Arabian Journal of Chemistry (2012) **5**, 297–307

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Corrosion inhibition of aluminum in 1 M H_3PO_4 solutions by ethanolamines

A.S. Fouda [a,*], **M. Abdallah** [b], **I.S. Ahmed** [b], **M. Eissa** [a]

[a] *Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura 35516, Egypt*
[b] *Department of Chemistry, Faculty of Science, Benha University, Benha, Egypt*

Received 26 January 2010; accepted 28 August 2010
Available online 7 September 2010

KEYWORDS

Corrosion;
Aluminum;
Quantum chemical calculation;
H_3PO_4;
Ethanolamines

Abstract The inhibitive effect of the investigated compounds (ethanolamine (I), diethanolamine (II) and triethanolamine (III)) on the corrosion behavior of aluminum in 1 M H_3PO_4 solution using weight loss, galvanostatic polarization and quantum chemical calculation methods was studied. The inhibition efficiency was found to depend on type and concentration of the additives and also on temperature. The effect of addition of halide ions to various concentrations of these compounds has also been studied. The apparent activation energy (E_a) and other thermodynamic parameters for the corrosion process have also been calculated and discussed. The galvanostatic polarization data indicated that these inhibitors were of mixed-type. The slopes of the cathodic and anodic Tafel lines (β_c and β_a) are approximately constant and independent of the inhibitor concentration. The adsorption of these compounds on aluminum surface has been found to obey the Freundlich adsorption isotherm. Some quantum chemical parameters and Mulliken charge densities for investigated compounds were calculated by the AM1 semi-empirical method to provide further insight into the mechanism of inhibition of the corrosion process. The theoretical results are then compared with experimental data.

1. Introduction

Aluminum has a remarkable economic and industrial importance owing to its low cost, light weight ($d = 2.71\ g/cm^3$), and high thermal and electrical conductivity. Most of well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen (Fox and Bradley, 1980; El Sayed, 1992; Schmitt, 1984; Sykes, 1990; Chatterjee et al., 1991; Rengamani et al., 1994; Gomma and Wahdan, 1994; Ajmal et al., 1994). Aluminum is used in hydrogen peroxide (H.T.P) processing and storage equipment partly because of its high corrosion resistance but also because it does not cause degradation of the peroxide. Aluminum has good resistance to petroleum products, and an Al–2Mg alloy is used for

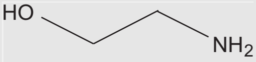
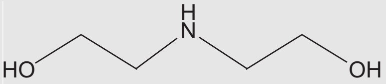
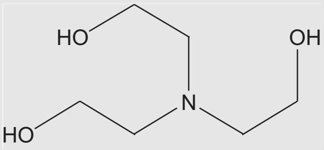
---

[*] Corresponding author. Tel.: +2 0502365730.
E-mail addresses: asfouda@mans.edu.eg, asfouda@hotmail.com (A.S. Fouda).

Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.08.020

Production and hosting by Elsevier

Table 1 Chemical and molecular structures of ethanolamines.

Inhibitor	Name	Structure	Mol. Wt.
(I)	Ethanolamine		61.083
(II)	Diethanolamine		105.136
(III)	Triethanolamine		149.189

tank-heating coils in crude-oil carriers. Aluminum is also used in the petroleum industry for sheathing for towers, heat exchangers, transport and storage tanks, and scrubbers. Most of well-known acid inhibitors are organic compounds containing N, S and O atoms (Aytac et al., 2005; Salghi et al., 2004; Muller, 2004; Foad El-Sherbini et al., 2003; Metroke et al., 2004; McCafferty, 2003; Bereket and Pinarba, 2004; Oguzie, 2007; Yurt et al., 2006; Cook and Taylor, 2000; Garrigues et al., 1996; Fouda et al., 1986; Metikos-Hukovic et al., 1998, 1995, 1994a,b; Abdel-Aal et al., 1990). The majority are nitrogen-containing compounds. Many N-heterocyclic compounds with polar groups and or π-electrons are efficient corrosion inhibitors in acidic solutions. Organic molecules of this type can adsorb on the metal surface and form a bond between the N electron pair and/or the π-electron cloud and the metal, thereby reducing the corrosion in acidic solution.

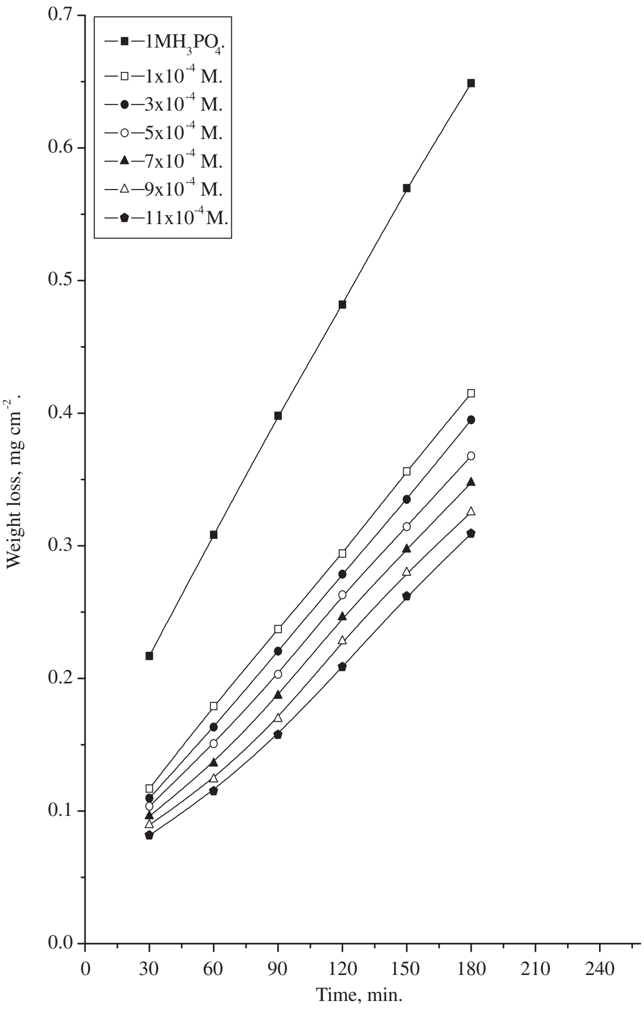


Figure 1 Weight loss–time curves for the corrosion of aluminum in 1 M H3PO$_4$ in the absence and presence of different concentrations of compound (III) at 30 °C.

Quantum-chemical calculations have been widely used to study reaction mechanism. They have also proved to be a very important tool for studying corrosion inhibition mechanism (Obot and Obi-Egbedi, 2008a,b; Obot et al., 2009).

The present study aimed to investigate the efficiency of ethanolamines as corrosion inhibitors for aluminum in 1 M H_3PO_4 solutions at different temperatures and in presence of halide ions by different techniques.

2. Experimental techniques

2.1. Materials

Chemical composition of aluminum is (wt.%): Si 0.4830, Fe 0.1799, Cu 0.0008, Mn 0.0083%, Mg 0.4051, Zn 0.0165, Ti 0.0145, Cr 0.0040, Ni 0.0047, Al the remainder.

Table 2 Values of % inhibition efficiencies of inhibitors for the corrosion of aluminum in 1 M H_3PO_4 from weight loss measurements at different concentrations at 30 °C.

Concentration (M)	% Inhibition efficiency (% IE)		
	(I)	(II)	(III)
1×10^{-4}	13.0	28.6	40.1
3×10^{-4}	17.6	31.5	43.2
5×10^{-4}	22.3	31.8	44.6
7×10^{-4}	27.1	36.5	48.8
9×10^{-4}	32.3	41.6	52.8
11×10^{-4}	37.2	45.6	56.8

Table 3 % Inhibition efficiency (% IE) at different concentrations of the investigated compounds with addition of 1×10^{-2}M KI, KBr and KCl for the corrosion of aluminum after 120 min immersion in 1 M H_3PO_4 at 30 °C.

Halide	Concentration *M*	% Inhibition efficiency (% IE)		
		(I)	(II)	(III)
KI	1×10^{-4}	32.1	42.9	48.5
	3×10^{-4}	35.6	45.9	52.0
	5×10^{-4}	40.6	50.0	56.1
	7×10^{-4}	44.2	53.6	60.6
	9×10^{-4}	48.4	58.8	64.3
	11×10^{-4}	52.5	60.5	68.0
KBr	1×10^{-4}	29.3	37.7	43.8
	3×10^{-4}	32.3	41.2	46.9
	5×10^{-4}	36.4	45.3	50.9
	7×10^{-4}	39.1	48.4	54.8
	9×10^{-4}	44.1	52.1	58.5
	11×10^{-4}	48.3	55.8	63.2
KCl	1×10^{-4}	23.7	31.1	41.2
	3×10^{-4}	27.6	35.1	45.7
	5×10^{-4}	32.0	39.7	50.2
	7×10^{-4}	36.7	43.7	54.5
	9×10^{-4}	40.4	47.4	58.2
	11×10^{-4}	43.6	51.1	61.4

2.2. Inhibitors

Ethanolamine, diethanolamine and triethanolamine were obtained from Aldrich and were used as received. The main functional group is hydroxyl and nitrogen atoms. Table 1 shows the molecular structure of these ethanolamines.

2.3. Solutions

Phosphoric acid (85%, specific gravity = 1.69) solution was prepared by diluting the appropriate volume of the concentrated chemically pure acid, with doubly distilled water and its concentration was checked by standard solution of NaOH. About 100 ml stock solutions (10^{-3} M) of compounds (1–3) were prepared, then the required concentrations of these inhibitors (1×10^{-4} to 11×10^{-4} M) were prepared by dilution with doubly distilled water. About 100 ml stock solutions (1 M) of halide salts (BDH grade) were prepared by dissolving an accurate quantity of each material in the appropriate volume of doubly distilled water, from these stock solutions exactly 1×10^{-2} M was prepared by dilution with doubly distilled water. Alkaline degreasing mixture was prepared as before (El Hosary et al., 1972). The solution of the degreasing mixture was heated to 80–85 °C before being used for degreasing the aluminum pieces for 30 s.

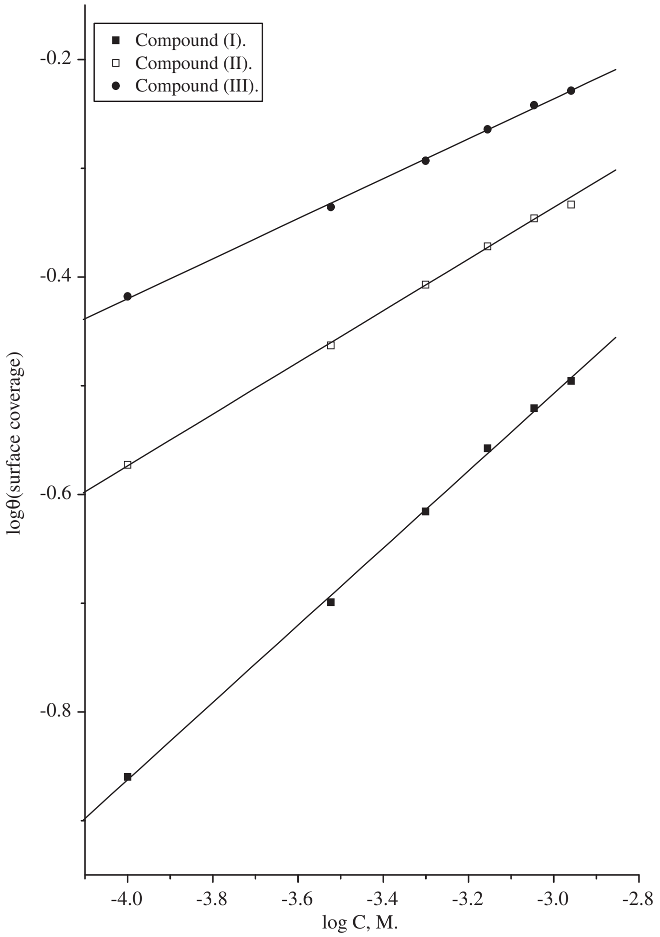


Figure 2 Curve fitting of corrosion data for aluminum in 1 M H_3PO_4 in the presence of different concentrations of the investigated compounds to Freundlich adsorption isotherm at 30 °C.

Two different techniques have been employed for studying the inhibition of corrosion of aluminum by these compounds, these are: chemical technique (weight loss method) and electrochemical technique (galvanostatic polarization method).

2.4. Chemical technique (weight loss method)

The reaction basin used in this method was a graduated glass vessel of 6 cm inner diameter having a total volume of 250 ml. About 100 ml of the test solution was employed in each experiment. The test pieces were cut into 2 × 2 cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in alkaline degreasing mixture, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended by suitable glass hooks at the edge of the basin, and under the surface of the test solution by about 1 cm. After specified periods of time, the test pieces were taken out of the test solution, rinsed in doubly distilled water, dried as before

Table 4 Equilibrium constant and adsorption free energy of the investigated compounds adsorbed on aluminum surface.

Inhibitors	$-\Delta G^\circ_{\mathrm{ads}}$ (kJ mol^{-1})	$K \times 10^{-2}$ (M^{-1})
(I)	6.8	27.7
(II)	7.9	43.1
(III)	8.2	48.4

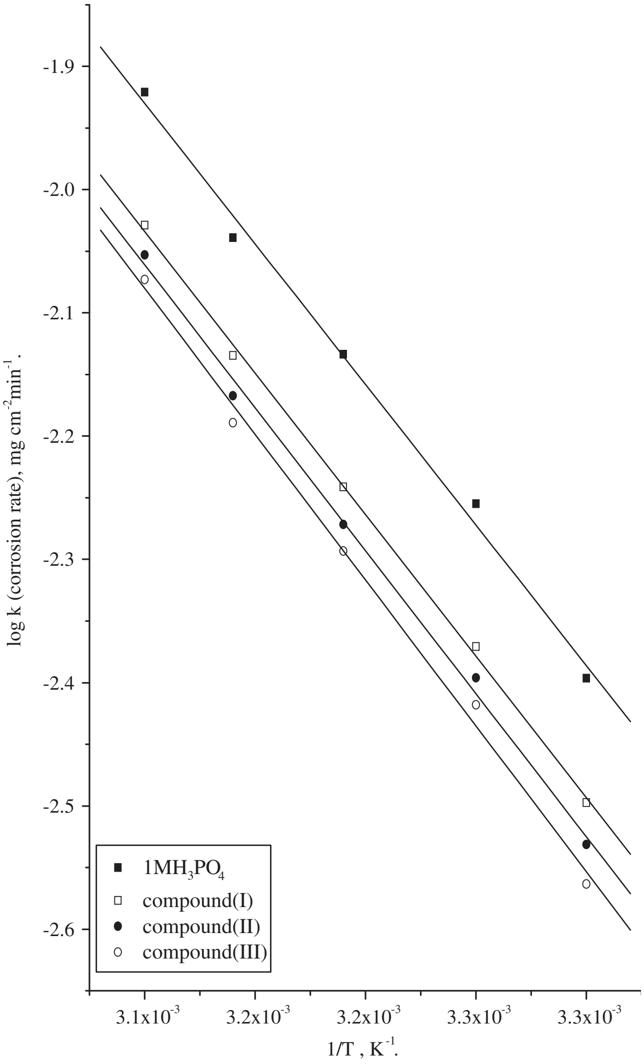


Figure 3 Log corrosion rate–$1/T$ curves for the corrosion of aluminum in 1 M H_3PO_4 at 5×10^{-4} M after 120 min for the investigated compounds.

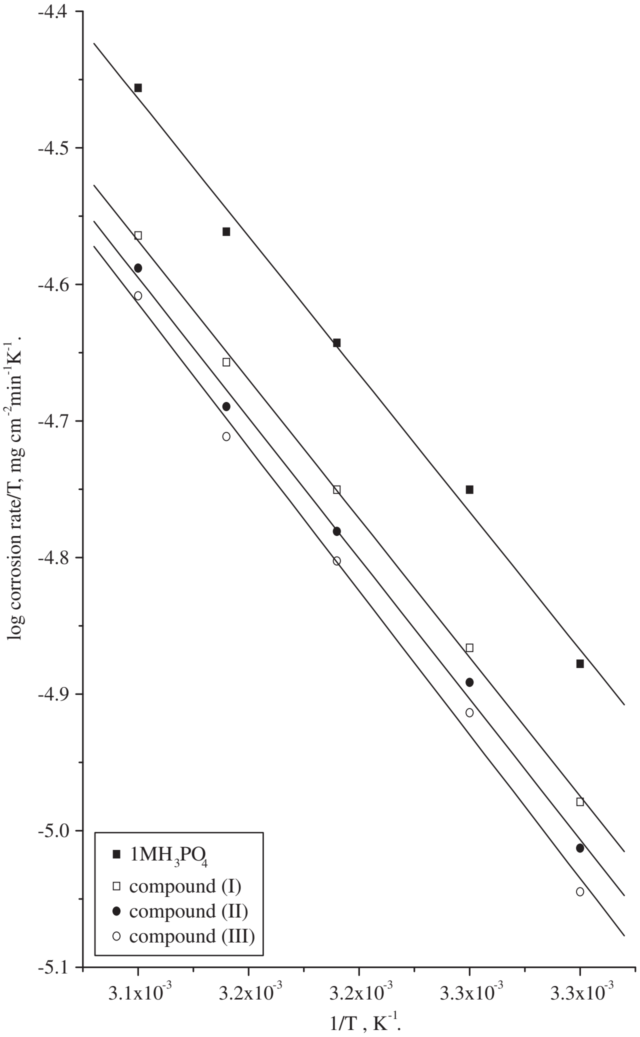


Figure 4 Log (corrosion rate/T)–($1/T$) curves for the corrosion of aluminum in 1 M H_3PO_4 at 5×10^{-4} M after 120 min for the investigated compounds.

Table 5 Activation parameters of the corrosion of aluminum in 1 M H_3PO_4 at 5×10^{-4} M after 120 min immersion for the investigated compounds.

Inhibitors	Activation parameters		
	E_a^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J mol^{-1} K^{-1})
Free acid	43.7	38.6	63.2
(I)	44.0	38.9	163.0
(II)	44.4	39.4	162.1
(III)	45.3	40.2	161.0

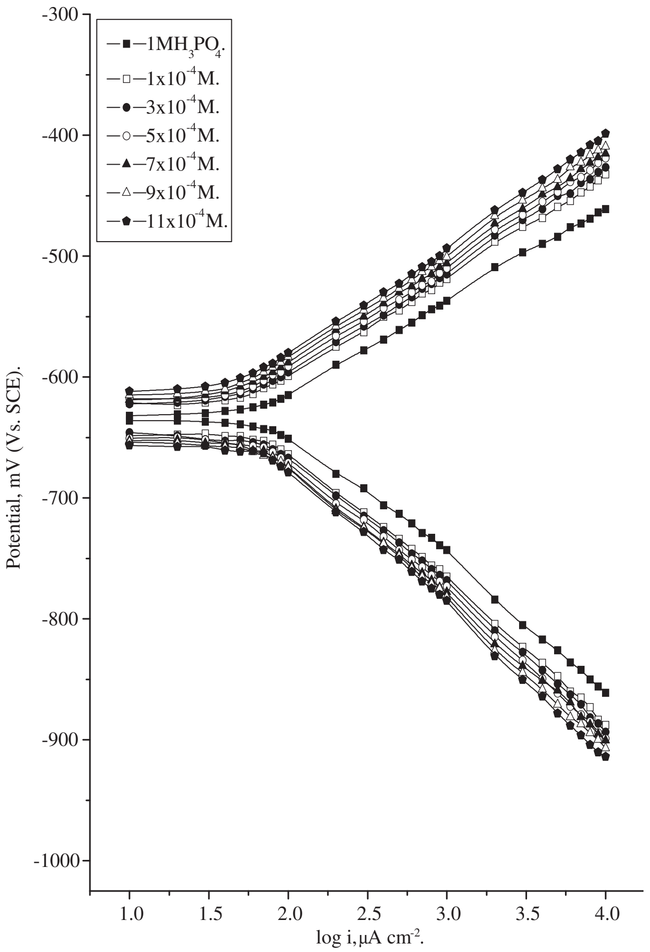


Figure 5 Galvanostatic polarization curves for the corrosion of aluminum in 1 M H_3PO_4 in the absence and presence of different concentrations of compound (III) at 30 °C.

and weighed again. The average weight loss at a certain time for each set of the test pieces was recorded to the nearest 0.0001 g.

2.5. Electrochemical technique (galvanostatic polarization method)

Three different types of electrodes were used during polarization measurements: the working electrode was aluminum electrode, which was cut from aluminum sheets. The electrodes were of dimensions 1 cm × 1 cm and were welded from one side to a copper wire used for electric connection. The samples were embedded in glass tube using epoxy resin. Saturated calomel electrode (SCE) and a platinum foil as reference and auxiliary electrodes, respectively, were used.

A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 30 min was given for the system to attain a steady state. Both cathodic and anodic polarization curves were recorded galvanostatically using Amel Galvanostat (Model-549) and digital Multimeters (Fluke-73) were used for accurate measurements of potential and current density. All the experiments were carried out at 30 ± 1 °C by using ultra circulating thermostat.

Table 7 Quantum chemical parameters obtained by MNDO SCF-MO method for investigated compounds.

Inhibitor	I	II	III
E_{Homo}(eV)	−10.156	−9.796	−9.568
E_{Lumo}(eV)	2.808	2.261	1.974
ΔE (eV)	12.964	12.057	11.542
I_p (eV)	10.156	9.796	9.568
Molecular weight	61.083	105.136	149.189

Table 6 Electrochemical parameters for aluminum in 1 M H_3PO_4 in the absence and presence of different concentrations of inhibitors at 30 °C.

Inhibitors	Concentration (M)	$-E_{\text{corr}}$ (mV)	I_{corr} (μA cm^{-2})	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	θ	% IE
(I)	0	630	66.4	89	78	–	–
	1×10^{-4}	630	55.6	90	79	0.162	16.2
	3×10^{-4}	629	53.9	91	80	0.189	18.9
	5×10^{-4}	628	50.9	93	80	0.234	23.4
	7×10^{-4}	628	46.8	102	81	0.298	29.8
	9×10^{-4}	627	43.4	103	82	0.346	34.6
	11×10^{-4}	626	40.8	104	83	0.385	38.5
(II)	1×10^{-4}	629	46.4	100	82	0.301	30.1
	3×10^{-4}	628	44.7	102	83	0.327	32.7
	5×10^{-4}	627	44.5	104	85	0.330	33.0
	7×10^{-4}	626	41.5	107	85	0.375	37.5
	9×10^{-4}	624	38.6	110	86	0.419	41.9
	11×10^{-4}	623	36.1	112	87	0.457	45.7
(III)	1×10^{-4}	625	38.8	103	81	0.415	41.5
	3×10^{-4}	624	37.1	107	82	0.442	44.2
	5×10^{-4}	623	35.5	108	84	0.466	46.6
	7×10^{-4}	623	33.8	112	87	0.491	49.1
	9×10^{-4}	622	31.3	113	88	0.528	52.8
	11×10^{-4}	620	28.22	114	91	0.575	57.5

2.6. Methods of calculations

Quantum calculations were carried out using the AM1 (Austin model 1) semi-empirical SCF-MO methods in the MOPAC 2000 program of CS ChemOffice packet program version 8 for Windows (CS ChemOffice Pro). Calculations were performed on an IBM compatible Intel Pentium IV 2.8 GHz computer.

3. Results and discussion

3.1. Weight loss measurements

Weight loss of aluminum was determined, at various time intervals, in the absence and presence of different concentrations of the investigated compounds. The obtained weight loss time curves are represented in (Fig. 1) for inhibitor (III) that is the most effective one. Similar curves were obtained for other inhibitors (not shown). The degree of dissolution, of course, is dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion is given with respect to area and time. Corrosion rates can be evaluated by measuring either the concentration of the dissolved metal in solution by chemical analysis or by measuring weight of a specimen before (W_A) and after (W_B) exposure and applying Eq. (1).

$$\Delta W = (W_B - W_A) \quad (1)$$

The percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) of the investigated compounds were computed by the following Eqs. (2) and (3), respectively:

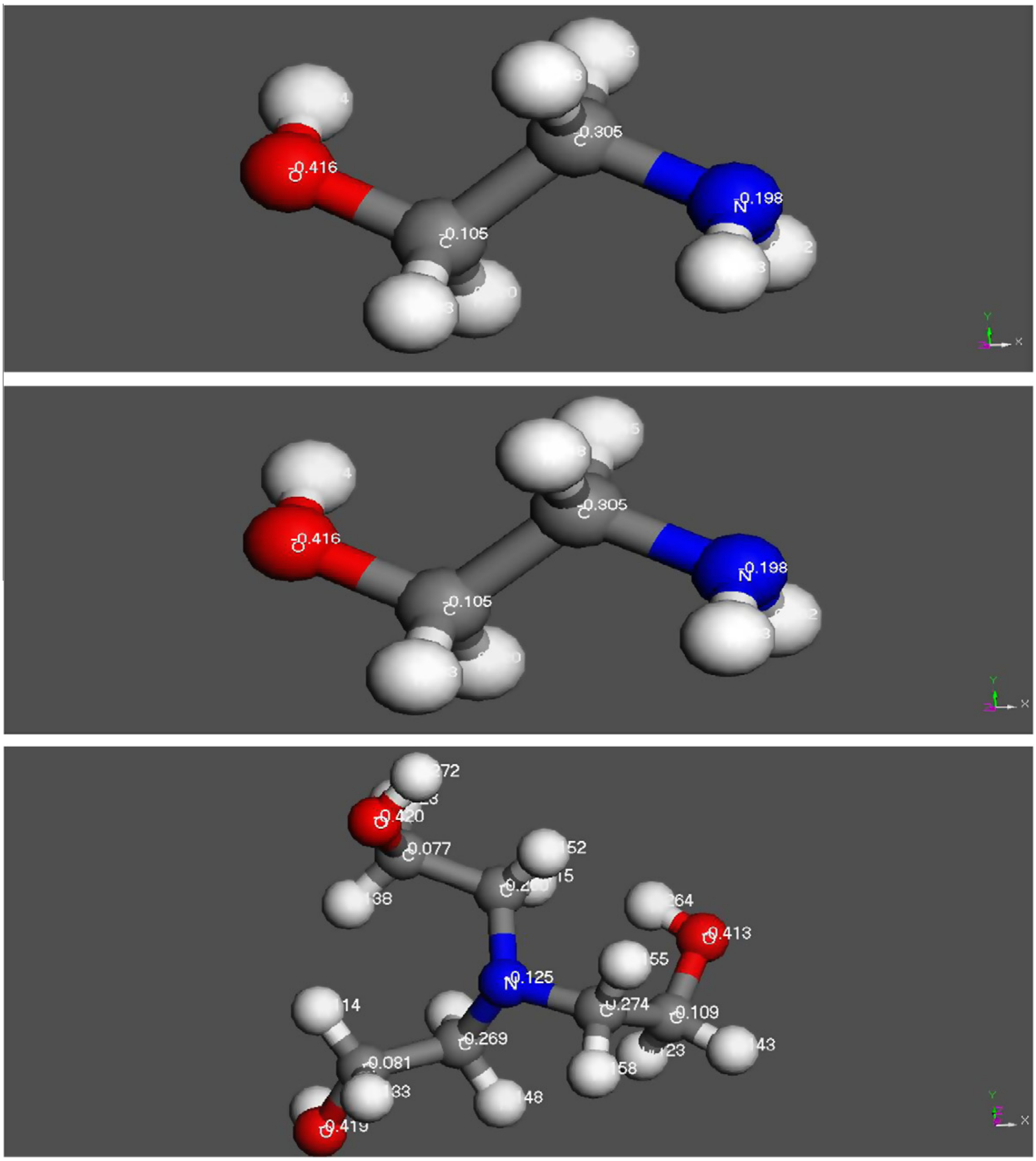


Figure 6 The three-dimensional structure of the three compounds (I–III).

$$\%IE = [1 - (\Delta W_{\text{inh}}/\Delta W_{\text{free}})] \times 100 \qquad (2)$$

$$\theta = [1 - (\Delta W_{\text{inh}}/\Delta W_{\text{free}})] \qquad (3)$$

where ΔW_{inh} and ΔW_{free} are the weight losses of metal per unit area in the presence and absence of the inhibitors, respectively, at the given time period and temperature.

In order to get a comparative view, the variation of the inhibition efficiency (% IE) of the investigated compounds with their molar concentrations was calculated according to Eq. (2). The values obtained are summarized in Table 2.

Careful inspection of these results showed that, at the same inhibitor concentration, the order of decreasing inhibition efficiency of the investigated compounds is as follows: III > II > I.

3.2. Synergistic effect

The corrosion of aluminum in 1 M phosphoric acid in the absence and presence of different concentrations of the investigated compounds with the addition of a specific concentration (10^{-2} M) of KI, KBr and KCl, was studied. Addition of halides further increased the inhibition efficiency value (Table 3). This may be attributed to the stabilization of adsorbed halide ions by means of electrostatic interaction with the inhibitor which leads to greater surface coverage and hence greater inhibition (Maitra et al., 1983; Gomma, 1998). This synergistic effect was observed to increase in the order: $Cl^- < Br^- < I^-$. Similar observations have been reported before (Ebenso, 2002; Oza and Sinha, 1982). This trend was explained on the basis of

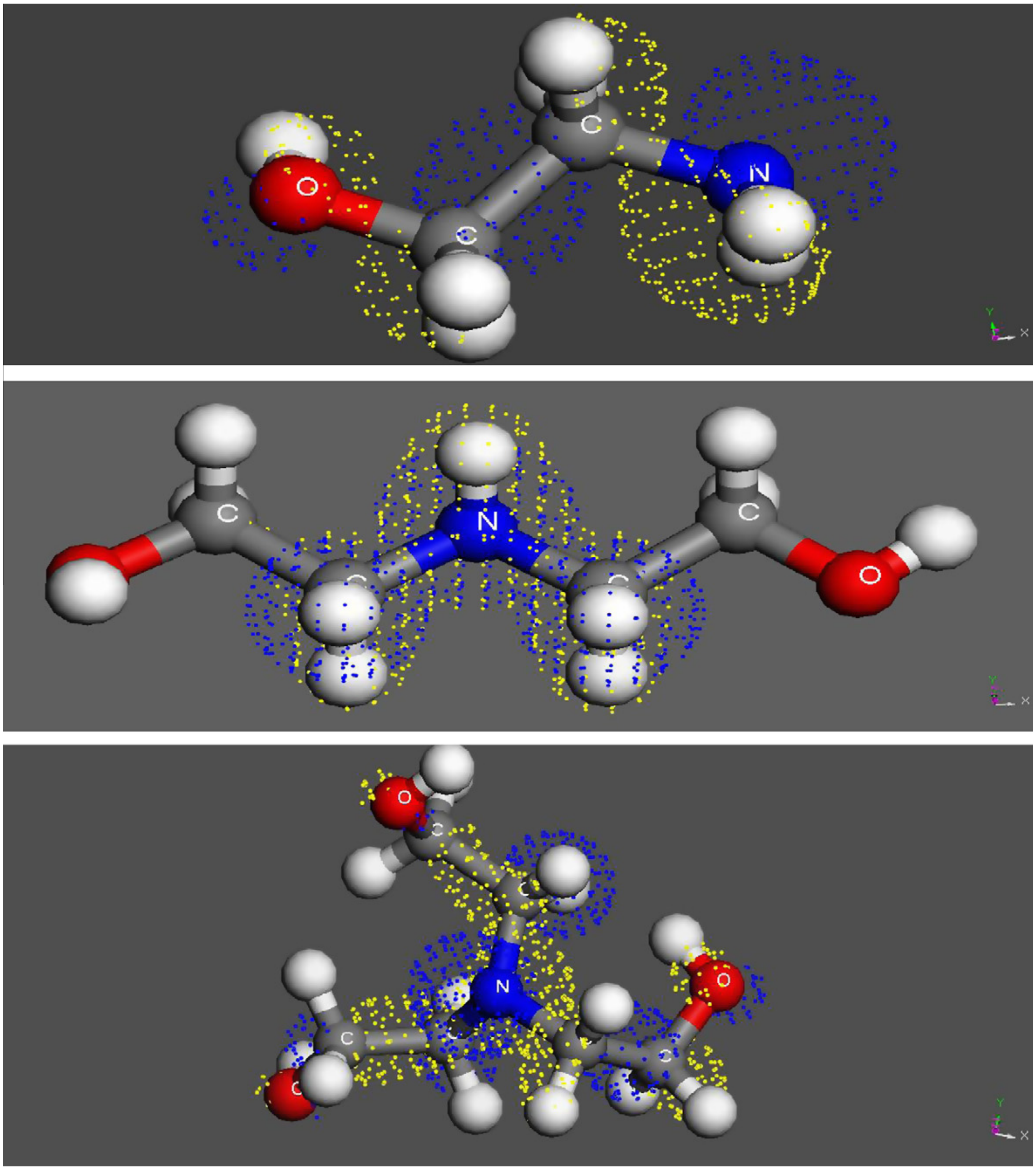


Figure 7 The frontier molecular orbital density distribution of the three compounds (I–III)-HOMO.

radii and electronegativity of the halide ions. Electronegativity decreases as follows: Cl^- (3.0) > Br^- (2.8) > I^- (2.5). Also their ionic radii decrease in the order: I^- (0.135 nm) > Br^- (0.114 nm) > Cl^- (0.09 nm). This suggests that the iodide ion radius is more predisposed to adsorption than bromide and chloride ions.

The order of decreasing inhibition efficiency of the investigated compounds on the addition of a specific concentration of the halide ions is as follows: III > II > I.

The synergistic inhibition effect was evaluated using a parameter, S_θ, obtained from the surface coverage values (θ) of the anion, cation and both. Aramaki and Hackerman (1969) calculated the synergism parameter, S_θ, using the following equation:

$$S\theta = 1 - \theta_{1+2}/1 - \theta'_{1+2} \quad (4)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, θ_1 = surface coverage by anion, θ_2 = surface coverage by cation and θ'_{1+2} = measured surface coverage by both the anion and the cation.

The values of S_θ are nearly equal to unity, which suggest that the enhanced inhibition efficiency caused by the addition of halide ions individually to the investigated compounds is due to the synergistic effect.

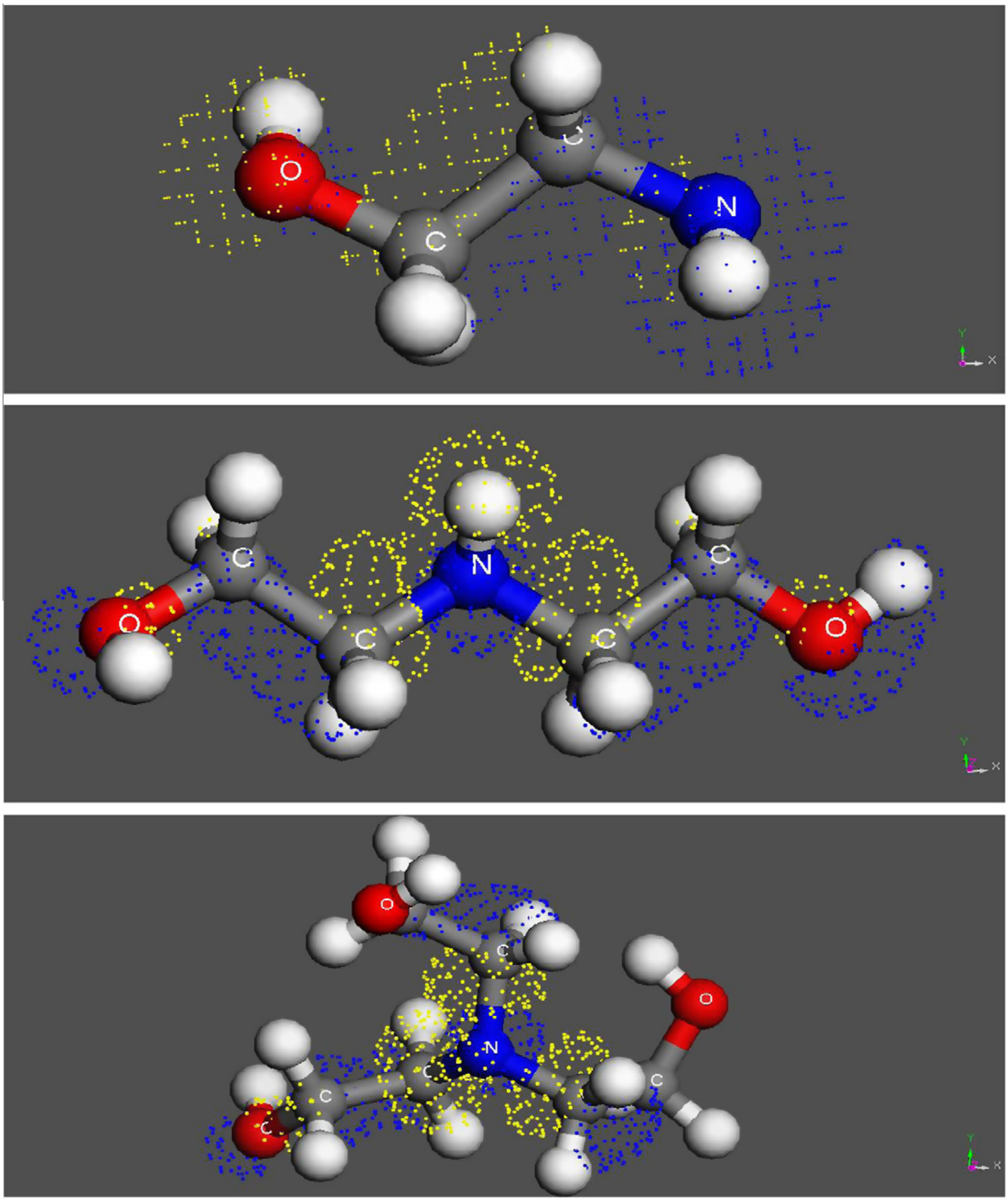


Figure 8 The frontier molecular orbital density distribution of the three compounds (I–III)-LUMO.

3.3. Adsorption isotherm

Adsorption isotherm equations are generally of the form (Khamis et al., 2000):

$$f(\theta, x)\exp(-a, \theta) = K\,C \tag{5}$$

where: $f(\theta, x)$ is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm. a is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface. From this equation $\log\theta = \log K + n\log C\ (0 < n < 1)$ Plots of $\log\theta$ vs. $\log C$ (Freundlich adsorption plots) for adsorption of the investigated compounds on the surface of aluminum in 1 M H_3PO_4 at 30 °C is shown in (Fig. 2). The data gave straight lines of intercept $\log K$ and slope (n) indicating that Freundlich adsorption isotherm is valid for these compounds.

All adsorption expressions include the equilibrium constant of the adsorption process, K, which is related to the standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) by the following equation (Kliskic et al., 1997; Abdallah, 2000):

$$K = (1/55.5)\exp(-\Delta G^{\circ}_{\text{ads}}/RT) \tag{6}$$

where R is the universal gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in mol l^{-1}.

The values of $\Delta G^{\circ}_{\text{ads}}$ and K were calculated and are listed in Table 4, It is clear that the value of $\Delta G^{\circ}_{\text{ads}}$ increases with the increasing solvation energy of adsorbed species which in turn increases with increasing the size of the molecule (Blomgren et al., 1961). The negative values of $\Delta G^{\circ}_{\text{ads}}$ obtained herein, indicate that the adsorption process of these compounds on the metal surface is a spontaneous one.

3.4. Effect of temperature and activation parameters of inhibition process

The effect of temperature on the corrosion rate of aluminum in 1 M H_3PO_4 over the temperature range of (30–50 °C) in the absence and presence of different concentrations of the investigated compounds has been studied. The % inhibition efficiency is found to decrease with increasing temperature; this indicated that, these compounds are physically adsorbed on the aluminum surfaces.

Plots of logarithm of corrosion rate ($\log k$), with reciprocal of absolute temperature ($1/T$) for aluminum in 1 M H_3PO_4 at 5×10^{-4} M after 120 min for the investigated compounds are shown in (Fig. 3). As shown from this figure, straight lines with slope of $-E^{*}_{a}/2.303R$ and intercept of A were obtained according to Arrhenuis-type equation:

$$k = A\exp(-E^{*}_{a}/RT) \tag{7}$$

where: k is the corrosion rate, A is a constant that depends on a metal type and electrolyte, E^{*}_{a} is the apparent activation energy.

Plots of log (corrosion rate/T) vs. $1/T$ for aluminum in 1 M H_3PO_4 at 5×10^{-4} M after 120 min for the investigated compounds are shown in (Fig. 4). As shown from this figure, straight lines with slope of ($-\Delta H^{*}/2.303R$) and intercept of ($\log R/Nh + \Delta S^{*}/2.303R$) were obtained according to transition state equation:

$$\text{Rate} = RT/Nh\ \exp(\Delta S^{*}/R)\exp(-\Delta H^{*}/RT) \tag{8}$$

where: h is Planck's constant, N is Avogadro's number, ΔH^{*} is the activation enthalpy and ΔS^{*} is the activation entropy.

The calculated values of the apparent activation energy, E^{*}_{a}, activation enthalpies, ΔH^{*} and activation entropies, ΔS^{*} are given in Table 5. The entropy of activation (ΔS^{*}) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step (Gomma and Wahdan, 1995; Marsh, 1988; Soliman, 1995). The value of the activation energy for the corrosion of aluminum in 1 M H_3PO_4 solution in the absence of additives is equal to 43.7 kJ mol^{-1}, which is in the same order of the magnitude as those observed by Yadav et al. (1999). Inspection of Table 5 shows that higher values were obtained for E^{*}_{a} and ΔH^{*} in the presence of inhibitors indicating the higher protection efficiency observed for these inhibitors (Yurt et al., 2005). There is also a parallelism between increases in inhibition efficiency and increases in E^{*}_{a} and ΔH^{*} values.

The order of decreasing inhibition efficiency of the investigated compounds as gathered from the increase in E^{*}_{a} and $\Delta H^{*}_{\text{ads}}$ values and decrease in $\Delta S^{*}_{\text{ads}}$ values, is as follows: III > II > I.

3.5. Galvanostatic polarization measurements

Fig. 5 shows the galvanostatic polarization curves for aluminum dissolution in 1 M H_3PO_4 in the absence and presence of different concentrations of inhibitors (3) at 30 °C. Similar curves were obtained for other inhibitors (not shown).

The numerical values of the variation of corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), degree of surface coverage (θ) and inhibition efficiency (% IE) with the concentrations of the investigated compounds are given in Table 6.

According to Fig. 5 and associated parameters, it is shown that the addition of the inhibitors reduce efficiently both cathodic and anodic current density indicating that the investigated compounds act as mixed-type inhibitors towards aluminum (E_{corr} shifted slightly <40 mV) (Ashassi-Sorkhabi et al., 2004). The corrosion current density was found to decrease in the presence of the inhibitors accompanied by an increase of the inhibition efficiency values following the same order obtained before, i.e. III > II > I. The constant values of Tafel slopes (β_a and β_c), in the presence and absence of inhibitors indicate that there is no change in the mechanism of the process.

3.6. Prediction of theoretical parameters

The inhibition efficiency of inhibitors can be related to their molecular electronic structure (Mihit et al., 2010). The quantum chemical parameters of investigated compounds were calculated and listed in Table 7. Fig. 6 shows the three-dimensional structure of the three compounds, Fig. 7 shows the frontier molecular orbital density distribution of the three compounds-HOMO and Fig. 8 shows the frontier molecular orbital density distribution of the three compounds-LUMO. It is known that the more negative the atomic charges of the atom, the more easily the atom donates its electrons to the unoccupied orbital of metal (Fang and Li, 2005). AS shown from Fig. 6 the Mulliken charges on oxygen atoms are greater than Mulliken charges on nitrogen atom, but still nitrogen atom has negative charge. Thus these compounds can be adsorbed on the metal surface through donating their lone pair of electrons to the vacant p orbital of metal atom. Excellent inhibitors are usually those organic compounds that donate electrons to unoccupied orbital of the metal surface and also accept free electrons from the metal (Mohamed et al., 1990). It is well established in the literature that the higher the HOMO energy of the inhibitor, the greater the tendency of offering electrons to unoccupied d orbital of the metal, and the higher corrosion inhibition. In addition, the lower the values of the E_{LUMO}, the easier the acceptance of electrons from the metal surface. Compound (I) has the E_{HOMO} equal to -10.156 eV and E_{LUMO} equal to 2.808 eV. Accordingly, inhibitor (I) has the highest separation energy, ΔE, 12.964 eV, among the investigated compounds, which means the lowest reactivity of the inhibitor towards the metal surface and hence the lowest inhibition efficiency. Also, the calculations show that it has the higher ionization potential (I_p) which probably decreases its adsorption on the metal surface. On the other hand compound (III) has the lowest separation energy, ΔE. This leads to an increase in its reactivity towards the metal surface and accordingly increases its inhibition efficiency. This confirms that this inhibitor has the highest inhibition efficiency. So, according to the above the order of inhibition is as follows: III > II > I.

3.7. *Chemical structure of the inhibitors and its effect on the corrosion inhibition*

Inhibition efficiency of the additive compounds depends on many factors (Fouda et al., 2008), which include the number of adsorption active centers in the molecule and their charge density, molecular size, and mode of interaction with metal surface. It is generally believed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibitor action in aggressive acid media. The order of decreasing inhibition efficiency of these tested compounds is: III > II > I. Due to two reasons:

1. Presence of three electron-donating groups of compound (III) makes negative charge on nitrogen atom and liberations of three (OH) groups make this more basic & inhibition increased. So adsorption of this compound (III) on Al surface is favored than compound (II) which contain two electron-donating groups and compound (I) which contain one electron-donating groups and less basicity.
2. The values of pk_b for compounds (1–3) are 4.5, 5.1 and 6.2, respectively. From these values it is clear that the basicity increases and hence inhibition efficiency of these compounds decreases in the order: III < II < I.

The order of inhibition efficiency of the additives revealed by the weight loss method is further supported by both galvanostatic polarization measurement and quantum chemical calculations. The observed agreement among these independent techniques proves the validity of the results obtained and supports the explanation given for the effect of chemical structure on the inhibition action of the investigated compounds.

4. Conclusions

1. The investigated compounds are efficient inhibitors for aluminum dissolution in 1 M H_3PO_4.
2. The adsorption of these compounds on the aluminum surface was found to obey Freundlich adsorption isotherm.
3. From the effect of temperature, the activation parameters for the corrosion process (E_a^*, ΔH^* and ΔS^*) were calculated.
4. % IE increased in the presence of 1×10^{-2} M KI, KBr and KCl due to the synergistic effect.
5. Galvanostatic polarization data indicated that these compounds influence both cathodic and anodic processes, i.e., mixed-type inhibitors.
6. The order of the inhibition efficiency of the inhibitors as given by polarization measurements is in good agreement with that obtained from weight loss and quantum chemical calculations. This order was explained on the basis of the quantum chemical parameters, chemical structure and adsorption active centers of investigated compounds.

References

Abdallah, M., 2000. Bull. Electrochem. 16 (6), 258.

Abdel-Aal, M.S., Makhlouf, M.Th., Hermas, A.A., 1990. European Symposium on "Corrosion Inhibition" Ann. Univ. Ferrara, N.S.Sez., Suppl. 9, pp. 1143.

Ajmal, M., Mideen, A.S., Qurainhi, M.A., 1994. Corros. Sci. 36, 97.

Aramaki, K., Hackerman, N., 1969. J. Electrochem. Soc. 116, 568.

Ashassi-Sorkhabi, H., Majidi, M.R., Seyyedi, K., 2004. Appl. Surf. Sci. 225, 176.

Aytac, A., Ozmen, U., Kabasakaloglu, M., 2005. Mater. Chem. Phys. 89, 176.

Bereket, G., Pinarba, S.I., 2004. Corros. Eng. Sci. Techol. 39 (4), 308.

Blomgren, E., Bockris, J.O.M., Jesch, C., 1961. J. Phys. Chem. 65, 200.

Chatterjee, P., Banerjee, M.K., Mukherjee, P., 1991. Ind. J. Technol. 29 (5), 191.

Cook Jr., R.L., Taylor, S.R., 2000. Corrosion 56, 321.

CS ChemOffice Pro. Cambridge Scientific Computing Inc., Cambridge, MA, USA.

Ebenso, E.E., 2002. Mater. Chem. Phys. 96, 1.

El Hosary, A.A., Salah, M.R., Shams El Din, A.M., 1972. Corros. Sci. 12, 897.

El Sayed, A., 1992. J. Appl. Electrochem. 27, 193.

Fang, Y., Li, J., 2005. Appl. Surf. Sci. 252, 1596.

Foad El-Sherbini, E.E., Abd-El-Wahab, S.M., Deyab, M.A., 2003. Mater. Chem. Phys. 82, 631.

Fouda, A.S., Elewady, Y.A., Abo-El-Enien, O.M., Agizah, F.A., 2008. Anti-Corros. Method. M. 55 (6), 317.

Fouda, A.S., Moussa, M.N., Taha, F.I., El-Neanaa, A.I., 1986. Corros. Sci. 26, 719.

Fox, P.G., Bradley, P.A., 1980. Corros. Sci. 20, 643.

Garrigues, L., Pebere, N., Dabosi, F., 1996. Electrochim. Acta 41, 1209.

Gomma, G.K., 1998. Mater. Chem. Phys. 55, 241.

Gomma, G.K., Wahdan, M.H., 1994. Bull. Chem. Corros. Sci. 36, 79.

Gomma, G.K., Wahdan, M.H., 1995. Mater. Chem. Phys. 30, 209.

Khamis, E., Ameer, M.A., Al-Andis, N.M., Al-Senani, G., 2000. Corrosion 56 (2), 127.

Kliskic, M., Radosevic, J., Gndic, S., 1997. J. Appl. Electrochem. 27, 200.

Maitra, A., Singh, G., Chakraborty, B.B., 1983. Trans. SAEST 18, 335.

Marsh, J., 1988. Advanced Organic Chemistry, third ed. Wiley Eastern, New Delhi.

McCafferty, E., 2003. J. Electrochem. Soc. 150 (7), B342.

Metikos-Hukovic, M., Babic, R., Grubac, Z., Brinic, S., 1994a. J. Appl. Electrochem. 24, 325.

Metikos-Hukovic, M., Babic, R., Grubac, Z., Brinic, S., 1994b. J. Appl. Electrochem. 24, 772.

Metikos-Hukovic, M., Babic, R., Omanovic, S., Brinic, S., 1995. Br. Corros. J. 30, 288.

Metikos-Hukovic, M., Omanovic, S., Grubac, Z., Brinic, S., 1998. J. Appl. Electrochem. 28, 433.

Metroke, Tammy L., Gandhi, Jaspreet S., Apblett, Allen, 2004. Prog. Org. Coat. 50, 231.

Mihit, M., Laarej, K., Abou El Makarim, H., Bazzi, L., Salghi, R., Hammouti, B., 2010. Arab. J. Chem. 3 (1), 57.

Mohamed, A.K., Rakha, T.H., Moussa, M.N., 1990. Bull. Soc. Chem. Fr. 127, 375.

Muller, B., 2004. Corros. Sci. 46, 159.

Obot, I.B., Obi-Egbedi, N.O., 2008a. Colloids Surf. A Physicochem. Eng. Aspects 330, 207.

Obot, I.B., Obi-Egbedi, N.O., 2008b. Surf. Rev. Lett. 16 (6), 903.

Obot, I.B., Obi-Egbedi, N.O., Umoren, S.A., 2009. Corros. Sci. 51, 276.

Oguzie, E.E., 2007. Corros. Sci. 49 (3), 1527.

Oza, B.N., Sinha, R.S., 1982. Trans. SAEST 17, 282.

Rengamani, S., Muraliddharan, S., Kulamdainathan, M.A., Venteatakrishna, S., 1994. J. Appl. Electrochem. 24, 355.

Salghi, R., Bazzi, L., Hammouti, B., Bendou, A., Ait Addi, E., Kertit, S., 2004. Prog. Organ. Coat. 51, 113.

Schmitt, G., 1984. Br. Corros. J. 19, 165.

Soliman, M.S., 1995. Ph.D. Thesis, Alex. Univ., Egypt, 1995.

Sykes, M., 1990. Br. Corros. J 25, 175.

Yadav, P.N.S., Singh, A.K., Wadhwani, R., 1999. Corrosion 55 (10), 937.

Yurt, A., Bereket, G., Kivrak, A., Balaban, A., Erk, B., 2005. J. Appl. Electrochem. 35, 1025.

Yurt, A., Ulutas, S., Dal, H., 2006. Appl. Surf. Sci. 253 (2), 919.