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Tributylamine as corrosion inhibitor for mild steel in hydrochloric acid

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The corrosion inhibition of mild steel in 2 M hydrochloric acid solution by tributylamine has been investigated using the impedance technique. Tributylamine was studied in concentrations from 5×10^{-4} M to 1 M at a temperature of 298 K. The inhibitor mechanism was treated as a substitutional adsorption process according to *Flory-Huggins, Dhar-Flory-Huggins* and *Bockris-Swinkels* isotherms. The best approach was obtained using the latter. A structural parameter, the projected molecular area of tributylamine, was calculated to elucidate inhibitor orientation in the adsorption process.

1. Introduction

Inhibitors are chemical compounds whose presence in small quantities can retard metal corrosion in an aggressive environment. Selecting the appropriate inhibitor for a specific environment and metal is of great importance, since an inhibitor that protects one particular metal may accelerate the corrosion of another.

Amines are well known as corrosion inhibitors for mild steel [1, 2]. The presence of a heteroatom in an organic compound with unsaturated bonds causes an adsorption process on the metal surface which reduces metal dissolution [3]. Despite the widespread use of amines as corrosion inhibitors, their inhibition mechanism remains unexplained.

The effectiveness of different corrosion inhibitors has been studied as a function of the electron density of the donor atom in the inhibitor molecule [4], the molecular structure of the molecule and its size [5]. Molecular modeling is a suitable technique for studying molecular interaction in the range from 1 Å to 100 Å [6–8].

The aim of this paper is to analyse the relationship between the adsorption mechanism, molecular structure and inhibition efficiency of tributylamine as a corrosion inhibitor for mild steel in hydrochloric acid solution.

2. Material and methods

The mild steel used had the following composition (weight %): 0.08 C, <0.02 P, 0.21 Mn, <0.02 S, 0.05 Si, with the balance in Fe. The specimens were mechanically polished with different grades of emery paper (down to 600), degreased with acetone and dried. 2 M HCl acid was used as the blank corrosion test solution.

The inhibitor used was a commercial tributylamine, linear formula $(CH_3\,CH_2\,CH_2\,CH_2)_3N$, Merck AR grade, in concentrations of 5×10^{-4}, 1×10^{-3}, 5×10^{-3}, 5×10^{-2}, and 1 M. The working temperature was 298 K. The experimentation times were 2, 24, 48 and 72 h.

The electrochemical impedance spectroscopy (EIS) method was used in the frequency range from 55 kHz to 1 mHz, with a logarithmic sweeping frequency of 5 steps/decade. EIS involved the imposition of a 10 mV amplitude sine-wave. A Solartron 1250 Frequency Response Analyzer connected to a Solartron 1286 Electrochemical Interface was used. The counter electrode was a platinum gauze and a saturated calomel (SCE) electrode was used as reference. Data was generated at the rest potential.

3. Results and discussion

Fig. 1 shows three representative examples of *Nyquist* plots for mild steel immersed in 2 M HCl acid solution obtained after 2 h experimentation time in the presence and absence of the tributylamine inhibitor at 1 M and 5×10^{-2} M concentrations. The testing temperature was 298 K in all cases. Impedance diagrams for other times are not included because they do not supply any additional information. As can be seen, the *Nyquist* plot always appears as a depressed capacitive semicircle in the high- to intermediate-frequency range, i.e. a rotation of the centre of the capacitive semicircle by an angle (φ) below the real axis. Deviations of this kind, often referred to as frequency dispersion, have been attributed to non-homogeneous steel surfaces. Distributed circuit elements have been used to describe the experimental findings. A good approximation, widely used in corrosion studies, is the well-known *Cole-Cole* frequency dispersion formula [9]:

$$Z(j\omega) = R_s + \frac{R_p}{1 + (j\omega C_{dl} R_p)^{\alpha}}$$

where R_s is the solution resistance between the reference and working electrodes, α is an empirical exponent

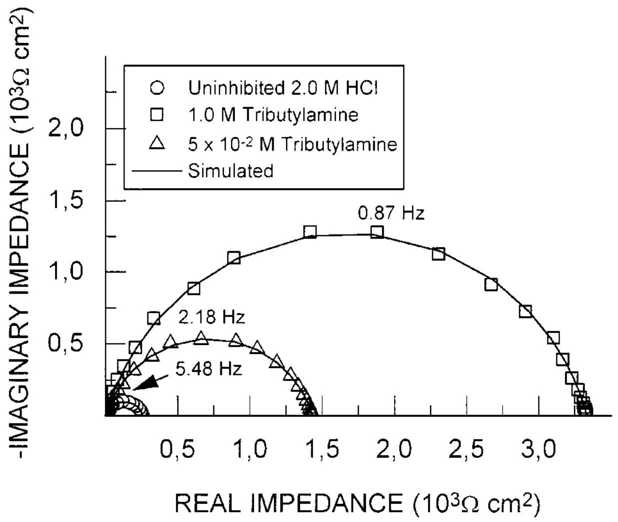


Figure 1 Typical impedance plots for mild steel in 2 M hydrochloric acid solution inhibited with 1 M and 5×10^{-2} M tributylamine concentrations after 2 h immersion at 298 K. The values of the fitted parameters are: (i) without inhibitor: $R_s = 2$ Ω cm^2, $R_p = 259.27$ Ω cm^2, $C_{dl} = 79.64$ μF cm^{-2}, $\alpha = 0.83$; (ii) with 1 M tributylamine: $R_s = 4$ Ω cm^2, $R_p = 3330.85$ Ω cm^2, $C_{dl} = 46.58$ μF cm^{-2}, $\alpha = 0.83$; and (iii) with 5×10^{-2} M tributylamine: $R_s = 4$ Ω cm^2, $R_p = 1428.67$ Ω cm^2, $C_{dl} = 57.71$ μF cm^{-2}, $\alpha = 0.82$.

$(0 < \alpha < 1)$ which is correlated to the angle of rotation (φ) through $\varphi = (1 - \alpha)\pi/2$, C_{dl} is the double-layer capacitance, and $j = (-1)^{1/2}$. Fig. 1 also includes simulated data. The simulation fitting procedure was carried out using the parameters indicated in the caption to Fig. 1. As can be seen, there is excellent agreement between the experimental and simulated results.

The *Nyquist* plots in Fig. 1 show that the mild steel-tributylamine system is under charge transfer resistance control, without any loops that could indicate inductive behaviour in the low-frequency region. Thus, it may be inferred that the inhibitor is selectively adsorbed in specific places on the mild steel surface. According to this inhibition mechanism the tributylamine inhibitor could be adsorbed at active points, thus causing the corrosion rate to drop.

R_s can be obtained from the abscissa axis intercept of the semicircle at $\omega \to \infty$, $R_s \approx 3$ Ω cm^2. R_p can be obtained from the diameter of the semicircle [10], i.e. the difference between the high- and low-frequency intercepts on the abscissa axis (Fig. 1), giving $R_p \approx 259$ Ω cm^2 in the absence of inhibitor and $R_p \approx 1429$ Ω cm^2 and $R_p \approx 3331$ Ω cm^2 for 5×10^{-2} M and 1 M inhibitor concentrations, respectively. The diameter of the semicircle (R_p) in Fig. 1 is associated with the steel corrosion rate, and a lower R_p implies higher corrosion.

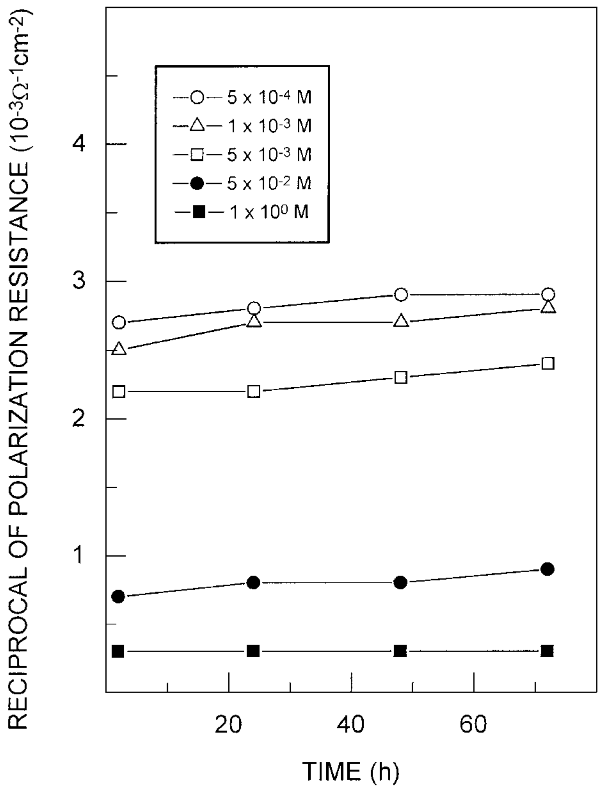


Figure 2 Reciprocal of polarization resistance against time at different inhibitor concentrations for mild steel in 2 M HCl acid solution at a temperature of 298 K.

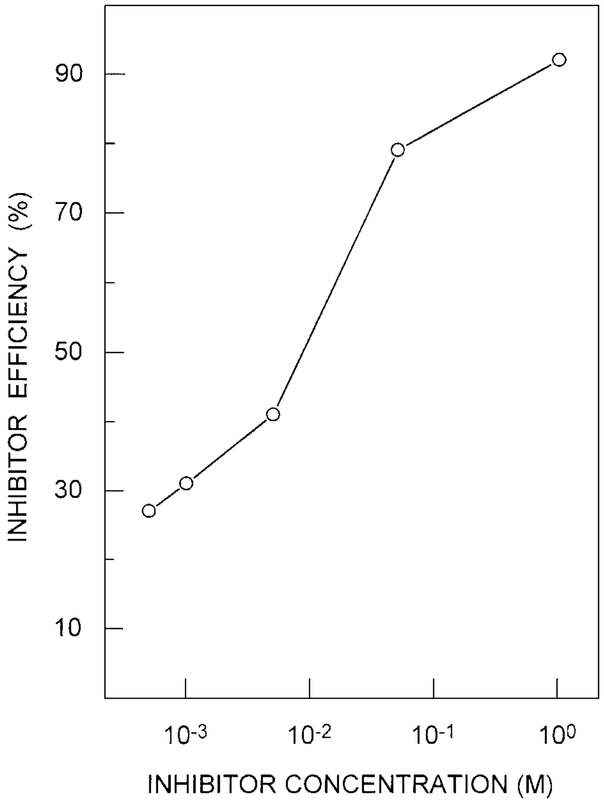


Figure 3 Inhibitor efficiency against inhibitor concentration for mild steel in 2 M HCl acid solution at a temperature of 298 K.

Fig. 2 depicts the reciprocal of the R_p results for the tributylamine inhibitor as a function of experimentation time and at a temperature of 298 K. It may be assumed, as an approximation, that the $(R_p)^{-1}$ parameter is directly related with the corrosion rate [10].

Fig. 3 shows the dependence of inhibitor efficiency on the amount of inhibitor. The percentage inhibitor efficiency is given by:

$$\frac{1/R_p - 1/R_{pi}}{1/R_p} \times 100$$

where R_p and R_{pi} represent polarization resistance in the absence and presence of inhibitor, respectively. The tested inhibitor proved to be highly efficient when very high concentrations were added.

According to *Bockris and Drazic* [11], the inhibition mechanism can be explained by the Fe-$(\mathrm{Ind})_{\mathrm{ads}}$ reaction intermediates: Fe + Inh $\Leftrightarrow$ Fe-$(\mathrm{Ind})_{\mathrm{ads}}$ $\Leftrightarrow$ $\mathrm{Fe}^{n+} + \mathrm{ne}^- + \mathrm{Inh}$, forming an adsorption layer, through the nitrogen atom of the inhibitor, which acts as a hindrance to the hydrochloric acid solution and enhances the protection of the metal surface [12]. At first when there is not enough Fe-$(\mathrm{Inh})_{\mathrm{ads}}$ to cover the metal surface, because the inhibitor concentration is low or because the adsorption rate is slow, metal dissolution takes place at sites on the mild steel surface free of Fe-$(\mathrm{Inh})_{\mathrm{ads}}$. With high inhibitor concentration a compact and coherent inhibitor overlayer is formed on the mild steel surface, reducing chemical attack of the metal.

The adsorption of an organic adsorbate on the surface of a mild steel electrode is regarded as a substitutional adsorption process between the organic compound in the aqueous phase ($\mathrm{Org}_{\mathrm{aq}}$) and the water molecules adsorbed on the mild steel surface ($\mathrm{H_2O_{ams}}$):

$$\mathrm{Org}_{\mathrm{aq}} + X\mathrm{H_2O_{ams}} \Leftrightarrow \mathrm{Org}_{\mathrm{ams}} + X\mathrm{H_2O_{aq}} \qquad (1)$$

where X is the size ratio, i.e. the number of water molecules replaced by one adsorbate molecule. When the equilibrium of the process described in Equation 1 is reached, it is possible to obtain different expressions of the adsorption isotherm plots, and thus the degree of surface coverage (θ) can be plotted as a function of the concentration of tributylamine inhibitor in the hydrochloric acid solution. The θ was calculated from the inhibitor efficiency relationship [13]: $\frac{1/R_{\mathrm{p}} - 1/R_{\mathrm{pi}}}{1/R_{\mathrm{p}}}$.

3.1. Adsorption isotherm plots

The isotherms most used are [14–16]:

(i) *Frumkin:*

$$kc = \left(\frac{\theta}{1-\theta}\right)\exp(-2a\theta) \qquad (2)$$

where c is the inhibitor concentration, a is the interaction term parameter ($a > 0$ lateral attraction and $a < 0$ repulsion between adsorbed organic molecules), k is the equilibrium constant of the adsorption reaction given by: $k = (1/55.5)\lfloor\exp(-\Delta G^0_{\mathrm{ads}}/RT)\rfloor$, the value 55.5 is the concentration of water in the solution in mol/l, R is the gas constant (8.314 J/mol K), T is the absolute temperature, and $\Delta G^0_{\mathrm{ads}}$ is the adsorption energy, $\Delta G^0_{\mathrm{ads}}$ can be calculated using the ordinate axis intercept of the straight line ($\log k$), see Figs 4–6 below. The application of the *Frumkin* isotherm to study the adsorption mechanism of amine compounds as inhibitors on mild steel in hydrochloric acid solution has been described elsewhere [1, 2].

(ii) *Flory-Huggins:*

$$kc = \frac{\theta}{X(1-\theta)^X} \qquad (3)$$

where X is the number of water molecules replaced by one molecule of organic adsorbate, see Equation 1.

(iii) *Dhar-Flory-Huggins:*

$$kc = \frac{\theta}{e^{(X-1)}(1-\theta)^X} \qquad (4)$$

(iv) *Bockris-Swinkels:*

$$kc = \frac{\theta}{(1-\theta)^X}\,\frac{[\theta + X(1-\theta)]^{(X-1)}}{X^X} \qquad (5)$$

All the above isotherms have the form $f(\theta, X)\exp(-a\theta) = kc$ where $f(\theta, X)$ is the configurational term, which depends essentially on the physical model and assumptions underlying the derivation of the isotherm, and $\exp(-a\theta)$ is the interaction term, which depends on the strength of the interaction [17, 18].

Equations 3–5 may be written as $\log[f(\theta, X)] = \log c + \log k$. A plot of $\log[f(\theta, X)]$ against $\log c$, for a specified value of X, is a straight line with a slope of unity, and the ordinate axis intercept gives the $\log k$ value.

Fig. 4 shows a *Flory-Huggins* isotherm plot for values of X up to 5, using results for 2 h experimentation time. Fig. 5 shows a *Dhar-Flory-Huggins* isotherm plot, and Fig. 6 a *Bockris-Swinkels* isotherm plot. Tables I–IV summarize meaningful parameters for the three isotherms examined and all the times tested.

It can be observed, from the slopes of Figs 4–6 and the correlation coefficient (CC) of Tables I–IV, that the three isotherms examined yield similar results. Nevertheless, the best approach is obtained with the *Bockris-Swinkels* isotherm, in which the slope for $X = 3$ remains constant, close to a unity value, for the four times tested. A value of X equal to 3 means that one molecule of tributylamine replaces 3 molecules of water on the mild steel surface.

The adsorption energy of water molecules on mild steel is high [14]. Thus, the first effect of tributylamine inhibitor is to replace a water molecule with a molecule of tributylamine adsorbate. Equations 3–5 take into account the number of water molecules displaced. In a second step the free amine can bond to the metal surface. This means that if the amount of tributylamine in the solution is low, the mild steel corrosion rate may increase due to the possible formation of intermediate products which reduce inhibitor efficiency.

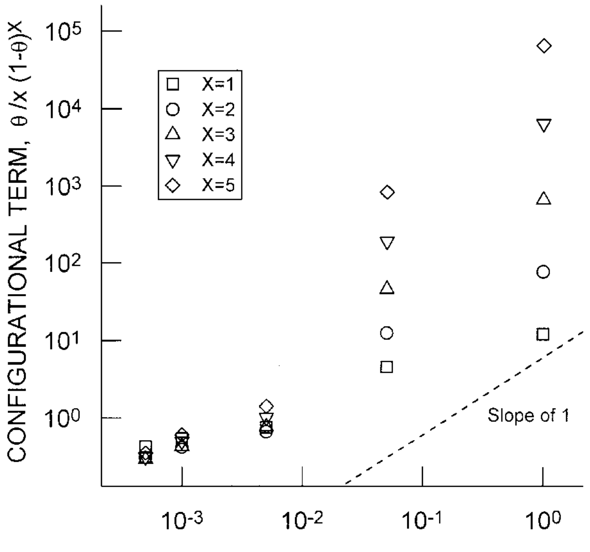


Figure 4 *Flory–Huggins* isotherm plot against inhibitor concentration for mild steel in 2 M HCl acid solution, at 298 K, for 2 h experimentation, and for values of X up to 5.

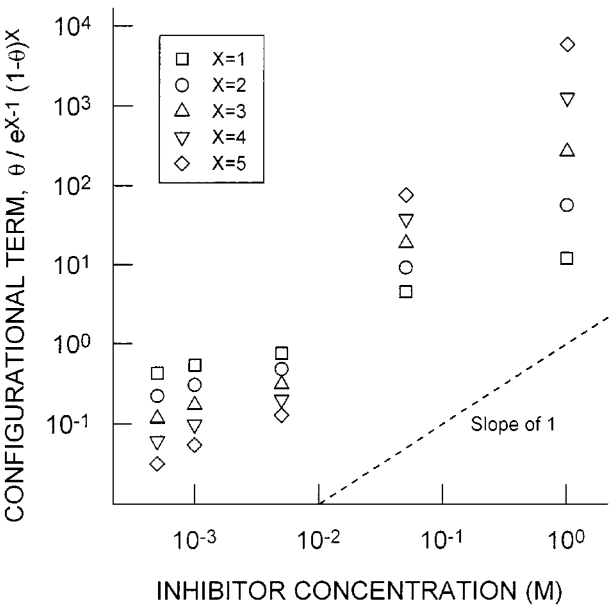


Figure 5 *Dhar-Flory–Huggins* isotherm plot against inhibitor concentration for mild steel in 2 M HCl acid solution, at 298 K, for 2 h experimentation, and for values of *X* up to 5.

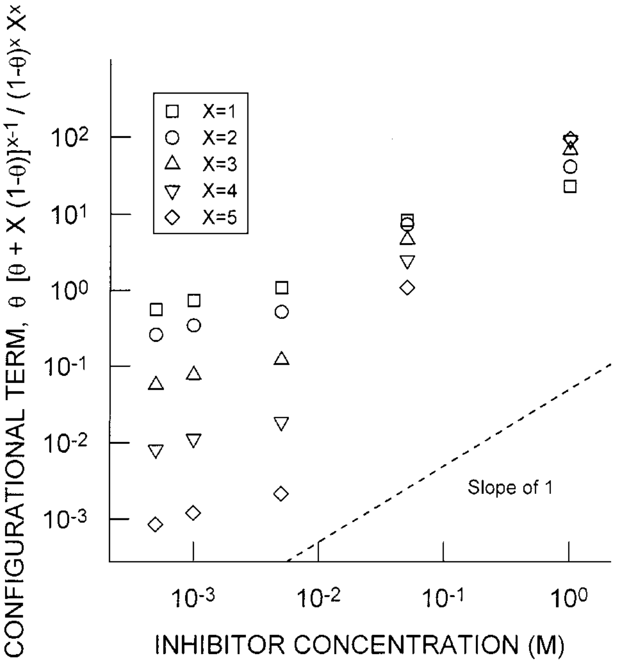
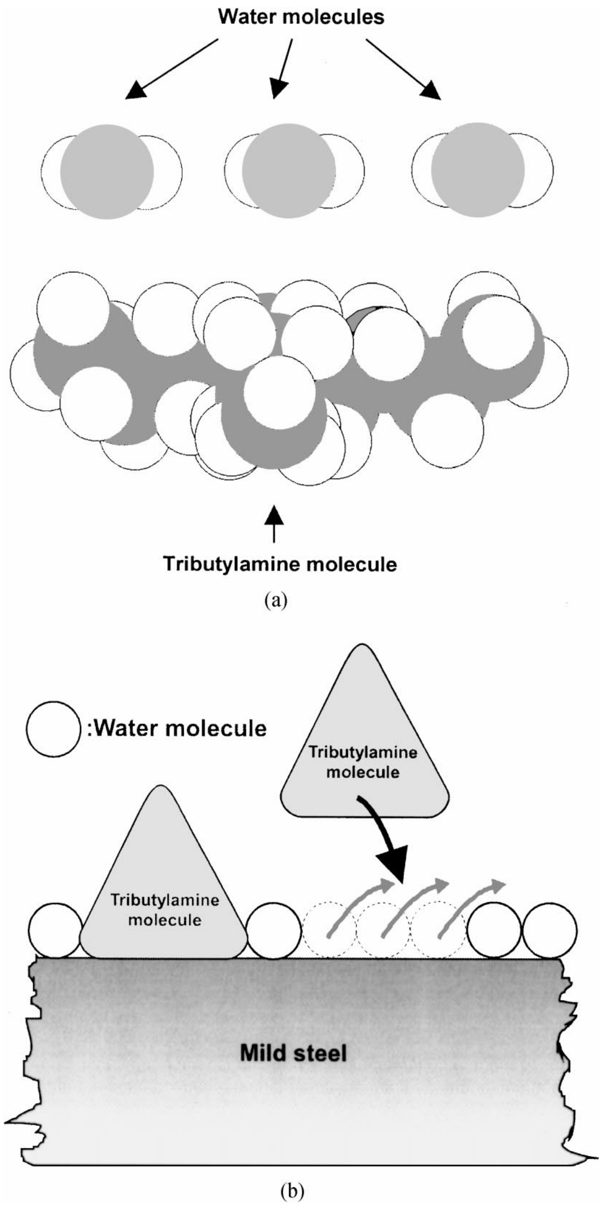


Figure 6 *Bockris-Swinkels* isotherm plot against inhibitor concentration for mild steel in 2 M HCl acid solution, at 298 K, for 2 h experimentation, and for values of *X* up to 5.

3.2. Orientation of tributylamine on the mild steel surface

The purpose of this section is to calculate the optimal orientation of tributylamine for adsorption on the mild steel surface using molecular models. Fig. 7a shows the



(a)

(b)

Figure 7 Tributylamine molecule adsorbed onto mild steel electrode. (a) Top view; (b) Schematic representation of the displacement process (front view).

TABLE I Adsorption isotherm parameters for tributylamine onto mild steel in 2 M HCl solution at 298 K and for 2 h experimentation

	Flory-Huggins			*Dhar-Flory-Huggins*			*Bockris-Swinkels*		
X	Slope	log(*k*)	$(CC)^2$	Slope	log(*k*)	$(CC)^2$	Slope	log (*k*)	$(CC)^2$
1	0.4641	1.1108	0.9668	0.4641	1.1108	0.9668	0.5200	1.4099	0.9650
2	0.7702	1.9024	0.9661	0.7702	1.7692	0.9661	0.7048	1.6219	0.9672
3	1.0764	2.8190	0.9649	1.0764	2.4275	0.9649	0.9844	1.7912	0.9626
4	1.3826	3.7867	0.9640	1.3826	3.0859	0.9640	1.2996	1.8857	0.9578
5	1.6887	4.7824	0.9633	1.6887	3.7442	0.9633	1.6261	1.8902	0.9550

CC: correlation coefficient.

TABLE II Adsorption isotherm parameters for tributylamine onto mild steel in 2 M HCl solution at 298 K and for 24 h experimentation

	Flory-Huggins			*Dhar-Flory-Huggins*			*Bockris-Swinkels*		
X	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2
1	0.4819	1.1000	0.9821	0.4819	1.1000	0.9821	0.5412	1.3994	0.9806
2	0.7902	1.8744	0.9801	0.7902	1.7411	0.9801	0.7226	1.5953	0.9804
3	1.0985	2.7737	0.9778	1.0985	2.3822	0.9778	0.9973	1.7403	0.9728
4	1.4068	3.7242	0.9761	1.4068	3.0234	0.9761	1.3080	1.8101	0.9667
5	1.7151	4.7027	0.9749	1.7151	3.6645	0.9749	1.6313	1.7921	0.9635

TABLE III Adsorption isotherm parameters for tributylamine onto mild steel in 2 M HCl solution at 298 K and for 48 h experimentation

	Flory-Huggins			*Dhar-Flory-Huggins*			*Bockris-Swinkels*		
X	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2
1	0.4946	1.1041	0.9799	0.4946	1.1041	0.9799	0.5559	1.4040	0.9782
2	0.8066	1.8788	0.9780	0.8066	1.7455	0.9780	0.7374	1.5995	0.9786
3	1.1185	2.7784	0.9756	1.1185	2.3869	0.9756	1.0127	1.7440	0.9712
4	1.4304	3.7291	0.9739	1.4304	3.0283	0.9739	1.3242	1.8129	0.9648
5	1.7423	4.7079	0.9726	1.7423	3.6697	0.9726	1.6487	1.7939	0.9611

TABLE IV Adsorption isotherm parameters for tributylamine onto mild steel in 2 M HCl solution at 298 K and for 72 h experimentation

	Flory-Huggins			*Dhar-Flory-Huggins*			*Bockris-Swinkels*		
X	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2	Slope	log(k)	(CC)^2
1	0.4984	1.0778	0.9800	0.4984	1.0778	0.9800	0.5607	1.3750	0.9790
2	0.8085	1.8319	0.9756	0.8085	1.6986	0.9786	0.7390	1.5565	0.9755
3	1.1187	2.7109	0.9720	1.1187	2.3195	0.9720	1.0096	1.6787	0.9651
4	1.4289	3.6411	0.9696	1.4289	2.9403	0.9696	1.3162	1.7235	0.9580
5	1.7390	4.5993	0.9679	1.7390	3.5611	0.9679	1.6365	1.6817	0.9545

area occupied by a vertically-oriented adsorbed tributylamine molecule to be about 33 Å^2 (the projected area of a rectangle surrounding a molecule), as compared with 45 Å^2 for the horizontal orientation (the projected area of a triangle surrounding a molecule). These values were obtained after minimum energy configuration calculations using the *HyperChem Program*. The area occupied by a vertically-adsorbed water molecule is in the range from 8.3 Å^2 to 12 Å^2 [14, 19, 20]. Thus, a vertical orientation of tributylamine displaces 3 molecules of water ($X = 3$, Equations 3–5) while a horizontal orientation of tributylamine displaces 4 molecules of water. The schematic representation of the displacement process is shown in Fig. 7b. This result corroborates the vertical adsorption of tributylamine pointed out previously using interaction term (a) in Equation 2 [1].

4. Conclusions

The inhibition mechanism of tributylamine on mild steel in hydrochloric acid solution seems to be that of selective adsorption at active points. Tributylamine was chemically adsorbed on the mild steel surface according to a *Bockris-Swinkels* isotherm, with one tributylamine molecule replacing 3 molecules of water. The inhibition efficiency of tributylamine increases as the inhibitor concentration is raised.

It has been demonstrated that the projected molecular area method is a good approach to correlate the effectiveness of film-forming corrosion inhibitor on mild steel in hydrochloric acid solution and the concentration of tributylamine.

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