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Corrosion inhibition of Al–bronze in acidified 4% NaCl solution

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The synergistic effect between either benzotriazole (BTA) or thiourea (TU) and iodide ion are used to retard the dissolution of Al–bronze alloy in deaerated solution of acidified 4% NaCl of pH 1.8–2 at 60 °C; this is shown by the weight loss and polarization techniques. Iodide ion alone has no effect on the dissolution of the alloy but addition of 100 p.p.m. KI to 300 p.p.m. of both BTA and TU improved the inhibition efficiency to 92% and 78.8%, respectively, and also decreased the anodic current density in both media.

1. Introduction

Copper-based alloys have long enjoyed commercial popularity as condenser and heat exchanger materials. Among them, the Al–bronzes exhibit excellent mechanical and chemical properties [1–9].

The corrosion of copper-based alloys and their inhibition by organic inhibitors in acid solution have been studied by several authors [10–15]. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial cleaning, acid descaling and oil-well acidizing.

Corrosion inhibition by benzotriazole (BTA) has been extensively studied, especially because of its high efficiency in the corrosion protection of copper and copper alloys exposed to a variety of attacking media [16–21]. It is generally assumed that BTA forms a polymeric cuprous complex on the metal surface which prevents further copper dissolution.

The effect of dibutyl thiourea (DBTU) on the corrosion of the copper–nickel alloy in acidified seawater was examined at 60 °C [22]. The results indicate that the compound (DBTU) is decomposed at the brass surface.

Potassium iodide (KI) improves the efficiency of some inhibitors against iron corrosion [23–25]. A recent study [26] shows that a synergistic effect exists between BTA and iodide ions in the case of corrosion of copper in sulphuric acid.

In the present study two different acid inhibitors BTA and TU are evaluated towards corrosion inhibition of Al–bronze in acidified 4% NaCl of pH $\cong$ 1.8–2.0. Addition of KI to both inhibitors are essentially studied to show the nature of the chemisorbed layer on the alloy surface.

2. Experimental procedure

2.1. Chemicals and materials

The inhibitors, acid NaCl were reagent grade and were used as supplied. Solutions were prepared using doubly distilled water.

Each experiment was performed using deaerated solution of 4% NaCl in the presence of 10^{-2} M HCl of pH 1.8–2, stirred by a magnetic stirrer.

The source of the aluminium bronze alloy is the same as that of Ateya [9], with the following composition: 7 Al, 0.04 Fe, 0.01 Ni, 0.04 Si, 0.0006% Mg, and the remainder is Cu.

2.2. Weight-loss test

The corrosion rate (CR) of Al–bronze was determined by the weight loss method as mg $cm^{-2} h^{-1}$. The Al–bronze test coupons were in the form of rectangles of sides $1 \times 4 \times 0.1$ cm thick. The procedure followed was similar to that reported previously [27].

The corrosion rates of the test coupons immersed in deaerated solution of acidified 4% NaCl of pH 1.8–2 were determined over several temperature settings of 25, 30, 40, 50 and 60 °C.

The effect of both BTA and TU inhibitors on the dissolution kinetics was measured at 60 °C in absence and presence of different concentrations of KI additives.

2.3. Electrochemical measurements

The polarization measurements were recorded using a Wenking potentiostat (model POS 73). Briefly, tests were conducted on the test electrodes with sides $1.2 \times 1 \times 0.1$ cm thick after cleaning. The anodic polarization scans were conducted in deaerated solutions of acidified 4% NaCl at 60 ± 2 °C using a Pt counter electrode and an external saturated calomel reference electrode (SCE) interfaced to the test solution via a salt bridge assembly and luggin capillary. The test solution was continuously stirred, and before use the Al–bronze electrodes were pretreated as in the case of weight loss measurements. Prior to commencing the polarization measurements the samples were kept at -600 mV versus SCE for 30 min in the test environment, to reduce the oxides (mainly copper oxide) on the sample surfaces before carrying out the measurement [26]. After that the inhibitor was injected into the electrolyte and the potential was then scanned from −600 to +600 mV versus SCE at a scan rate of 10 mV min^{-1}.

3. Results and discussion

3.1. Weight-loss results

The curves of Fig. 1 represent the variation of the weight loss with time of Al–bronze immersed in deaerated solutions of acidified 4% NaCl of pH 1.8–2 at temperatures varying between 25 and 60 °C. The curves show two rates of dissolution, which have been reported previously [27] in the case of brass in the same medium; a linear relation started at a limited value of copper concentration of the corrodent due to the autocatalytic effect on the formation and dissolution of cuprous chloride (CuCl).

The effect of BTA and TU on the dissolution of Al–bronze in the test solution was examined at 60 °C, which is the temperature commonly adopted during the acid cleaning of the distillers. The measurements were carried out in the usual manner in which the test coupons were exposed to test solution containing a definite inhibitor concentration. At increasing time intervals the specimens were withdrawn, washed, dried, weighed and reintroduced into the same solution for subsequent evaluation.

Fig. 2 shows the effect of increasing BTA concentration on the dissolution of Al–bronze in acidified 4% NaCl solution. The curve for 0 p.p.m. represents the inhibitor-free solution. Observation of the curves of this figure reveals that BTA causes slight inhibition effect between 100 and 600 p.p.m. By increasing the concentration of the inhibitor to above 800 p.p.m. retards the dissolution of alloy till 20 h and after that the dissolution is almost completely stopped due to the formation of a more protective film of BTA, which prevents the adsorption of anions. On the other hand, the corrosion rate (CR) which was calculated during the linear relation is very low, and the inhibition efficiency amounts to above 99.5% (Table I).

The effect of TU additives on the dissolution of Al–bronze in the test solution was also examined at 60 °C. The concentration of the inhibitor added varied between 100 and 300 p.p.m. (Fig. 3). As is evident from the curves, TU extended the first dissolution period of Al–bronze (to about 50 h at 300 p.p.m.) but increased the CR with respect to the TU-free solution (Table I). This behaviour has been reported previously for dibutylthiourea [22] and can be attributed to its decomposition at 60 °C on the electrode surface (70 Cu/30 Ni alloy) and the products of decomposition are either inactive or weaker inhibitors than the mother substance.

3.2. Electrochemical measurements

The anodic polarization behaviour of Al–bronze in the test solutions containing different additives of BTA is shown in Fig. 4. In all cases except the inhibitor free curve (●), the initial active region is followed by passivation behavior and two anodic current peaks are observed, I and II. The two peaks in each curve are followed at higher potentials by a slight decrease in the current density. Several studies [28–31] suggest that peak I is associated with oxidation of copper to Cu^{I} and peak II is associated with oxidation of Cu^{I} to Cu^{II} state.

Solutions containing increasing amounts of BTA shift the positions of the active peaks I and II to more negative values and decrease the time of its formation.

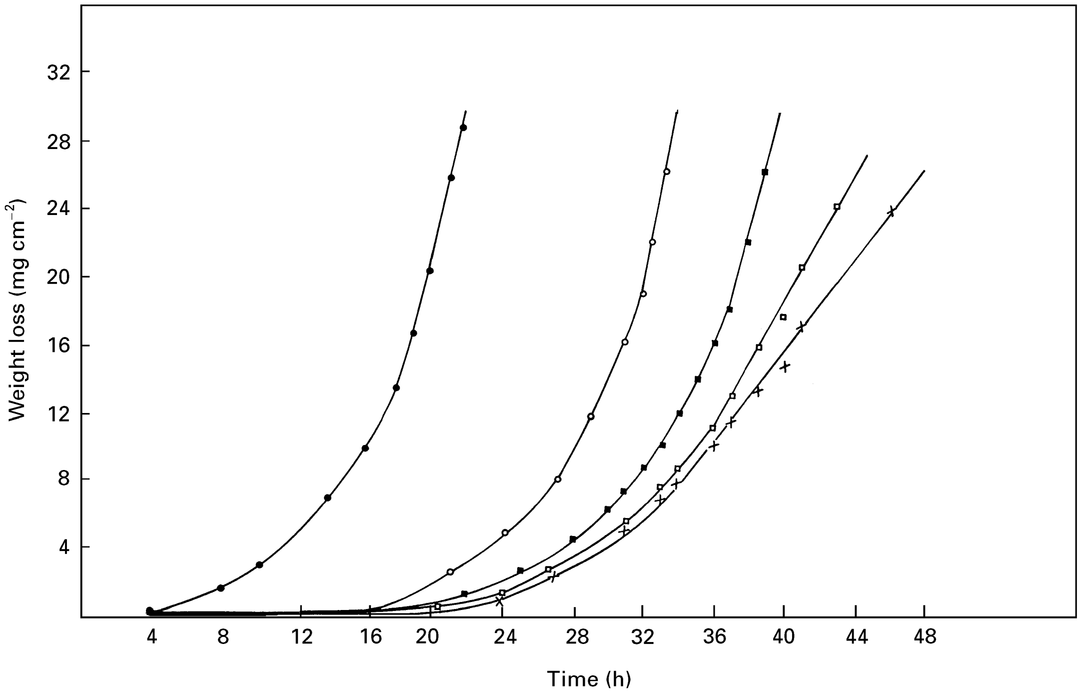


Figure 1 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at different temperatures. (●) 60 °C; (○) 50 °C; (■) 40 °C; (◇) 30 °C; (×) 25 °C.

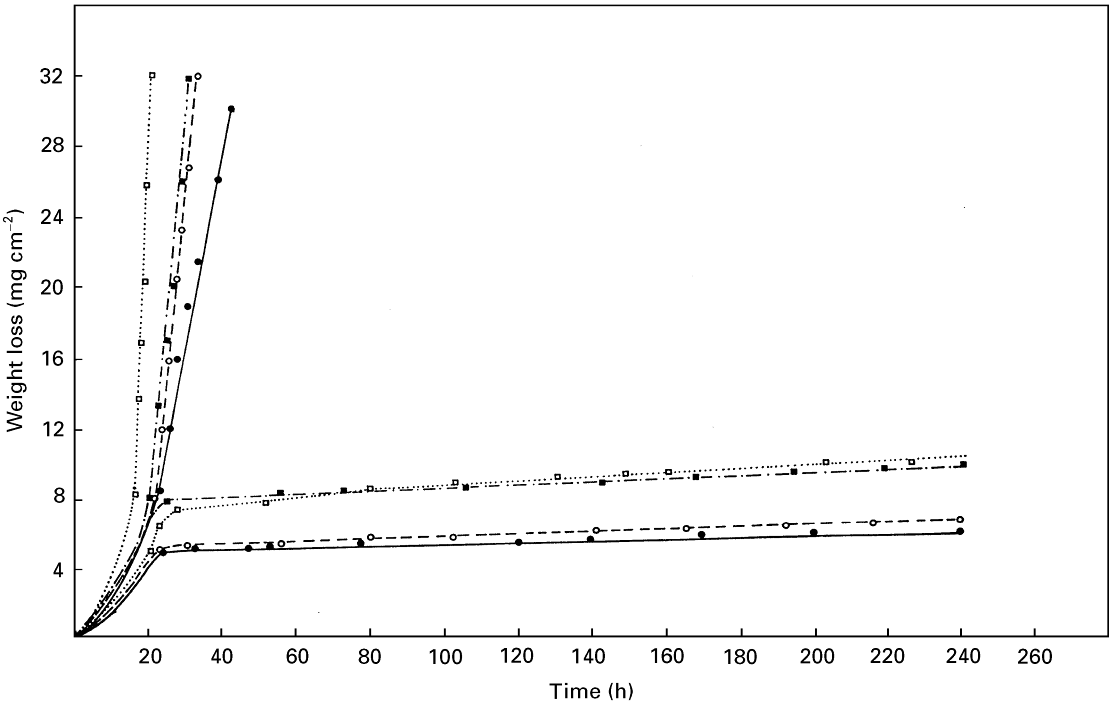


Figure 2 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of different additions of BTA in p.p.m. (□) 0; (■) 100; (○) 300; (●) 600 (upper curves); (□) 1000; (■) 800; (○) 1100; (●) 1200 (lower curves).

TABLE I Percentage inhibition efficiency of inhibitor concentrations on the corrosion rate (CR) of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C

Inhibitor concentration (p.p.m.)	CR (mg cm^{-2}h^{-1})				Inhibition efficiency (%)			
	BTA	BTA + 100 KI	TU	TU + 100 KI	BTA	BTA + 100 KI	TU	TU + 100 KI
Zero	4.15	4.15	4.15	4.15	–	–	–	–
100	2.80	1.20	6.40	2.80	32.5	71.10	− 54.20	32.50
200	–	0.50	6.00	1.80	–	88.00	− 44.50	56.60
300	1.64	0.34	4.25	0.88	60.4	92.00	− 3.60	78.80
600	1.00	–	–	–	75.9	–	–	–
800–1000	0.02				99.5			
1100–1200	0.01				99.8			

$$\% \text{ Inhibition efficiency} = \frac{\mathrm{CR}_{\mathrm{inh.free}} - \mathrm{CR}_{\mathrm{inh.}}}{\mathrm{CR}_{\mathrm{inh.free}}} \times 100$$

On the other hand, the active current peaks and current densities more than 300 mV decrease hand in hand with additive concentration up to 1000 p.p.m. Due to the formation of a more protective adsorbed film, the active current peaks and current density (more than 300 mV) decreases to about 10 000 μA and 480 μA, respectively, as shown in Table II, so that the active current peak I represents the time needed to form a BTA protective film.

It is found from the polarization curves that addition of 100 p.p.m. BTA decreases the dissolution of the alloy, while in case of weight loss measurements the effective concentration is above 600 p.p.m. This difference occurs because the time of immersion in the latter case is more than in the first which allow a higher concentration of the dissolved Cu^{2+}. This higher concentration leads to an increase in the dissolution of the alloy due to the autocatalytic effect [27] which retards the adsorption of the inhibitor.

Inspection of the TU polarization curves of Fig. 5 shows that the curve obtained when adding 100 p.p.m. TU shows pronounced irregularities especially from −150 mV to +150 mV. Increasing the additive concentration to 200 p.p.m. gives the same result but at lower current density. At 300 p.p.m. the curves have generally the same features but with less irregularities, however they have a slight decrease in the current density in comparison with BTA (Table II). The active current peaks and the current densities (more than 300 mV) decrease with increasing concentration of thiourea, as shown in Table II. By increasing concentration from 100 to 300 p.p.m. of TU the active current peak I and current density (more than 300 mV) decrease from 120 000 to 30 000 μA and 30 000 to 14 000 μA, respectively. In this case, there is a decrease in the dissolution of the alloy in comparison with the weight loss measurement which shows that TU acts as a promotor. This is because in the case of anodic

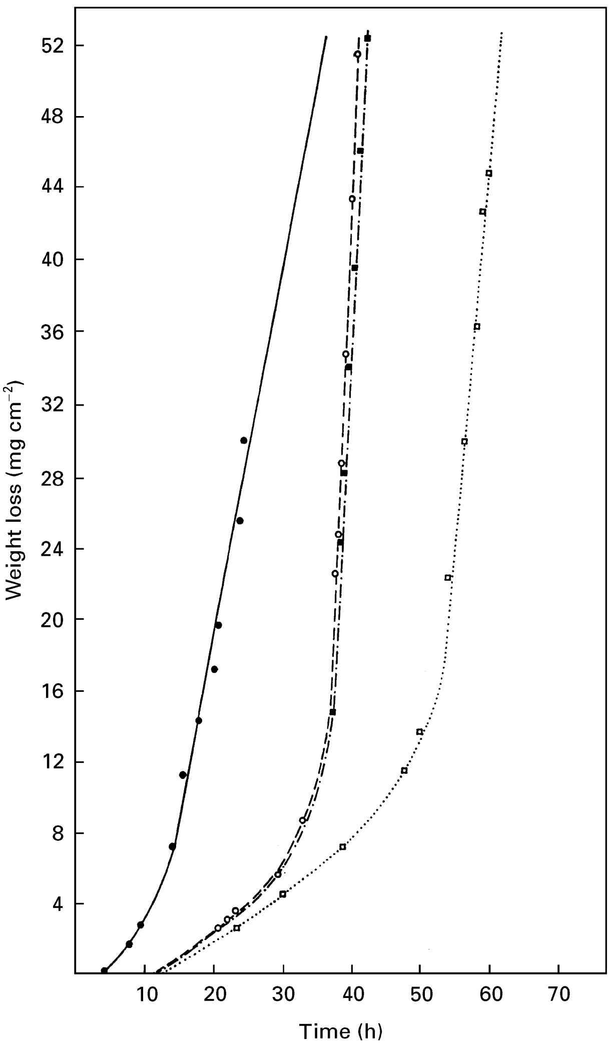


Figure 3 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of different additions of TU in p.p.m. (●) 0; (○) 100; (■) 200; (□) 300.

polarization the test time and the electrode surface area are very small in comparison with that of weight loss, so that the number of TU molecules that decompose is small, besides the decrease in the concentration of the copper ions which acts in the dissolution due to autocatalysis as mentioned above.

3.3. Synergistic inhibition

It can be seen from Fig. 6 that the slow dissolution period is extended to ≃ 40 h in the presence of 100 p.p.m. KI addition to different concentrations of BTA, but in the absence of KI it is at ≅ 15 h. The corrosion rate and inhibition efficiency calculated from the curves of Fig. 6 indicate that the CR decreases and the inhibition efficiency increases with 100 p.p.m. KI additive, as shown in Table I.

Fig. 7 shows the effect of increasing BTA concentration in presence of 100 p.p.m. KI on the dissolution of the alloy in the test solution during anodic polarization.

The curve for 0 p.p.m. BTA represents the inhibitor-free solution. Observation of the curves of this figure reveals that addition of 100 p.p.m. KI to test solution increases the current at potentials more than 500 mV. The linear increase of the logarithm of current with the potential at more oxidizing potentials where the CuI or CuCl film is not stable [26] represents charge-transfer or mixed control for Cu dissolution to Cu^{2+} ions from a film-free surface. As evident from the curves, the addition of 100 p.p.m. KI to different concentrations of BTA (100 to 300 p.p.m.) retards the dissolution of the alloy. The decrease in the current density probably is due to the change in the nature of the inhibitor film which becomes more

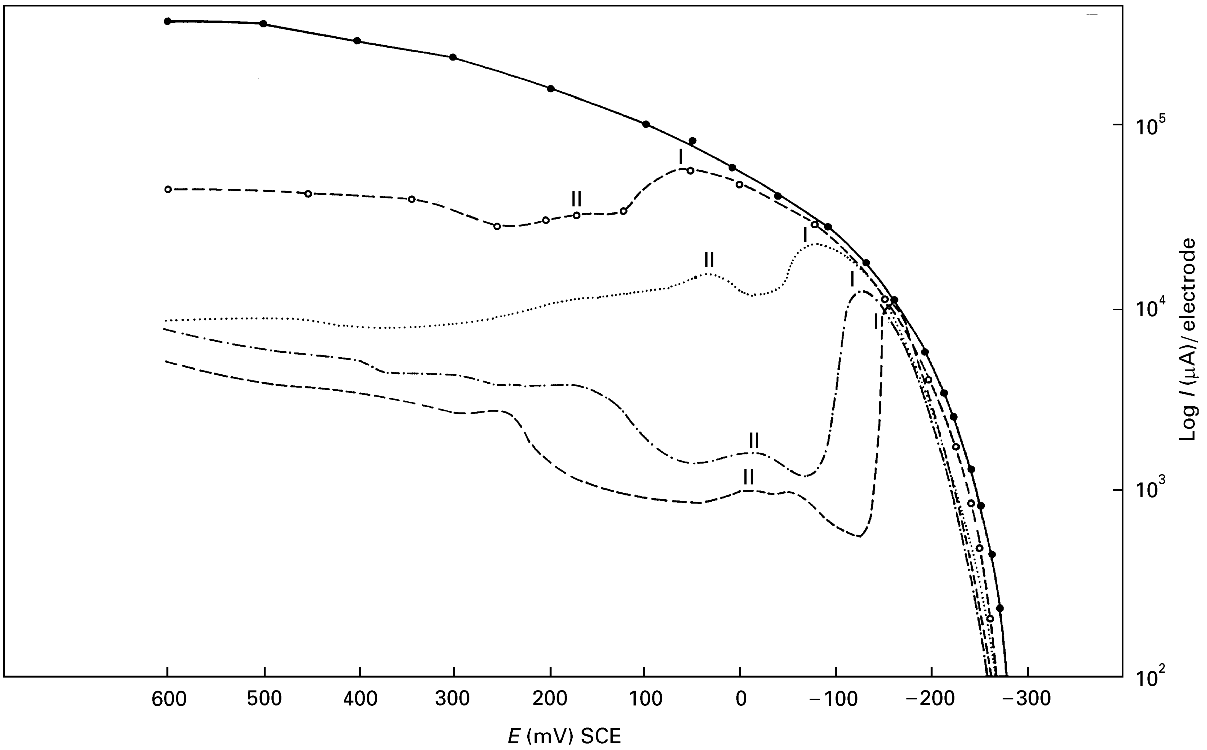


Figure 4 Anodic polarization curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of different additions of BTA in p.p.m. (●) 0; (○) 100; (·····) 300; (–·–) 600; (–––) 1000.

TABLE II Variation of the active current peak *I* and current density with the different concentrations of inhibitors in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C

Inhibitor concentration (p.p.m.)	Active current peak, *I* (μA)				Current density (μA)			
	BTA	BTA + 100 KI	TU	TU + 100 KI	BTA	BTA + 100 KI	TU	TU + 100 KI
Zero	–	–	–	–	32 000	32 000	32 000	32 000
100	54 000	32 000	120 000	42 000	20 000	8 000	30 000	5 800
200	–	22 000	38 000	26 000	–	2 500	22 000	5 600
300	20 000	13 000	30 000	22 000	5 000	2 200	14 000	4 800
600	12 000				780			
1000	10 000				480			

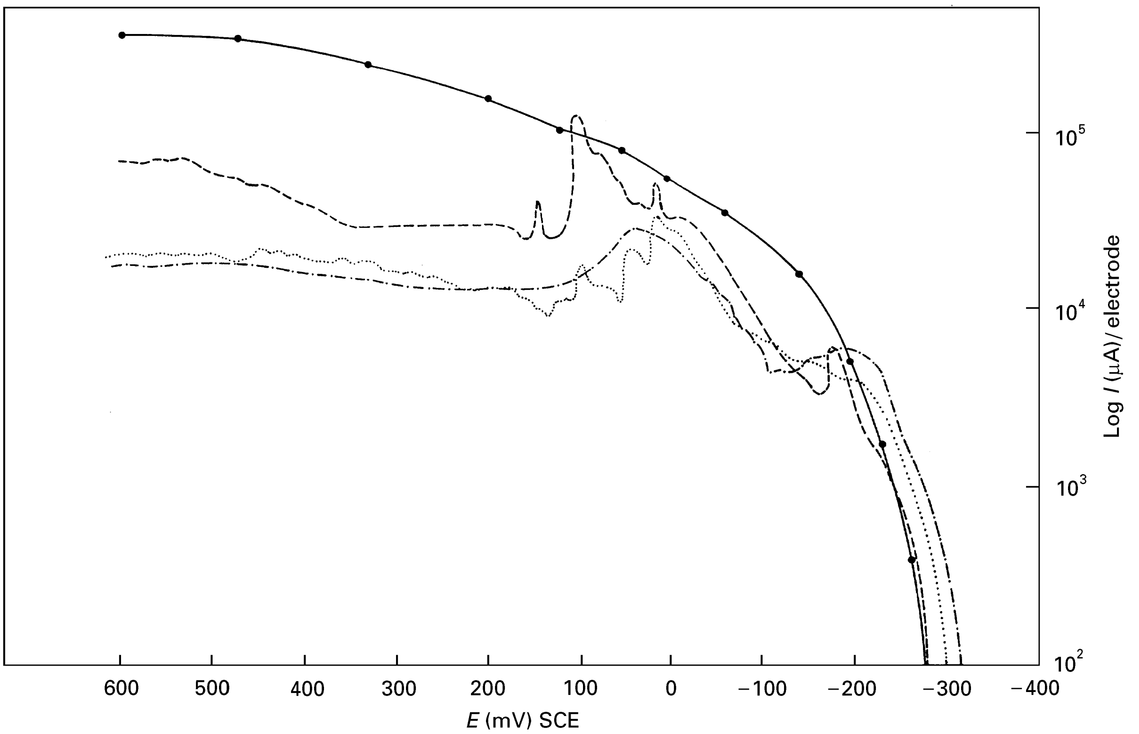


Figure 5 Anodic polarization curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of different additions of TU in p.p.m. (—) 0; (– – –) 100; (···) 200; (–·–) 300.

protective. Also, the corresponding decrease in CD by increasing the concentration of BTA in the presence of 100 p.p.m. KI is higher than the sum of the individual effects of BTA and KI.

Moreover Table II indicates that there is a decrease in the values of the active current peak I and current densities measured in comparison with the corresponding values in the absence of KI additive.

These results support the conclusion that KI improves the efficiency of BTA as a corrosion inhibitor, i.e. there is a synergistic inhibition.

In a similar manner curves of Fig. 8 represent the effect of increasing the TU concentration (100 to 300 p.p.m.) in the presence of 100 p.p.m. KI on the dissolution of Al–bronze in the test solution. The curves show that addition of KI to TU causes an extention of the slow dissolution period which increases with increasing the concentration of TU. On the other hand, the slope of the linear dissolution period (CR) of the curves decreases with the increase of additive content.

From the results of Table I, we see that addition of KI to TU in the test solution decreases the corrosion rate (CR). The inhibition efficiency amounts to above 78% in the presence of 100 p.p.m. KI at 300 p.p.m. TU while at the same concentration of TU in the absence of KI, it acts as a promotor.

The general effect of both KI and TU on the polarization behaviour in the test solution was not similar to that observed in TU alone as shown in Fig. 9. There are no irregularities in the curves in the presence of 100 p.p.m. KI addition; however there is a decrease in the active current peak I and the current density as shown in Table II. At the same time, addition of 100 p.p.m. KI to 300 p.p.m. TU decreases the value of the active current peak I from 30 000 to 22 000 μA and

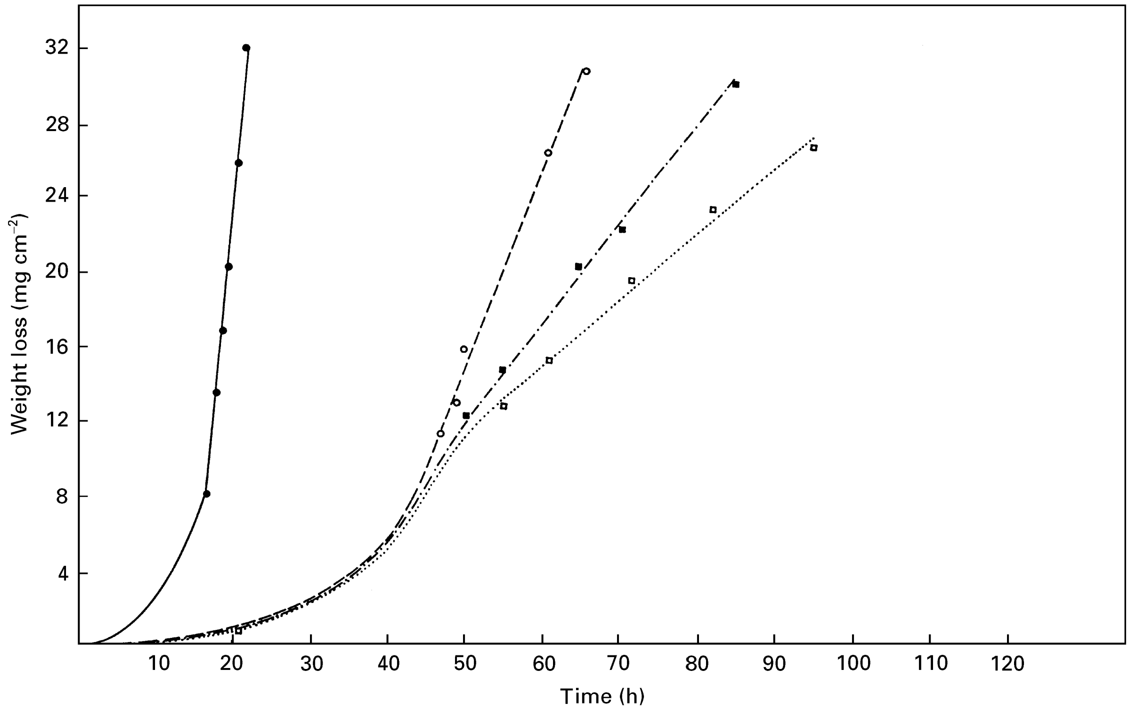


Figure 6 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of 100 p.p.m. KI and different additions of BTA in p.p.m. (●) 100; (○) 100 p.p.m. KI + 100; (◆) 100 p.p.m. KI + 200; (◇) 100 p.p.m. KI + 300.

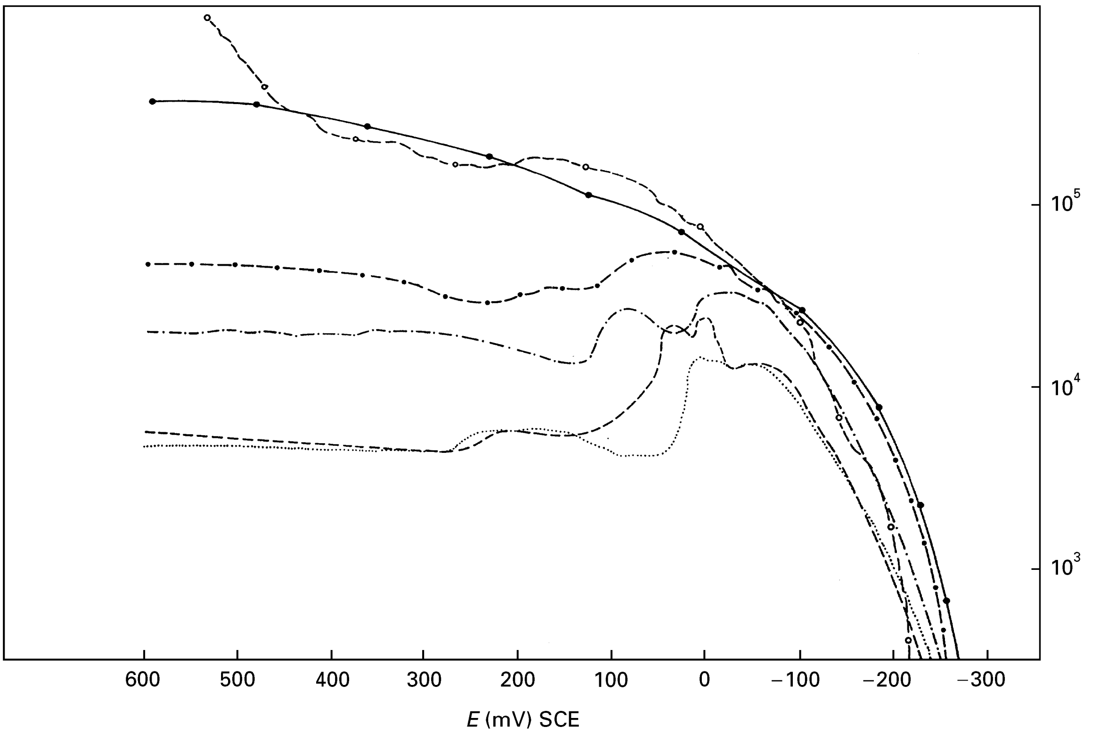
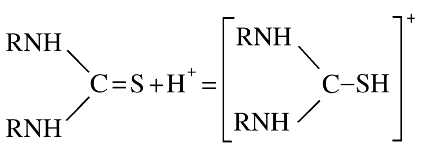


Figure 7 Anodic polarization curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of 100 p.p.m. KI and different additions of BTA. (○) 100 p.p.m. KI; (●) 0 p.p.m. BTA; (•) 100 p.p.m. BTA; (–·–) 100 p.p.m. KI + 100 p.p.m. BTA; (–––) 100 p.p.m. KI + 200 p.p.m. BTA; (····) 100 p.p.m. KI + 300 p.p.m. BTA.

the current density from 14 000 to 4800 μA. Both these effects indicate that KI with TU acts as inhibitor through the synergistic action for the dissolution of Al–bronze.

In view of the many investigations carried out [32–34] and the three theories existing (proposed different models), concerning the nature of the halide–organic inhibitor film [25], it is intended to try to explain the synergistic effect in the present results.

Iofa *et al.* [35, 36, 37] assume that many organic inhibitors in acid electrolytes become protonated, changing into cations according to the following reaction [38]



$$(\mathrm{RNH})_2\mathrm{C{=}S} + \mathrm{H^+} = \left[(\mathrm{RNH})_2\mathrm{C{-}SH}\right]^+$$

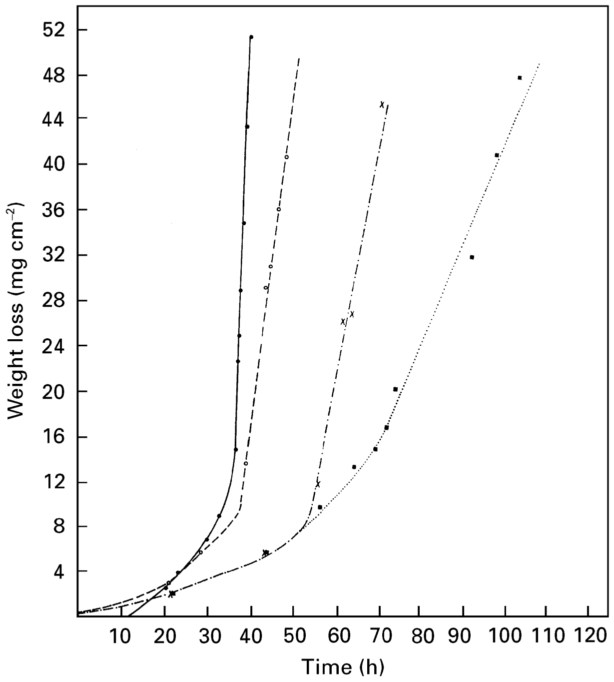


Figure 8 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of 100 p.p.m. KI and different additions of TU in p.p.m. (●) 100; (○) 100 p.p.m. KI + 100; (×) 100 p.p.m. KI + 200; (■) 100 p.p.m. KI + 300.

In the same manner [23]

$$C_6H_4N_3H + H^+ = C_6H_4N_3H_2^+$$

The adsorption of these cations is facilitated in the presence of halide ions [25] which form intermediate bridges, the negative ends of the halogen–metal dipoles being oriented toward the solution. Thus, halide ions alter the properties of the surface so that the adsorption of organic cations on it becomes possible.

Several workers [25, 40] shows that BTA and iodide themselves do not react strongly with each other to form new phases but the synergistic effect mentioned above actually due to the formation of a new complex formed by cuprous, BTA$^-$ and iodide ions. Also, the corrosion of copper in acid media in the presence of these inhibitors have been studied [25, 40, 42]. The results of these studies have shown that:

(a) Potassium does not and iodide does participate in the formation of the inhibitor film.
(b) Copper is mainly present in the film in a cation form.
(c) Copper species exist on the surface in the form of cuprous rather than cupric ion.

From all these points, we can conclude that the organic cations themselves, like [BTA]$^+$ are weakly adsorbed on Al–bronze, since the metal surface is positively charged in acid media. However, the iodide ions are adsorbed onto the surface and decrease the positive charge of the Cu, due to the formation of copper-iodide dipoles, which produce a negative adsorption potential, facilitating the adsorption of organic cations [BTA]$^+$, making the film thicker. Therefore, the inhibitor film may be Cuprous iodide benzotiazole complex Cu (IBTA) complex [26]. The Cu (IBTA) film has a greater inhibiting effect (as shown from Fig. 7) as a result of its protective and compact nature. Also the results obtained from the KI–TU couples agree with typical Cu–I–organic inhibitor film (CuITU). This film is highly resistive to heat decomposition and has a more protective and compact nature on Al–bronze exposed to acidified 4% NaCl solutions at 60 °C.

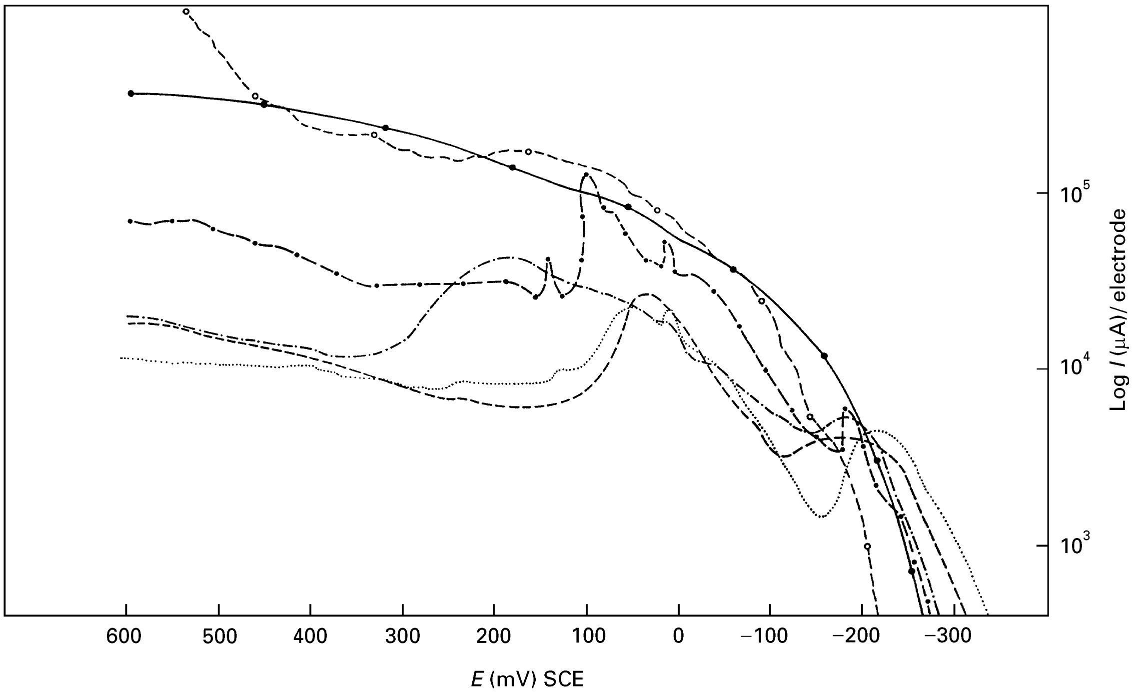


Figure 9 Anodic polarization curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at 60 °C in the presence of 100 p.p.m. KI and different additions of TU. (○) 0 p.p.m. KI; (●) 0 p.p.m. TU; (•) 100 p.p.m. TU; (–·–) 100 p.p.m. KI + 100 p.p.m. TU; (– – –) 100 p.p.m. KI + 200 p.p.m. TU; (···) 100 p.p.m. KI + 300 p.p.m. TU.

4. Conclusions

1. The dissolution of Al–bronze in acidified 4% NaCl of pH 1.8–2.0 in the temperature range 25–60 °C was characterized by a two dissolution rates, one is slow followed by a stage where the loss in weight increased linearly with immersion time. The corrosion rate increased with rise of temperature.
2. The higher efficiency of BTA at 60 °C was recorded only in solutions containing more than 600 p.p.m. of the additive.
3. Thiourea caused the elongation of the slow dissolution period and promoted the dissolution along the linear relation.
4. BTA and TU decreased the produced current density during the anodic polarization technique.
5. The dissolution of the alloy under above conditions was synergitically inhibited by the couples of iodide ion with both BTA and TU.
6. The couples with both media significantly decrease the corrosion rate and current density.

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