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Inhibiting and accelerating effects of some quinolines on the corrosion of zinc and some binary zinc alloys in HCl solution

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The effect of quinoline, benzo(f)quinoline and 8-hydroxyquinoline on the electrochemical and corrosion behaviour of zinc, Zn–2% Cd and Zn–2% Pb alloys in deaerated 0.1 M HCl solution was studied using the potentiostatic technique. Although quinoline inhibited the corrosion of zinc at all examined concentrations, it accelerated the corrosion of the alloys. As an inhibitor, quinoline was found to have a predominant anodic effect and its adsorption conformed with the Temkin isotherm. At concentrations $> 10^{-4}$ M, benzo(f)quinoline inhibited the corrosion of both zinc and the alloys. Inhibition was found to be predominantly anodic without changing the mechanism of zinc dissolution. Inhibition by 8-hydroxy quinoline was found to be purely anodic occurring by surface chelation, resulting in a change of the mechanism of zinc dissolution.

1. Introduction

The surface morphology of metallic electrodes was found to be one of the important factors affecting the inhibiting action of organic corrosion inhibitors [1]. Kerby *et al.* [2, 3] found that zinc deposits contaminated with either lead or cadmium have characteristic morphologies and orientation which are different from pure zinc. Zinc used in Leclanché batteries contains lead (1.03%) which is added as a grain refiner and cadmium (0.04%) which is added to increase the hardness of the metal [4]. The present work is a continuation of previous studies on the inhibition of zinc corrosion using organic and inorganic compounds [5–8]. This paper is devoted to the comparison of the inhibiting action of some quinolines on pure zinc, Zn–2% Cd and Zn–2% Pb alloys in HCl solution in order to reveal the role of alloying elements. The potentiostatic technique was used.

2. Experimental details

2.1. *Corrosion inhibitors*

Reagent grade (B.D.H.) quinoline (Q), 8-hydroxy quinoline (HQ) and benzo(f)quinoline (BQ) were used without further purification. The inhibitor solution was prepared by dissolving the appropriate amount in 10 ml methanol (p.a. Merck). The desired volume was added to the electrolyte (200 ml).

2.2. *Electrolyte*

A solution of 0.1 M HCl (pH 1) was made up from AnalaR reagent and bidistilled water and was deaerated using oxygen-free nitrogen for 6 h before the electrode was inserted into the cell. Nitrogen bubbling was continued throughout the run. The pH of the solution was adjusted by the addition of NaOH.

2.3. *Zinc and zinc alloys specimens*

Zinc specimens were cut from specpure zinc rods (Johnson Matthey London) 20 mm long and 6 mm diameter. The binary Zn–2% Cd and Zn–2% Pb alloys were prepared from extra pure zinc, cadmium and lead (Merck) by vacuum melting in Pyrex glass tubes following the method described by Marshall *et al.* [9]. Alloy specimens were machined in cylindrical form 20 mm long and 5 mm diameter. They were inserted in Teflon mounts in such a way that only the flat surface was in contact with the solution.

2.4. *Potential and polarization measurements*

Before potential measurements, the specimens were cleaned cathodically in 0.25 M H_2SO_4 solution (0.1 M HCl was used for Zn–2% Pb alloy) with vigorous hydrogen evolution to remove any surface contamination and air formed oxide. This was preceded by surface polishing using successive grades of emery paper. Before use, an electrode was degreased with absolute ethanol (AR grade) washed with bidistilled water and inserted into the polarization cell which has been described elsewhere [10]. Stirring of the solution was achieved using a Gallenkamp SS-34 magnetic stirrer and the stirring speed was kept constant during the run. The equilibrium potentials were measured with a Tinsley 3387 E potentiometer using a saturated calomel electrode (SCE) half cell. Potentials are quoted

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with respect to SCE at 30 ± 0.1° C. The potential of the working electrode was controlled by a standard potentiostat Wenking ST 72 (Gerhard Bank Elektroniks, Germany). The current density (c.d.)-time curves were recorded by a compensation recorder of type Flachschreiber, Gila (DLH Lauman, Germany). Corrosion rates (I_{corr}) were determined by the polarization curves extrapolation procedure. For the case where the cathodic reaction is diffusion controlled ($b_c = \infty$), corrosion rates were determined by polarization resistance measurements at the open circuit corrosion potential (E_{corr}) by application of the Stern-Geary equation following the procedure described by Baugh [11]. All polarization experiments were duplicated.

3. Results and discussion

3.1. *Behaviour in uninhibited acid solution*

Figure 1 compares the polarization curves (measured under steady state conditions) for zinc with those of Zn-2% Cd and Zn-2% Pb alloys in deaerated 0.1 M HCl solution. It can be seen that the presence of either cadmium or lead results in a large shift in both cathodic and anodic branches of the polarization curve of zinc towards lower current densities. The larger shift occurs with the Zn-2% Pb alloy. This can be attributed to the high hydrogen overvoltage on lead than on either zinc or cadmium (lead and cadmium were found to have higher hydrogen overvoltage than zinc [4]). It can also be observed that in spite of such shift, both cathodic and anodic Tafel slopes (b_c and b_a) are not appreciably affected ($b_c = 154 \pm 7\,\text{mV}$ and $b_a = 41 \pm 3\,\text{mV}\,\text{dec}^{-1}$). This suggests that the presence of either cadmium or lead as minor alloying elements does not affect the mechanism of either the hydrogen evolution reaction or zinc dissolution. The latter values for b_c and b_a are in satisfactory agreement with those obtained by several authors for pure zinc and battery zinc alloy in HCl and acidic NH_4Cl solutions [4, 7, 12]. The values obtained for the corrosion rate of zinc and the alloys (Table 1) indicate that the corrosion rates of the investigated alloys are markedly lower than that of pure zinc and the alloy containing lead has the lowest corrosion rate.

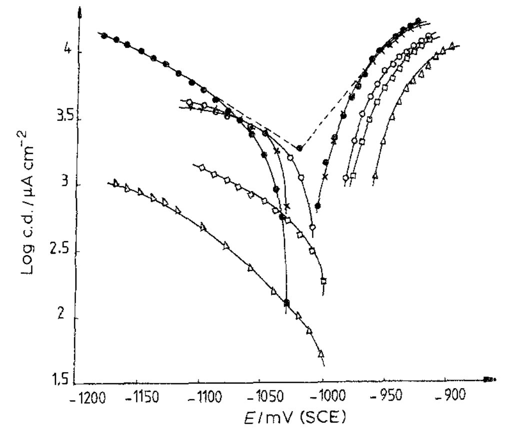

Fig. 2. Potentiostatic polarization curves of zinc in 0.1 M HCl solution (pH 1) in presence of quinoline. (●) pure medium, (x) 10^{-5} M Q, (○) 10^{-4} M, (□) 5 × 10^{-4} M (△) 10^{-3} M.

3.2. *Behaviour in the presence of quinolines*

The results obtained for the electrochemical and corrosion behaviour of zinc and the investigated alloys in the absence and the presence of 10^{-5}–10^{-3} M Q (Figs 2 and 3 and Table 1) indicate that although Q inhibits zinc corrosion at all examined concentrations, it accelerates the corrosion of the alloys. The marked shift of both cathodic and anodic branches of the original polarization curve of zinc (that of the uninhibited acid solution) towards lower current densities, together with the appreciable positive shift in the corrosion potential (E_{corr}) at concentrations $\geq 10^{-4}$ M suggests a predominant anodic effect [13].

For the alloys, the curves shown in Fig. 3 (these curves are representative for both Zn-2% Cd and Zn-2% Pb alloys) reveal that, in spite of the parallel shift in the anodic branches of the polarization curves towards lower current densities in the presence of Q, the cathodic branches show a marked shift towards higher current densities, resulting in a sharp increase

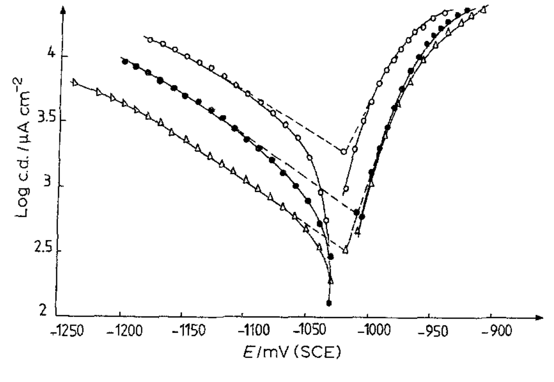

Fig. 1. Potentiostatic polarization curves of zinc and its binary alloys in 0.1 M HCl solution (pH 1). (○) pure zinc. (●) Zn-2% Cd alloy, (△) Zn-2% Pb alloy.

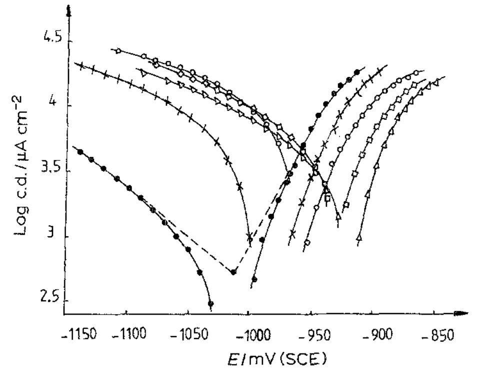

Fig. 3. Potentiostatic polarization curves of Zn-2% Cd alloy in 0.1 M HCl solution (pH 1) in presence of quinoline. (●) pure medium, (x) 10^{-5} M Q, (○) 10^{-4} M, (□) 5 × 10^{-4} M, (△) 10^{-3} M.

Table 1. Effect of quinoline on the electrochemical and corrosion behaviour of zinc and some zinc binary alloys in 0.1 M HCl solution

Specimen	Q Conc. /M	$-E_{corr}$ /mV (SCE)	I_{corr} /μA cm^{-2}	$-b_c$ /mV	b_a /mV	IE /%
Pure zinc	0	1022	1788	147	44	
	10^{-5}	1020	1560	168	46	+12.8
	10^{-4}	1002	1048	160	44	+41.4
	5×10^{-4}	992	309	159	36	+82.7
	10^{-3}	986	75	146	36	+95.8
Zn-2% Cd alloy	0	1010	589	154	44	
	10^{-5}	989	2818	145	48	−378.4
	10^{-4}	963	5495	130	50	−832.9
	5×10^{-4}	935	3301	132	42	−460.4
	10^{-3}	915	2041	131	40	−246.5
Zn-2% Pb alloy	0	1017	356	161	45	
	10^{-5}	993	3948	156	50	−1008.9
	10^{-4}	969	4465	158	40	−1154.2
	5×10^{-4}	954	3805	157	50	−968.8
	10^{-3}	942	2958	142	50	−730.9

in the corrosion rate (the corrosion process of zinc in acid solutions was found to be cathodically controlled [14]). This is associated with a decrease in the cathodic Tafel slope which is more pronounced with the Zn–2% Cd alloy. The marked positive shift in corrosion potential and the decrease in anodic current density in the presence of Q, suggest that this compound acts as an anodic type inhibitor. Similar results were obtained by Hoar and Holiday [15] for the inhibition of mild steel corrosion in H_2SO_4 solution by 2,6-dimethylquinoline.

The curves shown in Fig. 4 (these curves are representative for both zinc and the alloys) reveal that the presence of 8-hydroxyquinoline (HQ) shifts the cathodic branches of the original polarization curves of zinc and the alloys towards higher current density. This is associated with a marked decrease in the cathodic Tafel slope, suggesting a decrease in the energy barrier for H^+ ion discharge [16]. On the other hand, the pronounced shift in the anodic branches of the original polarization curves towards lower current densities with the marked increase in the anodic Tafel slope denote inhibition of the anodic type, associated with a change in the mechanism of zinc dissolution. Values of the corrosion rate given in Table 2 indicate corrosion acceleration at all HQ concentrations. Such acceleration ($IE < 0$) is relatively greater for the alloys than for zinc.

The results obtained in the presence of benzo(f)-quinoline (BQ) (Figs 5, 6 and 7 and Table 3) reveal that BQ acts as corrosion inhibitor at concentrations $> 10^{-4}$ M. An inspection of the curves shown in Figs 6 and 8 indicates that at concentrations $> 10^{-5}$ M BQ, the cathodic branches of the polarization curves of both zinc and Zn–2% Pb alloy do not have well defined Tafel regions and attain limiting currents by slight cathodic polarization. This indicates that the hydrogen evolution reaction becomes substantially diffisuion controlled. Similar results were obtained by Leroy [17] for zinc in Na_2SO_4/HCl solution mixture (pH 2) containing *n*-butyl thioglycolate and by Baugh [4] for zinc and zinc battery alloy in $NaClO_4$ and NaCl solutions of pH 3.8. For such a case (where $b_c = \infty$) corrosion rates were determined from the polarization resistance, R_p, (linear polarization plots for zinc and Zn–2% Pb alloy are shown in Figs 8 and 9) using the

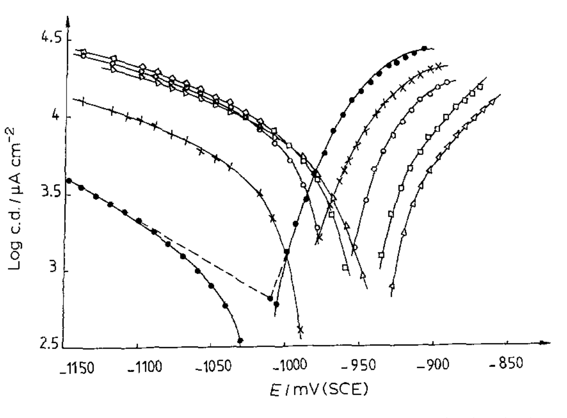

Fig. 4. Potentiostatic polarization curves of Zn–2% Cd alloy in 0.1 M HCl solution (pH 1) in presence of 8-hydroxyquinoline. (●) pure medium, (x) 10^{-5} M HQ, (○) 10^{-4} M, (□) 5×10^{-4} M, (△) 10^{-3} M.

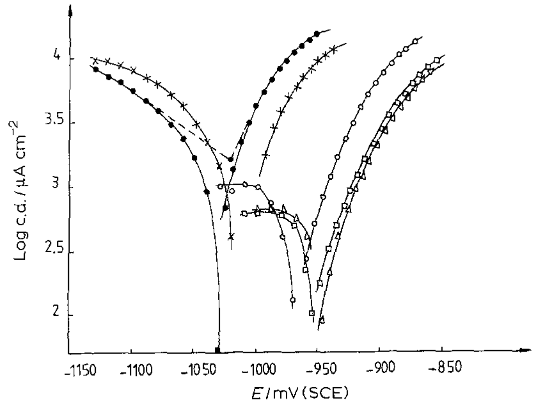

Fig. 5. Potentiostatic polarization curves of zinc in 0.1 M HCl solution (pH 1) in presence of benzo(f)quinoline. (●) pure medium, (x) 10^{-5} M BQ, (○) 10^{-4} M, (□) 5×10^{-4} M, (△) 10^{-3} M.

Table 2. Effect of 8-hydroxyquinoline on the electrochemical and corrosion behaviour of zinc and some zinc binary alloys in 0.1 M HCl solution

Specimen	HQ Conc. /M	$-E_{corr}$ /mV (SCE)	I_{corr} /μA cm^{-2}	$-b_c$ /mV	b_a /mV	IE /%
Pure zinc	0	1022	1788	147	44	
	10^{-5}	1018	2089	138	64	−16.8
	10^{-4}	1003	3162	141	72	−76.8
	5×10^{-4}	1002	2344	135	84	−31.1
	10^{-3}	994	2089	130	82	−16.8
Zn-2% Cd alloy	0	1010	589	154	41	
	10^{-5}	983	2089	127	53	−254.7
	10^{-4}	969	3081	108	106	−423.1
	5×10^{-4}	952	3162	105	104	−436.8
	10^{-3}	938	2511	116	102	−326.3
Zn-2% Pb alloy	0	1017	356	158	41	
	10^{-5}	1003	1820	132	53	−411.2
	10^{-4}	995	2041	129	106	−473.3
	5×10^{-4}	988	1096	131	104	−207.9
	10^{-3}	983	1000	131	102	−180.9

Stern–Geary equation:

$$I_{corr} = \frac{1}{2.303R_p}\left(\frac{b_a b_c}{b_a + b_c}\right) \qquad (1)$$

The polarization resistance, R_p, is defined as the tangent of the polarization curve at E_{corr}:

$$R_p = \left(\frac{dE}{dI}\right)_E = E_{corr} \qquad (2)$$

For a diffusion controlled cathodic process Equation 1 reduces to

$$I_{corr} = \frac{b_a}{2.303}\frac{1}{R_p} \qquad (3)$$

The data given in Table 3, indicate aproximately equal values for the inhibition efficiency of BQ for the alloys. Such values are markedly lower than those obtained for zinc at the same BQ concentration. The curves shown in Figs 5, 6 and 7 reveal considerable parallel displacement of the anodic branches of the original polarization curves towards lower current densities at all examined concentrations of BQ. This suggests inhibition of the anodic type without an effect on the mechanism of zinc dissolution. The predominance of anodic inhibition of BQ conforms with the experimental observation concerning the large positive shift in the corrosion potentials of zinc and the alloys on addition of the organic compound (ΔE_{corr} ranges from +77 to +110 mV at 10^{-3} M BQ).

3.3. *Mechanism of inhibition and acceleration of zinc corrosion and the effect of alloying elements*

According to Antropov [18], the potential of zinc on the correlative scale (ϕ scale) in acidic solutions is almost equal to −0.23, indicating that zinc is negatively charged at the corrosion potential (E_{corr}). On the other hand quinolines (as tertiary bases) undergo protonation in aqueous acid solutions [19, 20] accord-

Table 3. Effect of benzo(f)quinoline on the electrochemical and corrosion behaviour of zinc and some zinc binary alloys in 0.1 M HCl solution

Specimen	BQ Conc. /M	$-E_{corr}$ /mV (SCE)	I_{corr} /μA cm^{-2}	$-b_c$ /mV	b_a /mV	IE /%
Pure zinc	0	1022	1788	147	44	
	10^{-5}	1012	2398	164	50	−34.1
	10^{-4}	960	1984	∞	38	−10.9
	5×10^{-4}	949	353	∞	44	+80.3
	10^{-3}	945	267	∞	41	+85.1
Zn-2% Cd	0	1010	589	154	42	
	10^{-5}	976	2187	168	46	−271.3
	10^{-4}	948	851	183	46	−44.5
	5×10^{-4}	918	347	216	40	+41.1
	10^{-3}	911	186	214	34	+68.4
Zn-2% Pb alloy	0	1017	356	158	38	
	10^{-5}	984	724	280	31	−103.4
	10^{-4}	944	816	∞	25	−129.2
	5×10^{-4}	915	203	∞	28	+42.9
	10^{-3}	907	113	∞	26	+68.3

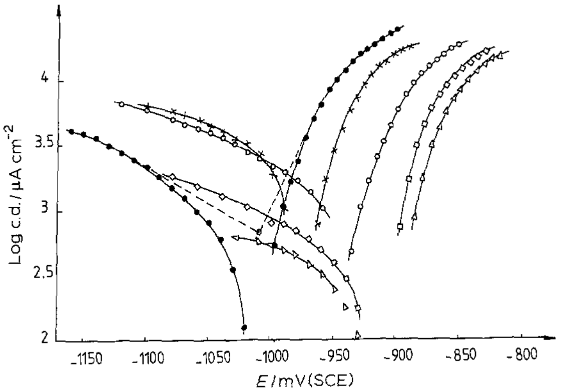

Fig. 6. Potentiostatic polarization curves of Zn–2% Cd alloy in 0.1 M HCl solution (pH 1) in presence of benzo(f)quinoline. (●) pure medium, (x) 10^{-5} M BQ, (○) 10^{-4} M, (□) 5×10^{-4} M, (△) 10^{-3} M.

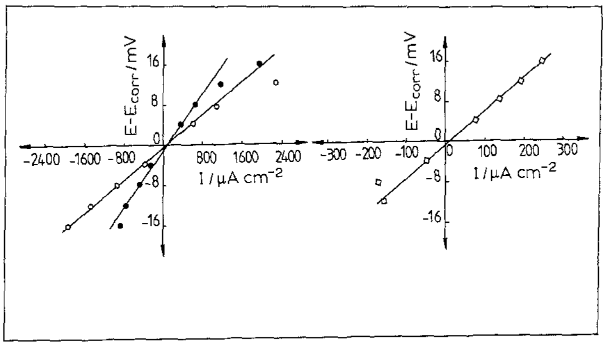

Fig. 8. Linear polarization plots for zinc in 0.1 M HCl solution (pH 1) in presence of benzo(f)quinoline. (○) 10^{-4} M BQ. (●) 5×10^{-4} M, (□) 10^{-3} M.

ing to the following equation:

$$B + H_3O^+ \rightleftharpoons (BH)^+ + H_2O \tag{4}$$

where B refers to Q, HQ and BQ.

The relative strength of a base B in an acidic solution is defined as being proportional to its basicity constant i.e. the equilibrium constant K_b for Equation 4 (pK_b for Q in 0.5 M HCl solution was found to be 9.1 [20]). Thus, the initial step of adsorption may involve the free base molecules and/or the protonated ones. The predominance of anodic inhibition of the examined quinolines suggests an appreciable contribution to the inhibition process via chemisorption of the free base molecules at the corrosion potential or under conditions of anodic polarization [21–23]. This may take place by sharing electrons of the N-atom and zinc surface atoms or via interaction of the π-electrons of the aromatic ring of the organic molecules, which should be oriented parallel to the metal surface. It was assumed by several authors [22, 23, 24], that the adsorbed quinoline cations can be deprotonated either by increasing potential [23] or, most easily, if the adsorbed ions are oriented perpendicularly to the metal surface with N-atom next to the metal [22, 24].

The increase in the anodic Tafel slope (b_a) in the presence of HQ suggests a mode of inhibition involving an interposition of the organic compound into the charge transfer process of zinc dissolution [25]. Leroy [17] reported that inhibition of zinc corrosion by HQ is attributed to its capability for surface chelation with zinc.

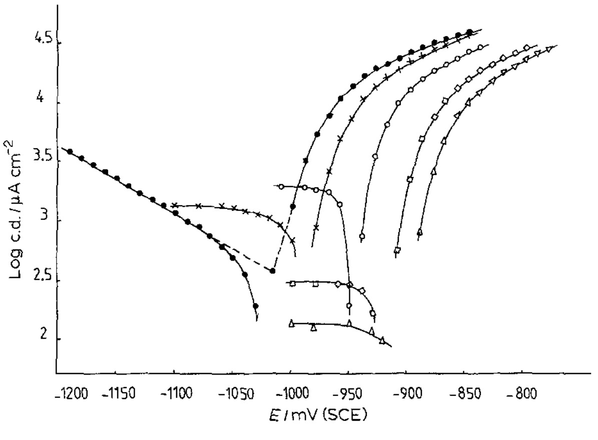

Fig. 7. Potentiostatic polarization curves of Zn–2% Pb alloy in 0.1 M HCl solution (pH 1) in presence of benzo(f)quinoline. (●) pure medium, (x) 10^{-5} M BQ, (○) 10^{-4} M, (□) 5×10^{-4} M, (△) 10^{-3} M.

The accelerating effect of the examined quinolines on the hydrogen evolution reaction (under cathodic polarization) can be explained on the basis of a reactive coverage, with the adsorbate involved in the mechanism according to the following reaction sequence [18, 26]:

$$(BH)^+_{ads} + e^- = (BH)_{ads} \tag{5}$$

$$(BH)_{ads} = (B)_{ads} + H_{ads} \tag{6}$$

$$2H_{ads} = H_2 \tag{7}$$

The above reaction is assumed to be catalysed by zinc, the catalytic activity of which seems to be markedly increased by the presence of either lead or cadmium. It may be suggested that the presence of either lead or cadmium surface atoms gives rise to the creation of active sites which increase the activity of zinc as a catalyst.

3.4. *Adsorption isotherms*

For quinoline with pure zinc, assuming no change in the mechanism of both the hydrogen evolution reaction and zinc dissolution, the degree of coverage θ_{inh}

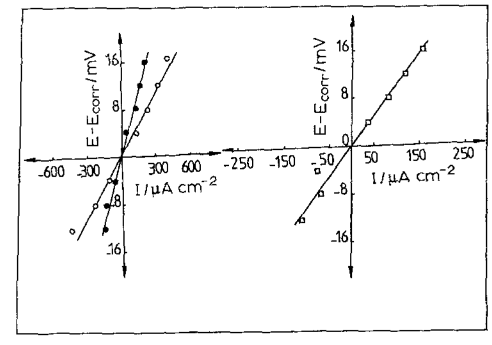

Fig. 9. Linear polarization plots for Zn–2% Pb alloy in 0.1 M HCe solution (pH 1) in presence of benzo(f)quinoline. (○) 10^{-4} M BQ. (●) 5×10^{-4} M, (□) 10^{-3} M.

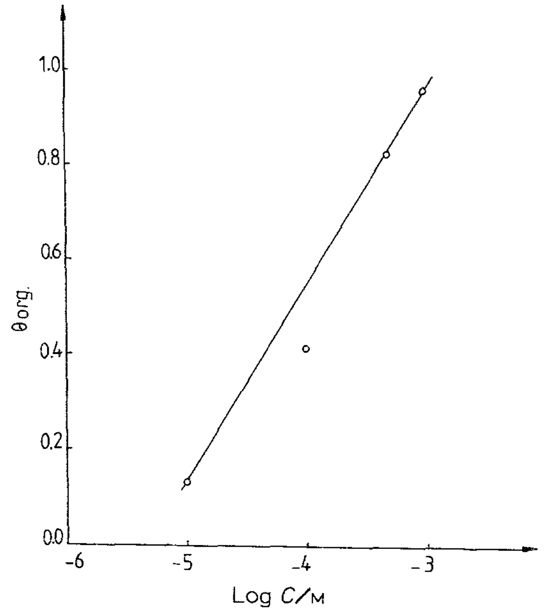

Fig. 10. Adsorption isotherm of quninoline on zinc in 0.1 M HCl solution (pH 1).

can be obtained using the equation:

$$\theta_{\text{inh}} = 1 - (I_{\text{inh}}/I_{\text{uninh}}) \qquad (8)$$

The adsorption isotherm obtained from Equation 8 is shown in Fig. 10. This isotherm follows that of Temkin which characterizes the chemisorption of uncharged substances on heterogeneous surfaces [27]. For such an isotherm θ_{inh} is a linear function of log C according to the equation:

$$\theta = \frac{1}{f} \ln B^{*}C \qquad (9)$$

where B^* is the adsorption equilibrium constant, f is the heterogeneity factor of the metal surface and C is the bulk concentration of the adsorbate.

4. Conclusions

The following points are made:

(i) The presence of either cadmium or lead as minor alloying elements with zinc (2 wt %) markedly hindered its corrosion in pure HCl solution.

(ii) Quinoline acted as a mixed type inhibitor for pure zinc and as an anodic type inhibitor for both Zn–2% Cd and Zn–2% Pb alloys. Inhibition occurred via chemisorption of the free molecules.

(iii) 8-Hydroxyquinoline was found to be an anodic type inhibitor for both pure zinc and the alloys and inhibition occurred via surface chelation, resulting in a change in the mechanism of zinc dissolution.

(iv) At concentrations $> 10^{-4}$ M, benzo(f)quinoline acted as a mixed type inhibitor with a predominant anodic effect without changing the mechanism of zinc dissolution.

(v) Adsorbed protonated molecules of the quinolines imparted a catalytic effect on the hydrogen evolution reaction and consequently accelerated zinc corrosion. Such catalytic effect was increased by the presence of either cadmium or lead surface atoms.

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