M; 3: 0.1 M; 4: 0.2 M; 5: 0.5 M.

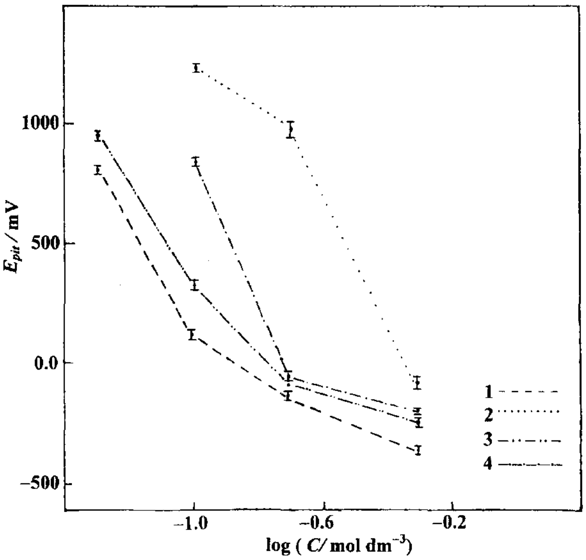

Fig. 5. Variation of E_{pit} with the log. of aggressive Cl^- ion concentration in the absence and presence of oxo-anions 1: 0.0 M; 2: 0.1 M CrO_4^{2-}; 3: 0.1 M WO_4^{2-}; 4: 0.1 M MoO_4^{2-}.

larization curve of tin in citrate solution containing CrO_4^{2-} only, shows a low steady state current compared with the value obtained in CrO_4^{2-} free citrate solution. This may be attributed to the fact that CrO_4^{2-} is considered as a strong oxidizer which inhibits the anodic reaction.[29] Therefore, it acts as an adsorption inhibitor[27,30] and pH buffering agent[25] in a way which facilitates surface oxidation. Moreover, the reduction of CrO_4^{2-} leads to the formation of a mixed oxide of spinel structure.[31] Similar results were reported for tin in aqueous solution of CrO_4^{2-} anion.[19] Addition of low concentrations (0.05—0.2 M) of Cl^- showed no significant effect on the anodic polarization behavior of tin. This suggests a strong adsorption and/or incorporation of CrO_4^{2-} anion on the surface film impeding the aggressive effect of Cl^- ions. However, 0.5 mol dm^{-3} of Cl^- ion broke down the passive layer and induced pitting corrosion. The potential at which the passive current increases rapidly is taken as the pitting potential (E_{pit}, see Fig. 1). Figure 5 shows clearly that with increasing $Cl^- > 0.05$ mol dm^{-3}, the E_{pit} was shifted to negative values. This indicates that the penetration of oxide film by aggressive ions takes place at preferential sites. Competitive adsorption of both Cl^- and CrO_4^{2-} depends on their concentrations. The reduction of oxo-anions is also assumed to supply oxygen atoms, leading to displacement of Cl^- ions.[32] It is to be noted that, in the presence of CrO_4^{2-} with < 0.5 mol dm^{-3} Cl^- ion, the break down of the oxide film does not occur. This is evidence that the complete displacement of CrO_4^{2-} anions by Cl^- ions will not occur except in the presence of 0.5 mol dm^{-3} Cl^-. Figure 6c shows that no pits were formed in the solution of 0.1 mol dm^{-3} citrate, 0.1 mol dm^{-3} CrO_4^{2-} and 0.1 mol dm^{-3} Cl^- ion at 1.0 V.

The influence of WO_4^{2-} anions is shown in Fig. 3. The curves exhibited active-passive transition similar to that shown for citrate solution. The passive current as well as the passive potentials are slightly affected by increasing the Cl^- content of the solutions. Inorganic inhibitors can be roughly classified into passivators, adsorbates and substances forming salts that deposit on the metal surface or complexes species incorporated in the surface film.[11,14,19,27,33—35] Another point of view about the inhibitive action of oxo-anions has been stated by Mikhailovskii.[36] He assumed that the inhibition should be attributed to the OH^- ion which formed during reduction process and not to the respective anion or its reduction product.

With 0.1 mol dm^{-3} WO_4^{2-}, lower 0.1 mol dm^{-3} Cl^- may induce pitting corrosion as compared with the 0.5 mol dm^{-3} Cl^- needed to break down the passivity of tin in the presence of 0.1 mol dm^{-3} CrO_4^{2-}. Figure 3 shows that E_{pit} decreased (shifted to more negative values) with increasing Cl^- concentration, as shown in Fig. 5. This suggests that Cl^- may have reduced the WO_4^{2-} anions to hydrated chloro complexes of lower valent *W* which precipitate on the surface film and block the active sites.[37] A yellow deposit was observed covering the electrode surface. The limit of protection of such a deposit results in the break down and continuous dissolution of metal in the high 0.5 mol dm^{-3} Cl^-. Similar results were obtained for inhibition of Zn in KCl solutions containing WO_4^{2-} anion.[17] The SEM of Fig. 6d shows the precipitate formed at some sites as well as the appearance of a few pits.

The curves in Fig. 4 demonstrate the effect of MoO_4^{2-} on the potentiodynamic anodic polarization behavior of tin in citrate solutions in the absence and presence of various concentrations of Cl^-. In the former, the anodic polarization curve shows low steady state passive current. This suggests that MoO_4^{2-} passivates the surface and a thin protective film of SnO or $Sn(OH)_4$ containing MoO_4^{2-} passivating film coexists.[19] A similar view was recorded for Al in deaerated Cl^- solution containing MoO_4^{2-} anions.[15] With Cl^-, behavior analogous to that obtained in solutions containing the same concentration of WO_4^{2-} was seen especially for 0.1, 0.2, and 0.5 mol dm^{-3} of Cl^-. With 0.05 mol dm^{-3} pitting attack does not occur, but the passive region current was higher. This indicates that Cl^- does not strongly attack the

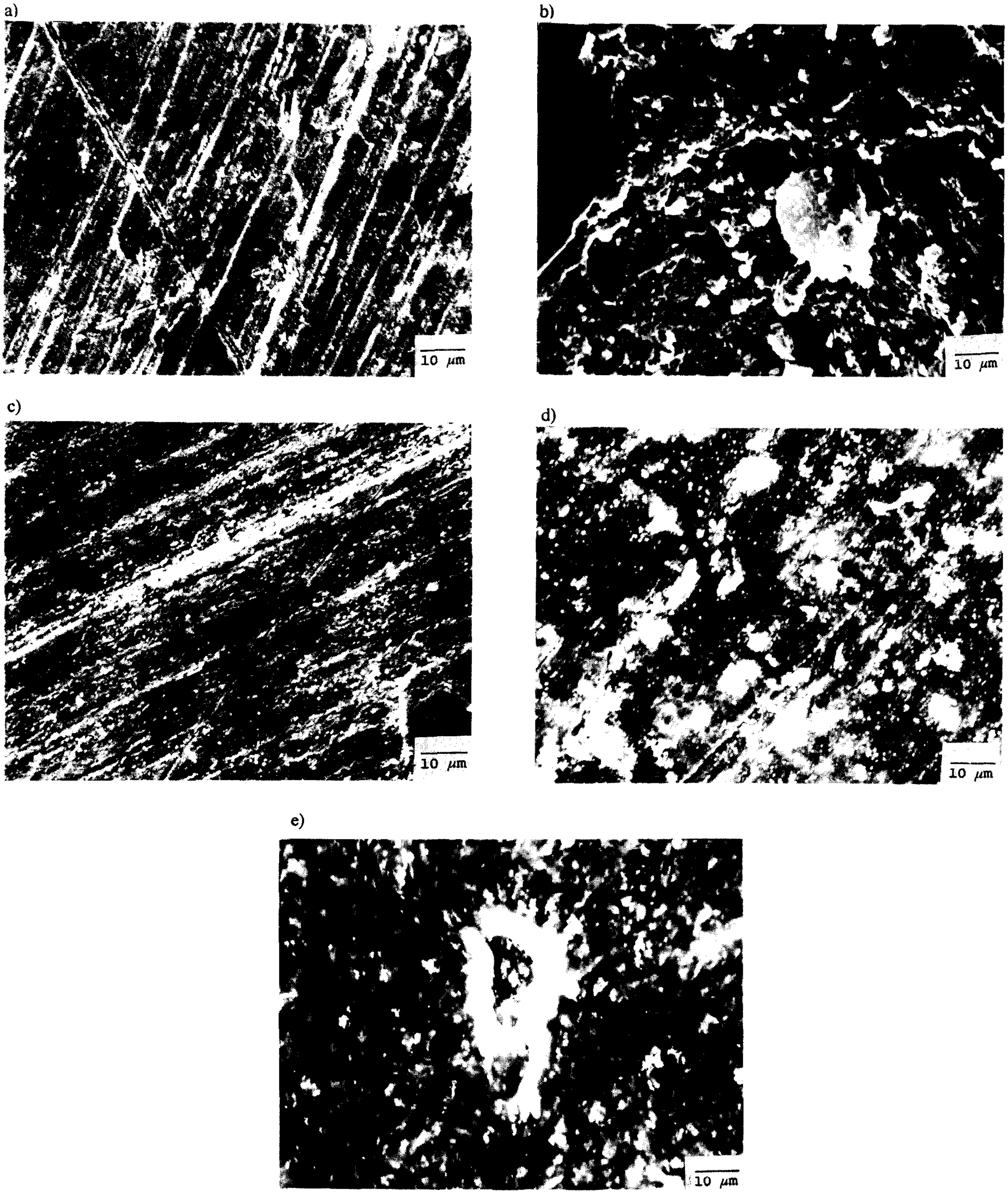

Fig. 6. SEM micrographs of tin after the experiment in: a-0.1 M citrate, b-0.1 M citrate+0.1 M Cl^- ions, c-0.1 M citrate+0.1 M Cl^- ions+0.1 M $CrO_4{}^{2-}$, d-0.1 M citrate+0.1 M Cl^- ions+0.1 M $WO_4{}^{2-}$, e-0.1 M citrate+0.1 M Cl^- ions+0.1 M $MoO_4{}^{2-}$.

formed protective film. Increasing the Cl^- concentration increases pitting and E_{pit} was shifted to more negative values (Fig. 5). The pitting attack was followed by a steady current, which could be attributed to the formation of polymolybdate layer which impedes the penetration of Cl^- ions to the metal/film interface.[15] Similarly, Ogura and Ohama[34] pointed out that molybdate anions form polymolybdate species which adsorped or precipitated on the metal surface.

The SEM micrograph Fig. 6e showed a large pit on the electrode surface in equimolar citrate-chloride 0.1 mol dm^{-3}

in the presence 0.1 mol dm^{-3} MoO_4^{2-}. Ruijini and Ives[12] reported that MoO_4^{2-} anions added to Cl^--containing solutions inhibited pit nucleation on stainless steel but did not hinder pit development. They also found that pit growth was prevented in MoO_4^{2-}-containing solutions when the pits were of small size.

Figure 7 compares the inhibitive action of these additives at 0.1 mol dm^{-3} of each and at the same potential of +1000 mV. It shows that Cl^- raises the current flowing along the passive region as a whole. The resistance of Sn to pitting attack by Cl^- ions can be detected from the change of the dissolution current density "Δi".[38] Here $\Delta i = i_{Cl^-} - i_n$, where i_n and i_{Cl^-} are the current density measured at a certain potential (+1000 mV), in the absence and presence of Cl^-, respectively. It can be seen that $\log \Delta i$ is linearly related to $\log C_{Cl^-}$ without and with constant inhibitor concentration (0.1 M) in citrate solution according to

$$\log \Delta i = a + b \log C_{Cl^-}. \text{ (where } a \text{ and } b \text{ are constants)}$$

It is found that Δi values decrease in the order

$$\text{oxo-anion free solution} > MoO_4^{2-} > WO_4^{2-} > CrO_4^{2-}$$

These values of Δi can be taken as a measure for the resistivity to pitting attack by Cl^- ions under potentiodynamic polarization conditions[38] according to the order given above. This suggests that CrO_4^{2-} anions directly interfere in the anodic dissolution which could occur through the formation of chloro-and chloro(oxo) complexes by reduction of CrO_4^{2-} to Cr(III) producing oxide anions.[14] This explains the tendency of CrO_4^{2-} to aid oxide film formation and the total absence of pits in the solution containing equimolar concentration (0.1 M) of Cl^-–CrO_4^{2-}. In solutions containing WO_4^{2-} and MoO_4^{2-}, the inhibition may be related to the chemical reaction occurring on the surface (formation of hydrated chloro-complexe of low valent W, forming poly-molybdate species), while localized attack proceeded. This suggestion is confirmed by SEM micrographs (see Figs. 6d and 6e).

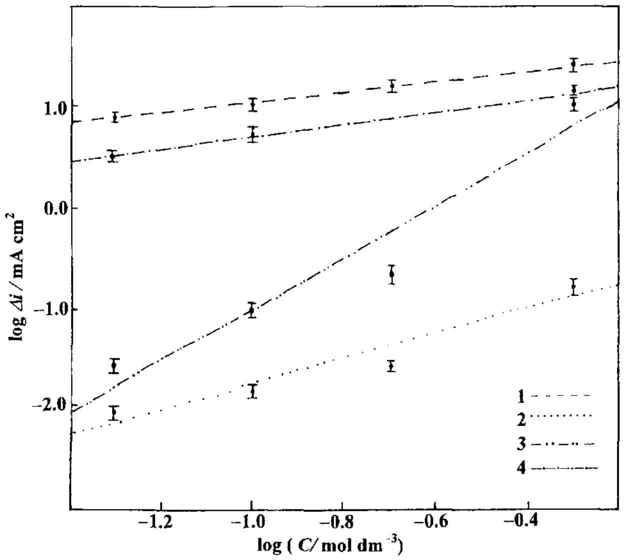

Fig. 7. Dissolution current density change "Δi" in the presence of oxo-anions. 1: 0.0 M; 2: 0.1 M CrO_4^{2-}; 3: 0.1 M WO_4^{2-}; 4: 0.1 M MoO_4^{2-} (measured at +1000 mV vs. SCE) as a function of Cl^- ions concentrations.

3. Effect of Oxo-Anions in the Presence of 0.1 mol dm^{-3} Aggressive Ion: Typical potentiodynamic anodic polarization curves of tin in aerated equimolar 0.1 mol dm^{-3} solution of citrate-Cl^- ions in the absence and presence of various concentrations of CrO_4^{2-} anions are given in Fig. 8. These curves demonstrated that, in the presence of low concentrations (10^{-3} and 10^{-2} M) of the CrO_4^{2-}, the metal dissolution is simulated.[19] A similar view was reported for tin in aerated 0.1 mol dm^{-3} NaCl solutions containing CrO_4^{2-} anions of concentrations 10^{-4} and 10^{-3} mol dm^{-3}.[5] Similar results were recorded in the absence and presence of WO_4^{2-} and MoO_4^{2-} anions. At high concentrations (0.05 and 0.1 M), the anodic polarization curves showed the inhibition effect of these compounds.

To clarify the acceleration effect of the additives (CrO_4^{2-}, WO_4^{2-}, and MoO_4^{2-}) at lower concentrations (10^{-3} and 10^{-2} M) and their inhibiting effect at high concentrations (0.05 and 0.1 M), a study of potentiostatic current–time transients for tin in 0.1 mol dm^{-3} equimolar solutions of citrate-chloride was carried out. Figure 9 shows the results within the active dissolution peak at −100 mV in the absence and presence of lower concentrations of CrO_4^{2-}. These can be divided into three stages. In the first stage, the current increases to a maximum, while in the second stage a decrease in the anodic current occurred. Finally, a steady anodic current is attained. These stages showed metal dissolution resulting in rapid decay of the current density. It is observed that the maximum current density of the first stage decreases with an increase of CrO_4^{2-} concentration (in agreement with the results of EIS, which will be discussed later). However, the anodic current of the steady state is much higher at lower concentrations than that in the absence of the additives. The curves in Fig. 10 exhibit an acceleration effect for lower concentrations at steady state current values in the passive region (+500 mV). Similar trends in the absence and presence of WO_4^{2-} and MoO_4^{2-} in both active and passive regions

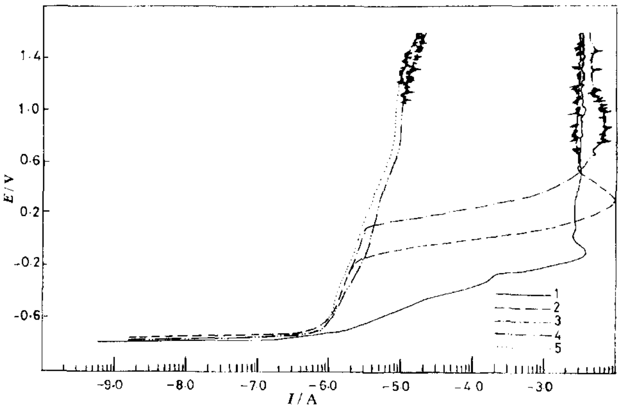

Fig. 8. Potentiodynamic anodic polarization curves for tin electrode in 0.1 mol dm^{-3} citrate+0.1 mol dm^{-3} NaCl in the presence of various CrO_4^{2-} anion concentrations 1: 0 M; 2: 10^{-3} M; 3: 10^{-2} M; 4: 5×10^{-2} M; 5: 10^{-1} M.

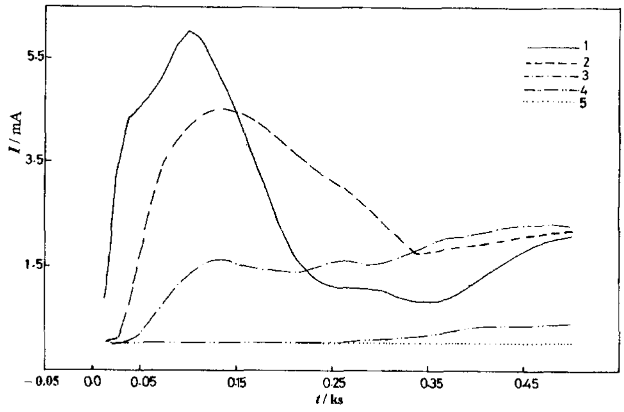

Fig. 9. Effect of $CrO_4{}^{2-}$ ions concentrations on potentiostatic transients for tin anodes in 0.1 mol dm^{-3} citrate-chloride ions at active dissolution peak (−100 mV vs. SCE). 1: 0 M; 2: 10^{-3} M; 3: 10^{-2} M; 4: 5×10^{-2} M; 5: 10^{-1} M.

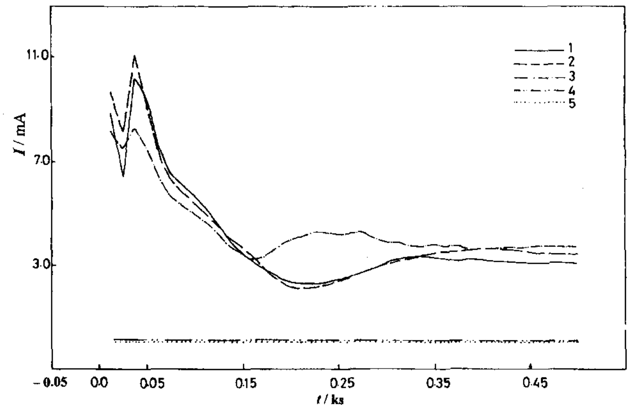

Fig. 10. Effect of $CrO_4{}^{2-}$ ions concentrations on potentiostatic transients for tin anodes in 0.1 mol dm^{-3} citrate-chloride ions in passive region (+500 mV vs. SCE). 1: 0 M; 2: 10^{-3} M; 3: 10^{-2} M; 4: 5×10^{-2} M; 5: 10^{-1} M.

were recorded. Accordingly, these results can be correlated with the potentiodynamic results, in which addition of the investigated additives increases the steady state of current density at both active and passive regions only at lower concentrations and diminishes it at higher concentrations (0.05 and 0.1 M).

Figure 12 represents the complex-plane impedance plots of tin in 0.1 mol dm^{-3} equimolar solution of citrate-Cl$^-$ in the absence and presence of Na_2MoO_4 (10^{-3} to 10^{-1} M). Such plots exhibit only semicircular behavior, indicating that the reaction is under charge transfer control.[39] The polarization resistance (R_p) values are calculated from the differences in impedance at lower and higher frequencies, as suggested by El-Sayed.[40] To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of impedance is maximum ($-Z^{=}_{\mathrm{max}}$) is found and C_{dl} values are obtained from the following equation:

$$f(-Z^{=}_{\mathrm{max}}) = 1/2\pi C_{dl} R_p.$$

Table 1 gives the values of pH, R_p polarization resistance and C_{dl} for tin in 0.1 mol dm^{-3} citrate-chloride ion containing various concentrations of the investigated additives ($CrO_4{}^{2-}$, $WO_4{}^{2-}$, and $MoO_4{}^{2-}$) in active region (−200 mV vs. SCE). The increase of R_p values with concentration of the additive was in the following sequence:

$$CrO_4{}^{2-} > WO_4{}^{2-} > MoO_4{}^{2-}$$

It is interesting that $CrO_4{}^{2-}$ leads to significantly higher R_p values compared with $WO_4{}^{2-}$ and $MoO_4{}^{2-}$, which reflects that the $CrO_4{}^{2-}$ anions remain the best inhibitor to retard the corrosion of tin. This order is in good agreement with the observed potentiostatic transient results at the same potential region (−200 mV vs. SCE), as shown in Fig. 11. The above observation is supported by the values of C_{dl} in the presence of different concentrations of the additives. Thus, the values of C_{dl} decrease with increasing of the inhibitor concentration. This effect may be attributed to saturation of the free vacancies of the electrode surface by chemisorbed

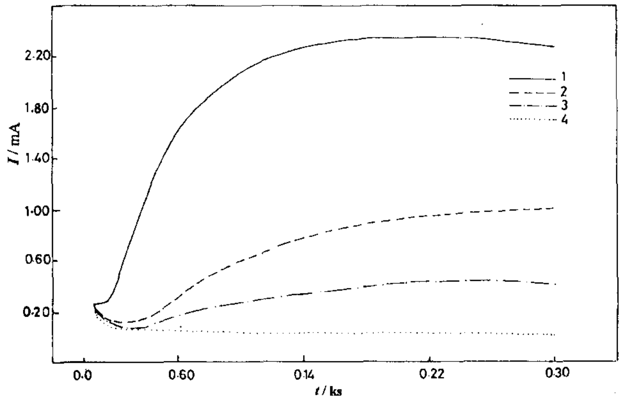

Fig. 11. Potentiostatic transients for tin anodes in 0.1 mol dm^{-3} citrate-chloride ions in the presence of 0.1 M oxo-anions: 1: free; 2: $MoO_4{}^{2-}$; 3: $WO_4{}^{2-}$; 4: $CrO_4{}^{2-}$ (at −200 mV vs. SCE).

Table 1. Effect of Group 6 Oxo-Anions on the EIS Parameters of Tin in the Citrate-Chloride Solution at −200 mV vs. SCE

Concn of additive	$CrO_4{}^{-2}$			$WO_4{}^{-2}$			$MoO_4{}^{-2}$		
mol dm^{-3}	pH	R_p/Ω cm^2	C_{dl}/μF cm^2	pH	R_p/Ω cm^2	C_{dl}/μF cm^2	pH	R_p/Ω cm^2	C_{dl}/μF cm^2
0.0	7.8	236	270	7.8	240	268	7.8	231	271
10^{-3}	8.6	1900	156	8.5	1420	161	8.3	1107	170
10^{-2}	9.0	2570	107	8.8	1730	112	8.6	1354	120
5×10^{-2}	9.8	3310	82	9.6	2890	93	8.8	2700	101
10^{-1}	10.4	3500	75	10.2	3050	81	9.0	2886	86

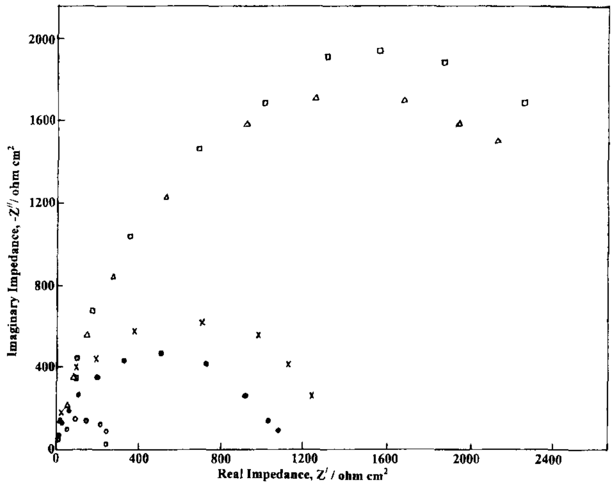

Fig. 12. Complex-plane impedance plots of tin in 0.1 M citrate-chloride ions (at −200 mV vs. SCE) in the presence of MoO_4^{2-} ions: ○: 0; •: 10^{-3} M; ×: 10^{-2} M; △: 5×10^{-2} M; □: 10^{-1} M.

anions accompanied by a decrease in the C_{dl} values.[6]

However, the observed discrepancy with potentiodynamic results, especially at lower concentrations (10^{-3} and 10^{-2} M) of the additives, can be explained as follows: the corrosion rate of tin in citrate-Cl^- ions solution increases gradually over longer periods of measurements even in the presence of additives at lower concentrations. Prolonged potentiodynamic measurements (50 min) in the solution allows for the formation of soluble tin citrate or tin chloride complex, presumably as more anodic sites are exposed to the dissolution process.[41] This may be the reason why the impedance studies in which measurements are taken in a short time (6 min) fail to reveal the acceleration of anodic dissolution. However, in other techniques such as potentiodynamic and potentiostatic studies (only at steady state of current values) longer periods of immersion allow for the metal dissolution and more anodic sites are exposed to the corrosion process.

Conclusion

The following points can now be made:

i) The localized corrosion of Cl^- in 0.1 mol dm^{-3} citrate is evident for all examined concentrations and pitting potentials are shifted towards more negative values with increasing Cl^- concentrations.

ii) Lower current values in the presence of equimolar citrate–oxo-anions with addition of Cl^-in various concentrations are observed compared with the values obtained in the absence of these oxo-anions. Thus, these oxo-anions may create a certain impediment or barrier to the attack of the aggressive Cl^- ions on the metal surface.

iii) Oxo-anions inhibit the anodic dissolution and the passivity breakdown in equimolar (0.1 M) citrate-chloride at higher concentrations but accelerate them at lower concentrations.

iv) The order of oxo-anions inhibiting effect on the aggressive Cl^- ions is as follows:

$$CrO_4^{2-} > WO_4^{2-} > MoO_4^{2-},$$

indicating that CrO_4^{2-} is more strongly adsorbed than the other investigated anions and exhibits a greater inhibition effect to prevent the pitting corrosion, probably through its ability to repair defects in the oxide film.

v) The impedance technique shows that inhibition of the anodic dissolution increases with increasing concentrations of the investigated additives.

References

1 S. C. Britton, C. Chem, M. A., F. I. M., F. I. Corrosion T. and F. R. I. C., "Tin Versus Corrosion," Tin Research Institute, I. T. R. Publication No. 510, 1975.

2 H. Leidheiser, Jr., A. F. Rauch, E. M. Ibrahim, and R. D. Granata, *J. Electrochem. Soc.*, **129**, 1651 (1986).

3 J. C. Skerlock and S. C. Britton, *Br. Corros. J.*, **8**, 210 (1973).

4 P. W. Board and R. V. Holland, *Br. Corros. J.*, **4**, 162 (1969).

5 M. S. Abd El Aal and F. H. Assaf, *J. Electrochem. Soc. India*, **30**, 38 (1981).

6 S. S. Abd El Rehim, A. A. El Samahi, and A. El Sayed, *Br. Corros. J.*, **20**, 196 (1985).

7 A. M. Azzam, S. S. Abd El Rehim, and M. H. Fawzy, *Appl. Chem. Biotchnol.*, **23**, 563 (1973).

8 V. K. Gouda, E. N. Rizkalla, S. Abd El Wahab, and E. M. Ibrahim, *Corros. Sci.*, **21**, 1 (1981).

9 M. Seruga, M. Metikos-Hukovic, T. Valla, M. Milun, H. Hoffschultz, and K. Wandelt, *J. Electroanal. Chem.*, **407**, 83 (1996).

10 A. El Sayed, F. H. Assaf, and S. S. Abd El Rehim, *Hung. J. Indust. Chem.*, **19**, 207 (1991).

11 K. Ogura and T. Majima, *Electrochim. Acta*, **24**, 325 (1979).

12 G. Roujini and M. B. Ives, *Corrosion*, **45**, 572 (1989).

13 M. Stern, *J. Electrochem. Soc.*, **105**, 638 (1958).

14 C. M. A. Brett, I. A. R. Gomes, and J. P. S. Martins, *J. Appl. Electrochem.*, **24**, 1158 (1994).

15 W. C. Moshier and G. P. Davis, *Corrosion*, **46**, 43 (1990).

16 G. A. Dorsey, *Plating*, **59**, 948 (1972).

17 A. M. Shams El Din, S. M. Abd El Haleem, and J. M. Abd El Kader, *J. Electroanal. Chem.*, **65**, 335 (1975).

18 A. M. Shams El Din and S. M. Abd El Haleem, *Werkst. Korros.*, **8**, 571 (1974).

19 D. Bijimi and D. R. Gabe, *Br. Corros. J.*, **18**, 88 (1983).

20 R. E. Van de Leest and G. Krijl, *Thin Solid Films*, **72**, 237 (1983).

21 S. S. Abd El Rehim, A. El-Sayed, and A. A. Samahi, *Surf. Coat. Technol.*, **27**, 205 (1986).

22 F. Rashwan, A. El-Sayed, and H. Mohran, *Bull. Electrochem. India*, **9**, 57 (1993).

23 R. G. P. Elbourne and G. S. Buchanan, *J. Inorg. Nucl. Chem.*, **32**, 493 (1970).

24 J. C. Sherlock and S. C. Britton, *Br. Corros. J.*, **7**, 180 (1972).

25 A. E. Smith, *Analyst*, **98**, 209 (1973).

26 F. H. Assaf, A. El Sayed, and S. S. Abd El Rehim, *Bull. Electrochem. India*, **7**, 445 (1991).

27 M. Drogowska, H. Menard, and L. Brossard, *J. Appl. Electrochem.*, **27**, 169 (1997).

28 F. M. Abd El Wahab, J. M. Abd El Kader, H. A. El Shayeb, and A. M. Shams El Din, *Corros. Sci.*, **18**, 997 (1978).

29 Z. Szklarska-Smialowska, "Proceedings of the 7th. European Sympsium on Corrosion Inhibitors," Ann. Uni. Ferrara N.S.,

Sez. V., Suppl. N. 9,979 (1990).

30 J. G. N. Thomas and T. J. Nurce, *Br. Corros. J.*, **2**, 13 (1967).

31 R. H. Abu Zahra and A. M. Shams El Din, *Corros. Sci.*, **5**, 517 (1965).

32 J. Augustynski, "Passivity of Metals," ed by R. P. Frankenthal and J. Kruger, The Electrochemical Society, Princeton, NJ (1978).

33 H. H. Uhlig and P. J. King, *J. Electrochem. Soc.*, **1**, 106 (1959).

34 K. Ogura and T. Ohama, *Corrosion*, **40**, 47 (1984).

35 Ya. M. Kolotyrkin, R. M. Lazorenko-Manevich, and L. A. Sokolova, *J. Electroanal. Chem.*, **228**, 301 (1987).

36 Yu. N. Mikhailovskii, *Zashch. Met.*, **20**, 179 (1984).

37 S. Glasstone and A. Hickling "Electrolytic Oxidation and Reduction," Chapman and Hall, London (1935), p. 134.

38 S. M. Abd El Haleem, *Br. Corros. J.*, **11**, 215 (1976).

39 R. Babic, M. Metikos-Hukovic, Z. Grubac, and S. Brinic, *Br. Corros. J.*, **30**, 288 (1995).

40 A. El-Sayed, *J. Appl. Electrochem.*, **27**, 193 (1997).

41 S. Rengamani, S. Muralidharan, M. Anbu. Kulandainathan, and S. Venkatakrishna Iyer, *J. Appl. Electrochem.*, **24**, 355 (1994).