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EVALUATION OF THE PERFORMANCE OF SOME CHEMICAL INHIBITORS ON CORROSION INHIBITION OF COPPER IN ACID MEDIA

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ABSTRACT

The inhibition of copper corrosion by Naphthylamine (NA), Ethylenediamine (EDA), Tetraethylenepentamine (TEPA), Diethylenetriamine (DETA), and Phenylenediamine (PDA) in 5% HCl have been investigated by weight loss technique at different temperatures. The results were compared with Benzotriazole (BTA), the common inhibitor used for inhibition of copper corrosion in different environments. The BTA film formed on the copper surface obeys Langmuir Adsorption Isotherm. While NA, EDA, TEPA, and DETA appear to obey the Freundlich Adsorption Isotherm. In the other hand, the two-adsorption isotherms were unsuitable to represent the data of PDA. Results also showed that the Kinetic-Thermodynamic Model was suitable to fit the experimental data of the most inhibitors of the present study.

INTRODUCTION

Due to its good corrosion resistance in water and its excellent heat conductivity, copper and its alloy are used widely in heating systems and condensers. 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 which when added in small concentration to environment effectively checks, decrease or prevent the reaction of metal with environment (1). It must be clearly understood that no universal corrosion inhibitor exists. Each inhibitor must be tailored to the specific corrosion problem that needs solution (2). 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. 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 corrosion (3). 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 form (4).

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* **(5)**. The simplest isotherm was first obtained in 1916 by Irvan Langmuir (5). This isotherm can be represented as;

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

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 became 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 Freundlich (6),

$$\theta = KC^{n} \qquad \ldots(2)$$

K, is equilibrium constant, C is inhibitor concentration, n is positive generally not integer constant, and (θ) is surface coverage. The surface coverage of inhibitor at a given concentration is calculated using the following equation:

$$\theta = \left\{ 1 - \left(\frac{W_{in}}{W_{un}} \right) \right\} \qquad \ldots(3)$$

Where the W_{in} and W_{un} are the weight loss corrosion rates with and without inhibitor respectively.

Recent researches have looked in to the action of adsorptive inhibitors from purely mechanistic kinetic point of view (7,8). 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 H_2SO_4 (8) and aluminum in HCL (9). In this model, (y) is the number of inhibitor molecules occupying one active site. This model can be given by the following equation;

$$\left(\frac{\theta}{1-\theta} \right) = K`[C]^{y} \qquad \ldots(4)$$

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;

$$K = K`^{\left(\frac{1}{y}\right)} \qquad \ldots\ (5)$$

The present work is an attempt to evaluate some corrosion inhibitors for copper in HCl. Some amines, which used in the past as corrosion inhibitors for another metals, such as Fe and Al, in another acids such as H_2SO_4, H_3PO_4 and HNO_3 are tested here for the corrosion of copper in HCl.

EXPERIMENTAL

The corrosion behavior of copper-nickel alloys, which used widely in many industrial equipments, was studied using weight loss in absence and presence of Benzotriazole (BTA), Naphthylamine (NA), Ethylenediamine (EDA), Tetraethylenepentamine (TEPA), Diethylenetriamine (DETA), and Phenylenediamine (PDA) in 5% HCl solution at different temperature (35, 45, and 55 C^{o}), and different inhibitor concentrations (1, 5, 10, and 15 g/l).

Locally produced hydrochloric acid supplied by AL-Furat Company for Chemicals Industries was used as a corrosive solution. The material of electrode was a copper-nickel alloy, which have the following analysis obtained by Specialized Institute of Engineering Industries shown in table (1) below: -

Table (1) Analysis of Cu-Ni alloy.

Compound	%	Compound	%
Sn	0.148	Ni >	2.4
Fe >=	0.2	Pb	0.0583
Zn	0.1374	Si	0.0202
Al	0.015	S	0.017
P	0.0003	As	0.0056
Sb >=	0.5	Cu	About 90

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 cm^2) to corrosive media. Specimens were cleaned by washing with detergent and flushed with tap water followed by distilled water, degreased by analar benzene and acetone, then annealed in vacuums to 600 C^o 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 with running tap water followed by distilled water then dried with clean tissue, degreased with benzene, dried, degreased with acetone, dried, and finally left in desicater 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-cm^3 solution of corrodant contained in a conical flask. They were exposed for a period of three hour 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 present work the units of corrosion rate were g/m^2.day (gmd).

RESULTS AND DISCUSSIONS

The corrosion rate increases with temperature increasing, generally, the addition of inhibitors reduces the corrosion rate, and the reductions depend on the type of inhibitor. Among all the inhibitors tested, *BTA* is the best one as shown in figure (1). As the concentration of BTA increased from (1 to 15 g/l) the corrosion rate decreased to a very low values. At 35 ^oC, the corrosion rate decreased from 12.5 gmd, when there is no inhibitor, to 0.0193 gmd at 15g/l-inhibitor concentration, with a maximum efficiency of 99.8 %. When the temperature increased, the corrosion rate also increased slowly. BTA still effective to less extent. Generally, efficiency of BTA decreased slightly with increasing in temperature.

The rest inhibitors, approximately, give the same behavior; the corrosion rate decreases with increasing the inhibitors concentrations, and increases with temperature increasing.

The order of inhibition of inhibitors evaluated by weight loss technique was as follows: -

BTA > NA > EDA > TEPA > DETA > PDA

The effect of temperature in presence of BTA is clear as shown in figure (2). The corrosion rate increase when the temperature increased, at any inhibitor used, and at inhibitor concentration.

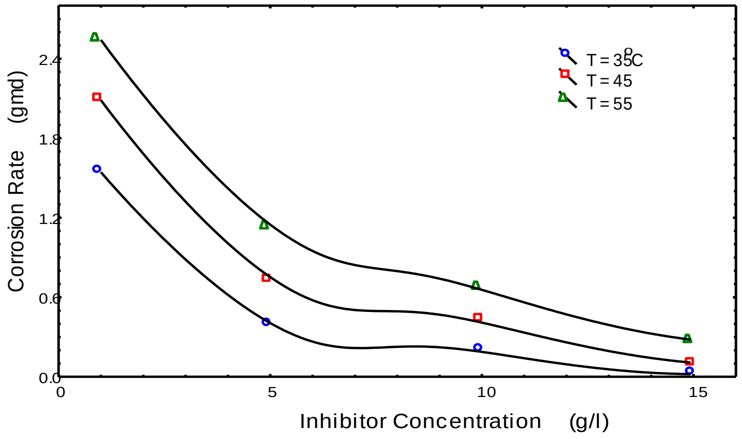


Fig. (1) **Effect of the Concentration of BTA on the corrosion of Cu-Ni**

Alloy in 5% HCl Acid.

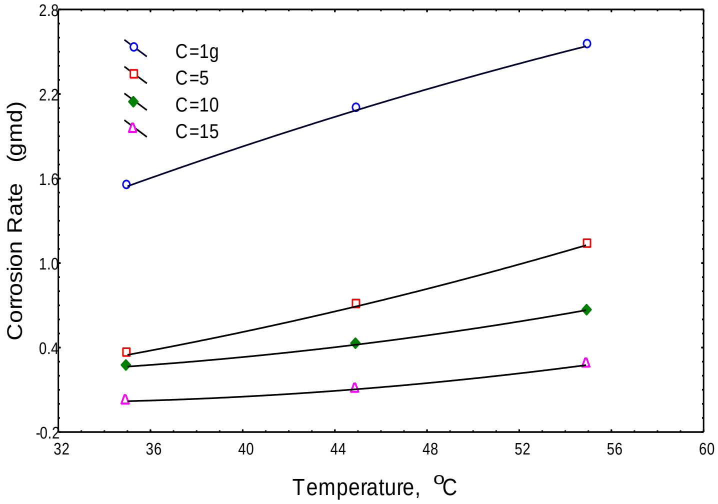


***Fig. (2)* Effect of Temperature on the Corrosion Rate of Cu-Ni alloy In Presence of BTA as Inhibitor in 5% HCl Acid.**

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 gives:

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

Equation (6) can be plotted as $\left(\frac{C}{\theta}\right)$ vs. C, as shown in figure (3). The higher value of K indicates that the inhibitor is strongly adsorbed on the metal surface. From fig. (3) and table (2), we can see that BTA follows Langmair adsorption isotherm, values of K decreases from (5.586 to 4.762 l/g) when the temperature increased from 35C^{o} to 45 C^{o}, this may be due to the de-sorption of inhibitor, further increase in temperature to 55 ^{o}C, did not effect the value of K. It is clear that the highest value of K was 5.586 l/g at 35 ^{o}C, this suggest that at 35 C^{o} BTA gives the highest coverage at any concentration, and the lowest value was 4.762 l/g at 45 ^{o}C and 55 ^{o}C, which gives the lowest coverage, this similarity between the values of K at 45 ^{o}C and 55 ^{o}C due to the close range of the surface coverage, which is ranged, from (0.868-0.99) at 45^{o}C, and from (0.878-0.987) at 55^{o}C. Langmuir adsorption isotherm fit the corrosion rate data of BTA strongly, and this is clear from the values of correlation coefficient, R, which has an average value of 0.9999 at different temperatures, this leads to suggest that BTA molecules form a monolayer on the metal surface. The values of y, (the number of inhibitor molecules occupying one active site in the metal surface), were approximately near unity, with an average value of 1.04, specially at 45 ^{o}C and 55 ^{o}C, which indicate that each molecule of BTA occupying one active site on Cu-Ni alloy surface, then it form a monolayer of inhibitor molecules.

The relation between surface coverage and the concentration of NA becomes linear when Freundlich adsorption isotherm is applied. This suggest that the corrosion rate data for NA is follow Freundlich adsorption isotherm, with K values of 0.1614, 0.1099, and 0.0895 l/g at 35,45and 55 C^o respectively, which in the same order and gives the same behavior as in Langmuir adsorption isotherm. The average value of (n) was 0.703 at different temperature, which is in agree with typical value of n= 0.6 (91). Generally, values of K obtained from the two-adsorption isotherms were in a good agreed with the values obtained from kinetic-thermodynamic models (0.22, 0.151, and 0.123 l/g) at 35,45and 55 C^o, respectively. The values of y at different temperatures were near unity (1.19 to 1.154), which indicate that NA molecules were attached to one active site of Cu-Ni alloy.

For EDA, there is a good agreement between the adsorption isotherms and kinetic-thermodynamic model, as it is shown from the values of K obtained from different models. The best fit was obtained by Freundlich adsorption isotherm, the values of K approximately constant with increasing of temperature.

For TEPA, the best fit to the data was by using Freundlich adsorption isotherm with an average value of correlation coefficient of 0.995,as shown in fig. (6). The values of equilibrium constant were increased slightly with temperature, which indicate, that there is some improvement in surface coverage with increasing in temperature. Values of K obtained from kinetic-thermodynamic model are differing from that obtained from adsorption isotherm, which indicate that this model did not represent the corrosion rate data of TEPA.

Again, in the case of DETA, Freundlich adsorption isotherm fit the corrosion rate data with an average correlation coefficient of 0.9854, which is more than the average correlation coefficient of Langmuir adsorption isotherm, (i.e., 0.8948). Also, there is some increasing in the values of K with increasing in temperature. The values of K obtained from the two-adsorption isotherm were in the same order, while the values that obtained from kinetic-thermodynamic model were lower, and y<1. Fig. (8).

Non of the adsorption isotherm used in present work are represent the corrosion rate data of PDA, this may be due to a low surface coverage of this inhibitor and low ability to form a layer on the metal surface. Kinetic-thermodynamic model slightly fit the corrosion rate data with K values in the same order as the values obtained from the adsorption isotherms. Generally, the values of K are approximately constant with an average value of 0.021 l/g.

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 equation $^{(10)}$:

$$K = \left(\frac{1}{55.55}\right)\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad \dots (7)$$

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.

The values of ΔG_{ads}, heat of adsorption of BTA, were obtained using the values of K from adsorption isotherm and kinetic-thermodynamic models. These values are given in tables (2), (3), and (4). According to Langmuir adsorption isotherm the values of ΔG_{ads}, were around (-22 kJ/mol.), this indicates that the process under study is spontaneous, and the inhibitor is chemically adsorbed on the metal surface, because the values of ΔG_{ads} for BTA on Cu-Ni alloy in 5% HCL in the range of chemical adsorption processes for organic inhibitor in aqueous media, which lies between –21 to –42 kJ/mol. $^{(10)}$.

The values of ΔG_{ads} for the last five inhibitors, as shown in tables (2), (3), and (4), were in the range of (-3.418 to -14.28 kJ/mol.), which indicate the weak adsorption of these inhibitors to the metal surface, also, these values are much lower than the values obtained with BTA. The values of K were also much lower these obtained with BTA.

Table. (2) Adsorption Constants, and heats of adsorption from Langmuir *Isotherm Models*.

Inhibitor	T (°C)	K (l/g)	ΔG_{ads} (kJ/mol.)	R
BTA	35	5.586	-22.093	0.99993
	45	4.762	-22.389	0.999923
	55	4.762	-23.093	0.99989
NA	35	0.1603	-13	0.9851
	45	0.106	-12.329	0.9725
	55	0.089	-12.24	0.99109
TEPA	35	0.115	-12.15	0.95489
	45	0.143	-13.121	0.9727
	55	0.18	-14.161	0.97755
PDA	35	0.02	-7.671	0.98296
	45	0.025	-8.510	0.2068
	55	0.0116	-6.683	0.6095

Table. (3) **Adsorption Constants, Heats of Adsorption, and n From Freundlich Isotherm Models.**

Inhibitor	T (°C)	K (l/g)	n	ΔG_{ads} (kJ/mol.)	R
BTA	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
EDA	35	0.1698	0.532	-13.15	0.9967
	45	0.1954	0.460	-13.95	0.9971
	55	0.1496	0.526	-13.66	0.9994
TEPA	35	0.131	0.452	-12.484	0.99182
	45	0.148	0.455	-13.211	0.997246
	55	0.188	0.378	-14.279	0.99516
DETA	35	0.039	0.471	-9.381	0.99447
	45	0.054	0.546	-10.546	0.96312
	55	0.0656	0.672	-11.408	0.99861

Table. (4) **Adsorption Constants, heats of adsorption, and y from**

Kinetic-Thermodynamic Models.

Inhibitor	T (ºC)	K (l/g)	y	ΔG_{ads} (kJ/mol.)	R
BTA	35	3.67	1.31	-21.018	0.89
	45	5.53	1.003	-22.784	0.9406
	55	8.803	0.813	-24.768	0.95529
NA	35	0.22	1.199	-13.811	0.9776
	45	0.151	1.176	-13.265	0.9861
	55	0.123	1.154	-13.122	0.9948
EDA	35	0.160	0.925	-12.996	0.9715
	45	0.152	0.793	-13.282	0.9789
	55	0.107	0.802	-12.742	0.9950
TEPA	35	0.0447	0.621	-9.73	0.9925
	45	0.065	0.652	-11.036	0.95252
	55	0.074	0.575	-11.737	0.9928
DETA	35	0.002	0.512	-1.775	0.99248
	45	0.0106	0.631	-6.241	0.95252
	55	0.0393	0.833	-10.011	0.99284
PDA	35	0.0038	0.722	-3.418	0.97802
	45	0.0444	1.168	-10.028	0.97838
	55	0.0325	1.319	-9.493	0.98551

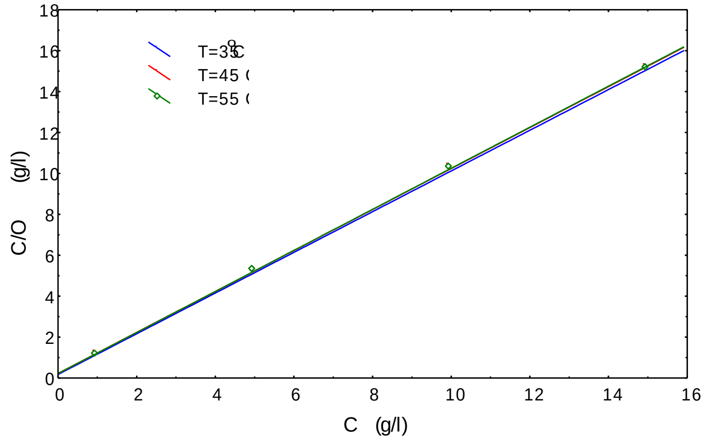


Fig. (3) Langmuir Adsorption Isotherm of BTA on Cu-Ni Alloy*In 5% HCl Acid.*

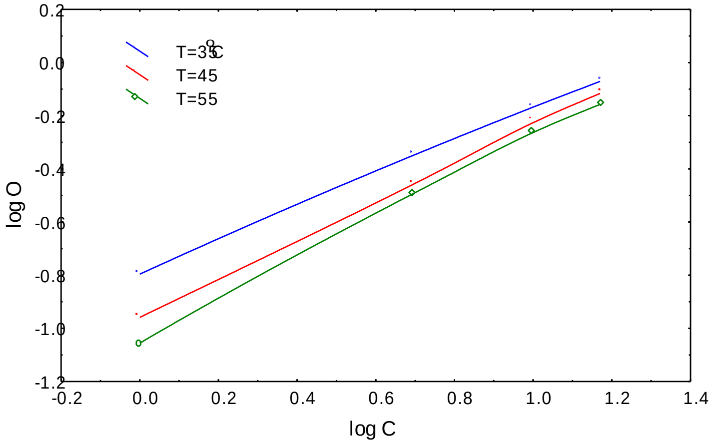


Fig. (4) Freundlich Adsorption Isotherm of NA on Cu-Ni AlloyIn 5% HCl Acid.

Fig. (5) Freundlich Adsorption Isotherm of EDA on Cu-Ni Alloy In 5% HCl Acid.

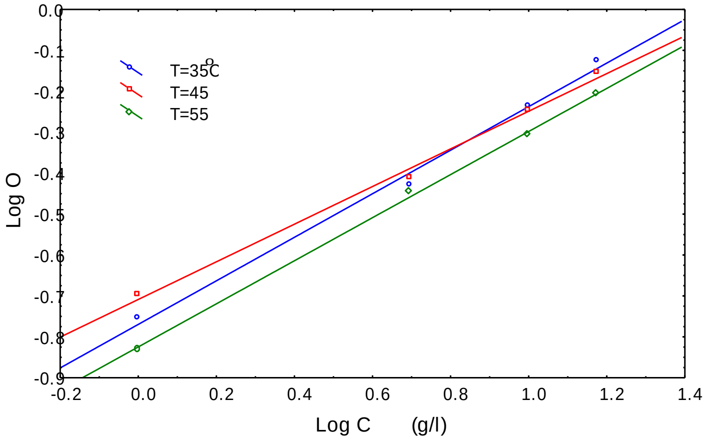
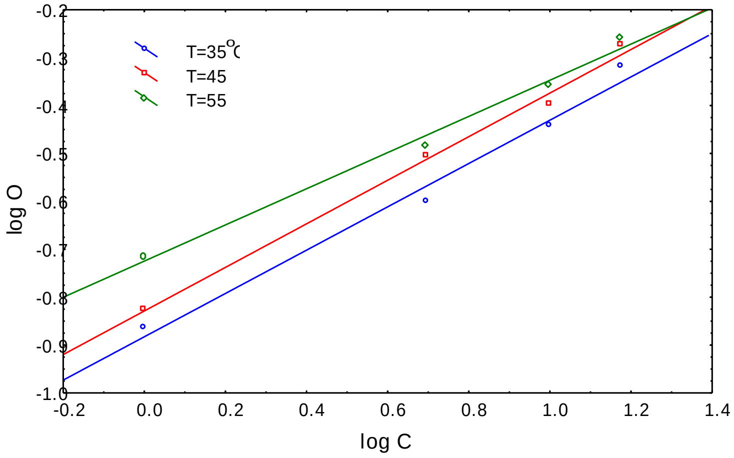


Fig. (6) Freundlich Adsorption Isotherm of TEPA on Cu-Ni Alloy in 5% HCl Acid.



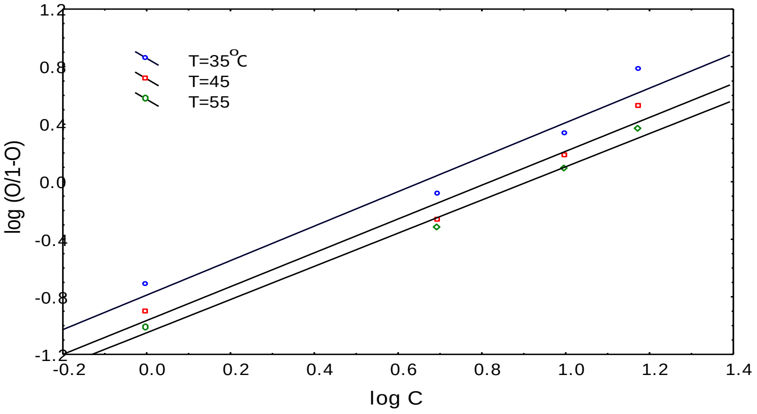


Fig. (7) Kinetic-Thermo. Model for the Corrosion of Cu-Ni Alloy in 5% HCl Acid in Presence of NA.

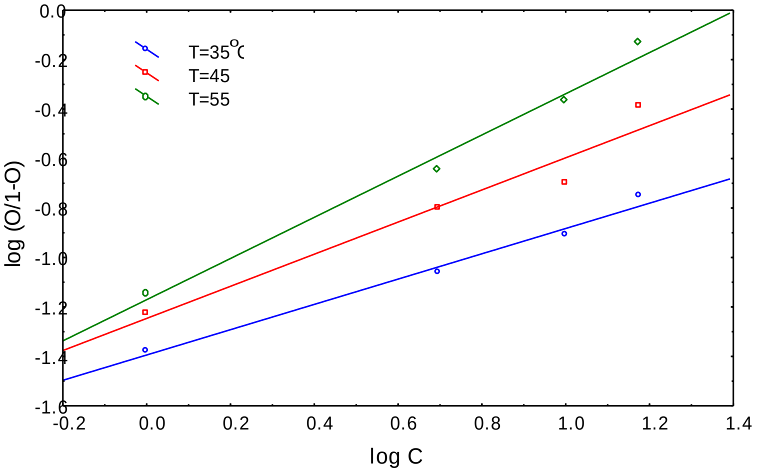


Fig. (8) Kinetic-Thermo. Model for the Corrosion of Cu-Ni Alloy in 5% HCl Acid in Presence of DETA.

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 is an effective inhibitor for copper in static hydrochloric acid solution. Maximum inhibitor efficiency is 99.8% at 15 g/l and 35 °C. Other chemicals (i.e. NA, EDA, TEPA, DETA, and PDA) were ineffective inhibitors even at high level of inhibitor concentration (i.e. 15 g/l). The BTA film formed on the copper surface obeys Langmuir Adsorption Isotherm

$\left(\theta = \dfrac{KC}{1+KC}\right)$. While NA, EDA, TEPA, and DETA appear to obey the Freundlich Adsorption Isotherm $\left(\theta = KC^{n}\right)$. In the other hand, the two-adsorption isotherms were unsuitable to represent the data of PDA. Results also showed that the Kinetic-Thermodynamic Model $\left(\dfrac{\theta}{1-\theta} = \mathrm{K}'C^{y}\right)$was suitable to fit the experimental data of the most inhibitors of the present study. The values of y (i.e. the number of inhibitor molecules occupying one active site on the metal surface) obtained from the present work were near unity, which indicate the formation of monolayer on the metal surface.

Values of heat of adsorption $\left(\Delta G_{ads}\right)$were higher in the case of BTA than the values of other inhibitors, which indicate the strong binding of BTA to the metal surface as compared with other inhibitors used. The order of inhibition of inhibitors evaluated by weight loss technique were as follows: -

BTA > NA > EDA > TEPA > DETA > PDA

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