

PHYSICOCHEMICAL PROBLEMS  
OF MATERIALS PROTECTION

# Influence of N-Thiazolyl-2-cyanoacetamide Derivatives on the Corrosion of Aluminum in 0.01 M Sodium Hydroxide<sup>1</sup>

M. Abdallah<sup>a, c</sup>, O. A. Hazazi<sup>a</sup>, A. F. Saad<sup>a, d</sup>, S. El-Shafei<sup>b</sup>, and A. S. Fouda<sup>b</sup>

<sup>a</sup>Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al Mukarramah, Saudi Arabia

<sup>b</sup>Chemistry Department, Faculty of Science, Mansoura University, Mansoura Egypt

<sup>c</sup>Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

<sup>d</sup>Chemistry Department, Faculty of Science, Assuit University, Assuit, Egypt

e-mail: metwally555@yahoo.com, oahazazi@hotmail.com

Received July 10, 2013

**Abstract**—The effect of N-thiazolyl-2-cyanoacetamide derivatives on the corrosion of aluminum in 0.01N sodium hydroxide has been studied using weight-loss and galvanostatic polarization techniques. The inhibition efficiency was found to increase with increasing the concentration of inhibitor and with decreasing temperature. The inhibition process was explained in terms of its adsorption on the aluminum surface. The adsorption is obeyed Frumkin isotherm. The addition of Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions to N-thiazolyl-2-cyanoacetamide derivatives enhanced the inhibition efficiency due to synergistic effect. Polarization data suggested that the additives used as mixed type inhibitors. Some activated thermodynamic parameters were calculated and explained.

DOI: 10.1134/S2070205114050025

## 1. INTRODUCTION

Aluminum and its alloys have proved to be strategically important materials due to their high technological value and wide range of industrial and house hold applications [1–3]. Their usefulness is derived from their very good physical and mechanical properties such as their high strength-to-weight ratio, recyclability, good machining properties, as well as their outstanding resistance to corrosion. The corrosion resistance of aluminum and its alloys is attributable to the formation of a stable protective thin film of aluminum oxide when first produced and exposed to the atmosphere. The protective oxide film is of amphoteric character and easily dissolved in strong acidic and alkaline media [4, 5] leading to a sequence electrochemical reaction.

Corrosion control of aluminum and its alloys can be enhanced by the addition of some inorganic substances to the corroding medium. The substances include phosphates, chromates, dichromates, silicates, bromates, arsenates, tungstates, molybdates, chlorides and their likes [6–9]. These inorganic inhibitors exhibit toxic effects and are therefore not environmentally friendly. As a result, several corrosion researchers have started using environmental friendly natural products as corrosion inhibitors [10–14]. Such naturally occurring substances of both plant and animal origin which are readily available, cheap, renewable, ecofriendly and ecologically acceptable, have

been successfully used as a replacement for the organic and inorganic inhibitors.

List of organic compounds and natural occurring substance were used to control the corrosion of aluminum in alkaline medium [16–28].

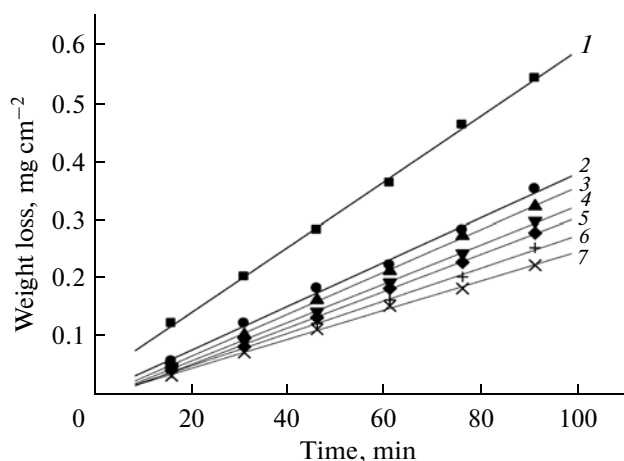
The aim of this work is to study the inhibitive action of N-thiazolyl-2-cyanoacetamide toward the corrosion behavior of aluminum in 0.01N sodium hydroxide using the weight-loss and galvanostatic polarization measurements. The effect of temperature on the corrosion of Al in free and inhibited alkaline solution was also investigated.

## 2. EXPERIMENTAL METHODS

The Aluminum metal used in this investigation has chemical composition 99.99% provided by “aluminum Company of Egypt, Nagh Ammady”. For weight loss measurements, the reaction basin used in this method was a graduated glass vessel having a total volume of 100 ml. 50 ml of the test solution was employed in each experiment. The test pieces were 2.0 × 2.0 × 0.2 cm<sup>3</sup>. The samples were first mechanically polished with a fine grade emery paper in order to obtain a smooth surface, followed by ultra-sonically degreasing with acetone and then rinsed with distilled water, 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.

The percentage inhibition efficiency (% IE) and a parameter (θ) which represents the part of the metal

<sup>1</sup> The article is published in the original.



**Fig. 1.** Weight-loss as a function of time for aluminum in 0.01 M NaOH solution in absence and presence of compound (c) at 30°C. 1) Blank 2)  $1 \times 10^{-6}$  M 3)  $3 \times 10^{-6}$  M 4)  $5 \times 10^{-6}$  M 5)  $7 \times 10^{-6}$  M 6)  $9 \times 10^{-6}$  M 7)  $11 \times 10^{-6}$  M.

surface covered by the inhibitor molecules were calculated using the following equations:

$$\%IE = \left[ \frac{1 - W_{\text{add}}}{W_{\text{free}}} \right] \times 100 \quad (1)$$

$$\theta = \left[ \frac{1 - W_{\text{add}}}{W_{\text{free}}} \right], \quad (2)$$

where,  $W_{\text{free}}$  and  $W_{\text{add}}$  are the weight loss of Al coupons in absence and presence of inhibitors, respectively.

For galvanostatic polarization measurements, a cylindrical rod embedded in araldite with exposed surface of 0.66 cm<sup>2</sup> was used. The electrode was polished with different grades emery paper, degreased with acetone and rinsed by distilled water. Galvanostatic polarization measurements were carried out using EG&G model 173 potentiostat/ galvanostat. Three compartment cell with a saturated calomel reference electrode and platinum foil auxiliary electrode was used. Solutions were not deaerated to make the conditions identical to weight loss measurements. All the experiments were carried out at  $30 \pm 1^\circ\text{C}$  by using ultra circulating thermostat.

The percentage inhibition efficiency (%IE) was calculated from corrosion current density values using the equation.

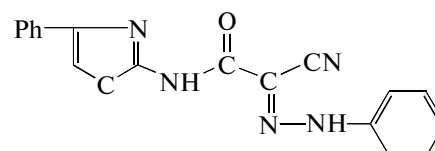
$$\%IE = \left[ 1 - \frac{I_{\text{add}}}{I_{\text{free}}} \right] \times 100, \quad (3)$$

where,  $I_{\text{free}}$  and  $I_{\text{add}}$  are the corrosion current densities in absence and presence of inhibitors.

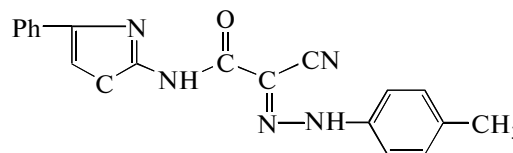
#### Organic Additives

The selected organic inhibitors used in this study were N-Thiazolyl-2-Cyanoacetamide derivatives.

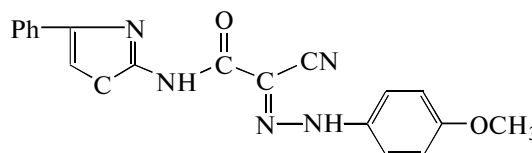
[a]-N-(4-phenylthiazol-2-yl)-2-phenylazo-2-cyanoacetamide.



[b]-N-(4-phenylthiazol-2-yl)-2-(p-tolylazo)-2-cyanoacetamide.



[c]-N-(4-phenylthiazol-2-yl)-2-(p-methoxyphenylazo)-2-cyanoacetamide.



### 3. RESULTS AND DISCUSSION

#### 3.1. Weight Loss Measurements

Figure 1 shows the weight loss-time curves of aluminum in 0.01M sodium hydroxide in absence and presence of different concentrations of the compound (a) as an example of the tested compounds. Similar curves were obtained for the other two compounds (not shown). Inspection of this figure, it is clear that by increasing the concentration of this compound, the weight loss of aluminum samples are decreased. This means that the presence of these compounds retards the corrosion of aluminum in 0.01M sodium hydroxide or in other words, these compounds act as an inhibitor.

The linear variation of weight loss with time in uninhibited and inhibited 0.01M NaOH indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed onto the metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

From the calculated values of % I.E given in Table 1, the order of the inhibition efficiencies of the selected N-thiazolyl-2-cyanoacetamide derivatives decreases in the following sequences: Compound (c) > Compound (b) > Compound (a). The explanation of this order will be discussed later

#### 3.2. Effect of Temperature

The effect of rising temperature on the corrosion rate of aluminum in 0.01 M sodium hydroxide solu-

**Table 1.** Values of protection efficiencies (%P) for N-Thiazolyl-2-cyanoacetamide derivatives for the corrosion of aluminum in 0.01 M NaOH after 75 minutes immersion at 30°C

10 <sup>6</sup> Conc., M	1	3	5	7	9	11
Compound (a)	14.60	15.99	20.69	23.75	26.28	28.00
Compound (b)	24.68	26.75	30.43	34.60	36.89	38.84
Compound (c)	37.19	38.84	42.95	48.45	51.95	53.90

**Table 2.** Activation parameters of the dissolution of aluminum in 0.01 M NaOH in the presence of  $5 \times 10^{-6}$  M N-Thiazolyl-2-cyanoacetamide

Inhibitors	$E_a^*$ , kJ mol <sup>-1</sup>	$\Delta H^*$ , kJ mol <sup>-1</sup>	$-\Delta S^*$ , Jmol <sup>-1</sup> K <sup>-1</sup>
Free NaOH	23.68	21.08	217.10
Compound (a)	26.23	23.63	210.74
Compound (b)	28.60	25.99	204.18
Compound (c)	31.68	29.08	195.92

tions in absence and presence of  $5 \times 10^{-6}$  M of the N-thiazolyl-2-cyanoacetamide derivatives was studied using weight loss measurements. Similar curves were obtained to Fig. 1 (not shown). It is clear that, the rate of corrosion increases as the temperature increases. This indicates that the rising of temperature decrease the inhibition processes and the best inhibition efficiency is obtained at 30°C.

The apparent activation energy ( $E_a^*$ ) of the corrosion of aluminum in 0.01 M NaOH solutions in the absence and presence of the N-thiazolyl-2-cyanoacetamide derivatives at different temperatures were calculated from the Arrhenius equation [29, 30].

$$R_{\text{corr}} = A \exp(-E_a^*/RT) \quad (4)$$

and the logarithmic form :

$$\log R_{\text{corr}} = \log A - E_a^*/2.303RT \quad (5)$$

where,  $R_{\text{corr}}$  is the corrosion rate,  $A$  is Arrhenius constant,  $R$  is the gas constant and  $T$  is the absolute temperature.

Figure 2 shows Arrhenius plot ( $\log R_{\text{corr}}$  vs  $1/T$ ) for uninhibited aluminum electrode in 0.01M NaOH and in presence of compounds a, b and c. The values of  $E_a^*$  obtained from the slope of the straight lines are listed in Table 2. Inspection of Table (2), it is clear that the values of  $E_a^*$  increases in the presence of the inhibitors. This was attributed to an appreciable decrease in the adsorption process of the inhibitor on the metal surface with increase of temperature and corresponding increase in the reaction rate because of the greater area of the metal that is exposed to sodium hydroxide solution.

The enthalpy change of activation ( $\Delta H^*$ ) and the entropy change of activation ( $\Delta S^*$ ) for corrosion of

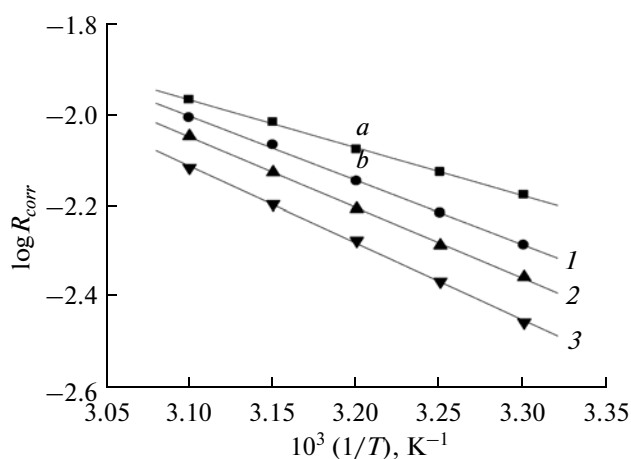
aluminum in 0.01M NaOH solution devoid of and containing  $5 \times 10^{-6}$  M of each used additives are obtained by the transition state equation:

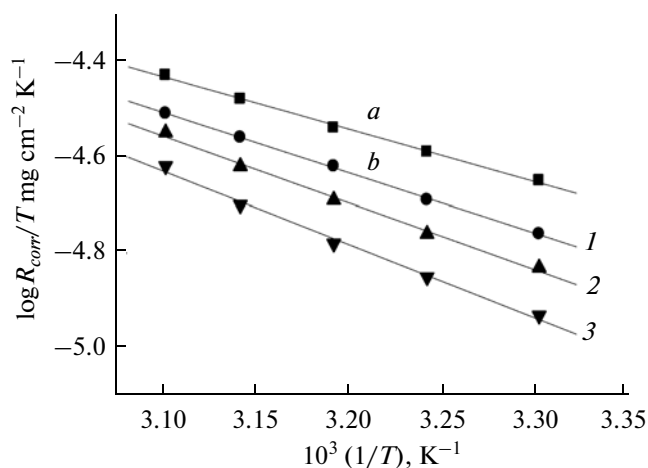
$$R_{\text{corr}} = RT/Nh \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \quad (6)$$

where,  $N$  is Avogadro number and  $h$  is the Plank's constant.

Figure 3 shows a plot of  $\log(R_{\text{corr}}/T)$  vs.  $1/T$  for uninhibited aluminum electrode in 0.01M NaOH and in the presence of compounds a, b and c. The above plots give a straight lines with a slope of  $(-\Delta H^*/2.303R)$  and an intercept of  $[\log(R/Nh) + \Delta S^*/2.303R]$ . The obtained values of  $\Delta H^*$  and  $\Delta S^*$  are listed in Table (2).

The positive values of  $\Delta H^*$  reflect that the process of adsorption of the inhibitors on the aluminum surface is endothermic process. The values of  $\Delta S^*$  in the

**Fig. 2.** log corrosion rate vs.  $1/T$  curves for aluminum in 0.01 M NaOH solution in absence and presence of  $5 \times 10^{-6}$  M of N-Thiazolyl-2-cyanoacetamide derivatives. (a) Blank (b) in presence of: 1) compound (a) 2) compound (b) 3) compound (c).

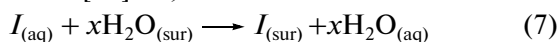


**Fig. 3.**  $\log R_{\text{corr}}/T$  vs.  $1/T$  curves for aluminum in 0.01 M NaOH solution in absence and presence of  $5 \times 10^{-6}$  M of N-Thiazolyl-2-cyanoacetamide derivatives. (a) Blank (b) in presence of: 1) compound (a) 2) compound (b) 3) compound (c).

presence and absence of the inhibitors is negative. This implies that the activation complex is the rate determining step represents association rather than dissociation indicating that a decrease in disorder takes place on going from reactants to the activated complex [31].

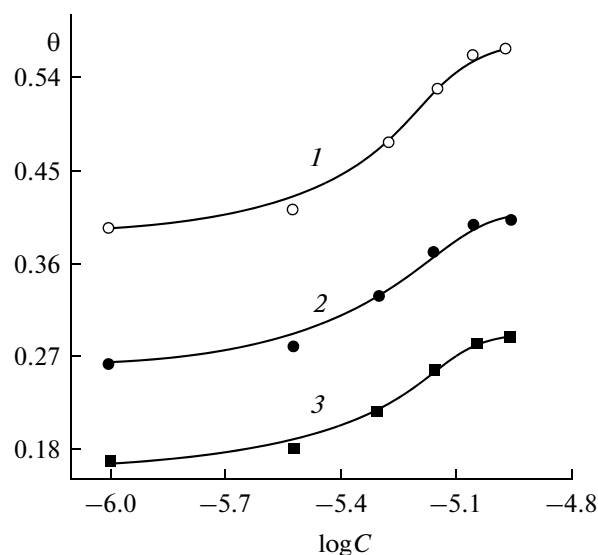
### 3.3. Adsorption Isotherm

N-thiazolyl-2-cyanoacetamide derivatives inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitution process in which an inhibitor molecule ( $I$ ) in the aqueous phase substitutes an “ $x$ ” number of water molecules adsorbed on the metal surface [32] vis,



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 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. Actually an adsorbed molecule may make the surface more difficult or less difficult for another molecule to become attached to a neighboring site and multilayer adsorption may take place. There may be more or less than one inhibitor molecule per surface site. Finally, various surface sites could have varying degrees of activation.

A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experiment data of the present work. The best fit was



**Fig. 4.** Curve fitting of corrosion data for aluminum in 0.01 M NaOH solution in presence of N-Thiazolyl-2-cyanoacetamide derivatives to Frumkin isotherm at 30°C. 1) compound (a) 2) compound (b) 3) compound (c).

obtained with Frumkin isotherm according to the following equation [33]:

$$KC = \theta / (1 - \theta) \exp(-2a\theta) \quad (8)$$

where,  $a$  is a parameter characterizing the interaction between the adsorbed particles is the equilibrium constant of the adsorption reaction,  $C$  is the inhibitor concentration in the bulk of the solution and  $\theta$  is the surface coverage. The surface coverage, i.e., the fraction of the surface covered by the inhibitor molecules,  $\theta$  were calculated from the following known equation:

$$\theta = 1 - (W'/W) \quad (9)$$

where, the meaning of  $W'$  and  $W$  as before.

Plots of  $\theta$  vs.  $\log C$  are shown in Fig. 4. The data gave S-shape curves indicating that Frumkin's isotherm is valid for these compounds.

### 3.4. Synergistic Effect

The effect of  $1 \times 10^{-3}$  M of  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions on the corrosion inhibition of aluminum in 0.01M NaOH solution in presence and absence of the N-thiazolyl-2-cyanoacetamide derivatives was studied by the weight loss method. Similar curves were obtained to Fig. 1 (not shown).

The values of inhibition efficiency (%I.E) for various concentrations of inhibitors in the presence of specific concentration of these cations at 30°C are given in Table 3.

The synergistic inhibition effect was evaluated using a parameter,  $S_0$ , obtained from the surface coverage values ( $\theta$ ) of the anion, cation and both. Aramaki and Hackerman [34] calculated the synergism parameter  $S_0$  using the following equation.

**Table 3.** Values of protection efficiencies (%P) of different N-Thiazolyl-2-cyanoacetamide derivatives in the presence of  $1 \times 10^{-3}$  M  $\text{MCl}_2$  for the corrosion of aluminum in 0.01M NaOH after 75 minutes immersion at 30°C

Salt	$10^6$ [Inh.], M	1	3	5	7	9	11
$\text{MgCl}_2$	Compound (a)	49.25	53.55	56.99	60.86	63.87	67.53
	Compound (b)	53.33	56.99	60.65	63.23	66.24	69.03
	Compound (c)	62.15	64.73	67.10	68.60	71.83	74.19
$\text{CaCl}_2$	Compound (a)	53.76	57.63	60.43	63.87	66.67	69.25
	Compound (b)	58.28	60.65	63.01	66.24	69.68	72.26
	Compound (c)	66.67	69.25	71.40	73.12	75.48	77.63
$\text{SrCl}_2$	Compound (a)	57.85	61.08	63.87	66.45	69.25	72.04
	Compound (b)	62.15	64.52	66.88	69.46	72.04	74.62
	Compound (c)	71.61	73.76	75.91	77.42	79.35	81.51
$\text{BaCl}_2$	Compound (a)	62.37	64.73	67.10	69.89	72.69	75.05
	Compound (b)	66.24	68.17	70.54	72.90	75.27	77.63
	Compound (c)	76.56	77.63	79.14	81.29	83.23	84.73

**Table 4.** Synergism parameter ( $S_0$ ) of N-Thiazolyl-2-cyanoacetamide derivatives in the presence of  $1 \times 10^{-3}$  M  $\text{MCl}_2$  for the corrosion of aluminum in 0.01M NaOH after 75 minutes immersion at 30°C

Salt	$10^6$ [Inh.], M	1	3	5	7	9	11
$\text{MgCl}_2$	Compound (a)	0.947	1.018	1.038	1.097	1.149	1.248
	Compound (b)	0.909	0.959	0.995	1.001	1.052	1.112
	Compound (c)	0.934	0.976	0.976	0.924	0.960	1.006
$\text{CaCl}_2$	Compound (a)	0.957	1.027	1.038	1.093	1.146	1.213
	Compound (b)	0.935	0.964	0.974	1.003	1.078	1.142
	Compound (c)	0.976	1.030	1.033	0.993	1.015	1.067
$\text{SrCl}_2$	Compound (a)	0.975	1.039	1.057	1.094	1.154	1.240
	Compound (b)	0.958	0.994	1.011	1.031	1.087	1.160
	Compound (c)	1.065	1.122	1.140	1.099	1.120	1.200
$\text{BaCl}_2$	Compound (a)	0.976	1.024	1.037	1.089	1.161	0.976
	Compound (b)	0.960	0.990	1.016	1.038	1.098	0.960
	Compound (c)	1.152	1.176	1.176	1.185	1.232	1.152

$$S_0 = 1 - \theta_{1+2}/1 - \theta'_{1+2} \quad (10)$$

where:

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2);$$

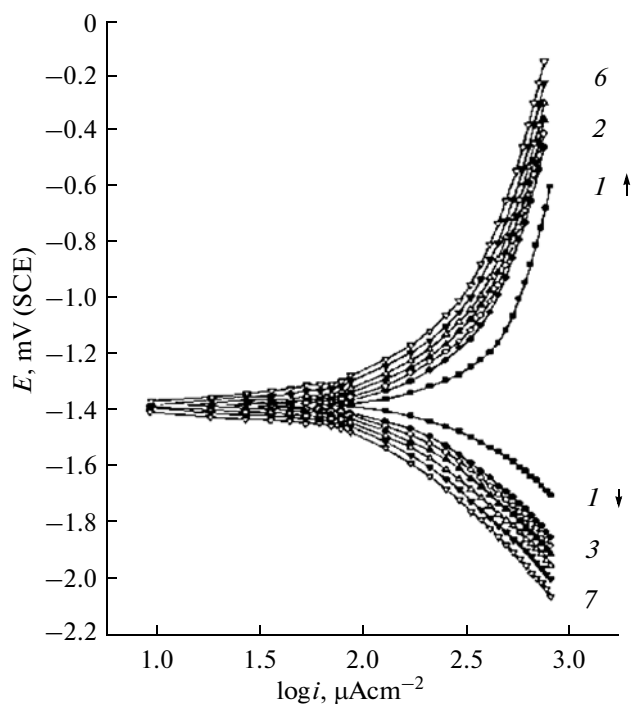
$\theta_1$  = surface coverage by anion;

$\theta_2$  = surface coverage by cation;

$\theta'_{1+2}$  = measured surface coverage by both the anion and cation.

We calculate synergism parameters from the above equation and the corresponding values are shown in Table 4. It is clear from this table that, the values of  $S_0$  are nearly equal to unity, which suggest that the enhanced inhibition efficiencies caused by the addition of cations to the selected organic compounds is due mainly to the synergistic effect.

It has been noticed that addition of cations ( $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$ ), in general, improves the inhibitive action of the organic substances in alkaline solutions. This may be due to the fact that the cations e.g.  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  are chemisorbed on aluminum in this medium, as has already been proved by radio-tracer study[35]. Also from Tables (3) we observe that the protection efficiency of the corrosive medium +  $1 \times 10^{-3}$  M cations + inhibitor exceeds the inhibition efficiency of the corrosive medium + inhibitor. This can be explained on the basis that the inhibitor ( $\text{In}^-$ ) at high concentration tends to withdraw the cations on the surface of the aluminum into the solution [36]. Hence coadsorption of cations and inhibitor ions is possible ( $\text{In}^-\text{Ba}^{2+}$  or  $\text{Ba}^{2+}\text{In}^-$ ) the extent of desorption of cations from the surface depends on the



**Fig. 5.** Galvanostatic polarization curves for dissolution of aluminum in 0.01 M NaOH solution in absence and presence of compound C at 30°C. 1) Blank 2)  $1 \times 10^{-6}$  M 3)  $3 \times 10^{-6}$  M 4)  $5 \times 10^{-6}$  M 5)  $7 \times 10^{-6}$  M 6)  $9 \times 10^{-6}$  M 7)  $11 \times 10^{-6}$  M.

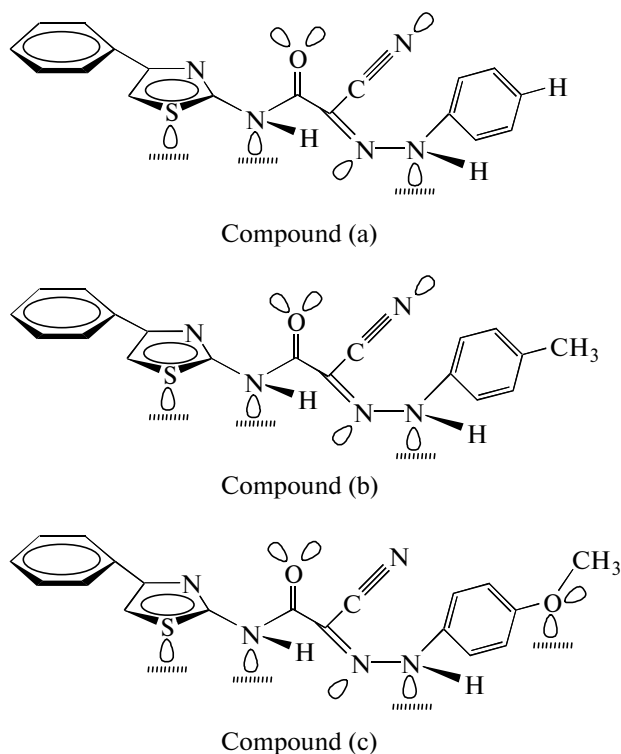
extent of adsorption of inhibitor ion ( $\text{In}^-$ ), which is a function of the concentration of the inhibitor.

From the results obtained the order of decreasing inhibition efficiency is  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ . This has a qualitative correspondence to the increasing atomic weights of these cations and it may be explained on the basis of their basicity which increases by increasing atomic weights.

### 3.5. Galvanostatic Polarization Measurement

Figure 5 shows the galvanostatic polarization curves of aluminum electrode in 0.01 M NaOH solution in the absence and presence of different concentrations of compound (c) as an example of the tested compounds. Similar curves were obtained for the other two compounds (not shown). The anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel constants were calculated from the linear region of the polarization curves. The corrosion current density ( $I_{\text{corr}}$ ) was determined from the intersection of the linear parts of the anodic and cathodic curves with the stationary corrosion potential ( $E_{\text{corr}}$ ).

Table 5 shows the effect of inhibitor concentrations on the corrosion parameters such as, corrosion potential  $E_{\text{corr}}$ , corrosion current density  $I_{\text{corr}}$ , anodic and cathodic Tafel constants ( $\beta_a$  &  $\beta_c$ ), surface coverage ( $\theta$ ) and percentage inhibition efficiency (% I.E).



**Fig. 6.** Skeletal representation of the mode of adsorption of N-thiazolyl-2-cyanoacetamide derivatives.

Inspection of this Table:

1. The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of N-thiazolyl-2-cyanoacetamide derivatives increased both cathodic and anodic overvoltage and caused mainly parallel displacement to the more negative and positive values, respectively.

2. The corrosion potential is shifted to more negative direction, the corrosion current density decreases and the inhibition efficiency increases indicating the inhibiting effect of these compounds toward the dissolution of aluminum in 0.01 N NaOH solutions.

3. The order of increased inhibition efficiency of these additives is: Compound (c) > Compound (b) > Compound (a). This is also in agreement with the observed order of corrosion inhibition by the weight-loss method.

4. The data suggest that these compounds behave as mixed-type inhibitors, but the anode is more polarized when an external current density was applied ( $\beta_a > \beta_c$ ).

5. The corrosion potential ( $E_{\text{corr}}$ ) values shifted to less negative values by increasing the concentration of N-thiazolyl-2-cyanoacetamide derivatives.

**Table 5.** Effect of N-Thiazolyl-2-cyanoacetamide derivatives on the free corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), Tafel slopes ( $\beta_a$  &  $\beta_c$ ), protection efficiency (%P) and degree of surface coverage ( $\theta$ ) of aluminum in 0.01N NaOH at 30°C

Inhibitor	$10^6$ Conc., M	$-E_{\text{corr}}$ , mV	$I_{\text{corr}}$ , $\mu\text{A cm}^{-2}$	$\beta_a$ , mV dec $^{-1}$	$\beta_c$ , mV dec $^{-1}$	$\theta$	%P
Compound (a)	0	1203	938.41	4897	2326	—	—
	1	1207	777.00	4902	2331	0.172	17.20
	3	1209	757.11	5147	2569	0.193	19.32
	5	1210	705.50	5387	2817	0.248	24.82
	7	1212	674.44	5637	3057	0.281	28.13
	9	1213	652.10	5985	3397	0.305	30.51
	11	1215	640.56	6223	3642	0.317	31.74
Compound (b)	0	1203	938.41	4897	2326	—	—
	1	1209	674.62	4909	2339	0.281	28.11
	3	1211	651.07	5180	2581	0.306	30.62
	5	1212	614.56	5447	2832	0.345	34.51
	7	1214	587.44	5702	3095	0.374	37.40
	9	1216	556.76	6025	3447	0.407	40.67
	11	1219	524.48	6356	3740	0.441	44.11
Compound (c)	0	1203	938.41	4897	2326	—	—
	1	1212	560.14	4929	2356	0.403	40.31
	3	1214	539.30	5208	2609	0.425	42.53
	5	1215	508.99	5484	2873	0.458	45.76
	7	1217	469.86	5743	3145	0.499	49.93
	9	1219	445.18	6095	3506	0.526	52.56
	11	1221	420.31	6441	3808	0.552	55.21

### 3.6. Studying the Correlation Between Inhibition Action and Chemical Structure of the Inhibitors

The inhibiting effect of N-thiazolyl-2-cyanoacetamide derivatives towards the corrosion behavior of aluminum in 0.01MNaOH was studied using weight loss and galvanostatic polarization techniques. The inhibiting efficiency was found to depend on the nature and concatenation of the inhibitor. As the concentration of the inhibitors increases the observed corrosion parameters led to

- The linear variation of the weight loss with time.
- The decrease in inhibition efficiency with increasing the temperature.
- Increase of surface coverage
- The corrosion current density decreases
- The parallel shift in Tafel lines to higher potential regions.

This indicates that the corrosion inhibition occurs by adsorption of the inhibitors at the electrode solution interface [37]. The nature of inhibitor interaction on metal surface during corrosion inhibition has been known from its adsorption characteristics [38]. However, inhibition efficiency of additive compounds depends [39] on many factors which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes.

It was found that, the order of inhibition efficiency of the N-thiazolyl-2-cyanoacetamide derivatives decreases in the following order:

$$c > b > a$$

Skeletal representation of the mode of adsorption of the studied N-thiazolyl-2-cyanoacetamide derivatives is shown in Fig. (6) and clearly indicates the active adsorption sites. As shown in this Figure, these organic compounds contain three active centers, so there is no effect of the active centers on percentage inhibition.

Variation in structure of inhibitor molecules (a)–(c) takes place through the phenylazo group. So, the inhibition efficiency will depends on this part of the molecule. This order of decreased inhibition efficiency of the additives can be accounted for in terms of polar effect [40] of the *p*-substituents on the phenylazo group. Compound (c) is the most efficient inhibitor because of the presence of highly electron releasing *p*-OCH<sub>3</sub> ( $\sigma = -0.23$ ) which enhances the delocalized  $\pi$ -electrons on the molecule. Compound (b) comes after compound (c) in inhibition efficiency this is due to the presence of *p*-CH<sub>3</sub> group which is an electron donating group with negative Hammett constant ( $\sigma = -0.17$ ). Also this group will increase the electron charge density on the molecule but with lesser amount than *p*-OCH<sub>3</sub> group in compound (c). Compound (a) with Hammett constant ( $\sigma = 0.0$ ) comes after compound (b) in percentage inhibition efficiency, because H-atom in *p*-position has no effect on the charge density on the molecules.

The order of inhibition efficiency of the additives revealed by the weight loss method is further supported by galvanostatic polarization measurement. 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.

## REFERENCES

- Caporali, S., Fossati, A., Lavacchi, A., et al., *Corrosion Sci.*, 2008, vol. 50, p. 534.
- Fang, H., Chen, K., Zhang, Z., and Zhu, C., *Trans. Nonferrous Met. Soc. China*, 2008, vol. 18, p. 28.
- Rosaliza, R., Wan Nik, W.B., and Senin, H.B., *Mater. Chem. Phys.*, 2008, vol. 107, p. 281.
- Oguzie, E.E., Onuoha, G.N., and Ejike, E.N., *Pigment Resin Technol.*, 2007, vol. 36, p. 44.
- Nnanna, L.A., Onwuagba, B.N., Mejeha, I.M., and Okeoma, K.B., *Afr. J. Pure Appl. Chem.*, 2008, vol. 4, p. 11.
- Zhang, H. and Zuo, Y., *Appl. Surf. Sci.*, 2008.
- Oguzie, E.E., *Portugaliae Electrochem. Acta*, 2008a, vol. 26, p. 303.
- Ebenso, E.E., *Bull. Electrochem.*, 2004, vol. 20, p. 551.
- Mejeha, I.M., Uroh, A.A., Okeoma, K.B., and Alozie, G.A., *Afr. J. Pure Appl. Chem.*, 2010, vol. 4 p. 158.
- Coleman, A.J., McMurra, H.N., Williams, G., et al., *Sci. Forum.*, 2006, vol. 629, p. 519.
- Rajendran, S., Ganga, V., Arockia Selvi, S.J., and John Amalr, A., *Bulletin of Electrochem.*, 2005, vol. 21, p. 367.
- Rajendran, S., Shanmugapriya, S., Rajalakshmi, T., and Amalraj, A.J., *Corrosion*, 2005, vol. 61, p. 685.
- Anthony, N., Malarivizhi, E., Maheswari, P., et al., *Ind. J. Chem. Tech.*, 2004, vol. 11, p. 346.
- Rajendran, S., Amalraj, A.J., Joice, M.J., et al., *Corrosion Rev.*, 2004, vol. 22, p. 233.
- Rajendran, S., Thangavelu, C., and Venkatesh, T., *Der Chemica Sinica*, 2012, vol. 3, p. 1475.
- Omar, A. and Hazazi Abdallah, M., *Int. J. Electrochem. Soc.*, 2013, vol. 8, p. 8138.
- Fouda, A.S., Abdallah, M., Ahmed, I.S., and Eissa, M., *Arab. J. of Chem.*, 2012, vol. 5, p. 297
- Abdallah, M., Zaafarany, I., Al-Karane, S.O., and Abd El-Fattah, A.A., *Arab. J. of Chem.*, 2012, vol. 5, p. 225.
- Rajendran, S., Manivanna, M., Sahayaraj, J.W., and Selvi, J.A., *SAEST*, 2006, vol. 41, p. 63.
- Rajendran, S., Muthulakshmi, S., Rajeswari, R., and Vijitha, A., *Ind. J. Electrochem. Soc.*, 2005, vol. 54, p. 50.
- Santhini, N. and Jeyaraj, T., *J. Chem. Pharm. Res.*, 2012, vol. 4, p. 3550.
- Beulah, J.R., Rani, T.S., and Jeyaraj, T., *J. Chem. Pharm. Res.*, 2012, vol. 4, p. 3541.
- Lakshmi, K., Praba Rajam, S., and Subramaniya, A., *J. Chem. Pharm. Res.*, 2012, vol. 4, p. 337.
- Rajendran, S., Thangavelu, C., and Annamalai, G., *J. Chem. Pharm. Res.*, 2012, vol. 4, p. 4836.
- Edrah, S. and Hasan, S.K., *Appl. Sci. Res.*, 2010, vol. 6, p. 1045.
- Vasanthi, B.J., Ravikumar, L., and Selvaraj, A., *Materials and Corrosion*, 2008, vol. 59, p. 14.
- Abood, H.A. and Basrah, J., *Science C*, 2011, vol. 28, p. 74.
- Oguzie, E.E., *Corrosion Sci.*, 2007, vol. 49, p. 1527.
- Putilova, I., Balezin, S., Barannik, I.N., and Bishop, V.P., *Metal. Corrosion Inhibition*, Oxford: Pergamon, 1960, p. 196.
- Abdallah, M., *Corrosion Sci.*, 2004, vol. 46, p. 1981.
- Abdallah, M., Asghar, B., Zaafarany, I., and Sobhi, M., *Protection of Metals and Physical Chemistry of Surfaces*, 2013, vol. 49, p. 485.
- Zaafarany, I. and Abdallah, M., *Int. J. Electrochem. Sci.*, 2010, vol. 5, p. 18.
- Fouda, A.S., Al-Sarawy, A.A., Ahmed, F.Sh., and El-Abbasy, H.M., *Corrosion Sci.*, 2009, vol. 51, p. 485.
- Aramaki, K. and Hackerman, N., *J. Electrochem. Sci.*, 1969, vol. 116, p. 568.
- Sekerka, I., *Werks. U. Korros.*, 1959, vol. 10, p. 383.
- Rudresh, H.B. and Mayann, S.M., *J. Electrochem. Soc.*, 1977, vol. 124, p. 340.
- Rudresh, H.B. and Mayann, S.M., *Surf. Technol.*, 1977, vol. 6, p. 139.
- Murakawa, T., Kato, T., Nagura, S., and Hackerman, N., *Corrosion Sci.*, 1968, vol. 8, p. 438.
- Fouda, A.S., Mousa, M.N., Taha, F.I., and Elneanaa, A.I., *Corrosion Sci.*, 1986, vol. 26, p. 719.
- Hammett, L.P., *Physical Organic Chemistry*, N.Y.: McGro-Hill Book Co., 1940.

SPELL: 1. recyclability, 2. amphoteric, 3. deaerated