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Substitutional inhibition mechanism of mild steel hydrochloric acid corrosion by hexylamine and dodecylamine

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Abstract

Hexylamine and dodecylamine were investigated as inhibitors of mild steel hydrochloric acid corrosion, in concentrations from 1×10^{-6} to 1.0 M, at a temperature of 298 K. For a given inhibitor concentration, dodecylamine showed higher effectiveness than hexylamine. The inhibitor mechanism was treated as a substitutional adsorption process according to Flory–Huggins (FH), Dhar–Flory–Huggins (DFH) and Bockris–Swinkels (BS) isotherms. The best approach was obtained using FH and DFH isotherms, with one molecule of inhibitor replacing three molecules of water. A structural parameter, the projected molecular area of these two inhibitors, was calculated to elucidate inhibitor orientation in the adsorption process.

1. Introduction

Amines are well known as corrosion inhibitors for mild steel. The relatively high water solubility of low molecular weight amines is advantageous in their use as corrosion inhibitors [1, 2]. The presence of a heteroatom in an organic compound with unsaturated bonds causes an adsorption process on the mild steel surface which reduces metal corrosion. Inhibition efficiency generally increases with the number of carbon atoms in the amine alkyl chain up to C_9–C_{12}. Further increases in chain length to more than 12 carbons brings about little further improvement because of the decreased solubility and increased steric hindrance to adsorption [3, 4]. Despite the widespread use of amines as corrosion inhibitors, the inhibition mechanism remains unexplained.

The effectiveness of a corrosion inhibitor can be studied as a function of the electron density of the donor atom in the inhibitor molecule [5], the molecular structure of the molecule and its size [6]. Molecular modelling is a suitable technique for studying molecular interaction in the range from 1 to 100 Å [7–9].

The aim of this work is to analyse the relationship between the substitutional adsorption mechanism, molecular structure and inhibition efficiency of hexylamine and dodecylamine as corrosion inhibitors for mild steel in hydrochloric acid solution at a temperature of 298 K.

2. Experimental details

The mild steel used had the following composition (wt %): 0.045 C, 0.011 P, 0.360 Mn, 0.015 S, 0.010 Si, the balance being Fe, corresponding to an ASTM A-619 Specification cold-rolled sheet. The specimens were mechanically polished with different grades of emery paper, down to 600, degreased with acetone and dried. 2.0 M HCl acid was used as the blank corrosion test solution.

Commercial hexylamine ($CH_3(CH_2)_5NH_2$) and dodecylamine ($CH_3(CH_2)_{11}NH_2$) were used (Merck AR grade) in the concentration range from 1×10^{-6} to 1.0 M. The working temperature was 298 K and the experimentation time 24 h.

Gravimetric measurements were carried out in triplicate using a Mettler analytical balance, model AJ150, precision ±0.1 mg. The reproducibility of the experiments was higher than 95%.

3. Results and discussion

Figure 1 depicts the dependence of inhibitor efficiency on the amount of inhibitor. The percentage inhibitor efficiency is given by

$$\frac{W_o - W_i}{W_o} \times 100 \tag{1}$$

where W_o and W_i represent weight loss in the absence and presence of inhibitor, respectively.

Figure 1 shows that dodecylamine is a more efficient inhibitor of mild steel hydrochloric acid corrosion than hexylamine. This behaviour may be interpreted as due to the higher molecular weight of dodecylamine. Additionally, the dissociation constant (pK_a), 10.56 for

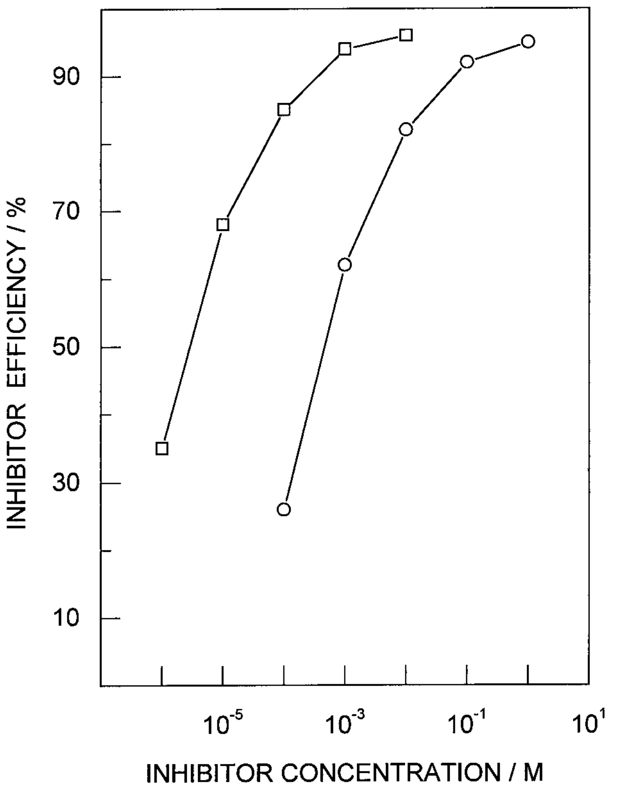

Fig. 1. Inhibitor efficiency against inhibitor concentration for mild steel in 2.0 M HCl acid solution at a temperature of 298 K. Key: (○) hexylamine and (□) dodecylamine.

hexylamine and 10.63 for dodecylamine, indicates that dodecylamine has a slightly more basic character than hexylamine and is more easily adsorbed by chemisorption, which initiates by the partial transfer of electrons from the dodecylamine to the metal. Table 1 includes mild steel corrosion rate in the presence and absence of inhibitors. It can be seen that the corrosion rate is lower in the presence of dodecylamine than in the presence of hexylamine.

The capacitance of the organic coating (C_{oc}) formed on mild steel is given by $C_{oc} = \varepsilon\varepsilon_o A(\lambda)^{-1}$, where ε is the dielectric constant of the amine, $\varepsilon_o = 8.85 \times 10^{-14}$ F cm^{-1} is the dielectric constant of a vacuum, $A = 1$ cm^2 is the exposed area of the mild steel test electrode and λ is the thickness of the organic coating. For a value of C_{oc} of about 1×10^{-6} F deduced from impedance results (not included) and a mean value for ε of 2 [1], the resulting thickness was 17.7×10^{-8} cm, which means a stable adsorbed film of inhibitor.

Table 1. Mild steel corrosion rate in the presence and absence of inhibitor

Inhibitor concentration/M	Corrosion rate × 10^6/kg m^{-2} s^{-1}							
	0	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Hexylamine	2.8	–	–	2.1	1.1	0.5	0.2	0.1
Dodecylamine	2.8	1.8	0.9	0.4	0.2	0.1	–	–

According to Bockris and Drazic [10], the inhibition mechanism can be explained by the Fe–(Inh)$_{ads}$ reaction intermediates

$$\mathrm{Fe} + \mathrm{Inh} \leftrightarrow \mathrm{Fe{-}(Inh)_{ads}} \leftrightarrow \mathrm{Fe}^{n+} + n\mathrm{e}^- + \mathrm{Inh} \tag{2}$$

This Fe–(Inh)$_{ads}$ intermediate forms an adsorption layer through the nitrogen atom of the inhibitor. The adsorption layer acts as a hindrance to the hydrochloric acid solution and enhances the protection of the metal surface. Initially when there is insufficient Fe–(Inh)$_{ads}$ 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–(Inh)$_{ads}$. 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 compound on the surface of a mild steel electrode is regarded as a substitutional adsorption process between the organic compound in the aqueous phase (Org$_{aq}$) and the water molecules adsorbed on the mild steel surface (H_2O_{ad})

$$\mathrm{Org_{aq}} + X\,\mathrm{H_2O_{ad}} \leftrightarrow \mathrm{Org_{ad}} + X\,\mathrm{H_2O_{aq}} \tag{3}$$

where X is the size ratio, that is, the number of water molecules replaced by one organic molecule [11]. When the equilibrium of the process described in Equation 3 is reached, it is possible to obtain different expressions for the adsorption isotherm plots, and thus the degree of surface coverage (θ) can be plotted as a function of the concentration of hexylamine or dodecylamine inhibitors in the hydrochloric acid solution. The value of θ was calculated from the inhibitor efficiency relationship

$$\theta = \frac{W_o - W_i}{W_o} \tag{4}$$

3.1. *Adsorption isotherm plots*

The most commonly used substitutional isotherms are Flory–Huggins [12], Dhar–Flory–Huggins [12] and Bockris–Swinkels [13]

(i) Flory–Huggins

$$kc = \frac{\theta}{X(1-\theta)^X} \tag{5}$$

(ii) Dhar–Flory–Huggins

$$kc = \frac{\theta}{\mathrm{e}^{(X-1)}(1-\theta)^X} \tag{6}$$

(iii) Bockris–Swinkels

$$kc = \frac{\theta}{(1-\theta)^X}\frac{[\theta + X(1-\theta)]^{(X-1)}}{X^X} \tag{7}$$

where X is the number of water molecules replaced by one molecule of organic compound (see Equation 3), c is

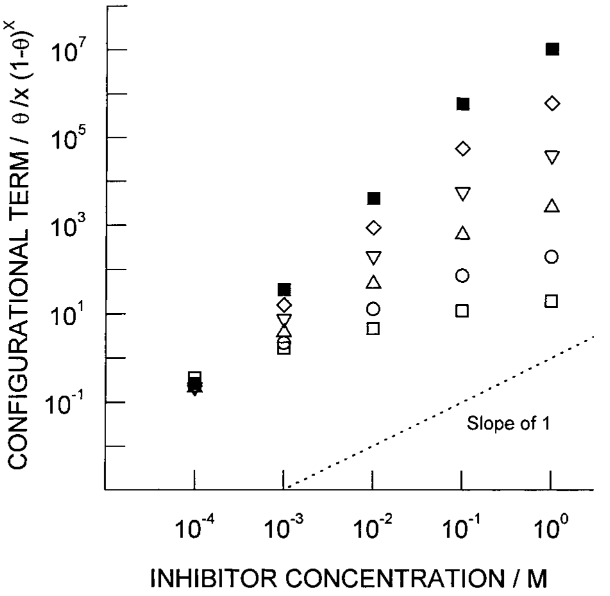

Fig. 2. Flory–Huggins isotherm plot against inhibitor concentration for mild steel in 2.0 M HCl acid solution, at 298 K, for 24 h experimentation and for values of X up to 6. Key: (□) $X = 1$, (○) $X = 2$, (△) $X = 3$, (▽) $X = 4$, (◇) $X = 5$ and (■) $X = 6$.

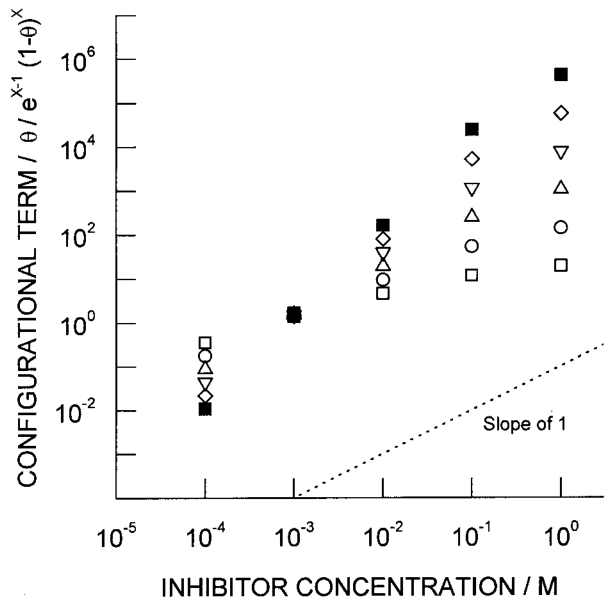

Fig. 3. Dhar–Flory–Huggins isotherm plot against inhibitor concentration for mild steel in 2.0 M HCl acid solution, at 298 K, for 24 h experimentation and for values of X up to 6. Key: (□) $X = 1$, (○) $X = 2$, (△) $X = 3$, (▽) $X = 4$, (◇) $X = 5$ and (■) $X = 6$.

the inhibitor concentration, and k is the equilibrium constant of the adsorption reaction given by $k = (1/55.5)[\exp(-\Delta G^{\circ}_{\text{ads}}/RT)]$. The value 55.5 is the concentration of water in the solution in M, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, and $\Delta G^{\circ}_{\text{ads}}$ is the adsorption energy. $\Delta G^{\circ}_{\text{ads}}$ can be calculated using the ordinate axis intercept of the straight line (log k), see Figures 2–4 below.

Equations 5–7 may be written as

$$\log[f(\theta,X)] = \log c + \log k \qquad (8)$$

where $f(\theta,X)$ is the configurational term, which depends essentially on the physical model and assumptions underlying the derivation of the isotherm [12, 13].

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.

Figures 2, 3 and 4 show Flory–Huggins, Dhar–Flory–Huggins and Bockris–Swinkels isotherm plots, respectively, for values of X up to 6, using hexylamine compound. Plots for dodecylamine inhibitor are not included since they do not supply any additional information to Figures 2–4.

Tables 2 and 3 summarize relevant parameters for the three isotherms and the two organic compounds examined.

From the slopes and the correlation coefficients (CC) in Tables 2 and 3 it can be seen that the three isotherms examined yield similar results. Nevertheless, the best approach for both hexylamine and dodecylamine inhibitors is obtained with the Flory–Huggins and Dhar–Flory–Huggins isotherms, in which the slope for $X = 3$ remains constant, and close to a value of unity. On the other hand, the Bockris–Swinkels isotherm is the best approach for $X = 4$. This undefined value may be resolved using parameters of the projected molecular area.

A value of $X = 3$ means that one molecule of hexylamine or dodecylamine replaces three molecules of water on the mild steel surface. The first effect of the hexylamine/dodecylamine inhibitor is to replace one water molecule with one molecule of the inhibitor

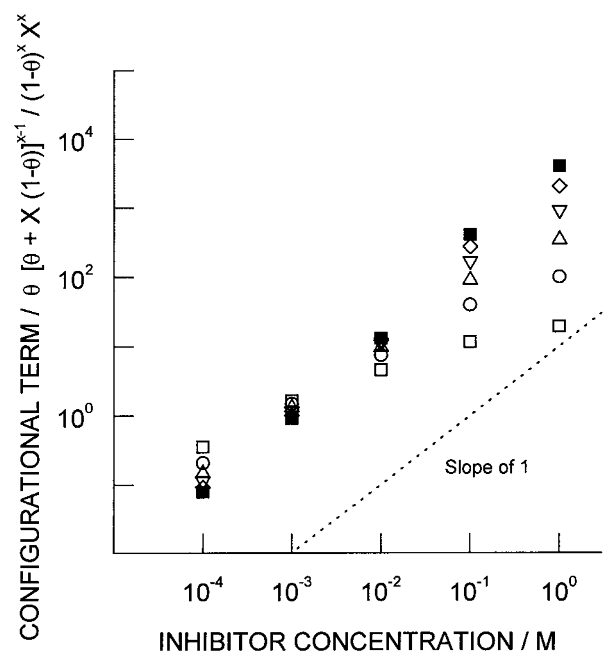

Fig. 4. Bockris–Swinkels isotherm plot against inhibitor concentration for mild steel in 2.0 M HCl acid solution, at 298 K, for 24 h experimentation and for values of X up to 6. Key: (□) $X = 1$, (○) $X = 2$, (△) $X = 3$, (▽) $X = 4$, (◇) $X = 5$ and (■) $X = 6$.

Table 2. Adsorption isotherm parameters for hexylamine onto mild steel in 2.0 M HCl solution at 298 K and for 24 h

X	Flory–Huggins			Dhar–Flory–Huggins			Bockris–Swinkels		
	Slope	log (k)	(CC)^2	Slope	log (k)	(CC)^2	Slope	log (k)	(CC)^2
1	0.4314	1.4141	0.9663	0.4314	1.4141	0.9663	0.4314	1.4141	0.9663
2	0.7331	2.4552	0.9836	0.7331	2.3220	0.9836	0.6786	2.1466	0.9870
3	1.0349	3.6213	0.9885	1.0349	3.2298	0.9885	0.8574	2.6639	0.9939
4	1.3366	4.8386	0.9906	1.3366	4.1377	0.9906	0.9972	3.0615	0.9962
5	1.6383	6.0838	0.9916	1.6383	5.0456	0.9916	1.1112	3.3812	0.9966
6	1.9400	7.3468	0.9923	1.9400	5.9535	0.9923	1.2067	3.6457	0.9962

CC: correlation coefficient

Table 3. Adsorption isotherm parameters for dodecylamine onto mild steel in 2.0 M HCl solution at 298 K and for 24 h

X	Flory–Huggins			Dhar–Flory–Huggins			Bockris–Swinkels		
	Slope	log (k)	(CC)^2	Slope	log (k)	(CC)^2	Slope	log (k)	(CC)^2
1	0.4166	2.3437	0.9719	0.4166	2.3437	0.9719	0.4166	2.3437	0.9719
2	0.7314	4.1273	0.9832	0.7314	3.9940	0.9832	0.6818	3.7160	0.9860
3	1.0463	6.0358	0.9862	1.0463	5.6443	0.9862	0.8819	4.7330	0.9905
4	1.3612	7.9955	0.9875	1.3612	7.2946	0.9875	1.0427	5.5421	0.9916
5	1.6761	9.9832	0.9881	1.6761	8.9450	0.9881	1.1768	6.2112	0.9913
6	1.9909	11.9886	0.9885	1.9909	10.5953	0.9885	1.2912	6.7785	0.9903

CC: correlation coefficient

compound. Equations 5–7 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 hexylamine/dodecylamine in the solution is low, the mild steel corrosion rate may increase due to the possible formation of intermediate products that reduce inhibitor efficiency [14].

3.2. *Projected molecular area of hexylamine/dodecylamine inhibitors*

The purpose is to calculate the optimal orientation of hexylamine/dodecylamine for adsorption on the mild steel surface using molecular models. Figure 5 (upper right corner) shows that the area occupied by a vertically-oriented adsorbed hexylamine/dodecylamine molecule is about $17\ \mathring{\mathrm{A}}^2$ (the projected area of a rectangle surrounding a molecule), as compared with $\sim 50\ \mathring{\mathrm{A}}^2$ for hexylamine and $\sim 85\ \mathring{\mathrm{A}}^2$ for dodecylamine for the horizontal orientations (Figure 5). These values were obtained after configuration calculations using the HyperChem Program and the values of van der Waal's atomic radii [15]. The area occupied by a vertically-adsorbed water molecule is $\sim 8\ \mathring{\mathrm{A}}^2$ [14, 16, 17]. Thus, a vertical orientation of hexylamine or dodecylamine displaces three molecules of water, $X = 3$ in Equations 5–7, while a horizontal orientation of hexylamine/dodecylamine displaces 5–6 and 9–10 molecules of water, respectively. These data corroborate the displacement of 3 molecules of water noted above using adsorption isotherms.

4. Conclusions

Dodecylamine gives higher inhibition efficiency for mild steel hydrochloric acid corrosion than hexylamine. Hexylamine and dodecylamine were chemically adsorbed on the mild steel surface according to Flory–Huggins and Dhar–Flory–Huggins isotherms, with one hexylamine or dodecylamine molecule replacing three

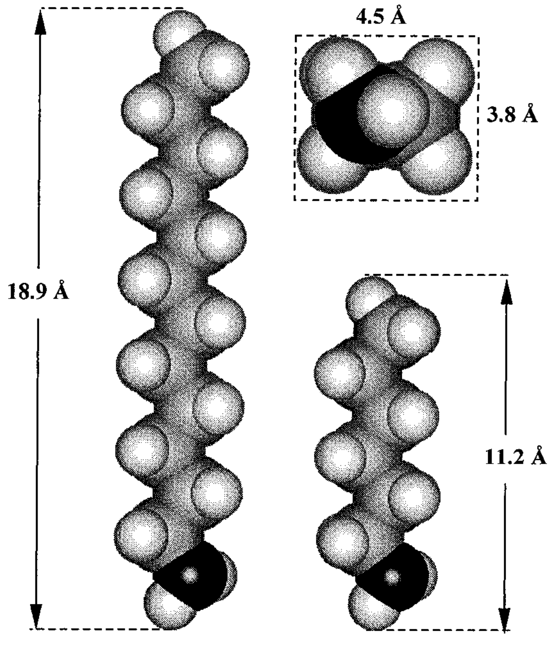

Fig. 5. Front view of hexylamine (bottom right) and dodecylamine (left) molecules adsorbed onto mild steel electrode. Top view (upper right corner).

molecules of water. The projected molecular area method is a good approach for correlating the effectiveness of film-forming corrosion inhibitor on mild steel in hydrochloric acid solution and the concentration of hexylamine and dodecylamine.

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