Inhibitive Effect of FA Derivatives on Mild Steel Corrosion in the Presence of Formic Acid

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ABSTRACT: The influence of selected long-chain FA hydrazides and thiosemicarbazides on the corrosion inhibition of mild steel in the presence of 20% formic acid was studied. The inhibition efficiency of these compounds varied with concentration, temperature, and immersion time. All the FA derivatives in the formic acid solution followed Temkin's adsorption isotherm. The activation energies and free energies of adsorption of all the hydrazides and thiosemicarbazides also were calculated. Potentiodynamic polarization studies indicated that all the tested compounds were of mixed type. Electrochemical impedance spectroscopy was also used to investigate the mechanism of corrosion inhibition.

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KEY WORDS: Corrosion inhibitors, electrochemical impedance spectroscopy, fatty acid hydrazides, fatty acid thiosemicarbazides, mild steel, potentiodynamic polarization, Temkin's adsorption isotherm.

The use of corrosion inhibitors has increased considerably in recent years as awareness of corrosion has expanded. Organic compounds are widely used in various industries as corrosion inhibitors in acidic environments (1–3). The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. It has been observed that adsorption depends mainly on the presence of π-electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel.

Most of the research on the corrosion of metals by organic compounds has been done in mineral acids, but little has been reported in organic acids (4–6). Mild steel is used in fabrication of containers such as reaction vessels and storage tanks, for industries that either manufacture or use formic acid as reactant. A survey of the literature reveals that corrosion inhibitors derived from FA potentially constitute an important class of corrosion inhibitors. Some ethoxylated FA derivatives are effective inhibitors of corrosion of mild steel in acidic solutions (7). Badran *et al.* (8,9) reported more than 90% inhibition efficiency (%IE) for a few modified epoxides of linseed oil and oleic acid in 0.05 N HCl. Quraishi *et al.* have synthesized and studied various FA derivatives as corrosion inhibitors (10–13). Here the corrosion-inhibiting properties of long-chain FA hydrazides and thiosemicarbazides on mild steel in formic acid are described.

MATERIALS AND METHODS

Weight loss measurements. Corrosion experiments were carried out using cold rolled mild steel in 20% formic acid. The

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mild steel sample ($2.0 \times 2.0 \times 0.25$ cm) had the following percentage composition: C, 0.14; Mn, 0.35; Si, 0.17; S, 0.025; P, 0.03; the remainder Fe. The experiments were performed as per ASTM standard G1-72 (14).

Potentiodynamic polarization studies. For potentiodynamic polarization studies, mild steel strips of the same composition as that used in the weight loss experiments, embedded in the affixing material araldite (Aldrich Chemical Co., St. Louis, MO) with an exposed area of 1.0 cm², were used, and the experiments were carried out at a temperature of $26 \pm 2°C$, as per ASTM standards G3-74 and G5-87 (14). Potentiodynamic polarization studies were carried out using a potentiostat/galvanostat (model 173; EG&G, Gaithersburg, MD), universal programmer (model 175; EG&G), and X-Y recorder (model RE 0089; EG&G). A platinum foil was used as the auxiliary electrode, and a saturated calomel electrode was used as reference.

Electrochemical impedance studies. Impedance measurements were performed for the mild steel in 20% formic acid in the absence and presence of 100 and 500 ppm of 1-decene-4-phenyl-thiosemicarbazide (DPTS) at E_{corr} with the ac voltage amplitude of +5 mV in the frequency range 5 Hz–100 kHz. A time interval of a few minutes was given for the open circuit potential (o.c.p.) to reach a steady value. All the measurements were carried out at $26 \pm 2°C$ using potentiostat/galvanostat PARC (model 273A; EG&G), a lock-in amplifier (model 5301A; EG&G).

Analyzed reagent grade formic acid (Merck India Ltd., Bombay, India) and double-distilled water were used for preparing the solutions of 20% formic acid for all the experiments. The inhibitors were synthesized in our laboratory following procedures reported elsewhere (15,16), and all the compounds were characterized through their spectral data. Their purity was confirmed by TLC. Names and molecular structures are presented in Scheme 1.
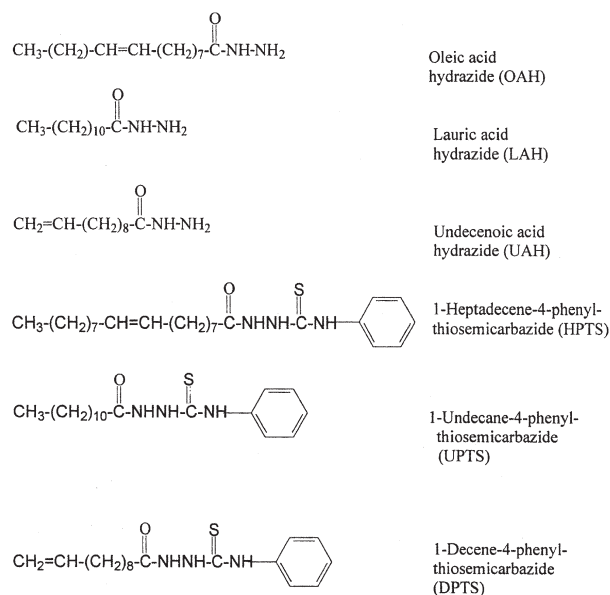
RESULTS AND DISCUSSION

Weight loss measurements. The values for %IE and corrosion rate, obtained by the weight loss method at different concentrations of hydrazides and thiosemicarbazides in 20% formic acid at 30°C, are summarized in Table 1. The %IE and surface coverage (θ) were calculated using the following equations (11):

$$\%\text{IE} = [(W^0 - W)/W^0] \times 100 \qquad [1]$$

$$\theta = [(W^0 - W)/W^0] \qquad [2]$$

where W^0 and W are the corrosion rate in the absence and presence of inhibitors, respectively. Table 1 and Figures 1A and 1A′

CH$_3$-(CH$_2$)-CH=CH-(CH$_2$)$_7$-C-NH-NH$_2$ Oleic acid hydrazide (OAH)

CH$_3$-(CH$_2$)$_{10}$-C-NH-NH$_2$ Lauric acid hydrazide (LAH)

CH$_2$=CH-(CH$_2$)$_8$-C-NH-NH$_2$ Undecenoic acid hydrazide (UAH)

CH$_3$-(CH$_2$)$_7$-CH=CH-(CH$_2$)$_7$-C-NHNH-C-NH⟨phenyl⟩   1-Heptadecene-4-phenyl-thiosemicarbazide (HPTS)

CH$_3$-(CH$_2$)$_{10}$-C-NHNH-C-NH⟨phenyl⟩   1-Undecane-4-phenyl-thiosemicarbazide (UPTS)

CH$_2$=CH-(CH$_2$)$_8$-C-NHNH-C-NH⟨phenyl⟩   1-Decene-4-phenyl-thiosemicarbazide (DPTS)

SCHEME 1

indicate that IE increases with increasing inhibitor concentration. Maximal IE was obtained at 500 ppm. Among the FA derivatives tested as inhibitors for corrosion of mild steel in 20% formic acid, the order of %IE of hydrazides at maximal concentration (i.e., 500 ppm) was undecenoic acid hydrazide > lauric acid hydrazide > oleic acid hydrazide. For thiosemicarbazides at maximal concentration of 500 ppm, the order was DPTS > 1-undecane-4-phenyl-thiosemicarbazide > 1-heptadecene-4-phenyl-thiosemicarbazide. Among the FA derivatives, undecenoic acid (C$_{11}$), bearing a (–C=C–) double bond at the terminal position, exhibited the best performance as a corrosion inhibitor. The high IE exhibited by these compounds may be attributed to their adsorption on the metal surface through polar groups as well as through π-electrons. The greater coverage of the metal surface by these compounds thereby leads to higher %IE. The derivatives of oleic acid showed lower %IE than lauric acid derivatives because the compounds with chains greater than 11 carbons in length have less efficiency (17).

Corrosion inhibition tests were carried out on mild steel by varying acid concentrations, immersion times, and temperatures in the presence of 500 ppm inhibitor. Figures 1B and 1B′ indicate that the maximal %IE for all compounds occurred at 20% formic acid and that %IE decreased as the acid concentration increased beyond 20% to increased aggressiveness of the acid (18). The effect of immersion time on %IE of the FA derivatives (Fig. 1C) was to decrease %IE with an increase in test duration. This effect may be attributed to factors such as increases in cathodic or hydrogen evolution kinetics or to an increase in a ferrous ion concentration (19). The effect of temperature on the %IE of the FA derivatives is shown in Figures 1D and 1D′. %IE gradually decreased with an increase in temperature from 30 to 50°C for the hydrazides, which may be due to the desorption of inhibitor from the metal surface; for thiosemicarbazides %IE did not change significantly with an increase in temperature, indicating that the inhibitive film

formed on the metal surface is protective in nature at higher temperature.

Activation energy (E_a) values were calculated using the Arrhenius equation (20,21):

$$\ln (r_2/r_1) = -E_a\, \Delta T/(R \times T_2 \times T_1) \qquad [3]$$

where r_1 and r_2 are corrosion rates at temperatures T_1 and T_2, respectively, and ΔT is the difference in temperature ($T_2 - T_1$). The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation:

TABLE 1
Corrosion Parameter[a] for Mild Steel in 20% Formic Acid in the Absence and Presence of Five Concentrations of Six Inhibitors

Concentration (ppm)	Weight loss (g)	%IE[b]	Corrosion rate (mmpy)
20% Formic acid	0.3081	—	14.31
Oleic acid hydrazide (OAH)			
25	0.0790	74.31	3.67
50	0.0725	76.48	3.37
100	0.0495	83.92	2.30
300	0.0213	93.05	0.99
500	0.0163	94.76	0.75
600	0.0160	94.82	0.74
Lauric acid hydrazide (LAH)			
25	0.0615	80.01	2.86
50	0.0529	82.87	2.45
100	0.0325	89.46	1.51
300	0.0183	94.06	0.85
500	0.0085	97.27	0.39
600	0.0082	97.34	0.34
Undecenoic acid hydrazide (UAH)			
25	0.0539	82.52	2.50
50	0.0239	92.24	1.11
100	0.0164	94.68	0.76
300	0.0069	97.76	0.37
500	0.0058	98.11	0.27
600	0.0054	98.25	0.25
1-Heptadecene-4-phenyl-thiosemicarbazide (HPTS)			
25	0.0287	90.68	1.33
50	0.0179	92.66	1.05
100	0.0122	94.33	0.81
300	0.0096	96.85	0.45
500	0.0060	98.01	0.28
600	0.0058	98.11	0.27
1-Undecane-4-phenyl-thiosemicarbazide (UPTS)			
25	0.0138	96.92	0.44
50	0.0082	97.34	0.38
100	0.0057	97.97	0.29
300	0.0047	98.46	0.22
500	0.0046	98.53	0.21
600	0.0043	96.60	0.26
1-Decene-4-phenyl-thiosemicarbazide (DPTS)			
25	0.0068	97.76	0.32
50	0.0060	98.01	0.28
100	0.0056	98.18	0.26
300	0.0038	98.74	0.18
500	0.0035	98.88	0.16
600	0.0032	98.95	0.15

[a]Determined from weight loss measurements.
[b]Inhibition efficiency, determined as %IE = $[(W^0 - W)/W^0] \times 100$, where W^0 and W are the corrosion rate in the absence and presence of inhibitors. Abbreviation: mmpy, millimeters per year.
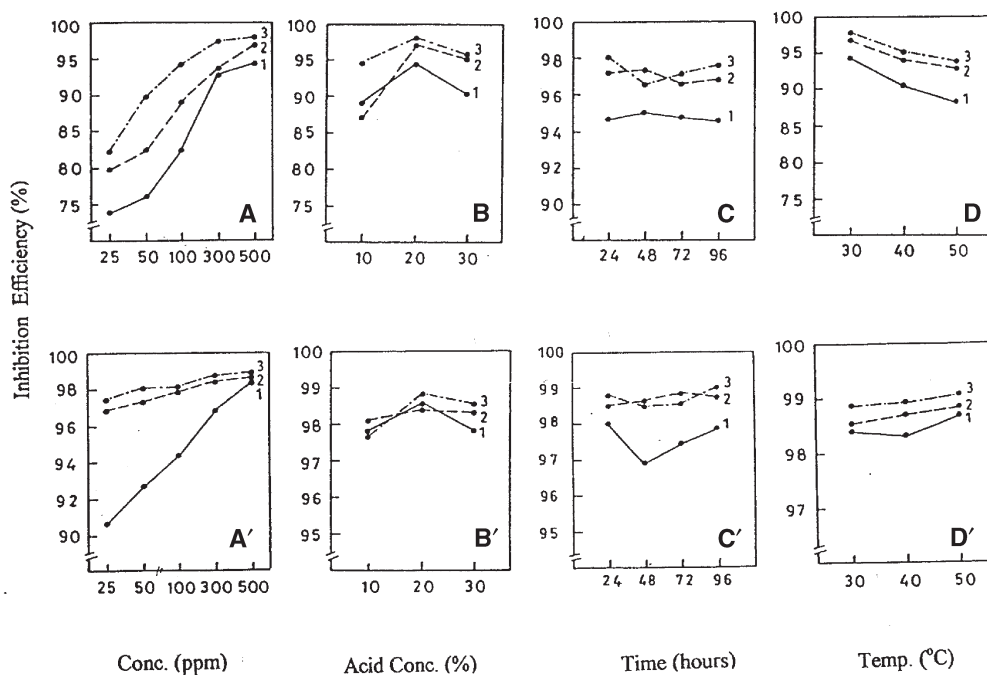
FIG. 1. Variation in inhibition efficiency of FA hydrazides with (A) concentration of inhibitors, (B) acid concentration, (C) immersion time, and (D) temperature [1: oleic acid hydrazide (OAH); 2: lauric acid hydrazide (LAH); 3: undecenoic acid hydrazide (UAH)] and of FA thiosemicarbazides with (A') concentration of inhibitors, (B') acid concentration, (C') immersion time, and (D') temperature [1: 1-heptadecene-4-phenyl-thiosemicarbazide (HPTS); 2: 1-undecane-4-phenyl-thiosemicarbazide (UPTS); 3: 1-decene-4-phenyl-thiosemicarbazide (DPTS)].

$$\Delta G_{ads} = - RT \ln (55.5 \; K) \qquad [4]$$

and K is given by

$$K = \theta/C \, (1 - \theta) \qquad [5]$$

where θ is the degree of coverage on the metal surface given by the ratio IE/100 (22,23), C is the concentration of inhibitor in moles/liter, and K is the equilibrium constant. The calculated values of E_a and ΔG_{ads} are given in Table 2. The values of $-\Delta G_{ads}$ for all the compounds at 30, 40, and 50°C were ≤40 kJ/mol except for HPTS, UPTS, and DPTS at 50°C, indicating that the inhibitor molecules are physically adsorbed on the mild steel surface (24). The low and negative value of ΔG_{ads} also suggests the strong interaction of the inhibitor molecules on the mild steel surface. The E_a values of all the inhibited systems were higher in the case of FA derivatives of hydrazides and lower in case of thiosemicarbazides than that of uninhibited systems. Putilova *et al.* (25) indicated that inhibitors having higher E_s values than that of uninhibited systems are effective at room temperature and less effective at higher temperature and vice versa.

To understand the mechanism of corrosion inhibition, the data were tested graphically by fitting them to various isotherms. The degree of surface coverage (θ) for different inhibitor concentrations was evaluated from weight loss values. A straight line was obtained by plotting log ($\theta/1 - \theta$) vs. log C (Fig. 2), suggesting that the adsorption of hydrazides and thiosemicarbazides to the metal surface occurs according to Langmuir's adsorption isotherm.

Potentiodynamic polarization studies. Corrosion parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), and %IE obtained from potentiodynamic polarization curves of mild steel in 20% formic acid at 26 ± 2°C in the absence and the presence of inhibitors are given in Table 3. The I_{corr} value decreased significantly, and b_a (anodic Tafel slope) and b_c (cathodic Tafel slope) showed no significant change

TABLE 2
Activation Energy[a] (E_a) and Free Energy of Adsorption[a] (ΔG_{ads}) for Mild Steel in 20% Formic Acid in the Absence and Presence of Inhibitors

Inhibitor concentration[b] (ppm)	E_a (kJ·mol⁻¹)	$-\Delta G_{ads}$ (kJ·mol⁻¹)		
		30°C	40°C	50°C
20% Formic acid	51.28	—	—	—
OAH (500)	83.13	32.62	32.92	33.31
LAH (500)	88.11	34.35	33.44	34.02
UAH (500)	97.05	35.10	34.06	34.23
HPTS (500)	34.51	36.92	37.69	40.46
UPTS (500)	42.47	37.14	38.74	40.21
DPTS (500)	44.32	37.75	39.12	40.75

[a]Calculated from the Arrhenius equation, $\ln (r_2/r_1) = -E_a \, \Delta T/(R \times T_2 \times T_1)$, where r_1 and r_2 are corrosion rates at temperatures T_1 and T_2, respectively, and ΔT is the difference in temperature ($T_2 - T_1$). Free energy of adsorption is determined as $\Delta G_{ads} = - RT \ln (55.5 \, K)$ and $K = \theta/C \, (1 - \theta)$, where θ is the degree of coverage on the metal surface, C is the concentration of inhibitor in moles/liter, and K is the equilibrium constant.
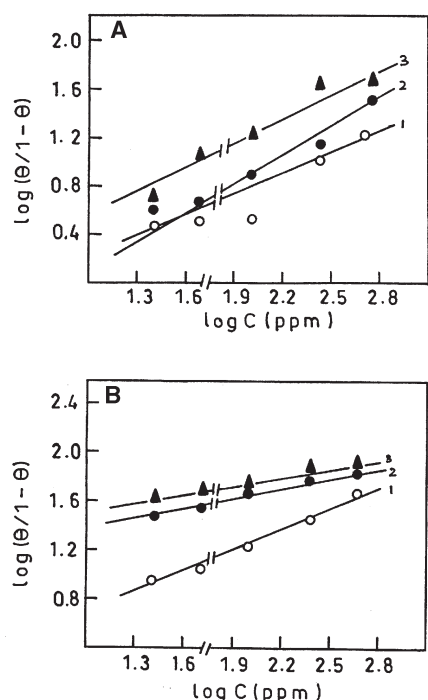[b]For other abbreviations see Table 1.

FIG. 2. Temkin's adsorption isotherm plots for adsorption of inhibitors in 20% formic acid on a mild steel surface: (A) FA hydrazides (1: OAH; 2: LAH; 3: UAH); (B) FA thiosemicarbazides (1: HPTS; 2: UPTS; 3: DPTS). θ, degree of coverage; for abbreviations see Figure 1.

(Fig. 3), suggesting that they are mixed-type inhibitors, i.e., they inhibit corrosion by slowing down both anodic and cathodic corrosion processes.

Electrochemical impedance studies. Impedance diagrams obtained for the frequency range 5 Hz–100 kHz at E_{corr} for mild steel in 20% formic acid are shown in Figure 4. The impedance diagrams are not perfect semicircles, and this difference has been attributed to frequency dispersion (26). The values of R_t and C_{dl} were obtained using the Nyquist and Bode plots, respectively (27). The %IE was calculated using the equation

$$\%IE = \frac{(1/R_{t0}) - (1/R_{ti})}{(1/R_{t0})} \times 100 \qquad [6]$$

where R_{t0} and R_{ti} are charge transfer resistance without and with inhibitor, respectively. The values R_t, C_{dl}, and %IE are given in Table 4. Values of R_t increase with an increase in inhibitor concentration (DPTS), and this in turn leads to an increase in the IE. The addition of DPTS to 20% formic acid lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor.

Mechanism of corrosion inhibition. Inhibition of corrosion of mild steel in acidic solution in the presence of FA hydrazides and thiosemicarbazides can be explained on the basis of molecular adsorption through lone pairs of electrons of nitrogen, sulfur, and oxygen and through π-electrons present in the molecule. The difference in IE may be attributed to the presence of the $CS-NHC_6H_5$ group in the thiosemicarbazide molecules, which facilitates greater adsorption of thiosemicarbazides

TABLE 3
Electrochemical Polarization Parameters for the Corrosion of Mild Steel in 20% Formic Acid Containing Maximal Concentrations of Various Inhibitors at 26 ± 2°C

Concentration[a]	E_{corr}[b] (mV vs. SCE)	b_a[c] (mV·decade^{-1})	b_c[d] (mV·decade^{-1})	I_{corr} (mA·cm^{-2})	IE (%)
20% Formic acid	−416	68	104	0.350	
OAH	−390	52	94	0.085	75.71
LAH	−396	56	98	0.075	78.52
UAH	−404	44	110	0.050	85.21
HPTS	-402	54	120	0.076	78.28
UPTS	−422	50	100	0.039	88.85
DPTS	−424	44	80	0.036	89.71

[a]Concentration: 500 ppm of each compound except for formic acid.
[b]E_{corr}, corrosion potential; SCE, saturated calomel electrode.
[c]b_a, anodic Tafel slope.
[d]b_c, cathodic Tafel slope.
[e]I_{corr}, corrosion current density. For other abbreviations see Table 1.

TABLE 4
Electochemical Impedance Parameters for the Corrosion of Mild Steel in 20% Formic Acid Containing Different Concentrations of DPTS at 26 ± 2°C

Concentration	R_t[a] (Ω m^2)	C_{dl}[b] (µF·cm^{-2})	IE (%)
20% Formic acid	75.00	1862.09	—
DPTS			
100 ppm	312.50	508.11	75.38
500 ppm	1231.48	197.24	93.76

[a]R_t, charge transfer resistance.
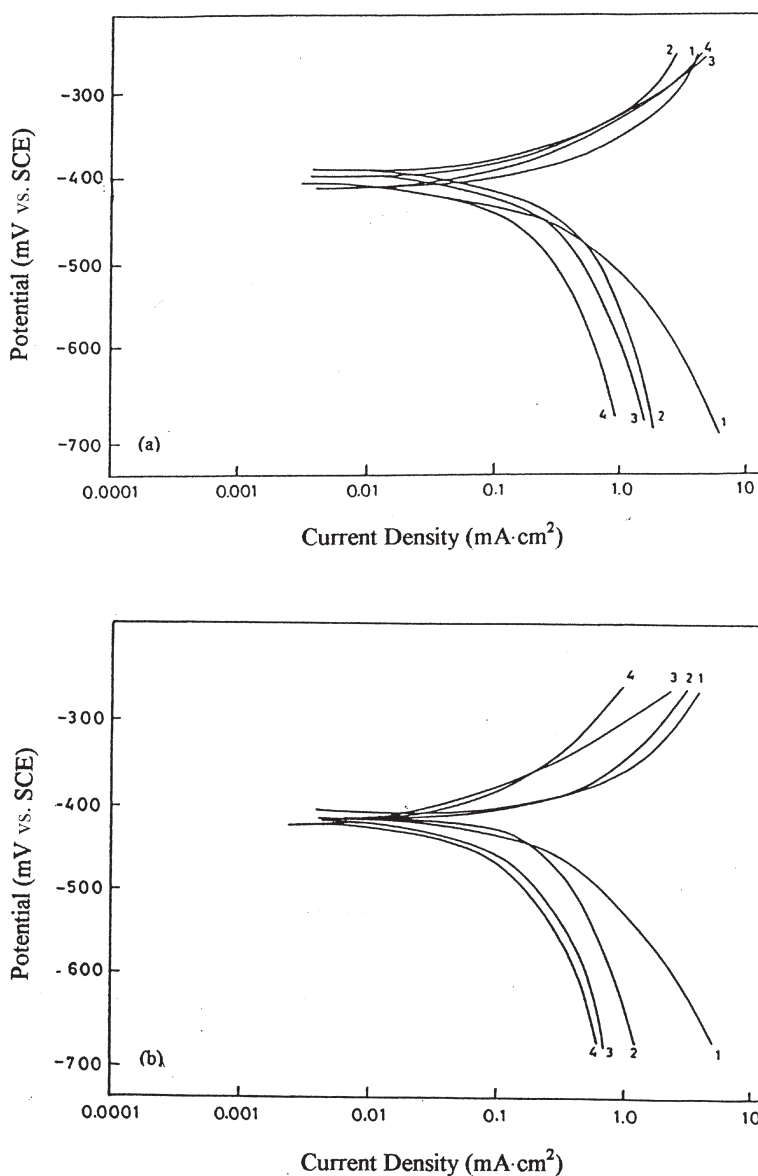[b]C_{dl} Double-layer capacitance. For other abbreviations see Tables 1 and 3.

FIG. 3. Potentiodynamic polarization curves of inhibitors at 500 ppm concentration of (A) FA hydrazides (1: blank; 2: OAH; 3: LAH; 4: UAH); (b) FA thiosemicarbazides (1: blank; 2: HPTS; 3: UPTS; 4: DPTS), SCE, saturated calomel electrode; for other abbreviations, see Figure 1.

through polarizable sulfur and phenyl groups on the metal surface, thereby giving higher IE than hydrazides.

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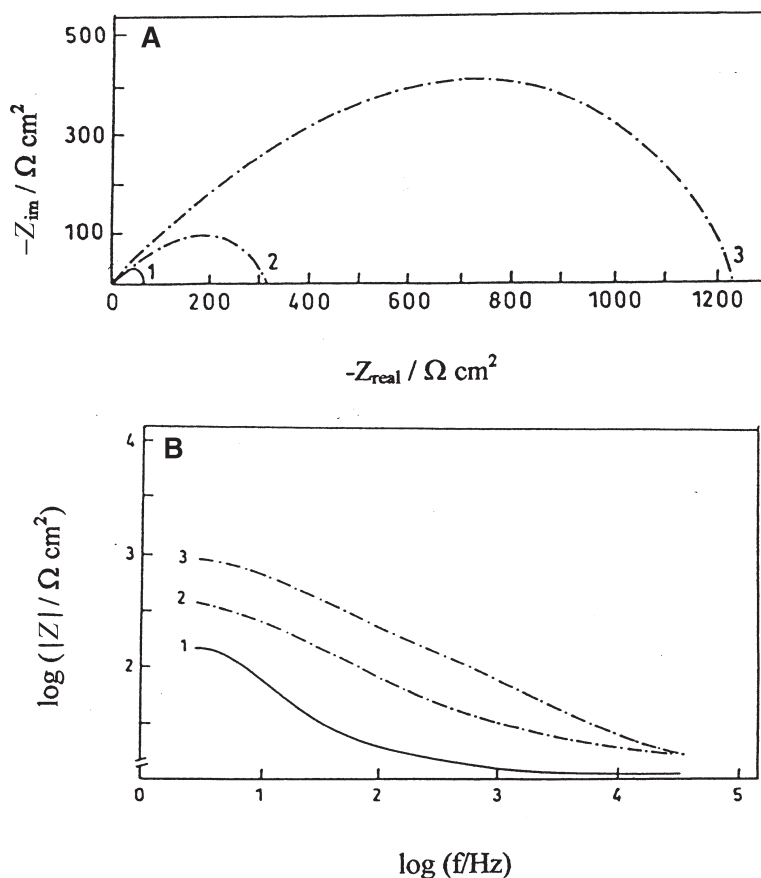
FIG. 4. Electrochemical impedance plots: (A) Nyquist plot and (B) Bode plot for mild steel in the absence and presence of various concentrations of DPTS (1: blank; 2: 100 ppm; 3: 500 ppm). f = frequency in Hz; for other abbreviation see Figure 1.

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