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## Adsorption Isotherm of Some Triazoles as Corrosion Inhibitors of Mild Steel in Acids.

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### Abstract:

Two absorption isotherm were studied is represent the absorption mechanism of benzotriazole, aminotriazole, and 1,2,4-triazole, which used as a corrosion inhibitors for mild steel in acids. Langmuir adsorption isotherm model was more suitable for representing the corrosion rate data than the Freundlich adsorption isotherm model.

### الخلاصة:

تم استخدام ميكانيكيتين لتوضيح عملية امتصاص البنزوترايزول، الامينوترايزول و الترايزول على سطح الحديد والذين استخدموا كمثبطات لكبح عملية تآكل الحديد في الأوساط الحمضية. وقد تم اختبار موديلين رياضيين لتمثيل عملية الامتصاص وهي موديل لانكمر Freundlich و موديل فريندلخ Langmuir adsorption isotherm model عند ظروف مختلفة. الاستفادة من بيانات معدلات التآكل عند

### Key words:

Langmuir adsorption isotherm, Freundlich adsorption isotherm, Surface Coverage, Heat of adsorption.

### Introduction:

An important phenomenon of surfaces is that known as adsorption, this term is used to describe the existence of a higher concentration of any particular substance at the surface of liquid or solid than is present in the bulk of the medium. An equation relates the amount of substance

attached to surface to its concentration in gas phase or in solution at fixed temperature, is known as an adsorption isotherms<sup>(1)</sup>.

The simplest isotherm was first obtained in 1916 by Irvan Langmuir<sup>(1)</sup>. The basis of derivation of this isotherm is that all parts of the surface behave in exactly the same way as far as absorption is concerned, and supposing a unimolecular layer of substance can be adsorbed on the surface of solid. Langmuir supposed that after equilibrium is established, adsorbed molecules cover a fraction  $\theta$  of the surface, and a fraction  $(1-\theta)$  will not be covered. The rate of absorption is:

$$R_a = k_a [C](1-\theta) \quad \dots (1)$$

where:

$k_a$ , is constant relating to absorption process.  $C$ , concentration of molecules in the solution.

The rate of desorption is;

$$R_d = k_d \theta \quad \dots (2)$$

At equilibrium the rate of absorption and desorption are equal,

$$k_a [C](1-\theta) = k_d \theta \quad \dots (3)$$

or,

$$\left( \frac{\theta}{1-\theta} \right) = \left( \frac{k_a}{k_d} \right) [C] \quad \dots (4)$$

The ratio  $(k_a/k_d)$  is equilibrium constant,  $K$ , so

$$\left( \frac{\theta}{1-\theta} \right) = K [C] \quad \dots (5)$$

or

$$\theta = \frac{KC}{1+KC} \quad \dots (6)$$

Equation (6) holds over fairly wide range of temperature. The Langmuir isotherm type is based on the simplest of assumption; all sites on the surface are assumed to be the same, and there is no interaction between adsorbed molecules. Systems that obey this

equation are often referred to ideal absorption. Systems frequently deviate significantly from Langmuir equation. This may be because the surface is not uniform, and also there may be interaction between adsorbed molecules, a molecule attached to surface may make it more difficult, or less difficult, for another molecules to become attached to a neighboring site, and this will lead to deviation from the ideal absorption equation.

Non-ideal system can sometimes be fitted to an empirical absorption isotherm of Freundlich<sup>(2)</sup>,

$$\theta = KC^n \quad \dots (7)$$

K, is equilibrium constant, and, n is positive and generally non integer constant. These isotherms assume an exponential distribution of absorption site energies.

There are also another isotherms suggested by many scientists, such as, Frumkin isotherm<sup>(3)</sup>, Flory-Huggins isotherm<sup>(4)</sup>, Hill-de Boer<sup>(5,6)</sup>, and Parson's isotherm<sup>(7)</sup>, and another isotherms that are used to evaluate the absorption mechanism of many inhibitors.

From the values of equilibrium constants, which obtained from different isotherms, the values of heat of absorption,  $\Delta G_{ads}$ , can be obtained using the following equation<sup>(8)</sup>:

$$K = \left( \frac{1}{55.55} \right) \exp \left( - \frac{\Delta G_{ads}}{RT} \right) \quad \dots (8)$$

The value of (55.5) is the water concentration in solution expressed in M, (i.e., ~1000 g/l). R and T are the gas constant (= 8.314 J.mol<sup>-1</sup>K<sup>-1</sup>) and absolute temperature respectively. Table 4 shows the values of  $\Delta G_{ads}$  which evaluated from the values of equilibrium constants, K, that obtained from Langmuir adsorption isotherm equation.

Sathanandhn et al<sup>(9)</sup>, studied the corrosion rates of mild steel in HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HNO<sub>3</sub> in presence of different concentration of benzotriazole, aminotriazole, and 1,2,4-triazole. They found that the corrosion rates decreased with increasing in inhibitor concentrations, and they obtained the values of inhibitors efficiencies.

The present paper, is an attempt to understand the mechanism of absorption of trizoles on mild steel surface using the corrosion rate data obtained by Sathanandhn et al <sup>(9)</sup>. They used weight loss technique to obtain the corrosion rate data. HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HNO<sub>3</sub> of 0.1 N concentration were used as a corrosive solution. Duplicated mild steel specimens of size (5 x 1.25 x 0.3 cm) abraded, cleaned and degreased. Specimens were immersed in the corrosive medium. The corrosion tests were carried out at room temperature (about 30<sup>0</sup>C) for 3h in absence and presence of (2-20 mM) of inhibitors.

### Results and Discussions:

The surface converge data obtained at different inhibitors concentration for the corrosion of mild steel in (0.1 N) HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HNO<sub>3</sub> are listed in tables 1, 2, and 3.

Table 1: Surface coverage  $\theta$  of Benzotrizole in 0.1 N acids

C mM	HCl	H <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	HNO <sub>3</sub>
2	0.88	0.85	0.69	0.81
5	0.97	0.91	0.69	0.86
10	0.98	0.95	0.89	0.91
20	0.96	0.82	0.98	0.93

Table 2: Surface coverage  $\theta$  of Aminotrizole in 0.1 N acids.

C mM	HCl	H <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	HNO <sub>3</sub>
2	0.66	0.55	0.66	0.40
5	0.38	0.67	0.67	0.36
10	0.73	0.72	0.69	0.52
20	0.74	0.72	0.82	0.63

Table 3: Surface coverage  $\theta$  of 1,2,4-trizole in 0.1 N acids.

C mM	HCl	H <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	HNO <sub>3</sub>
2	-0.13	-0.36	0.37	0.07
5	0.45	0.83	0.67	0.35

10	0.88	0.63	0.68	0.37
20	0.78	0.87	0.69	0.40

The corrosion rate data and surface converge data can be used to analyze the absorption mechanism. Rearrange Langmuir adsorption isotherm equation will give:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \dots (9)$$

Equation (9) can be plotted as  $\left(\frac{C}{\theta}\right)$  vs. C, as shown in figures (1-3).

The Freundlich Adsorption isotherm can also be applied. Freundlich model equation (7) can be rearranged as:

$$\log \theta = \log K + n \log C \quad \dots (10)$$

Which can be plotted as  $\log \theta$  vs.  $\log C$ . From the intercept of these two equation the values of K can be obtained. The linear adsorption isotherm equations which shown in figures (1-6) were plotted as a least square curves in order to explain the deviations of points from no linearity. Note that the values of the slopes and intercepts were taken from the line equations. The higher value of K indicate that the inhibitor is strongly adsorbed on the metal surface. Figures (3-6) shows Freundlich isotherm model. The values of K, n, and R (R, is correlation coefficient) which obtained from the two absorption models are given in tables 4 and 5.

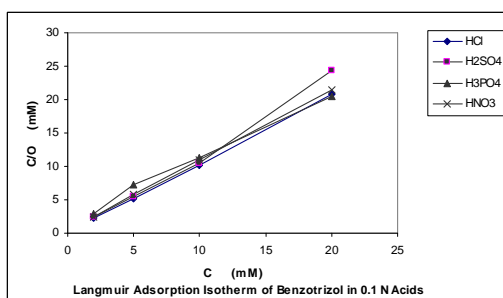


Fig. 1

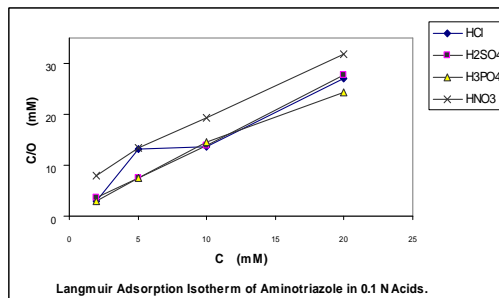


Fig. 2

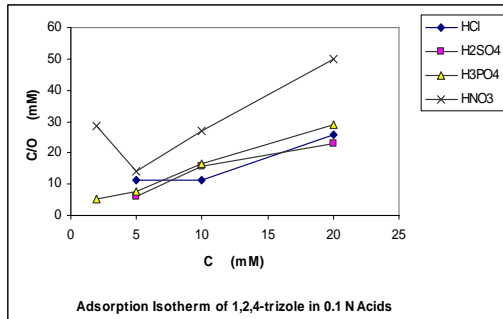


Fig. 3

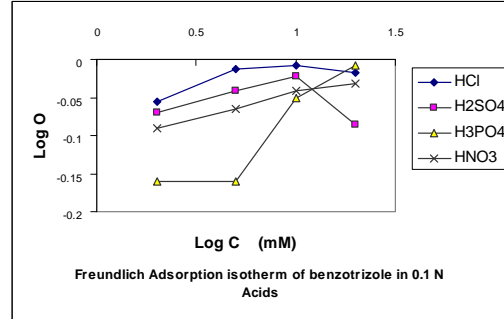


Fig. 4

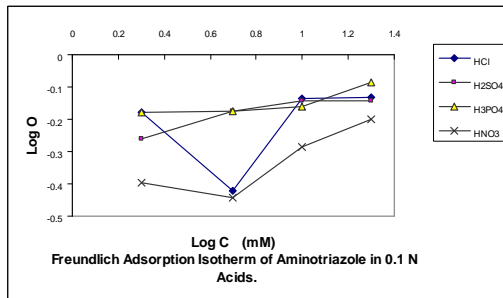


Fig. 5

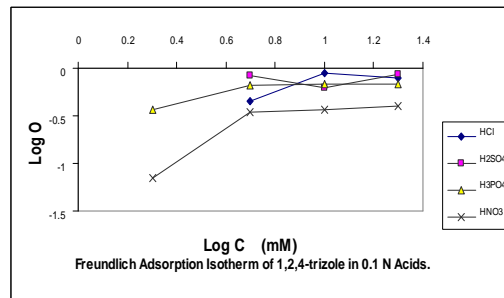


Fig. 6

As shown in figure (1-6) , Langmuir adsorption isotherm model is more suitable to represent the corrosion rate data than Freundlich adsorption isotherm model. And the values of  $R$  in the case of Langmuir adsorption isotherm model approach unity with average value of about (0.998) which indicate a higher correlation between the variables (i.e. surface coverage and inhibitor concentration), while the average values of  $R$  obtained with Freundlich adsorption isotherm model were about (0.722). These values relatively far from unity as compared with the values obtained with Langmuir adsorption isotherm model which indicate a weak correlation between the two variables. Khadom and Yaro <sup>(10,11)</sup> apply Langmuir adsorption isotherm model

and Freundlich adsorption isotherm model to study the mechanism of adsorption of some chemical inhibitors for the corrosion of steel and copper in acid solutions.

Table 4: Langmuir absorption isotherm model data.

inhibitor	acid	K (mM <sup>-1</sup> )	$\Delta G_{ads}$ (kJ/mol)	R
benzotrizole	HCl	22.22	-17.9	0.9998
	H <sub>2</sub> SO <sub>4</sub>	2.242	-12.2	0.9999
	H <sub>3</sub> PO <sub>4</sub>	0.45	-8.1	0.9988
	HNO <sub>3</sub>	1.459	-11.1	0.9969
aminotrizole	HCl	0.313	-7.2	0.9560
	H <sub>2</sub> SO <sub>4</sub>	1.313	-10.8	0.9990
	H <sub>3</sub> PO <sub>4</sub>	0.677	-9.1	0.9950
	HNO <sub>3</sub>	0.218	-6.3	0.9830
1,2,4-trizole	HCl	0.251	-6.64	0.9490
	H <sub>2</sub> SO <sub>4</sub>	0.405	-7.8	0.9602
	H <sub>3</sub> PO <sub>4</sub>	0.479	-8.3	0.9951
	HNO <sub>3</sub>	0.064	-3.2	0.8272

Table 5: Freundlich absorption isotherm model data.

inhibitor	acid	K (mM <sup>-1</sup> )	n	R
benzotrizole	HCl	0.88	0.038	0.75
	H <sub>2</sub> SO <sub>4</sub>	0.88	0.005	0.07
	H <sub>3</sub> PO <sub>4</sub>	2.20	0.27	0.98
	HNO <sub>3</sub>	2.21	0.27	0.98
aminotrizole	HCl	0.49	0.11	0.34
	H <sub>2</sub> SO <sub>4</sub>	3.59	0.12	0.92
	H <sub>3</sub> PO <sub>4</sub>	4.52	0.087	0.84
	HNO <sub>3</sub>	0.31	0.218	0.84
1,2,4-trizole	HCl	0.27	0.395	0.77
	H <sub>2</sub> SO <sub>4</sub>	0.71	0.035	0.14
	H <sub>3</sub> PO <sub>4</sub>	0.36	0.259	0.84

	HNO <sub>3</sub>	0.06	0.727	0.85
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Benzotriazole effectively decreases the corrosion rate in all the acids studied. However, the values of K is greater in HCl (22.22 mM<sup>-1</sup>), this agree with value of surface coverage , which is highest in the case of benzotriazole in HCl with average value of (0.948). the values of K were lower for H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HNO<sub>3</sub> with average surface coverage of (0.883, 0.813, and 0.877) respectively.

Langmuir absorption isotherm model fit the corrosion rate data of benzotriazole strongly and this clear from the values of correlation coefficient, R, which has an average value of (0.9989) at different acids. This leads to suggest that benzotriazole form a monolayer on the metal surface. Freundlich absorption isotherm model of benzotriazole gives a value for K which deviate from these which obtained with Langmuir absorption isotherm model. These values were lower in the case of HCl and H<sub>2</sub>SO<sub>4</sub>. Therefore, Freundlich absorption isotherm model did not agree with Langmuir absorption isotherm model nor the values of surface coverage obtained by Sathanandhn et al <sup>(9)</sup>. So this model failed in representing the corrosion rate data, which is also clear from the low value of correlation coefficients (average values of R=0.695) and figure 2. The average values of constant (n) was 0.146, this value was far from the typical value of n=0.6 <sup>(2)</sup>.

The values of K were lower in the case of aminotriazole as compared with benzotriazole. The adsorption is relatively higher with H<sub>2</sub>SO<sub>4</sub>, HCl, and H<sub>3</sub>PO<sub>4</sub>, and it decreased to less extent in the case of HNO<sub>3</sub>. these result agree with surface coverage data obtained by Sathanandhn et al <sup>(9)</sup>, which they found that aminotriazole gives a surface coverage of about 0.7 in H<sub>2</sub>SO<sub>4</sub>, HCl, and H<sub>3</sub>PO<sub>4</sub>, and much less in HNO<sub>3</sub>. Again, from figures 2 and 5, and from table 4 and 5, Langmuir absorption isotherm model was more suitable than Freundlich absorption isotherm model, which is clear from the values of R, that it approach unity in the case of Langmuir absorption isotherm.



The values of surface coverage were lower in the case of 1,2,4-triazole, the maximum value obtained was 0.87. Generally, as shown in figure 3 and figure 6, both absorption isotherm can represent the corrosion rate data. Langmuir absorption isotherm gives a straight lines with some deviation at low concentration of inhibitor, this may due to that the inhibitor can not make a monolayer on the metal surface at low concentration. This deviation may the reason that the values of correlation coefficient, R, has a value approximately far from unity, or may to the existence of interaction forces among their adsorbed molecules. The lines become approximately linear at high concentration, The values of K obtained from the both isotherms approximately the same, the highest value of K obtained with H<sub>3</sub>PO<sub>4</sub> which in a good agreement with the values of surface coverage of average value of (0.603). the lower value of K obtained with HNO<sub>3</sub>, this also agree with the lower value of surface coverage of average value of (0.3).

According to Langmuir absorption isotherm the values of  $\Delta G_{ads}$ , were negative, this indicates that the process under study is spontaneous. The values of  $\Delta G_{ads}$  for the aminotriazole and 1,2,4-triazole inhibitors, as shown in table 4, were in the range of (-3.2 to -10.8 kJ/mol.), which indicate the weak absorption of these inhibitors to the metal surface, also, these values are much lower than the values obtained with benzotriazole, which ranged from (-8.1 to -17.9 kJ/mol), this behavior indicates the strong absorption of benzotriazole as compared with other inhibitors.

### Conclusions:

The present study indicate that benzotriazole, aminotriazole, and 1,2,4-triazole obey Langmuir absorption isotherm model. This model was approximately suitable to explain the mechanism of absorption of these inhibitor with some deviation in the case of 1,2,4-triazole in different acids. The behavior of inhibitors obtained using Langmuir

absorption isotherm model was in good agreement with that obtained by Sathanandhn et al <sup>(9)</sup>, while Freundlich absorption isotherm model failed in representing the corrosion rate data, specially in presence of benzotrazizole and aminotrizole.

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