

Heterocyclic anils as corrosion inhibitors of mild steel in formic and acetic acid solutions

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Effects of four corrosion inhibitors namely, 4-(N, N-dimethylamino) benzylidene imino-3-propyl-5-mercapto-1,2,4-triazole(DIPMT), 4-benzylidene imino-3-propyl-5-mercapto-1,2,4-triazole (BIPMT), 4-salicylidene imino-3-propyl-5-mercapto-1,2,4-triazole (SIPMT) and 4-cinnamalidene imino-3-propyl-5-mercapto-1,2,4-triazole (CIPMT) against corrosion of mild steel in aqueous solutions of 20% formic acid and 20% acetic acid using weight loss and potentiodynamic polarization and impedance methods were studied. All tested inhibitors showed good inhibition efficiency (IE). The IE was found to vary with concentration, temperature, immersion time, and concentration of acid solution. The potentiodynamic polarization results revealed that all the compounds were mixed type inhibitors. The adsorption of these compounds on the mild steel surface exposed to both acids has been found to obey Langmuir adsorption isotherm.

Keywords: Mild steel, heterocyclic anils, Langmuir adsorption isotherm, potentiodynamic polarization, impedance.

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Corrosion behaviour of iron and mild steel in organic acid solutions has attracted the attention of several investigators¹⁻³. Corrosion studies on metals in organic acid solutions are scarce in comparison with similar studies in mineral acids⁴⁻⁷. Mild steel is used in fabrication of reaction vessels, storage tanks by industries, which either manufacture or use organic acids as reactant. Organic acids rank among the most important chemicals in industry today. The reactive carboxyl group –COOH makes them a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibers.

In the present investigation, a few heterocyclic anils namely, 4-(N, N-dimethylamino) benzylidene imino-3-propyl-5-mercapto-1, 2, 4-triazole(DIPMT), 4-benzylidene imino-3-propyl-5-mercapto-1,2,4-triazole (BIPMT), 4-salicylidene imino-3-propyl-5-mercapto-1,2,4-triazole (SIPMT) and 4-cinnamalidene imino-3-propyl-5-mercapto-1,2,4-triazole (CIPMT) have been synthesized and studied for their inhibiting

properties on mild steel in 20% formic and acetic acid. These inhibitors are selected on the basis of the following facts: (i) these inhibitors can be synthesized conveniently from relatively cheap raw materials, (ii) the presence of aromatic rings, the electronegative nitrogen, the easily polarisable sulphur and readily solubilizing hydroxy group in aqueous acid medium is likely to induce greater adsorption of these compounds on the metal surface leading to the effective inhibition.

Experimental Procedure

Materials

Colled rolled mild steel strips [composition: C = 0.14, Mn = 0.35, Si = 0.17, S = 0.025, P = 0.03 (wt. %) and the remainder Fe] were used. For weight loss measurements, strips having dimensions 2 × 2 × 0.25 cm were used, while mild steel specimens with an exposed area of 1 cm² were used for potentiodynamic polarization and impedance studies. 20% formic and 20% acetic acid solutions were used for all the experiments.

Double distilled water and analytical reagent-grade formic and acetic acid were used for preparing

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all experimental test solutions. Inhibitors were synthesized in the laboratory following the procedure reported elsewhere⁸. Synthesized compounds were characterized through their spectral data and their purity was confirmed by thin layer chromatography (TLC). Names and structural formulae of the inhibitors examined are given in Table 1.

Weight loss studies

Weight loss experiments were performed in accordance with ASTM methods^{9,10}. Tests were conducted in 20% formic acid and acetic acid solutions for 24 h at 30 °C with different concentrations of inhibitors, in 20% formic acid and acetic acid containing 300 ppm of each inhibitor at different immersion times, over the temperatures 30, 40 and 50 °C for 24 h, and in 10 to 30% formic and acetic acid containing 300 ppm of each inhibitor at 30 °C for 24 h. Specimens were taken in duplicate and all the values reported here are average.

Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out at temperature 26 ± 2 °C and a scan rate of 1 mVs^{-1} using an EG & G Princeton Applied Research

(PAR) model 173 potentiostat/galvanostat, a model 175 universal programmer, and a model RE 0089 X-Y recorder. A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) was used as reference electrode.

Electrochemical impedance studies

Electrochemical impedance studies were carried out at room temperature using an EG & G Potentiostat/Galvanostat (model 273A) and EG & G Lock-in-Amplifier (model 5301A) using an IBM computer. In this technique a three electrode assembly which consists of mild steel strip as working electrode, platinum as auxiliary electrode and calomel as reference electrode was used.

Results and Discussion

Weight loss studies

Values of the percentage of the inhibition efficiency (IE) and corrosion rate (CR) obtained by weight-loss measurements at different concentrations of these compounds in 20% formic acid and 20% acetic acid are given in Tables 2 and 3, respectively. It has been found that all these compounds inhibit

Table 1 — Name and molecular structures of the compounds used

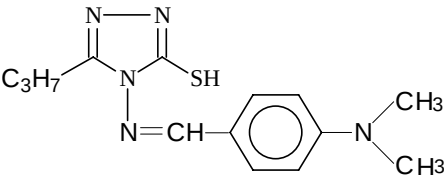
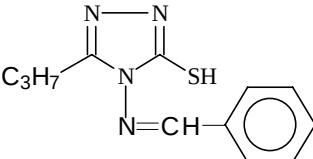
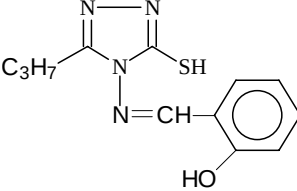
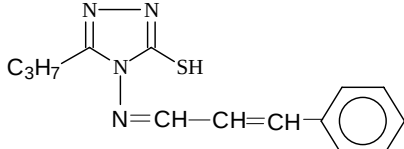
S.No.	Structure	Name and Abbreviation
1		4-(N,N-dimethylamino)benzylideneimino-3-propyl-5-mercapto-1,2,4-triazole (DIPMT)
2		4-benzylideneimino-3-propyl-5-mercapto-1,2,4-triazole (BIPMT)
3		4-salicylideneimino-3-propyl-5-mercapto-1,2,4-triazole (SIPMT)
4		4-cinnamalideneimino-3-propyl-5-mercapto-1,2,4-triazole (CIPMT)

Table 2—Corrosion parameters for mild steel in 20 % formic acid in the absence and presence of different concentrations of inhibitors at 30 °C for 24 h from weight loss measurements

Inhibitor concentration (ppm)	Weight loss (mg)	IE (%)	CR (mmpy)
Blank average			
DIPMT	311.06	-	14.45
50	18.1	94.18	0.84
100	15.6	94.98	0.72
150	11.5	96.30	0.53
200	9.9	96.82	0.46
250	7.5	97.59	0.35
300	7.2	97.69	0.33
350	7.1	97.72	0.33
BIPMT			
50	12.4	96.01	0.58
100	9.6	96.91	0.45
150	7.2	97.69	0.33
200	6.4	97.94	0.30
250	6.1	98.04	0.28
300	5.6	98.20	0.26
350	5.6	98.20	0.26
SIPMT			
50	8.9	97.14	0.41
100	7.9	97.46	0.37
150	6.4	97.94	0.30
200	5.6	98.20	0.26
250	5.0	98.40	0.23
300	3.4	98.91	0.16
350	3.4	98.91	0.16
CIPMT	7.2	97.69	0.33
50			
100	6.1	98.04	0.28
150	4.7	98.49	0.22
200	3.7	98.81	0.17
250	2.5	99.20	0.12
300	2.2	99.29	0.10
350	2.1	99.32	0.10

Table 3—Corrosion parameters for mild steel in 20 % acetic acid in the absence and presence of different concentrations of inhibitors at 30 °C for 24 h from weight loss measurements

Inhibitor concentration (ppm)	Weight loss (mg)	IE (%)	CR (mmpy)
Blank average			
DIPMT	151.87	-	7.05
50	15.6	89.72	0.72
100	13.9	90.85	0.65
150	11.8	92.23	0.55
200	10.9	92.82	0.51
250	9.1	94.01	0.42
300	8.8	94.21	0.41
350	8.8	94.21	0.41
BIPMT		92.03	0.56
50	12.1		
100	8.9	94.14	0.41
150	7.0	95.39	0.33
200	6.3	95.85	0.29
250	5.9	96.12	0.27
300	5.5	96.38	0.26
350	5.4	96.44	0.25
SIPMT	7.9	94.80	0.37
50			
100	6.6	95.65	0.31
150	5.7	96.25	0.26
200	5.3	96.51	0.25
250	4.8	96.84	0.22
300	3.1	97.96	0.14
350	3.1	97.96	0.14
CIPMT			
50	6.9	95.46	0.32
100	5.9	96.12	0.27
150	4.1	97.30	0.19
200	3.2	97.89	0.15
250	2.1	98.62	0.10
300	2.0	98.68	0.09
350	1.8	98.81	0.08

corrosion of mild steel in all cases. It has been observed that IE for all of these compounds increases with increasing concentration (Figs 1a and 2a). The maximum IE of each compound was achieved at 300 ppm and a further increase in concentration did not show any appreciable change in the performance of inhibitors.

The influence of temperature on IE is shown in Figs 1b and 2b. It is observed that with increase in temperature the IE initially increases slightly and then decreases on further increase in temperature. The decrease of IE with temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperatures^{11,12}. Figs 1c and 2c

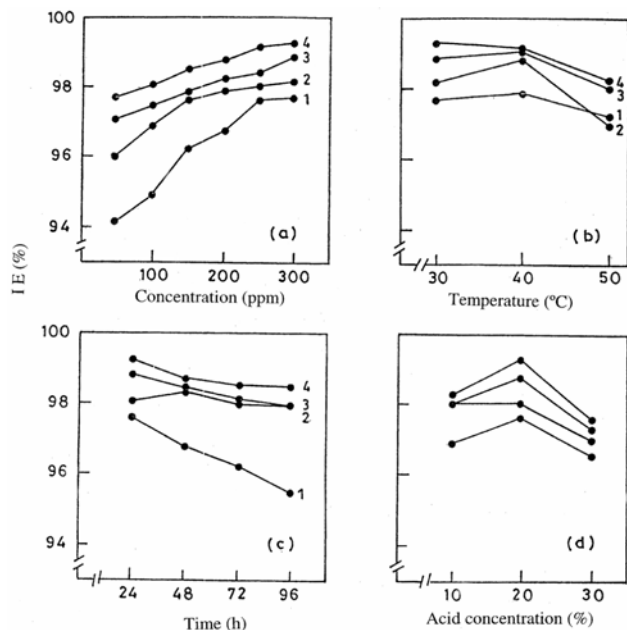


Fig. 1 — Variation of inhibition efficiency with (a) inhibitor concentration (b) solution temperature (c) immersion time (d) acid concentration, in 20% formic acid (1, DIPMT; 2, BIPMT; 3, SIPMT; 4, CIPMT)

show the variation of the IE at 300 ppm with immersion time. It is observed that the IE of all the compounds decreases with increasing immersion time from 24 to 96 h.

The effect of acid concentration of formic and acetic acid for 24 h of exposure at 300 ppm of all the compounds on IE is shown in Figs 1d and 2d. It is found that with increase in concentration of formic acid, the IE initially increases and attains a maximum value at 20% concentration of formic and acetic acid and decreases on further increase in the acid concentration to 30%.

The values of activation energy (E_a) were calculated using the Arrhenius equation^{13,14},

$$\ln(r_2/r_1) = -E_a \Delta T / (R \times T_2 \times T_1)$$

where r_1 and r_2 are the corrosion rates at temperatures T_1 and T_2 , respectively, and $\Delta T = T_1 - T_2$. The free energy of adsorption (ΔG_{ads}) at different temperatures were calculated using following equation¹⁵,

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

Where $K = \theta/C$ ($1-\theta$), θ is the degree of coverage on the metal surface given by the ratio¹¹ IE/100, C is

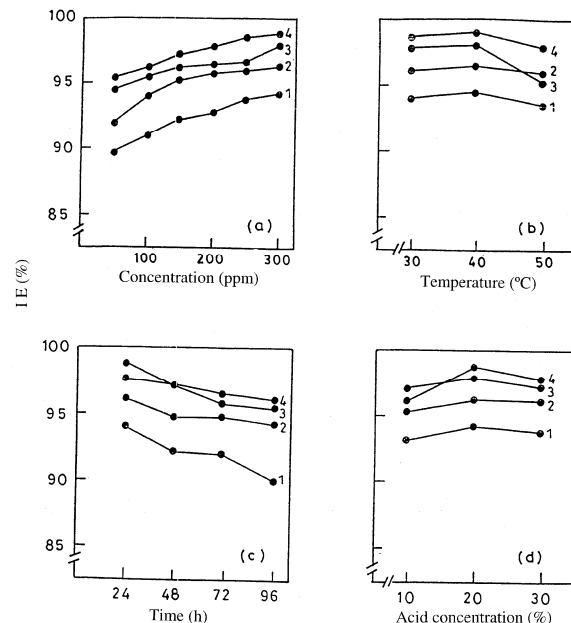


Fig. 2 — Variation of inhibition efficiency with (a) inhibitor concentration (b) solution temperature (c) immersion time (d) acid concentration, in 20% acetic acid (1, DIPMT; 2, BIPMT; 3, SIPMT; 4, CIPMT)

Table 4 — Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 20% formic acid and 20% acetic acid in the absence and presence of various inhibitors with optimum concentration

System	E_a (K. cal/mole)	$-\Delta G_{ads}$ (K. cal/mole)		
		30 °C	40 °C	50 °C
20% formic acid	12.05	-	-	-
DIPMT	14.48	8.87	9.22	9.31
BIPMT	17.58	8.88	9.55	9.07
SIPMT	18.17	9.20	9.61	9.43
CIPMT	21.37	9.52	9.67	9.52
20% Acetic acid	6.11	-	-	-
DIPMT	7.54	8.24	8.55	8.71
BIPMT	6.83	8.45	8.75	8.97
SIPMT	14.11	8.82	9.14	8.94
CIPMT	10.87	9.14	9.44	9.43

the concentration of inhibitor in (mol/L) and K is the equilibrium constant. The values of E_a and ΔG_{ads} are given in Table 4. The low and negative values of free energy of adsorption indicate spontaneous adsorption of inhibitors on the mild steel surface. The negative values of ΔG_{ads} also suggest the strong interaction of the inhibitor molecules with the mild steel surface^{16,17}. It was found that E_a was higher in the presence

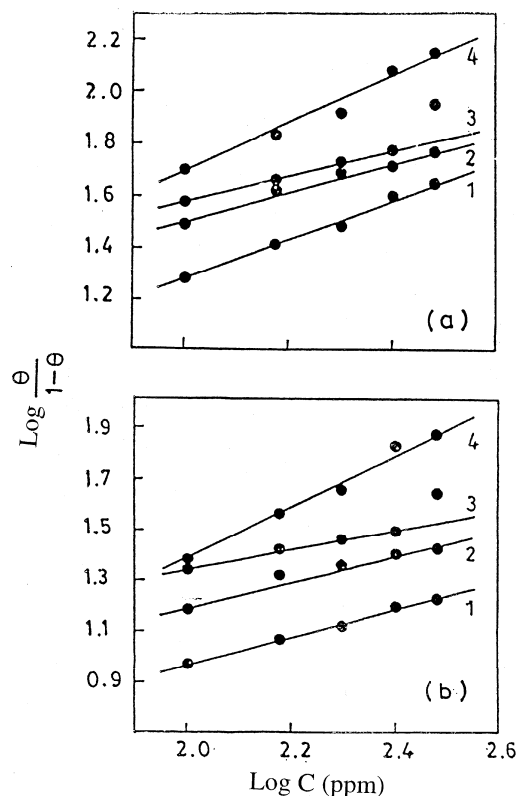


Fig. 3 — Langmuir adsorption isotherm plots for the adsorption of various inhibitors in (a) 20% formic acid and (b) 20% acetic acid, on the surface of mild steel (1, DIPMT; 2, BIPMT; 3, SIPMT; 4, CIPMT)

Table 5 — Electrochemical polarization parameters for the corrosion of mild steel in 20% formic and acetic acid in the absence and presence of various inhibitors with optimum concentration at $26 \pm 2^\circ\text{C}$

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
20% Formic acid	-498	0.25	-
DIPMT	-495	0.015	94.0
BIPMT	-490	0.006	97.6
SIPMT	-485	0.005	98.0
CIPMT	-485	0.003	98.8
20% Acetic acid	-495	0.14	-
DIPMT	-490	0.06	57.14
BIPMT	-490	0.035	75.00
SIPMT	-492	0.030	78.57
CIPMT	-486	0.027	80.71

of inhibitors indicating that these inhibitors are more effective at lower temperature¹².

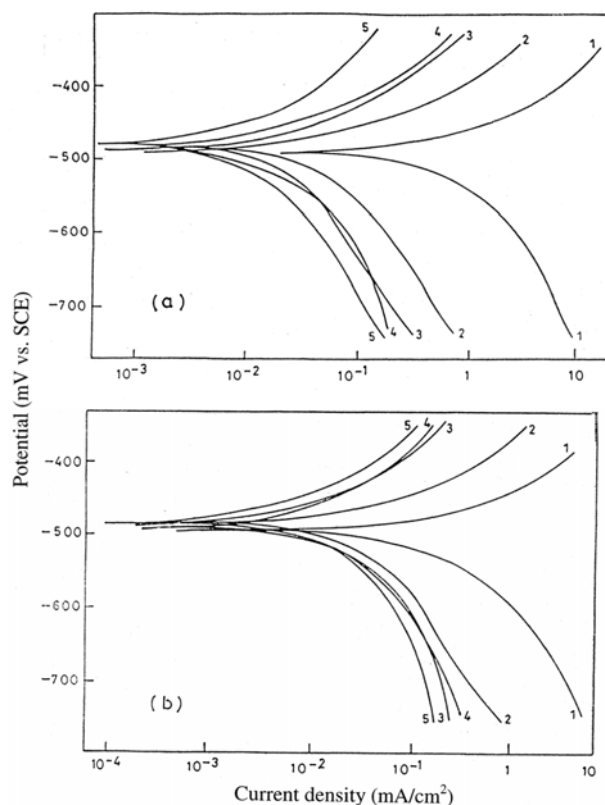


Fig. 4 — Typical potentiodynamic curves for mild steel in (a) 20% formic acid and (b) 20% acetic acid in the presence and absence of inhibitor containing 300 ppm concentration (1, Blank; 2, DIPMT; 3, BIPMT; 4, SIPMT; 5, CIPMT)

Adsorption isotherm

The surface coverage values (θ) were evaluated using corrosion rate values (CR) obtained from weight loss method. θ values for different concentrations of inhibitors were tested graphically by fitting to various isotherms. A plot of $\log \theta/(1-\theta)$ against $\log C$ for different concentrations shows a straight line indicating that adsorption from both acids follows the Langmuir adsorption isotherm¹⁸ (Figs 3a and b).

Potentiodynamic polarization studies

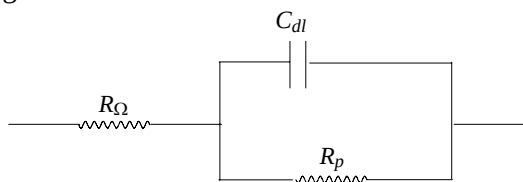
The d. c. polarization behaviour of mild steel in 20% formic acid and 20 % acetic acid in the absence and presence of 300 ppm inhibitor concentration is shown in Figs 4a and 4b. Electrochemical parameters such as corrosion current density (I_{corr}) and corrosion potential (E_{corr}) calculated from Tafel plots are given in Table 5. Potentiodynamic polarization experiments were carried out to know the electrochemical nature of the inhibitors. These studies show that the inhibitors are of three types i. e. anodic, cathodic and mixed type.

The maximum decrease in I_{corr} was observed at 300 ppm concentration for each inhibitor. Maximum decrease in I_{corr} was observed for CIPMT indicating that CIPMT is most effective corrosion inhibitor. Similar trend was observed in weight-loss method. E_{corr} values do not show any significant change in the presence of all the compounds suggesting that all these compounds are mixed type inhibitors.

The inhibition of corrosion of mild steel in the acids by the anils can be explained on the basis of molecular adsorption. Among the compounds investigated in the present study CIPMT has been found to give the best inhibitor performance. This can be explained on the basis of presence of an additional π -bond between the carbon atoms ($-\text{C}=\text{C}-$) in conjugation with azomethine ($-\text{N}=\text{C}=\text{}$) group. This leads to greater surface coverage, thereby giving higher inhibition efficiency. The reason for this is the least steric hindrance due to planarity of this additive (CIPMT). Others will face greater steric hindrance. BIPMT will also have very less steric hindrance due to planer nature but higher conjugation in CIPMT makes it a better adsorbing inhibitor.

Electrochemical impedance studies

The electrical equivalent circuit for the system is given below—



R_{Ω} = uncompensated resistance,

R_p = polarization resistance and

C_{dl} = double layer capacitance

Impedance diagrams obtained for the frequency range of 5 Hz-100 kHz at E_{corr} for mild steel in 20% formic acid are shown in Figs 5a and 5b. The impedance diagrams are not perfect semicircles, and this difference has been attributed to frequency dispersion¹⁹. The values of charge-transfer resistance (R_t), and double-layer capacitance (C_{dl}) can be evaluated using the Nyquist and Bode plots²⁰. The IE was calculated using the Eq.,

$$IE = \frac{(1/R_{t0}) - (1/R_{ti})}{(1/R_{t0})} \times 100$$

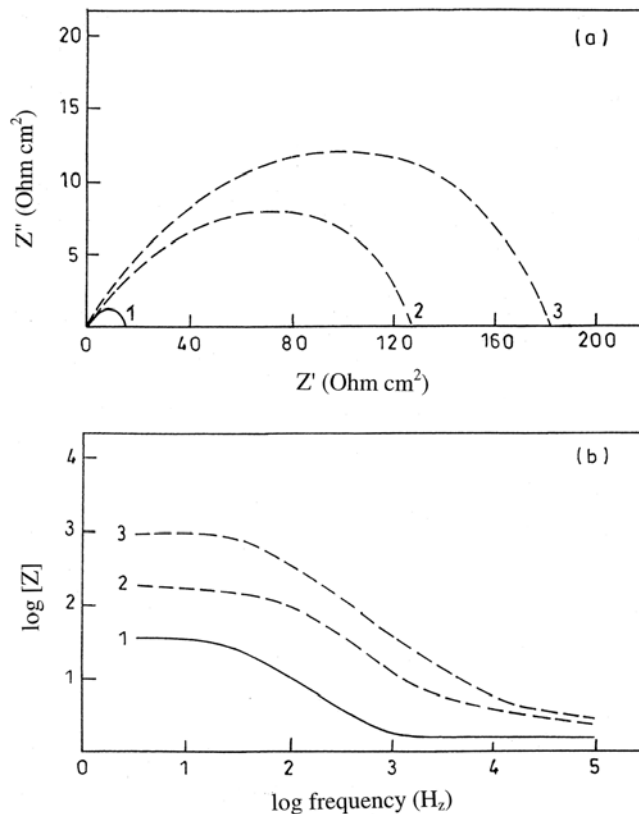


Fig. 5 — (a) Nyquist plot and (b) Bode plot for mild steel in the absence and presence of various concentrations of CIPMT 1. Blank; 2. 100 ppm; 3. 300 ppm

Table 6 — Electrochemical impedance parameters for mild steel in 20% formic acid containing different concentration of CIPMT

Concentration (ppm)	R_t ($\Omega\text{-cm}^2$)	C_{dl} (m f cm^{-2})	IE (%)
20% Formic acid CIPMT	15.56	1513.57	-
100	192.51	79.43	91.75
300	240.00	25.12	93.78

where R_{t0} and R_{ti} are the charge transfer resistance without and with inhibitor, respectively, and are given in Table 6. Values of R_t increase with increase in inhibitor concentration (CIPMT) and this in turn leads to an increase in the IE. The addition of CIPMT to 20% formic acid lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor²¹.

Conclusions

From the results of the studies performed the following can be concluded,

- (i) All investigated inhibitors namely DIPMT, BIPMT, SIPMT and CIPMT are effective inhibitors for corrosion of mild steel in 20% formic acid and 20% acetic acid solutions.
- (ii) Inhibition of corrosion of mild steel surface in acid solutions is by a mechanism of adsorption of these compounds on the metal surface.
- (iii) All the compounds behave as mixed type inhibitors.
- (iv) Their adsorption on the mild steel surface in 20% formic acid and 20% acetic acid solutions obeys Langmuir adsorption.

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