Fatty Acid Triazoles: Novel Corrosion Inhibitors for Oil Well Steel (N-80) and Mild Steel

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ABSTRACT: Three fatty acid triazoles, namely, 3-undecane-4-aryl-5-mercapto-1,2,4-triazole (triazole 1), 3(heptadeca-8-ene)-4-aryl-5-mercapto-1,2,4-triazole (triazole 2), and 3(deca-9-ene)-4-aryl-5-mercapto-1,2-4-triazole (triazole 3) were synthesized and their corrosion-inhibiting action in 15% hydrochloric acid was evaluated by weight-loss method and electrochemical techniques. Electrochemical polarization studies at room temperature indicated that all the triazoles are mixed-type inhibitors, i.e., they inhibit both anodic and cathodic reactions. The adsorption of these compounds onto mild steel from 15% HCl followed Temkin's adsorption isotherm.

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KEY WORDS: Corrosion inhibition, fatty acid triazole, mild steel, oil well tubular steel, Temkin's adsorption isotherm.

Acidification of petroleum oil wells is an important stimulation technique for enhancing oil production. Hydrochloric acid (15–28%) is commonly used for acidification. Because of the aggressive nature of the acid, inhibitors are commonly used to reduce the aggressive attack of the acid on oil well tubing and casing materials during acidization (1).

A literature survey (2–5) on high-temperature acid corrosion inhibitors indicates that a variety of organic compounds are effective corrosion inhibitors during acidification including acetylenic alcohols, aromatic aldehydes, alkenyl phenones, nitrogen-containing heterocyclics, and imminium salts. Among these compounds acetylenic alcohols are widely used as acidifying inhibitors in industry because of their commercial availability and cost effectiveness. However, these inhibitors are effective only at high concentration and produce toxic vapors during the acidification process (6). Because of this, there is a need for developing new acidifying corrosion inhibitors.

Continuing our work on developing acidifying corrosion inhibitors (7–11), we synthesized three fatty acid triazoles and evaluated their corrosion-inhibiting properties on mild steel and N-80 (oil-well tubular steel) in 15% HCl at boiling temperature (105 ± 2°C) and at room temperature (28 ± 2°C). The selection of this type of fatty acid derivatives was made because they are environmentally benign and have low toxicity (12,13). A literature survey indicated that no work has been reported on the use of fatty acid derivatives of triazoles as corrosion inhibitors.

MATERIAL AND METHODS

Weight-loss measurements. Experiments were conducted using oil-well steel (N-80) and cold-rolled mild steel in 15% HCl. The mild steel sample (2.0 × 2.0 × 0.6 cm)—having a composition C, 0.14%; Mn, 0.35%; Si, 0.17%; S, 0.025%; P, 0.03%; remainder Fe—and N-80 steel (2.0 × 1.0 × 0.7 cm) were used for weight-loss measurement studies. The experiments were performed in a 500-mL three-neck round-bottomed flask, to which a condenser was attached, for 0.5 h at 105 ± 2°C as per ASTM G 1-72 (14). Corrosion rates are expressed as mmpy (millimeters per year).

Electrochemical studies. For potentiodynamic polarization studies, mild steel strips and N-80 steel of the same composition were embedded in araldite (a fixing material, made up of epoxy resin) with an exposed area of 1.0 cm^2, and the experiments were carried out at a constant temperature of 28 ± 2°C as per ASTM G 3-74 and G 5-87 (14). 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, Darmstadt, Germany) and doubled-distilled water were used for preparing test solutions of 15% HCl for all experiments. The inhibitors were synthesized in the laboratory following procedures reported elsewhere (12,13), and all compounds were characterized from their spectral data. Names and molecular structures are presented in Scheme 1.

RESULTS AND DISCUSSION

Weight-loss measurements. The values of percentage inhibition efficiency (%IE) and corrosion rate obtained by weight-loss methods at different fatty acid triazole concentrations in 15% HCl under boiling conditions at 105 ± 2°C are summarized in Table 1. The %IE and surface coverage (θ) were calculated using the following equations(15):

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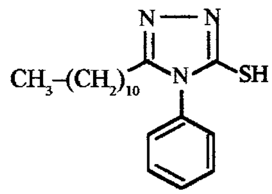
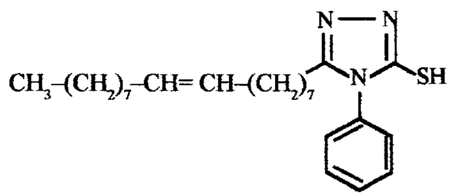
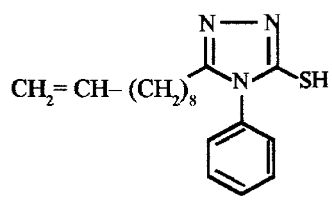


3-Undecane-4-aryl-5-mercapto-1,2,4-triazole
(Triazole 1)



3-(Heptadeca-8-ene)-4-aryl-5-mercapto-1,2,4-triazole
(Triazole 2)



3-(Deca-9-ene)-4-aryl-5-mercapto-1,2,4-triazole
(Triazole 3)

SCHEME 1

TABLE 1
Corrosion Parameters for Mild Steel in Boiling 15% HCl (105 – 2¡C) in Absence and Presence of Different Concentrations of Various Inhibitors[a]

Concentration (ppm)	Weight loss (g)	IE (%)	CR (mmpy)
15% HCl	7.60	—	14,420
Triazole 1			
1,000	4.39	42.31	8,319
2,000	4.00	47.50	7,569
3,000	3.80	50.15	7,195
4,000	3.31	56.52	6,270
5,000	3.03	60.20	5,739
Triazole 2			
1,000	2.95	61.23	5,591
2,000	2.09	72.52	3,962
3,000	1.52	80.05	2,877
4,000	1.13	85.18	2,141
5,000	0.72	90.53	1,365
Triazole 3			
1,000	3.70	51.42	7,005
2,000	1.64	78.50	3,100
3,000	0.34	95.52	640
4,000	0.32	95.73	616
5,000	0.29	96.20	548

[a]As determined from weight-loss measurements. IE, inhibition efficiency; CR, corrosion rate, determined as millimeters per year (mmpy); Triazole 1; 3-undecane-4-aryl-5-mercapto-1,2,4-triazole; Triazole 2; 3-(heptadeca-8-ene)-4-aryl-5-mercapto-1,2,4-triazole; Triazole 3; 3-(deca-9-ene)-4-aryl-5-mercapto-1,2,4-triazole.

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

Concentration (ppm)	0.5 h		3.0 h		6.0 h	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
15% HCl	—	3,140	—	2,380	—	1,813
Triazole 3						
3,000	84.87	475	95.53	106	93.27	122
5,000	91.81	257	91.30	207	88.95	200

[a]As determined from weight-loss measurements. For abbreviations see Table 1.

$$\%IE = [(W^0 - W)/W^0] \times 100 \quad [1]$$

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

where W^0 and W are the weight loss in the absence and presence of inhibitors, respectively. Table 1 indicates that %IE increases with increasing inhibitor concentration. Maximal %IE is obtained at 5000 ppm. All three fatty acid triazoles exhibited good corrosion inhibition at 5000 ppm. Triazole 3 gave the highest inhibition efficiency (96.2%) whereas Triazoles 2 and 1 showed 90.5 and 60.2% inhibition efficiency, respectively, at a concentration of 5000 ppm.

Table 2 summarizes the values of % IE and corrosion rate of N-80 (oil-well tubular steel) for Triazole 3 for immersion times of 0.5, 3.0, and 6.0 h at a temperature of 105 ± 2°C in 15% boiling HCl at concentrations of 3000 and 5000 ppm.

The effectiveness of a compound as a corrosion inhibitor depends on the structure of the organic compound (15). High corrosion-inhibiting properties of triazoles may be attributed to the lone electron pair present on N and S atoms and the π-electrons of the heterocyclic ring, which favor adsorption of these compounds on the metal surface leading to higher inhibition efficiency. The lateral interaction of long-chain hydrocarbons is mutual and can result in the formation of a thick network that further facilitates the formation of a compact film of inhibitor on the metal surface. Triazole 3, having a double bond at the terminal position, exhibited the best performance as corrosion inhibitor (17). That the compound exhibited the highest inhibition efficiency may be attributed to its adsorption on the metal surface through polar groups as well as through π-electrons of the double bond. This leads to greater coverage of the metal surface by these compounds,

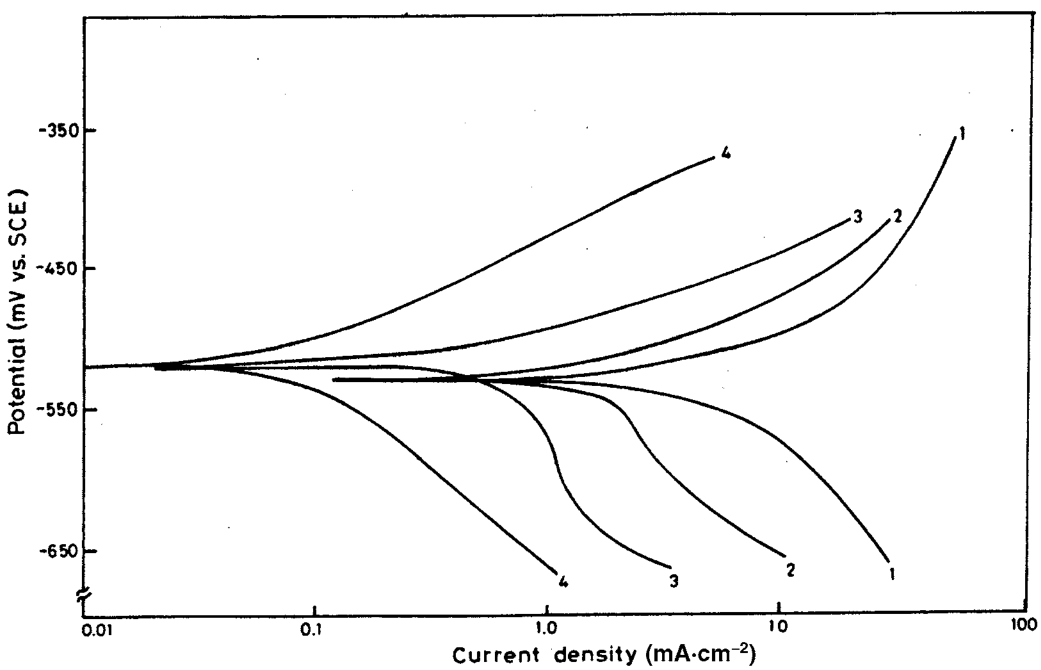


FIG. 1. Anodic and cathodic potentiodynamic polarization curves for mild steel in 15% HCl in the presence and absence of various inhibitors at 500 ppm. (**1**) 15% HCl, (**2**) Triazole 1 (3-undecane-4-aryl-5-mercapto-1,2,4-triazole), (**3**) Triazole 2 [3-(heptadeca-8-ene)-4-aryl-5-mercapto-1,2,4-triazole], (**4**) Triazole 3 [3-(deca-9-ene)-4-aryl-5-mercapto-1,2,4-triazole]; SCR, saturated calomel electrode.

TABLE 3
Electrochemical Polarization Parameters for the Corrosion of Mild Steel in 15% HCl Containing Optimal Concentrations of Various Inhibitors at 28 – 2¡C

Concentration (ppm)	E_{corr} (mV vs. SCE)	I_{corr}[a] ($mA \cdot cm^{-2}$)	IE (%)
15% HCl	–539	3.50	—
Triazole 1			
500	–539	0.58	83.37
Triazole 2			
500	–525	0.16	95.25
Triazole 3			
500	–515	0.03	99.14

[a]SCE, saturated calomel electrode. I_{corr} represents corrosion current density as determined by the extrapolation method as described in Application Note of EG&G, Princeton Applied Research (Gaithersburg, MD). The intersection of extrapolated curves at current axis (x-axis) gives the value of I_{corr}. For abbreviations see Table 1.

TABLE 4
Electrochemical Polarization Parameters[a] for the Corrosion of N-80 Steel in 15% HCl Containing Optimal Concentrations of Various Inhibitors at 28 – 2¡C

Concentration (ppm)	E_{corr} (mV vs. SCE)	I_{corr} ($mA \cdot cm^{-2}$)	IE (%)
15% HCl	–548	0.47	—
Triazole 3			
500	–535	0.20	57.44

[a]For abbreviations see Tables 1 and 3.

thereby giving higher inhibition efficiency. Triazole 1 showed the lowest inhibition efficiency due to the absence of a double bond in the hydrocarbon chain. Triazole 2, containing an internal double bond at position 8, showed less inhibition efficiency than Triazole 3, containing a π-bond and 10 carbon atoms, because compounds containing >10 carbon atoms show less inhibition efficiency owing to decreased solubility and increased steric hindrance to adsorption (18).

Electrochemical measurements. The potentiodynamic anodic and cathodic polarization curves of mild steel carried out in 15% HCl containing 500 ppm concentrations of all the triazoles are shown in Figure 1. Various electrochemical parameters calculated for the curves are given in Table 3. It can be seen that I_{corr} values decrease significantly in the presence of the triazoles. These observations indicate that the triazoles studied are effective inhibitors for the corrosion of mild steel in 15% HCl. Figure 2 shows the polarization behavior of N-80 steel in 15% HCl at room temperature in the absence and presence of 500 ppm of Triazole 3. The electrochemical parameters obtained from the curves are given in Table 4. The results show that these triazoles do not cause any significant change in corrosion potential values, indicating that they are mixed-type inhibitors.

Mechanism of corrosion inhibition. To understand the mechanism of corrosion inhibition, one must know the adsorption behavior of the organic compounds on the metal surface (19). The degree of surface coverage (θ) for different inhibitor concentrations has been evaluated from weight-loss values. The data were tested graphically by fitting to various isotherms. Straight lines were obtained by plotting θ vs. log C for Triazoles 1–3 (Fig. 3), suggesting that the adsorption of these compounds from the acid on a mild steel surface follows Temkin's adsorption isotherm.

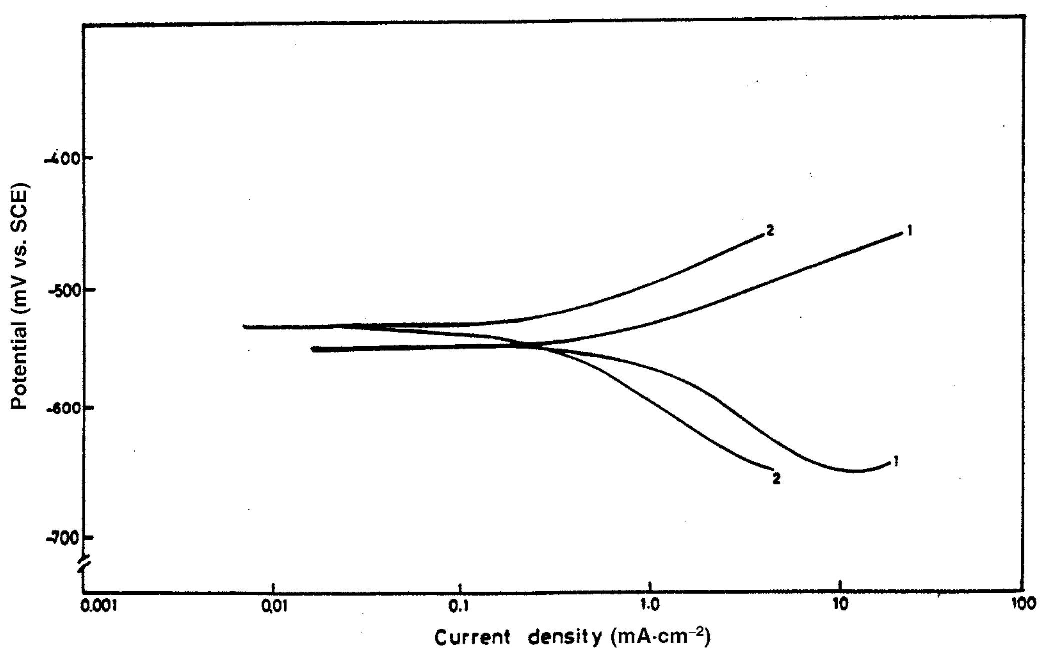


FIG. 2. Anodic (upward curving) and cathodic (downward curving) potentiodynamic polarization curves for N-80 steel in 15% HCl in the presence and absence of inhibitors at 500 ppm. (**1**) 15% HCl, (**2**) Triazole 3. For abbreviations see Figure 1.

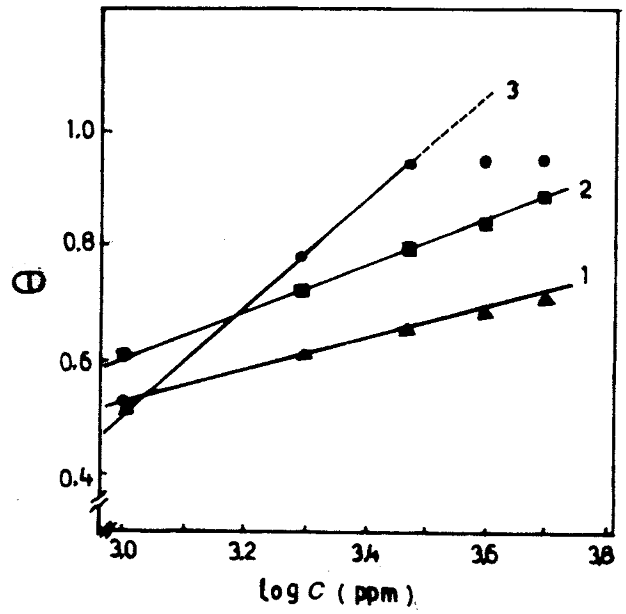


FIG. 3. Temkin's adsorption isotherm plots for the adsorption of various inhibitors in 15% boiling HCl on the surface of mild steel. (**1**) Triazole 1, (**2**) Triazole 2, (**3**) Triazole 3. θ, fractional surface converage; *C*, concentration of thiazole; for other abbreviations see Figure 1.

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