

Adsorption and Inhibitive Properties of Tetradecyltriméthylammonium Chloride for the Corrosion of Carbon Steel in Acid Sulfuric

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Abstract - The inhibition effect of a cationic surfactant: Tetradecyltriméthylammonium chloride (TDMA) on the corrosion of carbon steel in 0.5 M H₂SO₄ has been investigated by means of weight loss measurements, kinetics and thermodynamics studies. The high inhibition efficiency of TDMA was due to the adsorption of inhibitor molecules on the metal surface. The decrease of surface area available for electrode reactions to take place is due to the formation of a protective film. Activation energy and enthalpic of activation in the presence and absence of TDMA were determined by measuring the temperature dependence of the corrosion current. On the account of R² this adsorption process well fitted into Langmuir, Flory- Huggins Frumkin and Temkin model The results of the investigation show that this compound has excellent inhibiting properties for mild steel corrosion in sulfuric acid and revealed clearly that TDMA inhibition activity proceeds via a chemisorption, the best isotherm fit for the TDMA has been resolved to be the Langmuir isotherm model.

Keywords – Tetradecyltriméthylammonium chloride, Mild steel, Corrosion inhibitors, Sulfuric acid, Weight loss method, Adsorption isotherm, thermodynamics

I. INTRODUCTION

Mild steel is widely used as a constitutional material in many industries due to its good mechanical properties and low cost. Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. Corrosion problems arise as a result of interaction of the aqueous solutions with C-steel, especially during the pickling process in which the alloy is brought in contact with high concentrated. The corrosion inhibitors of metallic materials in acidic media by different types of organic compounds have been widely studied [1-6]. Most organic inhibitors are substances with at least one functional group considered as the reaction centre for the adsorption process. The adsorption of inhibitors is related to the presence of heteroatom as nitrogen, oxygen, phosphorus and sulphur, as well as triple bond or aromatic ring in their molecular structures [7-12]. Over the years the addition of high molecular weight organic compounds like surfactants to acid media in order to reduce the rate of corrosion attack has been proved to be a very useful method. These compounds were expected to possess high inhibition efficiencies for acidic corrosion environments because of the presence of a long hydrocarbon chain that ensures large surface coverage and the presence of multiple active centers for adsorption. Ionic and non-ionic surfactants have been reported to be good inhibitors for iron corrosion in acid media [13–17].

The application of surfactants as corrosion inhibitors has been widely studied, and adsorption of these molecules on the metal surface was found to be responsible of the corrosion inhibition of the metal [18–19]. Adsorption results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution, thus diminishing the overall corrosion rate. The relationship between the adsorption of surfactants and their molecular structure has attracted the attention of many investigators [20–25].

The aim of this study is to investigate the efficiency of cationic surfactant, Tétradecyltriméthylammonium chloride (TDMA), for the inhibition of corrosion of carbon steel in H₂SO₄ 0.5 M. The effects of inhibitor concentration and temperature on the performance and extent of adsorption of TDMA are studied.

II. EXPERIMENTAL

II. 1. Inhibitor

Tetradecyltriméthylammonium chloride (TDMA), used as the inhibitor. The cationic surfactant was produced from Sigma- Aldrich. Fig. 1 shows the molecular structure of the TDMA.

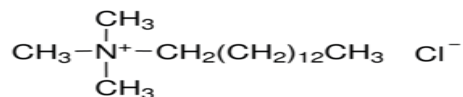


Figure 1: Tetradecyltriméthylammonium chloride (TDMA)

II.2. Materials

Tests were performed on a mild steel of the following composition:

Table 1: Chemical composition (wt. %) of mild steel

Element	wt. %
C	0,21
Si	0,38
P	0,09
S	0,05
Mn	0,05
Al	0,01
Fe	Balance

II.3. Solutions

The acidic solution 0,5M H₂SO₄ was prepared by dilution of Analytical Grade 98% H₂SO₄ with distilled water. Gravimetric methods are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 30 ml. The steel specimens used have rectangular shapes 3.5cm×1cm×0.1cm. For each sample, three tests are realized and the corresponding average value is calculated. The samples were weighted with an uncertainty of 10⁻⁴ g. The immersion time for weight loss amounts is 6h for all the temperatures. The concentration range of inhibitor (TDMA) employed was varied from 75 to 325 ppm.L⁻¹.

II.4. Weight loss measurements

The carbon steel sheets of 3.5cm ×1cm× 0.1cm were abraded with series of emery paper (grade 320-500-800) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in 30 ml beaker, which contained 30 ml hydrochloric acid with and without addition of different concentrations of TDMA. All the aggressive acid solutions were open to air. After 6 h, the specimens were taken out, washed, dried, and weighed accurately. Experiments were carried out in triplicate. The average weight loss of three parallel mild steel sheets could be obtained. Then the tests were repeated at different temperatures and 0,5M H₂SO₄ concentration.

III. RESULTAT

III.1. Effect of inhibitor concentration

The corrosion rate (W_{corr}) of carbon steel investigated in this study was calculated using the following equation:

$$W_{\text{corr}} = \frac{\Delta m}{S \cdot t} \quad (1)$$

Δm is the weight loss ($m_i - m_f$) in mg with m_i and m_f being the initial and final masses of the carbon steel specimen, before and after corrosion tests, respectively. S (cm²) is the exposed surface area of the specimen and t (h) is its immersion time in the investigated solution. The corrosion rate (W_{corr}) is therefore measured in (mg.cm⁻².h⁻¹).

The inhibition efficiency IE (%) and the degree of surface coverage (θ) of the inhibitor molecule adsorbed on the steel surface were estimated using following equations (2) and (3), respectively, where, $W_{\text{corr (free)}}$ and $W_{\text{corr (inh)}}$ are the corrosion rates in absence and presence of the corrosion inhibitors, respectively.

$$\text{IE (\%)} = \frac{W_{\text{corr (free)}} - W_{\text{corr (inh)}}}{W_{\text{corr (free)}}} \times 100 \quad (2)$$

$$\theta = \frac{W_{\text{corr (free)}} - W_{\text{corr (inh)}}}{W_{\text{corr (free)}}} \quad (3)$$

The weight loss method of monitoring corrosion rate and inhibition efficiency is useful owing to its simple application and good reliability [35-36]. The weight loss study was performed with various concentrations of TDMA, to study the influence of various concentrations of TDMA on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 solution at 298° K for a period of six hours. Table 2 reports the percentage efficiency and corrosion rate in the absence and presence of different concentrations of TDMA. Fig. 1 shows the corrosion rate (W_{corr}) values of mild steel in the 0.5 M H_2SO_4 solution without and with different concentrations of TDMA. In the acidic medium, it is obvious that the TDMA effectively inhibits the corrosion rate of mild steel in HCl. THE Corrosion rate decreases noticeably with an increase in TDMA concentration. At the maximum concentration of 325 ppm TDMA, the corrosion rate values from 0.66 was decreased to 0, 06.

Table 2. Corrosion parameters for mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of TDMA at 298° K.

[TDMA] (ppm)	W_{corr} ($\text{mg.cm}^{-2}.\text{h}^{-1}$)	IE (%)	θ
Blank	0.66	-	
75	0.11	83.01	0.83
125	0.09	85.00	0.85
175	0.09	86.16	0.86
225	0.08	86.80	0.87
275	0.07	89.60	0.89
325	0.06	90.00	0.90

The results show a positive correlation between the concentration of surfactant and the corrosion rate for mild steel in 0.5 M H_2SO_4 solution. This trend may result from the fact that the amount adsorbed and the coverage of inhibitor molecules on the mild steel surface increased with the increase of the surfactant concentration, thus the mild steel surface is efficiently blocked from the hydrochloric acid.

This tremendous change in the corrosion rate values had a very strong impact on the inhibition efficiency, which in its turn increases with increasing the TDMA concentrations as depicted from table 2 and plotted in figure 2 reaching the highest value of ca. 90.00 % at a TDMA concentration of 325 ppm.

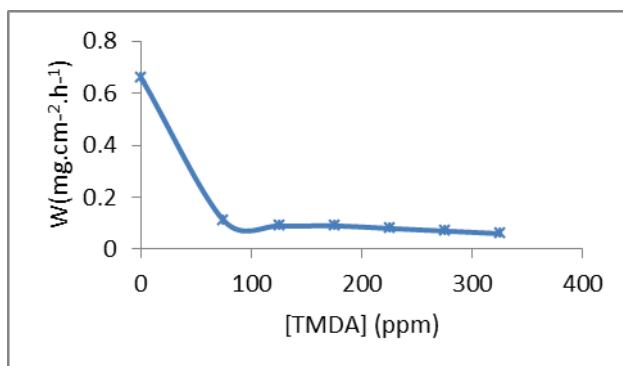


Figure 2. Variation of the corrosion rate W_{corr} of carbon steel with the concentration of TDMA in 0.5 M H_2SO_4 at 298° K.

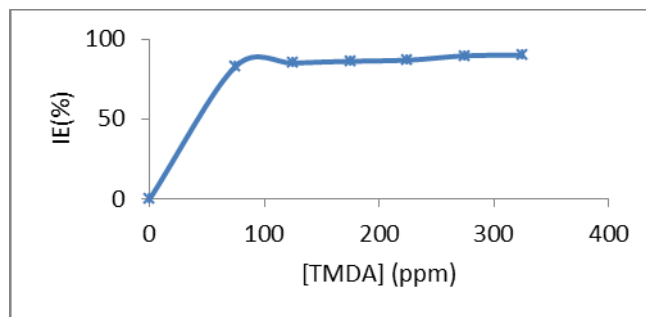


Figure 3. Variation of the inhibition efficiency IE (%) of carbon steel corrosion with the concentration of TDMA in 0.5 M H₂SO₄ at 298° K.

III.2. Effect of Temperature

The effect of temperature on the inhibited solution-metal reaction is highly complex. Many changes may occur on the metal surface, such as rapid etching and desorption of inhibitor, or the inhibitor itself undergoing decomposition and/or rearrangement. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the absence and presence of inhibitor gives some insights into the possible mechanism of inhibitor adsorption [26– 30]. The study of the effect of temperature on the corrosion rate and inhibition efficiency facilitates the calculation of kinetic and thermodynamic parameters for corrosion and inhibition processes. In the current investigation the results indicated that inhibition efficiency of TDMA increase with the increase in temperature. In order to evaluate the adsorption of inhibitors and to calculate thermodynamic and activation parameters of the corrosion processes of the mild steel in acidic media, the effect of temperature on the corrosion parameters was studied using the gravimetric technique. Measurements were made in the temperature range 298-333 °k in the absence and presence of 325 ppm /L of TDMA during 6h immersion period.

Table 3. Corrosion parameters of acid Corrosion of mid steel with 325 ppm of TDMA at various temperatures at 6 h immersion time.

T (°K)	$W_{\text{corr}}(\text{free})$	$W_{\text{corr}}(\text{inh})$	IE (%)	Θ
298	0.66	0.07	90.00	0.90
303	0.98	0.09	91.10	0.91
313	0.73	0.22	92.04	0.92
323	5.56	0.31	94.38	0.94
333	7.64	0.39	94.95	0.95

The values of the percentage IE (%) and corrosion rates obtained from weight loss measurements for the different concentrations of TDMA in 0.5 M H₂SO₄ are presented in Table 3. The results reveals that the corrosion rate in all cases increases with increasing temperature, as expected. From this table, the figure 4 was plotted. An eye-catching feature in figure 4 is that the acceleration of the corrosion rate with increasing temperature is far low in the presence of 325 ppm of TDMA compared with inhibitor-free solution. In fact, while the corrosion rate reaches an extreme value of ($W_{\text{corr}}(\text{inh}) = \text{ca. } 7.64 \text{ mg.cm}^{-2}\text{.h}^{-1}$) at 333 K in the blank 0.5 M H₂SO₄ compared with its initial value of ($W_{\text{corr}}(\text{inh}) = \text{ca. } 0.66 \text{ mg.cm}^{-2}\text{.h}^{-1}$), this behavior is almost ten-fold lower in the presence of 325 ppm of TDMA where the corrosion rate increased from ($W_{\text{corr}}(\text{inh}) = \text{ca. } 0.07 \text{ mg.cm}^{-2}\text{.h}^{-1}$) to ($W_{\text{corr}}(\text{ free}) = \text{ca. } 0.39 \text{ mg.cm}^{-2}\text{.h}^{-1}$) only. A very interesting feature depicted in table 3 is the increase of the inhibition efficiency with increasing temperature which is of practical interest in processes requiring the protection of the material at high temperature [31]. A maximum value of ca. 94.95% was reached in the present study at 333°K as displayed in figure 5. The observed increase in IE(%) with increase in temperature is an indication that the adsorption of the inhibitor on the electrode surface leads to the formation of a barrier between the metal surface and the corrosion medium, thereby reducing the metal reactivity and some molecules of surfactant become better adsorbed at higher temperature and so contribute more to the overall inhibiting effect.

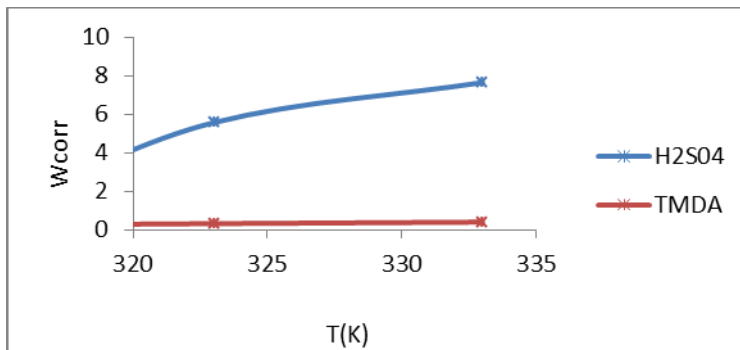


Figure 4. Effect of temperature on the corrosion rate of carbon steel in 0.5 M H2SO4 In the absence (Wcorr (free)) and the presence (Wcorr (inh)) of 325 ppm of TDMA.

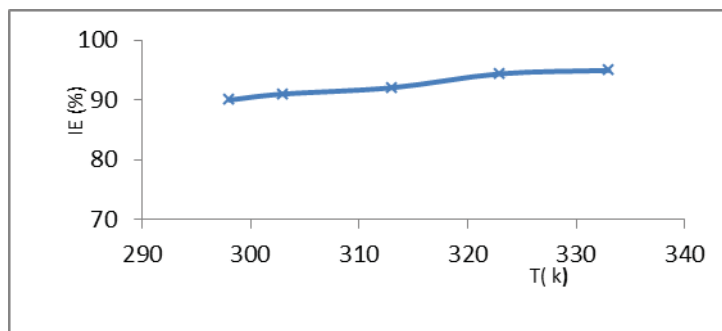


Figure5. Effect of temperature (296 °K–343 °K) on the inhibition efficiency IE (%) of carbon steel corrosion in a (325 ppm of TDMA + 0.5 M H2SO4) solution.

Similar increase in the inhibition efficiency has been observed in literature at several metals [32-34]. The most probable interpretation of this behavior is that the inhibition mechanism proceeds through a chemical adsorption (chemisorptions) of TMDA molecules onto the carbon steel surface and this indeed increases with rising temperature [35].

The apparent activation thermodynamic parameters, namely the activation energy (E_{app}), the activation enthalpy (ΔH_{app}) and the activation entropy (ΔS_{app}) of the corrosion process under study can be calculated [36-38] using Arrhenius equation [39]:

$$\log W_{corr} = \log A - \frac{E_{app}}{2.303RT} \quad (4)$$

And the alternative formulation of Arrhenius equation, the transition-state equation:

$$\log \left(\frac{W_{corr}}{T} \right) = \left[\left(\log \frac{R}{hN} \right) + \left(\frac{\Delta S_{app}}{2.303R} \right) \right] - \frac{\Delta H_{app}}{2.303RT} \quad (5)$$

where E_{app} is the apparent effective activation energy, A ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) is the Arrhenius pre-exponential factor, R is the universal gas constants ($8.3144621 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), N is Avogadro’s number ($6.02252 \times 10^{23} \text{ mol}^{-1}$) and h is Plank’s constant ($6.626176 \times 10^{-34} \text{ J}\cdot\text{s}$). A plot of \log of corrosion rate vs. $1/T$ gave a straight as shown in Fig. 6 with a slope of $-E_{app}/2.303R$. The value of the activation energy is listed in Table 4. The data shows that the thermodynamic activation function (E_{app}) of the corrosion in mild steel in 0.5M H_2SO_4 solution in the presence of TMDA is lower than those in the free acid solution indicating that the surfactant exhibits high IE (%) at elevated

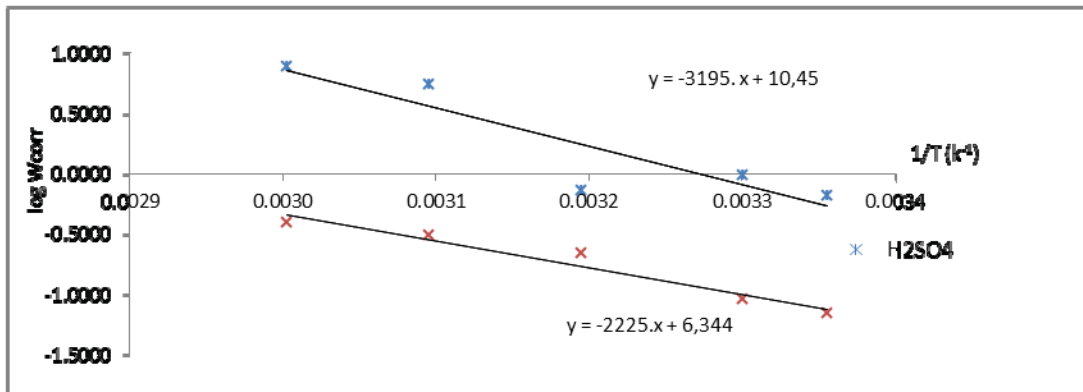


Figure6. Arrhenius plots for mild steel corrosion in 0.5 M H₂SO₄ solutions without and with TMDA

temperatures. An increase in inhibition efficiency with rise in temperature with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of chemical (molecular) nature [40]. A plot of $\log W_{\text{corr}}$ against $(1/T)$ gives a straight line as displayed in figure 6.

The value of (A) was calculated from the y-intercept of respective lines. The slopes of these plots ($-E_{\text{app}}/RT$) yielded the values of the activation energy (E_{app}) both in the absence and presence of the inhibitor. All results are tabulated in table 4.

Table 4: Activation parameters of the dissolution of steel in 0.5M H₂SO₄ in the absence and presence of inhibitor.

	$A(\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1})$	$E_{\text{app}}(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H_{\text{app}}(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S_{\text{app}}(\text{kJ}\cdot\text{mol}^{-1})$
H ₂ SO ₄	$2,84\cdot 10^{10}$	$6,12\cdot 10^4$	$5,86\cdot 10^4$	-53,56
H ₂ SO ₄ + TMDA	$2,21\cdot 10^6$	$4,26\cdot 10^4$	$4,00\cdot 10^4$	-132,25

And a plot of $\log (W_{\text{corr}}/T)$ against $(1/T)$ is displayed in figure 7 for the corrosion of carbon steel in 0.5 M H₂SO₄ in both the absence and presence of TMDA. Each obtained straight line has a slope of $(-\Delta H_{\text{app}}/R)$ and an intercept of $(\log[R/Nh] + \Delta S_{\text{app}}/R)$ from which the values of ΔH_{app} and ΔS_{app} were calculated, respectively. These results are tabulated in table 4, as well.

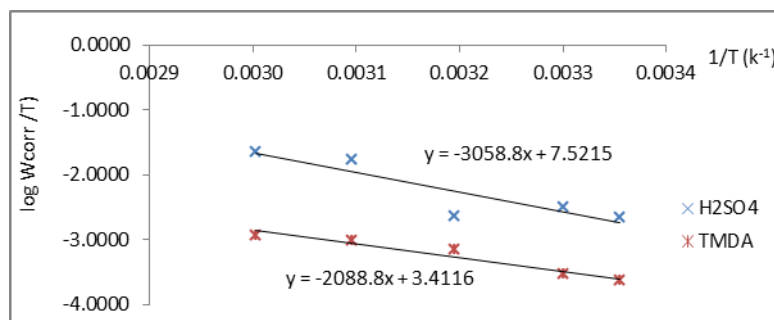


Figure7. Transition-state plots for carbon steel corrosion W_{corr} in 0.5M H₂SO₄ in the presence and absence of 325 ppm of TMDA.

The decrease of the apparent activation energy in the presence of inhibitor suggests that the inhibitor's presence further supports the proposed chemisorption mechanism [41]. Lower value of E_{app} in inhibited system compared to the blank is indicative of a chemisorption mechanism, while higher values of E_{app} suggest a physical adsorption mechanism. The same tendency applies to the Arrhenius pre-exponential factor as similarly observed in other studies [42- 43]. This increase in the value of the pre-exponential factor (A) induces the increase of the corrosion rate (W_{corr}) showing that the investigated (TMDA) compound is a highly effective inhibitor since it shows high

inhibition efficiency even at low activation energy. The value obtained of the ΔH_{app} confirm the exothermic behavior of the adsorption process of TMDA on the mild steel surface in sulfuric acid. While an endothermic adsorption process ($\Delta H_{app} > 0$) is attributed unequivocally to chemisorption, an exothermic adsorption process ($\Delta H_{app} < 0$) may involve either physisorption or chemisorption or a mixture of both processes [44, 45]. In the present work, the values of ΔS_{ads} in the absence and presence of the inhibitor is large and negative, is explained by the possibility of formation of iron complex on the metal surface [46, 47], or inhibitor molecules may freely move in the bulk of solution before the adsorption process, while with progress in adsorption the inhibitor molecules were orderly adsorbed on the metal surface, which resulted in the decrease in entropy [48].

III.3. Adsorption isotherms

The inhibiting action of organic compounds usually is attributed to interactions with metallic surfaces by adsorption. The adsorption process is influenced by the structure of the organic compounds, the charge distribution in the molecules, the nature of the surface-charged metals and the types of media used. The adsorption of an organic adsorbate at a metal-solution interface can be represented as a substitutional adsorption process combining the organic molecules in the aqueous solution, and the water molecules on the metallic surface . [50]:



Where $\text{PEGME}_{\text{sol}}$ and $\text{PEGME}_{\text{ads}}$ are the surfactant molecules in the acid solution and adsorbed on the metallic surface, respectively, $\text{H}_2\text{O}_{\text{ads}}$ is the water molecules in the metallic surface, n is the size ratio representing number of water molecules replaced by one molecule of inhibitor during adsorption process. The degree of surface coverage Θ can be plotted as a function of the concentration of the inhibitor under test. The fractional surface coverage (Θ) was found maximum at the higher concentration (325 ppm) of TMDA at 6 h immersion period (Table-1). It is assumed that the water molecules dipoles have to be oriented and their orientation depends on the metal charge adapting the suitable adsorption isotherm [51-52].

However, accounted that the relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature is known as isotherm; thus the following insight into the adsorption process. Several adsorption isotherm were attempted to fit surface coverage values to classical isotherm of Langmuir, Flory-Huggins, Temkin, Frumkin, [53.56]. Furthermore, the value of the correlation (R^2) was used to determine the best fit isotherm which was obtained for Langmuir, Flory-Huggins, Frumkin isotherms and Temkin.

III.3.1. Langmuir Adsorption Isotherms

The surface coverage Θ data are very useful on discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium condition. The dependence of the fraction of the surface covered Θ on the concentration C of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Fig. 6 shows the linear plots for C/Θ versus C , suggesting that the adsorption obeys the Langmuir's isotherm. Langmuir adsorption isotherm is mathematically expressed as:

$$C_{\text{inh}}/\Theta = C_{\text{inh}} + 1/K_{\text{ads}} \quad (7)$$

where C_{inh} is inhibitor concentration, K_{ads} is the adsorptive equilibrium constant, representing the degree of adsorption (i.e., the higher value of K_{ads} indicates that the inhibitor is strongly adsorbed on the metal surface); the value of K_{ads} obtained from the reciprocal of intercept of Langmuir plot lines and the slope of these lines is near unity, meaning that each inhibitor molecule occupies one active site on the metal surface. Figure 8 shows the plots of C_{inh}/θ versus C_{inh} . The linear plot was obtained indicating that the experimental data obtained fits the Langmuir adsorption isotherm.

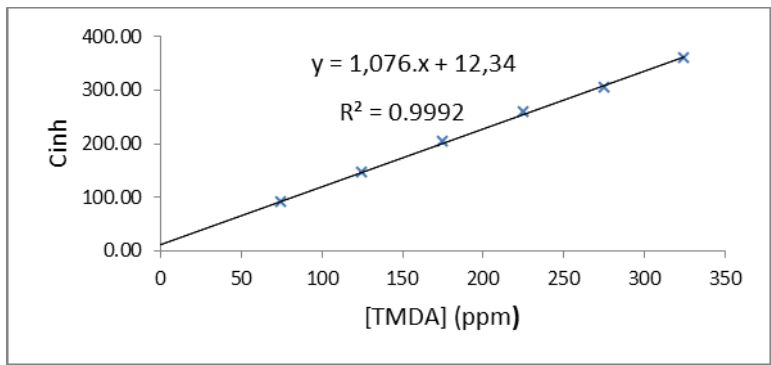


Figure8. Langmuir adsorption isotherm of TMDA on carbon steel surface in 0.1M H2SO4 at 30° C

Moreover, the essential characteristic Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L [57], which describes the type of isotherm and is defined by:

$$R_L = \frac{1}{1 + K_{ads} C}$$

The smaller R_L value indicates a highly favorable adsorption. If $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable. The estimated value of R_L for TMDA at 325 ppm was found less than unity, confirming that the adsorption processes is favorable.

The value of K_{ads} is given in Table 2. The equilibrium constant of adsorption process (K_{ads}) is related to the free energy of adsorption (ΔG°_{ads}) by the equation:

$$K_{ads} = \frac{1}{55.5} \exp\left[\frac{-\Delta G^\circ_{ads}}{RT}\right] \tag{8}$$

Where R is the gas constant (8.314 kJ/mol); and T is the temperature (K). The constant value of 55.5 is the concentration of water in solution in mol.L⁻¹.

The value of ΔG°_{ads} was evaluated using Equation (8) for the 325 pp of TMDA and presented in Table 5. The high value of K_{ads} and negative value of ΔG°_{ads} suggested that, inhibitor molecules strongly adsorb on the carbon steel surface. The value of ΔG°_{ads} indicates the spontaneous adsorption of TMDA on the mild steel. Generally, values of ΔG°_{ads} up to -20 kJ mol⁻¹ are consistent with electrostatic interaction between the charged metal and charged molecules, which signifies physical adsorption while values more negative than -40 kJ mol⁻¹ signifies

Table 5. Thermodynamic parameters for the adsorption of TMDA onto the carbon steel surface in 0.5 M H2SO4

Inhibitor	Slope	K_{ads}	R^2	ΔG°_{ads}
TMDA	1.076	$8.010 \cdot 10^4$	0.999	-37.98

chemical adsorption [58-59]. The calculated ΔG°_{ads} value was -37.98 kJ mol⁻¹ indicated that adsorption mechanism of the investigated surfactant is typical of chemical adsorption. The lower value of activation energy in presence of TMDA than in its absence (Table 5) further corroborated the chemical mode of adsorption.

III.2. Flory-Huggins Isotherm

Flory-Huggins adsorption isotherm is calculated from the experimental data and can be expressed according to Equation 9 [60]:

$$\text{Log} \frac{\theta}{C} = \text{Log} K_{ads} + x \text{Log} (1 - \theta) \tag{9}$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule. As shown in Figure 9, the plot of $\text{log}(\theta / C)$ against $\text{log}(1 - \theta)$ for different concentrations shows a straight line indicating that adsorption follows the Flory–Huggins adsorption isotherm, (slope 2.213) with $R^2 = 0.876$. The value of the size parameter (x) is approximately 2. This indicates that the adsorbed specie of the inhibitor is bulky since it could displace more than one water molecule from the metal steel surface [61]. The calculated ΔG_{ads}

for the inhibitor on the surface of mild steel is given -43.32 kJ/mol, it corroborates that the adsorption process is chemisorption. The value of ΔG_{ads}° is too negative indicating that TMDA is strongly adsorbed on the steel surface and ensuring the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface.

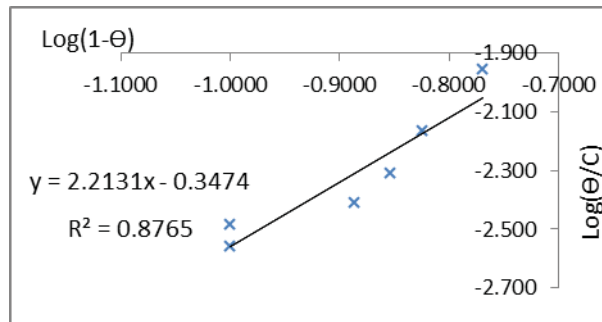


Figure9. Flory-Huggins adsorption isotherm of TMDA on carbon steel surface in 0.5M H2SO4 at 298°K

III.3. Frumkin Adsorption Isotherm

Frumkin isotherm is an extension of Langmuir isotherm. It states that adsorbed molecules do interact and affect further adsorption by either repulsion or attraction of molecules. Considering the Frumkin isotherm commonly used to quantify the interactions occurring between corrosion inhibitor and a metal surface and it is expressed by the relationship [62]:

$$\log C \cdot \frac{\theta}{1-\theta} = 2.303 \log K_{ads} + 2a\theta \quad (10)$$

Where θ is the degree of surface coverage, a is the interaction term parameter describing the interaction in adsorbed layer (if $a > 0$, there is a lateral attraction, if $a < 0$, there is a lateral repulsion between the adsorbing molecules), C (in ppm/L) is the inhibitor concentration, where K_{ads} is the adsorption-desorption constant. The Frumkin adsorption isotherm is a general expression since the limiting case for which $a = 0$ is representative of an interaction free behavior between adsorbed species and defines the Langmuir isotherm [63]. Equation 10 was used to plot the

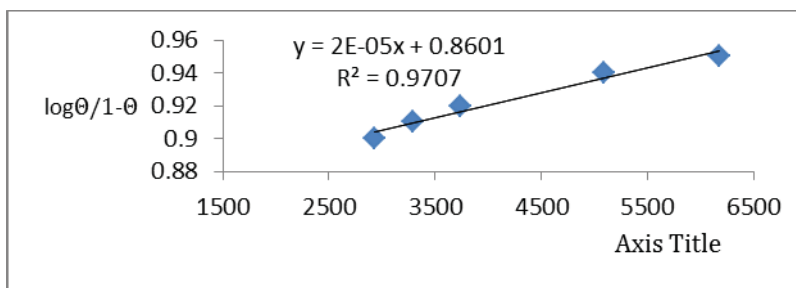


Figure10. Frumkin adsorption isotherm of TMDA on carbon steel surface in 0.5M H2SO4 at 298°K

Frumkin isotherm ($\log C \cdot \theta/(1-\theta)$ versus θ) shown in Figure 10. The existence of adsorption interactions between adsorbed TMDA and the metal surface is thus confirmed since most of the experimental data fit nicely into the Frumkin isotherm plot, the slight S-shape. The value of the adsorption parameter a is positive suggesting the attractive behavior of the inhibitor on the surface of mild steel [64]

III.3.4. Temkin Adsorption Isotherm

The Temkin isotherm mostly favours chemisorption and an indication of interaction of uncharged molecules on a heterogeneous surface. The equation for this model is given by equation [65]:

$$\ln \left(\frac{\theta}{1-\theta} \right) = K_{ads} \cdot C \quad (12)$$

where a is molecules interaction parameter, Θ is the degree of surface coverage, K_{ads} is equilibrium constant of adsorption process and C is the concentration of TMDA. The surface coverage values (θ) evaluated at different concentrations of TMDA in 0.5M H_2SO_4 were tested graphically by fitting to suitable adsorption isotherm. The plot of θ versus $\log C$ (Figure 10) shows a straight line indicating that the adsorption of the compound on the composite surface follows Temkin adsorption isotherm. The applicability of Temkin adsorption isotherm verifies the assumption of mono-layer adsorption on a uniform homogeneous composite surface with an interaction in the adsorption layer [66]. The value of the adsorption parameter a positive suggesting the attractive behavior of the inhibitor on the surface of mild steel [67]. The calculated ΔG°_{ads} is -34.93 kJ/mole.

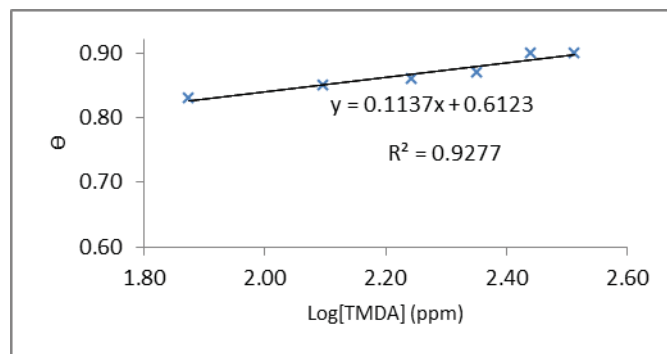


Figure 11. Temkin adsorption isotherm of TMDA on carbon steel surface in 0.1M H_2SO_4 at 30° C

Obtained value of ΔG°_{ads} is negative, indicative of spontaneity of the adsorption process and the stability of the adsorbed species on the metal surface [24]. The value of ΔG°_{ads} for the Temkin isotherm is around -40 kJ/mol, supportive of earlier proposed chemisorption as the mechanism of the adsorption process [68-70].

IV. CONCLUSION

The results obtained show that TMDA is a good corrosion inhibitor for mild steel under acidic conditions. The inhibitive action of TMDA toward the corrosion of mild steel could be attributed to the adsorption on the metal surface. The adsorbed layer acts as a barrier between the metal surface and aggressive solution leading to a decrease in the corrosion rate. Given this inhibition efficiency, the value of Gibb's free energy of adsorption indicate that TMDA is chemically adsorbed on the surface and spontaneous following its correspondence to the following adsorption models: the Langmuir, Frumkin, Flory-Huggins and Temkin. The interactions of the adsorbed molecules of the inhibitor are attractive and bulky on the metal surface. From the study of the effect of temperature, it was found that IE (%), very interestingly, increased with increasing temperature reaching a peak at 343° K (IE(%)) = ca. 97.5%) which is of a practical interest in several industrial processes. There is an adequate change of the apparent activation energy when compared to that in the case of uninhibited solutions. The lower activation energy of the corrosion process in the presence of the corrosion inhibitor, when compared to that in its absence demonstrated the chemisorptive nature of the adsorption.

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