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Acrylonitrile derivatives as corrosion inhibitors for Cu10Ni alloy in 0.5 M hydrochloric acid solution

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Corrosion inhibition of Cu10Ni alloy in 0.5 M HCl solution using acrylonitrile derivatives namely: (E)-2-(1H-indole-3-carbonyl)-3-(2-oxo-2-phenylethylthio)-3-(phenylamino)acrylonitrile(a),(E)-2-(1H-indole-3-carbonyl)-3-mercapto-3-(phenylamino)acrylonitrile(b)and(Z)-2-(1H-indole-3-carbonyl)-3 phenylacrylonitrile (c) was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM). Effect of temperature on the efficiency of the corrosion inhibition process was studied and the values of thermodynamic activation parameters were calculated and discussed. The inhibition was found to increase with increasing inhibitor concentrations and decreases with increasing temperature. Polarization data indicate that the examined acrylonitrile derivatives act as mixed type (cathodic/anodic) inhibitors. EIS results show that the change in impedance parameters with the concentration of the acrylonitrile derivatives studied is indicative of the adsorption of acrylonitrile derivatives molecules on Cu10Ni alloy surface. The adsorption of investigated compounds on Cu10Ni alloy surface has been found to obey Langmuir adsorption isotherm.

Key words: Corrosion inhibition, hydrochloric acid (HCl), Cu10Ni alloy, acrylonitrile derivatives.
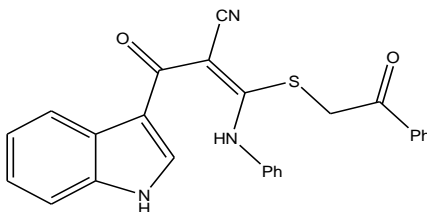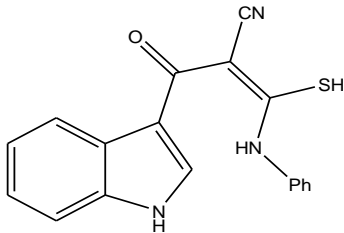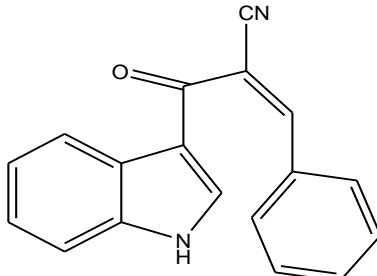
INTRODUCTION

Copper and Cu10Ni alloys (also known as cupronickels) have been used for over 50 years for seawater piping and heat exchangers because they have good corrosion resistance. It is well known that the addition of nickel to copper, as an alloying component, to form Cu10Ni alloys, gives rise to the production of a corrosion resistant material (Igual et al., 2004; Ismail et al., 2006; Gilbert et al., 1995; Jones, 1996) Copper and its alloys are industrial materials with a wide variety of applications due to electrical, thermal, mechanical and corrosion resistance properties, among others. However, in the presence of oxygen, chlorides, sulphates or nitrates ions they are exposed to localized corrosion (Rosa et al.,

2008; Alfantazi et al., 2009). The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated. Amongst them there are inorganic inhibitors (Igual et al., 2004), but in much greater numbers there are organic compounds and their derivatives such as azoles (Sherif, 2006; Sherif and Park, 2006a and b, Sherif et al., 2007), amines (Ehteshamzade and Hosseini, 2006) amino acids (Matos et al., 2004) and many others. It is noticed that, the presence of heteroatom such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the

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Table 1. The investigated inhibitors and their chemical structures.

Inhibitor	Chemical structure	Name	Molecular weight
a		(E)-2-(1H-indole-3-carbonyl)-3-(2-oxo-2-phenylethylthio)-3-(phenylamino)acrylonitrile	437.51 $C_{26}H_{19}N_3O_2S$
b		(E)-2-(1H-indole-3-carbonyl)-3-mercapto-3-(phenylamino)acrylonitrile	319.38 $C_{18}H_{13}N_3OS$
c		(Z)-2-(1H-indole-3-carbonyl)-3-phenylacrylonitrile	272.30 $C_{18}H_{12}N_2O$

presence of vacant d orbital in copper ions that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, π-electrons, is also present (Antonijevic and Petrovic, 2008).

This work the study of the corrosion inhibition of Cu10Ni alloy in HCl solution by acrylonitrile compounds using different techniques such as potentiodynamic polarization, electrochemical impedance (EIS) spectroscopy and electrochemical frequency modulation (EFM).

EXPERIMENTAL

Materials

The chemical composition (wt %) of Cu10 Ni is: 88Cu%, 10%Ni, 2%Fe.

Solutions

Hydrochloric acid (37%) solution was prepared from chemically pure grade (BDH) by appropriate dilution, and then standardized using sodium carbonate. Double distilled water was used throughout all the experiments.

Inhibitors

The inhibitors used in this study were selected from acrylonitriles derivatives (El-Newehi, 2009) and their chemical structures are shown in Table 1.

Potentiodynamic polarization method

For the potentiodynamic polarization experiments, electrochemical cell with a three electrode configuration was used. A standard calomel electrode (SCE) and a platinum electrode were used as a reference and counter electrodes, respectively. Cu 10Ni electrodes were cut from the Cu10Ni sheets, of thickness 0.1 mm. The electrodes were of dimensions 1 × 1 cm and were weld from one side to a copper wire used for electric connection. The samples were embedded in glass tube of just larger diameter than the samples. Epoxy resin was used to stick the sample to glass tube .The working electrode was polarized at -0.8 V to +0.8 V with scanning rate of 5 mVs^{-1}. From this study we obtained corrosion current density (i_{corr}), corrosion potentials (E_{corr}), cathodic and anodic Tafel slopes (β_c), (β_a) and surface coverage (θ). The inhibition efficiency and surface coverage were calculated from
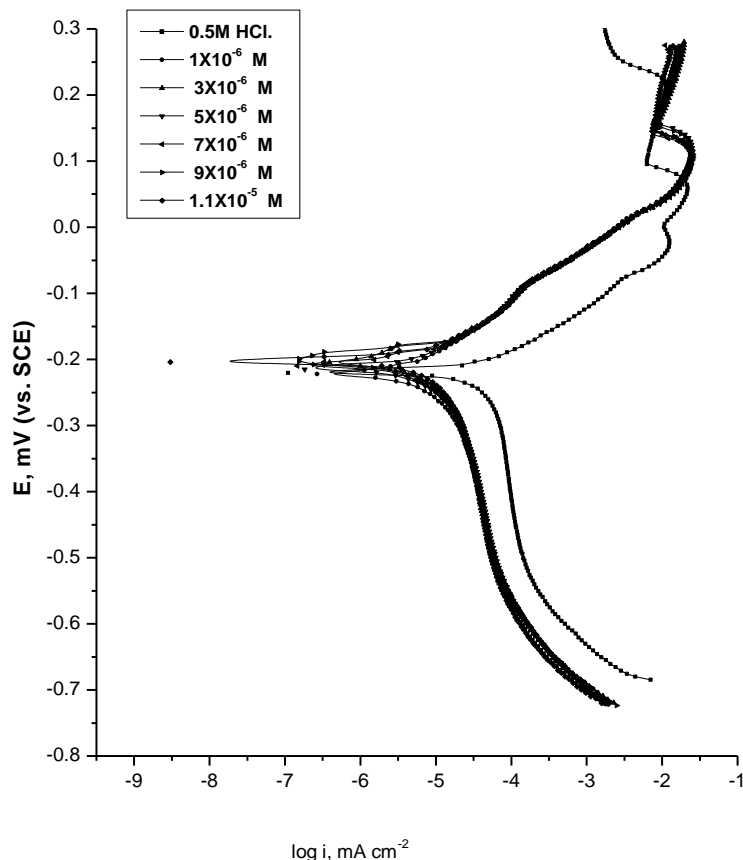
Figure 1. Potentiodynamic polarization curves of Cu10Ni alloy in 0.5 M HCl in the absence and presence of compound (a) at different concentrations at 25°C.

corrosion current density using the following formula

$$\eta \% = \theta \times 100 = [(i_{corr} - i'_{corr}) / i_{corr}] \times 100 \qquad (1)$$

where i_{corr} and i'_{corr} are the corrosion current densities obtained in the absence and presence of the inhibitors, respectively.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy experiments were conduct at $25 \pm 1°C$ with respect to corrosion potential, E_{corr}, over a frequency range of 100 kHz to 10 m Hz with a signal amplitude perturbation of 5 mV s^{-1}. Data were presented as Nyquist and Bode plots. Degree of surface coverage, θ, and IE % were calculated using the following equation:

$$\eta \% = \theta \times 100 = [1 - (R°_{ct} / R_{ct})] \times 100 \qquad (2)$$

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

Electrochemical frequency modulation (EFM)

EFM measurements were performed with applying potential perturbation signal with amplitude of 10 mV with two sine waves of 2 and 5 Hz. The electrochemical studies were performed using Gamry Potentiostat/Galvanostat (Gamry PCI 300/4) with a Gamry framework system based on ESA 300. Gamry applications include software DC105 for corrosion, EIS 300 for EIS and EFM 140 for electrochemical frequency modulation measurements, and Echem Analyst version 5.5 software packages for data fitting. The working electrode was immersed in the acid solution for 30 min in order to attain the steady-state (open circuit) potential before the electrochemical tests.

RESULTS AND DISCUSSION

Potentiodynamic polarization

The potentiodynamic polarization curves for Cu10Ni alloy in 0.5 M HCl solutions containing different concentrations of compound (a) at 25°C are shown in Figure 1. Similar curves were obtained for other compounds (not shown). Potentiodynamic polarization parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) cathodic and anodic Tafel slope (β_c and β_a), degree of surface coverage (θ), and percentage inhibition

Table 2. Data from potentiodynamic polarization of Cu10Ni alloy in 0.5 M HCl containing different concentrations of investigated compounds at 25°C.

| Inhibitor	Conc., M	-E_{corr}, mV vs.SCE	i_{corr}, μA cm^{-2}	$β_a$, mVdec^{-1}	$β_c$, mVdec^{-1}	θ	η %
Blank	0.5M HCl	221	129.00	390	335	–	–
a	1 × 10^{-6}	221	14.35	153	381	0.889	88.9
	3 × 10^{-6}	205	10.05	136	347	0.922	92.2
	5×10^{-6}	213	9.00	137	305	0.930	93.0
	7 × 10^{-6}	210	8.29	140	319	0.936	93.6
	9 ×10^{-6}	204	6.73	145	277	0.948	94.8
	11 × 10^{-6}	204	6.28	131	291	0.951	95.1
b	1 × 10^{-6}	204	21.16	149	526	0.836	83.6
	3 × 10^{-6}	210	18.21	149	492	0.859	85.9
	5 × 10^{-6}	209	16.22	145	424	0.874	87.4
	7 × 10^{-6}	209	14.73	144	455	0.886	88.6
	9 ×10^{-6}	210	10.39	144	291	0.920	92.0
	11 × 10^{-6}	214	10.23	144	333	0.921	92.1
c	1 × 10^{-6}	214	22.96	156	451	0.822	82.2
	3 × 10^{-6}	212	18.21	150	416	0.834	83.4
	5 ×10^{-6}	209	16.22	151	458	0.859	85.9
	7 × 10^{-6}	214	14.73	148	425	0.875	87.5
	9 × 10^{-6}	215	10.39	155	419	0.887	88.7
	11 × 10^{-6}	204	10.23	140	382	0.904	90.4

efficiency (IE%) are summarized in Table 2 for the corrosion of Cu10 Ni alloy in 0.5 M HCl in the absence and presence of different concentration of inhibitors. The results show that the corrosion current (i_{corr}) decreases with increasing the inhibitor concentration and hence, the inhibition efficiency increases. The order of inhibition efficiency of investigated compounds is as follows: a > b > c (Table 3). A compound can be classified as an anodic-or cathodic-type inhibitor when the change in the E_{corr} value is larger than 85 mV (Musa et al., 2010). Since the largest displacement exhibited by these inhibitors was 17 mV at 25°C (Table 2). It may be concluded that these molecules should be considered as a mixed-type inhibitor, meaning that the addition of these inhibitors to 0.5 M HCl solution both reduces the anodic dissolution of Cu10Ni alloy and also to retards the cathodic hydrogen evolution reaction.

Adsorption is the mechanism generally accepted to explain the inhibitory action of organic corrosion inhibitors. The adsorption of inhibitors can affect the corrosion rate in two ways: (i) by decreasing the available reaction area, the so-called geometric blocking effect and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring in the inhibitor-free metal in the course of the inhibited corrosion process. It a difficult task to determine which aspects of the inhibiting effect are connected to the geometric blocking action and which are connected to the energy effect. Theoretically, no shifts in E_{corr}, should be observed after addition of the corrosion inhibitor if the geometric blocking effect is stronger than the energy effect (de Souzaf, 2009). No change observed in E_{corr} values upon addition of inhibitors indicates that geometric blocking effect is stronger, although the energy effect cannot be ignored.

Adsorption isotherm

Organic molecules like inhibitors molecules inhibit the corrosion process via their adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, $L_{inh.}$, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface (Pardo et al., 2006) vis,

$$L_{inh\,(aq)} + x\,H_2O_{(sur)} \rightarrow L_{inh\,(sur)} + x\,H_2O_{(aq)} \qquad (3)$$
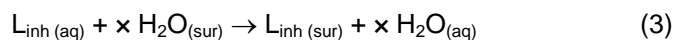
where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the
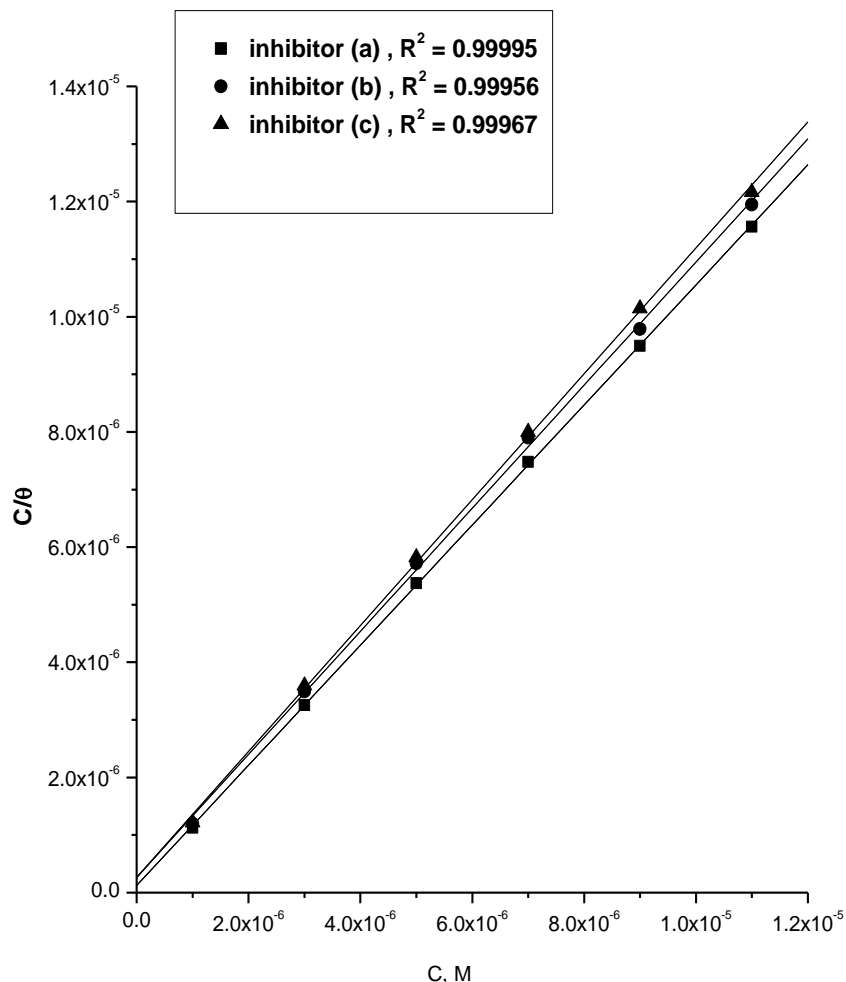
Figure 2. Curve fitting of corrosion data for Cu10Ni alloy in 0.5 M HCl in presence of different concentrations of inhibitors corresponding to Langmuir adsorption isotherm at 25°C.

nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface (El-Awady and Ahmed, 1985). To obtain more information about the interaction between the acrylonitrile molecules and the alloy surface, different adsorption isotherms were tested. The degree of surface coverage, θ at different concentrations of the acrylonitrile in 0.5 M HCl solutions was determined from the corresponding electrochemical polarization measurements. The obtained values of θ were fitted to different isotherms including Langmuir, Frumkin, Temkin, etc. The Langmuir isotherm, Equation (4), was verified only in the case of investigated compounds on Cu10Ni, which is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby

sites being occupied or not.

$$C / \theta = 1/ K + C \tag{4}$$

where C is the concentration of inhibitor, θ the fractional surface coverage and K is the adsorption equilibrium constant related to the free energy of adsorption ΔG^o_{ads} as Lipkowski and Ross (1992):

$$K = 1/ 55.5 \exp (-\Delta G^o_{ads}/ RT) \tag{5}$$

where R is the universal gas constant, T is the absolute temperature. The value 55.5 is the concentration of water on the metal surface in mol/ L.

Figure 2 shows Langmuir adsorption isotherm for the adsorption of investigated compounds on Cu10Ni alloy surface. Values of adsorption parameters deduced from the isotherm are presented in Table 4. From the results obtained, it is significant to note that the R^2 values and

Table 3. Inhibition efficiency of Cu10Ni alloy in 0.5 M HCl in the presence of different concentrations of compounds (a, b, c) 25°C.

Conc. × 10 6 (M)	% η		
	a	b	c
1	88.9	83.	82.2
3	92.2	85.9	83.4
5	93.0	87.4	85.9
7	93.6	88.6	87.5
9	94.8	92.0	88.7
11	95.1	92.1	90.4

Table 4. Equilibrium constant (K) and free energy of adsorption (ΔG°ads), for the adsorption of inhibitors on Cu10Ni alloy at 25°C.

Inhibitor	Kinetic model		Langmuir	
	$K \times 10^{-7} M^{-1}$	$-\Delta G^\circ_{ads} kJ mol^{-1}$	$K \times 10^{-7} M^{-1}$	Slope
a	30.1	58.3	2.6331	1.05815
b	8.1	55.1	2.6109	1.1017
c	6.9	54.7	1.2323	1.12659

the slopes values of the plots are very close to unity, which indicates a strong adherence of the adsorption data to the assumptions establishing Langmuir adsorption isotherm. Also, it is found that the data fit the kinetic thermodynamic model of (El-Awady and Ahmed 1985) the adsorption isotherm relationship which is represented by Equation (6):

$$\log (\theta/ 1-\theta) = \log k` + y \log C \qquad (6)$$

where: y is the number of inhibitor molecules occupying one active site of the metal surface and 1/y is the number of the surface active sites occupied by one inhibitor molecule. Plot log (θ/ 1-θ) against log C, a straight line obtained as shown in Figure 3 with intercept of log k`, slope of (y) and K calculated from $K = k`^{(1/y)}$ as shown in Table 4.

From previous results, the large values of K imply better efficient adsorption and better inhibition efficiency (Abd El-Rehim et al., 2001). The negative value of -ΔG°ads indicates that the adsorption process is spontaneous. The higher values of ΔG°ads and K indicate the strong adsorption of these inhibitors and stability of the adsorbed layer on the Cu10Ni alloy surface (Popova et al., 2003). It is well known that ΔG°ads value up to - 20 kJ mol⁻¹ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol⁻¹ involve sharing or transfer of electron from the inhibitor molecule to the metal surface to form a coordinate bond (chemisorption) (Bensajjay et al., 2003).

The values of ΔG°ads obtained are more negative than -40 kJ mol⁻¹ indicating that the adsorption of compounds a, b, and c on Cu10Ni alloy in 0.5 M HCl solutions was mixed one, chemisorption and physisorption.

Effect of temperature

The effect of temperature (25 – 55) ±1°C on the corrosion behavior of Cu10Ni in 0.5 M HCl in the absence and presence of 11×10⁻⁶ M of the inhibitors was studied using potentiodynamic polarization measurements. The activation energy (E^*_a) for the corrosion process can be calculated from Arrhenius equation:

$$i_{corr} = A \exp (-E^*_a/RT) \qquad (7)$$

where i_{corr} is the corrosion rate, A is the Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of (log i_{corr}) against (1/T) are shown in Figure 4, straight lines obtained and from the slopes of these lines E^*_a can be determined. The values of E^*_a obtained are listed in Table 5, these results show that the E^*_a value of 0.5 M HCl containing inhibitors is higher than that without inhibitors. The higher values of E^*_a indicated the presence of energy barrier on the Cu10Ni surface (Putilova et al., 1960). The activation energy increases with increasing the efficiency of the investigated compounds as follows: a > b > c.

Enthalpy and entropy of activation (ΔH* and ΔS*) are calculated from transition state theory using the following
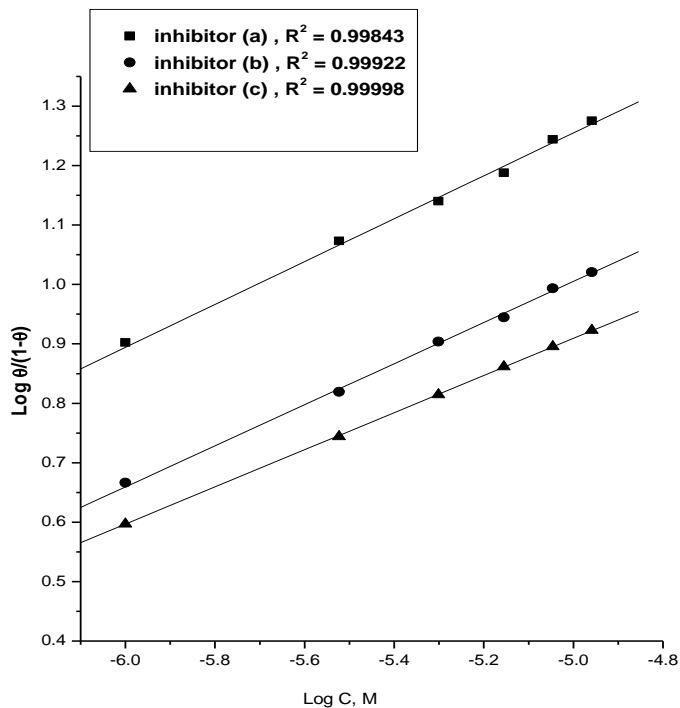
Figure 3. Curve fitting of corrosion data for Cu10Ni alloy in 0.5 M HCl in presence of different concentrations of inhibitors corresponding to kinetic model at 25°C.
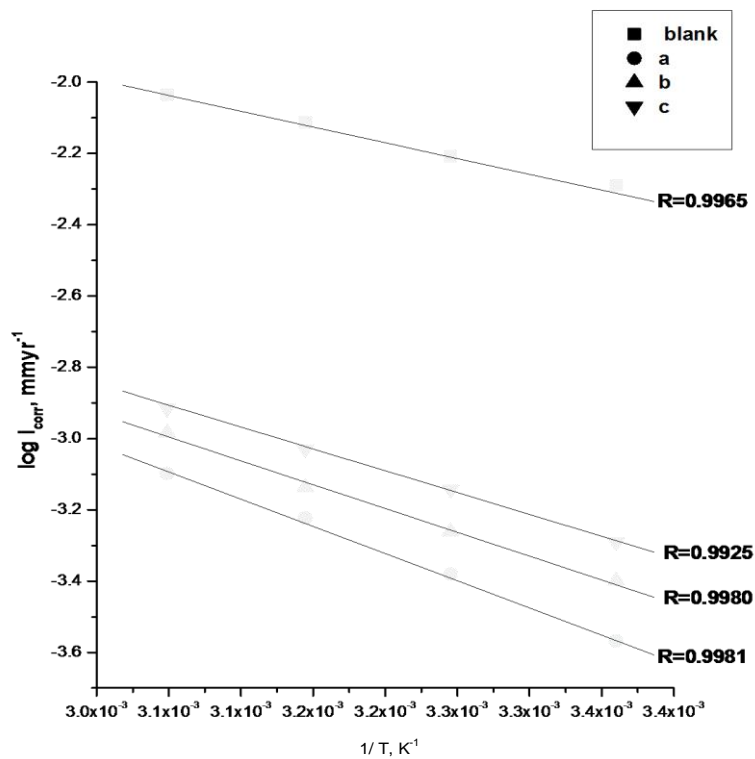

Figure 4. log i_{corr} - 1/T curves for Cu10Ni alloy dissolution in 0.5 M HCl in the absence and presence of 11×10^{-6} M different inhibitors at different temperatures.

Table 5. Effect of different temperatures on the activation energy (E_a^*), activation enthalpy (ΔH^*) and activation entropy (ΔS^*) of Cu10Ni alloy corrosion in 0.5 M HCl in the absence and presence of 11×10^{-6} M different inhibitors.

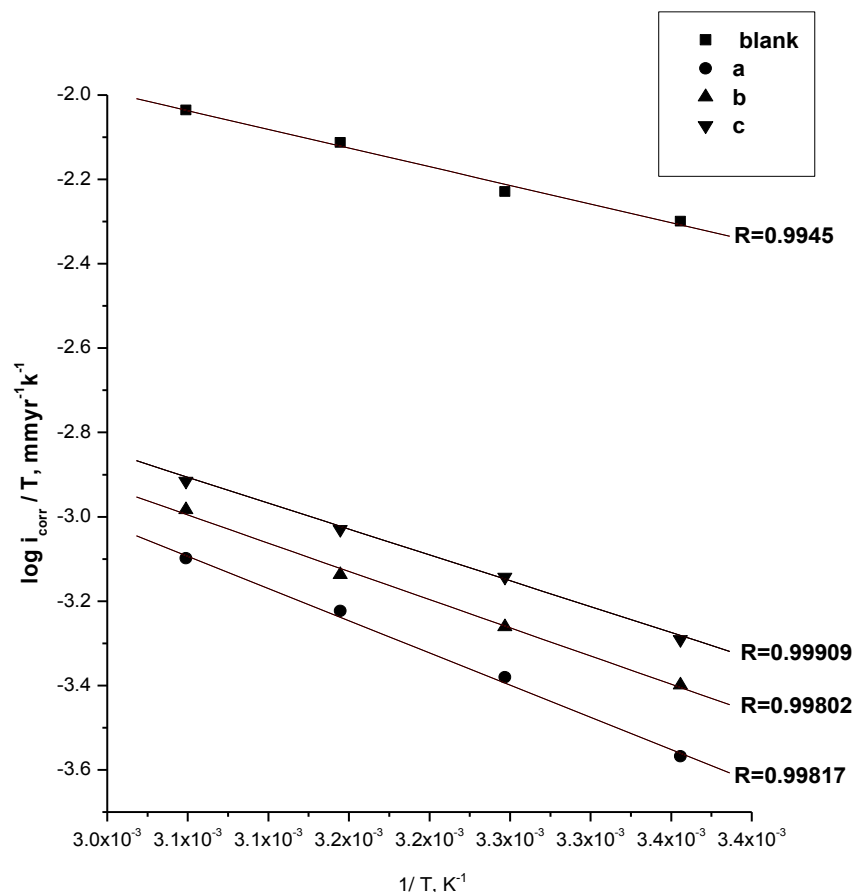| Inhibitor	ΔE_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1} K^{-1}
blank	19.6	7.4	50.8
a	31.8	12.7	33.6
b	28.2	11.1	42.8
c	26.1	10.2	47.5

Figure 5. log i$_{corr}$/T - 1/T curves for Cu10Ni alloy dissolution in 0.5 M HCl in the absence and presence of 11×10^{-6} M different inhibitors at different temperatures.

equation (Haladky et al., 1980):

$$i_{corr} = RT/Nh \exp (\Delta S^* /R) \exp (-\Delta H^* /RT) \qquad (8)$$

where $k = i_{corr}$, N is Avogadro's number and h is the Planck' constant .plot of (log i$_{corr}$ / T) against 1/T straight lines obtained as shown in Figure 5. The values of ΔH^* calculated from the slope of these lines and the values of ΔS^* calculated from the intercepts of these lines are recorded in Table 5. The positive values of ΔH^* reflect the endothermic corrosion process and on Cu10Ni alloy surface. The values of ΔS^* in the absence and presence of inhibitors are large and negative this indicate that the activated complex in the rate determining step represents an association rather than dissociation step.

Electrochemical impedance spectroscopy (EIS)

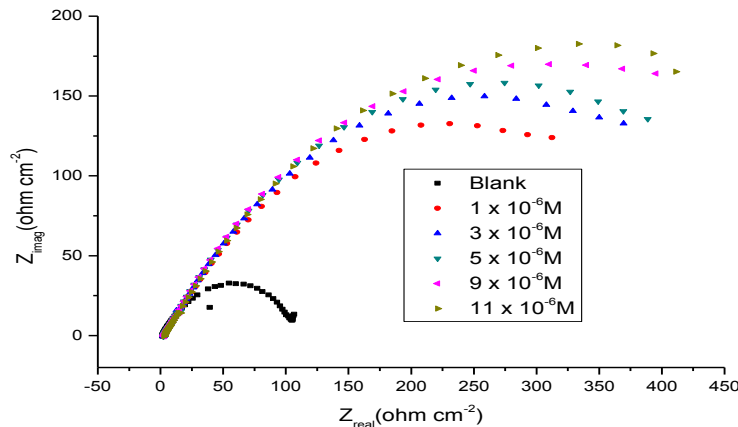The results of the potentiodynamic polarization

Figure 6. 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°C.

Table 6. Electrochemical kinetic parameters obtained from EIS technique for the corrosion of Cu10Ni alloy in 0.5 M HCl at different concentrations of investigated compounds at 25°C.

Comp.	Conc., M	R_{ct} Ω cm^2	C_{dl} × 10^{-3} µF cm^{-2}	θ	% η
	Blank	108.4	3.554	–	–
	1×10^{-6}	542.1	1.963	0.800	80.0
a	3×10^{-6}	595.9	1.343	0.818	81.8
	5×10^{-6}	616.0	1.208	0.824	82.4
	9×10^{-6}	688.2	0.917	0.842	84.2
	11×10^{-6}	742.8	0.716	0.854	85.4
	1×10^{-6}	411.5	1.480	0.737	73.7
	3×10^{-6}	482.4	1.296	0.775	77.5
b	5×10^{-6}	551.0	9.258	0.803	80.3
	9×10^{-6}	633.5	0.611	0.829	82.9
	11×10^{-6}	629.4	0.287	0.828	82.8
	1×10^{-6}	400.7	1.233	0.729	72.9
	3×10^{-6}	449.5	0.983	0.759	75.9
c	5×10^{-6}	473.4	0.617	0.771	77.1
	9×10^{-6}	560.4	0.541	0.807	80.7
	11×10^{-6}	565.1	0.461	0.808	80.8

experiments were confirmed by impedance measurements, since the electrochemical impedance spectroscopy (EIS), is a powerful technique in studying corrosion mechanisms and adsorption phenomena. EIS measurements were carried out for corrosion of Cu10Ni alloy in 0.5 M HCl in the absence and presence of inhibitor compounds (a, b, c) at 25 ± 1°C. The obtained Nyquist plot for compound (a) are shown in Figure 6. It has been reported (Jones, 1996) that the semicircles at high frequencies are generally associated with the relaxation of electrical double-layer capacitors, and the diameters of the high-frequency capacitive loops can be considered as the charge-transfer resistance. The diagram of the capacitive loop obtained increases in the presence of inhibitor and was indicative of the degree of inhibition of the corrosion process. The high frequency limits corresponding to the solution resistance R_s (Ω), while the lower frequency limits corresponds to (R_{ct} + R_s). The low frequency contribution showed the kinetic response of the charge transfer reaction (Mansfeld, 1990). The impedance parameter such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency (% IE) were calculated and are listed in Table 6. The R_{ct} values increase and the C_{dl}
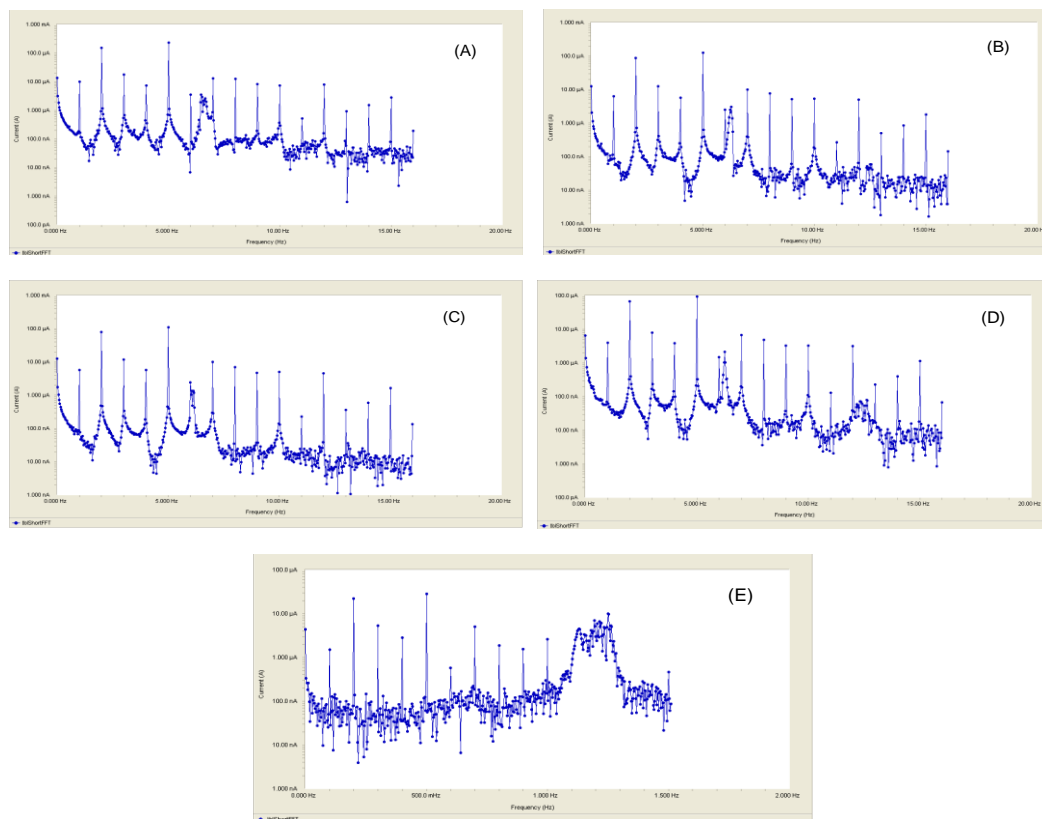
Figure 7a-e. The EFM charts for Cu10Ni alloy in 0.5 M HCl solution in the absence and presence of different concentrations of compound (a) at 25°C.

values decrease with increasing concentration of the inhibitors and hence, the inhibition efficiency (% IE) increases. The high R_{ct} values associated with slower corroding system (Khaled, 2003; Babic-samardzija et al., 2005). The inhibition efficiency obtained from impedance measurements are in good agreement with those obtained from potentiodynamic polarization studies (a > b > c).

Electrochemical frequency modulation (EFM) method

The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. Intermodulation spectra obtained from EFM measurements in absence and presence of compound (a) are presented in Figure 7a - e as examples of Cu10Ni alloy in 0.5 M HCl solutions at 25°C. Each spectrum is a current response as a function of frequency. The two large peaks are the response to the 2 and 5 Hz excitation frequencies. These peaks are used by the EFM 140 software package to

calculate the corrosion current and Tafel constants.

The calculated corrosion kinetic parameters at different concentrations of the investigated extract in 0.5 M HCl at 20°C (i_{corr}, β_a, β_c, CF-2, CF-3 and % η) are given in Table 7. From Table 7, the corrosion current densities decrease by increasing the concentration of inhibitors and hence, inhibition efficiency increases. The causality factors in Table 7 are very close to theoretical values which according to EFM theory should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors in Table 7 indicate that the measured data are of good quality (Abd El Rehim et al., 2006). The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to the perturbation amplitude was too small or the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well. It can be seen that the inhibition efficiency is in the order: a > b > c.

Inhibition mechanism

The adsorption of investigated compounds can be attributed to the presence of polar unit having atoms of

Table 7. Data from electrochemical frequency modulation of Cu10Ni alloy in 0.5 M HCl containing different concentrations of compound (a) at 25°C.

Inhibitor	Conc., M	i_{corr}, µA cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	C.R. mpy	θ	% η
	Blank	153.0	46	60	2.12	3.06	70.3	–	–
a	3 × 10^{-6}	83.95	44	61	2.06	2.80	38.6	0.451	45.1
	5 ×10^{-6}	71.98	42	61	2.05	2.71	33.1	0.530	53.0
	7 × 10^{-6}	66.70	47	64	2.06	2.93	30.7	0.564	56.4
	11 × 10^{-6}	17.67	36	65	1.91	3.83	8.1	0.884	88.4
b	3 × 10^{-6}	93.72	45	62	2.02	2.71	43.1	0.387	38.7
	5×10^{-6}	80.45	47	66	2.02	2.61	36.9	0.474	47.4
	7 × 10^{-6}	77.38	40	57	2.07	3.02	35.6	0.494	49.4
	11 × 10^{-6}	24.36	40	76	1.96	3.28	11.1	0.841	84.1
c	3 × 10^{-6}	106.3	45	60	2.07	2.77	48.9	0.305	30.5
	5 × 10^{-6}	94.45	39	56	2.09	3.94	43.4	0.383	38.3
	7 × 10^{-6}	84.21	39	55	2.09	3.09	38.8	0.449	44.9
	11 × 10^{-6}	26.95	30	55	1.96	3.58	12.4	0.823	82.3

nitrogen, sulphur and oxygen and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pair of hetero-atoms and л-electrons of aromatic ring (Ahamad et al., 2010). These compounds may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor–acceptor interactions between the л -electrons of aromatic ring and vacant d-orbital of surface iron atoms, (iii) interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms. The neutral molecules may be adsorbed on the surface of Cu10Ni alloy through the chemisorption mechanism, involving the displacement of water molecules from the Cu10Ni alloy surface and the sharing electrons between the hetero- atoms and the alloy. The inhibitor molecules can also adsorb on the Cu10Ni alloy surface on the basis of donor–acceptor interactions between л -electrons of the aromatic ring and vacant d-orbitals of the alloy surface.

Compound (a) is the most efficient inhibitor, due to its higher molecular size and the presence of extra active sites such as O atom and phenyl ring. Compound (b) comes after compound (a) in inhibition efficiency, due to its lower molecular size than compound (a) and the absence of some active centers (O atom and phenyl ring). Compound (c) is the least efficient one, due to its lower molecular size than compounds (a) and (b) and the absence of some active centers such as NH, S, O and phenyl ring.

Conclusions

The main conclusions are as follows:

1. Acrylonitrile derivatives show good inhibitive action against the corrosion of Cu10Ni alloy in 0.5 M HCl solutions.
2. The value of inhibition efficiency increases with increasing inhibitor concentration and decreases with increasing temperature.
3. The adsorption of acrylonitriles derivatives on Cu10Ni alloy obeys Langmuir adsorption isotherm.
4. Polarization data indicate that the examined acrylonitriles derivatives act as mixed type inhibitors.
5. There is a good agreement between the data obtained from the different techniques.

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