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Corrosion Behaviour of Tin in Stagnant Salt Solutions

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The corrosion behaviour of tin in stagnant solutions of Cl^-, SO_4^{2-}, S^{2-}, HPO_4^{2-} CO_3^{2-}, NO_3^-, I^-, SO_3^{2-}, NO_2^-, $C_6H_5COO^-$, CrO_4^{2-} and vanadate ions has been studied individually. This type of study has been achieved by using potential-time, weight-loss measurements and polarization technique as well. The results obtained indicate that the corrosion behaviour of tin depends on the nature and the concentration of the anion used, and the whole process is mainly under anodic control.

INTRODUCTION

It is well known that corrosion is an electrolytic character of solutions containing metals and it depends upon the electrochemical conditions under which the reaction occurs on the metal surface[1–4]. Moreover, both metallurgical and environmental factors have a remarkable influence on the rate, as well as, on the distribution of corrosion. Benzoate and phenyl acetate buffer solutions[5] were considered as inhibitors of steel and iron corrosion in the galvanic-couples of steel with Al, Cu, Ni, Cr and with alloy of Fe-Sn. Potential-time curves were determined for uniformly prepared surface of chemically pure tin in $NaHCO_3$ and Na_2CO_3 solutions[6]. Schmidt *et al*[7] used tin-sheet (99.8% pure) and tin-plate in NaCl solution separately, with and without oxygen. They found that the corrosion of pure tin was greater in NaCl (10 g. dm^{-3}) and less in the absence of oxygen. Hoar[8] studied the attack on tin by salt solutions of alkali metals. Sanyol[9] and others[10,11] also studied the corrosive inhibiting action of sodium benzoate on tin.

In addition to these, Shams El-Din and his co-workers[12], as well as Nakai[13] and Ragheb *et al.*[18] studied the anodic oxidation of tin galvanostatically in NaOH and H_3PO_4 solutions.

The solubility of the reaction product between the metal and the corrosive medium was extensively studied by Frasch[14]. Gendan[15] and Almond[16] worked on tin and tin coated with copper in Na_2CO_3 and formic acid solutions, respectively. Kim[17] used the radioactive-tracer method to follow the distribution of tin in the reaction products. Rapid detinuing in different concentrations of nitric acid[19,20], or organic acids[21] and in plain food-cans (due to the presence of nitrate as a conservative substance[22]) was successively studied. Tin-based binary alloys were examined by changing their composition and the corrosion phenomenon was well studied in different acid solutions[23-26]. The rate of corrosion was found to be increased by increasing the mechanical vibration of the tin-electrode in solution under question[27]. It was also found to be dependent on the pH values and the concentrations of the chloroorganic acids used[28]. Thiosemicarbazide[29] in alkaline solution was found to inhibit the corrosion of tin-lead alloy by a maximum of 42%.

EXPERIMENTAL

Materials

Tin$^-$ electrode used in this type of work (Johanson and Mattey, London) was in the form of a rod, one cm in length and 0.5 cm in diameter. Before every measurement, tin electrode surface was degreased and abraded successively with very fine emery-paper and with a soft cloth, whereby it attained a rather smooth bright surface. It was then thoroughly washed with distilled water and rinsed with the electrolyte to be used. electrical contact was achieved by soldering a 1 mm. thick copper wire to the end of the rod. The copper wire was isolated from the solution by a pyrex glass tube fitted tightly to the tin sample. A constant pre-determined area (0.5 cm^2) was always exposed to the test solution by waxing the edge of the electrode. Measurements of the corrosion rate were made by using sheet specimens of apparent surface-area of 20 cm^2.

The electrode was abraded successively down to "00" grade emery-paper. In order to obtain the exact data, average values of 2–3 runs with a new clean electrode surface and a fresh electrolyte were taken. Stock solutions of the tested salts were prepared by dissolving the appropriate amounts in doubly distilled water and then diluted as required. All the salts used were of analytical grade.

The cell used for the polarization measurements was composed of two compartments, separated by a fritted glass-disc to prevent mixing of anolyte and catholyte. Critical current density for passivation was adopted using the procedure of Uhlig and Woodside[30] technique. Potential data were measured with reference to a saturated calomel electrode (SCE) with a fine lugging capillary tube positioned close to the electrode surface in order to minimise ohmic potential drop.

Measurements

1. Potential-Time Measurements: The cell used was in the form: calomel electrode/ electrolyte/working electrode. The E.M.F. of the cell was measured by a potentiometer until a steady-state value was reached at 30°C.

2. Determination of Critical-Current Densities for Passivation: The procedure of Uhlig and Woodside[30] was adopted. The tin electrode was first cathodically treated and then was anodically polarized with successive increasing current densities, whereby the corresponding potentials were recorded.

3. Weight-loss Technique: The tin samples (2 × 5 × 0.5) cm were abraded with different grades of emery-paper; washed by acetone; weighed and then each sample was immersed in 100 ml pyrex glass-beaker containing 60 ml of the solution to be tested. The samples were then cleaned by brushing it under running water to remove corrosion products, then dried and reweighed. All the experiments were carried out in air-thermostat adjusted at 30°C. The solution lost by evaporation during the period of the test was compensated by adding distilled water. The results were duplicated and the mean values were computed.

4. Linear-Polarization Measurements: The rates of corrosion were determined by linear-polarization technique.

RESULTS AND DISCUSSION

A. Results

1. Potential-time measurements: The variation of tin electrode potential under open-circuit conditions in salt solutions was followed as a function of time till the steady-state values were established (Fig. 1 as an example). The

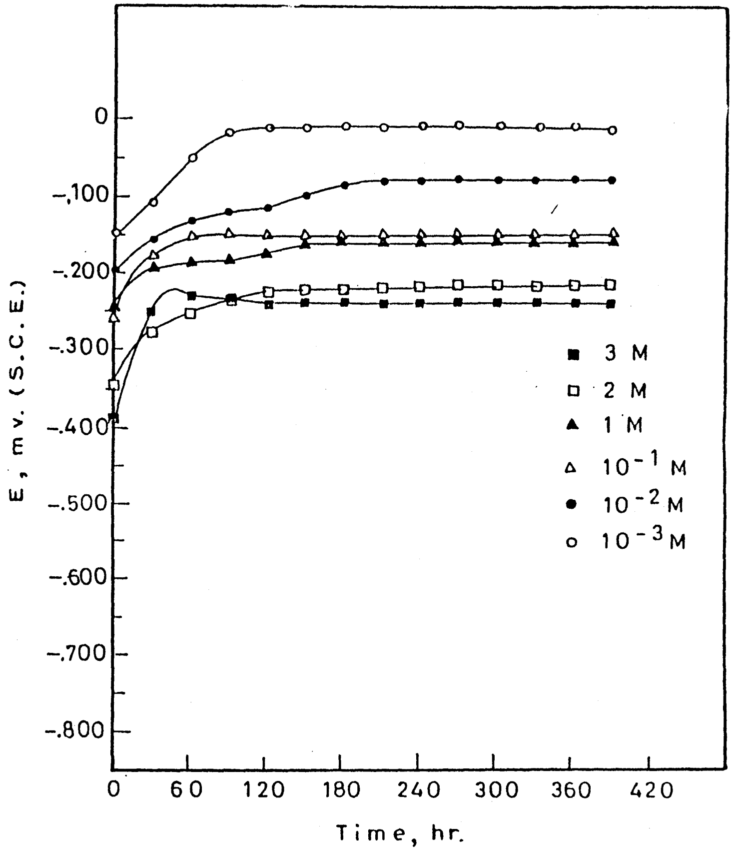

Fig. 1 Relation between potential and time for tin in KNO_3 solution at 30°C

concentration of the test solutions (containing anions suggested for study) varied between 10^{-3}–3 M. The experimental results are tabulated in Table 1.

The time necessary for reaching the steady state potential was ranged from 120 to 180 minutes (figures are not shown). For the inhibiting anions, nitrite, benzoate, chromate and vanadate, the steady-state potentials of tin in their solutions approached more noble values as it can be seen from Table 1. On the other hand, the tin-electrode potential was shifted towards the less noble values on immersing in relatively concentrated solutions.

2. *Effect of Salt Concentration on the Steady-State Potential of Tin*: Figs. 2 and 3 represent the variation of the steady-state potential of tin in the presence of aggressing and inhibiting anions, respectively as a function of log molar

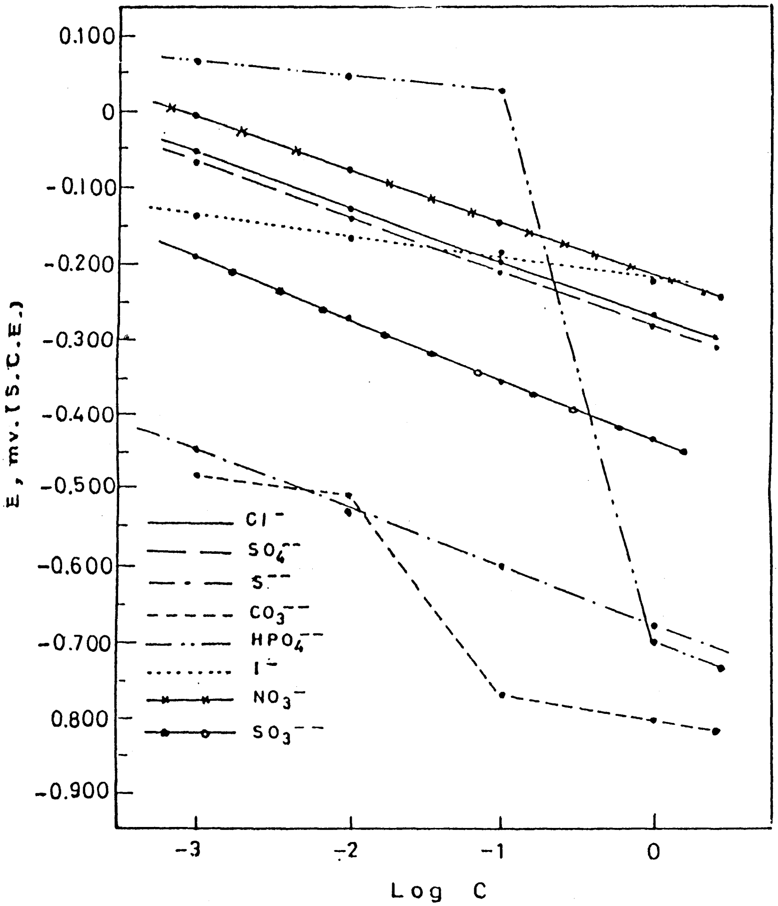

Fig. 2 Relation between E/log C for corrosive anions for tin.

TABLE 1

INITIAL (E_1) AND FINAL (E_2) STEADY STATE POTENTIAL (E_{corr}) IN mV FOR TIN IN THE TESTED SALT SOLUTION FOR DIFFERENT CONCENTRATIONS (SCE)

Conc. (M)	KCl		K_2SO_4		K_2S		K_2HPO_4		K_2CO_3		KNO_3		KI		K_2SO_3		KNO_2		$C_6H_5COO^-$		CrO_4^{--}		Vanadate	
	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
3	440	300	—	—	—	—	740	725	800	850	390	260	—	—	450	425	140	+60	205	+10	—	—	—	—
2	305	290	290	300	—	—	580	700	780	825	350	240	—	—	390	400	100	+50	260	30	260	+50	—	—
1	550	250	310	260	705	700	525	675	690	780	250	180	450	425	200	380	450	25	225	50	190	25	—	—
10^{-1}	490	215	410	200	650	605	450	+25	650	760	160	160	340	325	320	330	460	40	400	190	290	50	600	325
10^{-2}	360	160	305	190	650	550	260	+50	405	525	200	100	250	260	250	260	400	150	325	250	295	110	650	440
10^{-3}	315	60	290	150	500	450	150	+60	350	450	150	50	390	225	390	240	500	160	500	460	295	125	700	570

concentration of the salt solution. The results indicate the occurrence of a linear logarithmic segment in the E/log C lines.

On using the aggressive anion solutions (Cl^-, SO_4^{2-}, S^{2-}, HPO_4^{2-}, CO_3^{2-}, NO_3^-, I^-, SO_3^{2-}) the increase of the anion concentration was accompanied by a sharp decrease (negativation) in the steady-state potential. The initial parts of all the curves shown in Fig. 2 are more or less linear and the respective slopes of these linear parts for the above-mentioned anions are about (–63) mV for Cl^-; (–65) mV for SO_4^{2-}; (–75) mV for SO_3^{2-}; (–75) mV for S^{2-}; (–20) mV for HPO_4^{2-}; (–25) mV for CO_3^{2-}; (–45) mV for NO_3^- and (–62) mV for I^-. In the case of CO_3^{2-} although there is a break in the E/log C mV line, yet the two parts are approximately parallel and the slopes of the two linear parts are 40 mV. The curve representing CO_3^{2-} shows an initial potential drift towards the more negative values (relatively greater than the rest of the aggressive anions), up to a concentration of 10^{-2} M, followed by a region of concentration independence up to 10^{-1} M, and then the potential shifts slightly towards the more negative values.

In conclusion, it could be stated that the nature of the aggressive anion exerts

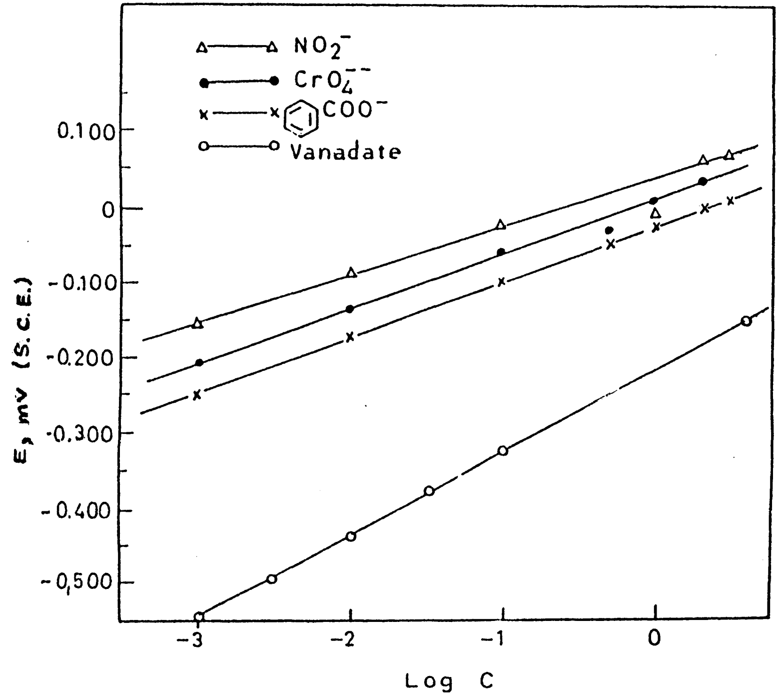

Fig. 3 Relation between E/log C for tin in aerated solution of inhibitive anion.

a profound effect on the position of the potential–log C curve and this is the case of HPO_4^{2-}. However, at any concentration the negativation of the potential increases in the order:

$$CO_3^{2-} > S^{2-} > SO_3^{2-} > SO_4^{2-} > Cl^- > I^- > NO_3^- > HPO_4^{2-}$$

On the other hand, and as is shown in Fig. 3, the increase in the concentration of the inhibiting anions (NO_2^-, $C_6H_5COO^-$, CrO_4^{2-} and vanadate) was accompanied by a slight decrease in the steady-state potential of tin. Moreover, the shift was observable and sharp in the case of vanadate, and considerably less for benzoate as compared with NO_2^- and CrO_4^{2-} which have a passive potential around (–150) and (–600) mV, respectively. The passive potential was (–210) mV in the case of benzoate.

3. *Weight-Loss Technique:* The corrosion rates (dw/dt vs. t) in the stimulating salt solutions were nearly similar and straight lines were obtained (Fig. 4). It could be concluded that the rates decreased in the order $CO_3^{2-} > S^{2-} = SO_3^{2-} > SO_4^{-2} > Cl^- > I^- > NO_3^- > HPO_4^{2-}$. The values of corrosion rate were tabulated in Table 2.

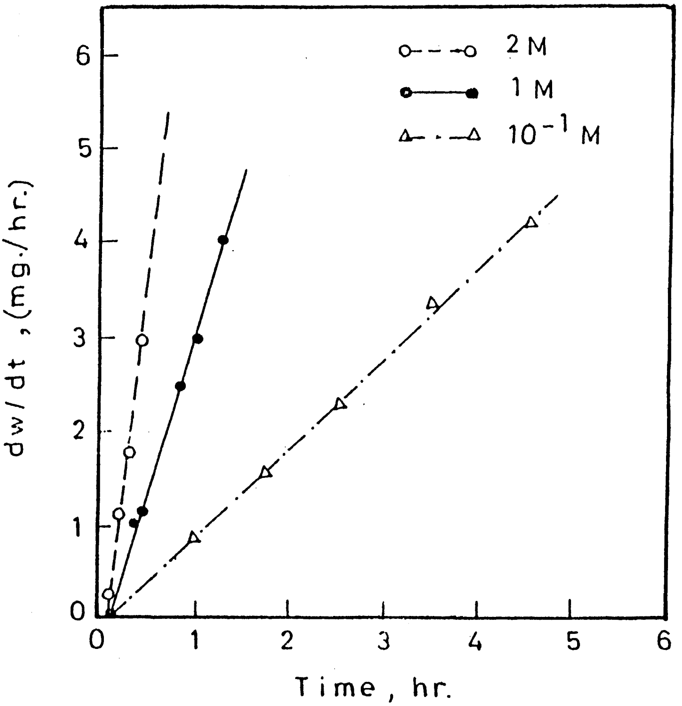

Fig. 4 Relation between wt. loss and time for tin in KNO_3 solution at 30°C.

TABLE 2
CORROSION RATES OF TIN IN DIFFERENT STAGNANT SALT SOLUTIONS (10^{-1} M) AT 30°C

Anion	Corrosion rate ($mg/cm^2/hr$)	Anion	Corrosion rate ($mg/cm^2/hr$)
CO_3^{2-}	1.380	NO_3^-	0.500
S^{2-}	0.780	HPO_4^{2-}	0.020
SO_3^{2-}	0.780	NO_2^-	0.070
SO_4^{2-}	0.700	$C_6H_5COO^-$	0.060
Cl^-	0.680	CrO_4^{2-}	0.050
I^-	0.550	VO_4^{2-}	0.010

4. *Linear-Polarization Method:* The corrosion rate of tin was also determined by using the linear-polarization method. The corrosion rate (dE/dT) was mathematically calculated from the equations:

$$I_{corr.} = \frac{0.029}{Slope} = Am/cm^2$$

$$dE/dT = \frac{I_{corr.}}{Valency} \times \frac{Atomic\ weight}{Faraday} = g/cm^2/sec$$

The relation between the molar concentration of the tested salt solutions and the corrosion rates of tin gave always straight lines as is shown in Fig. 5. It could be concluded that the rate was decreased in the order

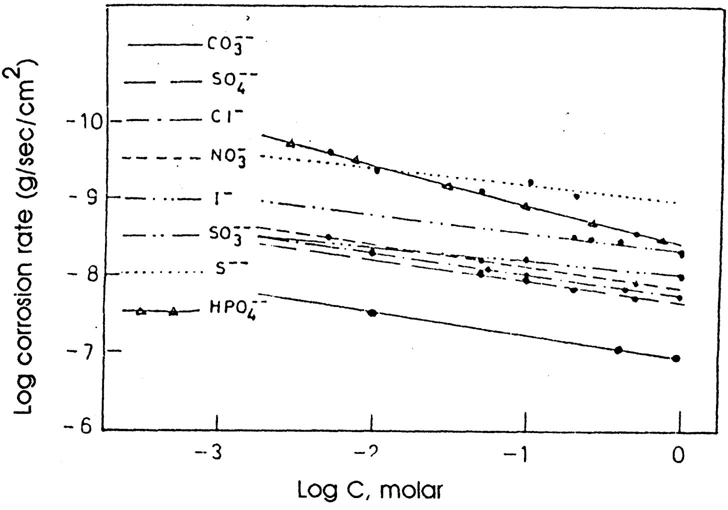

Fig. 5 Relation between log corrosion rate and log C for tin in aggressive solutions.

$CO_3^{2-} > SO_4^{2-} > Cl^- > NO_3^- > I^- > S^{2-} = SO_3^{2-} > HPO_4^{2-}$. This is somewhat simillar to the order obtained from the weight-loss technique.

5. *Anodic-Polarization Measurements:* The critical current densities for passivation were measured for tin in the aggressive anion solutions as well as in the inhibiting anion solutions, (Table 3). Fig. 6 represents the relation between log current density (c.d.) and log C of tin in different corrosive anion solutions. It is clear that, on increasing the applied c.d., the electrode potential changes slightly at first till it reaches a definite critical value, then it shifts abruptly in the noble direction. The values of the limiting current depend on the concentration of the solutions as well as on the nature of the anion used. In contrary, on using inhibiting anion solutions and at relatively lower concentrations, tin was passivated at much higher c.d. compared with those required in the case of concentrated solutions. The results are given in Table 3. From this table it could be seen that the values of log c.d. are increased by increasing the concentration of the aggressive anions used (i.e., proportional relation), whereas, it decreased by increasing the concentration of the inhibiting anions used (i.e., inversely proportional relation). All the curves obtained in both cases are nearly straight lines, (Fig. 6). The order of decreasing the passivation is as follows:

$$CO_3^{2-} > S^{2-} = SO_3^{2-} > SO_4^{2-} > Cl^- > NO_3^- > I^- > HPO_4^{2-}$$

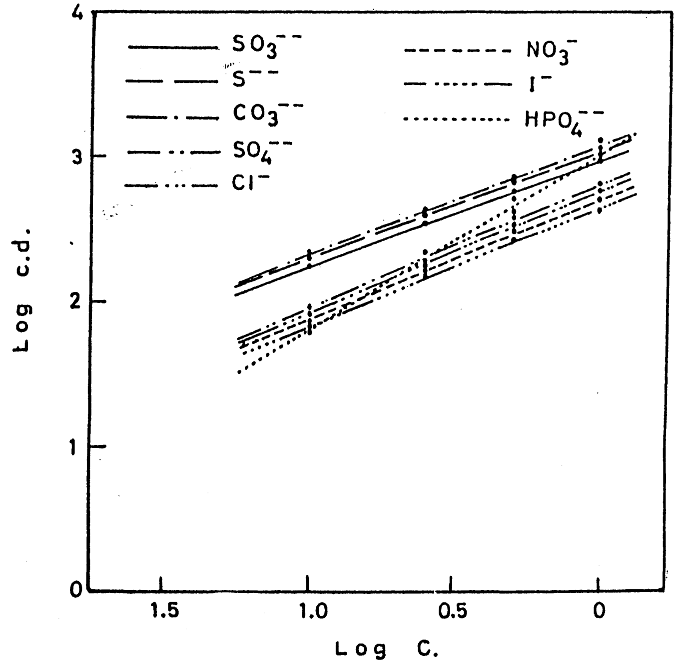

Fig. 6 Relation between log c.d. and log C for tin in different corrosive anions.

TABLE 3
CRITICAL CURRENT DENSITIES FOR PASSIVATION OF TIN IN DIFFERENT AGGRESSIVE AND INHIBITING ANION SOLUTIONS

Anions	Conc., (M)	log c.d., (MA/cm^2)	Anions	Conc., (M)	log c.d., (MA/cm^2)
Cl^-	1	2.90	I^-	1	2.60
	5×10^{-1}	2.50		5×10^{-1}	2.40
	25×10^{-2}	2.25		25×10^{-2}	2.15
	1×10^{-1}	1.95		1×10^{-1}	1.80
SO_4^{2-}	1	2.70	SO_3^{2-}	1	3.00
	5×10^{-1}	2.50		5×10^{-1}	2.75
	25×10^{-2}	2.25		25×10^{-2}	2.50
	1×10^{-1}	1.90		1×10^{-1}	2.25
S^{2-}	1	3.05	NO_2^-	1	2.15
	5×10^{-1}	2.80		5×10^{-1}	2.30
	25×10^{-2}	2.60		25×10^{-2}	2.45
	1×10^{-1}	2.30		1×10^{-1}	2.55
HPO_4^{2-}	1	3.00	$C_6H_5COO^-$	1	1.80
	5×10^{-1}	2.70		5×10^{-1}	1.90
	25×10^{-2}	2.30		25×10^{-2}	2.00
	1×10^{-1}	1.80		1×10^{-1}	2.10
CO_3^{2-}	1	3.10	$C_rO_4^{2-}$	1	2.00
	5×10^{-1}	2.85		5×10^{-1}	2.15
	25×10^{-2}	2.60		25×10^{-2}	2.35
	1×10^{-1}	1.80		1×10^{-1}	2.45
NO_3^-	1	2.70			
	5×10^{-1}	2.49			
	25×10^{-2}	2.25			
	1×10^{-1}	1.90			

B. Discussion

From the results reported in this work, it is clear that the potential values of tin-electrode are characterised by an initial rapid shift followed by gradual small drifts towards the negative values, which are in accordance with the corrosion properties of the aggressive anions. The time required to reach the steady-state varies according to the nature and the concentration of the anion used. The negativation is larger at higher concentrations (Table 1). The concentration has a little effect on tin-electrode potential in solution containing the aggressive anions higher than 1 M.

In dilute solutions (conc. 10^{-3}–10^{-1} M), the potential and the corrosion rate vary with the variation in the type and the concentration of the anions. Generally, any increase in the aggressive anions concentration leads to an increase in the electrode potential as well as the corrosion-rate of tin. These results are in good agreement with those reported by Tomashov[31] and Speller[32].

Moreover, this concentration increase leads to a decrease in the oxygen concentration and this is due to the salting out effect.

It is reported[31,32] that the solubility of oxygen decreases in the order NO_3^- > Cl^- > SO_4^{2-}, it strongly depends on both type and concentration of the anion used, and its relation with the concentration is exponential. It could be concluded that the anion of comparatively less salting out effect has less corrosive action. Individually, any increase in the anion concentration (10^3 – 1 M) will be accompanied by a decrease in the oxygen concentration, and will give slight increase in both potential and corrosion-rate. It is most probable that the increase in anion's concentration could lead to a relative increase in the anodic area, and then decreases the anodic polarization with the establishment of a more negative overall measured potential of the system. Thus the whole process becomes mainly under anodic control.

If the decrease in the oxygen-concentration is considered seprarately from that of the salt present, it might lead to one of the following situations:

(i) Increase in cathodic-polarization with a negative shift in potential accompanied in the same time with a decrease in the corrosion rate.

(ii) Decrease in the cathodic area leading to a negative shift in potential and to an increase in the corrosion rate.

The described behaviour in both cases (i) and (ii) could possibly be used to explain the results of the present work leading to important conclusions. Consequently, the increase in the aggressive anions concentration as well as the decrease in the oxygen concentration, both lead to an increase in the anodic area and thus the reaction is mainly under anodic control.

However, there are evidences[33,34] to indicate the dependence of the steady-state corrosion potential on the ratio of anodic/cathodic areas. Thus, the increase of aggressive anion concentrations enchances the destruction of the oxide-film, while the competing oxide-film repair is impeded.

The critical current density for passivation was taken as a measure of the mobility of the metals[33,35] as well as for testing the effectiveness of inhibitors[36]

In the presence of inhibiting anions, the negativation of potential with the simultaneous decrease in corrosion rate (the order is NO_2^- > $C_6H_5COO^-$ > CrO_4^{2-} > Vanadate) indicates that the corrosion in the tested inhibiting anions is mainly under cathodic control. This may be explained on the promise that the adsorption of these anions interferes with the cathodic depolarization of tin by oxygen. The function of the inhibitors is to block the pores of the oxide-film. Thus, the passive potential is most probably due to the high resistance[37] resulting from blocking the pores by the adsorbed inhibitor which leads to a very low current density at the cathode. Consequently, the local anode becomes polarized to the open circuit potential. In this way local potential differences on the surface are eliminated and there is no longer any driving-force for local corrosion cells.

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