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Phenothiazine as inhibitor of the corrosion of cadmium in acidic solutions

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The corrosion of cadmium in 0.5 M $HClO_4$, CH_3COOH or 0.25 M H_2SO_4 in the absence and presence of small amounts of phenothiazine (10^{-6}–10^{-4} M) as an inhibitor has been studied using both electrochemical impedance spectroscopy (EIS) and Tafel-plot techniques. Measurements were carried out at cathodic, open circuit and anodic potentials at different temperatures. In $HClO_4$ and H_2SO_4 solutions the inhibition efficiency increases as both the concentration of phenothiazine and the temperature are increased. The effect of temperature in CH_3COOH solution gives an opposite effect, that is, a decrease in the inhibition efficiency with increasing temperature. This behaviour is attributed to competitive adsorption between the inhibitor molecules and the acetate ions at the metal–solution interface. Phenothiazine can be considered as an inhibitor of mixed type with more pronounced effects in the anodic direction. The thermodynamic parameters in $HClO_4$ containing the inhibitor were evaluated using the Bockris–Swinkels adsorption isotherm with $n = 4$ as the configurational function. These parameters reveal that phenothiazine is adsorbed on the cadmium surface in molecular form with a strong interaction between the metal and the inhibitor.

1. Introduction

Cadmium and its alloys find extensive application in industry, for example, as coatings for steel and aluminium to provide surface protection. In spite of numerous publications on cadmium in alkaline solutions containing organic compounds [1], very little work has been done on the corrosion inhibition of cadmium in acidic media [2, 3]. Phenothiazine and its derivatives have only been used (in our laboratory) as corrosion inhibitors for zinc in NH_4Cl solutions [4].

The present paper describes a study of the inhibition of the corrosion of cadmium by phenothiazine in $HClO_4$, H_2SO_4 and CH_3COOH solutions at different temperatures. The mechanism of inhibition is discussed on the basis of an adsorption isotherm, as well as the calculated thermodynamic parameters. Two electrochemical methods are used to carry out the measurements: (a) electrochemical impedance spectroscopy (EIS) and (b) Tafel plot extrapolation.

2. Experimental details

0.5 M solutions of $HClO_4$, CH_3COOH and 0.25 M H_2SO_4 were prepared from Analar reagent and bidistilled water and were deaerated by oxygen free nitrogen for at least 5 h.

Measurements were performed on a planar cadmium disc electrode ($A = 0.125\ cm^2$) of specpure 99.999% (Aldrich) grade embedded in an Araldite holder. Prior to each measurement the electrode was polished with successive grades of emery paper, degreased in pure ethanol and washed in running bidistilled water before being inserted in the polarization cell. The reference electrode was a saturated calomel electrode to which all potentials are referred. The cell description is given elsewhere [5].

The electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 10 kHz to 0.02 Hz. An amplitude of 5 mV peak to peak was used for the a.c. signal for all EIS measurements. The Tafel-plot technique was carried out in a potential range of −200 mV to +100 mV with respect to the open circuit (OC) potential. Simultaneous EIS and Tafel-plot measurements were carried out on the cadmium electrode in different acids with and without the inhibitor at four different temperatures using a potentiostat/galvanostat (model 273), a frequency response analyser (model 5208) and a personal computer. Details of the experimental procedures have been described elsewhere [6]. SEM micrographs were made using a Jeol JSM 5300 scanning electron microscope.

Reagent grade (Aldrich production) phenothiazine was used without further purification. The inhibitor solution was prepared by dissolving the appropriate amount in 10 ml AnalaR methanol. The desired volume was added to the electrolyte (250 ml containing 10% by volume AR methanol).

3. Results and discussion

3.1. *Behaviour in perchloric and sulfuric acid solutions*

Figure 1 represents polarization curves for cadmium in 0.5 M $HClO_4$ with and without addition of different phenothiazine concentrations. It can be seen

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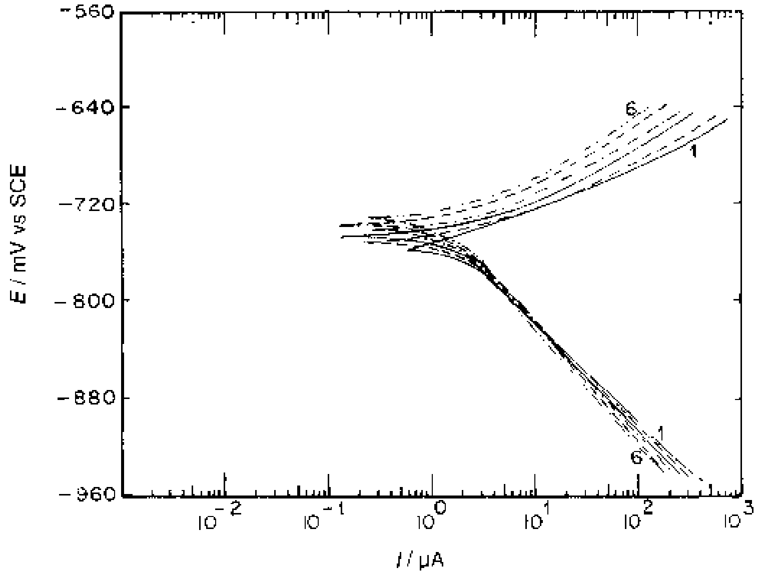

Fig. 1. Tafel plots for cadmium in 0.5 M $HClO_4$ (dE/dt = 1 mV s^{-1}) and in the presence of phenothiazine; (1) 0.0, (2) 10^{-6}, (3) 10^{-5}, (4) 2×10^{-5}, (5) 5×10^{-5}, (6) 10^{-4} M at 30 °C, A = 0.125 cm^2.

that the presence of phenothiazine results in a marked shift in the anodic branches and a slight shift in the cathodic branches of the polarization curves towards lower current densities. The positive shift in the corrosion potential (E_{corr}) indicates that the anodic process is much more affected than the cathodic. This suggests that phenothiazine acts predominantly as an anodic inhibitor. Similar curves are obtained in 0.25 M H_2SO_4, using the same phenothiazine concentrations. The fact that b_c and b_a in Table 1 are almost the same in uninhibited and inhibited solutions suggests that the inhibitory action of phenothiazine reduces the surface area available for hydrogen evolution and anodic cadmium dissolution without affecting their mechanism.

The EIS data obtained for cadmium in 0.5 M $HClO_4$ and 0.25 M H_2SO_4 solutions in the absence and presence of phenothiazine within the concentration range 10^{-6} to 10^{-4} M at three different potential points, are given in Tables 2 and 3. From these data the inhibition efficiency (I%) can, as reported elsewhere [7], be calculated according to the following equation:

$$I\% = \frac{C_{dl} - C_{inh}}{C_{dl}} \times 100 = \Theta \times 100 \qquad (1)$$

Table 1. Tafel parameters and corrosion current density obtained by Tafel extrapolation and polarization resistance methods on cadmium in 0.5 M $HClO_4$ without and with the addition of phenothiazine at E_{corr} (30 °C)

Additive conc./ M	*Tafel extrapolation method*			*Impedance method*
	b_c / mV (decade)$^{-1}$	b_a /mV(decade)$^{-1}$	i_{corr} / μA cm^{-2}	i_{corr} /μA cm^{-2}
0	90	45	29	33
10^{-6}	91	45	23	26
10^{-5}	91	46	15	17
2×10^{-5}	92	46	13	16
5×10^{-5}	92	46	12	15
1×10^{-4}	92	46	12	14

Table 2. Effect of phenothiazine on E_{corr}, impedance parameters and inhibition efficiency of cadmium in 0.5 M $HClO_4$ solution at cathodic, open circuit and anodic potentials, A = 0.125 cm^2 (25 °C)

Concentration / M		*at −200 mV*				*at 0.0 mV*				*at + 50 mV*			
	E_{corr}/mV	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%
0	−746	15	0.596	22	–	3	7.79	23	–	2	0.562	45	–
10^{-6}	−745	15	0.644	21	4	3	7.79	23	–	2	1.02	37	17
10^{-5}	−741	15	0.677	18	18	3	9.58	18	21	2	2.20	24	46
2×10^{-5}	−736	15	0.753	17	22	3	10.79	16	30	2	2.34	18	60
5×10^{-5}	−729	15	0.854	16	27	3	10.79	15	35	2	2.44	15	66
1×10^{-4}	−726	15	0.902	15	31	3	10.79	15	35	2	2.77	13	71

Table 3. Effect of phenothiazine on E_{corr}, impedance parameters and inhibition efficiency of cadmium in 0.25 M H_2SO_4 solution at cathodic, open circuit and anodic potentials, $A = 0.125$ cm^2 (25 °C)

Concentration / M		*at −200 mV*				*at 0.0 mV*				*at + 50 mV*			
	E_{corr}/mV	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%	R_s/Ω	R_p/kΩ	C_{dl}/μF	I/%
0	−776	5	1.80	10	–	4	4.19	27	–	13	0.115	1700	–
10^{-6}	−774	5	1.80	10	–	4	4.89	21	22	13	0.163	638	62
10^{-5}	−771	5	2.00	8	20	4	7.26	15	44	13	0.29	131	94
2×10^{-5}	−768	5	2.25	7	30	4	7.69	13	51	13	0.35	100	92
5×10^{-5}	−767	5	2.35	6	40	4	8.50	12	55	13	0.270	131	92
1×10^{-4}	−766	5	2.35	6	40	4	7.27	14	48	13	0.270	131	92

where C_{dl} and C_{inh} are the electrode capacitance in the absence and presence of additive, respectively, and Θ is the surface coverage. It is found that I%, at a cathodic potential of −200 mV vs OC, is relatively small and gradually increases as the potential shifts anodically (+50 mV vs OC). These results suggest that retardation of the electrode processes occurs, especially at anodic sites, as a result of coverage the majority of active sites of the cadmium surface by the inhibitor molecules. The inhibitive effect of the additive molecules in H_2SO_4 is probably caused by hindering the adsorption of sulfate ions on the cadmium surface, thus preventing dissolution. Similar behaviour was previously reported by Mrowczynski *et al.* [12] for corrosion inhibition of iron in sulfate solution.

Figure 2 is a complex-plane impedance diagram for the cadmium electrode in 0.5 M $HClO_4$ in the presence of various concentrations of phenothiazine in the anodic potential region at 30 °C. The equivalent circuit models for this system are shown in Fig. 3 as previously reported [8]. The equivalent circuit model in Fig. 3(a) can be given in a simplified equivalent circuit model as in Fig. 3(b). The measured complex-plane impedance plot is similar to that calculated by the equivalent circuit model.

The corrosion current density (i_{corr}) data were calculated using the polarization resistance (R_{P}) obtained from the impedance measurements, together with the Stern–Geary equation:

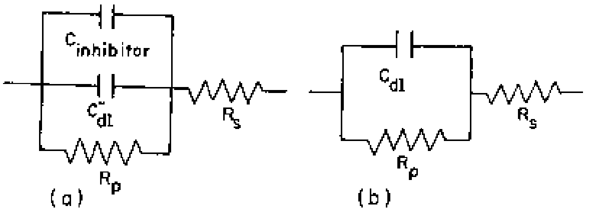

Fig. 3. Equivalent circuit model (a) can be given in a simplified equivalent circuit model (b). R_{s} and R_{p} are solution and polarization resistances, respectively. $C_{\mathrm{inhibitor}}$ is the capacitance of parts that the inhibitor is adsorbed, C^{-}_{dl} is the capacitance of parts that the inhibitor is not adsorbed, and C_{dl} is the apparent double layer capacitance.

$$i_{\mathrm{corr}} = \frac{b_{\mathrm{a}} b_{\mathrm{c}}}{2.303 R_{\mathrm{p}} A (b_{\mathrm{a}} + b_{\mathrm{c}})} \tag{2}$$

where $R_{\mathrm{p}} = \lim_{f \to 0} (Z^{-} - R_{\mathrm{s}})$, A is the electrode surface area and b_{a} and b_{c} are the Tafel slopes of the anodic and cathodic processes, respectively. The observed i_{corr} values (Table 1) obtained from Tafel extrapolation are in good agreement with those calculated from the polarization resistance of the impedance measurements at E_{corr}. The foregoing results confirm the recent discussion concerning the use of impedance measurements as a fast sensitive technique in testing inhibitor efficiency [9].

To elucidate the nature of the adsorption of phenothiazine (chemisorption or physical adsorption), the effect of temperature on the inhibitive efficiency in

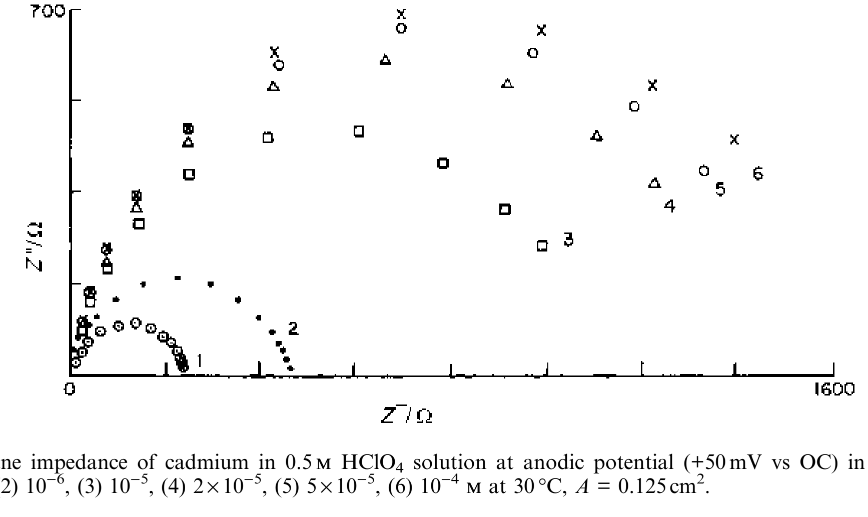

Fig. 2. Complex-plane impedance of cadmium in 0.5 M $HClO_4$ solution at anodic potential (+50 mV vs OC) in the presence of phenothiazine; (1) 0.0, (2) 10^{-6}, (3) 10^{-5}, (4) 2×10^{-5}, (5) 5×10^{-5}, (6) 10^{-4} M at 30 °C, A = 0.125 cm^2.

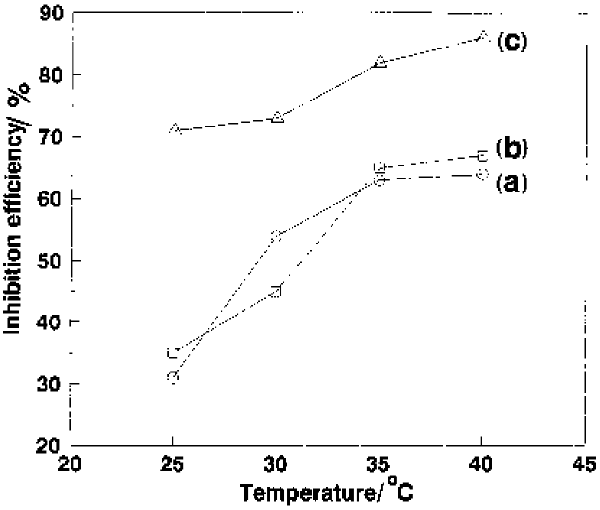

Fig. 4. Influence of temperature on inhibition efficiency of phenothiazine for cadmium in 0.5 M $HClO_4$ containing 10^{-4} M of inhibitor at (a) cathodic, (b) open circuit and (c) anodic potentials.

Table 4 Apparent activation energies of cadmium in 0.5 M $HClO_4$ and 0.25 M H_2SO_4 solutions containing phenothiazine

*Additive conc./*M	Q/kJ mol^{-1}	
	$HClO_4$	H_2SO_4
0	34.4	87.9
10^{-6}	30.6	72.6
10^{-5}	28.6	55.4
2×10^{-5}	19.1	51.6
5×10^{-5}	17.2	47.8
1×10^{-4}	13.3	45.9

0.5 M $HClO_4$ and 0.25 M H_2SO_4 containing 10^{-4} M phenothiazine was studied (Figs 4 and 5). In the absence of the additive the corrosion rate increases with temperature. Moreover, the inhibition efficiency of the additive is found to increase with rising temperature at all examined potentials. It is observed that the effect of temperature on $I\%$ is more pronounced at both cathodic and OC potentials than at anodic potential. The value of $I\%$ in H_2SO_4 is not appreciably affected by the rise in temperature at anodic potentials. This behaviour can be attributed to near complete coverage (92%) of the surface at low temperature, but at higher temperatures little opportunity for extra adsorption is available.

The values of the apparent activation energy (Q), were calculated from Arrhenius plots and are given in Table 4. The activation energy decreases as the phenothiazine concentration increases from 10^{-6} to 10^{-4} M in both $HClO_4$ and H_2SO_4. This can be explained as due to the enhancement of the inhibitor adsorption on to the metal surface at higher temperatures [10]. Thus an increase in the surface coverage is expected. Similar results were obtained by Abdel Aal *et al.* [4] for corrosion inhibition of zinc by *N*-acetylphenothiazine in acidic NH_4Cl. The decrease in activation energy with increasing additive concentration, in addition to the increase in $I\%$ in the presence of inhibitor with temperature, are suggestive of chemisorption of the inhibitor molecules on the metal surface [11].

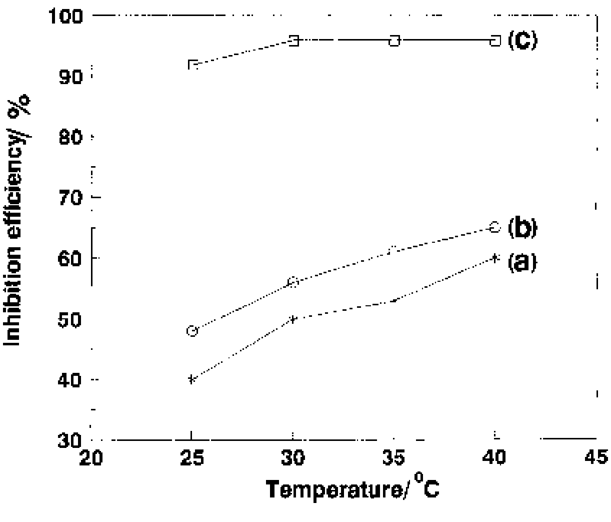

Fig. 5. Influence of temperature on inhibition efficiency of phenothiazine for cadmium in 0.25 M H_2SO_4 containing 10^{-4} M of inhibitor at (a) cathodic, (b) open circuit and (c) anodic potentials.

3.2. *Behaviour in acetic acid solution*

The data obtained for EIS of cadmium in 0.5 M CH_3COOH solution in the absence and presence of the different phenothiazine concentrations are given in Table 5. It is observed that by increasing the additive concentration R_p values are significantly increased, and the C_{dl} values of the electrode are decreased. Based on the approximate equal values of $I\%$ in both the cathodic and anodic regions in the presence of 10^{-4} M phenothiazine at 25 °C the additive can be considered as a mixed type inhibitor [3]. But the low $I\%$, especially in the anodic region of inhibitor (compared to that observed in $HClO_4$ and H_2SO_4), suggests that it is adsorbed on the relatively small, uncovered area of cadmium. According to Antropov [13, 14], the potential of cadmium on measuring (ϕ_{scale}) in acidic solutions is almost equal to +0.17 V, indicating that cadmium is positively charged at E_{corr}. Therefore, the free acetate ions are likely adsorbed on the metal surface, leading to a decrease in the true surface area available for the adsorbed phenothiazine molecules.

It is interesting to observe that the behaviour of cadmium in plain acetic acid solution at different temperatures is contrary to that observed in both $HClO_4$ and H_2SO_4 solutions, especially in the anodic region (see Fig. 7). This indicates that the increase in temperature leads to a lower corrosion rate. SEM micrographs of surfaces after experiments at anodic potential in 0.5 M CH_3COOH at both 25 and 50 °C are shown in Fig. 6(a) and (b), respectively.

The relationship between $I\%$ and temperature in the presence of 10^{-4} M phenothiazine in acetic acid solution is shown in Fig. 8. The $I\%$ decreases with increasing temperature at all examined potentials. However, a sharp decrease in $I\%$ is observed in the

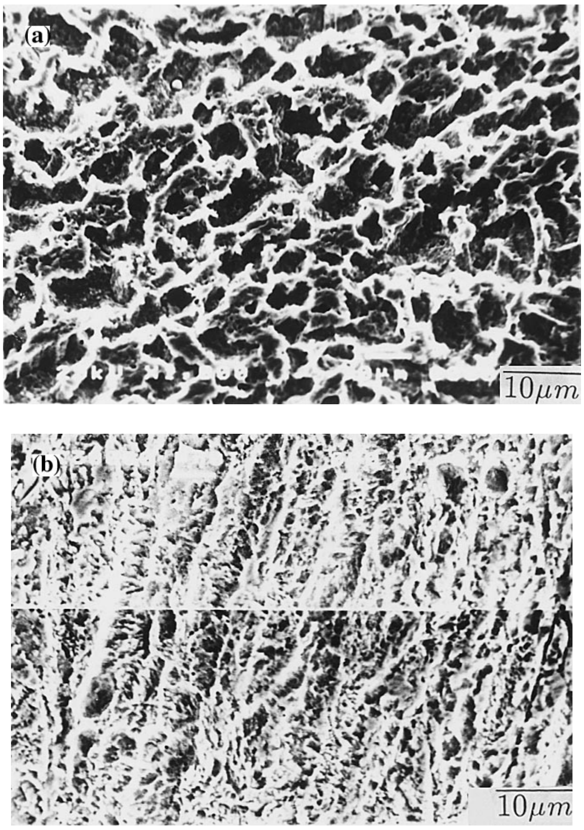

Fig. 6. SEM micrographs of cadmium surface after the experiment in 0.5 M CH_3COOH at (a) 25 °C and (b) 50 °C.

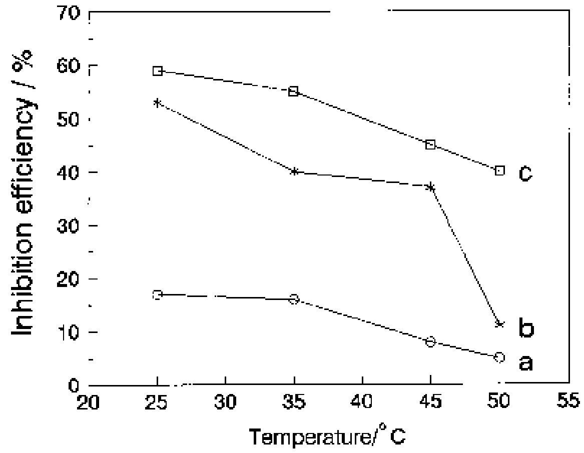

Fig. 8 Influence of temperature on inhibition efficiency of phenothiazine for cadmium in 0.5 M CH_3COOH containing 10^{-4} M of inhibitor at (a) open circuit, (b) cathodic and (c) anodic potentials.

cathodic region at higher temperature (50 °C), which may be due to a pronounced adsorption-interaction between the acetate ions and the metal surface. This suggests the presence of competitive adsorption between the inhibitor and the acetate ions. This behaviour is supported by the marked decrease in the positive shift in E_{corr} in the presence of the additive with increasing temperature. These results explain why phenothiazine is a more efficient inhibitor at lower temperatures than at higher ones in acetic acid solution.

3.3. *Adsorption isotherms*

The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitor [15]. The metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process [16], the thermodynamics of which depend on the number (*n*) of water molecules replaced by the inhibitor molecule (*n* is the configurational function, or the size factor, and is related to the mode of adsorption of the inhibitor molecules). Precise evaluation of the standard free energy (ΔG°_a) of a solvent-substitution adsorption process has been made using an adsorption

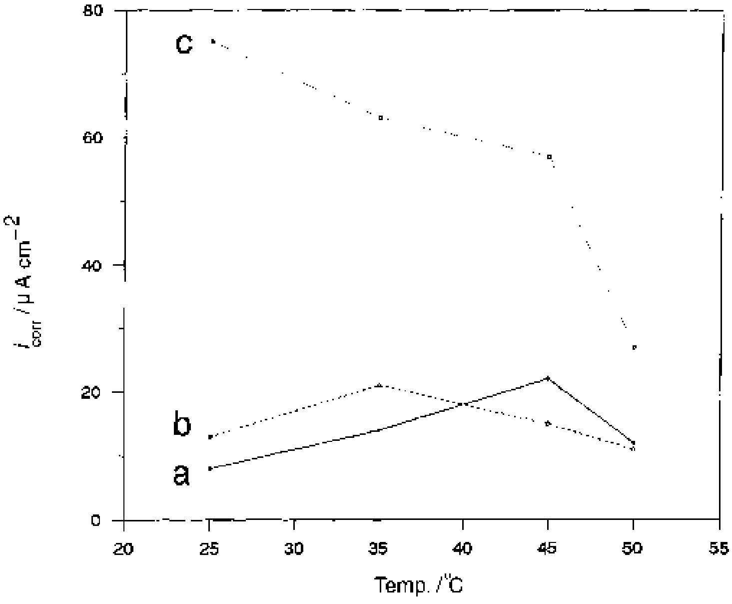

Fig. 7. Effect of temperature on corrosion current density of cadmium in 0.5 M CH_3COOH at (a) cathodic, (b) open circuit and (c) anodic potentials.

Table 5. Effect of phenothiazine on E_{corr}, impedance parameters and inhibition efficiency of cadmium in 0.5 M *CH_3COOH solution at cathodic, open circuit and anodic potentials, $A = 0.125\ cm^2$ (25 °C)*

Concentration / M		*at −200 mV*				*at 0.0 mV*				*at + 50 mV*			
	E_{corr}/mV	R_s/kΩ	R_p/kΩ	C_{dl}/μF	*I*/%	R_s/kΩ	R_p/kΩ	C_{dl}/μF	*I*/%	R_s/kΩ	R_p/kΩ	C_{dl}/μF	*I*/%
0	−770	1.40	17	15	–	1.336	6.66	23	–	1.288	1.5	241	–
10^{-6}	−768	1.40	17	13	13	1.336	6.66	23	0	1.288	1.92	186	22
10^{-5}	−760	1.40	20.23	10	33	1.366	7.10	21	9	1.288	2.77	148	38
2×10^{-5}	−754	1.40	22.92	9	40	1.336	7.34	19	17	1.288	3.72	120	50
5×10^{-5}	−748	1.40	25.61	8	46	1.336	7.34	19	17	1.288	4.05	104	56
1×10^{-4}	−743	1.40	28	7	53	1.336	7.34	19	17	1.288	4.06	98	59

isotherm [17] by introducing the configurational function in Θ. Graphical representation of Fig. 9 was made to evaluate the probable value of *n* [18]. It is found that the straight line with *n* = 4 passes through the origin indicating that 4 is the most probable value for the additive. It is known [19] that water forms groups of 4 to 5 molecules in tetrahedral arrangement which are displaced from the surface as a result of adsorption [20].

The values of ΔG_a° were calculated for various concentrations of inhibitor in $HClO_4$ solution with different Θ values ($n = 4$) and are found to be almost constant, which indicates the absence of lateral interaction among the inhibitor molecules on the electrode surface [21]. The free energy, heat and entropy of adsorption (ΔG_a°, ΔH_a° and ΔS_a°, respectively) were calculated and are depicted in Table 6. The large negative values of ΔG_a° of adsorption are usually characteristic of strong interaction [11]. The negative values of ΔH_a° indicate that the adsorption of inhibitor molecules is an exothermic process [22]. The magnitudes of the values of ΔS_a° and ΔH_a° are characteristic of the occurrence of a replacement process during adsorption of inhibitor molecules on the metal surface [23].

Table 6. Thermodynamic parameters for adsorption of phenothiazine onto a cadmium surface in 0.5 M *$HClO_4$ solution at 30* ° C

Additive conc./M	$-\Delta G_a^\circ$ ($n = 4$)/kJ mol^{-1}	ΔS_a° /J K^{-1}	$-\Delta H_a^\circ$ /KJ mol^{-1}
1×10^{-6}	33.2	91.7	5.4
1×10^{-5}	31.5	91.7	3.7
2×10^{-5}	32.4	91.7	4.6
5×10^{-5}	32.2	91.7	4.4
1×10^{-4}	32.2	91.7	4.4

The Bockris–Swinkels adsorption isotherm can not be applied in its ideal case in both H_2SO_4 and CH_3COOH solutions. This may be due to the relatively high adsorption affinity of sulfate and acetate ions on the electrode surface. The Temkin adsorption isotherm [3] (Θ_{org} against log *C*) is found to be ideally obeyed (see Fig. 10).

3.4. *Mode of adsorption*

Phenothiazine can be chemisorbed as a tridentate surface ligand in which the surface coordination is either through both the sulfur atom and two benzene rings or solely through the sulfur centre alone. The

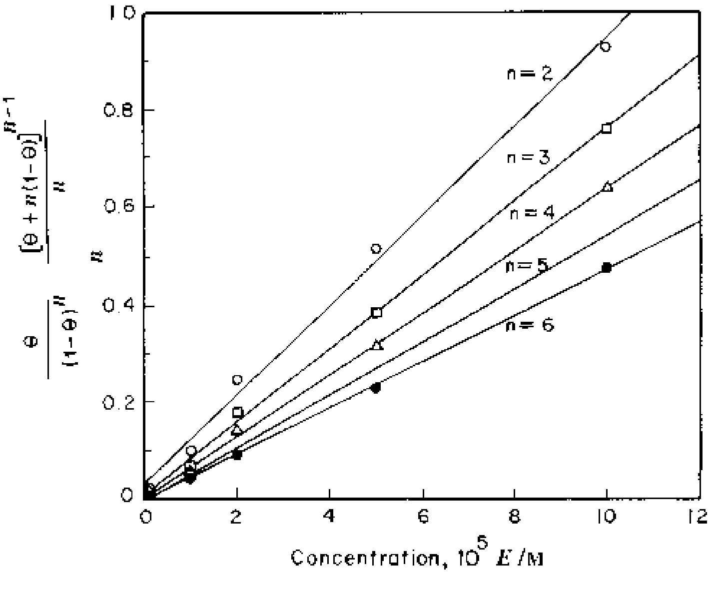

Fig. 9. Bockris-Swinkels adsorption isotherms for adsorption of phenothiazine on cadmium in 0.5 M $HClO_4$ in cathodic potential region at 30 °C.

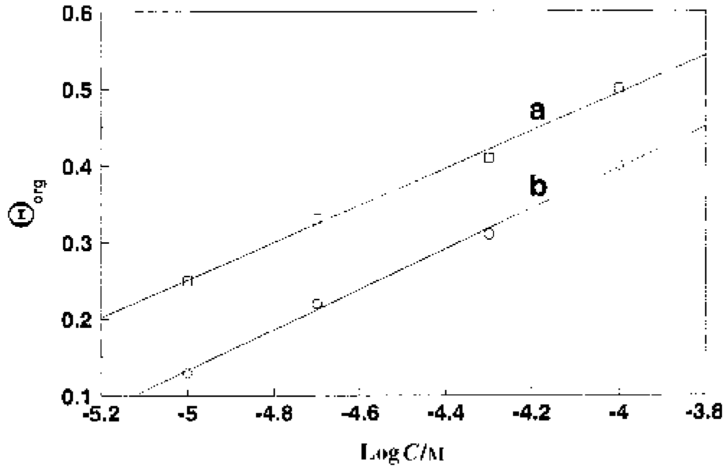

Fig. 10. Temkin adsorption isotherm for phenothiazine on cadmium in both (a) H_2SO_4 and (b) CH_3COOH in cathodic potential region at 35 °C.

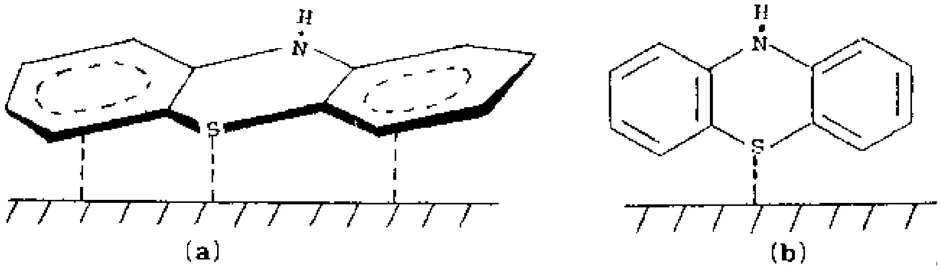

Fig. 11. Mode of adsorption of phenothiazine.

two possible modes are depicted in Fig. 11. Previously, it was concluded that the mode of adsorption depends on the affinity of the metal towards the Π-electrons of the ring system [11]. Metals such as cadmium, which have greater affinity towards aromatic moieties were found to adsorb aniline and benzene thiols in a flat orientation [3]. Thus, in the case of the cadmium/acid system, it is reasonable to assume that the inhibitor is adsorbed in a flat orientation through a tridentate form (see Fig. 11 (a)).

4. Conclusions

(i) Phenothiazine is strongly adsorbed on cadmium in $HClO_4$ and H_2SO_4 solutions, predominantly in the anodic region.
(ii) The inhibition efficiency (I%) increases as both the inhibitor concentration and the temperature are increased. The decrease in activation energy with increasing additive concentration, in addition to the increase in I% in the presence of the inhibitor with temperature, are suggestive of chemisorption.
(iii) In CH_3COOH solution the corrosion rate of cadmium decreases as the temperature rises, especially in the anodic region, due to more even distribution of the accumulated acetate ions on the electrode surface. In the presence of the additive I% decreases with increasing temperature as a result of competitive adsorption between the inhibitor and acetate ions at the electrode surface.
(iv) The Bockris–Swinkels adsorption isotherm fits the Cd/$HClO_4$ system well. While the Temkin relation is found to be ideally obeyed in both H_2SO_4 and CH_3COOH solutions.

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