Enaminonitrile derivatives as corrosion inhibitors for Cu10Ni alloy in 0.5 M HCl solutions

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ABSTRACT

The adsorption and inhibition efficiency effect of enaminonitrile derivatives on the Cu10Ni alloy in 0.5 M HCl were investigated using electrochemical techniques (potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM)). The inhibition efficiency of the inhibitors increased with increasing the concentration of the derivatives and decreased with increasing the temperature. Polarization curves revealed that these compounds are mixed type inhibitors. The adsorption of these compounds follows Temkin adsorption isotherm. Some thermodynamic parameters of activation and adsorption processes were also determined and discussed.

Keywords: Corrosion inhibition, Cu-Ni alloy, HCl, enaminonitrile derivatives
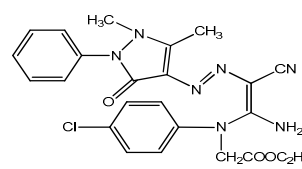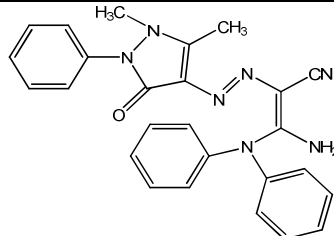_____

INTRODUCTION

The widespread use of copper alloys depends on a combination of good corrosion resistance, excellent workability, high thermal and electrical conductivities and attractive mechanical properties [1-2]. The electrochemical behavior of cupronickels has extensively studied under different experimental conditions using various techniques [3-12]. It was reported that the increase of Ni content improves the corrosion resistance of the alloy at high chloride concentration (> 0.5 M) [13]. The interest in studying the corrosion and electrochemical characteristics of Cu10Ni alloys arose because of their good corrosion resistance and the resistance of copper alloys to biological residues. Therefore, most of the studies focused on their behavior in marine environment. Studies were performed in chloride [14-16], in either natural or synthetic sea water, in the absence [4&17] or presence of sulfide [18-19], to understand the corrosion mechanism under different conditions; however, studies in alkaline medium [20-23] or in acidic sulfate [24] have also been reported.

The aim of this article is to use the investigated compounds as a corrosion inhibitor for Cu10Ni alloy in 0.5 M HCl solution. Measurements were conducted under different experimental conditions using various corrosion monitoring techniques, such as potentiodynamic polarization (Tafel polarization), electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM).

MATERIALS AND METHODS

The working electrode was made from Cu10Ni rod. The rod was mounted into a glass tube and fixed by araldite leaving a circle surface geometry of 1 cm diameter to contact the test solution. Prior to each experiment, the working electrode was polished with a different grades of emery paper up to 1200 grit, rinsed with acetone and finally with doubly distilled water. The auxiliary electrode was platinum wire, while a saturated calomel electrode (SCE) connected to conventional electrolytic cell of capacity 100 ml.

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The experiments were conducted in 0.5 M HCl solution and with different concentration $(1\times10^{-6} – 1\times10^{-4}$ M) of organic compounds. The structures and molecular weights of the investigated organic compounds are shown in Figure (1). All solutions were freshly prepared using analytical grade reagents and doubly distilled water. All experiments were performed at required temperature ±1 ^oC.

No.	Structures and names	Chemical formula	Mol. Wt.
A	ethyl 2-(((*Z*)-1-amino-2-cyano-2-((*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)vinyl)(4-chlorophenyl)amino)acetate	$C_{24}H_{24}ClN_7O$	493.95
B	(*Z*)-3-amino-2-((*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)-3-(diphenylamino)acrylonitrile	$C_{26}H_{23}N_7O$	449.51

Potentiodynamic polarization
Potentiodynamic polarization curves were recorded by changing the potential automatically from -600 mV to + 200 mV with scan rate 1mVs^{-1}

The inhibitive efficiency (% IE) was calculated employing Eq. (1):

$$\% \text{ IE} = \Theta \text{ x } 100 = [1 – (i_{inh} / i_{free})] \text{ x } 100 \qquad (1)$$

where i_{inh} and i_{free} are the corrosion current with and without inhibitor, respectively.

Electrochemical impedance spectroscopy
Electrochemical impedance spectroscopy measurements were carried out in frequency range of 100 kHz to 0.1 Hz to using ac signals of amplitude of peak to peak at respective potentials. The inhibition efficiencies (% IE) and the surface coverage (θ) obtained from the impedance measurements are defined by the following Eq. (2):

$$\% \text{ IE} = [1 – (R_{ct} / R`_{ct})] \text{ x}100 \qquad (2)$$

where R_{ct} and R'_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively.

Electrochemical frequency modulation
Electrochemical frequency modulation measurements were carried out using potential perturbation signals with amplitudes of mV. The experiments were carried out using two frequencies, 2 Hz and 5 Hz. The higher frequency must also be sufficiently low that the charging of the double layer does not contribute to current response [25]. This technique is fast, nondestructive and has internal self check in the form of two causality factors [25-26].

Before polarization, EIS and EFM experiments the open circuit potential (OCP) of the working electrode, which was measured as a function of time during 30 minute, the time needed to achieve a steady state.

Electrochemical experiments were performed using a typical three-compartment glass cell consisted of the Cu10Ni alloy specimen as working electrode (1 cm^2), saturated calomel electrode (SCE) as a reference electrode and a platinum foil (1 cm^2) as a counter electrode. The reference electrode was connected to a Luggin capillary and the tip

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of the Luggin capillary is made very close to the surface of the working electrode to minimize IR drop. All the measurements were done in solutions open to atmosphere under unstirred conditions. All potential values were reported versus SCE. Prior to every experiment, the electrode was abraded with successive different grades of emery paper, degreased with acetone and washed with bidistilled water and finally dried.

All electrochemical measurements are carried out using Potentiostat /Galvanostat / ZRA (Gamry PCI 300/4). This includes Gamry Framework system based on the ESA400, and a personal computer with DC 105 software for dc corrosion measurements, EIS300 software for impedance measurements and EFM140 software for electrochemical frequency modulation. Echem Analyst software 5.1 was used for plotting, graphing and fitting data. To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case at the same conditions.

RESULTS AND DISCUSSION

Potentiodynamic polarization
Polarization curves were shown in Figure (1) for Cu10Ni alloy in 0.5 M HCl in the absence and presence of different concentrations of compound A at 30°C. Similar curves were obtained for compound (B) but not shown. It is clear that both anodic metal dissolution and cathodic H$_2$ reduction reactions were inhibited when investigated inhibitors were added to 0.5 M HCl and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors. This behavior indicates that the undertaken additives act as mixed-type inhibitors [27]. The values of corrosion potential, E$_{corr}$, corrosion current density j$_{corr}$, Tafel slopes (β_a & β_c), corrosion rate CR and inhibition efficiency obtained from these measurements are summarized in Table (1). It is clear from this Table that the corrosion current density decreases with increasing the concentration of the investigated compounds. Moreover the negative shift of corrosion potential indicates that the investigated compounds are mixed-type inhibitors but mainly cathodic inhibitor than anodic one [28-29].

The decrease in the corrosion current density and the increase in the inhibition efficiency may be attributed to the adsorption of the investigated compounds on the alloy surface.
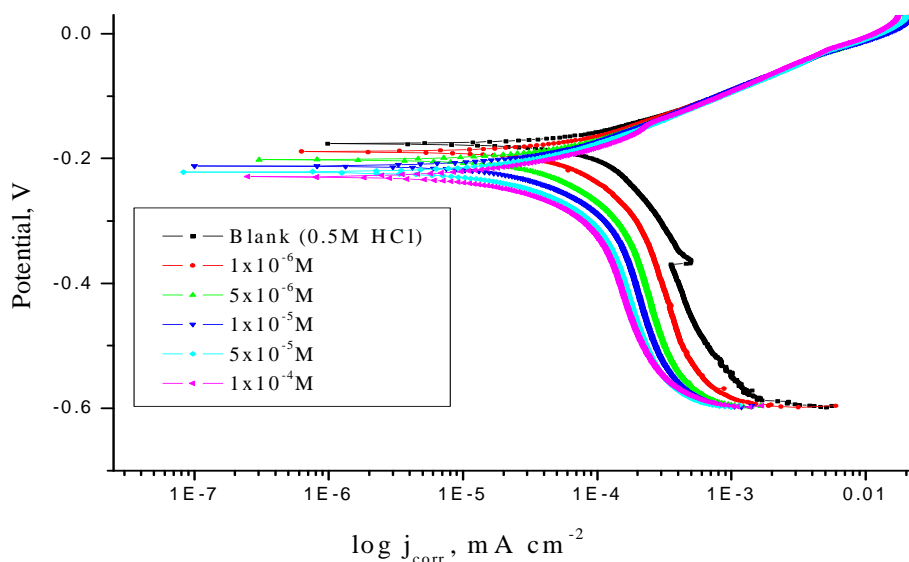

Figure 1 Potentiodynamic polarization curves for the dissolution of Cu10Ni alloy in 0.5 M HCl in the absence and presence of different concentrations of compound A at 30 ^{o}C

Electrochemical impedance spectroscopy
The effect of inhibitor concentration on the impedance behavior of Cu10Ni alloy in 0.5 M HCl solution at 25 ℃ is presented in Fig. 3. The curves show a similar type of Nyquist plots for Cu10Ni alloy in the presence of various concentrations of inhibitor (A). Similar curves were obtained for other inhibitor but not shown. The existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of

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interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface [30].

Table 1 The effect of concentration of the investigated compounds on the free corrosion potential (E_{corr}), corrosion current density (j_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (% IE), degree of surface coverage (θ) and corrosion rate (CR) for the corrosion of Cu-10Ni alloy in 0.5 M HCl at 30°C

| Compound	Conc. μM	$-E_{corr}$ mV	j_{corr} $\mu A\ cm^{-2}$	β_a $mVdec^{-1}$	β_c $mVdec^{-1}$	θ	% IE	CR $mm\ y^{-1}$
Free acid	0.0	176	152.0	101	408	---	---	69.6
	1	189.0	108.0	98.4	455.7	0.289	28.9	49.4
	5	202.0	73.8	94.5	378.2	0.514	51.4	33.7
(A)	10	212.0	44.4	86.4	219.7	0.708	70.8	20.3
	50	222.0	34.7	85.9	201.1	0.772	77.2	15.9
	100	229.0	33.8	91.9	205.1	0.778	77.8	15.5
	1	192	117.0	130	400	0.230	23.0	53.47
	5	202	86.90	115	343	0.428	42.8	39.7
(B)	10	224	50.40	118	373	0.668	66.8	23.0
	50	253	41.10	131	315	0.730	73.0	18.8
	100	230	34.10	91	192	0.776	77.6	15.6
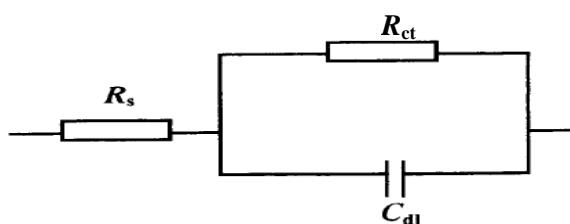
Figure 2 The equivalent circuit model used to fit the experimental results

Table 2 Electrochemical kinetic parameters obtainefrom EIS technique for the corrosion of Cu10Ni alloy in 0.5 M HCl at different concentrations of investigated compounds at 30°C

Compound	Conc., μM	R_p $\Omega\ cm^2$	C_{dl} $F\ cm^{-2}$	θ	% IE
Blank	0.0	82.7	1.2×10^{-4}	---	---
	1	398.8	2.5×10^{-5}	0.793	79.3
	5	432.0	2.3×10^{-5}	0.809	80.9
A	10	453.5	2.2×10^{-5}	0.818	81.8
	50	544.4	1.8×10^{-5}	0.848	84.8
	100	671.7	1.5×10^{-5}	0.877	87.7
	1	214.4	4.6×10^{-5}	0.614	61.4
	5	292.3	3.4×10^{-5}	0.718	71.8
B	10	383.7	2.5×10^{-5}	0.785	78.5
	50	479.8	2.2×10^{-5}	0.828	82.8
	100	556.6	1.8×10^{-5}	0.852	85.2

Electrochemical kinetic parameters obtained by EIS technique for the corrosion of Cu10Ni alloy in 0.5 M HCl at different concentrations of investigated compounds at 30°C were reported in Table (3). It is clear from the Table that the polarization resistance increases with increasing the concentration of the investigated compounds while C_{dl} values tend to decrease. The decrease in C_{dl} is due to the adsorption of the investigated compounds on the alloy surface [31] and it can be explained on the basis that the double layer between charged alloy surface and the solution is considered as an electrical capacitor. The decrease in the capacitance may be attributed to the formation of protective layer on the alloy surface [32].
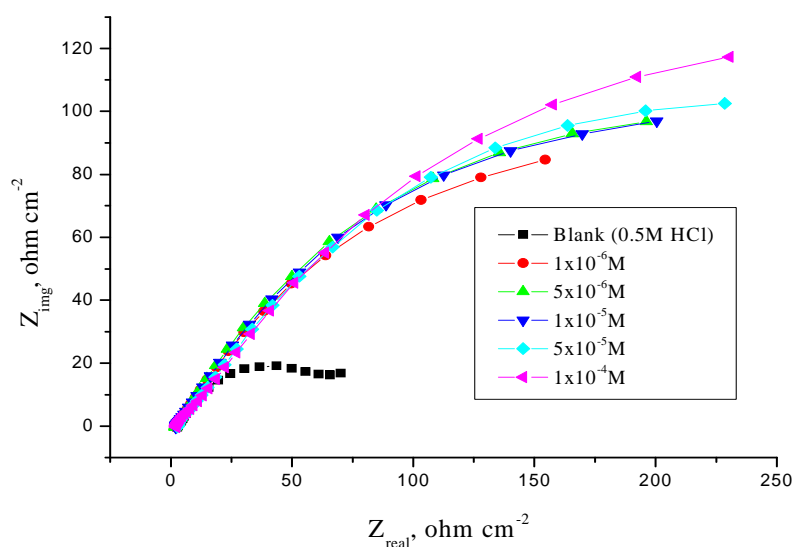
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Figure 3 The Nyquist plot for Cu10Ni alloy in 0.5 M HCl solution in the absence and presence of different concentrations of compound A at 25 ºC

Electrochemical frequency modulation

The EFM technique is used to calculate the anodic and cathodic Tafel slopes as well as the corrosion current densities for the investigated compound. Figures (3a and 3b) show the EFM intermodulation spectra (spectra of current response as a function of frequency) of Cu10Ni alloy in 0.5 M HCl and in presence of 1×10^{-4} M of compound A, respectively as an example. The calculated electrochemical parameters (j_{corr}, β_c, βa, CF-2, CF-3 and % IE) are given in Table (4). The values of causality factors obtained in absence and presence of investigated compounds are approximately equal the theoretical values (2 and 3) indicating that the measured data are of high quality [33]. It shown from the Table that the corrosion current density decreases with increasing the concentration of the investigated compounds with respect to blank and hence the inhibition efficiency increases and indicate that the investigated compounds inhibit the acid corrosion of the alloy through adsorption.
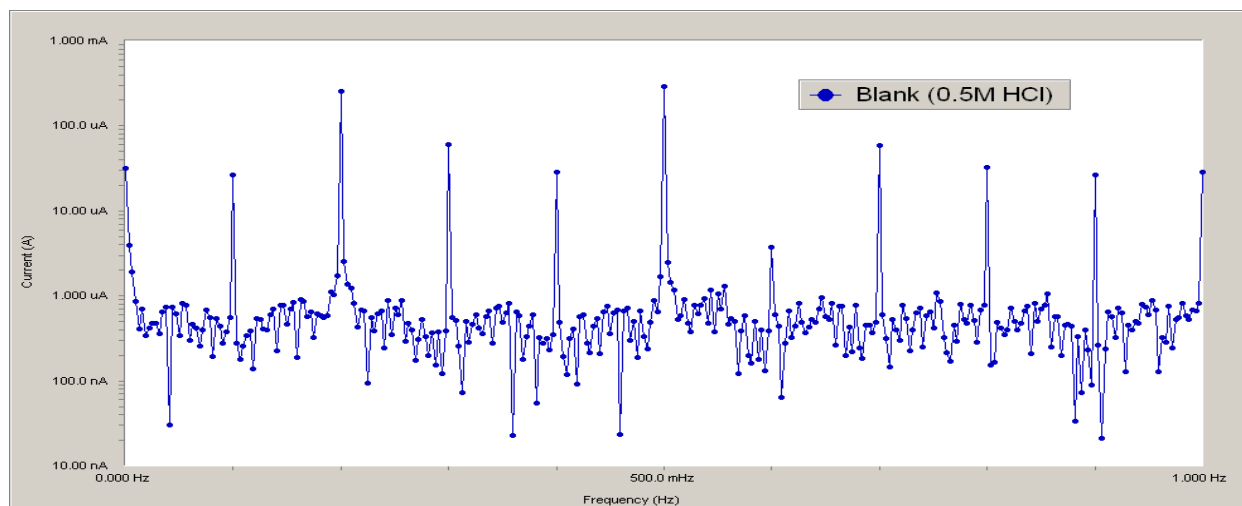

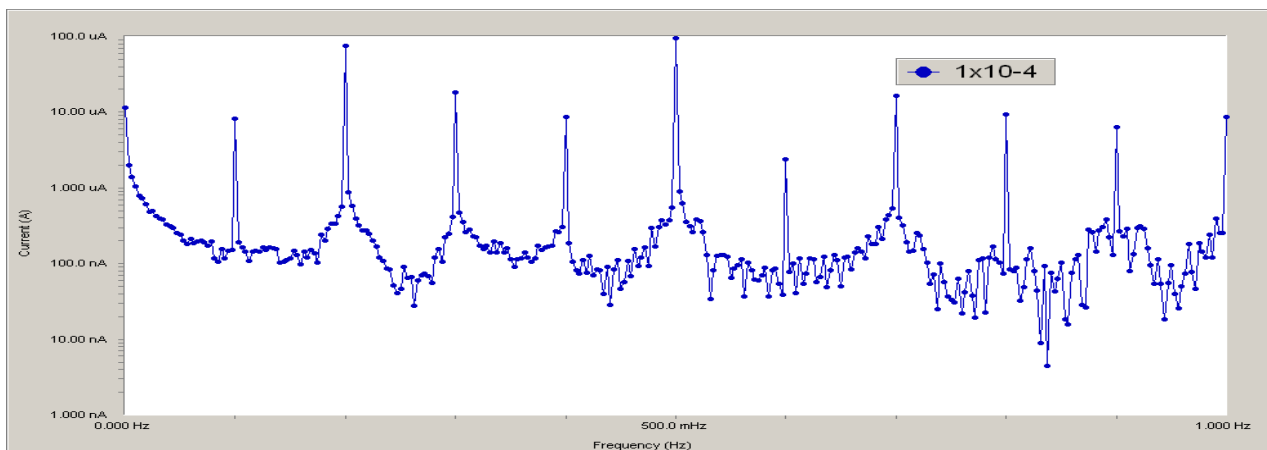**Figure 3 a EFM intermodulation spectra of Cu10Ni alloy in 0.5 M HCl**

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Figure 3 b   EFM intermodulation spectra of Cu10Ni alloy in 0.5 M HCl in the presence of 1x10^{-4} of compound (A)

Table 4 Electrochemical kinetic parameter obtained by EFM technique for the corrosion of Cu10Ni alloy in 0.5 M HCl at different concentration of the investigated compounds

Compound	Conc., μM	i_{corr}, μA cm^2	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	θ	% IE
Blank	0.0	165.6	31	54	2.0	3.5	---	---
	1	75.5	34	41	1.9	3.5	0.544	54.4
	5	72.0	32	54	2.0	3.4	0.559	59.9
A	10	56.6	29	44	2.0	3.5	0.658	65.8
	50	51.9	29	45	1.9	3.4	0.686	68.6
	100	45.9	29	45	2.0	3.5	0.722	72.2
	1	90.8	33	52	2.1	3.5	0.452	45.2
	5	87.8	34	45	2.0	3.3	0.469	46.9
B	10	77.8	37	63	2.1	3.0	0.530	53.0
	50	62.0	33	50	2.0	3.5	0.626	62.6
	100	53.6	32	48	2.0	3.5	0.676	67.6

Adsorption isotherm

It is widely acknowledge that adsorption isotherm provide useful insight onto the mechanism of the corrosion inhibition as well as the interaction among the adsorbed molecules themselves and their interaction with the electrode surface [34].

The protection efficiency has often been taken as a measure of the degree of surface coverage of the metal surface with particular inhibitor. With this definition, the degree of surface coverage (θ) can be calculated from Eq. (3):

$$\theta = \% \text{ IE} / 100 \tag{3}$$

The dependence of θ on inhibitor concentration (C) can be analyzed using Temkin isotherm

$$\theta = 2.303/a \log K_{ads} + 2.303/a \log C \tag{4}$$

where K_{ads} is the equilibrium constant of the adsorption reaction which related to standard free energy of adsorption ΔG°_{ads} by Eq. (5) [35]:

$$\log K_{ads} = -\log 55.5 - \Delta G^{\circ}_{ads} / 2.303RT \tag{5}$$

where the value of 55.5 is the concentration of water in solution in mole /L. Hence, a plot of θ versus logs C as shown in Fig. (4), give a straight line with a slope of 2.303/a and intercept equal 2.303/a log K_{ads}. From slope and intercept we can calculate the equilibrium constant of adsorption K_{ads}. The heat of adsorption ΔH°_{ads} could be calculated according to Van't Hoff equation [36]:

$$\log K_{ads} = \text{constant} - \Delta H^{\circ}_{ads}/2.303RT \tag{6}$$

In order to calculate heat of adsorption (ΔH°_{ads}), log K_{ads} was plotted against 1/T as shown in Fig (5). The straight lines were obtained with slope equal to ($-\Delta H^{\circ}_{ads}/2.303R$). Then according to the basic equation (7):

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$$\Delta G^{°}_{ads} = \Delta H^{°}_{ads} - T\Delta S^{°}_{ads} \qquad\qquad (7)$$

By introducing the obtained $\Delta G^{°}_{ads}$ and $\Delta H^{°}_{ads}$ vales in equation (7), the entropy of adsorption ($\Delta S^{°}_{ads}$) values were calculated at all studied temperatures. All estimated thermodynamic adsorption parameters for studied compounds on Cu10Ni alloy in 0.5 M HCl solution were listed in Table (4). From the listed data it can be conclude that:

a) K_{ads} values decrease with increasing the temperature from 25 – 55 °C
b) The negative values of $\Delta G^{°}_{ads}$ reflect that the adsorption of the investigated compounds on the alloy surface is spontaneous process [37].
c) $\Delta G^{°}_{ads}$ may increase (become less negative) with an increase of temperature which indicates the occurrence of exothermic process at which adsorption was unfavorable with increasing reaction temperature as the result of the inhibitor desorption from the alloy [38].
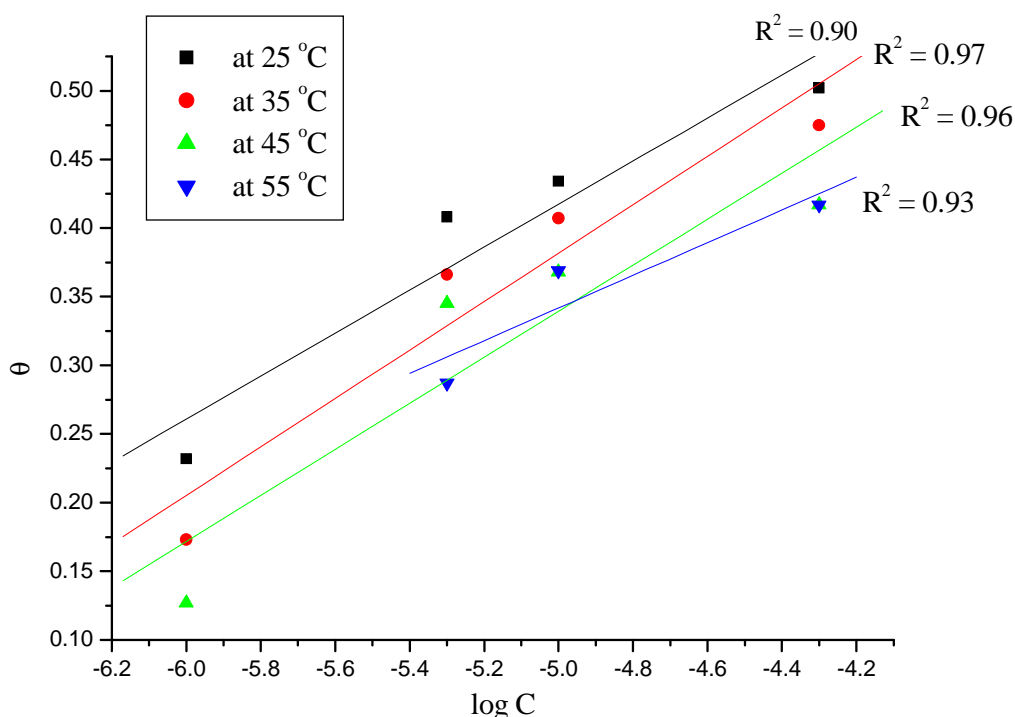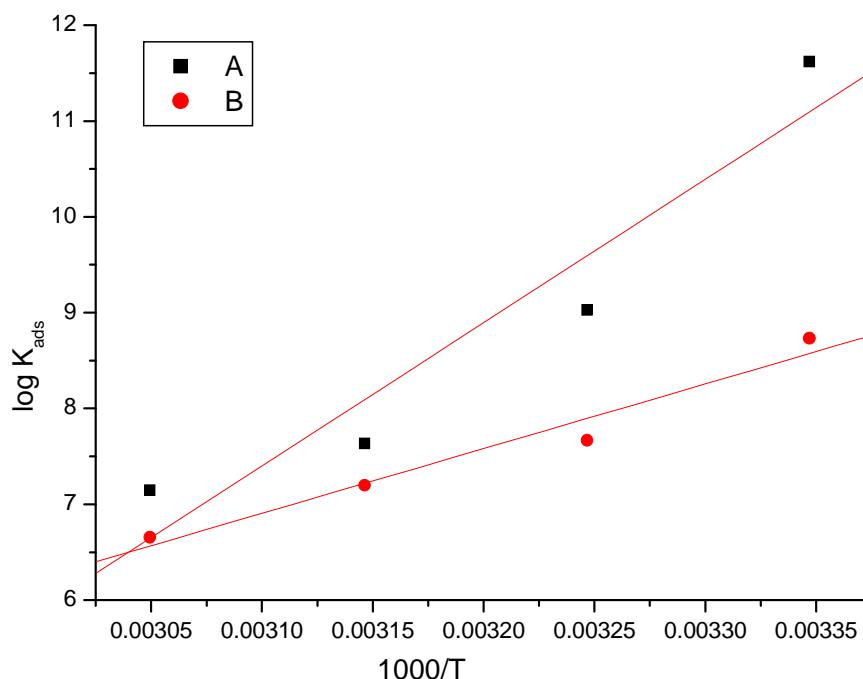

Figure 4 Temkin adsorption isotherm of compound (A) on Cu10Ni alloy in 0.5 M HCl at different temperatures

d) It is usually accepted that the values of $\Delta G^{°}_{ads}$ around -20 kJ mol^{-1} or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution while those around -40 kJ mol^{-1} or higher involve charge chairing or charge transfer between the charged metal and the organic molecules [41]. From the obtained values of $\Delta G^{°}_{ads}$ it was found that the existence of comprehensive adsorption (physical and chemical adsorption). That is to say, since the adsorption heat approached the general chemical reaction heat, the chemical adsorption occurs.

e) The negative sign of $\Delta H^{°}_{ads}$ reveals that the adsorption of the inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption [40]. In an exothermic process, physisorption is compared to chemisorption by considering the absolute value of adsorption enthalpy. Generally, enthalpy values up to 41.9 kJ mol^{-1} are related to the electrostatic interactions between charged molecules and charged metal (physisorption) while those around 100 kJ mol^{-1} or higher are attributed to chemisorption. The unshared electron pairs in the investigated molecules may interact with orbitals of the metal to provide a protective chemisorbed film [41]. In the investigated compound the absolute values of $\Delta S^{°}_{ads}$ are relatively high, approaching those typical of chemisorption. The values of $\Delta S^{°}_{ads}$ in the presence of the investigated compounds are larger and negative values that are accompanied with exothermic adsorption process [42].

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Table 4. Thermodynamic parameters for the adsorption of inhibitors on Cu10Ni alloy surface in 0.5 M HCl at different temperatures

Compound	Temp. °C	K_{ads} M^{-1}	$\Delta G°_{ads.}$ kJ mol^{-1}	$\Delta H°_{ads.}$ kJ mol^{-1}	$\Delta S°_{ads.}$ J mol^{-1}K^{-1}
Compound A	25	4.17×10^{11}	76.3		0.621
	35	7.2×10^{7}	57.1	261.3	0.66
	45	4.3×10^{7}	56.6		0.64
	55	1.4×10^{7}	55.9		0.62
Compound B	25	1.44×10^{9}	62.2		0.22
	35	1.6×10^{7}	53.4	127.5	0.24
	45	1.04×10^{7}	52.9		0.23
	55	1.0×10^{6}	48.8		0.24

Figure 5 plot of log K$_{ads}$ versus 1000/T of the investigated compounds at different temperatures

Effect of temperature

The effect of temperature on the corrosion rate of Cu10 Ni alloy was investigated in 0.5 M HCl solution in absence and presence of different concentration of the investigated compounds in the temperature range 25–55 °C. The values of corrosion parameters at different temperature were calculated from electrochemical frequency modulation data. In general, the corrosion rate which is represented by the corrosion current density j_{corr} which increase with increasing temperature and the process obey to the familiar Arrhenius equation [43-44].

$$\log j_{corr} = \log A - E^{*}_{a}/2.303RT$$

where A is the pre-exponential factor, E^{*}_{a} is the apparent activation energy of the process and R is the universal gas constant. A plot of log j_{corr} versus 1/T gave a straight line shown in Fig (6) with a slope equal $-E_{a}/2.303R$. The enthalpy of activation (ΔH^{*}) and the entropy of activation (ΔS^{*}) were obtained by aping the transition sate equation [45]

$$\log (j_{corr}/T) = \log (R/Nh) + (\Delta S^{*}/2.303R) - \log (\Delta H^{*}/2.303RT)$$

By plotting log (j_{corr}/T) versus 1/ gave a straight line shown in Fig (7) with a slope ΔH^{*}/R and intercept [log (R/Nh) + ΔS^{*}/2.303R]. All estimated thermodynamic activation parameters were tabulated in Table (5). It could be shown from the obtained data the presence of the investigated compounds lead to increase the apparent activation energy to a value larger than that of uninhibited solution suggesting that the higher energy barrier for the corrosion process in inhibited solution associated with physical adsorption or weak chemical bonding between the investigated

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compound and the alloy surface [46]. All values of E_a^* are larger than the analogous values of ΔH^* indicating that the corrosion process must involved a gaseous reaction, simply the hydrogen evolution reaction [47]. The entropy of activation ΔS^* in absence and presence of inhibitor has negative values this indicates that the activated complex in the rate determining step prefer association rather than dissociation, meaning that, a decrease in disordering takes place on going from reactants to the activated complex [48].
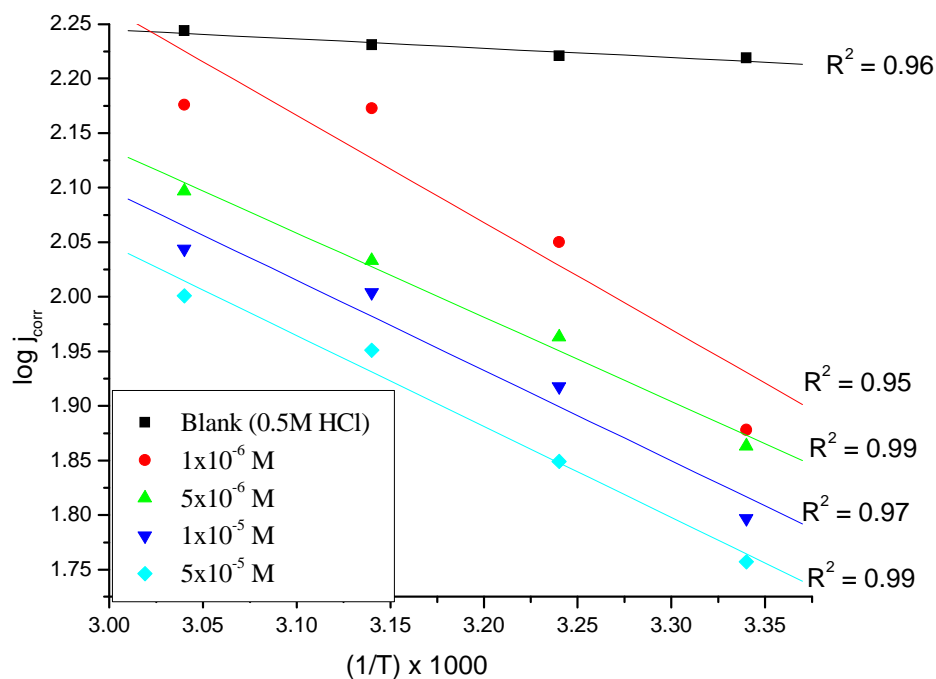

Figure 6 Arrhenius plots (log j_{corr} vs. 1/ T) for Cu10Ni alloy in 0.5 M HCl in the absence and presence of different concentration of compound A
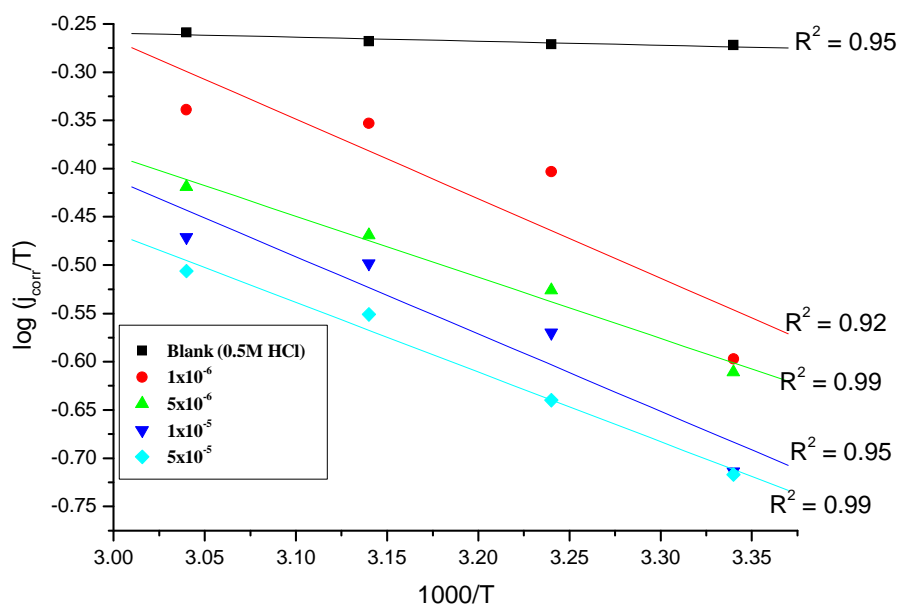

Figure 7 Transition state plots log j_{corr}/ T vs. (1/ T) for Cu-Ni alloy in 0.5 M HCl in the absence and presence of different concentration of compound A

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Table 5. Thermodynamic activation parameter for the dissolution of Cu10Ni alloy in 0.5 M HCl in the absence and presence of different concentrations of the investigated compounds

Conc. M	E^*_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
Compound A			
Blank	1.6	0.8	199.8
1x10^{-6}	14.7	12.1	168.2
5x10^{-6}	15.8	14.4	162.0
1x10^{-5}	17.0	15.3	152.6
5x10^{-5}	18.8	17.3	154.3
Compound B			
1x10^{-6}	14.0	11.5	171.0
5x10^{-6}	15.2	13.8	164.7
1x10^{-5}	16.0	14.5	159.0
5x10^{-5}	17.3	15.4	155.0

Mechanism of inhibition

Corrosion inhibition of copper – nickel alloy in HCl solution by the investigated compounds indicated from potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation techniques was found to be depending on the concentration and nature of the investigated compounds.

It is generally, assumed that adsorption of the inhibitor on the metal / solution interface is the first step in the action mechanism of the inhibitor in aggressive acid media. Four types of adsorption may take place during inhibition involving organic molecules at the metal / solution interface:1) Electrostatic attraction between charged molecules and charged metal 2) interaction of unshared pairs of electrons in the molecule with the metal 3) Interaction of π electrons with the metal 4) A combination of the above [49]

Concerning inhibitors, the inhibition efficiency depend on several factors; such as (i) The number of adsorption sites and their charge density, (ii) Molecular size, (iii) Mode of interaction with the metal surface and (iv) The formation of metallic complex [50]

The order of inhibition is decreased as the following order: A > B This is due to its larger molecular size and the presence of Cl group which has a dual effect (act as electron donor or electron acceptor) and hence Cl atom may act as donor atom which increases the electron charge density on the molecule and hence % IE increases.

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