

Development of Novel Acidizing Inhibitors for Carbon Steel Corrosion in 15% Boiling Hydrochloric Acid

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ABSTRACT

The inhibitive action of 1-cinnamylidene-3-thiocarbohydrazide (CTCH) and 1,1'-dicinnamylidene-3-thiocarbohydrazide (DCTCH) against the corrosion of carbon steel in 15% hydrochloric acid (HCl) was investigated using nonelectrochemical and electrochemical techniques. Potentiodynamic polarization studies revealed that the compounds were mixed-type inhibitors and exhibited more than 97% inhibition efficiency at 1,500 ppm of inhibitor concentration. The effect of temperature on the corrosion behavior of carbon steel in 15% HCl with 1,500 ppm of inhibitors was studied in the temperature range from 30°C to 110°C. The surface coverage (θ) increased linearly with the logarithm of the inhibitor concentration fitting a Temkin adsorption isotherm. Thermodynamic parameters including the free energy of adsorption, activation energy, enthalpy, entropy, and heat of adsorption were also calculated. The inhibitors reduced the hydrogen permeation current effectively through the steel surface. The protective film formed on the metal surface by the adsorption of organic compounds was confirmed using Fourier transform infrared (FTIR), ultraviolet (UV)-visible reflectance, and scanning electron microscopy (SEM) studies.

KEY WORDS: acidizing inhibitors, carbon steel, electrochemical studies, hydrochloric acid, hydrogen permeation studies

INTRODUCTION

Acidization of a petroleum oil well is one of the important stimulation techniques for enhancing oil produc-

tion. It is commonly brought about by forcing 15% to 28% hydrochloric acid (HCl) as a solution into the well to open up near-bore channels in the formation and, hence, to increase the flow of oil. To reduce the aggressive attack of the acid on tubing and casing materials, inhibitors are added to the acid solution during the acidizing process.¹ Effective acidizing inhibitors that are usually found in commercial formulations are acetylenic alcohols,²⁻⁵ alkenyl phenones,⁶ aromatic aldehydes,⁷⁻⁸ nitrogen-containing heterocyclics and their quaternary salts,⁹⁻¹¹ and condensation products of carbonyl compounds and amines.¹² Most of the efficient inhibitors used in industry are organic compounds that mainly contain nitrogen; sulfur atoms and multiple bonds are in the molecules through which they are adsorbed on the metal surface.¹³⁻²³ Among the various inhibitors available, acetylenic alcohols are used widely as acidizing inhibitors because of their commercial viability and effectiveness, but they are effective only at high concentrations and are extremely toxic.²⁴ In the present investigation, novel acidizing inhibitors that can effectively control the corrosion of oil-well equipment during acidization were synthesized and evaluated.

EXPERIMENTAL PROCEDURES

Material Preparation

Carbon steel strips of size 4.5 by 2 by 0.2 cm containing 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P, and the remainder Fe were used for mass-loss and hydrogen permeation studies. For electrochemical studies, carbon steel strips coated with

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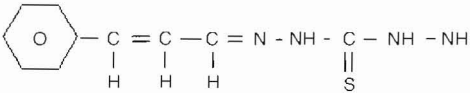
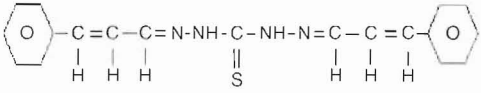
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TABLE 1

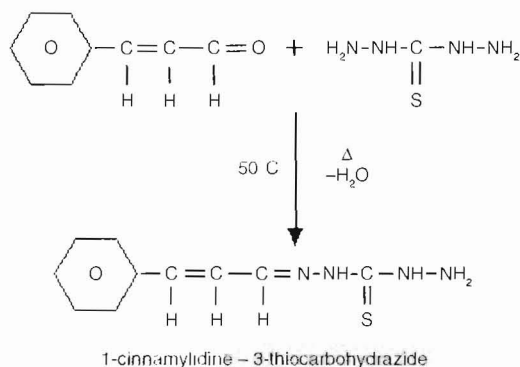
Molecular Formula, Molecular Weight, Structure, and Melting Point of the Synthesized Organic Compounds

Name of the Compound	Molecular Formula	Molecular Weight	Structure	Melting Point (°C)
1-cinnamylidene-3-thiocarbohydrazide (CTCH)	C ₁₀ H ₁₂ N ₄ S	220.20		163
1,1'-dicinnamylidene-3-thiocarbohydrazide (DCTCH)	C ₁₈ H ₁₆ N ₄ S	334.29		165

lacquer with an exposed area of 1 cm² were used. They were polished mechanically with emery papers of 1/0 to 4/0 grades. They were subsequently degreased with trichloroethylene (C₂HCl₃) before use. Analytical reagent (AR)-grade HCl and double-distilled water were used for preparing 15% HCl. All other chemicals used for synthesizing inhibitors were AR grade.

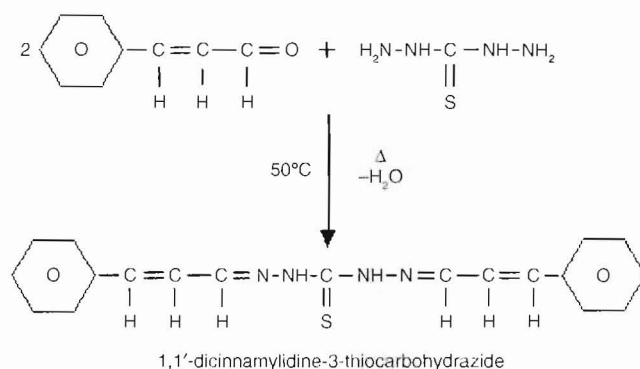
Synthesis and Characterization of Acidizing Inhibitors

Preparation of 1-Cinnamylidene-3-Thiocarbohydrazide (CTCH) — 10.6 gm (0.1 mole) of thiocarbonylhydrazide (TCH) was dissolved in 200 mL hot water and treated with 12.6 mL of cinnamaldehyde (C₉H₈O, 0.1 mole) in ethanol (C₂H₅OH, 30 mL) dropwise with constant stirring for 20 min at 50°C, then the mixture was allowed to stand overnight to give a yellow-colored solid compound, namely, 1-cinnamylidene-3-thiocarbohydrazide (CTCH). The obtained CTCH was recrystallized with equal ratio of acetone and ethanol to get pure yellow crystalline solid:



(2) Preparation of 1,1'-Dicinnamylidene-3-Thiocarbohydrazide (DCTCH) — 10.6 gm (0.1 mole) of TCH was dissolved in 200 mL hot water and treated with 25.2 mL of cinnamaldehyde (0.2 mole) in ethanol (60 mL) dropwise with stirring for 20 min at 50°C, then the mixture was allowed to stand overnight to

give a yellow-colored solid compound, namely, 1,1'-dicinnamylidene-3-thiocarbohydrazide (DCTCH):



The obtained 1,1'-dicinnamylidene-3-thiocarbohydrazide was recrystallized with an equal ratio of acetone and ethanol to get pure yellow crystalline solid. Synthesized compounds are solids and their melting points were determined using a melting point apparatus. The molecular formula, molecular weight, molecular structure, and melting point of synthesized organic compounds are given in Table 1.

Ultraviolet-Visible Spectral Studies

The UV-visible absorption spectra were recorded by dissolving a small quantity of inhibitor in acetone using an UV-visible spectrophotometer (Shimadzu UV-2401[†]). Before spectroscopic measurements, the base-line correction was made suitably using acetone. The spectra were recorded in the range between 300 nm and 800 nm. The spectrum for the precursors was also run to ensure the formation of the compounds.

Fourier Transform Infrared Spectral Studies

Fourier transform infrared (FTIR) spectrophotometry measurements were recorded using a FTIR spectrophotometer (Perkin Elmer Paragon model 500[†]) for the synthesized compounds to confirm the condensation products obtained by treating TCH with cinnamaldehyde. The spectra were determined in the mid-infrared region (MIR), which extended from

[†] Trade name.

4,000 cm⁻¹ to 400 cm⁻¹, using the potassium bromide (KBr) pellet technique.

Nonelectrochemical Methods

Mass-Loss Measurements — Carbon steel strips of size 4.5 by 2 by 0.2 cm were used for the determination of corrosion rate (CR) by mass-loss measurements. These specimens were given necessary pretreatment such as mechanical polishing with emery papers of 1/0 to 4/0 grades and degreased with trichloroethylene before use. The experimental solution used was 15% HCl in the absence and presence of different concentrations of inhibitors. The volume of acid used was 100 mL. The initial weight of the specimens was measured and then it was completely immersed into the experimental solution at 30°C. After 6 h, the specimens were taken out, washed thoroughly with distilled water, dried completely, and their final weights were measured. From the initial and final weights of the specimen, the loss in weights were calculated. The corrosion rate (mmpy) and inhibitor efficiency of the inhibitors can be calculated using the formula:

$$\text{Corrosion rate (mmpy)} = \frac{KW}{ATD} \quad (1)$$

where $K = 8.76 \times 10^4$ (constant), W = mass loss in g, A = area in cm², and D = density in gm/cm³ (7.86).

$$\text{Inhibition efficiency (\%)} = \frac{W_B - W_I}{W_B} \times 100 \quad (2)$$

where W_B and W_I are mass loss per unit time in the absence and presence of inhibitors.

Potentiodynamic Polarization Studies

Potentiodynamic polarization measurements were carried out using an electrochemical analyzer (EG&G model 6310¹). The polarization measurements were made to evaluate the corrosion current (I_{corr}), corrosion potential (E_{corr}), and Tafel slopes. Experiments were carried out in a conventional three-electrode cell assembly. The working electrode was a carbon steel specimen of 1 cm² area, which was exposed, and the rest was covered with red lacquer. A rectangular Pt foil was used as the counter electrode. To exert a uniform potential field on the working electrode, it was designed in such a way that the counter electrode was much larger in area compared to the working electrode. The reference electrode used was a saturated calomel electrode (SCE). The Luggin capillary arrangement was used to connect the working electrode to the SCE. To avoid the ohmic contribution, the Luggin capillary was kept close to the working electrode. A time interval of 10 min to 20 min was given for each experiment to attain the steady-state open-circuit potential. The polarization was carried from a cathodic

potential of $-800 \text{ mV}_{\text{SCE}}$ to an anodic potential of $-200 \text{ mV}_{\text{SCE}}$ at a sweep rate of 1 mV/s. From the polarization curves, Tafel slopes, E_{corr} , and I_{corr} were calculated. The inhibitor efficiency was calculated using the following formula:

$$\text{IE (\%)} = \frac{I_{\text{corr}} - I_{\text{corr}}^*}{I_{\text{corr}}} \times 100 \quad (3)$$

where I_{corr} and I_{corr}^* are corrosion currents in the absence and presence of inhibitors, respectively.

Impedance Measurements

The electrochemical alternating current (AC) impedance measurements were also performed using the commercial electrochemical analyzer over a frequency range of 100 kHz to 10 mHz. Experiments were carried out in the same cell that was used for potentiodynamic polarization studies. The working electrode was a carbon steel specimen of 1 cm² area, which was exposed, and the rest was covered with red lacquer. A rectangular Pt foil was used as the counter electrode. A sine wave with an amplitude of 10 mV was superimposed on the steady open-circuit potential. A time interval of 10 min to 20 min is given for each experiment to attain the steady-state open-circuit potential. Nyquist plots were obtained from the results of these experiments. From the plots, the charge-transfer resistance (R_t) was calculated and the double-layer capacitance was then calculated using the following equation:

$$C_{\text{dl}} = 1/2\pi f_{\text{max}} R_t \quad (4)$$

where R_t is charge-transfer resistance and C_{dl} is the double-layer capacitance.

The experiments were carried out in the absence and presence of different concentrations of inhibitors. The percentage of inhibition efficiency (IE) was calculated using the following equation:

$$\text{IE(\%)} = \frac{R_t^* - R_t}{R_t^*} \times 100 \quad (5)$$

where R_t^* and R_t are the charge-transfer resistances in the presence and absence of inhibitors, respectively.

Effect of Temperature

Mass-loss measurements were also performed in the range from 30°C to 110°C with 1,500 ppm concentration of inhibitors. The duration of the experiment was 1 h. Experiments were performed in a 500-mL, three-neck, round-bottom flask using a condenser, according to ASTM G1²⁵ at 110°C. From the initial and final weights of the specimen, the loss in weights was calculated and the efficiency of the inhibitors at various temperatures was also calculated.

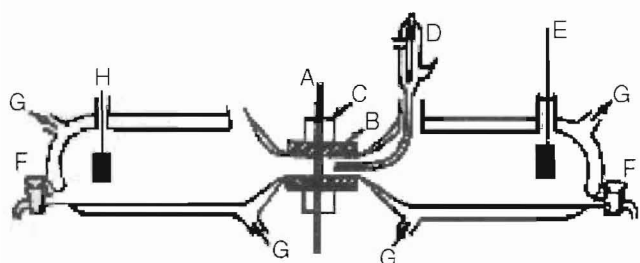


FIGURE 1. Permeation cell setup: (A) steel membrane, (B) PTFE bushings, (C) polyvinyl chloride (PVC) coupling, (D) reference electrode, (E) counter electrode, (F) tap, (G) water circulation, and (H) anode.

Surface coverage (θ) was also calculated from the mass-loss measurements using the formula:

$$\text{Surface coverage } (\theta) = \frac{W_B - W_I}{W_B} \quad (6)$$

where W_B is the mass loss in the absence of inhibitor and W_I is the mass loss in the presence of inhibitor.

Hydrogen Permeation Studies

Hydrogen permeation studies were carried out using a cell arrangement as described earlier.²⁶⁻²⁷ The specimen is fixed in between polytetrafluoroethylene (PTFE) bushings and clamped tightly. The Pd-coated side of the compartment is filled with 0.2 N sodium hydroxide (NaOH) solution, which is preelectrolyzed for a period of 24 h at a current density of 100 μA . The circuit is completed using a Hg/HgO/0.2 N NaOH reference electrode and a Pt auxiliary electrode. The other compartment facing the carbon steel is filled with the experimental solution. The cell is connected to a potentiostat and a constant potential of -300 mV is applied to the specimen on the anodic side. It has been shown earlier that -300 mV is the most suitable potential for ionizing the diffused hydrogen rapidly and efficiently at the Pd/0.2 N NaOH interface. The initial current gradually decreases and reaches a steady value. The nonplated side is allowed to corrode with free hydrogen evolution. A part of the hydrogen produced could penetrate through the membrane and get ionized at the Pd/0.2 N NaOH interface, which is accounted as permeation current using an X-Y/t recorder. The permeation current was measured in 15% HCl medium with and without inhibitors for the best inhibiting concentrations only, and the complete permeation cell setup is shown in Figure 1.

Surface Examination Studies

The carbon steel specimens were immersed in 15% HCl in the absence and presence of 1,500 ppm concentration of inhibitors for 6 h at 30°C. After 6 h, the specimens were taken out, dried, and kept in a desiccator. The protective film formed on the surface

was studied by FTIR, UV-visible reflectance, and scanning electron microscopy (SEM) studies.

Fourier Transform Infrared Spectral Studies

FTIR spectra were recorded using the commercial FTIR spectrophotometer for the carbon steel surface immersed in 15% HCl solution in the absence and presence of optimum concentration of inhibitors.

Ultraviolet-Visible Reflectance Studies

UV-visible reflectance spectral studies were made on the surfaces of polished, corroded, and corrosion-inhibited carbon steel specimens in the region of 200 nm to 800 nm using a UV-visible spectrophotometer (Hitachi model U-3400[†]).

Scanning Electron Microscopic Studies

Surface examination of carbon steel specimens were made using a JEOL[†] scanning electron microscope with the magnification of 1,000X for the carbon steel specimens immersed in 15% HCl solution for 6 h at 30°C in the absence and presence of optimum concentration of inhibitors.

RESULTS

Characterization of Synthesized Acidizing Inhibitors

Ultraviolet-Visible Spectral Studies — The UV-visible spectra of CTCH and DCTCH in acetone showed absorption bands at 384 nm and 385 nm, characteristic of $n-\pi^*$ transitions, confirming the presence of the C = N group in the molecule. Absorption bands in the region from 250 nm to 360 nm are characteristic of the C = N group. In the case of CTCH and DCTCH, the absorption maximum was shifted slightly toward longer wavelengths (Bathochromic shift) due to the presence of the auxochrome (NH_2) group.

Fourier Transform Infrared Spectral Studies — The absorption frequencies in the range from 1,690 cm^{-1} to 1,640 cm^{-1} are characteristic of the azomethine group $>\text{C} = \text{N}-$. In the case of CTCH and DCTCH, the $>\text{C} = \text{N}-$ stretching vibration frequency was shifted slightly toward lower frequencies due to delocalization of π electrons in the benzene ring and a lone pair of electrons present on the N and S atoms. The basic $>\text{C} = \text{N}-$ stretching vibrations were seen at 1,628 cm^{-1} and 1,629 cm^{-1} for CTCH and DCTCH, respectively, and their corresponding spectra are given in Figures 2(a) and (b).

Nonelectrochemical Methods

Mass-Loss Measurements — Mass-loss measurements were made for various concentrations of CTCH and DCTCH for the corrosion of carbon steel in 15% HCl for 6 h duration at 30°C (Table 2). Inhibition efficiency increased with the concentration from 500 ppm to 2,000 ppm. Maximum inhibition efficiency obtained

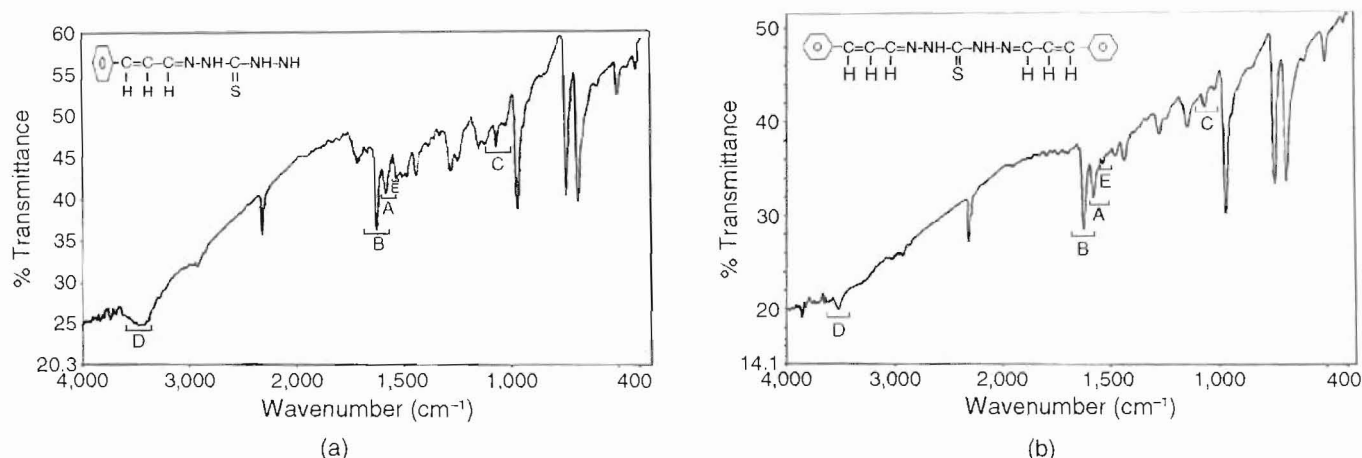


FIGURE 2. FTIR spectrum of (a) CTCH and (b) DCTCH: (A) C=C stretch vibrations, (B) C=N stretch vibrations, (C) C=S stretch vibrations, (D) NH-NH₂ stretching, and (E) NH bending.

with CTCH and DCTCH is 98.3% and 99.1% at 1,500 ppm. Further increases in the concentration of inhibitor from 1,500 ppm to 2,000 ppm had little effect on corrosion rate.

The effect of immersion time on corrosion rate and inhibition efficiency of the synthesized inhibitors with an optimum concentration at 30°C is given in Table 3. The inhibition efficiency of CTCH and DCTCH remained constant with the increase of immersion time from 6 h to 24 h. This suggests the inhibitors are stable and effective for a longer duration.

Potentiodynamic Polarization Measurements

Electrochemical corrosion kinetic parameters such as E_{corr} , I_{corr} , anodic and cathodic Tafel slopes (b_a and b_c), and percentage IE are given in Table 4. Polarization curves are shown in Figures 3(a) and (b) for the corrosion of carbon steel in 15% HCl at 30°C in the absence and presence of different concentrations of CTCH and DCTCH. The polarization curves revealed that the investigated compounds retarded the cathodic and anodic corrosion reactions. These results indicated that inhibitors exhibited cathodic and anodic inhibition effects. Therefore, inhibitors can be classified as inhibitors of relatively mixed effects (anodic/cathodic inhibition). The I_{corr} decreased with inhibitor concentration from 500 ppm to 2,000 ppm. The increase of concentration beyond 1,500 ppm had very little effect in the decrease of I_{corr} . Inhibition efficiencies obtained from I_{corr} values followed the same trend as mass-loss measurements.

Electrochemical Impedance Spectroscopy Measurements

Impedance diagrams obtained for the frequency range from 100 kHz to 10 mHz at the open-circuit potential in the absence and presence of different concentrations of CTCH and DCTCH in 15% HCl at 30°C

TABLE 2

Corrosion Parameters Obtained from Mass-Loss Measurements for the Corrosion of Carbon Steel in 15% HCl in the Absence and Presence of Different Concentrations of CTCH and DCTCH at 30°C for 6 h

Inhibitor Concentration (ppm)	Mass Loss (gms)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	1.6179	133.57	—
CTCH			
500	0.1455	12.01	91.0
1,000	0.0835	6.89	94.8
1,500	0.0274	2.26	98.3
2,000	0.0245	2.02	98.5
DCTCH			
500	0.0872	7.20	94.6
1,000	0.0484	4.00	97.0
1,500	0.0152	1.25	99.1
2,000	0.0126	1.04	99.2

TABLE 3

Effect of Immersion Time on Inhibition Efficiency of Carbon Steel in 15% HCl at 30°C in the Presence of 1,500 ppm of CTCH and DCTCH

Time (h)	Blank	CTCH		DCTCH	
	CR (mmpy)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
6	133.57	2.26	98.3	1.15	99.1
12	72.82	1.25	98.3	0.63	99.1
18	50.25	0.88	98.3	0.47	99.1
24	39.84	0.71	98.2	0.39	99.0

are shown in Figures 4(a) and (b). The impedance diagrams obtained having a semicircular appearance suggest that the corrosion of carbon steel is mainly controlled by a charge-transfer process. The impedance spectra (Nyquist plots) were analyzed by fitting

TABLE 4

Potentiodynamic Polarization Parameters for Carbon Steel in 15% HCl in the Absence and Presence of Different Concentrations of Inhibitors at 30°C

Inhibitor Concentration (ppm)	E_{corr} (mV _{SCE})	I_{corr} (mA/cm ²)	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-536	3.48	78	122	—
CTCH					
500	-554	0.37	80	124	89.4
1,000	-560	0.22	78	122	93.7
1,500	-532	0.10	74	118	97.1
2,000	-548	0.09	76	120	97.4
DCTCH					
500	-552	0.27	82	126	92.2
1,000	-558	0.13	84	126	96.3
1,500	-546	0.06	80	124	98.3
2,000	-534	0.05	82	126	98.6

the experimental data to a simple equivalent circuit model (Figure 5),²⁸⁻³¹ which included the solution resistance (R_s) and the constant phase element (CPE), which was placed in parallel to the R_t . The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to I_{corr} . Impedance of inhibited surface increased with inhibitor concentration in 15% HCl. The corrosion kinetic parameters such as R_i and C_{dl} ³²⁻³³ were derived from the Nyquist plots and percentage IE are given in Table 5. The R_i values increased and the C_{dl} value decreased with an increase in CTCH and DCTCH concentration. The decreased values of C_{dl} may be due to the replacement of water molecules at the electrode interface through adsorption by organic inhibitor molecules of lower dielectric constant.

Effect of Temperature

The corrosion rate and inhibition efficiency at various temperatures for the inhibitors are shown in Table 6. In acid solution, the logarithm of the corrosion rate is a linear function with $1/T$. Using Arrhenius theory, activation energies can be calculated using the equation:³⁴⁻³⁷

$$k = A \exp(-E_a/RT) \quad (7)$$

where k is the corrosion rate, E_a is the apparent effective activation energy, R is the universal gas constant, T is the absolute temperature, and A is the Arrhenius preexponential factor. Arrhenius plots of log of corrosion rate vs. $1/T$ gave straight lines (Figure 6).

Activation energies were calculated from the slopes of log corrosion rate vs. $1/T$ curves. The free energy of adsorption, ΔG_A^0 , at different temperatures were calculated using the equation:

$$\Delta G_A^0 = -RT \ln (55.5K) \quad (8)$$

and K is given by:

$$K = \frac{\theta}{C(1 - \theta)}$$

where 55.5 is the molar concentration of water in the solution, θ is the degree of surface coverage on the metal surface obtained from mass-loss measurements, C is the concentration of inhibitor in mole/L, T is the absolute temperature, R is the universal gas constant, and K is the adsorption equilibrium constant. The values of E_a and ΔG_A^0 are shown in Table 7. The IE of CTCH and DCTCH remained constant throughout the range of temperature studied. At 110°C, CTCH and DCTCH gave a very high IE of about 98.2% and 99.0%, respectively.

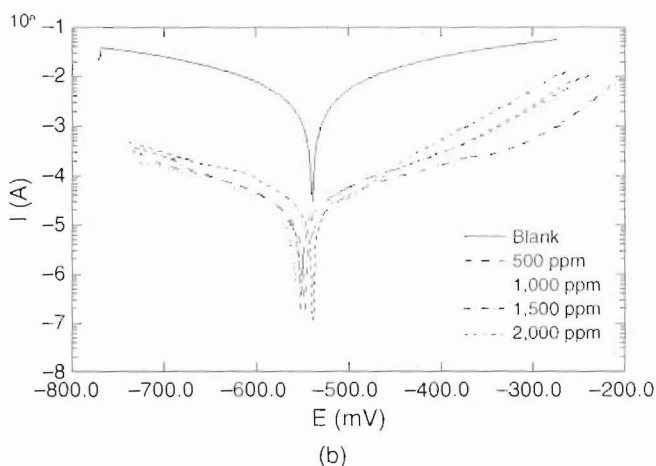
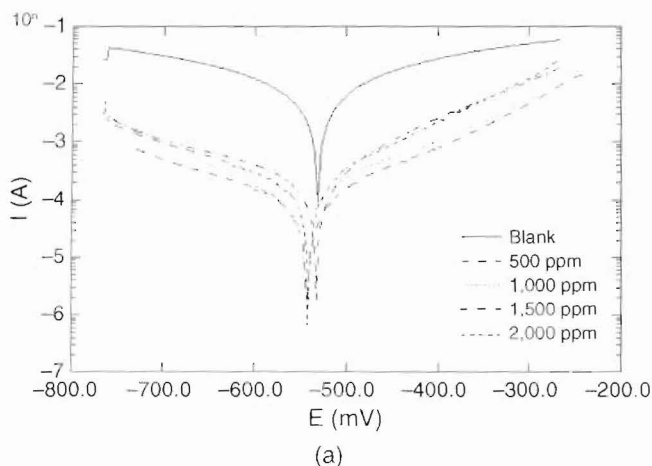


FIGURE 3. Potentiodynamic polarization curves for carbon steel in 15% HCl solution in the absence and presence of different concentrations of (a) CTCH and (b) DCTCH.

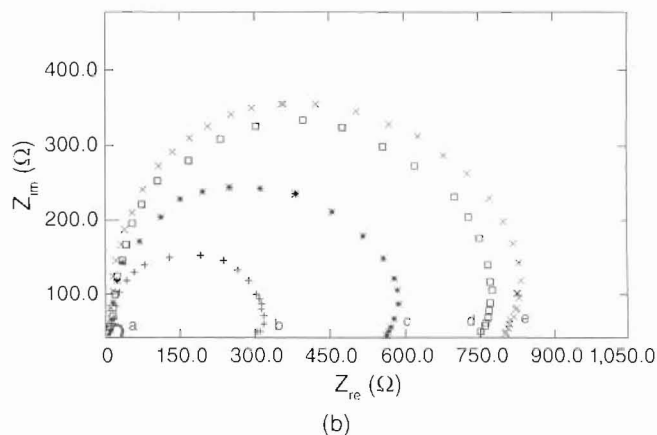
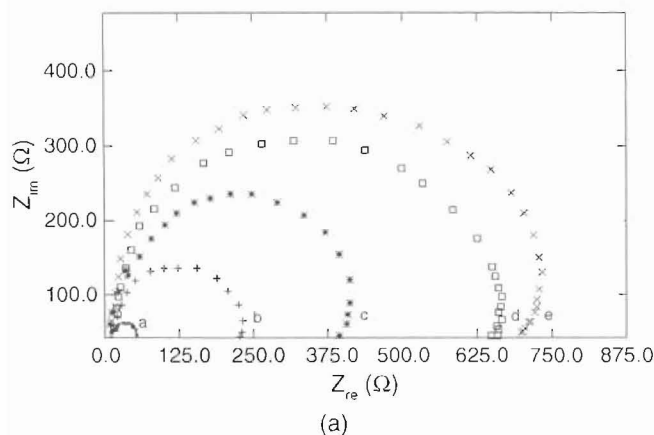


FIGURE 4. Impedance diagrams for carbon steel immersed in 15% HCl solution in the absence and presence of different concentrations of (a) CTCH and (b) DCTCH: (A) blank, (B) 500 ppm, (C) 1,000 ppm, (D) 1,500 ppm, and (E) 2,000 ppm.

An alternative formula³⁸ of the Arrhenius equation using the transition state is also given below:

$$\text{Rate} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_A^0}{R}\right) \exp\left(-\frac{\Delta H_A^0}{RT}\right) \quad (9)$$

where h is Planck's constant, N is Avogadro's number, ΔS_A^0 is the entropy of activation, and ΔH_A^0 is the enthalpy of activation. A plot of $\log (CR/T)$ vs. $1/T$ gave a straight line (Figure 7), with a slope of $(-\Delta H_A^0/2.303 R)$ and an intercept of $[\log (R/Nh) + (\Delta S/2.303R)]$, from which the values of ΔS_A^0 and ΔH_A^0 were calculated and given in Table 8. Higher values obtained for E_a and ΔH_A^0 in the presence of inhibitors indicate the higher protection efficiency. The heat of adsorption (Q_A) of the inhibitor can be calculated using Equation (10):³⁹⁻⁴⁰

$$Q_A = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \text{ kJ mol}^{-1} \quad (10)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 (K), respectively. The inhibition efficiencies of CTCH and DCTCH remains almost constant, suggesting the stability (effectiveness) of CTCH and DCTCH for a longer duration (Table 9).

Adsorption Isotherm

All adsorption isotherms are of the general form:

$$f(\theta, x) \exp(-2a\theta) = KC \quad (11)$$

where $f(\theta, x)$ is the configurational factor, which depends upon the physical model and the assumptions underlying the derivation of the isotherm.⁴¹ θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the size ratio of the

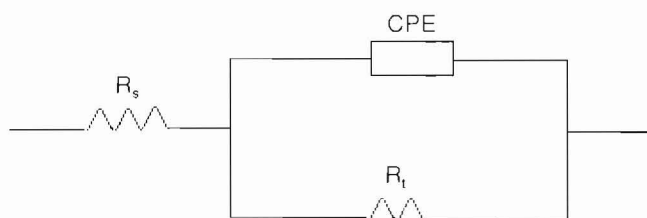


FIGURE 5. The equivalent circuit model used to fit the experimental EIS data.

TABLE 5

Impedance Parameters for Carbon Steel in 15% HCl in the Absence and Presence of Different Concentrations of Inhibitors at 30°C

Inhibitor Concentration (ppm)	R_t ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	Inhibition Efficiency (%)
Blank	29	272	—
CTCH			
500	230	34.15	87.4
1,000	402	19.61	92.8
1,500	665	12.01	95.6
2,000	696	11.35	95.8
DCTCH			
500	314	25.02	90.8
1,000	572	13.98	94.9
1,500	750	10.60	96.1
2,000	796	9.68	96.4

adsorbed organic molecule, a is the molecular interaction parameter, and K is the equilibrium constant of the adsorption process. Using the values of coverage (θ), Langmuir and Temkin isotherms were attempted for both the compounds under study. Langmuir's isotherm was first tested by plotting C/θ vs. C for all the compounds. A straight-line relationship was not obtained in both the cases, indicating that both of these

TABLE 6
Corrosion Rate and Inhibition Efficiencies for an Optimum Concentration (1,500 ppm) of Inhibitors on Corrosion of Carbon Steel in 15% HCl at Different Temperatures Obtained by Mass-Loss Method

Temperature (°C)	Blank	CTCH		DCTCH	
	CR (mmpy)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
30	311.17	5.24	98.3	2.68	99.1
50	891.27	15.05	98.3	7.69	99.1
70	2,511.87	42.35	98.3	23.62	99.1
90	6,309.57	112.11	98.2	62.01	99.0
110	14,417.00	255.96	98.2	140.31	99.0

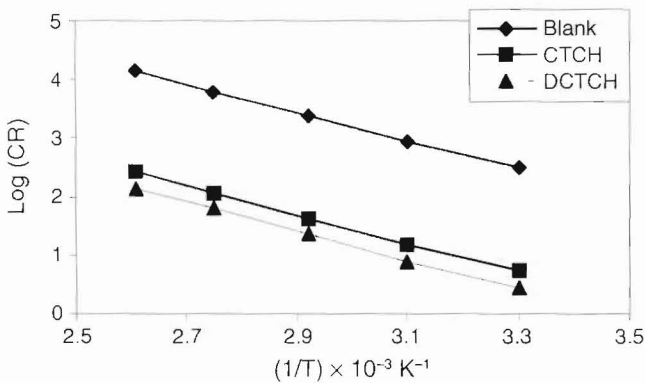


FIGURE 6. Arrhenius plots for carbon steel immersed in 15% HCl solution in the absence and presence of an optimum concentration of inhibitors.

compounds do not obey Langmuir’s isotherm. Temkin adsorption isotherm was tried by plotting θ vs. $\log C$ for all the compounds using Equation (12):

$$\exp(-2a\theta) = KC \tag{12}$$

and rearranging gives:

$$\theta = \frac{-1}{2a} \ln K - \frac{1}{2a} \ln C \tag{13}$$

A straight-line relationship was obtained by plotting θ against $\ln C$, suggesting that both of these compounds obey the Temkin adsorption isotherm. Figure 8 shows the isotherm plots for the inhibitors

studied for their adsorption on carbon steel in 15% HCl solution.

Hydrogen Permeation Studies

Permeation current vs. time curves for carbon steel in 15% HCl in the absence and presence of inhibitors are shown in Figure 9, and their corresponding values are given in Table 10. Both the compounds reduced the hydrogen permeation currents. A definite correlation existed between the extent of corrosion inhibition and the percentage decrease in hydrogen permeation current.

Surface Examination Studies

Fourier Transform Infrared Spectral Studies — The FTIR spectrum obtained for the carbon steel immersed in 15% HCl solution is shown in Figure 10(a). Spectrum of the film formed on the surface of the carbon steel immersed in 15% HCl solution containing optimum concentrations of inhibitors is given in Figures 10(b) and (c). Figures 10(b) and (c) have peaks corresponding to $>C = S-$ stretching frequency of organic compounds. This suggests that the sulfur atom is coordinated to Fe^{2+} , resulting in the formation of a Fe^{2+} – inhibitor complex on the metal surface. It is also inferred from the spectrum that $C = S$ stretching frequency decreases from $1,071\text{ cm}^{-1}$ to $1,051\text{ cm}^{-1}$, $1,072\text{ cm}^{-1}$ to $1,051\text{ cm}^{-1}$, for the studied inhibitors of CTCH and DCTCH, respectively, confirming the bond formation through the $>C = S$ group between the inhibitors and the carbon steel surface.

Ultraviolet-Visible Reflectance Studies — Inhibition of corrosion of carbon steel in 15% HCl solu-

TABLE 7
Values of Activation Energy and Free Energy of Adsorption on Corrosion of Carbon Steel in 15% HCl in the Absence and Presence of 1,500 ppm Concentration of Inhibitors at Various Temperatures

Inhibitor	E_a (kJ/mol)	$-\Delta G_a^0$ (kJ/mol)				
		30°C	50°C	70°C	90°C	110°C
Blank	46.33	—	—	—	—	—
CTCH	46.99	32.91	35.09	37.26	39.26	41.42
DCTCH	47.99	35.59	37.94	40.29	42.31	44.65

tion in the presence of inhibitors may be due to the formation of film on the metal surface. This is supported by UV-visible reflectance studies, carried out by using a spectrophotometer for carbon steel specimens immersed in 15% HCl alone and for specimens immersed in 15% HCl solution containing an optimum concentration of inhibitors. A comparison of reflectance curves drawn on a uniform scale for a polished carbon steel specimen, carbon steel specimen immersed in 15% HCl alone, and in the presence of CTCH and DCTCH are shown in Figure 11. The percentage of reflectance is maximum for a polished specimen and it has been reduced considerably in the case of specimens immersed in 15% HCl alone. A change in surface characteristics was caused by the corrosion of carbon steel specimen in 15% HCl solution alone. However, in the case of specimens immersed in 15% HCl solution containing an optimum concentration of inhibitors, reflectance has been reduced to only a very small extent. This shows that surface characteristics are not altered very much as a result of the formation of a film on the surface.

Scanning Electron Microscopy Studies — Surface examination studies through SEM at a magnification of 1,000X for the metal specimens dipped in 15% HCl at 30°C for 6 h in the absence and presence of optimum concentration of inhibitors are shown in Figures 12(a) through (c). In the absence of inhibitors, the corroded metal surface with etched grain boundaries are clearly seen (Figure 12[a]). In the case of film-forming inhibitors such as CTCH and DCTCH, the fully protected metal surface without any surface etching are observed.

DISCUSSION

Molecular structure is used to understand the inhibition efficiency of CTCH and DCTCH. Effective adsorption on the metal surface is due to the presence of N and S atoms, $-C=N$ group, and aromatic rings. DCTCH shows a slightly higher IE than CTCH. The substitution of terminal hydrogen on both sides of the hydrazino group of the TCH molecule had a dramatic influence on increasing the efficiency due to the increase of π – electron density on the ligating sulfur atom,⁴² leading to an easier electron transfer from the functional group ($C=S$) to the metal, producing

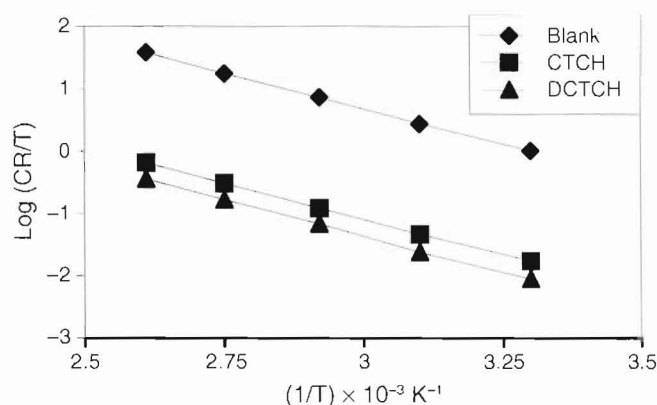


FIGURE 7. Plot of $\log (CR/T)$ vs. $1/T$ for carbon steel immersed in 15% HCl solution in the absence and presence of an optimum concentration (1,500 ppm) of inhibitors.

TABLE 8

Thermodynamic Activation Parameters for Carbon Steel in 15% HCl in the Absence and Presence of 1,500 ppm Concentration of Inhibitors

Inhibitor	ΔH_A^0 (kJ/mol)	ΔS_A^0 (J/mol K ⁻¹)	Q_A (kJ/mol)
Blank	43.56	-53.86	—
CTCH	44.00	-86.33	-0.70
DCTCH	45.02	-88.51	-1.28

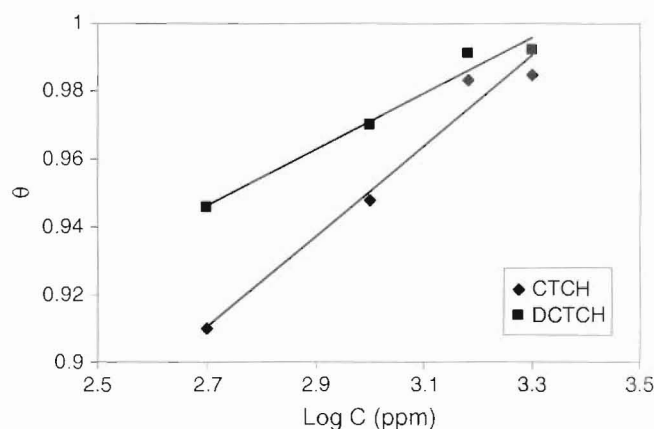


FIGURE 8. Temkin adsorption isotherm plots for the adsorption of different concentration inhibitors on the surface of carbon steel in 15% HCl solution.

TABLE 9

Effect of Immersion Time on Percentage Inhibition Efficiency of Carbon Steel in 15% HCl at 110°C in the Presence of 1,500 ppm Concentration of Inhibitors

Inhibitor	Corrosion Rate (mmpy)			Inhibition Efficiency (%)		
	Time (h)			Time (h)		
	1	3	6	1	3	6
Blank	14,417.00	9,927.18	7,269.76	—	—	—
CTCH	255.96	175.85	129.15	98.2	98.2	98.2
DCTCH	140.31	95.05	70.12	99.0	99.0	99.0

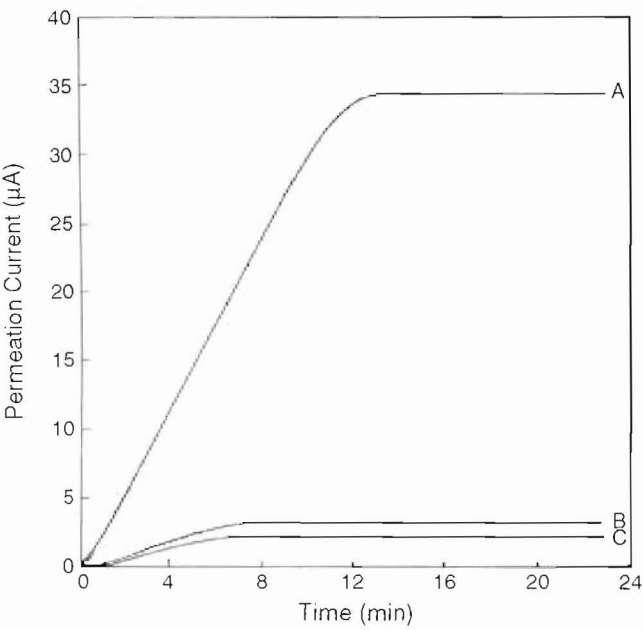


FIGURE 9. Hydrogen permeation current vs. time plots for carbon steel in 15% HCl solution in the absence and presence of an optimum concentration (1,500 ppm) of inhibitors: (A) blank, (B) CTCH, and (C) DCTCH.

greater coordinate bonding and, hence, greater adsorption and higher inhibition efficiency of DCTCH.

Temperature dependence of the IE and the comparison of the values of effective E_a of the corrosion process, both in the absence and in the presence of inhibitors, led to conclusions concerning the mechanism of the inhibiting action. The relationships between the temperature dependence of percentage inhibition efficiency of an inhibitor and the E_a found in its presence can be classified into three groups according to temperature effects.^{37,43-46}

- For inhibitors whose inhibition efficiency decreases with an increase in temperature, the value of the apparent E_a is greater than that obtained in the uninhibited solution.
- For inhibitors whose inhibition efficiency does not change with temperature, the apparent E_a does not change in the presence or absence of inhibitors.
- For inhibitors whose inhibition efficiency increases with an increase in temperature, the value of apparent E_a for the corrosion process is smaller than that obtained in the uninhibited solution.

Inspection of Tables 7 and 8 show that higher values were obtained for E_a and ΔH_A^0 in the presence of inhibitors indicating the higher protection efficiency observed for these inhibitors. There is also a parallelism between increases in inhibition efficiency and increases in E_a and ΔH_A^0 values. The low and negative values of ΔG_A^0 indicate the spontaneous adsorption of inhibitors on the surface of carbon steel. It is cur-

TABLE 10
Values of Hydrogen Permeation Current for the Corrosion of Carbon Steel in 15% HCl Alone and in the Presence of Inhibitors (1,500 ppm)

Inhibitor	Inhibitor Concentration (ppm)	Permeation Current (μA)	Decrease in Permeation Current (%)
Blank	—	34.5	—
CTCH	1,500	3.2	90.7
DCTCH	1,500	2.5	92.7

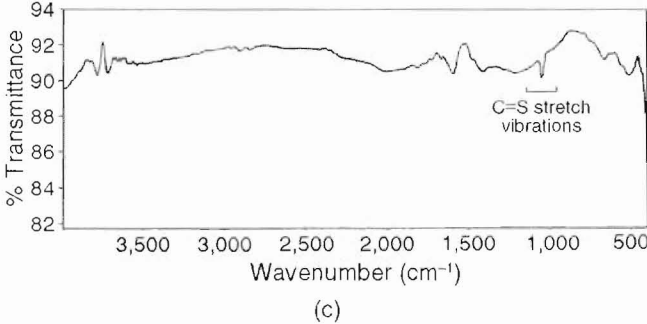
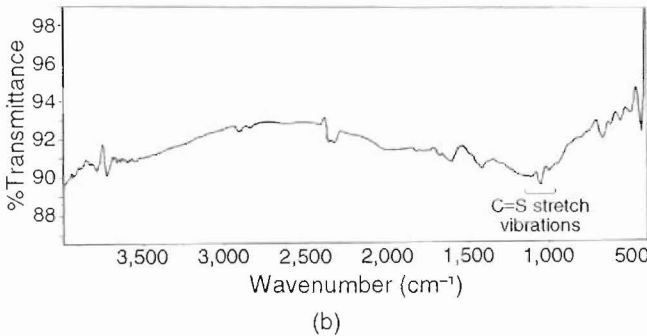
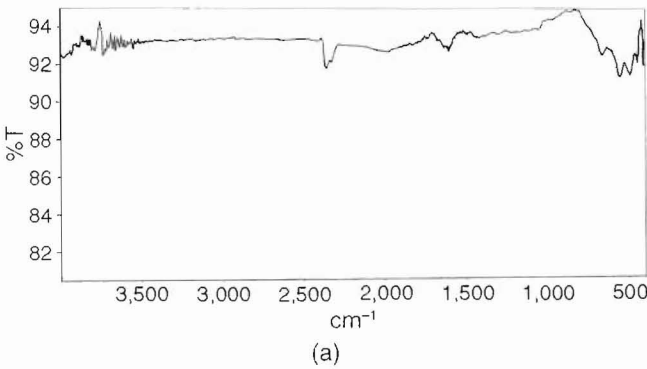


FIGURE 10. FTIR spectrum of the surface of carbon steel immersed in (a) 15% HCl solution, (b) 15% HCl solution containing 1,500 ppm of CTCH, and (c) 15% HCl solution containing 1,500 ppm of DCTCH.

rently recognized that the lowest values of ΔG_A^0 are associated with a physical adsorption process whereas values of ΔG_A^0 of the order of -42 KJ/mol or higher involve chemical adsorption.⁴⁷

The Q_A values are less negative while the free energies of adsorption are more negative in the case of

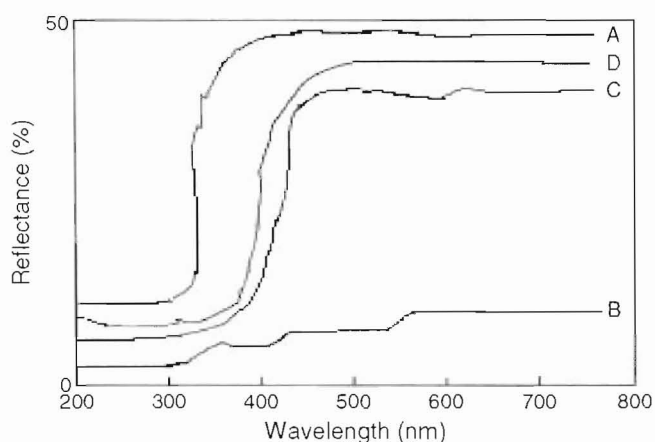
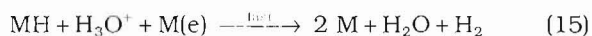


FIGURE 11. UV-visible reflectance curves for carbon steel specimens in 15% HCl solution in the absence and presence of 1,500 ppm of inhibitors: (A) polished, (B) blank, (C) CTCH, and (D) DCTCH.

inhibitors of CTCH and DCTCH. This suggests that there is a strong interaction of the inhibitor molecules with the metal surface, resulting in the spontaneous adsorption.

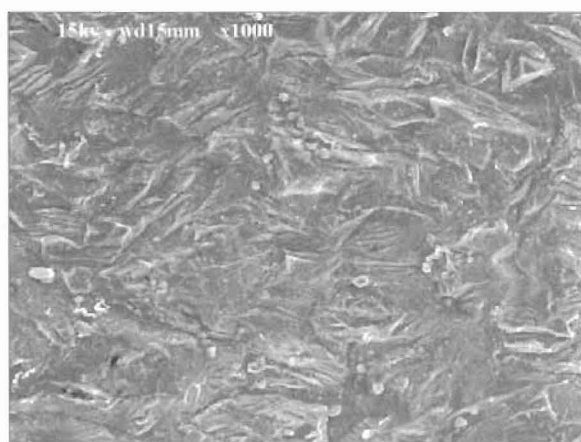
The reason for the reduced hydrogen permeation current in the presence of the inhibitors can be attributed to the slow discharge step followed by a fast electrolytic desorption step.



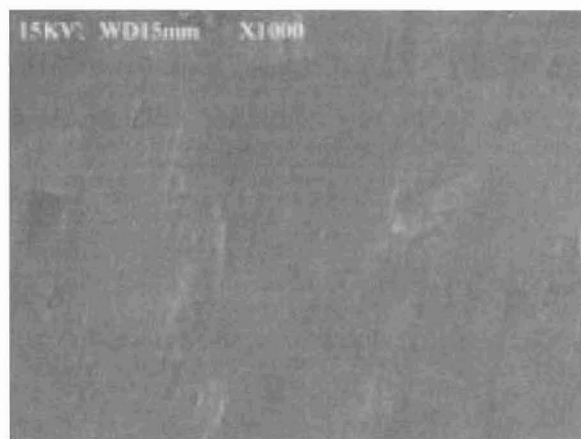
This sequence leads to lesser surface concentration of the adsorbed hydrogen atoms and the consequent reduction in the permeation currents.⁴⁸ Figure 13 shows the possible mechanism of hydrogen evolution and penetration in the absence and presence of inhibitors. Essentially, in the absence of the inhibitor, the hydrogen evolution reaction (HER) involves the hydrogen ions discharge on the steel surface followed by two reactions that correspond to hydrogen desorption (chemical or electrochemical recombination) and hydrogen absorption within the metal lattice (Figure 13[a]). Nevertheless, if there are adsorbed molecules of the organic compound in the steel surface, the recombination reaction of electrochemical-reduced hydrogen could be inhibited. Therefore, adsorbed atomic hydrogen activity may increase and as a result more hydrogen penetration was promoted into the steel (Figure 13[b]).

CONCLUSIONS

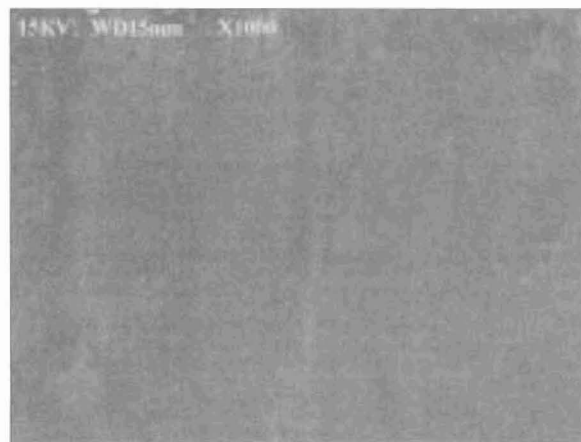
- ❖ CTCH and DCTCH were effective acidizing inhibitors for carbon steel in 15% HCl.
- ❖ The polarization curves revealed that the investigated compounds retarded the cathodic and anodic



(a)



(b)



(c)

FIGURE 12. SEM photograph of carbon steel immersed in (a) 15% HCl solution, (b) 15% HCl solution containing 1,500 ppm of CTCH, and (c) 15% HCl solution containing 1,500 ppm of DCTCH.

corrosion reactions. These results indicated that inhibitors exhibited cathodic and anodic inhibition effects. Therefore, inhibitors can be classified as an inhibitor of relatively mixed effect (anodic/cathodic inhibition).

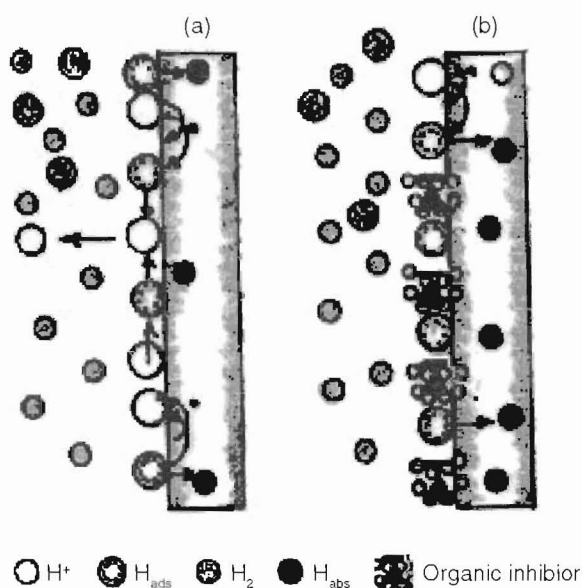


FIGURE 13. Schematic representation of HER: (a) in the absence of organic inhibitor and (b) in the presence of organic inhibitor.

- ❖ The adsorption of these compounds on a carbon steel surface in 15% HCl solution obeyed the Temkin adsorption isotherm.
- ❖ The FTIR, UV-visible reflectance spectra, and SEM analysis confirmed the highly protective nature of the metal surface by the inhibitors.

REFERENCES

1. G. Schmitt, *Br. Corros. J.* 19 (1984): p. 165.
2. F.A. Brudsi, T.W. Blecks, T.E. Sullivan, "Solution and Method for Selectivity Stripping Alloys (containing Nickel with Gold, Phosphorus, or Chromium from Stainless Steel and Related Nickel-Based Alloys)," U.S. Patent 4302246, 1981.
3. T.M. Muzyezko, S. Share, J.A. Martin, U.S. Patent 3105106, 1972.
4. B.F. Mago, "Poly(alkylene Oxide) Compositions," U.S. Patent 426,3167, 1987.
5. I.L. Rosenfeld, *Corrosion Inhibitors* (New York, NY: McGraw-Hill 1981), p. 98.
6. W.W. Frenier, F.B. Growcock, V.R. Lopp, *Corrosion* 44 (1988): p. 590.
7. W.W. Frenier, European Patent 047400, 1972.
8. F.B. Growcock, W.W. Frenier, P.A. Andreozzi, *Corrosion* 45 (1989): p. 1,007.
9. A. Cizek, "Corrosion Inhibition Using Mercury Intensifiers," U.S. Patent 4997040, 1991.
10. R.R. Annand, A.E. Woodson, "Inhibiting Acidic Corrosion of Ferrous Metals with Polyquaternary Amino Polymers," U.S. Patent 3982894, 1976.
11. K.D. Neemla, A. Jayaraman, R.C. Saxena, A.K. Agarwal, R. Krishna, *Bull. Electrochem.* 5 (1989): p. 250.
12. R.F. Monroe, C.H. Kucera, B.D. Oates, "Composition for Inhibiting Corrosion," U.S. Patent, 3007454, 1963.
13. M.A. Quraishi, R. Sardar, *Corrosion* 58 (2002): p. 103.
14. M.A. Quraishi, R. Sardar, *Corrosion* 58 (2002): p. 748.
15. L. Wang, *Corros. Sci.* 43 (2001): p. 2,281.
16. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.* 45 (2003): p. 33.
17. F. Bentiss, M. Lebrini, H. Vezin, M. Lagrenee, *Mater. Chem. Phys.* 87 (2004): p. 18.
18. P. Morales-Gil, G. Negron-Silva, M. Romero-Romo, C. Angeles-Chavez, Palomar-Pardave, *Electrochim. Acta* 49 (2004): p. 4,733.
19. E.A. Noor, *Corros. Sci.* 47 (2005): p. 33.
20. Z. Ait Chikh, D. Chebabe, A. Dermaj, N. Hajjaji, A. Srhiri, M.F. Montemor, M.G.S. Ferreira, A.C. Bastos, *Corros. Sci.* 47 (2005): p. 447.
21. M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, *Corros. Sci.* 47 (2005): p. 485.
22. S.S. Abdel-Rehim, K.F. Khaled, N.S. Abd-Elshafi, *Electrochim. Acta* 51 (2006): p. 3,269.
23. L. Wang, G.-J. Yin, J.-G. Yin, *Corros. Sci.* 43 (2001): p. 1,197.
24. D.D.N. Singh, A.K. Dey, *Corrosion* 49 (1993): p. 594.
25. ASTM G1-03, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens" (West Conshohocken, PA: ASTM International, 2003).
26. A. Subramania, N.T. Kalyana Sundaram, A.R. Sathya Priya, T. Vasudevan, *J. Appl. Electrochem.* 34 (2004): p. 693.
27. A. Subramanian, A.R. Sathya Priya, N.T. Kalyana Sundaram, T. Vasudevan, *Bull. Electrochem.* 20 (2004): p. 13.
28. A.E.I-Sayed, *Corros. Prev. Control* 43 (1996): p. 29.
29. I. Sekine, M. Sabongi, H. Hagiuda, T. Oshibe, M. Yuasa, T. Zmahoma, Y. Shibata, T. Wake, *J. Electrochem. Soc.* 139 (1992): p. 3,167.
30. F. Mansfeld, *Corrosion* 36 (1981): p. 301.
31. F. Mansfeld, M.W. Kendig, W.J. Lorenz, *J. Electrochem. Soc.* 132 (1985): p. 290.
32. T. Tsuru, S. Haruyama, *Boshoku Gijutsu (Corros. Eng.)* 27 (1978): p. 573.
33. E. McCafferty, N. Hackerman, *J. Electrochem. Soc.* 119 (1972): p. 146.
34. M.A.B. Christopher, A.R.G. Isabel, P.S.M. Jenny, *Corros. Sci.* 36 (1994): p. 15.
35. C.B. Breslin, W.M. Camol, *Corros. Sci.* 33 (1993): p. 327.
36. M.G.A. Khedr, M.S. Lashien, *Corros. Sci.* 33 (1992): p. 137.
37. T. Szauer, A. Brandt, *Electrochim. Acta* 26 (1981): p. 1,209.
38. S.S.A. Rehim, H.H. Hassan, A.A. Mohammed, *Mater. Chem. Phys.* 70 (2001): p. 64.
39. T.P. Hoar, R.D. Holiday, *J. Appl. Chem.* 3 (1963): p. 503.
40. E.E. Oguzie, *Mater. Chem. Phys.* 87 (2004): p. 212.
41. B.G. Ateya, B.E.El-Anadoul, F.M.El. Nizamy, *Corros. Sci.* 24 (1984): p. 509.
42. E. Khamis, M.A. Ameer, N.M. Al Andis, G. Al-Senani, *Corrosion* 56 (2000): p. 127.
43. Z.A.Foroulis, Proc. 6th European Symp. on Corrosion Inhibitors (Ferrara, Italy, 1985), p. 48.
44. Q.J. Slaiman, H.M.Al. Saaty, Proc. 7th European Symp. on Corrosion Inhibitors (Ferrara, Italy, 1990), p. 189.
45. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.* 45 (2003): p. 33.
46. O. Radovici, Proc. 2nd European Symp. on Corrosion Inhibitors (Ferrara, Italy, 1965), p. 178.
47. Emranuzzaman, T. Kumar, S. Vishwanathan, G. Udayabhanu, *Corros. Eng. Sci. Technol.* 39 (2004): p. 327.
48. R. Iyer, H. Pickering, *J. Electrochem. Soc.* 136 (1989): p. 2,463.