ADSORPTION MECHANISM OF BENZOTRIAZOLE FOR CORROSION INHIBITION OF COPPER-NICKEL ALLOY IN HYDROCHLORIC ACID

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ABSTRACT

The inhibition of copper corrosion by Benzotriazole (BTA) in 5% HCl has been investigated by weight loss technique at different temperatures. Langmuir adsorption isotherm, Freundlich Adsorption Isotherm and Kinetic-Thermodynamic Model were used to describe the adsorption process depending on values of surface converge. Maximum value of surface converge was 0.998 for BTA at 35 °C and 15 g/l inhibitor concentration, while the lower value was 0.868 at 55 °C and 1 g/l inhibitor concentration. The films formed on the copper-nickel alloy surface of BTA appeared to obey the Langmuir Adsorption Isotherm more than Freundlich adsorption isotherm. In the other hand, results showed that the Kinetic-Thermodynamic Model was unsuitable to fit the experimental data of the BTA of the present study.

Keywords: adsorption isotherms, corrosion inhibition, copper-nickel alloy, benzotriazole, inhibitor efficiency

INTRODUCTION

Copper and its alloys are commonly employed as a material in heating and cooling systems due to their good thermal conductivity and mechanical properties. Hydrochloric acid pickling is extensively used for the removal of rust and scale on heat transfer in several industrial processes. However, these systems should be regularly cleaned from carbonates and oxides that diminish their heating transmission. Diluted hydrochloric acid is used to clean these surfaces; a corrosion inhibitor is added to avoid the action of this acid on copper. Corrosion inhibitor is a chemical substance when it is added with little concentration to environment effectively checks, decreases or prevents the reaction of metal with environment¹. It must be clearly understood that no universal corrosion inhibitor exists. Each inhibitor must be tailored to the specific corrosion problem that needs solution. While the use of inhibitors for some types of corrosion can be similar to other, this similarity must be treated as coincidence. Most inhibitors have been developed by empirical experimentation. Amines and triazoles derivatives have been reported to be very effective inhibitors for copper in acidic solutions^{2,3}. The corrosion mechanism can vary considerably depending on the corrosive factors that are present. Similarly, the mechanism of inhibition will vary depending on the chemical nature of the inhibitor and the factor causing corrosion⁴. The most widely accepted postulated involves the formation of surface layers or films, which reduce the ease of access of the corrosive materials to the metal surface. Such scale can be formed naturally, or can be induced to form⁵. 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. The simplest isotherm was first obtained in 1916 by Irvan Langmuir⁶. This isotherm can be represented as;

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

Systems that obey this equation are often referred to ideal adsorption. 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 adsorption equation. Non-ideal system can sometimes be fitted to an empirical adsorption isotherm of Freundlich⁷

$$\theta = KC^n \quad (2)$$

K, is equilibrium constant, C is inhibitor concentration, n is positive generally not integer constant, and (θ) is surface coverage. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations⁸.

Recent researches have looked into the action of adsorptive inhibitors from purely mechanistic kinetic point of view^{9,10}. A kinetic-thermodynamic model for adsorption process at metal-solution interface has been suggested. This model has been tested on inhibition effect of number of open chain amines and one macrocyclic amine on the corrosion of steel in H₂SO₄¹⁰ and aluminum in HCl¹¹. In this model, (y) is the number of inhibitor molecules occupying one active site. This model can be given by the following equation;

$$\left(\frac{\theta}{1 - \theta} \right) = K[C]^y \quad (3)$$

Values of $y > 1$ implies the formation of multilayers of inhibitor on the surface of metal. Values of $y < 1$ mean a given inhibitor molecules will occupy more than one active site. K, corresponding to adsorption isotherm is given by;

$$K = K' \left(\frac{1}{y} \right) \quad (4)$$

The present work is an attempt to study the corrosion inhibition mechanism of Benzotriazole for copper-nickel alloy in 5% HCl at different temperatures. It has been reported by Loshkarav et al¹² that, BTA exist as protonated species C₆H₆N₃⁺ in acidic solution, as the undissociated compound C₆H₅N₃ in near neutral solutions, and as the simple anion C₆H₄N₃⁻ in alkaline solutions. The molecular structure of Benzotriazole is

EXPERIMENTAL WORK

The corrosion behavior of copper-nickel alloys, which used widely in many industrial equipments, was studied using weight loss in absence and presence Benzotriazole (BTA) in 5% HCl solution at different temperature (35, 45, and 55 °C), and different inhibitor concentrations (1, 5, 10, and 15 g/l).

Ring shape specimen of Cu-Ni alloy with dimension (2.22 cm) outside diameter, (1.5 cm) width, and (0.13 cm) thickness, exposing a surface area of about (10 cm²) to corrosive media. Specimens were washed by detergent and flushed by tap water followed by distilled water, degreased by analar benzene

and acetone, then annealed in vacuums to 600 °C for one hour and cooled under vacuum to room temperature. Before each run, specimens of Cu-Ni were abraded in sequence using emery paper of grade number 220,320, 400, and 600, then washed by running tap water followed by distilled water then dried by clean tissue, degreased with benzene, dried, degreased with acetone, dried, and finally left in desiccator over silica gel. Weighing the specimen was carried out using 4 decimals digital balance and its dimensions were measured with vernier. The metal samples for weight loss runs were completely immersed in 250-cm³ solution of corrodant contained in a conical flask. They were exposed for a period of three days at a desired temperature, acid concentration, and inhibitor concentration. Weight losses were determined in absence and presence of inhibitors. The data are expressed as mass loss per unit time per unit area; in the present work the units of corrosion rate were g/m².day (gmd). The chemical compositions of Cu-Ni alloy were (0.148 %Sn, 0.2%Fe, 0.134%Zn, 0.015%Al, 0.0003%P, 0.5%Sb, 0.0583%Pb, 0.0202%Si, 0.017%S, 0.0056%As, 10%Ni, and the reminder is Cu).

RESULTS AND DISCUSSIONS

The corrosion rates of Cu-Ni alloy in 5% HCl acid solution as a function of temperature in absence and presence of different inhibitors concentrations are summarized in Table (1) through 15 runs using weight loss technique. The following equation was used to calculate the inhibitor efficiency:

$$IE\% = \frac{W_{\text{uninhibit}} - W_{\text{inhibit}}}{W_{\text{uninhibit}}} \times 100 \quad (5)$$

Where $W_{\text{uninhibit}}$ and W_{inhibit} are the corrosion rates in absence and presence of inhibitor respectively. The primary step in the action of inhibitors in acid solution is generally agreed to be adsorption on the metal surface. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reaction occurred normally on the inhibitor-free area¹³. Accordingly, the fraction of surface covered with inhibitor species ($\theta = \frac{E}{100}$) can follow as a function of inhibitor concentration and solution

temperature. The surface coverage (θ) data are very useful while 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 corrosion rate increases with temperature increasing, generally, the addition of inhibitor reduces the corrosion rate, and the reductions depend on the concentration of inhibitors.

Table 1 Effect of Temperature and Inhibitor Concentration on the Corrosion of Cu-Ni alloy in 5% HCl Acid Solution.

Run	Inhibitor	C (g/l)	T (°C)	Rate (gmd)	IE (%)
1	Nil	Nil	35	12.5	
2			45	15.87	
3			55	20.83	
4	BTA	1	35	1.545	87.6
5		5		0.35	97.2
6		10		0.27	97.8
7		15		0.0193	99.8
8		1	45	2.088	87.8
9		5		0.695	95.6
10		10		0.422	97.3
11		15		0.105	99.3
12		1	55	2.543	86.8
13		5		1.131	94.5
14		10		0.668	96.8
15		15		0.277	98.7

The corrosion rate data can be used to analyze the adsorption mechanism, by using the value of θ as a function of inhibitor concentration. Rearranging Langmuir isotherm equation will give:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (6)$$

Equation (6) can be plotted as $\left(\frac{C}{\theta}\right)$ vs. C. The higher value of K indicates that the inhibitor is strongly adsorbed on the metal surface. From Table (2), and figure 1, the best fitting was obtained by Langmuir adsorption isotherm with high correlation coefficients (R) as compared with the other two models. As shown in Figure 2, the lines deviate from linearity in the case of Freundlich adsorption isotherm and average value of (n) was 0.0466 at different temperatures, which disagreed with typical value of n= 0.6¹⁴. Figure 3 shows the kinetic thermodynamic model for the adsorption of BTA on Cu-Ni surface. Generally, values of K obtained from the two-adsorption isotherms were in a good agreement with the values obtained from kinetic-thermodynamic models. The value of y was lower than unity indicating the formation of monolayer on the metal surface and this confirm the Langmuir behavior. Many of researchers apply adsorption isotherm in order to understand the mechanism of inhibitor adsorption, Ravera and Chavez¹⁵ studied the corrosion inhibition of copper in H2SO4 acid, the corrosion rate data obey Langmuir – Freundlich isotherm with high correlation coefficient.

Table 2 Adsorption Constants and heats of adsorption from Langmuir Isotherm, Freundlich Isotherm and Kinetic-Thermodynamic Models.

Langmuir Isotherm Model				
T (°C)	K (l/g)	ΔG_{ads} (kJ/mol.)	R	
35	5.586	-22.093	0.99993	
45	4.762	-22.389	0.999923	
55	4.762	-23.093	0.99989	
Freundlich Isotherm Model				
T (°C)	K (l/g)	n	ΔG_{ads} (kJ/mol.)	R
35	0.883	0.048	-17.37	0.9742
45	0.87	0.049	-17.894	0.99017
55	0.879	0.043	-18.485	0.9985
Kinetic-Thermodynamic Model				
T (°C)	K (l/g)	y	ΔG_{ads} (kJ/mol.)	R
35	3.67	1.31	-21.018	0.8987
45	5.53	1.003	-22.784	0.9406
55	8.803	0.813	-24.768	0.95529

Moreover, the essential characteristic Langmuir isotherm can be expressed in term of a dimensionless separation factor, R_L ¹⁶, which describes the type of isotherm and defined by:

$$R_L = \frac{1}{1 + KC} \quad (7)$$

The smaller R_L value indicates a highly favorable adsorption. If $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, and if $R_L = 0$ irreversible. Table 3 gives the estimated values of R_L for BTA at different concentrations. It was found that all R_L values are less than unity conforming that the adsorption processes is favorable. The values of R_L did not change as the temperature increased from 45 to 55 °C. This is because that the K (equilibrium constant) value is unchanged, and this mean that the amount of adsorbed inhibitor equal to desorbed one, in other words, the equilibrium process may be reached.

From the values of equilibrium constants, which obtained from different isotherms, the values of heat of adsorption, ΔG_{ads} , can be obtained using the following equation¹⁷

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

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 and absolute temperature respectively.

Table 3 The values of dimensionless separation factor R_L for BTA at various concentrations and temperatures.

BTA (g/l)	Temperature (°C)	R_L
1	35	0.151
5		0.0345
10		0.0175
15		0.0117
1	45	0.1735
5		0.0403
10		0.0205
15		0.0138
1	55	0.1735
5		0.0403
10		0.0205
15		0.0138

The values of ΔG_{ads} heat of adsorption were given in tables (2). The values of ΔG_{ads} for BTA inhibitor were in the range of (-17.37 to -24.76 kJ/mol.), which indicate the good adsorption of BTA inhibitor to the metal surface. The negative values of ΔG_{ads} ensures the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Generally, value of ΔG_{ads} up to -20 kJ.mol⁻¹ is consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption) while those around -40 kJ.mol⁻¹ or higher than that are associated with chemisorptions as a result of sharing or transferring of electrons from the organic molecules to the metal surface to form a coordinate type of bond^{18,19}. While other researchers suggested that the range of ΔG_{ads} of chemical adsorption processes for organic inhibitor in aqueous media lies between (-21 to -42 kJ.mol⁻¹)²⁰. Therefore, in the present work, the value of ΔG_{ads} has been considered within the range of chemical adsorption.

CONCLUSION

The corrosion rate of Cu-Ni alloy in 5% HCl acid solution, increased with increasing of temperature, and decreased with increasing of inhibitor concentration. BTA was very effective inhibitor with maximum inhibitor efficiency of 99.8% at 35 °C and 15 g/l inhibitor concentration, while the lower value was 86.8% at 55 °C and 1 g/l inhibitor concentration. BTA adsorption on the metal surface strongly obeyed Langmuir adsorption isotherm more than Freundlich adsorption isotherm. In the other hand, the values of γ (i.e. the number of inhibitor molecules occupying one active site on the metal surface) obtained from the Kinetic-Thermodynamic Model were near unity, which indicate the formation of monolayer on the metal surface. Values of heat of adsorption ΔG_{ads} were high and negative, which indicate the strong binding of inhibitor to the metal surface.

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Nomenclature

- C: inhibitor concentration (g.l⁻¹)
 IE%: inhibitor efficiency
 K: equilibrium constant (l.g⁻¹)
 n: Freundlich isotherm constant
 R: gas constant (8.314 J. mol⁻¹. K⁻¹)
 R_L : dimensionless separation factor
 T: temperature (°C)
 $W_{uninhibit}$ and $W_{inhibit}$: corrosion rates in absence and presence of inhibitor respectively (gmd).
 ΔG_{ads} : heat of adsorption (kJ.mol⁻¹)
 Θ : surface coverage.

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