

Effect of Cetyltrimethylammonium bromide Surfactant as Novel Inhibitor for the Corrosion of Steel in 0.5 M H₂SO₄

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Received: 5 November 2015 / Accepted: 12 November 2015 / Published: 1 January 2016

The effect of cationic surfactant, cetyltrimethylammonium bromide (Cetrimide) as corrosion inhibitor for steel in 0.5 M H₂SO₄ has been studied. The inhibition efficiency has been determined by weight loss and electrochemical impedance spectroscopy (EIS) measurements. Adsorption of Cetrimide on carbon steel in 0.5 M H₂SO₄ obeyed Langumir, Florry-Huggins and the Kinetic-Thermodynamic model. Effect of Cetrimide on the activation parameters of the corrosion reaction of steel in 0.5 M H₂SO₄ has been measured and discussed.

Keywords: Cationic surfactant, Acid Corrosion, Adsorption, Inhibition, Weight loss, Impedance.

1. INTRODUCTION

Carbon steel is the most important metal used in industry as construction metal [1] for metallurgical industries [2] and is used as construction material for pipes in oil and gas industry and transmission pipelines [3]. Sulfuric acid is used in many industrial applications such as, acid pickling, acid cleaning and descaling [4]. The drawback of using sulfuric acid in industry is the cause of corrosion of metals during the acid treatment [5]. Corrosion inhibitors are used to eliminate the undesirable effect of corrosion process and to prevent the metal dissolution [6]. Surfactants are widely used in our daily life and in industrial applications [7]. Using surfactants as corrosion inhibitors find little attention in the last years [8-12]. The advantages of using surfactants as corrosion inhibitors is its high inhibition efficiency, low price, low toxicity and easy production [13]. The mechanism of action of surfactants as corrosion inhibitor is adsorption on the metal surface in such a way that the polar or

ionic part (hydrophilic) attaches the metal surface while the non-polar part (hydrophobic) extends in the solution [14]. The adsorption behavior depends on the surfactant structure [9,15]. In general, the inhibition efficiency increase with increasing the molecular weight, number of carbon atoms in the molecule [11]. The inhibition efficiency of the surfactant increases with increasing the surfactant concentration in solution until approaches the critical micelle concentration (CMC) [1], above which, there is no further increase in the inhibition efficiency which remains constant for further increase in surfactant concentration. Many cationic surfactants have been used as corrosion inhibitors for steel in acidic media [16,17].

The aim of this study is evaluating the inhibition effect of cationic surfactant (Cetrimide) for the corrosion of carbon steel in sulfuric acid solution using chemical and electrochemical methods. The study will extend to explain the adsorption characteristics of Cetrimide at the steel/solution interface and its effect on the kinetics of the corrosion reaction.

2. EXPERIMENTAL

2.1 Materials and solutions

The carbon steel used in this study has the following chemical composition (wt %): C 0.21; S 0.04; Mn 2.5; P 0.04; Si 0.35; balance Fe. The sulfuric acid solution was prepared by dilution of analytical grade 98 % H₂SO₄ and Cetrimide was obtained from Alpha Chemika with molecular weight 364.45 g/mol, its molecular structure is shown in figure 1. Double distilled water was used in the preparation of test solutions in all measurements.

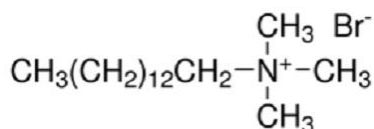


Figure 1. Chemical structure of Cetrimide.

2.2. Electrochemical measurements

Electrochemical measurements were carried out in a three electrode cell with carbon steel as working electrode that had the chemical composition previously mentioned in the gravimetric measurement. Graphite is used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The carbon steel used as working electrode is 6 mm diameter embedded in Teflon holder. Before each experiment, the working electrode was polished with a series of emery papers of different grit sizes (320-1000). After polishing, the carbon steel electrode was washed with double distilled water and dried at room temperature. All electrochemical studies were carried out with 604 Gill ACM instrument. The frequency range for EIS measurements was $0.01 \leq f \leq 3 \times 10^4$ Hz with applied potential signal amplitude of 10 mV around the rest potential.

2.3. Weight loss measurements

Rectangular specimens of carbon steel with dimensions (2.0 cm x 5.0 cm x 0.05 cm) were used during the weight loss measurements. The samples were prepared by abrading with a series of emery papers 320, 800, 1000 grades and washed with ethanol, rinsed in water and dried between filter paper. After weighting accurately, the specimens were immersed at 30 °C in 100 mL of 0.5 M H₂SO₄ with and without different concentrations of surfactant. After 2 hours the carbon steel samples were taken out, washed with distilled water, dried, re-weighted and the weight loss is calculated. The percentage inhibition (% P) and the surface coverage θ were calculated by the following equation [1]:

$$\% P = \frac{W_0 - W}{W_0} \times 100 = \theta \times 100 \tag{1}$$

Where, W₀ and W are the values of the average weight loss without and with the surfactant respectively.

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance spectroscopy results

Figure 2a, represents Nyquist plots for steel in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of Cetrimide.

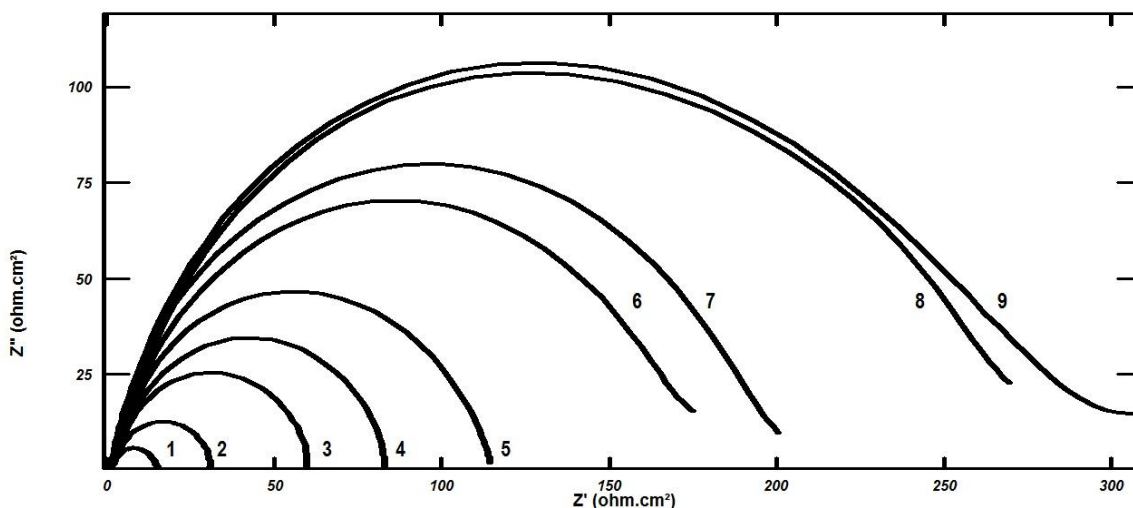


Figure 2a. Nyquist plots for steel in 0.5 M H₂SO₄ solution in absence and presence of different concentrations of Cetrimide. 1) 0.0 M; 2) 0.00005 M; 3) 0.000075; 4) 0.0001 M; 5) 0.00015; 6) 0.0002; 7) 0.00025 M; 8) 0.02 M; 9) 0.05 M.

The figure manifested only one depressed capacitive semicircle indicating the presence of the charge transfer resistance associated with the effect of ionic double-layer capacitance. The impedance

spectra for different Nyquist plots were analyzed by fitting the experimental data using Zsimpwin program to a simple equivalent circuit model, figure 2b.

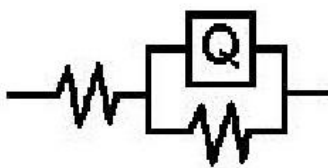


Figure 2b. The equivalent circuit model

The equivalent circuit model includes the solution resistance R_s and the constant phase element Q which is placed in parallel to charge transfer resistance element R_{ct} . The Q is used normally to replace the capacitor in the equivalent circuit to express the non-homogeneity in the system and is defined by two values, Q and n where; $0 \leq n \leq 1$. In case of $n = 1$, the Q values is replaced by the capacitance C . The values of the electrochemical parameters obtained from EIS for steel in 0.5 M H_2SO_4 solution containing different surfactant concentrations and the inhibition efficiency (% P) are given in table 1 and were calculated from impedance measurements using the relation.

$$\% \text{ inh.} = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100 \quad (2)$$

where, R_{ct0} and R_{ct} are the charge transfer resistance in absence and in presence of Cetrimide respectively.

Table 1. Electrochemical impedance parameters for steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of Cetrimide at 30 °C.

[Cetrimide] mol/L	R_s Ohm.cm ²	Q_{dl} F	n	R_{ct} Ohm.cm ²	% Inhibition
0.000000	1.071	0.00077	0.83	14.45	-
0.000050	1.297	0.00040	0.84	31.43	54.02
0.000075	1.196	0.00038	0.84	63.03	77.07
0.000100	1.165	0.00034	0.83	87.28	83.44
0.000150	1.060	0.00030	0.81	118.4	87.79
0.000200	0.804	0.00028	0.81	186.6	92.25
0.000250	0.075	0.00025	0.85	201.7	92.83
0.020000	0.770	0.00023	0.79	287.2	94.96
0.050000	0.750	0.00015	0.83	292.6	95.06

The results show that, R_{ct} values increase with increasing the Cetrimide surfactant concentration indicative of the formation of a protective layer on the electrode surface acts as a barrier for mass and charge transfer [18-20]. The capacitance of the electric double layer Q_{dl} decreases with increasing the surfactant concentration probably due to the adsorption of Cetrimide molecules at the steel surface to form an adherent film which increases the double layer thickness.

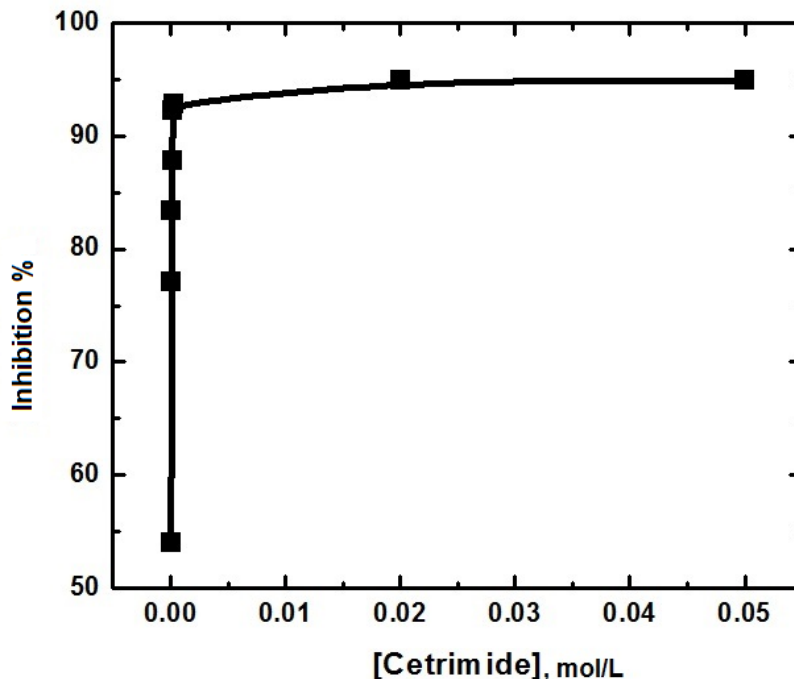


Figure 3. The relation between the percentage inhibition and the concentration of Cetrimide surfactant.

Figure 3, represents the variation of the percentage inhibition with the concentration of Cetrimide surfactant. The inhibition efficiency increases with increasing the surfactant concentration which indicates that the Cetrimide surfactant acts as corrosion inhibitor for steel in 0.5 M H₂SO₄ solution. The relation represents an adsorption isotherm in which the efficiency increases with increasing the concentration until leveling off indicating that the inhibition process is mainly controlled by adsorption of the surfactant at the steel surface until it reaches a point of saturation of the metal surface by the surfactant molecules.

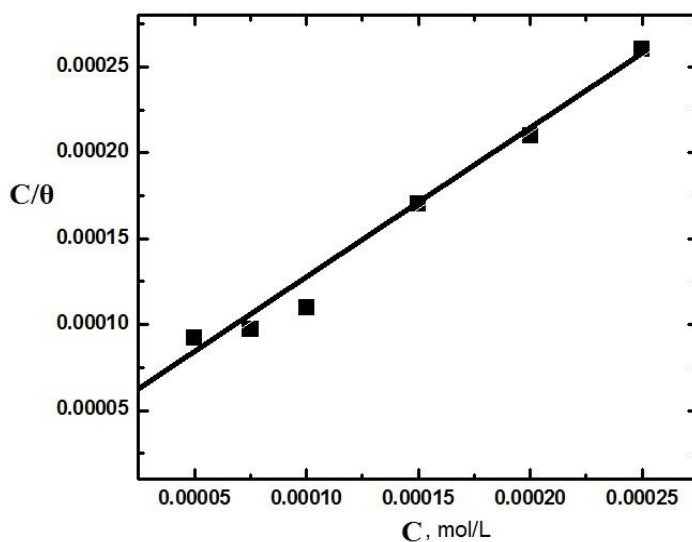


Figure 4. Application of the Langmuir isotherm to fit the experimental results of adsorption of Cetrimide on steel surface in 0.5 M H₂SO₄.

Figure 4 shows that Langmuir adsorption isotherm fit the experimental data and is given by the following equation [21-24]:

$$C/\theta = 1/K + C \quad (3)$$

Where C is the concentration of inhibitor (mol/L), K the adsorptive equilibrium constant and θ is the fraction of surface covered by inhibitor molecules.

The validity of the Langmuir isotherm is confirmed from the linearity of a graph requiring the slope of the graph to be unity. The slope of the graph is nearly 1 indicating that Langmuir adsorption isotherm is valid to fit the experimental data. This means that the adsorption process is ideal and there is no mutual interaction between the surfactant molecules at the metal/solution interface.

The adsorptive equilibrium constant K is related to the standard free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ according to the following equation [25-27]:

$$K = 1/C_{\text{solvent}} \exp(-\Delta G_{\text{ads}}^{\circ}/RT) \quad (4)$$

Where; R is the universal gas constant, T is the absolute temperature, C_{solvent} is the molar concentration of solvent which is in this case water and equal to 55.5 mol/L.

It is reported that values of $\Delta G_{\text{ads}}^{\circ}$ approximately -20 kJ/mol or lower are consistent with an electronic interaction between the inhibitor molecule and the metal surface (physisorption). Values higher than -40 kJ/mol are involved in charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption) [28-30]. The value of K equal 2.8×10^4 obtained from Langmuir isotherm gives $\Delta G_{\text{ads}}^{\circ}$ equals -35.91 kJ/mol indicative that the adsorption of Cetrimide on the steel surface is comprehensive (physical and chemical).

In a previous work, $\Delta G_{\text{ads}}^{\circ}$ of dodecyl trimethyl ammonium chloride (DTAC) surfactant on carbon steel in 0.5 M HCl solution was calculated and found to be -39.8 kJ/mol indicating a spontaneous adsorption of the surfactant on steel surface and suggesting a comprehensive adsorption (physical and chemical adsorption) might be occur [1,31]. El-Nemr et al [32], calculated $\Delta G_{\text{ads}}^{\circ}$ for the Cassia Fistula L. aqueous extract on steel in acidic solution. The value of $\Delta G_{\text{ads}}^{\circ}$ were ranged between -10.284 and -16.834 kJ/mol indicating that the adsorption of the extract on steel was typical of physical adsorption. The values of $\Delta G_{\text{ads}}^{\circ}$ for the adsorption of tween 80 on the carbon steel in sulfuric acid is -43 kJ/mol which indicates the chemisorption of tween 80 on the steel surface [24]. The $\Delta G_{\text{ads}}^{\circ}$ for Chitosan as a green inhibitor for copper corrosion in acid solution was calculated and found to be -42.2 kJ/mol indicating the strong interaction of chitosan on the copper surface which can be attributed to the presence of N atom and electrons in the inhibitor molecules ensuring the spontaneity of adsorption process and the stability of adsorption. In other words, the adsorption is more chemical than physical [33].

Flory-Huggins isotherm [34] and the Kinetic-Thermodynamic model [35,36] of adsorption have also been applied to fit the experimental results of the inhibition of the corrosion of steel in 0.5 M H_2SO_4 by Cetrimide. The results indicated that these two models fit the experimental data and give the same value of the binding constant K.

The performance of the adsorption of Cetrimide on the steel surface can be discussed on the basis of the suggestion that the Cetrimide molecule is adsorbed on the steel surface from the ionic (hydrophilic) part while the non-polar (hydrophobic) part extended in the solution surface. The counter

ion (Br^-) plays an important role in the adsorption process of Cetrimide on the steel surface, it forms an intermediate bridge between the steel surface and the surfactant cations [1].

3.2. Weight loss results

Table 2 represents the weight loss results for the corrosion of carbon steel in 0.5 M H_2SO_4 in the absence and the presence of different concentrations of Cetrimide after 2 hours of immersion

Table 2. Data of weight loss measurements for carbon steel in 0.5 M H_2SO_4 in the absence and the presence of different concentrations of Cetrimide after 2 hours immersion.

[Cetrimide] mol/L	Weight loss (g/cm^2)	%p
0.000000	0.3872	-
0.000050	0.1064	72.52
0.000075	0.0729	81.17
0.000100	0.0168	95.66
0.000250	0.0147	96.20
0.020000	0.0100	97.41

The data indicate that the inhibition efficiency increases with increasing the concentration of the surfactant and figure 5 shows a good agreement between the results obtained from the weight loss and impedance measurements.

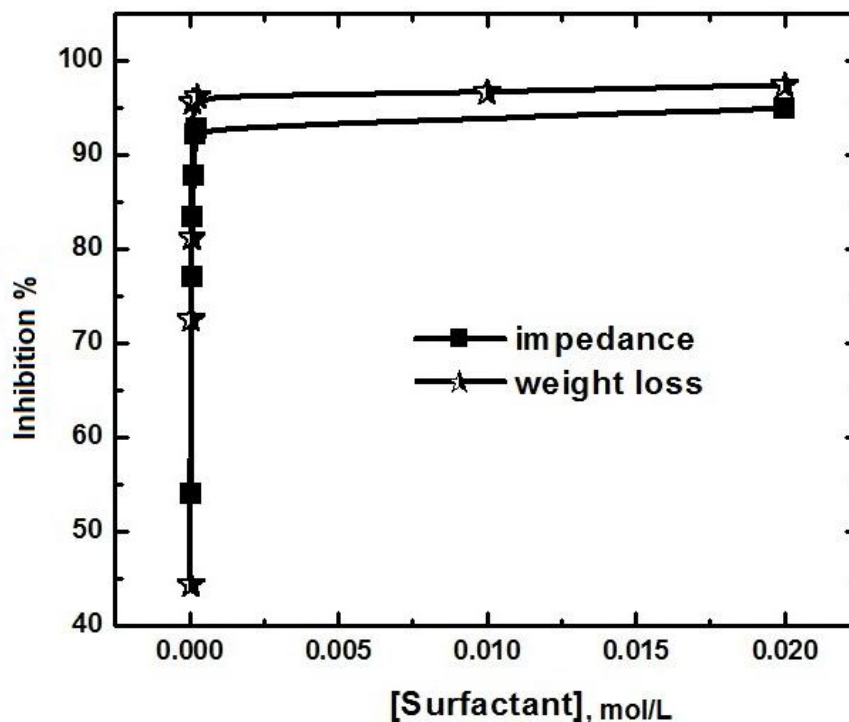


Figure 5. The relation between the percentage inhibition obtained from the impedance and weight loss measurements with the concentrations of Cetrimide surfactant.

3.3. Effect of temperature on the activation parameters of the corrosion reaction of steel with sulphuric acid in absence and presence of Cetrimide.

It has been reported that the logarithm of the rate of corrosion (expressed by W) is a linear function with 1/T [37-39]. We use the Arrhenius equation to investigate these phenomena and see how it correlates with the results we obtained using different concentrations of Cetrimide surfactant to reduce corrosion:

$$\ln W = \ln A - (E_a/RT) \tag{5}$$

Where E_a is the apparent effective activation energy, T is the absolute temperature, R is the universal gas constant and A is Arrhenius pre-exponential factor. The corrosion rates were taken from the weight loss measurements. An alternative formulation of the Arrhenius equation is the transition state equation shown below:

$$W = (RT/Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \tag{6}$$

Where; N is Avogadro's number, h the plank's constant, ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation.

Figures 6a and 6b show that linear plots are produced when we plot ($\ln W$) versus ($1/T$) and ($\ln W/T$) versus ($1/T$) using data collected in experiments where steel was immersed in 0.5 M H_2SO_4 in the absence or the presence of 0.000075 or of 0.0002 M Cetrimide. This data was used to calculate the values of the activation parameters E_a , ΔH^* and ΔS^* . The resulting values of the activation parameters are given in Table 3.

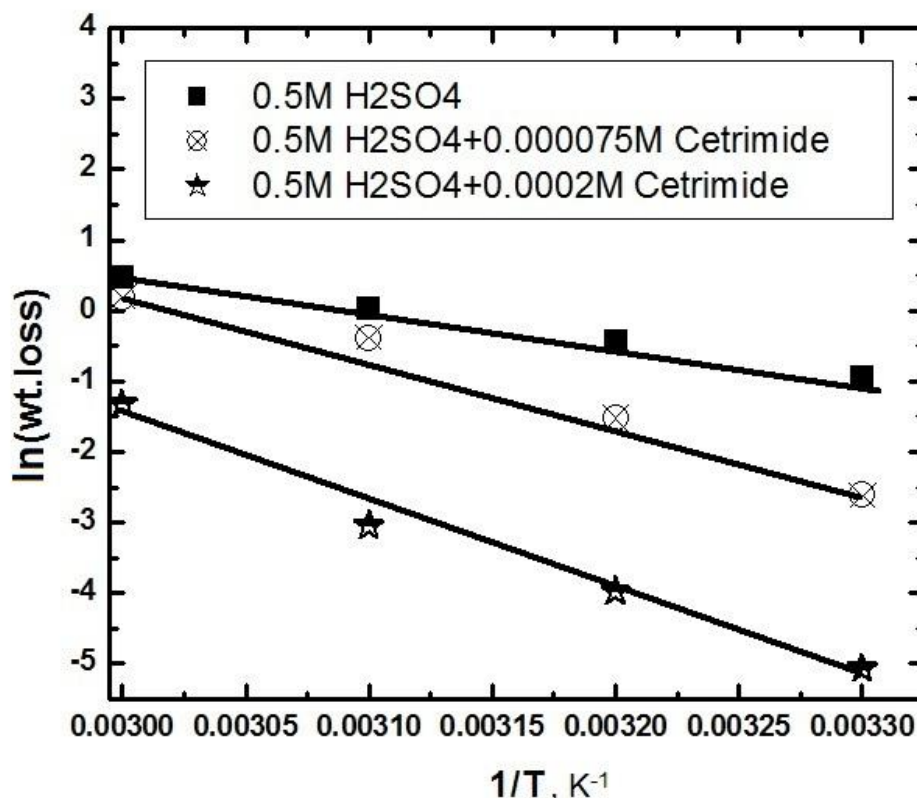


Figure 6a. Linear fit for ($\ln W$) data vs. ($1/T$) for steel dissolution in 0.5 M H_2SO_4 solutions in the absence and presence of Cetrimide.

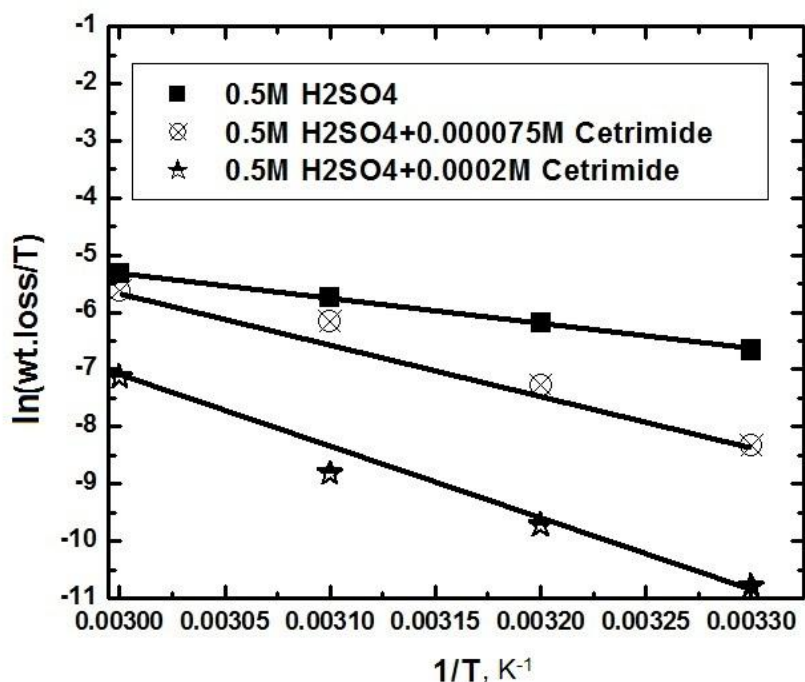


Figure 6b. Linear fit for (ln W/T) data vs. (1/T) for steel dissolution in 0.5 M H₂SO₄ solutions in the absence and presence of Cetrimide.

Table 3. Activation parameters of steel dissolution in 0.5 M H₂SO₄ in absence and presence of 0.000075 and 0.0002 M Cetrimide.

Solution composition	Activation parameters		
	E _a (kJ mol ⁻¹)	ΔH [*] (kJ mol ⁻¹)	ΔS [*] (J mol ⁻¹ K)
0.5 M H ₂ SO ₄	39.41	36.80	-131.34
0.5 M H ₂ SO ₄ + 0.000075 M Cetrimide.	79.54	76.93	-12.11
0.5 M H ₂ SO ₄ + 0.0002 M Cetrimide.	101.29	98.65	37.48

As observed from the data given in table 3, the activation energy E_a and the enthalpy change ΔH^{*} for the solutions containing the Cetrimide surfactant were higher than that for the solutions where no surfactant was added. This behavior is probably discussed on the basis that the energy barrier of the corrosion reaction of steel with sulphuric acid increases in presence of the surfactant due to the formation of an adsorbed layer of the surfactant at the steel/solution interface. The negative values of ΔS^{*} in absence of the surfactant implies that the activated complex represents association rather than a dissociation step [40,41]. Table 3 also illustrates that ΔS^{*} becomes less negative or (more positive) when the Cetrimide surfactant present in the solution. This means that the entropy increases in presence of Cetrimide which is the driving force for the adsorption of the surfactant onto the steel surface [42,43].

4. CONCLUSIONS

1) The cationic surfactant Cetrimide inhibits the corrosion of carbon steel in 0.5 M H₂SO₄ with efficiency more than 92.0 % in presence of 2×10^{-4} M Cetrimide.

2) Adsorption of Cetrimide on carbon steel in 0.5 M H₂SO₄ obeyed Langumir, Florry-Huggins isotherms and the Kinetic-Thermodynamic model. The linear fitting parameters showed a good agreement between the values of the binding constant K obtained from the three models, where the change in the standard free energy of adsorption indicated that the adsorption of Cetrimide on the steel surface is comprehensive (physical and chemical).

3) The values of the activation parameters of the corrosion reaction of steel with 0.5 M H₂SO₄ in the absence and presence of two different concentrations of Cetrimide indicated that the presence of the surfactant in the reaction medium increases both the energy barrier and the entropy of the reaction.

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