

Adsorption Mechanism of Some Chemical Amines Inhibitors for Corrosion Inhibition of Copper–Nickel Alloy in Hydrochloric Acid

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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. 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 0.856 for NA at 35 °C and 15 g/l inhibitor concentration, while the lower value was 0.01 for PDA at 55 °C and 1 g/l inhibitor concentration. The films formed on the copper–nickel alloy surface of NA, EDA, TEPA, and DETA appear to obey the Freundlich Adsorption Isotherm more than Langmuir 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.

Keywords: adsorption isotherms, corrosion inhibition, copper–nickel alloy, organic inhibitors

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 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. 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 [2–5]. 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 [6]. 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 [7]. 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 [8]. The simplest isotherm was first obtained in 1916 by Irvan Langmuir [8]. 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 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 [9]

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

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 concentrations [10].

Recent researches have looked in to the action of adsorptive inhibitors from purely mechanistic kinetic point of view [11, 12]. 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 [12] and aluminum in HCl [13]. 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 evaluate some corrosion inhibitors for copper-nickel alloy 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 5% HCl at different temperatures.

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 of Naphthylamine (NA), Ethylenediamine (EDA), Tetraethylenepentamine (TEPA), Diethylenetriamine (DETA), and Phenylenediamine (PDA) in 5% HCl solution at different temperature (35, 45, and 55 $^{\circ}C$), 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 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 $^{\circ}C$ 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 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 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 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 64 runs using weight loss technique. The following equation was used to calculate the inhibitor efficiency:

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

Where $W_{uninhibit}$ and $W_{inhibit}$ are the corrosion rates in absence and presence of inhibitor respectively.

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

Run	Inhibitors	C (g/l)	T (°C)	Rate (gmd)	IE (%)
1	Nil	Nil	35	12.5	
2			45	15.87	
3			55	20.83	
4	NA	1	35	10.5	16
5		5		6.875	45
6		10		4	68
7		15		1.8	85.6
8		1	45	14.01	11
9		5		10.313	35
10		10		6.341	60
11		15		3.65	77
12		1	55	19.021	8.8
13		5		14.032	32.3
14		10		9.374	55
15		15		6.249	70
16	EDA	1		10.312	17.5

17		5	35	7.843	37.25
18		10		5.274	57.8
19		15		3.125	75
20		1		12.692	20.03
22		5	45	9.744	38.6
23		10		6.874	56.68
24		15		4.741	70.126
25		1		17.741	14.83
26		5	55	13.324	36.03
27		10		10.554	49.33
28		15	55	7.875	62.193
29	TEPA	1		10.8	13.6
30		5	35	9.375	25
31		10		8	36
32		15		6.5	48
33		1		13.5	14.9
34		5	45	10.932	31.1
35		10		9.52	40
36		15		7.457	53
37		1		16.8	19.3
38		5	55	13.96	32.9
39		10		11.66	44
40		15		9.373	55
41	DETA	1		12.375	4
42		5	35	12	8
43		10		11.51	10.9
44		15		10.625	15
45		1		14.985	5.6
46		5	45	13.71	13.6
47		10		13	15
48		15		11.265	29
49		1		19.44	6.7
50		5	55	16.987	18.5
51		10		14.58	30
52		15		12.05	42.4
53	PDA	1		12.3	1.6
54		5	35	11.625	7
55		10		10.95	8.5

56	15		9.2	10
57	1		15.39	3
58	5	45	14.28	10
59	10		11.437	31
60	15		11.25	42
61	1		20.622	1
62	5	55	18.54	11
63	10		17.91	14
64	15		14.587	30

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 area [14]. Accordingly, the fraction of surface covered with inhibitor species ($\theta = \frac{IE\%}{100}$) can

followed 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 inhibitors reduces the corrosion rate, and the reductions depend on the type of inhibitors.

All tested 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: –

NA > EDA > TEPA > DETA > PDA

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:

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

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 Langmuir lines deviate from linearity in the case of NA, 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 (figure 2), with K values of 0.1614, 0.1099, and 0.0895 l/g at 35, 45 and 55 °C 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 [15]. Figure 3 shows the kinetic thermodynamic model for the adsorption of NA on Cu-Ni surface. 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°, respectively. The values of y at different temperatures were near unity (1.19 to 1.154), which indicates 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 (figure 4), the values of K approximately constant with increasing of temperature.

As shown in figure (5), for TEPA, the best fit to the data was by using Freundlich adsorption isotherm with an average value of correlation coefficient of 0.995. 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.

In the case of DETA, figure (6) shows that 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 $y < 1$.

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 [16]

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

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 were given in tables (2), (3), and (4). The values of ΔG_{ads} for the five inhibitors were in the range of (–3.418 to –14.28 kJ/mol.), which indicate the weak adsorption of these inhibitors to the metal surface. The negative value of ΔG_{ads}^o ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Generally, value of ΔG_{ads}^o 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 are associated with chemisorptions as a result of sharing or transfer of electrons from the organic molecules to the metal surface to form a coordinate type of bond [17,18]. While other researchers suggested that the range of ΔG_{ads}^o of chemical adsorption processes for organic inhibitor in aqueous media lies between –21 to –42 kJ.mol^{–1} [19]. Therefore, for present work the value of ΔG_{ads}^o has been considered within the range of physical adsorption.

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

Inhibit or	T (°C)	K (l/g)	ΔG_{ads} (kJ/mol.)	R
BTA	35	5.586	–22.093	0.99993
	45	4.762	–22.389	0.99992
	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.

Inhibit or	T (°C)	K (l/g)	n	ΔG_{ads} (kJ/mol.)	R
BTA	35	0.883	0.048	-17.37	0.974 2
	45	0.87	0.049	-17.894	0.990 17
	55	0.879	0.043	-18.485	0.998 5
EDA	35	0.1698	0.532	-13.15	0.996 7
	45	0.1954	0.460	-13.95	0.997 1
	55	0.1496	0.526	-13.66	0.999 4
TEPA	35	0.131	0.452	-12.484	0.991 82
	45	0.148	0.455	-13.211	0.997 24
	55	0.188	0.378	-14.279	0.995 16
DETA	35	0.039	0.471	-9.381	0.994 47
	45	0.054	0.546	-10.546	0.963 12
	55	0.0656	0.672	-11.408	0.998 61

Table 4 Adsorption Constants, heats of adsorption, and γ from Kinetic–Thermodynamic Models.

Inhibitor	T (°C)	K (l/g)	γ	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
ETA	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	0.978
					02
	45	0.0444	1.168	-10.028	0.978
					38
	55	0.0325	1.319	-9.493	0.985
					51

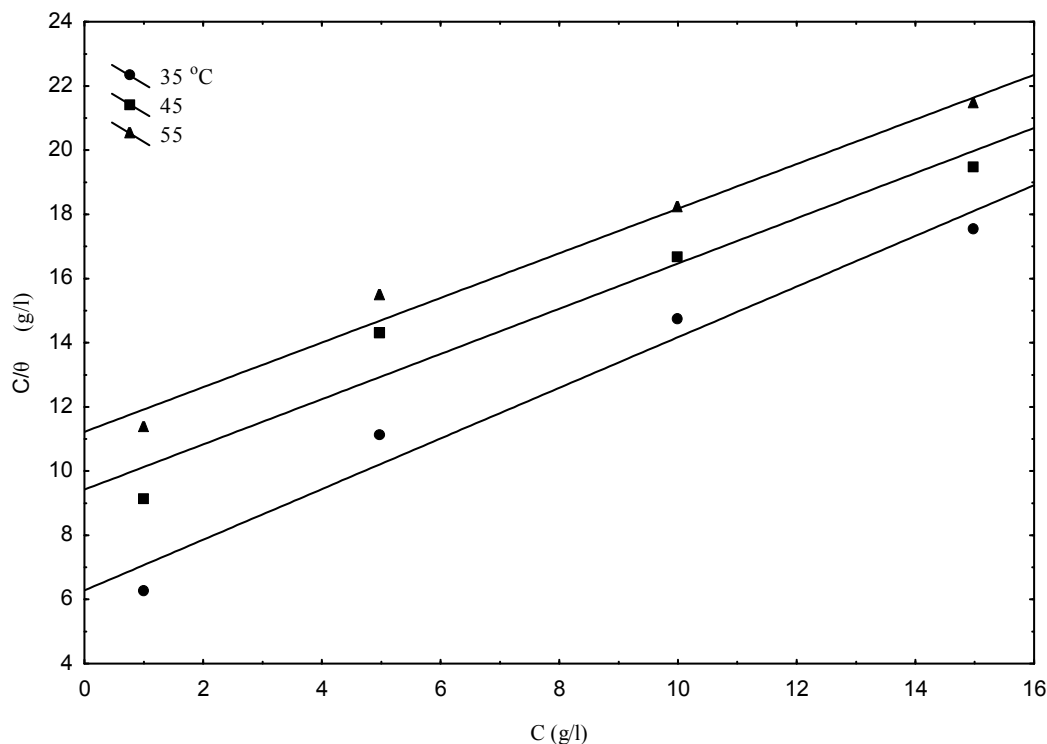


Fig. 1 Langmuir Adsorption Isotherm for Cu-Ni Alloy in 5% HCl in Presence of NA

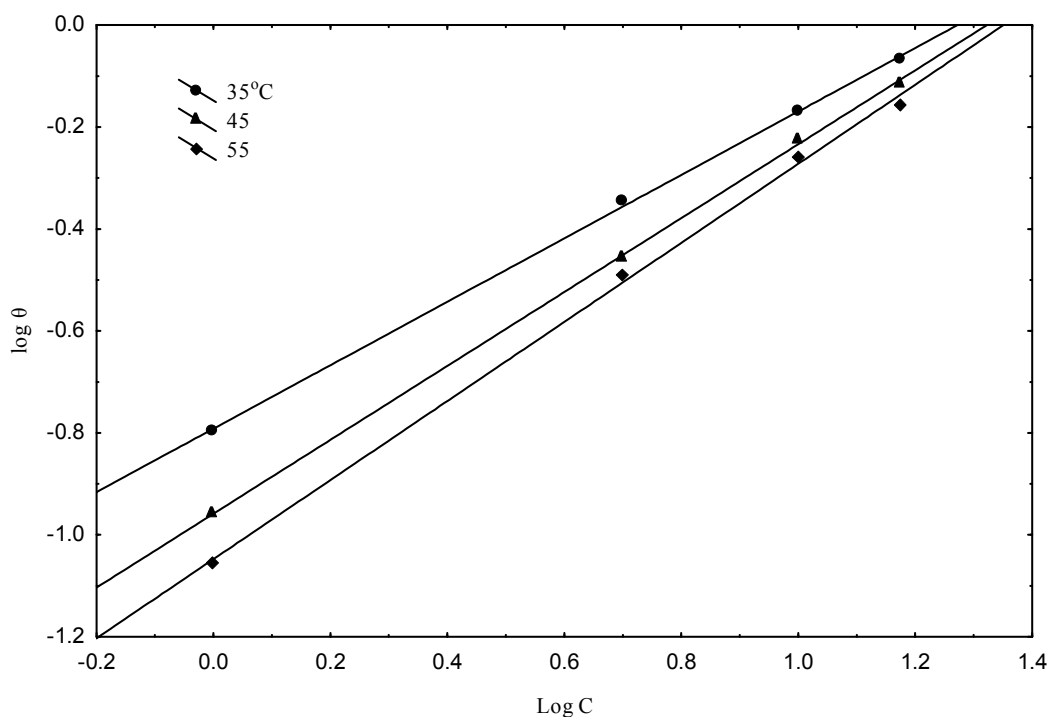


Fig. 2 Freundlich Adsorption Isotherm of NA on Cu-Ni Alloy in 5% HCl Acid at Different Temperatures.

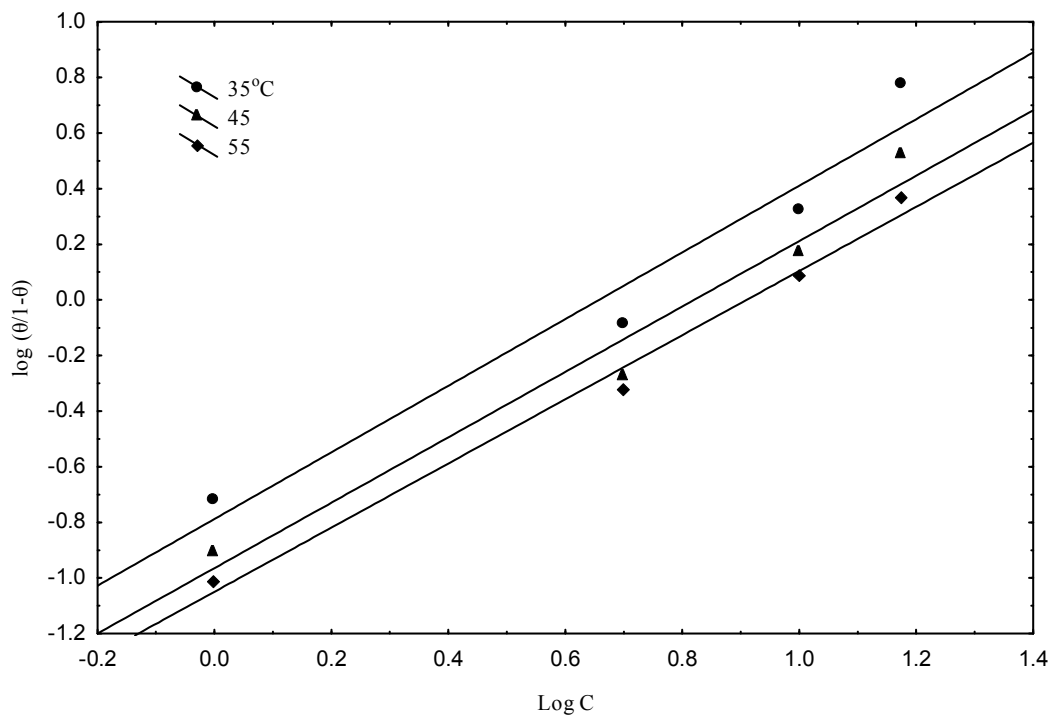


Fig. 3 Kinetic-Thermodynamic Model of NA on Cu-Ni Alloy in 5% HCl Acid at Different Temperatures.

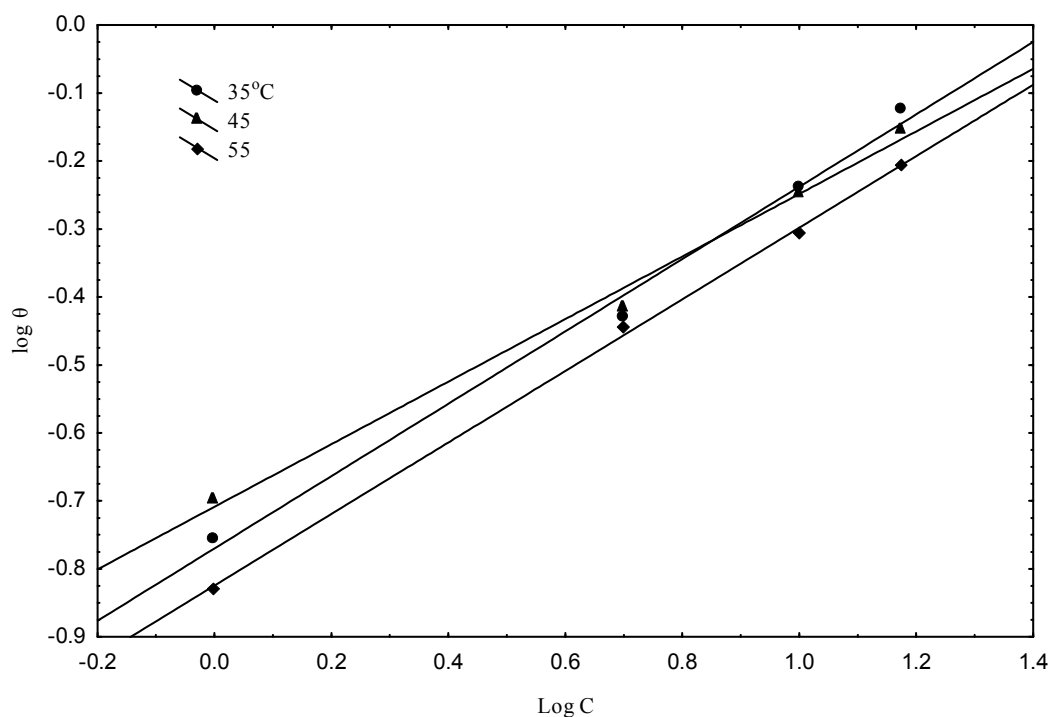


Fig. 4 Freundlich Adsorption Isotherm of EDA on Cu-Ni Alloy in 5% HCl Acid at Different Temperatures.

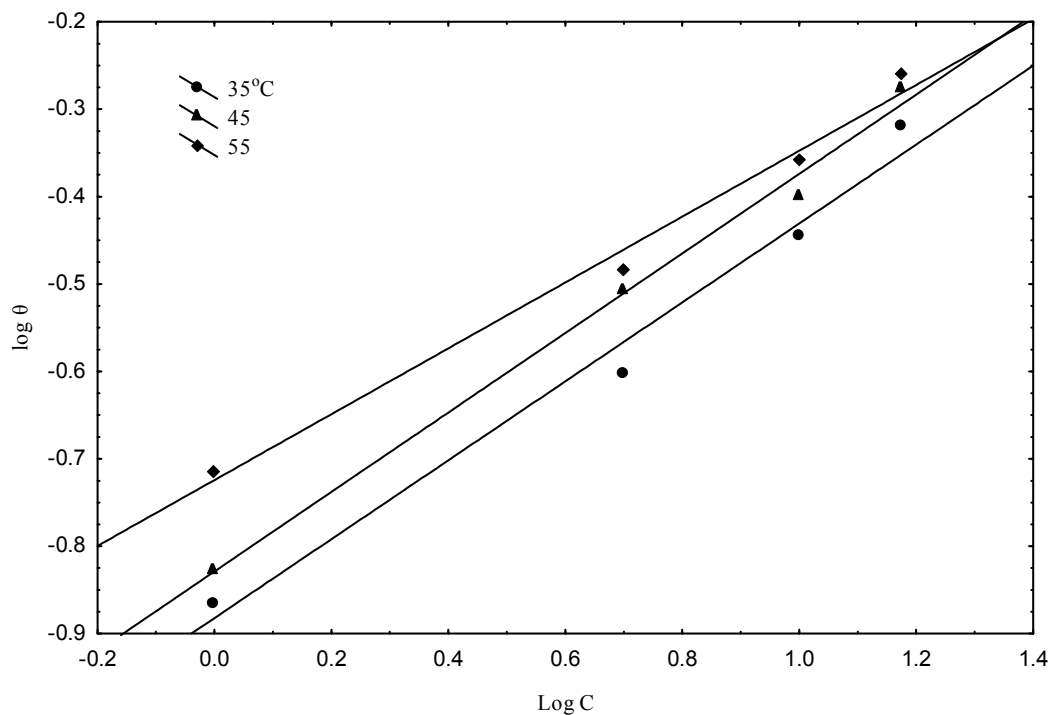


Fig. 5 Freundlich Adsorption Isotherm of TEPA on Cu-Ni Alloy in 5% HCl Acid at Different Temperatures.

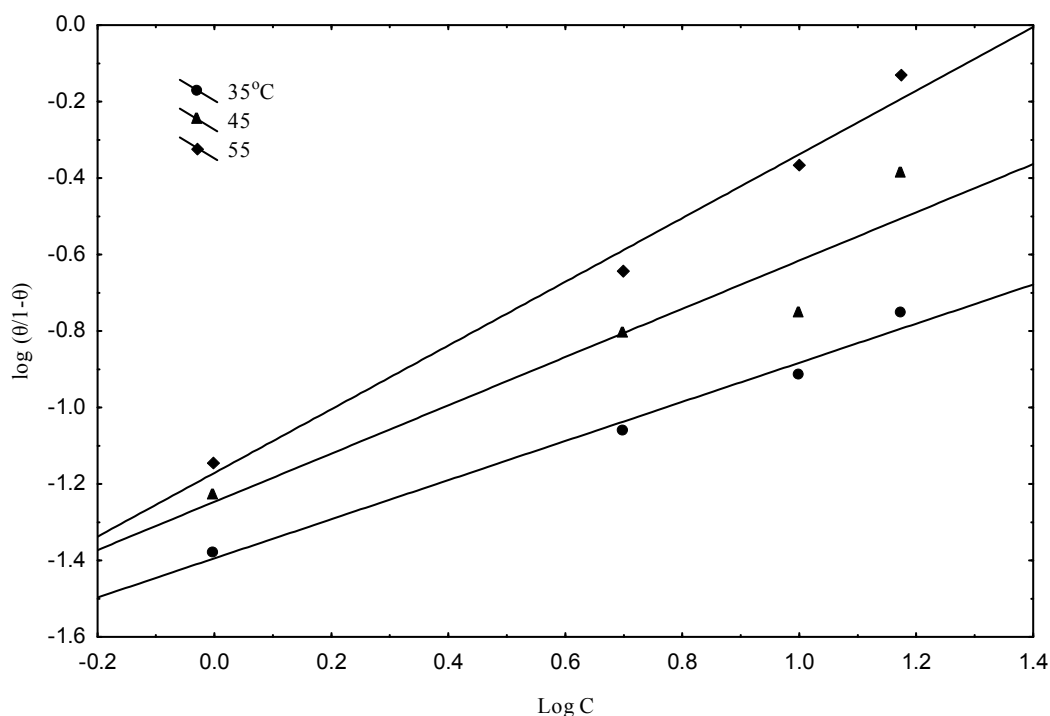


Fig. 6 Kinetic-Thermodynamic Model of DETA on Cu-Ni Alloy in 5% HCl Acid at Different Temperatures.

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. NA was the relatively the most effective inhibitor than the other. Other chemicals (i.e. EDA, TEPA, DETA, and PDA) were ineffective inhibitors even at high level of inhibitor concentration (i.e. 15 g/l). NA, EDA, TEPA, and DETA appear to obey the Freundlich adsorption isotherm more than Langmuir 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. 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 (ΔG_{ads}) were lower in the cases, which indicate the weak binding of inhibitors to the metal surface. The order of inhibition of inhibitors evaluated by weight loss technique were as follows; NA > EDA > TEPA > DETA > PDA

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