

Inhibitive Effect of Some New Triazole Derivatives on Mild Steel Corrosion in Formic and Acetic acid

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Abstract

Four organic inhibitors namely, 5-nonyl-4-phenyl-3-mercapto-1, 2,4-triazole (NPMT), 5-Undecyl-4-phenyl-3-mercapto-1, 2,4-triazole (UPMT), 5-Pentadecyl-4-phenyl-3-mercapto-1, 2,4-triazole (PPMT), 5-Heptadecyl-4-phenyl-3mercapto-1,2,4-triazole (HPMT) have been synthesized in the laboratory and their influence on the corrosion inhibition of mild steel (MS) in 20% formic acid and 20% acetic acid by weight loss and potentiodynamic polarization techniques were studied. Scanning electron microscopic study (SEM) was done to investigate the surface characterization of inhibited & uninhibited metal samples. The inhibition efficiency was found to vary with inhibitor concentration, immersion time, and acid concentration and solution temperature. Good inhibition efficiency (IE) was evidenced in both the acid solutions, even at concentration of 25 ppm. The adsorption of these compounds on the mild steel surface for both acids was found to obey langmuir's adsorption isotherm. The values of activation energy, free energy of adsorption, heat of adsorption, enthalpy of activation and entropy of activation were also calculated to elaborate the mechanism of corrosion inhibition. The potentiodynamic polarization data have shown that compounds studied are mixed type inhibitors. FT-IR & NMR Study were also done in order to confirm the composition of synthesised inhibitor.

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Introduction

Most of the researches on corrosion inhibition of metals have been done in mineral acids. Corrosion behaviour of iron and mild steel in organic acid solutions has attracted the attention of many investigators [1-3]. Mild steel is used in the fabrication of reaction vessels, storage tanks etc. by industries, which either manufacture or use organic acid as reactant. Organic acids rank among the most important chemicals in industry today. Rather than being used as final products, they serve as precursors to other chemicals. The reactive carboxyl group -COOH makes them a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibres.

Organic compounds containing heteroatoms such as O, N, S and multiple bonds in their molecules are of particular interest as they give better inhibition efficiency than those containing N or S atom alone [4-8]. A survey of literature reveals that corrosion inhibitors derived from triazoles constitute an important and potential class of corrosion inhibitors on mild steel in acidic medium [9-11]

In present investigation, the influence of four triazoles namely, 5-nonyl-4-phenyl-3-mercapto-1, 2,4-triazole (NPMT), 5-Undecyl-4-phenyl-3-mercapto-1, 2,4-triazole (UPMT), 5-Pentadecyl-4-phenyl-3-mercapto-1, 2,4-triazole (PPMT), 5-Heptadecyl-4-phenyl-3-mercapto-1, 2,4-triazole (HPMT) on corrosion inhibition of mild steel in 20% formic acid & 20% acetic acid have been reported.

Experimental

Material Preparation

AR grade formic and acetic acid (MERCK) and doubled distilled water were used for preparing test solutions of 20% formic acid and 20% acetic acid for all the experiments. The inhibitors were synthesized in the laboratory following the procedure described by Kittur et al. [12] and the compounds were characterized through their spectral data and their purity was confirmed by thin layer chromatography (TLC). Name & structural formulas of the condensation products are given in Table 1.

FT-IR Spectroscopy

The FT-IR spectroscopic study was used to investigate the purity of the synthesized compound. The results are listed below:

- i) 5-nonyl-4-phenyl-3-mercapto-1,2,4-triazole (NPMT) - IR (KBr): 1734(C=N), 1410 (C-N), 2362 (S-H), 2848 (C-H), 925 (C₆H₅), 1234 (CH₃) cm⁻¹.
- ii) 5-Undecyl-4-phenyl-3-mercapto-1,2,4-triazole (UPMT)- IR (KBr) 1606(C=N), 1313 (C-N), 1733 (S-H), 2984 (C-H), 999 (C₆H₅), 1252 (CH₃) cm⁻¹.
- iii) 5-Pentadecyl-4-phenyl-3-mercapto-1,2,4-triazole (PPMT)- IR (KBr): 1640(C=N), 1311 (C-N), 2354 (S-H), 2911 (C-H), 915 (C₆H₅), 1203 (CH₃) cm⁻¹.
- iv) 5-Heptadecyl-4-phenyl-3-mercapto-1,2,4-triazole (HPMT) - IR (KBr): 1558(C=N), 1315 (C-N), 2364 (S-H), 2850 (C-H), 917 (C₆H₅), 1203 (CH₃) cm⁻¹.

NMR Spectroscopy

NMR Spectral data (δCDCl₃)

7.388 (5H, C₆H₅), 1.180 (1H, SH), 0.983 (3H, CH₃), 2.245 (16H, (CH₂)₈)

Weight loss Determination

The mild steel samples having composition, (Wt %): 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and balance Fe has been used for the experiment. The mild steel sample of size 2.0 cm × 2.0 cm × 0.025 cm were used for weight loss measurement studies. Weight loss measurement studies were carried out at various temperatures ranging from 30 to 60°C for various immersion times from 24 to 120 hrs. The experiments were performed as per ASTM method described previously [13]. The inhibition efficiency of the inhibitors was calculated by using the following equation: -

$$IE = \frac{CR_o - CR_i}{CR_o} \times 100 \quad \text{-----(1)}$$

where

CR_o = Corrosion rate of blank formic and acetic acid

CR_i = Corrosion rate after adding inhibitors.

Electrochemical studies

For potentiodynamic polarization studies of mild steel strips of the above composition, coated with commercially available lacquer with an exposed area of 1.0 cm^2 were used and the experiments were carried out at temperature $(30 \pm 1 \text{ }^\circ\text{C})$. Equilibrium time leading to steady state of the specimens was 30 minutes. Sweep rate in potentiodynamic experiment was 1 mV/sec . Potentiodynamic polarization studies were carried out using an EG & G Princeton Applied research (PAR) potentiostat / galvanostat (model 173), a universal programmer (model 175) and a X-Y recorder (model RE0089). A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) was used as reference electrode. The CR was calculated using the following formula [14],

$$\text{CR} = \frac{0.13 \times I_{\text{corr}} \times \text{EW}}{D} \quad \text{----- (2)}$$

where,

I_{corr} = Corrosion current density in $\mu\text{A/cm}^2$.

EW = Equivalent weight of the metal in gram.

D = Density of the metal in g/cm^3 .

Scanning Electron Microscopy

Scanning electron microscope (SEM) Model No 435 VP LEO was used to study the morphology of corroded surface in presence and absence of inhibitors. The specimens were thoroughly washed with double distilled water before putting on the slide. The photographs have been taken from that portion of specimen from where better information was obtained. They were photographed at appropriate magnifications. To understand the morphology of the steel surface in absence and presence of inhibitors, the following cases have been examined.

- i) Polished mild steel specimen
- ii) Mild steel specimen dipped in 20% formic acid
- iii) Mild steel specimens dipped in 20% formic acid containing 500ppm concentration of UPMT inhibitors.

Results and Discussion

Weight loss studies

The values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained from weight loss method at different concentrations at 30°C are summarized in Table 2. It has been found that all of these compounds inhibit the corrosion of mild steel in formic and acetic acid solution, at all concentrations used in this study i.e., 25ppm – 500 ppm. It has also been observed that the inhibition efficiency for all of these compounds increases with the increase in concentration variation as shown in Fig.1a & 1'a.

It is observed that the tested triazoles shows a decrease in the inhibition efficiency with the increase in the immersion time from 24 to 120 hours in formic as well as in acetic acid. This shows the persistency of the adsorbed triazole over a longer test period. Inhibition efficiency of all the compounds against the immersion time is shown in Fig.1b & 1'b.

The variation of IE with solution temperature is shown in Fig. 1c & 1'c. It can be seen that IE for compounds such as NPMT, UPMT, PPMT and HPMT increases with increase in temperature from 30°C to 60°C indicating that the inhibitive film formed on the metal surface is protective in nature up to 60°C. The effect of acid concentration of formic and acetic acid is shown in Fig. 1d & 1'd'. With the increase in concentration of formic acid, the IE initially increases and attains maxima at 20% acid concentration and thereafter decreases on further increase in acid concentration to 30%. The IE decreases slightly with increase in acetic acid concentration.

The degree of surface coverage (θ) for different inhibitor concentrations in 20% formic acid and 20% acetic acid at 30°C over 24-hour immersion time was evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A plot of $\log (\theta/1-\theta)$ versus $1/T$ is shown in Figure 2a and 2'a. The plot gives the values of heat of adsorption (Q), which is determined from the slope ($= -Q/2.303R$). The values for the heat of adsorption are presented in Table 3. The values of heat of adsorption for the inhibitors in formic and acetic acid is found to be less than (-40kJ mol^{-1}); except for UPMT in formic acid. This indicates that all the inhibitors used except UPMT are adsorbed physically [15].

It has been reported by a number of authors [16-18] that, in acid solution, the logarithm of the corrosion rate is a linear function of $1/T$ (Arrhenius equation):

$$\text{Log (Rate)} = \frac{-E_a^0}{2.303RT} + A \quad \text{----- (3)}$$

where, E_a^0 is the apparent activation energy, R the general gas constant and A the Arrhenius pre exponential factor. A plot of \log (corrosion rate) versus $1/T$ gave straight lines as shown in Figure 2b and 2'b. The values of activation energy (E_a^0) obtained from the slope of the lines are given in Table 3. An alternative formula for the Arrhenius equation in the transition state equation:

$$\text{Rate} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \quad \text{----- (4)}$$

where, h is the Plank constant, N the Avogadro's number, ΔS^0 the entropy of activation, and ΔH^0 the enthalpy of activation. A plot of $\log (CR/T)$ versus $1/T$ should give a straight line, (Figure 2c and 2c') with a slope of $(-\Delta H^0 / 2.303 R)$ and an intercept of $[(\log (R / Nh) + (\Delta S^0 / 2.303 R))]$, from which the values of ΔS^0 and ΔH^0 were calculated and are listed in Table 3. The data show that the values of thermodynamic activation function (E_a^0) of the corrosion in mild steel in 20% formic acid and 20% acetic acid solution in the presence of the inhibitors are lower than those in the free acid solution, indicating that all the inhibitors exhibit high inhibition efficiency at elevated temperatures [19]. Such inhibitors are bound to the surface by specific adsorption forces or by chemisorption as a result of which a surface film of reaction product is formed [15]. The chemisorption process in the film formation with a strong attractive force is likely to be exothermic resulting in lowering of the activation energy [20]. The values of ΔH^0 (Table 3) is in the order $UPMT > NPMT > PPMT > HPMT$ which is an indicative of the existence of energy barrier at elevated temperature [19]. The values of activation ΔS^0 in the absence and presence of the inhibitors are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorderness takes during the course of transition from

reactants to the activated complex [21]. The average value for free energy of adsorption (ΔG_{ads}), calculated using the following equations [22] are given in Table 3.

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K) \quad \text{----- (5)}$$

and K is given by:

$$K = \theta/C (1 - \theta) \quad \text{----- (6)}$$

where, θ is degree of coverage on the metal surface, C is concentration of inhibitor in mol l^{-1} , K is equilibrium constant, R is a gas constant and T is temperature. It is found that the ΔG_{ads} values for the studied compound at higher temperature is less than -40 kJ mol^{-1} indicating that the triazoles are physically adsorbed on the metal surface except for a slight increase in ΔG_{ads} values for UPMT in formic acid, showing chemical adsorption [23].

The low and negative value of ΔG_{ads} indicates the spontaneous adsorption of inhibitor on the surface of mild steel [24]. It was also found that value of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova [19] has suggested that this type of inhibitor is effective up to higher temperature.

The Plot of log (weight loss) versus Immersion time as shown in Figure (2d), gave a straight line indicating that it follows first order reaction. The value of rate constant is calculated by using the first order rate law [25].

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \quad \text{----- (7)}$$

where $[A_0]$ is the initial mass of the metal and $[A]$ is the mass corresponding to time t. The half-life ($t_{1/2}$) values were calculated using the relationship [26].

$$t_{1/2} = 0.693/k \quad \text{----- (8)}$$

The values of rate constants and half-life ($t_{1/2}$) obtained from the above relations are summarized in Table 4. Half-life values were found to be constant at different immersion time. The order of effectiveness of inhibitors were observed as UPMT > NPMT > PPMT > HPMT in 20% formic acid and UPMT > NPMT > HPMT > PPMT in 20% acetic acid. The constant values of rate constant further confirmed that the corrosion of mild steel in

20% formic acid and in 20% acetic acid in presence of different inhibitor follows first order kinetics.

Application of Adsorption isotherm

The mechanism of corrosion inhibition may be explained on the basis of adsorption behaviour of inhibitors [27]. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight-loss data. Fitting of data to various isotherms was tested graphically. A plot of $\log \theta / (1 - \theta)$ vs. $\log C$ shows a straight line (Figure 3 & 3') indicating that adsorption follows the Langmuir isotherm.

$$\theta / (1 - \theta) = k C \exp (- G_{\text{ads}}/RT) \quad \text{----- (9)}$$

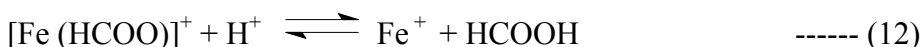
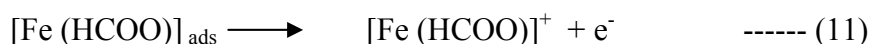
where G_{ads} is the free energy of adsorption and C is the inhibitor concentration.

Potentiodynamic polarization

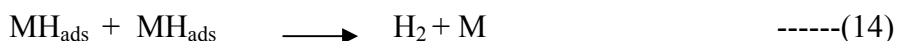
The cathodic and anodic polarization curves of mild steel in 20% formic and 20%acetic acid in the absence and presence of different inhibitors at 500-ppm concentration at 28 ± 2 °C are shown in (Figure 4 & 4'). Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and inhibition efficiency (IE) were calculated from Tafel plots and are given in Table 5. A maximum decrease in I_{corr} was observed for UPMT. It is also observed from Table 5 that (E_{corr}) values and Tafel slope constants b_a and b_c do not change significantly in inhibited solution as compare to uninhibited solution. It is seen from the results that triazoles do not shift E_{corr} values significantly thereby suggesting that they are mixed type inhibitors. This type of behaviour has been observed for mild steel in acid solution containing 2-hydrazino-6-methyl-benzothiazole [28].

Mechanism of corrosion inhibition

The corrosion of mild steel in non-aqueous and aqueous solution may occur in the following steps [29]:



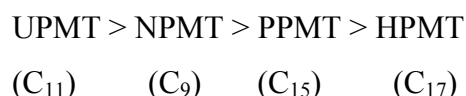
The evolution of hydrogen occurs due to the following cathodic reaction:



The adsorption of formate ions on the surface of iron is a prerequisite for the anodic dissolution to occur, thus the rate of corrosion should depend on the concentration of formate ion in the solution. The conductance of formic acid solution gradually increases in concentration range from 5% - 20%. As a result, the extent of adsorption of formate ion, as well as the rate of step (9) increases and consequently the rate of corrosion also increases.

The triazoles inhibit the corrosion by controlling both the anodic and cathodic reactions. In acidic solutions these compounds exist as protonated species. These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through the π - electrons of aromatic rings and lone pair of electrons of nitrogen and sulphur atoms [30].

Among the compounds investigated, the order of IE is:



UPMT gives the best performance as corrosion inhibitor. In general trend, the IE increases with increase in the chain length but it also decrease as we increase chain length after C_{11} due to decreased solubility and increased steric hindrance [31].

Conclusions

- (i) The triazole derivatives showed good performance as corrosion inhibitors in formic acid and acetic acid media.
- (ii) All of the four triazoles, inhibited corrosion by adsorption mechanism and the adsorption of these compounds from acid solution followed Langmuir's adsorption isotherm.
- (iii) All the compounds examined acted as mixed inhibitors in formic and acetic acid solutions.

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Table 1.

Name, structures and molecular weights of the compounds used

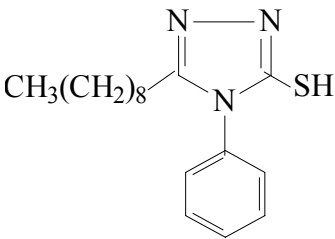
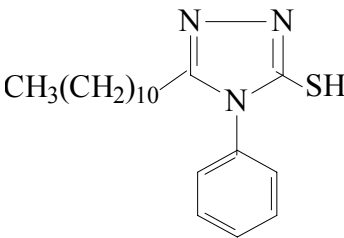
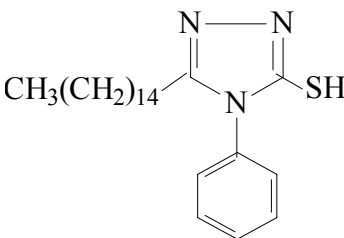
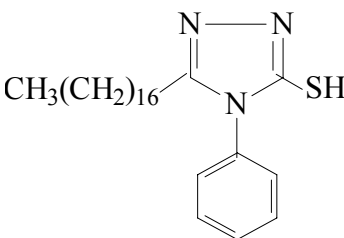
S No	Structure	Designation and abbreviation
1.		5-Nonayl- 4-Phenyl 3-mercapto-1,2,4 Triazole (NPMT)
2.		5-Undecyl- 4-Phenyl 3-mercapto1, 2,4 Triazole (UPMT)
3.		5-Pentadecyl- 4-Phenyl 3-mercapto1, 2,4 Triazole (PPMT)
4.		5-Heptadecyl- 4-Phenyl 3-mercapto1, 2,4 Triazole (HPMT)

Table 2

Corrosion parameters for mild steel in aqueous solution of 20% formic acid and 20%acetic acid in absence and presence of different concentrations of various inhibitors from weight loss measurements at 30 °C for 24 h.

Inhibitor Conc. (ppm)	20% Formic acid			20% Acetic acid		
	Weight loss (mg)	IE (%)	CR (mmpy)	Weight loss (mg)	IE (%)	CR (mmpy)
Blank	308.21	-	14.31	150.36	-	6.97
UPMT						
25	23.53	92.36	1.09	11.51	92.34	0.53
50	14.94	95.18	0.69	9.37	93.76	0.44
100	9.76	96.83	0.45	8.72	94.20	0.41
300	6.01	98.05	0.28	7.12	95.26	0.33
500	3.26	98.94	0.15	5.75	96.17	0.27
NPMT						
25	30.10	90.23	1.39	14.42	90.40	0.67
50	18.98	93.84	0.88	12.29	91.82	0.57
100	13.67	95.56	0.65	10.13	93.26	0.47
300	9.18	97.02	0.43	9.30	93.81	0.43
500	5.57	98.19	0.26	8.16	94.57	0.38
PPMT						
25	33.15	89.24	1.54	19.14	87.26	0.89
50	25.78	91.63	1.19	15.73	89.53	0.73
100	17.93	94.18	0.83	12.83	91.46	0.59
300	10.10	96.72	0.47	10.59	92.95	0.49
500	8.87	97.15	0.41	8.97	94.03	0.42
HPMT						
25	43.96	85.73	2.04	22.05	85.19	1.03
50	35.24	88.56	1.64	19.79	86.83	0.92
100	23.60	92.34	1.09	17.40	88.42	0.81
300	16.48	94.65	0.76	13.88	90.76	0.65
500	9.76	96.83	0.45	12.74	91.50	0.59

Table 3

Thermodynamic activation parameters for mild steel in 20% formic acid and 20%acetic acid in absence and presence of inhibitors of 500-ppm concentration.

Inhibitor concentration (ppm)	E_a (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	$-\Delta S$ (J mol ⁻¹ K ⁻¹)	$-\Delta G_{ads}$ (KJ mol ⁻¹)	$-Q$ (KJmol ⁻¹)
20% Formic acid	18.51	25.53	226.31	-	-
UPMT	6.38	31.93	270.36	41.89	51.05
NPMT	9.57	12.76	262.69	39.09	25.53
PPMT	15.95	9.57	255.99	38.23	15.96
HPMT	16.59	7.66	253.12	37.97	6.38
20% Acetic acid	19.15	28.72	222.49	-	-
UPMT	15.95	12.76	260.78	37.80	21.06
NPMT	12.76	9.57	255.04	36.07	17.03
PPMT	10.85	5.11	250.25	36.25	14.68
HPMT	9.57	4.79	245.46	35.18	5.74

Table 4

Half-life (h) values for the corrosion of mild steel at different immersion time in 20% formic acid and 20% acetic acid in absence and presence of inhibitors of 500-ppm concentration at 30° C.

Inhibitor concentration (ppm)	$k10^{-4}$	$t_{1/2}$
20%Formic acid	6.23±0.0075	1112.36
UPMT	1.24±0.0002	5588.71
NPMT	1.64±0.0001	4233.35
PPMT	2.22±0.0002	3116.01
HPMT	2.90±0.0004	2387.18
20%Acetic acid	4.03±0.0004	1717.89
UPMT	1.67±0.0002	4162.16
NPMT	2.24±0.0005	3093.75
PPMT	5.91±0.0009	1172.58
HPMT	3.05±0.0003	2272.43

Table 5

Electrochemical polarization parameters for the corrosion of mild steel in 20% formic acid and 20%acetic acid containing 500-ppm inhibitors at 30 °C.

Inhibitor concentration (ppm)	E_{corr} (mV)	I_{corr} (mA cm ⁻²)	IE (%)	b_a (mVdec ⁻¹)	b_c (mVdec ⁻¹)
20%Formic acid	-416	0.350	-	68	104
UPMT	-420	0.0035	99.02	64	106
NPMT	-402	0.0051	98.54	60	100
PPMT	-423	0.0094	97.30	66	112
HPMT	-395	0.0154	95.60	70	120
20%Acetic acid	-402	0.240	-	60	100
UPMT	-406	0.005	97.90	52	96
NPMT	-390	0.039	94.70	54	92
PPMT	-412	0.034	93.90	58	104
HPMT	-418	0.024	90.83	56	98

CAPTION FOR FIGURES

Fig. 1 —Variation of inhibition efficiency with (a) inhibitor concentration, (b) immersion time, (c) solution temperature, (d) acid concentration in 20% formic acid (1: UPMT; 2: NPMT; 3: PPMT; 4: HPMT)

Fig. 1' —Variation of inhibition efficiency with (a) inhibitor concentration, (b) immersion time, (c) solution temperature, (d) acid concentration in 20% acetic acid (1: UPMT; 2: NPMT; 3: PPMT; 4: HPMT)

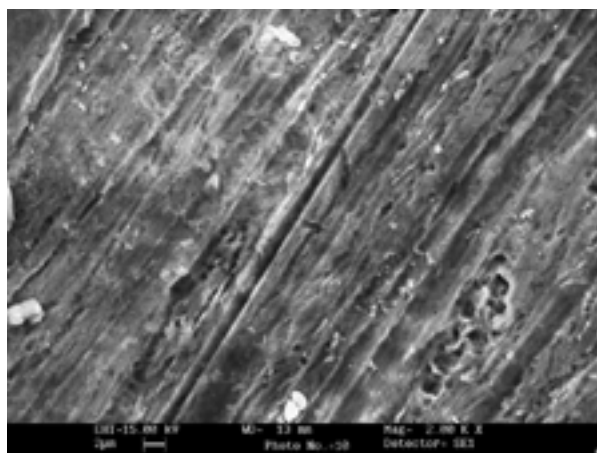
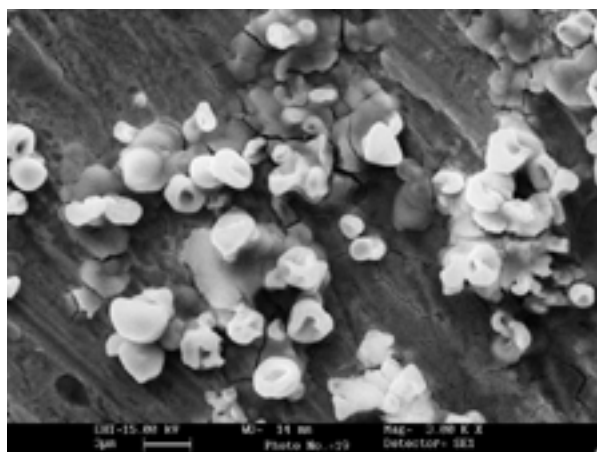
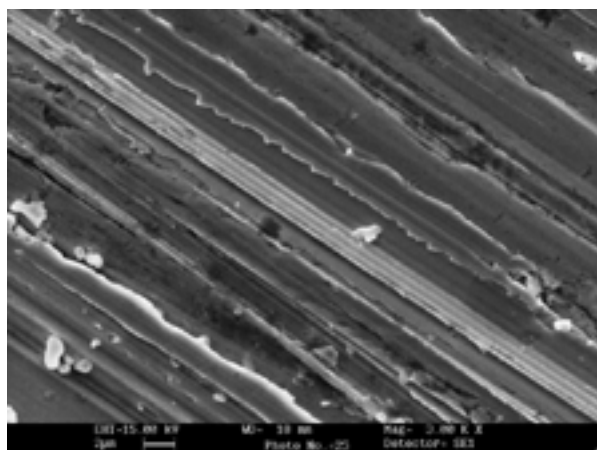
Fig. 2— (a) Adsorption isotherm plot for $\log (\theta / 1-\theta)$ versus $1/T$; (b) Adsorption isotherm plot for $\log (CR)$ versus $1/T$; (c) Adsorption isotherm plot for $\log (CR/T)$ versus $1/T$; and (d) Half-life plot for $\log (\text{weight loss})$ versus immersion time in 20% formic acid (1: UPMT; 2: NPMT; 3: PPMT; 4: HPMT; 5: Blank)

Fig. 2' — (a) Adsorption isotherm plot for $\log (\theta / 1-\theta)$ versus $1/T$; (b) Adsorption isotherm plot for $\log (CR)$ versus $1/T$; (c) Adsorption isotherm plot for $\log (CR/T)$ versus $1/T$; and (d) Half-life plot for $\log (\text{weight loss})$ versus immersion time in 20% acetic acid (1: UPMT; 2: NPMT; 3: PPMT; 4: HPMT; 5: Blank)

Fig. 3 — Langmuir's adsorption isotherm plots for the adsorption of various inhibitors on the surface of mild steel in a) 20% formic acid b) 20% acetic acid. (1: UPMT; 2: NPMT; 3: PPMT; 4: HPMT; 5: Blank)

Fig. 4 — Potentiodynamic polarization curves for aluminium containing 500-ppm concentration of various azathiones in a) 20% formic acid b) 20% acetic acid. (1:Blank; 2: HPMT; 3: PPMT; 4: NPMT; 5: UPMT)

Fig. 5 — Scanning electron micrographs for
a) Polished mild steel b) Mild steel in 20% formic acid c) Mild steel in 20% formic acid + 500ppm UPMT



Scanning electron micrographs for

- a) Polished mild steel b) Mild steel in 20% formic acid c) Mild steel in 20% formic acid + 500ppm UPMT

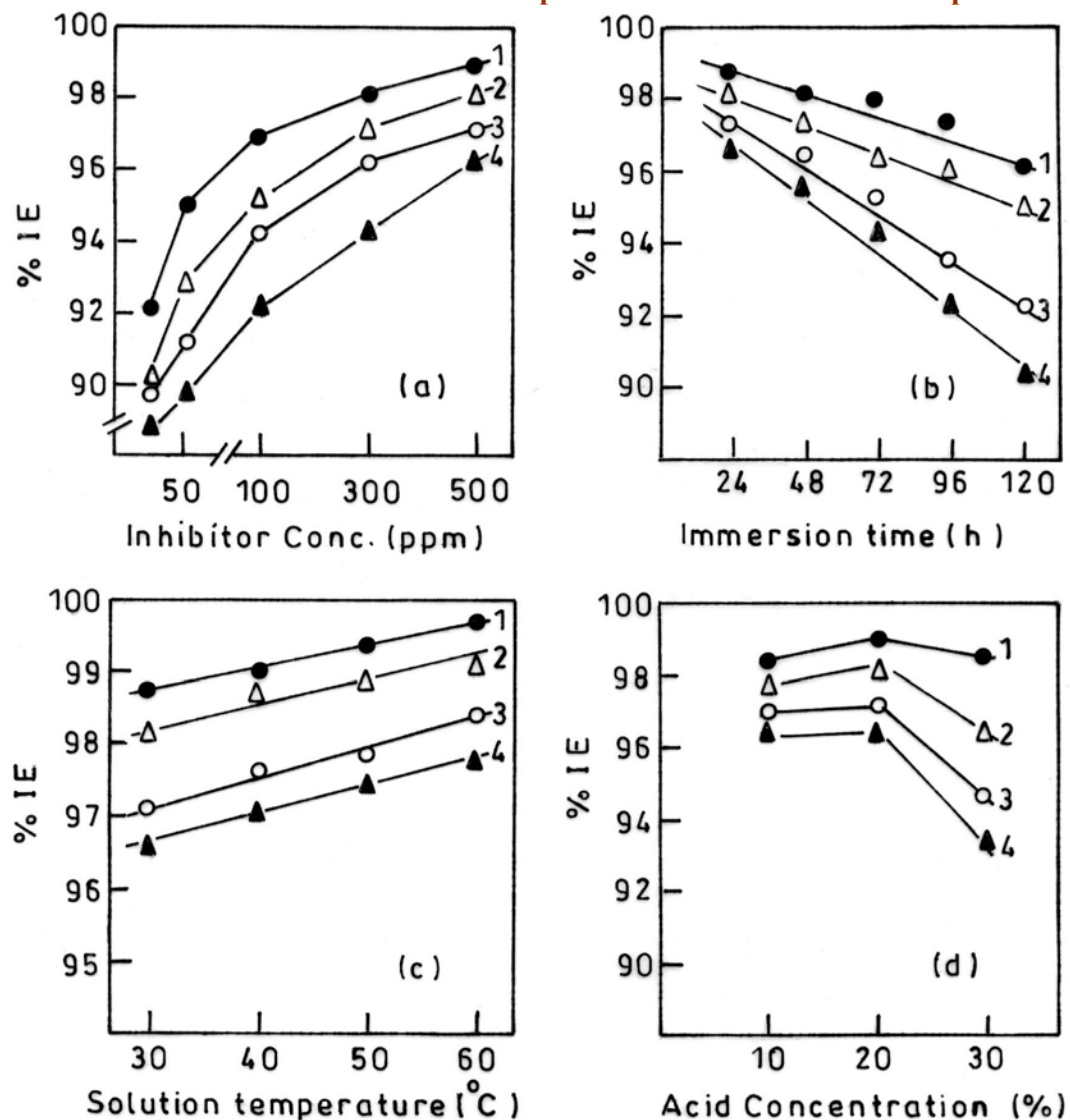


Fig. 1

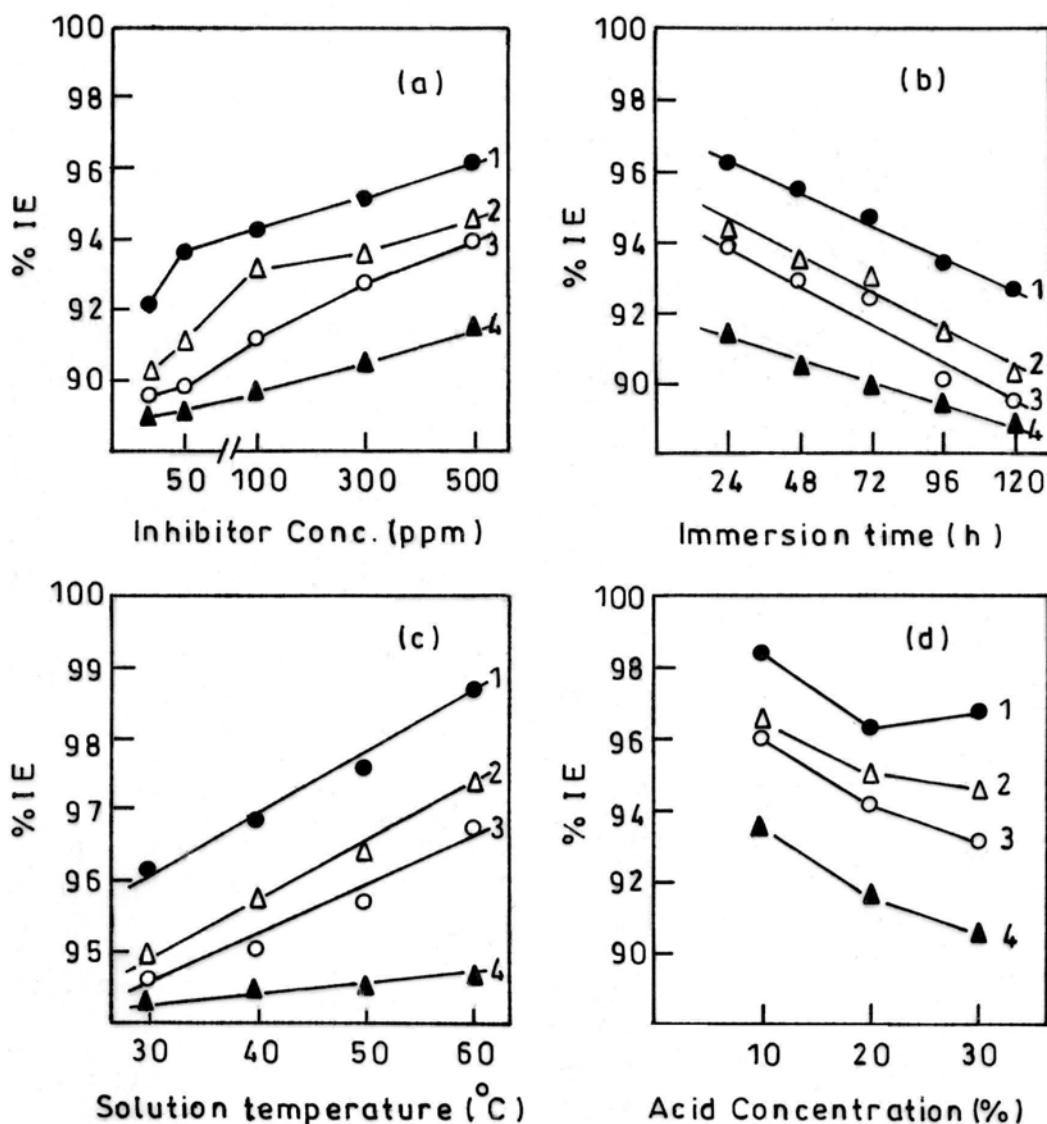


Fig.1'

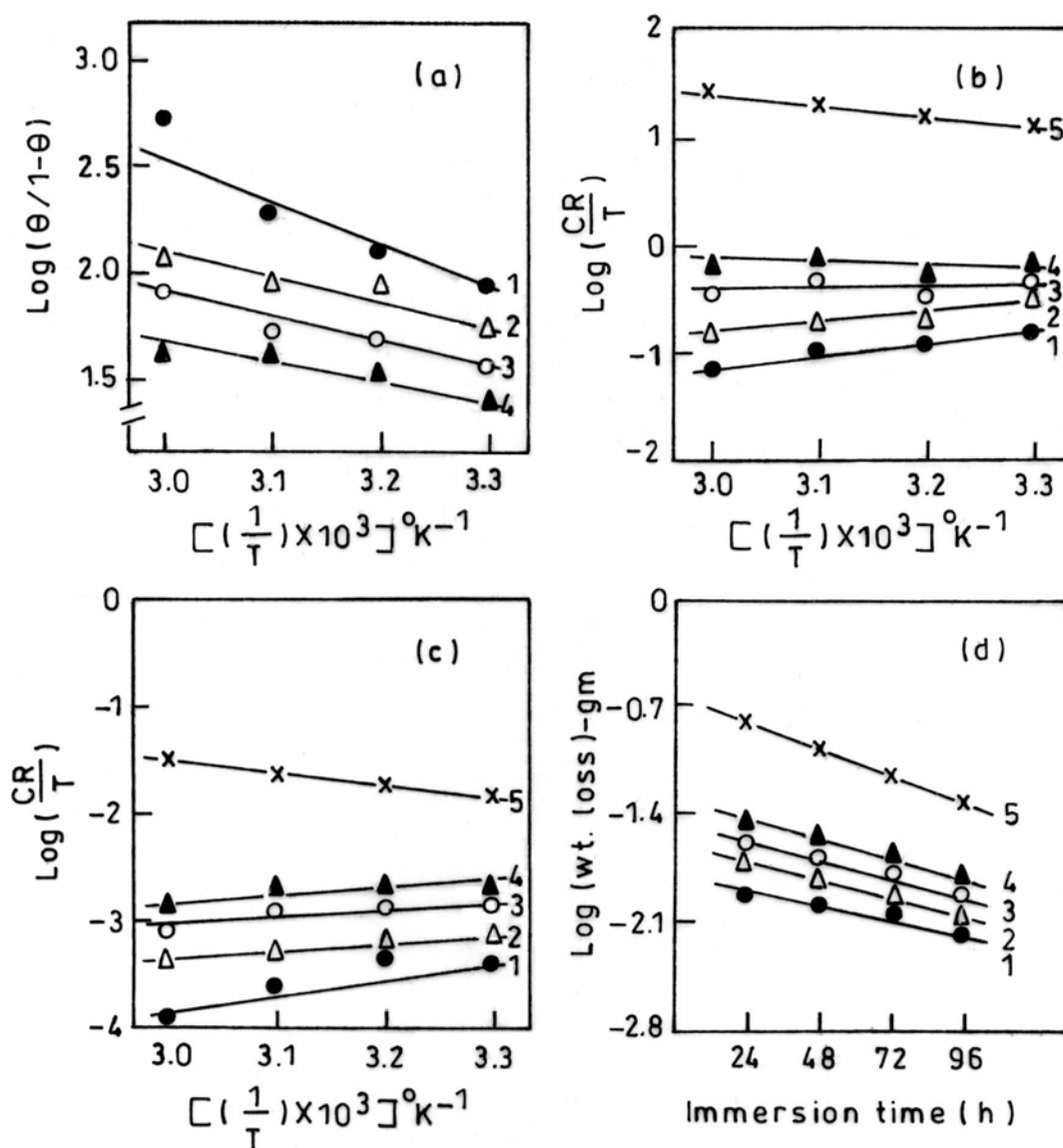


Fig. 2

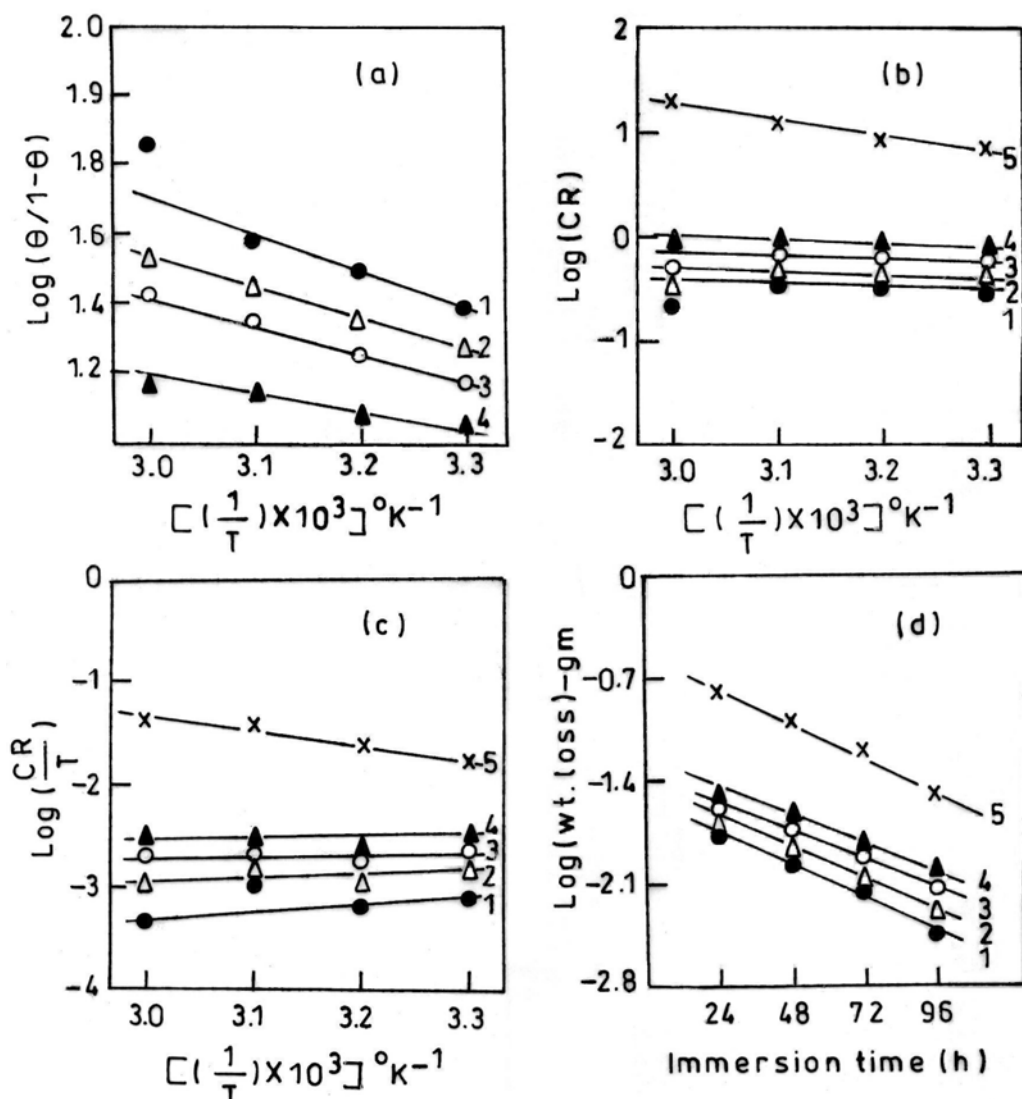


Fig. 2'

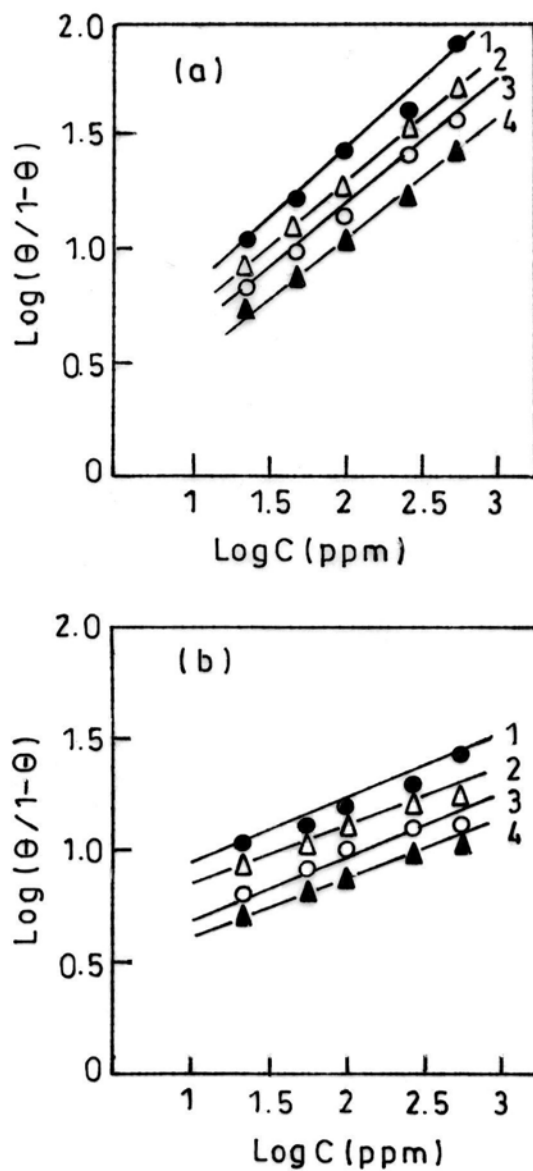


Fig. 3a & 3b

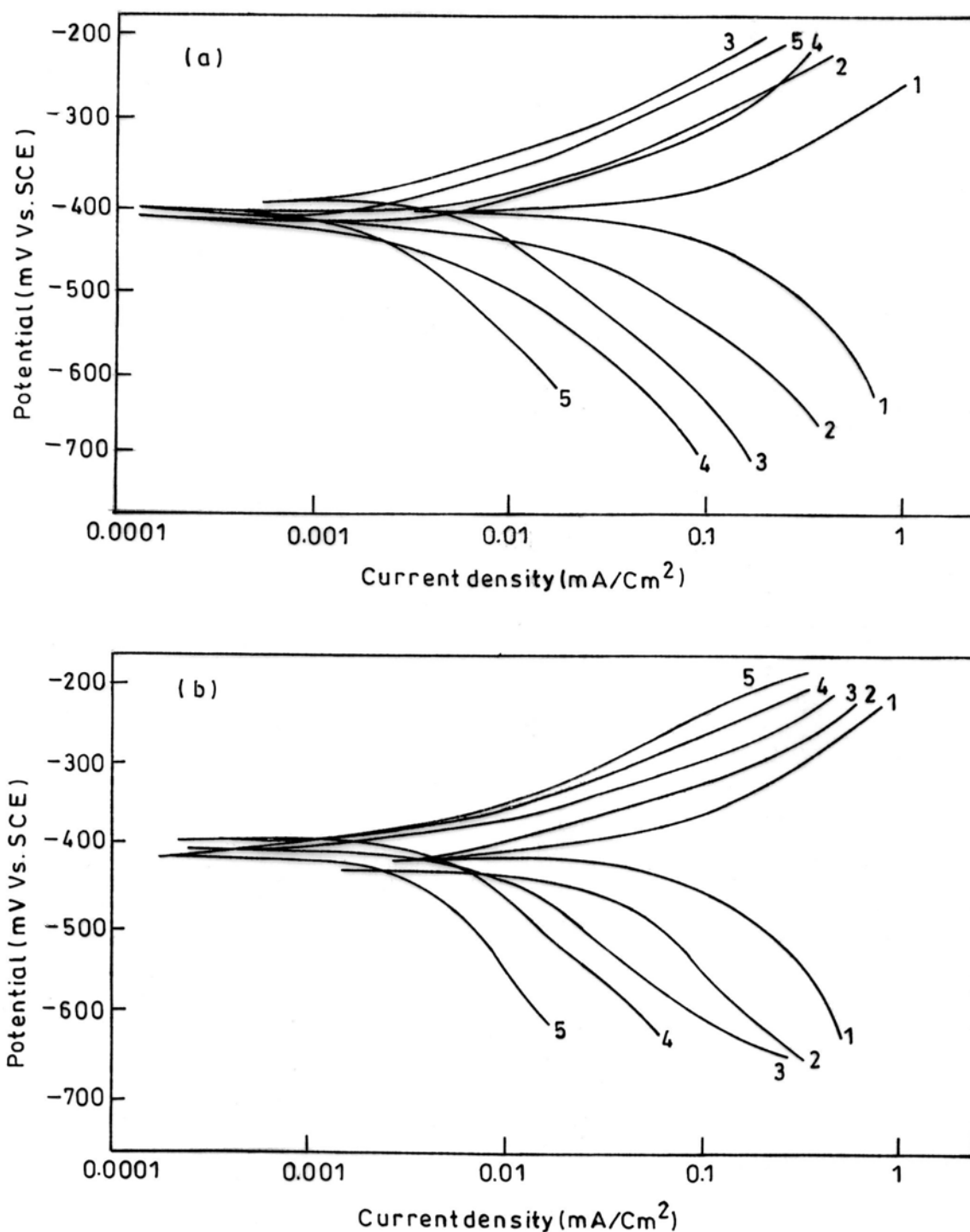


Fig. 4a & 4b