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Corrosion Inhibition Studies by Thiophene Derivative in the Presence of Surfactants on Carbon Steel in Hydrochloric Acid

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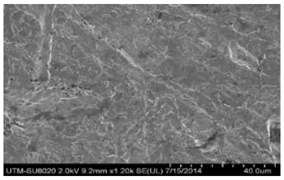
GRAPHICAL ABSTRACT



SEM image of carbon steel immersed in HCl + CTAB + methyl thiphene

ABSTRACT

In this work, the inhibition efficiency of three types of surfactants, namely sodium lauryl sulfate (SLS), cetyl trimethylammonium bromide (CTAB) and Polysorbate 80 (Tween 80), in the absence and presence of the thiophene derivative (2-methyl thiophene) on carbon steel in 2 M HCl was investigated at different concentrations, immersion times and temperatures. The studies were carried out through the weight loss and potentiodynamic polarization techniques. The inhibition efficiency increased with addition of the thiophene derivative to the corrosive media containing surfactants. It was found that the adsorption of the inhibitors on carbon steel surface followed the Langmuir adsorption isotherm. The morphology test was done on the carbon steel surface before and after placing in the inhibitor solutions using scanning electron microscopy (SEM). The results showed that the order of inhibition efficiency is SLS > CTAB > Tween 80.

Keywords: surfactant, corrosion, carbon steel, thiophene derivative, Langmuir adsorption

1. INTRODUCTION

Corrosion is a common process when it comes into contact with acidic solutions. It is known as an electrochemical reaction based on the universal laws of nature. The most important thing is how to reduce the corrosion rate. Carbon steel have been used in many industrial applications such as pipelines, tanks, casings, tubing and other equipment [1, 2]. Many studies show that surfactants have been used as a corrosion inhibition in acidic solutions [3-6]. In addition, organic compounds have been widely used as a corrosion inhibitor. Thiophene is one of the organic compounds that has an aromatic ring containing a sulfur atom. It can donate a lone pair of electrons to the d-orbital of metal surface, hence increase the inhibition efficiency [7].

Thus, in this study, three surfactants, namely sodium lauryl sulfate (SLS), cetyl trimethylammonium bromide (CTAB) and Tween 80 were used as corrosion inhibitors on carbon steel in 2 M HCl solution. Whereas, thiophene derivative was added to enhance the inhibition efficiency. The efficiency of surfactants were compared. The weight loss method and potentiodynamic polarization techniques were used to measure the inhibition efficiency. Surface morphology of carbon steel in acidic solution was imaged using a scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1 Test Solutions

A solution of 2 M HCl was prepared by diluting analytical grade 37% HCl with distilled water. Stock solutions of thiophene derivative and surfactants (SLS, CTAB and Tween 80) were prepared by diluting them with distilled water. The molarity of the thiophene derivative was kept constant at 2×10^{-5} M, whereas, the surfactant solutions were prepared in the range of 2×10^{-5} M to 5×10^{-3} M and diluted in 2 M HCl.

2.2 Weight Loss Technique

The experiments were performed with specimens having an area of 4 cm^2 and thickness 0.2 mm which were cut from a steel sheet. In order to obtain a smooth surface, the test specimens were abraded with an emery paper, followed by cleaning with ultrasonic degreasing in acetone and finally rinsed with distilled water. The weight loss method was carried out by immersing the test specimens in 100 mL acid solutions with and without the addition of the thiophene derivative for 2-6 h at

333-363 K. The specimens were weighed before and after the immersion. Triplicate sp7676ecimens were exposed for each condition and the mean weight losses was reported. The corrosion rates and inhibition efficiencies were calculated using the following equation:

$$\Delta W = (W_1 - W_2) / A \qquad (1)$$

$$I\% = ((\Delta CR - \Delta CR_i) / CR) \times 100 \qquad (2)$$

Where W_1 and W_2 are the weight of specimens before and after the reaction, A is the surface area in cm^2 and ΔCR and ΔCR_i are the corrosion rate in the absence and presence of the inhibitors, respectively.

2.3 Electrochemical Technique

For electrochemical measurements, an AUTOLAB PGP 201 potentiostat/galvanostat in a three-electrode arrangement was used. A platinum electrode and saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. Carbon steel specimen as a working electrode was pressure-fitted into a holder exposing only 1 cm^2 surface to the solution. The working electrode was immersed for 30 min at 303 K in an experimental solution before each electrochemical measurement was performed to obtain a stable open circuit potential (OCP).

The potential applied was from a low potential of -250 to +250 mV with a scan rate 2 mV min^{-1}. The current-potential curve was recorded by changing the electrode potential automatically. GPES 4.9 software was used to analyze polarization data in order to obtain the corrosion parameters including: corrosion potential (E_{corr}), polarization resistance (R_p) and corrosion current density (i_{corr}). Both of cathodic and anodic polarization curves can be determined through this technique. Corrosion currents can be calculated from extrapolation of Tafel lines to pre-determined open circuit potential [8]. From the obtained parameters, the inhibition efficiency were calculated using the relationship [9]:

$$I\% = ((i_{\mathrm{corr}} - i'_{\mathrm{corr}}) / i_{\mathrm{corr}}) \times 100 \qquad (3)$$

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and presence of the inhibitors, respectively.

2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an instrument that uses an electron beam to examine material on a very fine scale. It gives information on the surface topography and composition of metal used in absence and presence of inhibitors. The sample was fixed on a carbon tape and coated with platinum prior to imaging using JEOL JSM-638 OLA SEM.

3. RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

3.1.1 Effect of Inhibitor Concentration

The influence of inhibitor dose on the inhibition efficiency of the surfactant was showed in Table 1. As the surfactant concentration increased, the inhibition efficiency increased, but the corrosion rate decreased. In brief, increasing of surfactant concentration will increase a surface coverage of inhibitors on the metal surface. The large surface coverage caused a formation of protective layer on the surface and evaded corrosion-active species from reaching the surface. Additionally, it can avoid the corrosion process or slow it down [8]. Surfactants of CTAB and SLS in the presence of methyl thiophene reached a maximum efficiency, which is 87.80 % at an optimum dose of 1×10^{-3} M CTAB and 5×10^{-3} M SLS. The results indicated that the inhibitor efficiency was clearly dependent on its concentration.

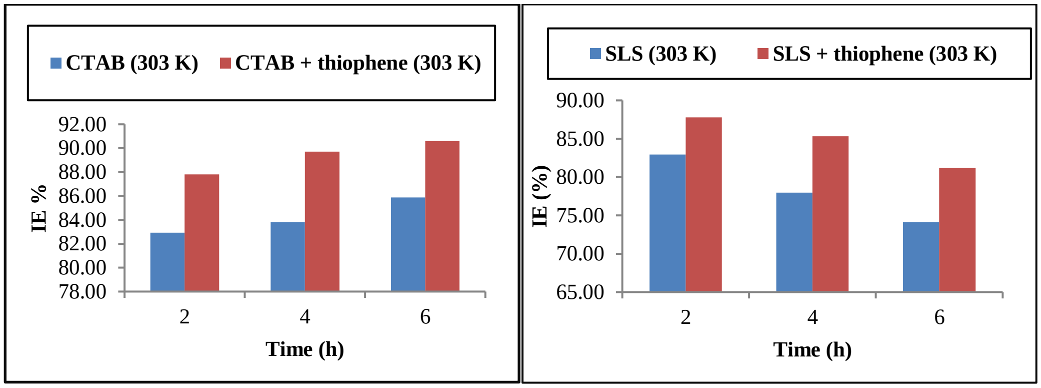
3.1.2 Effect of Exposure Time

Figure 1 showed the relationship between the exposure time (min) and the inhibition efficiency on carbon steel at optimum concentration of surfactants (1×10^{-3} M of CTAB and 5×10^{-3} M of SLS and Tween 80), in the absence and presence of 2×10^{-5} M methyl thiophene at 303 K. It showed that an extended time of exposure of carbon steel to the CTAB solution both in the absence and presence of the thiophene derivative in the aggressive medium led to an increase in inhibition efficiency. However, with increasing of immersion time of carbon steel in SLS surfactant, the efficiency was decreased. Meanwhile, the inhibition efficiencies of Tween 80 increased initially during immersion but decreased after 4 hours.

With the exposure time of 2-6 hours, 82.9 % and 87.8 % of inhibition efficiency of CTAB at optimum concentration (1×10^{-3} M) increased to 85.9 % and 90.6 % in the absence and presence of 2-methyl thiophene, respectively. Whereas, the efficiencies of SLS at an optimum concentration (5×10^{-3} M) was decreased from 82.9 % and 87.8 % to 74.1 % and 81.2 % in the absence and presence of thiophene, respectively. Efficiencies of Tween 80 increased from 78.1 % and 80.5 % to 82.4 % and 85.3 % after 2 hours but then decreased to 81.2 % and 82.4 % after 4 hours of immersion time.

Table 1 Corrosion inhibition efficiencies and activation energies of the inhibitors at 2 h of immersion time at 303 K

Inhibitor	Concentration (M)	*CR* (mg cm^{-2} h^{-1})	θ	Inhibition Efficiency (%)	Activation Energy, E_{ads} (kJ mol^{-1})
Blank	0	2.05	0	0	53.90
CTAB	2×10^{-5}	0.60	0.71	70.73	42.45
	1×10^{-4}	0.50	0.76	75.61	34.24
	2×10^{-4}	0.40	0.80	80.49	35.85
	1×10^{-3}	0.35	0.83	82.93	33.93
CTAB + thiophene	2×10^{-5}	0.55	0.73	73.17	43.02
	1×10^{-4}	0.45	0.78	78.05	33.69
	2×10^{-4}	0.30	0.85	85.37	34.89
	1×10^{-3}	0.25	0.88	87.80	36.36
SLS	1×10^{-4}	0.60	0.71	70.73	58.14
	5×10^{-4}	0.55	0.73	73.17	56.53
	1×10^{-3}	0.45	0.78	78.05	55.60
	5×10^{-3}	0.35	0.83	82.93	55.60
SLS + thiophene	1×10^{-4}	0.45	0.77	76.83	58.41
	5×10^{-4}	0.40	0.80	80.49	54.93
	1×10^{-3}	0.35	0.83	82.93	53.72
	5×10^{-3}	0.25	0.88	87.80	56.88
Tween 80	1×10^{-4}	0.60	0.71	70.73	50.96
	5×10^{-4}	0.55	0.73	73.17	48.72
	1×10^{-3}	0.50	0.76	75.61	44.85
	5×10^{-3}	0.45	0.78	78.05	34.96
Tween 80 + thiophene	1×10^{-4}	0.55	0.73	73.17	52.00
	5×10^{-4}	0.50	0.76	75.61	47.59
	1×10^{-3}	0.45	0.78	78.05	45.62
	5×10^{-3}	0.40	0.80	80.49	34.33



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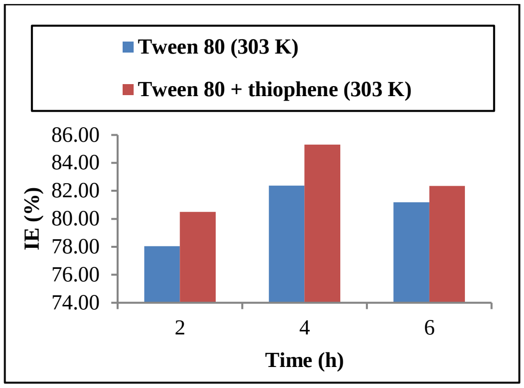
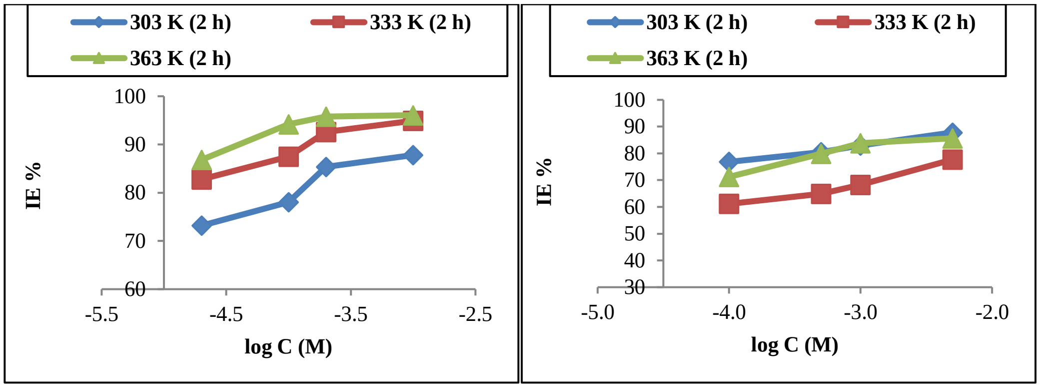


(c)

Figure 1 Effect of exposure time on the inhibition efficiency of (a) CTAB, (b) SLS and (c) Tween 80, in 2 M HCl in absence and presence of 2 × 10^{-5} M of methyl thiophene at 303 K.

3.1.3 Effect of Temperature

In general, the corrosion rate is affected by the temperature. In order to study the effect of temperature on corrosion rate of metal, an experiment was done by immersing the carbon steel in 2 M HCl at various temperatures between 303-363 K through a weight loss method. At 303-363 K, the inhibition efficiencies of CTAB and Tween 80 inhibitors in the absence and presence of methyl thiophene increased (Figure 2). It shows that the CTAB and Tween 80 surfactants were adsorbed on carbon steel surface by chemical adsorption. However, for the SLS inhibitor, the inhibition efficiency decreased from the temperature range 303-333 K but increased when the temperature reached at 363 K. In fact, at temperature 303 K and 363 K, the percentages of inhibition efficiency of SLS in the presence of methyl thiophene are similar. This can be seen in Figure 2. It means, the inhibitor was adsorbed physically onto the metal surface at the beginning and it turned to be chemically adsorbed when the temperature was elevated. From the results obtained, it shows that the inhibitors used in this study have a mixed physical and chemical adsorption [10]. At low temperature, SLS showed a good efficiency whereas, at high temperature, the increasing solubility of CTAB and Tween 80 prevented the corrosive active agent from reaching the metal surface.



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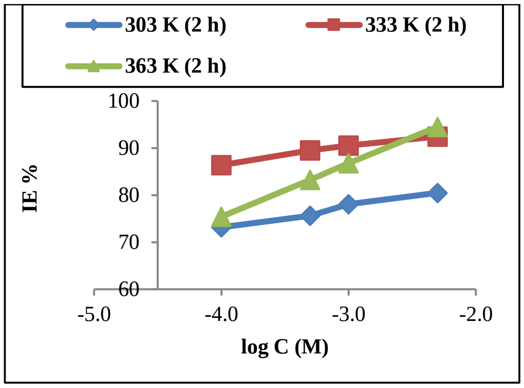


(c)

Figure 2 Effect of temperature on the inhibition efficiency for carbon steel in 2 M HCl in presence of 2 × 10^{-5} M of thiophene derivative and various concentrations of (a) CTAB, (b) SLS and (c) Tween 80, at 2 hours immersion time.

Figure 3 showed a plot of log corrosion rate (k) against 1/T for carbon steel in 2 M HCl in the present of methyl thiophene and various concentrations of CTAB where a straight line occurred. The three surfactants studied showed a similar behaviour. Arrhenius parameters were regarded as purely empirical quantities that enable us to discuss the corrosion rate as a function of temperature. One of these parameters is an activation energy that can be calculated from a slope of the straight line. The negative slope of E_a shows the adsorption of inhibitors on the surface metal [6]. Arrhenius equation can be expressed as:

$$\log k = (AE_a) / (2.303RT) \tag{14}$$

Where k is the corrosion rate of metal, A is the pre-exponential coefficient, E_a is the activation energy, T is the absolute temperature and R is the universal gas constant. The values of E_a on protected and unprotected of carbon steel in 2 M HCl was calculated and presented in Table 1. It showed that E_a values obtained in presence of inhibitors were smaller than that of the blank solution (2 M HCl) in the early immersion time. After some time, the values became higher than those in free acid solution indicating that physical and chemical adsorption may occur. In fact, when the E_a value increases, the energy barrier will increase accordingly. These phenomena will prevent the corrosion active agent from adsorbing onto the metal surface.

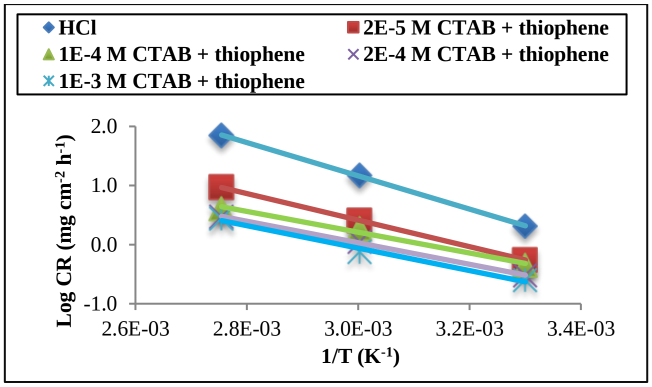


Figure 3 The relationship between log CR and $1/T$ for carbon steel dissolution in different concentrations of CTAB in presence of 2 × 10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time.

Moreover, from a transition state equation:

$$A + B \leftrightharpoons AB \rightarrow C \qquad (15)$$

$$[11] = K\,[12]\,[13] \qquad (16)$$

Thus, it can be written as:

$$\text{Rate} = k\,[11] \qquad (17)$$

By using the Van't Hoff equation, Arrhenius equation can be converted to an alternative equation as:

$$CR = RT/Nh \exp(\Delta S_{ads}/R) \exp(-\Delta H_{ads}/RT) \qquad (18)$$

where CR is the corrosion rate, N is the Avogadro's constant, h is the Plank's constant, ΔS_{ads} is the entropy of activation energy and ΔH_{ads} is the enthalpy of activation and R is the universal gas constant. In order to find ΔH_{ads}, a graph was plot between log CR/T and $1/T$ in presence of the thiophene derivative containing CTAB as seen in Figure 4. A straight line emerged and ΔH_{ads} can be calculated from the slope ($-\Delta H_{ads}/2.303R$). The calculated values of ΔH_{ads} are shown in Table 2. Consequently, the positive value of ΔH_{ads} proved that the adsorption of inhibitors onto the metal surface underwent an endothermic process. In effect, inhibition efficiency increased at high temperature.

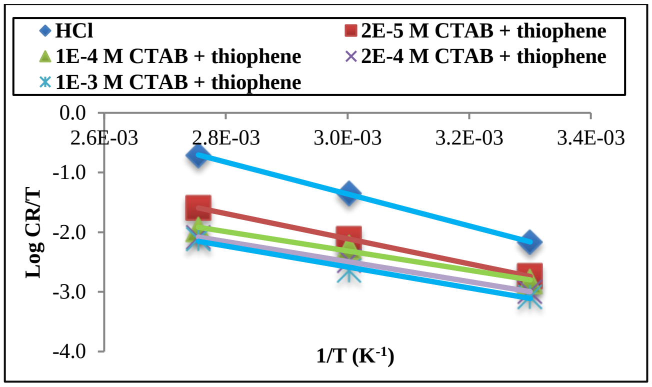


Figure 4 The relationship between log (CR/T) and $1/T$ for carbon steel dissolution in different concentrations of CTAB in presence of 2×10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time.

3.2 Adsorption Isotherm

The interaction which occurred between the metal surface and the inhibitor can be seen through a study of adsorption isotherm [10, 12]. In order to study the isotherm, the degree of surface coverage (θ) can be calculated using the equation:

$$\theta = (\Delta CR - \Delta CR_i) / \Delta CR \qquad (19)$$

$$C/\theta = 1/K_{ads} + C \qquad (20)$$

Where ΔCR and ΔCr_i are the corrosion rate in the absence and presence of the inhibitors, respectively, C is the inhibitor concentration, θ is the degree of surface coverage and K_{ads} is the standard adsorption equilibrium constant. Surface coverage values were tested graphically by plotting C/θ versus C. It was performed under different temperature through the weight loss method. Since the graph showed a straight line, the adsorption isotherm of inhibitors used obeys the Langmuir isotherm (Figure 5). All the surfactants (CTAB/SLS/Tween 80) showed a similar behaviour. Moreover, this result showed a good agreement with the isotherm in the potentiodynamic polarization technique (Figure 7). Since the environment was not exactly the same for both techniques, the correlation coefficient (r^2) values were not exactly the same. In conclusion, the protection layer that formed led to a monolayer. Furthermore, the adsorption cannot proceed above the monolayer coverage.

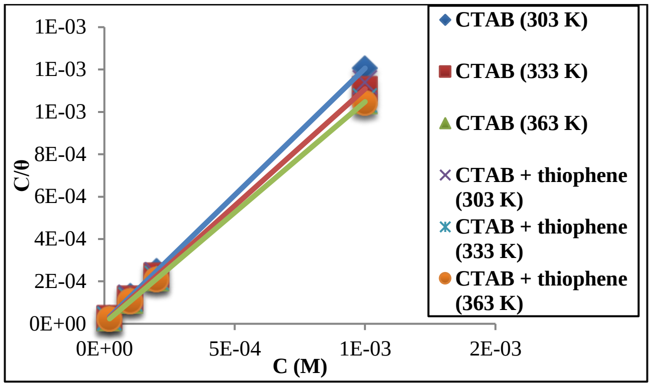


Figure 5 Langmuir adsorption model of various concentrations of CTAB in absence and presence of methyl thiophene by weight loss method on the carbon steel in 2 M HCl at 2 hours immersion times.

Table 2 Adsorption parameters obtained from the weight loss method at 2 hours immersion time

Inhibitor	**Concentration (M)**	**ΔH^{o}_{ads} (kJ mol^{-1})**	**ΔS^{o}_{ads} (J mol^{-1} K^{-1})**
Blank	-	51.15	-161.27
CTAB	2×10^{-5}	39.70	-258.31
	1×10^{-4}	31.49	-400.36
	2×10^{-4}	33.10	-376.27
	1×10^{-3}	31.18	-435.17
CTAB + thiophene	2×10^{-5}	40.27	-255.48
	1×10^{-4}	30.94	-423.49
	2×10^{-4}	32.14	-421.89
	1×10^{-3}	33.61	-399.91
SLS	1×10^{-4}	55.39	-155.89
	5×10^{-4}	53.78	-163.34
	1×10^{-3}	52.85	-169.33
	5×10^{-3}	52.85	-172.51
SLS + thiophene	1×10^{-4}	55.66	-157.14
	5×10^{-4}	52.18	-173.18
	1×10^{-3}	50.97	-180.65
	5×10^{-3}	54.13	-169.77
Tween 80	1×10^{-4}	48.21	-193.48
	5×10^{-4}	45.97	-209.37
	1×10^{-3}	42.10	-242.03
	5×10^{-3}	32.21	-396.97
Tween 80 + thiophene	1×10^{-4}	49.25	-189.19
	5×10^{-4}	44.84	-220.39
	1×10^{-3}	42.87	-238.80
	5×10^{-3}	31.58	-423.01

Standard adsorption equilibrium constant (K_{ads}) was related to a standard free energy of adsorption (ΔG^{o}_{ads}) by the following equation:

$$-\Delta G^{o}_{ads} = RT \ln(55.5\, K_{ads}) \qquad (21)$$

$$K_{ads} = \theta / C (1- \theta) \qquad (22)$$

Where R was the universal constant, T was the absolute temperature and the value 55.5 was the molar concentration of water in solution. By using equation 21, the standard free energy of adsorption (ΔG^o_{ads}) for SLS, CTAB and Tween 80 in the absence and presence of methyl thiophene were calculated (Table 3-5). The values of ΔG^o_{ads} which was between -30 kJ mol^{-1} and -50 kJ mol^{-1} indicated that the adsorption of inhibitors onto the metal surface was a mixed of physical and chemical adsorption since values of ΔG^o_{ads} around -20 kJ mol^{-1} or lower and -40 kJ mol^{-1} or higher were followed by the physisorption and chemisorption, respectively [10]. Therefore, inhibition efficiency increased at high temperature. Higher ΔG^o_{ads} values have showed a strong interaction and higher inhibition efficiency [10, 14]. The adsorption entropies (ΔS^o_{ads}) and adsorption enthalpies (ΔH^o_{ads}) are given in table 3. Entropy of inhibitor adsorption (ΔS^o_{ads}) was calculated using the equation:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (23)$$

The negative value of ΔS^o_{ads} proved that the adsorption process between inhibitor and metal surface is believed to be an exothermic process.

Table 3 The thermodynamic parameters for adsorption of the CTAB in the absence and presence of thiophene

Inhibitor	**Time (h)**	**Temperature (K)**	**Slope**	**Intercept**	**$K_{ads} \times 10^{-4}$ (M^{-1})**	**ΔG^0_{ads} (kJ mol^{-1})**
CTAB	2	303	1.1979	8×10^{-6}	12.50	-39.69
		333	1.1035	5×10^{-6}	20.00	-44.92
		363	1.0452	3×10^{-6}	33.33	-50.50
CTAB + thiophene		303	1.1299	9×10^{-6}	11.11	-39.39
		333	1.0473	6×10^{-6}	16.67	-44.41
		363	1.0388	2×10^{-6}	50.00	-51.73
CTAB	4	303	1.1893	4×10^{-6}	25.00	-41.43
		333	1.1387	7×10^{-6}	14.29	-43.98
		363	1.0864	9×10^{-6}	11.11	-47.19
CTAB + thiophene		303	1.108	7×10^{-6}	14.29	-40.02
		333	1.0701	7×10^{-6}	14.29	-43.98
		363	1.0805	7×10^{-6}	14.29	-47.95
CTAB	6	303	1.1612	3×10^{-6}	33.33	-42.16
		333	1.1661	1×10^{-5}	10.00	-43.00
		363	1.1576	2×10^{-5}	5.00	-44.78
CTAB + thiophene		303	1.0987	6×10^{-6}	16.67	-40.41
		333	1.1011	1×10^{-5}	10.00	-43.00
		363	1.1137	1×10^{-5}	10.00	-46.87

Table 4 The thermodynamic parameters adsorption of the SLS in the absence and presence of thiophene

Inhibitor	**Time (h)**	**Temperature (K)**	**Slope**	**Intercept**	**$K_{ads} \times 10^{-4}$ (M^{-1})**	**ΔG^0_{ads} (kJ mol^{-1})**
SLS		303	1.1946	6×10^{-5}	1.67	-34.61
		333	1.3052	0.0001	1.00	-36.62
		363	1.2144	9×10^{-5}	1.11	-40.24
SLS + thiophene	2	303	1.1305	5×10^{-5}	2.00	-35.07
		333	1.2665	0.0001	1.00	-36.62
		363	1.1612	3×10^{-5}	3.33	-43.55
SLS		303	1.2579	0.0001	1.00	-33.32
		333	1.7102	0.0001	1.00	-36.62
		363	1.3932	0.0002	0.50	-37.83
SLS + thiophene	4	303	1.1542	1×10^{-4}	1.00	-33.32
		333	1.4176	0.0002	0.50	-34.70
		363	1.2860	0.0001	1.00	-39.92
SLS		303	1.3147	0.0002	0.50	-31.58
		333	1.8236	0.0002	0.50	-34.70
		363	1.5451	0.0001	1.00	-39.92
SLS + thiophene	6	303	1.2134	1×10^{-4}	1.00	-33.32
		333	1.5063	0.0003	0.33	-33.58
		363	1.3843	0.0001	1.00	-39.92

Table 5 The thermodynamic parameters adsorption of the Tween 80 in absence and presence of thiophene.

Inhibitor	**Time (h)**	**Temperature (K)**	**Slope**	**Intercept**	**$K_{ads} \times 10^{-4}$ (M^{-1})**	**ΔG^0_{ads} (kJ mol^{-1})**
Tween 80		303	1.2750	3×10^{-5}	3.33	-36.36
		333	1.0954	3×10^{-5}	3.33	-39.95
		363	1.0555	7×10^{-5}	1.43	-41.00
Tween 80 + thiophene	2	303	1.2365	3×10^{-5}	3.33	-36.36
		333	1.0786	2×10^{-5}	5.00	-41.08
		363	1.0460	7×10^{-5}	1.43	-41.00
Tween 80		303	1.2104	2×10^{-5}	5.00	-37.38
		333	1.1049	4×10^{-5}	2.50	-39.16
		363	1.0748	0.0001	1.00	-39.92
Tween 80 + thiophene	4	303	1.1668	3×10^{-5}	3.33	-36.36
		333	1.0652	4×10^{-5}	2.50	-39.16
		363	1.0486	0.0001	1.00	-39.92
Tween 80		303	1.2273	2×10^{-5}	5.00	-37.38
		333	1.0723	4×10^{-5}	2.50	-39.16
		363	1.1039	0.0001	1.00	-39.92
Tween 80 + thiophene	6	303	1.2117	1×10^{-5}	10.00	-39.12
		333	1.0660	3×10^{-5}	3.33	-39.95
		363	1.0900	0.0001	1.00	-39.92

3.3 Potentiodynamic Polarization Curves

Figure 6 showed polarization curves of corrosion rate on carbon steel in 2 M HCl in the absence and presence of methyl thiophene with several concentrations of CTAB. Both of cathodic and anodic polarization curve can be determined through this technique. Corrosion currents can be calculated from extrapolation of Tafel lines to pre-determined open circuit potential [8]. From the polarization curve, inhibition efficiency of inhibitor can be calculated using the following equation:

$$I\% = \{(i_{corr} - i_{corr}(inh)) / i_{corr}\} \times 100 \qquad (24)$$

Where i_{corr} and $i_{corr(inh)}$ were the uninhibited and inhibited corrosion current densities, respectively. Other electrochemical parameter values were also calculated. For instance, the corrosion potential (E_{corr}), cathodic Tafel slope (B_c), anodic Tafel slope (B_a) and corrosion current density (i_{corr}) were stated in Table 6.

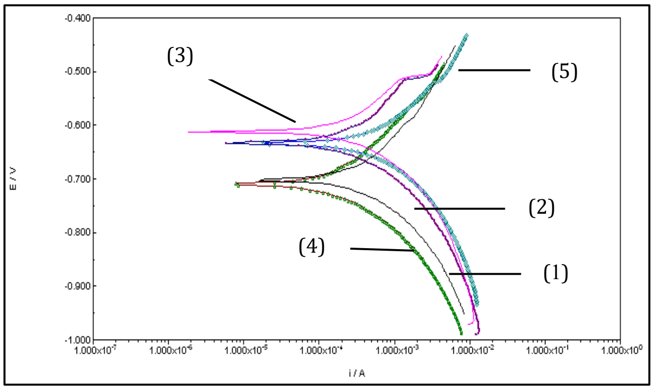


Figure 6 Polarization curves of CTAB for carbon steel in 2 M HCl in the absence of methyl thiophene: (1) 2 M HCl + 2 × 10^{-5} M CTAB, (2) 2 M HCl + 1 × 10^{-4} M CTAB, (3) 2 M HCl + 2 × 10^{-4} M CTAB, (4) 2 M HCl + 1 × 10^{-3} M CTAB and (5) 2 M HCl.

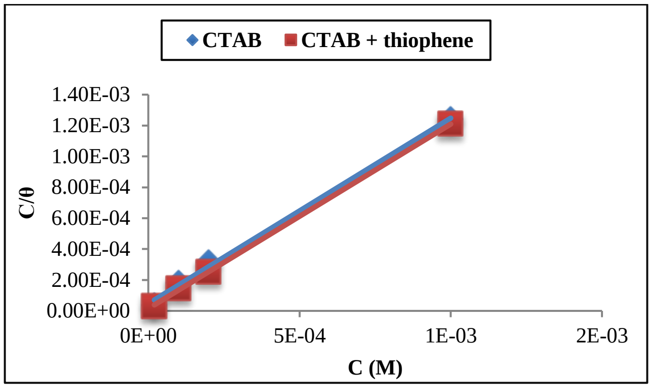


Figure 7 Langmuir isotherm adsorption model of CTAB in the absence and presence of methyl thiophene on steel surface by polarization technique.

From the findings it can be concluded that:

(i) E_{corr} values were shifted to more positive and more negative values. It means that the inhibitors used in this study are mixed type inhibitors [15]. Thus, they had the ability to inhibit both the anodic dissolution of steel and the cathodic H^+ ion reduction.

(ii) i_{corr} values decreased with increasing concentration of CTAB. Thus, the corrosion inhibition efficiency increased due to the formation of anodic protective films on the electrode surface [15]. This behavior proved that the inhibitors act as corrosion inhibitors for carbon steel in 2 M HCl.

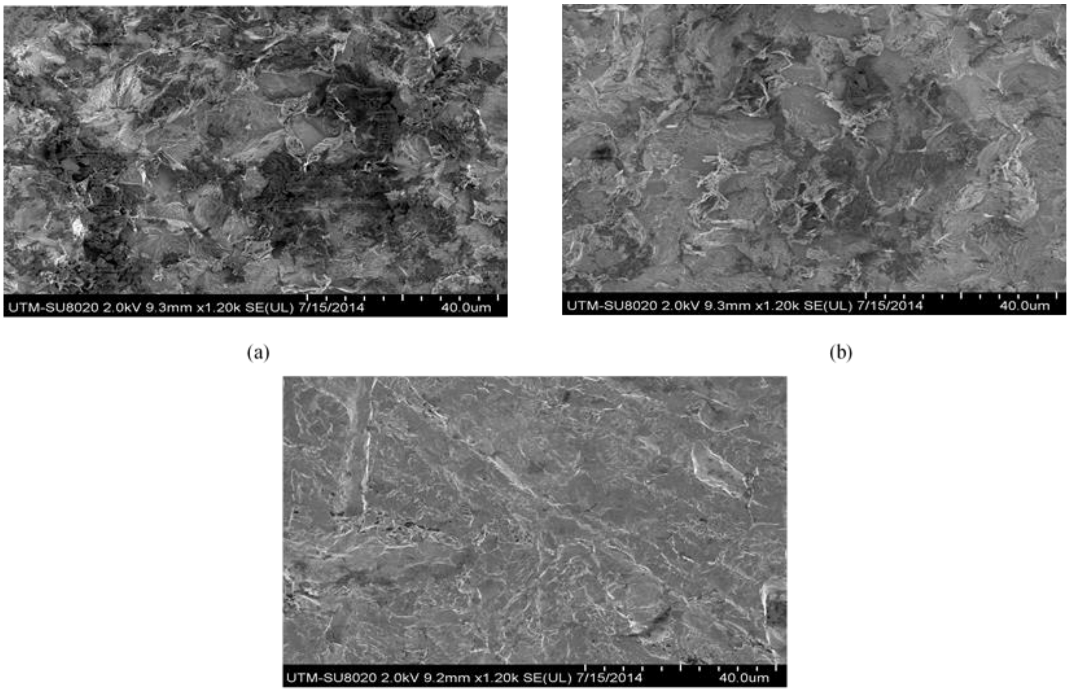
(iii) The value of Ba and Bc changed. It indicated that the mixed type inhibitor was used [10]. The change in β_c values indicates the influence of the inhibitor on the kinetics of hydrogen evolution. The shift in the anodic Tafel slopes (β_a) can be attributed to the chloride ion or inhibitor molecules adsorbed on the metal surface.

Table 6 Electrochemical parameters obtained from polarization curve.

Inhibitor	**Concentration (M)**	**E_{corr} (mV)**	**B_c (mV/dec)**	**B_a (mV/dec)**	**i_{corr} (mA cm^{-2})**	**θ**	**I%**
Blank	0	-634	246	266	0.324	0	0
CTAB	2×10^{-5}	-702	174	236	0.148	0.54	54.32
	1×10^{-4}	-612	163	346	0.144	0.56	55.56
	2×10^{-4}	-633	156	259	0.117	0.64	63.89
	1×10^{-3}	-709	138	183	0.063	0.81	80.52
CTAB + thiophene	2×10^{-5}	-606	134	233	0.111	0.66	65.74
	1×10^{-4}	-694	101	169	0.101	0.69	68.83
	2×10^{-4}	-619	118	159	0.066	0.80	79.63
	1×10^{-3}	-619	121	187	0.056	0.83	82.72
Blank	0	-634	246	266	0.324	0	0
SLS	1×10^{-4}	-660	204	150	0.162	0.50	50.00
	5×10^{-4}	-647	171	135	0.098	0.70	69.66
	1×10^{-3}	-689	60	66	0.068	0.79	79.01
	5×10^{-3}	-653	45	51	0.035	0.89	89.20
SLS + thiophene	1×10^{-4}	-690	142	130	0.141	0.56	56.48
	5×10^{-4}	-660	124	121	0.116	0.64	64.20
	1×10^{-3}	-666	88	92	0.055	0.83	83.02
	5×10^{-3}	-645	249	224	0.030	0.91	90.74
Blank	0	-461	155	204	0.336	0	0
Tween 80	1×10^{-4}	-460	132	209	0.185	0.45	44.94
	5×10^{-4}	-458	147	177	0.165	0.51	50.89
	1×10^{-3}	-458	105	172	0.097	0.71	71.13
	5×10^{-3}	-467	162	98	0.088	0.74	73.81
Tween 80 + thiophene	1×10^{-4}	-470	130	342	0.216	0.36	35.71
	5×10^{-4}	-467	119	328	0.147	0.56	56.25
	1×10^{-3}	-462	109	185	0.117	0.65	65.18
	5×10^{-3}	-466	109	211	0.082	0.76	75.60

3.4 Scanning Electron Microscopy (SEM)

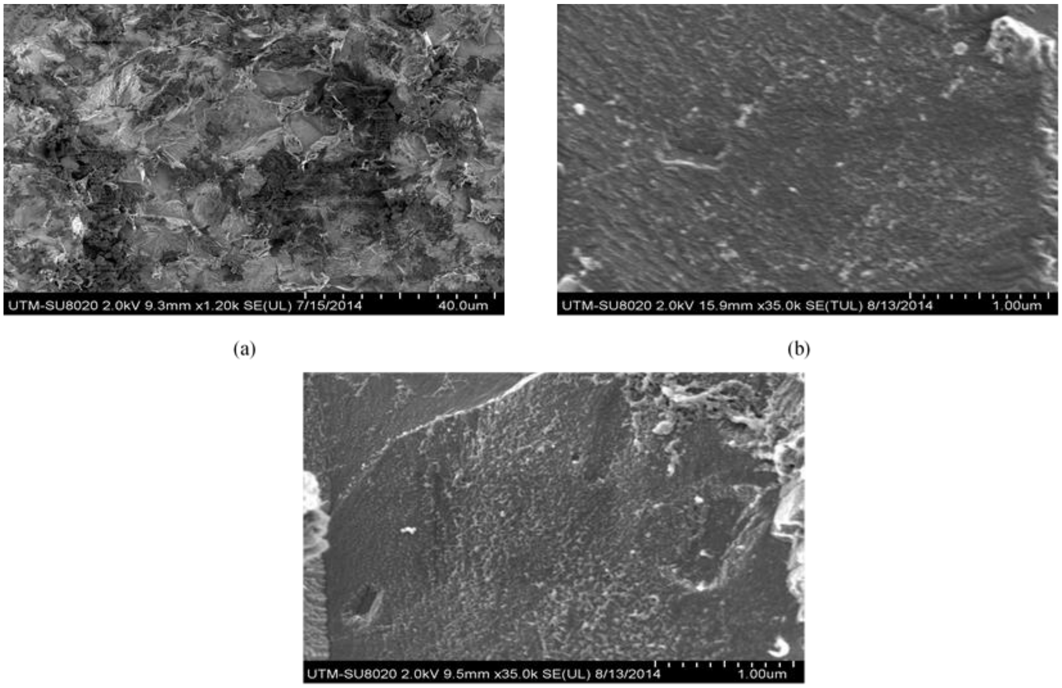
Scanning electron microscopy micrographs (Figure 8-10) of carbon steel were recorded in order to see the changes occurred during corrosion process before and after immersion in 2 M HCl with and without corrosion inhibitors. From the SEM micrograph, it shows that the steel surface was strongly damaged in the absence of inhibitors. However, in presence of surfactants (CTAB, SLS and Tween 80) and 2-methyl thiophene, the surface was remarkably improved. The surface of carbon steel immersed in mixture of surfactants and methyl thiophene were smoother when compared with that in surfactants alone. This observation suggested that surfactants in combination with methyl thiophene formed a protective layer over the metal surface and prevented the surface from being attacked by the acid.



(a) (b)

(c)

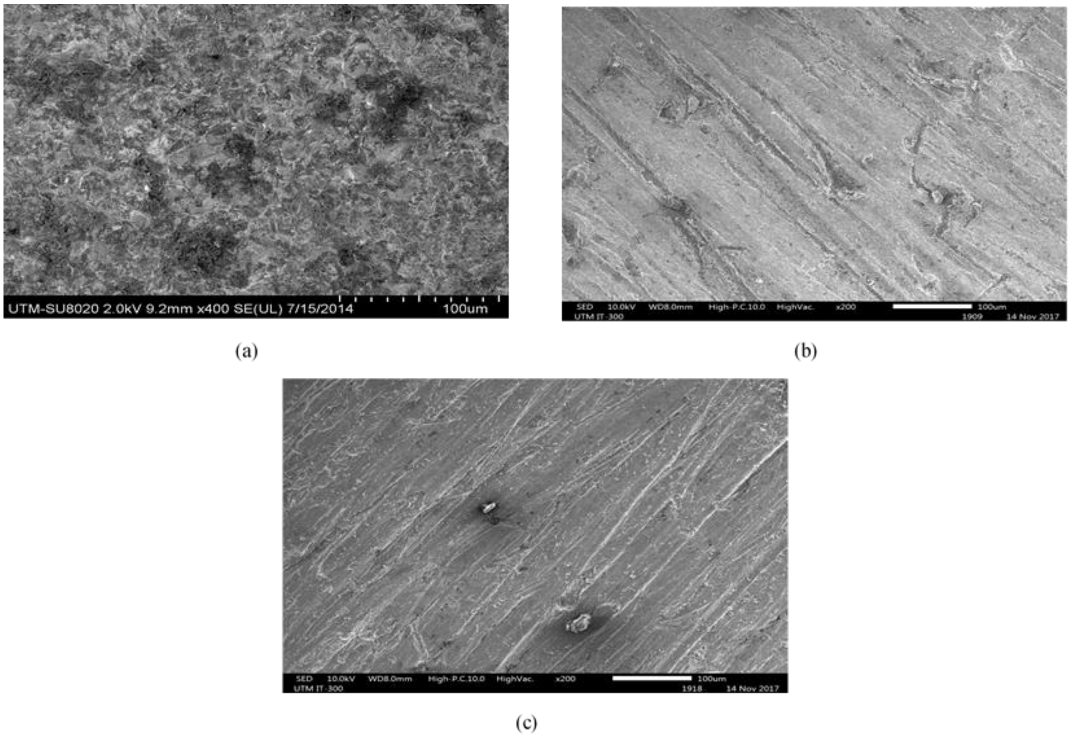
Figure 8 Scanning electron micrographs of carbon steel samples after immersed in: (a) 2 M HCl. (b) 2 M HCl + CTAB (1×10^{-3} M), (c) 2 M HCl + CTAB (1×10^{-3} M) + methyl thiophene (2×10^{-5} M)



(a) (b)

(c)

Figure 9 Scanning electron micrographs of carbon steel samples after immersed in: (a) 2 M HCl. (b) 2 M HCl + SLS (5×10^{-3} M), (c) 2 M HCl + SLS (5×10^{-3} M) + methyl thiophene (2×10^{-5} M)



(a) (b)

(c)

Figure 10 Scanning electron micrographs of carbon steel samples after immersed in: (a) 2 M HCl. (b) 2 M HCl + Tween 80 (5×10^{-3} M), (c) 2 M HCl + Tween 80 (5×10^{-3} M) + 2-methyl thiophene (2×10^{-5} M)

4 CONCLUSIONS

This paper discussed about the effects of surfactants (SLS/CTAB/Tween 80) concentration in a mixture with methyl thiophene as an inhibitor for corrosion inhibition of carbon steel. The efficiency of surfactant inhibitors increased in presence of 2-methyl thiophene. The values of adsorption free energy for all inhibitors (ΔG^{o}_{ads}) are between -30 kJ mol^{-1} and -50 kJ mol^{-1} which indicate that the inhibitors are a mixed-type. The inhibition efficiency of surfactants in presence of the thiophene derivative showed concentration-, time- and temperature-dependent. The addition of thiophene derivatives to acidic media containing surfactants (CTAB, SLS and Tween 80) enhanced the inhibition efficiency due to the electron transfer of the lone pair of electrons to the d-orbital of iron atom. From the weight loss method, SLS and CTAB gave the same value of inhibition efficiency, which is 87.80 % at 2 hours of immersion time. However, SLS showed the highest efficiency in the polarization method that is 90.74 % while the efficiency of CTAB reached 82.72 %. Thus, the most efficient surfactant in presence of the thiophene derivative as a corrosion inhibitor follows the order: SLS > CTAB >Tween 80. Both techniques of weight loss and potentiodynamic polarization showed that the adsorption isotherm followed the Langmuir isotherm.

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