Fatty Acid Derivatives as Corrosion Inhibitors for Mild Steel and Oil-Well Tubular Steel in 15% Boiling Hydrochloric Acid

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ABSTRACT: Selected hydrazides and thiosemicarbazides of fatty acids with 11, 12, and 18 carbon atoms were synthesized and evaluated as corrosion inhibitors on mild steel and oil-well steel (N-80) in boiling 15% hydrochloric acid solution, by weight loss method. Potentiodynamic polarization studies carried out on mild steel and N-80 steel at room temperature showed that all the tested compounds are of mixed type. Adsorption studies showed that all the investigated compounds followed Temkin's adsorption isotherm.

Paper no. J9195 in *JAOCS 77*, 265–268 (March 2000).

KEY WORDS: Corrosion inhibitors, fatty acid hydrazides, fatty acid thiosemicarbazides, mild steel, oil well tubular steel, potentiodynamic polarization, Temkin's adsorption isotherm.

Corrosion inhibitors are widely used over a range of corrosive environments. A variety of organic compounds are effective corrosion inhibitors under acid conditions including acetylenic alcohols, aromatic α-, β-unsaturated aldehydes, α-alkenyl phenones, nitrogen- and sulfur-containing heterocyclic compounds, quaternary ammonium salts, and condensation products of carbonyls and amines (1–4).

Among these compounds, acetylenic alcohols are widely used as acid inhibitors in industry because of their commercial viability and effectiveness. However, these inhibitors produce toxic vapors under acidic conditions, and are effective only at high concentration. Because of this, a need exists for development of new acidizing inhibitors.

Continuing our work on development of acid inhibitors (5–8), we have synthesized a few hydrazides and thiosemicarbazides of long-chain fatty acids with a view to evaluate their corrosion inhibition properties on mild steel and N-80 steel in 15% boiling hydrochloric acid (HCl). These fatty acid derivatives were chosen because they are more environmentally benign, less toxic, and more cost effective than acetylenic alcohols.

MATERIAL AND METHODS

Weight loss measurements. Corrosion experiments were carried out using N-80 steel (2.0 × 1.0 × 0.7 cm) and cold rolled mild steel in 15% HCl. The mild steel sample (2.0 × 2.0 × 0.6 cm) had the following percent composition: C, 0.14; Mn, 0.35; Si, 0.17; S, 0.025; P, 0.03; the remainder, Fe. The experiments were performed in a 500-mL three-neck round-bottomed flask using a condenser at 105 ± 2°C as per ASTM, G 1-72 (9).

Electrochemical studies. For potentiodynamic polarization studies, mild steel strips and N-80 steel of the same composition embedded in Araldite (Aldrich Chemical Co., St. Louis, MO) (a fixing material) with an exposed area of 1.0 cm^2 were used and the experiments were carried out at constant temperature of 28 ± 2°C as per ASTM G 3-74 and G 5-87 (9). Potentiodynamic polarization studies were carried out using a potentiostat/galvanostat (model 173; EG&G, Gaithersburg, MD), a universal programmer (model 175; EG&G), and X–Y recorder (model RE 0089; EG&G). A platinum foil was used as auxiliary electrode, and a saturated calomel electrode served as reference. Analyzed reagent-grade HCl (Merck India Ltd., Bombay, India) and double-distilled water were used for preparing test solutions of 15% HCl for all experiments. The inhibitors were synthesized in our laboratory following procedures reported elsewhere (10,11), and all compounds were characterized through their spectral data. Their purity was confirmed by thin-layer chromatography. Names and molecular structures are presented in Scheme 1.

RESULTS AND DISCUSSION

Weight loss measurements. The values of percentage inhibition efficiency (%I.E.) and corrosion rate obtained by the weight loss method at different concentrations of hydrazides and thiosemicarbazides in 15% HCl under boiling condition are summarized in Table 1. The %I.E. and surface coverage (θ) were calculated using the following equations (12):

$$\%\text{I.E.} = [(W^o - W)/W^o] \times 100 \qquad [1]$$

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

where W^o and W are the weight loss in the absence and presence of inhibitors, respectively. In Table 1, %I.E. increases

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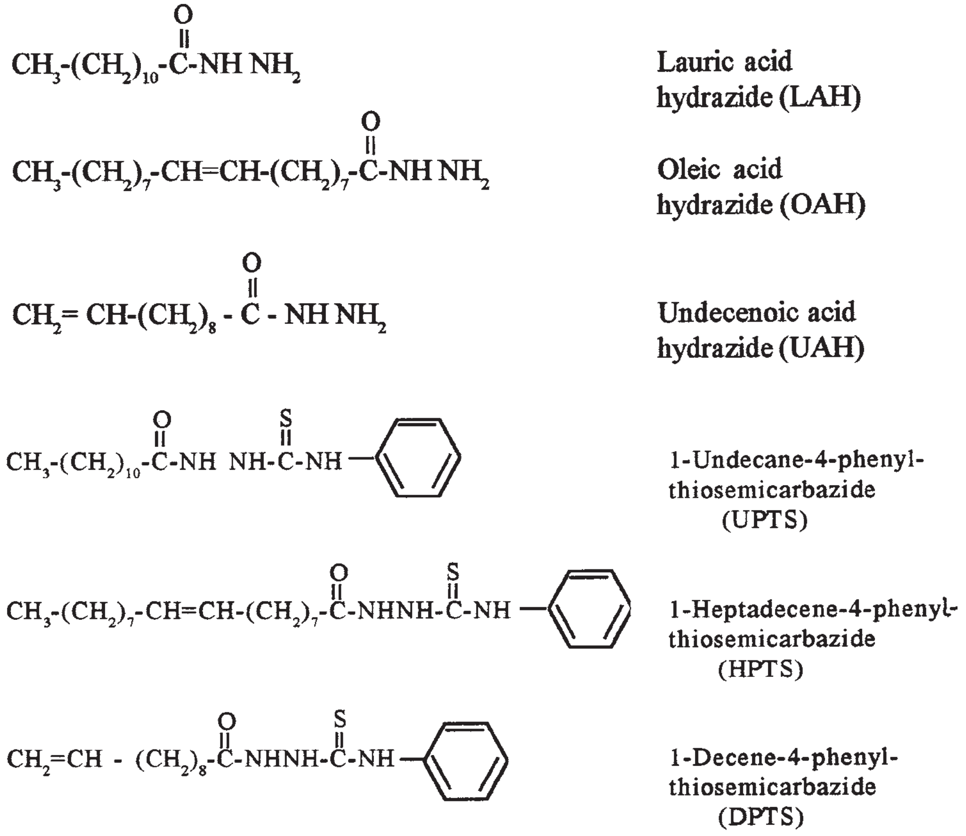

SCHEME 1

with increasing concentration of inhibitor. Maximal %I.E. was obtained at 5,000 ppm of inhibitor. Among the compounds tested as inhibitors for corrosion of mild steel in boiling 15% HCl, the order of %I.E. at maximal concentration (i.e., 5,000 ppm) was undecenoic acid hydrazide (UAH) > oleic acid hydrazide (OAH) > lauric acid hydrazide (LAH). For semithiocarbazides at the optimal concentration of 5,000 ppm, the order was 1-decene-4-phenyl-thiosemicarbazide (OPTS) > 1-heptadecene-4-phenyl-thiosemicarbazide (HPTS) > 1-undecane-4-phenyl-thiosemicarbazide (UPTS).

Corrosion inhibition tests at different immersion times also were carried out on N-80 steel under similar conditions using concentrations of 5,000 ppm UAH and DPTS (Table 2). UAH and DPTS were found to have inhibition efficiencies of 61.9 and 69.9%, respectively, at 0.5 h. The %I.E. for DPTS and UAH decreased with increasing test duration from 0.5 to 6.0 h. The decrease in inhibitor effectiveness at longer immersion times can be caused by various factors such as increase in cathodic or hydrogen evolution kinetics or increase in concentration of ferrous ions (1).

Potentiodynamic polarization studies. Corrosion parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and %I.E. obtained from potentiodynamic polarization curves of mild steel and N-80 steel in 15% HCl at 28 ± 2°C in the absence and presence of inhibitors are given in Table 3. The I_{corr} value decreases significantly in the presence of the fatty acid derivatives, indicating that the compounds are effective corrosion inhibitors. Also, these compounds do not cause any significant change in corrosion potential values, suggesting that they are mixed-type inhibitors, i.e., they inhibit corrosion by slowing down both anodic and cathodic corrosion processes.

A significant feature of the investigation is that the thiosemicarbazides of fatty acids showed better %I.E. than the respective hydrazides of fatty acids. This may be attributed to the high polarizibility of sulfur atoms of thiosemicarbazides, which facilitates greater adsorption of thiosemicarbazides than hydrazides, which have less polarizable nitrogen atoms.

Mechanism of corrosion inhibition. One plausible mechanism for the corrosion inhibition exhibited by the thiosemicarbazides and hydrazides used in this study is that of adsorption. Thiosemicarbazides and hydrazides can adsorb onto metal surfaces through lone pairs of electrons present on nitrogen or sulfur atoms and through π-electrons present in these molecules. To test this hypothesis, we plotted the surface coverage (θ) and log concentration values and obtained straight lines (Figs. 1and 2). These observations suggest adsorption of thiosemicarbazides and hydrazides to the mild steel surface/acidic solution interface occurs according to Temkin's adsorption isotherm (13).

TABLE 1
Corrosion Parameters[a] for Mild Steel in Boiling 15% HCl (105 ± 2°C) in the Absence and Presence of Five Concentrations of Six Inhibitors

Concentration (ppm)	Initial weight (g)	Weight loss (g)	I.E.[b] (%)	Corrosion rate (mmpy)
15% HCl	16.73	7.60	—	44,420
Lauric acid hydrazide (LAH)				
1000	16.98	2.78	63.5	5,268
2000	16.62	2.48	67.4	4,701
3000	17.02	2.26	70.3	4,278
4000	16.91	2.24	70.6	4,245
5000	16.43	2.18	71.3	4,134
Oleic acid hydrazide (OAH)				
1000	16.40	3.78	50.3	7,165
2000	16.62	2.27	70.2	4,301
3000	16.85	1.68	77.9	3,181
4000	17.04	1.30	82.9	2,464
5000	16.68	1.19	84.4	2,251
Undecenoic acid hydrazide (UAH)				
1000	16.46	2.95	61.2	5,593
2000	16.23	2.32	69.5	4,398
3000	16.82	1.53	79.9	2,897
4000	16.69	0.93	87.8	1,756
5000	16.68	0.73	90.4	1,380
1-Undecane-4-phenyl-thiosemicarbazide (UPTS)				
1000	17.12	6.31	17.1	11,950
2000	17.02	4.23	44.5	8,003
3000	16.32	3.20	58.0	6,056
4000	16.62	1.90	75.0	3,608
5000	16.49	1.69	77.8	3,207
1-Heptadecene-4-phenyl-thiosemicarbazide (HPTS)				
1000	16.77	5.18	32.0	9,803
2000	16.72	3.67	51.9	6,943
3000	16.53	2.89	62.1	5,465
4000	16.89	1.81	76.2	3,430
5000	16.58	1.05	86.1	1,999
1-Decene-4-phenyl-thiosemicarbazide (DPTS)				
1000	16.29	2.61	65.7	4,952
2000	16.99	1.89	75.1	3,591
3000	16.38	1.06	86.0	2,019
4000	16.66	0.46	93.9	879
5000	16.30	0.30	96.0	578

[a] Determined from weight loss measurements.
[b] Inhibition efficiency, determined as %I.E. = $[(W^o - W)/W^o] \times 100$, where W^o and W are the weight loss in the absence and presence of inhibitors. Abbreviation: mmpy, millimeters per year.

TABLE 2
Corrosion Parameters[a] for N-80 Steel in 15% HCl at 105 ± 2°C in Absence and Presence of Inhibitor

	0.5 h		3.0 h		6.0 h	
Concentration	I.E. (%)	C.R. (mmpy)	I.E. (%)	C.R. (mmpy)	I.E. (%)	C.R. (mmpy)
HCl (15%)	—	3140	—	2380	—	1813
UAH (5000 ppm)	61.9	1196	46.2	1280	43.1	1024
DPTS (5000 ppm)	69.9	946	92.5	178	90.8	166

[a] From weight loss measurements. C.R., corrosion rate; for other abbreviations see Table 1.

TABLE 3
Electrochemical Polarization Parameters for Corrosion of Mild Steel and N-80 Steel in 15% HCl Containing Various Inhibitors at 28 ± 2°C

Concentration[a]	Type of steel	E_{corr}[b] (mV vs. SCE)	I_{corr}[c] (m.A. cm^{-2})	I.E. (%)
15% HCl	Mild steel	–539	3.50	—
UAH 500	Mild steel	–540	0.52	85.0
OAH 500	Mild steel	–542	0.18	94.7
UAH 500	Mild steel	–543	0.14	96.0
UPTS 500	Mild steel	–543	0.09	97.4
HPTS 500	Mild steel	–534	0.05	98.6
DPTS 500	Mild steel	–534	0.03	99.0
15% HCl	N-80 steel	–548	0.47	—
UAH 500	N-80 steel	–539	0.31	34.0
DPTS 500	N-80 steel	–532	0.20	57.4

[a] Concentration in ppm except for HCl.
[b] E_{corr}, corrosion potential; SCE, saturated calomel electrode.
[c] I_{corr}, corrosion current density (milliamperes per centimeter^2); for other abbreviations see Table 1.

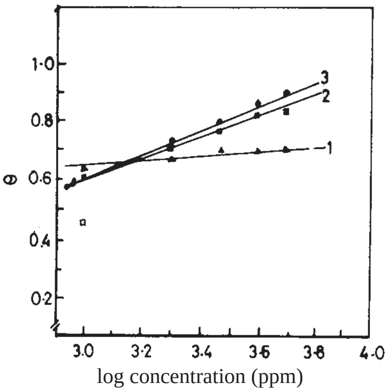

FIG. 1. Temkin's adsorption isotherm plots for the adsorption of three inhibitors in 15% boiling HCl on the surface of mild steel. (1) Lauric acid hydrazide; (2) oleic acid hydrazide; (3) undecenoic acid hydrazide; θ, surface coverage calculated as $\theta = (W^o - W)W^o$, where W^o and W are the weight loss in the absence and presence of inhibitors.

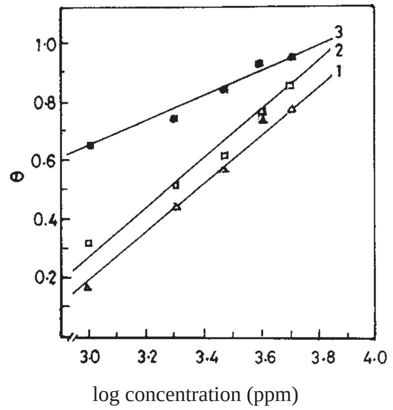

FIG. 2. Temkin's adsorption isotherm plots for the adsorption of three inhibitors in 15% boiling HCl on the surface of mild steel. (1) 1-Undecane-4-phenyl-thiosemicarbazide, (2) 1-heptadecene-4-phenyl-thiosemicarbazide, and (3) 1-decene-4-phenyl-thiosemicarbazide.

ACKNOWLEDGMENT

This work was financially supported by the Council of Scientific and Industrial Research, New Delhi, India.

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[Received April 1, 1999; accepted November 17, 1999]