

## Corrosion Inhibition of Copper-nickel Alloy: Experimental and Theoretical Studies

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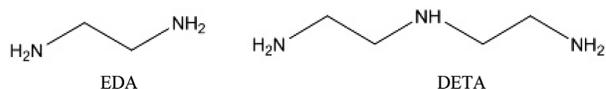
**ABSTRACT.** The corrosion inhibition of copper-nickel alloy by Ethylenediamine (EDA) and Diethylenetriamine (DETA) in 1.5M HCl has been investigated by weight loss technique at different temperatures. Maximum value of inhibitor efficiency was 75% at 35 °C and 0.2 M inhibitor concentration EDA, while the lower value was 4% at 35 °C and 0.01 M inhibitor concentration DETA. Two mathematical models were used to represent the corrosion rate data, second order polynomial model and exponential model respectively. Nonlinear regression analysis showed that the first model was better than the second model with high correlation coefficient. The reactivity of studied inhibitors was analyzed through theoretical calculations based on density functional theory (DFT). The results showed that the reactive sites were located on the nitrogen (N1, N2 and N4) atoms.

**Key words:** Alloy, Corrosion test, Molecular dynamic, Corrosion

### INTRODUCTION

Acid solutions are often used in industry for cleaning and pickling of metallic structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals and alloys in aggressive environments against corrosion is by adding organic or inorganic species to the solution in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate. The inhibition effectiveness might be due to the formation of thin layers of metal inhibitor complexes as TrabANELLI and his co-workers reported.<sup>1</sup> Generally, the diminution of the corrosion rate is a result of adsorption which makes, in acidic media, an effective blocking of the active sites of metal dissolution and/or hydrogen evolution. The adsorption requires the existence of attractive forces between the adsorbate and the metal. The principal types of interaction between an organic inhibitor and metal surface are physisorption, chemisorption or both of them. The adsorption of inhibitor is influenced by the nature and surface charge of the metal, the type of aggressive electrolyte, and temperature and the chemical structure of the inhibitor. Indeed, specific interaction between functional groups and the metal

surface and heteroatoms like nitrogen, oxygen, sulphur and phosphorus plays an important role in the inhibition process due to the free electron pairs they possess.<sup>2</sup> Several amines<sup>3-5</sup> exhibit good inhibitory effect in hydrochloric acid. The present study was undertaken to investigate the copper-nickel alloy corrosion inhibition in 1.5 M hydrochloric acid by Ethylenediamine (EDA) and Diethylenetriamine (DETA). The study was conducted by weight loss method. The thermodynamic parameters of molecule adsorption onto metal surface were determined and the nature of inhibitor adsorption process was also studied and discussed. The molecular structures of the two inhibitors are showed below.



### EXPERIMENTAL WORK

The corrosion behavior of copper-nickel alloy, which is used widely in many industrial equipments, was studied using weight loss method in the absence and presence of Ethylenediamine (EDA) and Diethylenetriamine (DETA) in 1.5M HCl solution at different temperatures (35, 45, 55

and 65 °C), and different inhibitor concentrations (0.01, 0.05, 0.1 and 0.2 M). 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<sup>2</sup>) 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 cm<sup>3</sup> 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 the absence and presence of inhibitors. The data are expressed as mass loss per unit time and per unit area; in the present work the units of corrosion rate were g/m<sup>2</sup>.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 remainder is Cu).

## THEORETICAL CALCULATIONS

The equilibrium geometries of the EDA and DETA molecules were optimized using energy minimization method implemented in DMol3 model in Material studio v.5.5, a high quality quantum mechanics computer program (available from Accelrys, San Diego, CA). These calculations employed an ab initio, local density functional (LDF) method with a double numericpolarization (DNP) basis set and a Becke–Perdew (BP).<sup>6,7</sup> The chemical reactivity of the different sites of the molecule was evaluated by Fukui indices, which are defined by<sup>5</sup>

$$f_k^+ = [q_k(N+1) - q_k(N)] \quad (1)$$

for nucleophilic attack, and

$$f_k^- = [q_k(N) - q_k(N-1)] \quad (2)$$

for electrophilic attack, where  $q_k(N)$ ,  $q_k(N-1)$ , and  $q_k(N+1)$  denote electronic populations of the atom  $k$  in neutral, cationic, and anionic systems, respectively. These quan-

tities were calculated using Mulliken Population Analysis.

## RESULTS AND DISCUSSIONS

### Activation Parameters

The corrosion rates of Cu-Ni alloy in 1.5 M HCl acid solution as a function of temperature in absence and presence of different inhibitors concentrations are summarized in Table 1 through 36 runs using weight loss technique. The following equations were used to calculate the

**Table 1.** Effect of temperature and inhibitor concentration on the corrosion of Cu-Ni alloy in 1.5 M HCl acid solution

Run	Inhibitor	T (°C)	C(M)	CR (gmd)	IE%
1	Blank	35		12.50	
2		45		15.87	
3		55		20.83	
4		65		30.55	
5	EDA	35	0.01	10.31	17
6			0.05	7.843	37
7			0.10	5.274	57
8			0.20	3.125	75
9		45	0.01	12.69	20
10			0.05	9.744	38
11			0.10	6.874	56
12			0.20	4.741	70
13		55	0.01	17.74	14
14			0.05	13.32	36
15			0.10	10.55	49
16			0.20	7.875	62
17	65	0.01	27.49	10	
18		0.05	22.91	25	
19		0.10	19.85	35	
20		0.20	13.74	55	
21	DETA	35	0.01	12.375	4
22			0.05	12	8
23			0.10	11.51	10
24			0.20	10.625	15
25		45	0.01	14.99	5
26			0.05	13.71	13
27			0.10	13.01	15
28			0.20	11.27	29
29		55	0.01	19.44	6
30			0.05	16.98	18
31			0.10	14.58	30
32			0.20	12.05	42
33	65	0.01	27.19	11	
34		0.05	23.22	24	
35		0.10	17.72	42	
36		0.20	12.22	60	

weight loss corrosion rate and inhibitor efficiency respectively:

$$CR = \frac{\text{weight loss (g)}}{\text{area (m}^2\text{)} \times \text{time (day)}} \quad (3)$$

$$IE\% = \frac{CR_{\text{uninhibit}} - CR_{\text{inhibit}}}{CR_{\text{uninhibit}}} \times 100 \quad (4)$$

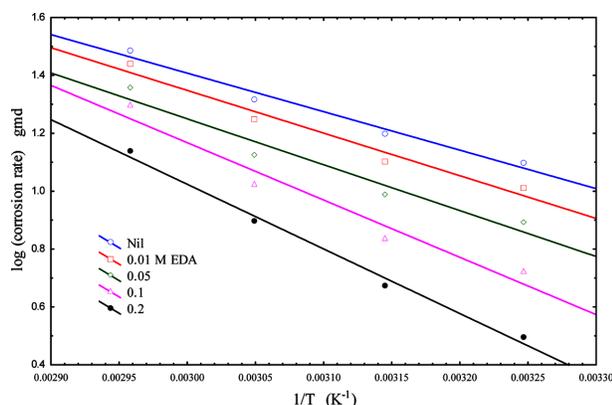
Where  $CR_{\text{uninhibit}}$  and  $CR_{\text{inhibit}}$  are the corrosion rates in absence and presence of inhibitors, respectively. Thermodynamic parameters of the corrosion reaction, namely activation energy  $E_{act}$ , entropy  $\Delta S_{act}$  and enthalpy  $\Delta H_{act}$  of activation were calculated using Arrhenius equation (Eq. 5) and its alternative formulation called transition state equation (Eq. 6). From the corrosion rate data at different temperatures in absence and presence of Ethylenediamine (EDA) and Diethylenetriamine (DETA) as corrosion inhibitors, Arrhenius and transition state plots were obtained. Activation energies were calculated from the Arrhenius plots, which represent the relationship between  $\log(CR)$  and the reciprocal of absolute temperature.<sup>8</sup>

$$\log CR = \log A - \frac{E_{act}}{2.303RT} \quad (5)$$

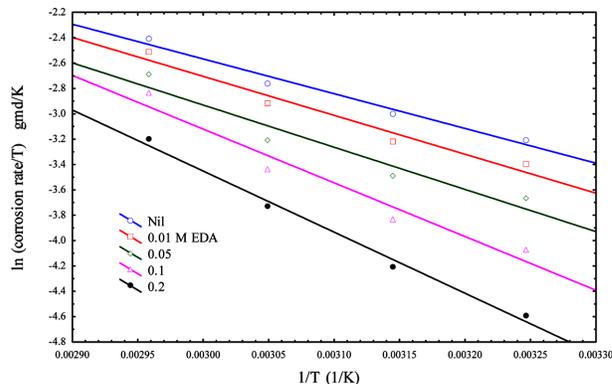
While the transition state equation can be defined as:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{act}}{R}\right) \exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad (6)$$

Where  $A$  is the frequency factor,  $T$  is the absolute temperature,  $R$  is the universal gas constant,  $h$  is Plank's constant, and  $N$  is Avogadro's number. The values of entropy of activation  $\Delta S_{act}$  and of the enthalpy  $\Delta H_{act}$  of activation were obtained by drawing of Eq. 6 as  $\log(CR/T)$  vs  $(1/T)$ . Figs. 1 and 2 show Arrhenius and transition state plots for



**Fig. 1.** Arrhenius Plot of Cu-Ni Alloy in 1.5 M HCl Containing Various Concentration of EDA.



**Fig. 2.** Transition state Plot of Cu-Ni Alloy in 1.5 M HCl Containing Various Concentration of EDA.

EDA at different conditions, similar plots were obtained for DETA but do not appear in this paper. The values of activation parameters were listed in Table 2. In case of EDA the values of  $E_{act}$  and  $\Delta H_{act}$  were higher as compared with uninhibited acid. This means that the corrosion reaction in presence of the inhibitor needs more energy to occur. While in the case of DETA the activation energy  $E_{act}$  and activation enthalpy  $\Delta H_{act}$  for an uninhibited acid were higher than in inhibited acid. The decrease in the value of activation energy appears to be paradoxical. However, Khadom and Yaro<sup>9</sup> attributed this to increased coverage of the metal surface by the inhibitor at higher temperatures and also suggested that the rate of formation of the chemisorbed passive film may be greater than its rate of dissolution at higher temperatures. El-Anadouli et al.<sup>10</sup> obtained values of activation energy for the corrosion of metal in acidic media in absence and presence of some inhibitors. They found that some inhibitors in the corrosive medium modify the kinetics of corrosion reaction by offering alternate reaction paths with lower activation energies. The value of  $E_{act}$  for copper-nickel alloy corrosion in uninhibited hydrochloric acid solution ( $21.71 \text{ kJ}\cdot\text{mol}^{-1}$ ) is in the same order of magnitude of some literature data for copper alloy in some acid solutions.<sup>11,12</sup> Table 2, shows that all the values of  $A$  are lower than that of the blank, which is an advantage for inhibiting the corrosion rate of metals. It is well known that the increase in  $A$  elevates the corrosion rate of metal.<sup>12</sup> As observed above, for all cases  $E_{act} > \Delta H_{act}$  by a value which approximately equal to  $RT$ . From the thermodynamic and kinetic point of view, the unimolecular reactions are characterized by following the equation<sup>13</sup>

$$E_{act} - \Delta H_{act} = RT \quad (7)$$

**Table 2.** Activation parameters for Cu-Ni alloy corrosion reaction in inhibited HCl

Inhibitor	C (M)	A (g/m <sup>2</sup> .day)	E <sub>act</sub> (kJ/mol)	ΔH <sub>act</sub> (kJ/mol)	ΔS <sub>act</sub> (kJ/mol.K)
	0	53333.5	21.71	19.14	-0.162
EDA	0.01	49928.3	21.514	26.5	-0.045
	0.05	44946.9	22.206	25.71	-0.0495
	0.10	432713.1	29.06	33.5	-0.028
	0.20	11494.4	38.77	42.52	0.0165
DETA	0.01	19833.5	19.215	16.82	-0.17
	0.05	3476.9	14.78	12.363	-0.184
	0.10	555.9	10.056	7.285	-0.201
	0.20	83.4	5.354	2.659	-0.217

The value of ΔS<sub>act</sub> is negative in absence of inhibitors. In absence of inhibitors the Transition State of the rate-determining recombination step represents a more orderly arrangement relative to the initial state, and hence, a negative value for ΔS<sub>act</sub> is obtained. It is still negative in presence of inhibitors but its magnitude decreases with increasing concentrations of inhibitors. This was because these compounds inhibited acid dissolution of metal by simple blocking on the surface without changing the mechanism of corrosion process.<sup>14</sup> According to Khadom et al.<sup>14</sup> the corrosion of metals in neutral or acidic solution is cathodically controlled by the hydrogen evolution reaction which occurs in two steps,



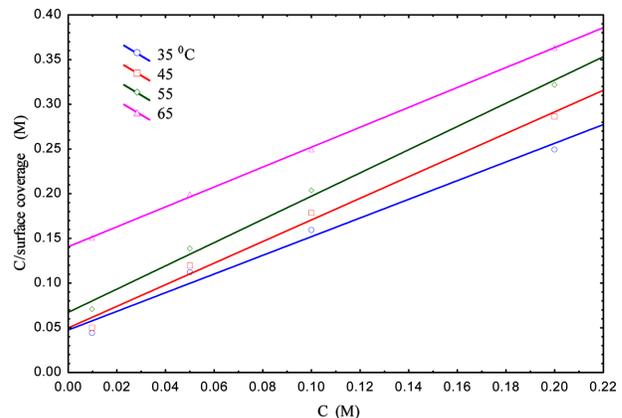
The rate-determining step for the hydrogen evolution reaction is the recombination of adsorbed hydrogen atoms to form hydrogen molecules (Eq. 8). In free acid solution the transition state of the rate determining recombination step represents a more orderly arrangement relative to initial state and hence a negative value for the entropy of activation is obtained. In presence of inhibitors, the entropy of activation still has a negative value but its magnitude decreases with increase of the inhibitor concentration in the case of EDA. In the presence of this compound, the recombination of adsorbed hydrogen atoms to form hydrogen molecules is hindered. In the case of DETA, the values of ΔS<sub>act</sub> are higher. So, this may be due to the new path of reaction, which reduced the values of E<sub>act</sub> and ΔH<sub>act</sub>, respectively. At the same time this path may have a more random recombination step.

### Adsorption Parameters

Surface coverage (θ) data are very useful while considering inhibitor adsorption characteristics. The primary

step in inhibitor action in the acid solution generally is agreed to be its adsorption on the metal surface. This involves the assumption that corrosion reactions are prevented from occurring over the area (or at active sites) on a metal surface that is covered by adsorbed inhibitor species, whereas these corrosion reactions normally occurred on inhibitor-free areas.<sup>15</sup> Accordingly, the fraction of surface covered with inhibitor species (θ = IE%/100) can follow as a function of inhibitor concentration and solution temperature. 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. Fraction dependence of surface covered θ on the concentration C of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Eq. 10 and Fig. 3 show linear plots when drawn as C/θ versus C, suggesting that adsorption is in line with Langmuir's isotherm:

$$\frac{C}{\theta} = \frac{1}{K_{Langmuir}} + C \quad (10)$$

**Fig. 3.** Langmuir adsorption isotherm of EDA on metal surface.

**Table 3.** Adsorption parameters for corrosion inhibition of Cu - Ni alloy in 1.5 M HCl

Inhibitor type	T (°C)	$K_{Langmuir}$ (M <sup>-1</sup> )	$\Delta G_{ads}^o$ (kJ/mol)	R	$K_{kinetic}$ (M <sup>-1</sup> )	y	$\Delta G_{ads}^o$ (kJ/mol)	R
EDA	35	9.1953	-12.880	0.9575	9.6160	0.925	-12.996	0.9715
	45	10.998	-13.771	0.9736	9.1352	0.793	-13.282	0.9789
	55	9.0150	-13.664	0.9851	6.4307	0.802	-12.742	0.9950
	65	9.1141	-13.712	0.9887	6.0316	0.772	-12.888	0.9333
DETA	35	3.61095	-9.104	0.9552	0.2063	0.512	-1.775	0.99248
	45	4.64265	-10.087	0.9797	1.0936	0.631	-6.241	0.95252
	55	6.08703	-11.156	0.9321	4.0545	0.833	-10.011	0.99284
	65	8.1225	-12.346	0.9431	7.1176	0.889	-12.131	0.9348

Where C is inhibitor concentration,  $K_{Langmuir}$  adsorptive equilibrium constant representing the degree of adsorption (i.e., the higher value of  $K_{Langmuir}$  indicates that the inhibitor is strongly adsorbed on the metal surface). As shown in Table 3, the value of  $K_{Langmuir}$  was obtained from the reciprocal of intercept of Langmuir plot line, and the correlation coefficients, R, of this line is near unity means that each inhibitor molecule occupies one active site on metal surface. It is a known fact that  $K_{Langmuir}$  denotes the strength between adsorbate and adsorbent. Large values of  $K_{Langmuir}$  imply more efficient adsorption and consequently better inhibition efficiency.<sup>16</sup> It is clear from Table 3 that values of  $K_{Langmuir}$  are low, indicating weak interaction between inhibitors and metal surface. It seems, therefore, that electrostatic interaction (physisorption) among inhibitor molecules existing as cations should prevail over molecular interaction, and this often results in strong interactions (chemisorption).<sup>17</sup> The equilibrium constant of adsorption  $K_{Langmuir}$  is related to the standard adsorption free energy ( $\Delta G_{ads}^o$ ) by the following equation:<sup>18</sup>

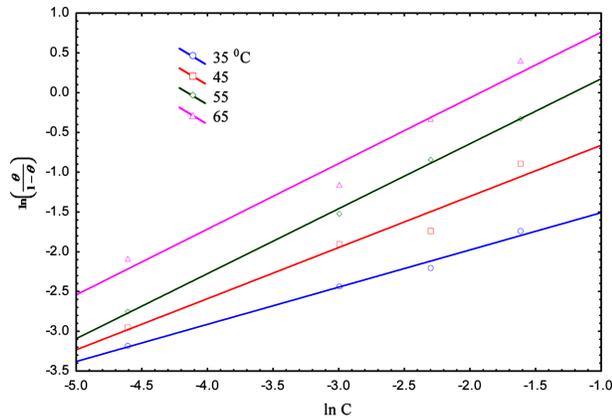
$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right) \quad (11)$$

Where, 55.5 is water concentration in solution expressed in molar (M), R is gas constant, and T absolute temperature. From Table 3, the average value of standard adsorption free energy ( $\Delta G_{ads}^o$ ) was -13.44 kJ.mol<sup>-1</sup> for EDA and -10.11 kJ.mol<sup>-1</sup>. The negative value of  $\Delta G_{ads}^o$  ensures spontaneity of the adsorption process and stability of adsorbed layer on metal surface. Generally, value of  $\Delta G_{ads}^o$  up to -20 kJ.mol<sup>-1</sup> is consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption) while those around -40 kJ.mol<sup>-1</sup> or higher are associated with chemisorptions as a result of sharing or transferring of electrons from organic molecules to metal surface to form a coordinate type of bond [18, 19], while other researchers suggested that the range of  $\Delta G_{ads}^o$  of chemical adsorption processes for organic inhibitor in

aqueous media lies between -21 to -42 kJ.mol<sup>-1</sup>.<sup>15</sup> One can see that the calculated  $\Delta G_{ads}^o$  values are less than 20 kJ.mol<sup>-1</sup>, indicating that the adsorption mechanism of EDA and DETA on Cu-Ni surface in 1.5 M HCl solution was typical of physisorption (Table 3). The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become a quasi-equilibrium state. In this case, it is reasonable to consider the quasi-equilibrium adsorption in thermodynamic way using the appropriate equilibrium isotherms. It is essential to know the mode of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. Some researchers have looked into the action of an adsorptive inhibitor from a purely mechanistic kinetic point of view.<sup>20</sup> This relation can be expressed as follow,  $\theta/1-\theta = K'C^y$ , or this equation can be written in linear form as;

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln K' + y \ln C \quad (12)$$

Where  $K'$  is a constant, and  $y$  is the number of inhibitor molecules occupying one active site. A plot of  $\ln(\theta/1-\theta)$  vs.  $\ln C$  gives a straight line of slope  $y$  and intercept of  $\ln K'$  (Fig. 4). Equilibrium constant corresponding to adsorption isotherm is given by,  $K_{kinetic} = K'^{1/y}$ . Values of  $y > 1$  imply the formation of multilayer of inhibitor on the surface of metal. Values of  $y < 1$  mean the molecules of a given inhibitor will occupy more than one active site. As shown in Table 3, the kinetic-thermodynamic model data were in a good agreement with that obtained by Langmuir adsorption isotherm model. The value of  $y$  was lower than unity indicating the formation of monolayer on the metal surface, and the values of  $K_{kinetic}$  were comparable. Experimental results obtained in this study were further fitted into Dubinin-Radushkevich isotherm model (D-RIM). This model was initially used to distinguish between



**Fig. 4.** Kinetic - thermodynamic isotherm for adsorption of DETA on metal surface.

physical and chemical adsorption for removal of some pollutants from aqueous solutions by adsorption on various adsorbents.<sup>21</sup> Recently, Noor<sup>22</sup> has applied this model in explaining the mechanism of adsorption of corrosion inhibitor onto a metal surface in acidic medium. The equation for the isotherm model can be expressed as:

$$\ln \theta = \ln \theta_{\max} - a \delta^2 \quad (13)$$

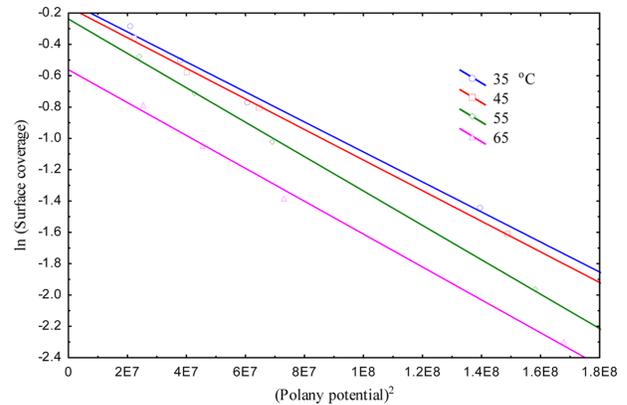
where  $\theta_{\max}$  is the maximum surface coverage and  $\sigma$  (Polanyi potential) can be correlated as:

$$\delta = RT \ln \left( 1 + \frac{1}{C} \right) \quad (14)$$

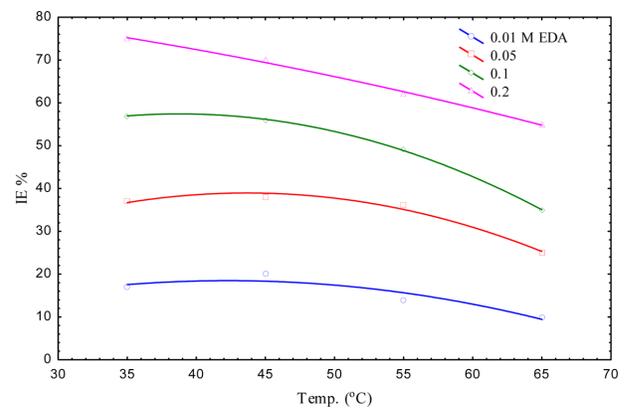
where  $R$  is the universal gas constant,  $T$  is the absolute temperature and  $C$  is the concentration of the inhibitor. The constant  $a$  gives the mean adsorption energy,  $E$ , which is the transfer energy of 1 mol of adsorbate from infinity (bulk solution) to the surface of the adsorbent.

$$E = \frac{1}{\sqrt{2a}} \quad (15)$$

The magnitude of  $E$  gives information about the type of adsorption. Values of  $E$  less than 8 kJ/mol indicates physical adsorption.<sup>22</sup> Fig. 5 shows the relationship between  $\ln \theta$  and  $\sigma^2$  for the corrosion rate data at different temperatures and the corresponding parameters from the regression analysis are listed in Table 4. It is clear from the table that the numerical values of  $E$  reflect physical adsorption mechanism. The values of  $\theta_{\max}$  (maximum surface coverage) for the two inhibitors are in good agreement which further corroborates the results obtained for the inhibition efficiency values.



**Fig. 5.** Dubinin-Radushkevich isotherm model for EDA.



**Fig. 6.** Effect of temperature on inhibitor efficiency of EDA.

**Table 4.** Adsorption parameters for corrosion inhibition of Cu - Ni alloy in 1.5 M HCl by Dubinin-Radushkevich isotherm model

Inhibitor type	T (°C)	$\theta_{\max}$	$a$ (mol <sup>2</sup> kJ <sup>-1</sup> )	$E$ (kJ.mol <sup>-1</sup> )
EDA	35	0.8	0.05	3.16
	45	0.8	0.07	2.67
	55	0.7	0.09	2.36
	65	0.7	1.01	0.71
DETA	35	0.4	0.38	1.14
	45	0.5	0.29	1.32
	55	0.4	0.21	1.56
	65	0.7	0.12	2.02

### Effect of Temperature on Inhibitor Efficiency

Table 1 shows the effect of temperature on the performance of the inhibitor. The addition of inhibitors reduces the corrosion rate at different temperatures. In the case of EDA, as shown in Fig. 5 the values of inhibitor efficiency decreased slightly with temperature raise, while in the case of DETA, as shown in Fig. 6, the inhibitor efficiency slightly increased with increasing in temperature, the maximum value was 60% at 0.2 M inhibitor concentra-

tion, and 65 °C and the minimum value was 4% at 0.01 M inhibitor concentration and 35 °C.

### Combined Influence of Temperature and Inhibitor Concentration on the Corrosion Rate

The experimental corrosion rate results in uninhibited and inhibited 1.5 M HCl acid as a function of temperature and inhibitor concentration are given in Table 1. Our previous models<sup>12</sup> can be suggested again to represent the corrosion rate data. Second order polynomial model was used to represent the temperature and inhibitor concentration effects as follows:

$$Y = a_1 + a_2X_1 + a_3X_1^2 + a_4X_1X_2 + a_5X_2 + a_6X_2^2 \quad (16)$$

$$Y = a_7\left(\frac{1}{X_1}\right)^{a_8} \exp\left(-\frac{a_9}{X_2}\right) \quad (17)$$

where;  $Y$ : Corrosion Rate (gmd),  $X_1$ : Inhibitor Concentration (M)  $X_2$ : Absolute Temperature (K) and,  $a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, a_9$ : are constants. These constants were evaluated by using non-linear estimation regression based on *Levenberg-Marquardt* method. Eq. 16 used as a first model ( $M_1$ ) to represent the results and yield the following equation for EDA (correlation coefficient  $R^2=0.9988$ ) and DETA ( $R^2=0.9945$ ) respectively:

$$Y = 880.15 + 96.71X_1 + 255.41X_1^2 - 0.59X_1X_2 - 6.11X_2 + 0.01X_2^2 \quad (16a)$$

$$Y = 380.96 + 420.66X_1 + 66.44X_1^2 - 1.43X_1X_2 - 3.33X_2 + 0.005X_2^2 \quad (16b)$$

While, Eq. 17 used as a second model ( $M_2$ ) to represent the results and yield the following equation for EDA (correlation coefficient  $R^2=0.9788$ ) and DETA ( $R^2=0.9368$ )

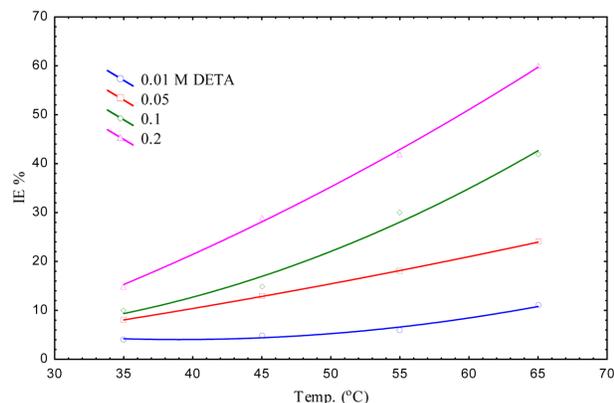


Fig. 7. Effect of temperature on inhibitor efficiency of DETA.

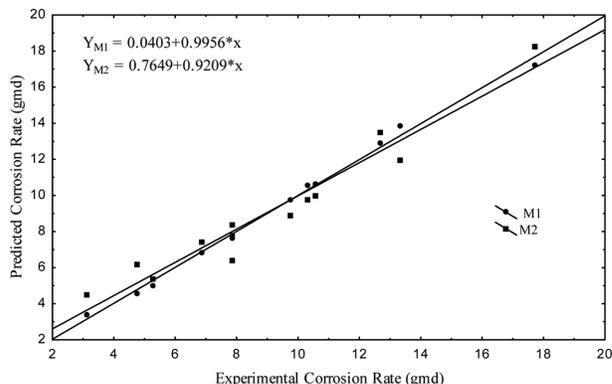


Fig. 8. The deviation of the Two Suggested Models from the Corrosion Rate data of Cu-Ni Alloy in Presence of EDA in 1.5 M HCl.

respectively:

$$Y = 90448.61\left(\frac{1}{X_1}\right)^{-0.27} \exp\left(-\frac{3147.43}{X_2}\right) \quad (17a)$$

$$Y = 1700.37\left(\frac{1}{X_1}\right)^{-0.11} \exp\left(-\frac{1633.1}{X_2}\right) \quad (17b)$$

Figs. 7 and 8 show these models against the experimental corrosion rate data. Also it could be seen the high fitting between experimental and predicted corrosion rates. The best fitting obtained with model  $M_1$ .

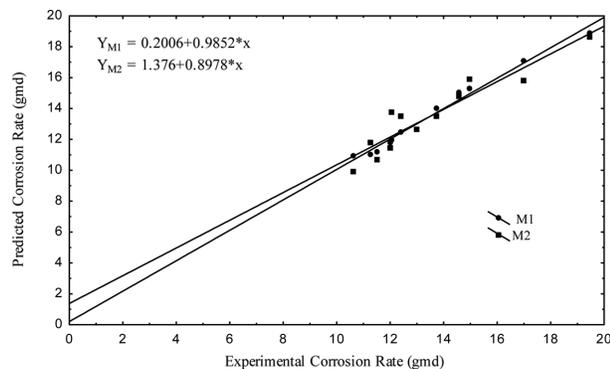
### Mechanism of Inhibition

The adsorption of inhibitors at metal/solution interfaces can markedly change the corrosion resisting properties of metals.<sup>23</sup> The efficiency of organic molecules as good corrosion inhibitors mainly depends on their adsorption ability on the metal surface. So, the investigation of the relation between corrosion inhibition and adsorption is of great importance. The cathodic reaction that occurs on the copper alloy surface in 1.5 M HCl is the oxygen reduction, Since Cu is nobler than  $H^+$  in the electromotive series, and a cathodic reaction other than the displacement of  $H^+$  must account for metal dissolution. This is readily available in terms of  $O_2$  reduction from solution.<sup>24</sup> Anodic dissolution of copper in chloride media has been studied extensively.<sup>25-29</sup> The accepted anodic reaction is the dissolution of copper through oxidation of Cu to  $Cu^+$ :



Then  $Cu^+$  reacts with chloride ion from the solution to form  $CuCl$ :



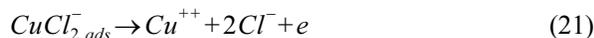


**Fig. 9.** The deviation of the Two Suggested Models from the Corrosion Rate data of Cu-Ni Alloy in Presence of DETA in 1.5 M HCl.

Insoluble CuCl precipitates on the copper surface. The CuCl species has poor adhesion, is unable to produce enough protection for the copper surface, and transforms to the sparingly soluble cuprous chloride complex,  $\text{CuCl}_2^-$ <sup>30</sup>



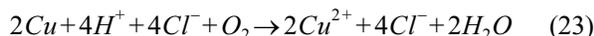
It has also been reported that the  $\text{CuCl}_2$  adsorbed on the surface dissolves by further oxidation:<sup>28</sup>



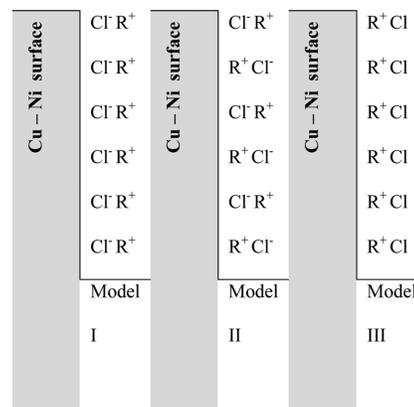
It is reported that the anodic dissolution of copper in the acidic chloride solution is controlled by both electro dissolution of copper and diffusion of  $\text{CuCl}_2$  to the solution bulk.<sup>28,30</sup> The cathodic corrosion reaction in an aerated acidic chloride solution is:



The total corrosion reaction of copper in acidic chloride solutions is as follows:



It is clear from the polarization experiments that the presence of inhibitors decreases the corrosion rate. In acidic solutions, organic inhibitors exist as cationic species  $\text{R}^+$ .<sup>31</sup> The protonated amines can be adsorbed on the metal surface on previously adsorbed chloride ions, since organic compounds with heteroatoms of N and S are able to adsorb on the metal surface even at high concentration of chloride ions.<sup>32</sup> Fig. 10 shows the three suggested inhibition mechanisms. In model I, at low concentrations,

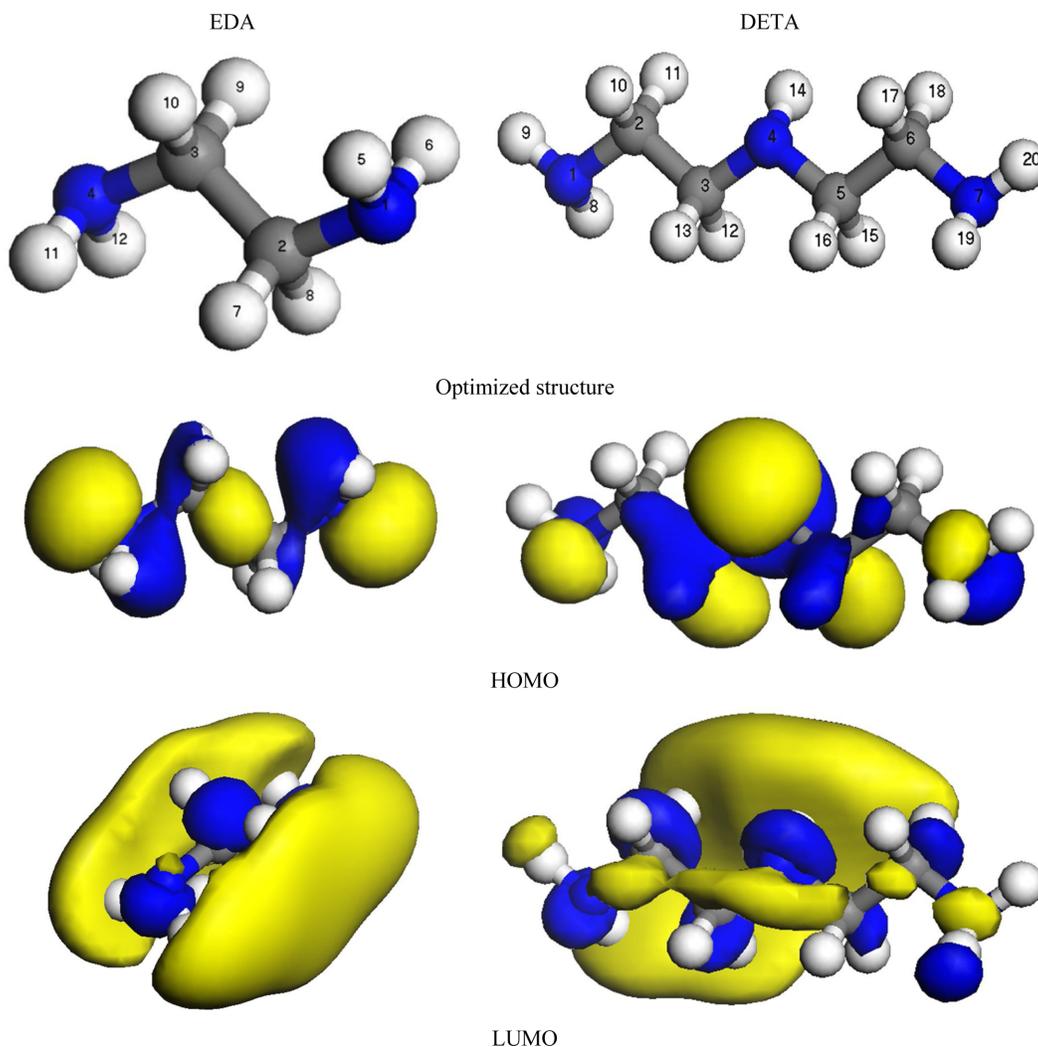


**Fig. 10.** Suggested inhibition models.

inhibitors cations ( $\text{R}^+$ ) from solution cluster around the chloride ions by coulombic attraction on the metal surface where chloride ions are already adsorbed, then as a result tend to be weakly bound to the chloride ions, resulting in low coverage of the electrode surface. Model II represents a situation of weak adsorption of chloride ions;  $\text{R}^+$  at high concentration tends to withdraw the chloride ions on the surface into the solution. Hence, co-adsorption of cations and chloride ions is possible as in model II, on increasing the concentration of inhibitors. The degree of desorption of chloride ions from the surface depends on the degree of adsorption of  $\text{R}^+$  which is a function of the concentration of EDA and DETA. When the concentration of these inhibitors are increased, the chloride ions on the surface provide a better electrostatic condition, which promotes a direct adsorption of cations on the surface through its polar group, as seen in model III.

### Theoretical Calculations

The optimized inhibitors molecules structures are shown in Fig. 11. Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms. Terms involving the frontier MO could provide a dominant contribution, because of the inverse dependence of stabilization energy on orbital energy difference. It has been reported in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO-HOMO energy gap decreased and the efficiency of inhibitor improved.<sup>33</sup> Quantum chemical parameters listed in Table 5 reveal that



**Fig. 11.** The frontier molecule orbital density distributions of EDA and DETA.

**Table 5.** Molecular properties of EDA and DETA calculated with DMol in Material Studio 5.5

	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)
EDA	-0.1787	0.0473	-0.226
DETA	-0.1773	0.0466	-0.224

EDA has higher HOMO with higher energy gap than DETA thus EDA exhibit more corrosion inhibition than DETA. In order to give further insight into the experimental results, ionization potentials are computed and the Fukui indices are used for predicting the preferential sites of electrophilic attack on both EDA and DETA. It is known that the Fukui indices were widely used as descriptors of site selectivity for the soft-soft reactions.<sup>34</sup> According to Li-Evans,<sup>35</sup> the favorite reactive site is that which possesses a high value of Fukui indices, thus we have cal-

**Table 6.** Fukui Indices for EDA and DETA calculated with DMol3 in Material Studio 5.5

Inh.	Atoms	Fukui indices
EDA	N1	0.196
	N2	0.196
DETA	N1	0.065
	N4	0.196
	N7	0.072

culated the electrophilic Fukui indices  $f_k^-$  defined by Eq. 2, for heteroatoms in systems. The results are given in Table 6. It turns out from the tabulated values that the nitrogen atoms (N1 and N2) in EDA possesses the largest value of Fukui indices while nitrogen atoms (N1 and N7) in DETA have small values of electrophilic Fukui indices, less than 0.08. Thus, the N1 and N2 atoms for EDA and N4 atom for DETA are more reactive for electrophilic

attack. The addition of nitrogen atom in DETA does affect the Fukui indices in N1 atom by reducing its value to more than a half, however, N4 keep its value after the addition of nitrogen atom. These results seem to indicate that the N4 in both molecules, which has a great nucleophilic character, is involved in the chemical reactivity of these molecules with the metal surface.

## CONCLUSION

The corrosion rate of Cu-Ni alloy in 1.5 M HCl acid solution, increased with increase in temperature, and decreased with increase in inhibitors concentration. The values of activation parameters from Arrhenius equation and transition state equation in inhibited acid solution are significantly influenced by inhibitor concentration. The two suggested mathematical models were suitable to represent the corrosion rate data. Nonlinear regression analysis shows that the first model was better than the second model with high correlation coefficient. Reactive sites for nucleophilic and electrophilic attacks were indicated using the Fukui functions and located on the nitrogen atoms for both inhibitors. Results showed that the N4 in both molecules (EDA and DETA) involved in the chemical reactivity of these molecules with the metal surface.

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