

## Some Thiazolidinone Derivatives as Inhibitors For The Corrosion of 6163 Aluminum in Phosphoric Acid Solution

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### Abstract

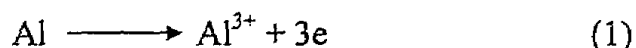
The influence of some thiazolidinone derivatives as corrosion inhibitors for 6163 aluminum in 3M phosphoric acid solution has been studied by weight-loss and galvanostatic polarization techniques. A significant decrease in the corrosion rate of aluminum was observed in the presence of these investigated inhibitors. The inhibition efficiency of these derivatives increases with increasing the inhibitor concentration and decreases with increasing temperature. The galvanostatic polarization studies revealed that these compounds behave as mixed -type inhibitors. The effect of temperature on corrosion inhibition has been studied and activation energies has been calculated. Some thermodynamic parameters for the corrosion process are calculated and discussed. Addition of small amounts of KI, KSCN, and KBr to the acidic medium containing the thiazolidinone derivatives increases the inhibition efficiency of the system due to the synergistic effect. The adsorption of the inhibitors on the aluminum surface is found to obey Temkin's adsorption isotherm. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

**Key words :** Corrosion, thiazolidinone derivatives, aluminum, H<sub>3</sub>PO<sub>4</sub>.

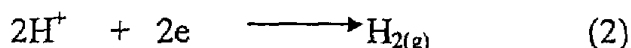
### 1. Introduction

Aluminum and its alloys are used widely in many industries owing to its low cost, light weight, high thermal & electrical conductivity and the study of its corrosion inhibition in pickling baths (acidic medium) is of great importance. Several researchers [1-33] have studied the corrosion inhibition of aluminum and its alloys in different aqueous solutions using organic inhibitors containing nitrogen, sulfur and oxygen atoms. These compounds can adsorb on the aluminum surfaces and block the active site decreasing the corrosion rate. The corrosion of aluminum proceeds via two possible reactions namely, the partial

anodic reaction that can be represented by the dissolution of metal according to the following reaction [30] :



And the partial cathodic reaction which can be represented by the overall reaction:



The aim of this work is to study: the corrosion inhibition of 6163 aluminum in 3M  $\text{H}_3\text{PO}_4$  by some thiazolidinone derivatives using weight-loss and galvanstatic polarization techniques, and to throw some light on the mechanism of the corrosion process.

## 2. Materials and methods

6163 Aluminum specimens of size 20x20x2 mm of the composition (in weight %): Zn = 0.08, Ti = 0.03, Si = 0.20, Cu = 0.02, Fe = 0.20 and the rest Al were used. The samples were polished successively with fine grade emery papers ,followed by ultrasonically degreasing with alkaline mixture, washed with bidistilled water and then dried at room temperature. A stock solution ( $10^{-3}\text{M}$ ) of each inhibitor was prepared by dissolving an accurately weighed quantity of inhibitor in an appropriate volume of absolute ethanol, then the required concentrations ( $5 \times 10^{-7}$  -  $15 \times 10^{-7}\text{M}$ ) were prepared by dilution with bidistilled water. Phosphoric acid solution (3M) was prepared by diluting the appropriate volume of the concentrated chemically pure acid, with bidistilled water and its concentration was checked by a prestandardized solution of NaOH . A stock solution of KI, KSCN and KBr (1M) was prepared using bidistilled water. All chemical used were of AR grade.

### 2.1. Preparation of Inhibitors

Thiazolidinone derivatives (Fig.1) were prepared according to methods described before [34-35] . In a typical preparation, 25 ml of bidistilled water containing 0.01 mole hydrochloric acid were added to 0.01 mole aniline or a 4-alkyl-

aniline. The resulting mixture stirred and cooled to 0°C, a solution of 0.01 mole sodium nitrite in 20 ml of water was added dropwise. The so formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mole 3-phenylamino-2-thioxo-4-thiazolidinone, in 20 ml of pyridine. The colored precipitate, which formed immediately, was filtered through sintered glass crucible, washed several times with water and ether. The crude product was purified by recrystallization from hot ethanol, yield 65% then dried in vacuum desiccator over P<sub>2</sub>O<sub>5</sub>.

## 2.2. Chemical measurements

For weight loss measurements, rectangular aluminum specimens of size 20x20x2 mm, were immersed in 100 ml of uninhibited and inhibited solutions at 30°C. This was conducted in covered beaker to prevent contact with air and allow the escape of evolved gases. After the required immersion time, the test specimen was removed, washed with bi-distilled water, dried between two filter papers and finally, weighed. The percentage inhibition efficiency (%I) of the inhibitor was calculated using the equation:

$$\% I = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100 \quad (3)$$

where:  $\Delta W$  and  $\Delta W_i$  are the weight losses per unit area in absence and presence of the inhibitor, respectively.

The degree of surface coverage ( $\theta$ ) was calculated using equation:

$$\theta = \frac{\Delta W - \Delta W_i}{\Delta W} \quad (4)$$

## 2.3. Electrochemical measurements

Polarization studies were carried out using 6163 aluminum specimens of the same compositions dipped in 3M H<sub>3</sub>PO<sub>4</sub> in the presence and absence of inhibitors. E vs. log I curves were recorded at temperature namely 30 °C. The corrosion kinetic parameters such as corrosion current ( $i_{corr.}$ ), corrosion potential ( $E_{corr.}$ ), cathodic Tafel slope ( $\beta_c$ ), and anodic Tafel slope ( $\beta_a$ ) were derived from the curves. The working

electrode (M) was 6163 aluminum wire embedded with an exposed area of 1 cm<sup>2</sup>. The polarization cell is a three electrode glass cell assembly as shown in (Fig. 2). A rectangular platinum foil was used as counter electrode (C). The area of the counter electrode was much larger compared to the area of the working electrode. This will exert an uniform potential field on the working electrode. Saturated calomel electrode (SCE) was used as reference electrode. A constant quantity of the test solution (100 ml) was taken in the polarization cell. The working electrode was polished with a fine grade emery paper and followed by ultrasonically degreasing with alkaline solution. The working and the reference electrodes were assembled and necessary connections were made with the instrument. A time interval of about 30 minutes was given for the system to attain a steady state and the open circuit potential (OCP) was noted. Both cathodic and anodic polarization curves were recorded galvanostatically using Amel Galvanostat (Model-549) and digital Multimeters (Fluke-73) for accurate measurements of potential and current density. Solutions were not de-aerated to make the conditions identical to weight loss measurements. All the experiments were carried out at 30±1 °C by using ultra circulating thermostat. The inhibition efficiency (%I) and degree of surface coverage (θ) are defined as:

$$\% I = \left( \frac{i_{free} - i_{inh.}}{i_{free}} \right) \times 100 \quad (5)$$

$$\theta = \frac{i_{blank} - i_{inhibited}}{i_{blank}} \quad (6)$$

where  $i_{free}$  and  $i_{inh.}$  are the corrosion currents in absence and presence of the inhibitor, respectively.

### 3. Results and Discussion

#### 3.1. Weight-Loss Measurements

Aluminum samples were dissolved under unstirred conditions in 3M H<sub>3</sub>PO<sub>4</sub> without and with various concentrations (5X10<sup>-7</sup> – 15X10<sup>-7</sup>) of different investigated compounds at 30 °C. Fig. 3 shows the effect of the period of immersion on the corrosion of aluminum in presence and absence of different concentrations of

compound (e) in acidic medium. The other curves of the rest compounds are similar and not shown. The extent of the decrease in weight loss was found to depend on the type of the inhibitor and its concentration. The inhibition efficiency (% I) of various inhibitors was found to be in the order (Table 1):

*Compound (e) > compound (d) > compound (c) > compound (b) > compound (a).*

Table ( 1 ): %Inhibition of Al dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of different concentrations of thiazolidinone derivatives at 30°C and at 210 min. immersion.

Concentration M	%Inhibition (%I)				
	(a)	(b)	(c)	(d)	(e)
5x10 <sup>-7</sup>	14.2	17.4	23.4	29.2	33.3
7x10 <sup>-7</sup>	16.9	21.9	28.8	33.6	36.4
9x10 <sup>-7</sup>	23.8	25.7	31.6	38.7	41.1
11x10 <sup>-7</sup>	28.8	32.4	37.5	42.1	44.9
13x10 <sup>-7</sup>	35.1	37.5	41.6	47.0	49.4
15x10 <sup>-7</sup>	41.0	43.6	50.7	53.3	55.2

### 3.2. Synergistic Effect

The effect of I<sup>-</sup>, SCN<sup>-</sup> and Br<sup>-</sup> anions on the corrosion inhibition of aluminum in 3M H<sub>3</sub>PO<sub>4</sub> in presence and absence of thiazolidinone derivatives was studied using weight loss method. Fig. 4 represents the weight loss time curve for Al dissolution in absence and present of different concentrations of compound (e) without and with addition of 0.01 M KBr at 30 °C . The other curves of the rest compounds are similar and not shown. The values of inhibition efficiency (% I) for various concentrations of inhibitors in the presence of specific concentrations of these anions are given in Tables (2-4).

Table (2): %Inhibition of aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of different concentrations of thiazolidinone derivatives with addition of 0.01 M KI at 30 °C and at 210 min. immersion .

Concentration M	%Inhibition (%I)				
	(a)	(b)	(c)	(d)	(e)
5x10 <sup>-7</sup>	58.2	61.7	65.2	70.1	75.9
7x10 <sup>-7</sup>	60.6	64.0	66.7	71.6	77.0
9x10 <sup>-7</sup>	62.4	65.2	68.3	73.4	78.0
11x10 <sup>-7</sup>	64.9	67.3	70.4	74.3	78.9
13x10 <sup>-7</sup>	67.0	69.8	72.8	75.9	80.2
15x10 <sup>-7</sup>	69.4	71.6	74.7	77.4	81.1

Table (3): %Inhibition of aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of different concentrations of thiazolidinone derivatives with addition of 0.01 M KSCN at 30 °C and at 210 min. immersion.

Concentration M	%Inhibition (%I)				
	(a)	(b)	(c)	(d)	(e)
5x10 <sup>-7</sup>	48.3	50.7	54.7	59.0	63.2
7x10 <sup>-7</sup>	50.7	53.8	57.1	61.1	64.8
9x10 <sup>-7</sup>	52.9	56.5	59.6	63.3	66.3
11x10 <sup>-7</sup>	54.7	59.3	61.4	64.8	67.9
13x10 <sup>-7</sup>	57.1	62.1	64.2	67.6	70.9
15x10 <sup>-7</sup>	59.0	64.2	66.3	69.4	73.4

Table (4): %Inhibition of aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of different concentrations of thiazolidinone derivatives with addition of 0.01 M KBr at 30 °C and at 210 min. immersion

Concentration M	%Inhibition (%I)				
	(a)	(b)	(c)	(d)	(e)
5x10 <sup>-7</sup>	42.2	44.8	46.9	51.0	54.4
7x10 <sup>-7</sup>	43.9	47.2	49.7	53.4	57.1
9x10 <sup>-7</sup>	46.0	49.4	51.9	55.2	60.1
11x10 <sup>-7</sup>	47.8	51.9	54.3	58.3	62.9
13x10 <sup>-7</sup>	51.9	54.9	56.8	61.1	66.3
15x10 <sup>-7</sup>	54.9	57.1	58.9	63.5	69.0

It is observed that (% I) of the inhibitors increases on addition of these different anions due to synergistic effects[36]. The strong chemisorption of these anions on the metal surface is responsible for the synergistic effect of these ions in combination with cation of the inhibitor. The cation is then adsorbed by coulombic attraction on the metal surface where these anions are already adsorbed by chemisorption. Stabilization of these adsorbed anions with cations leads to greater surface coverage and therefore greater inhibition. The synergistic inhibition effect was evaluated using a parameter, ( $S_{\theta}$ ), obtained from the surface coverage values ( $\theta$ ) of the anion, cation and both. Aramaki and Hackerman [37] calculated the synergism parameter ( $S_{\theta}$ ) using the following equation:

$$S_{\theta} = \frac{1-\theta_{1+2}}{1-\theta_1-\theta_2} \quad (7)$$

where:

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

$\theta_1$  and  $\theta_2$  : are surface coverage for anion and cation respectively;  
 $\theta_{1+2}$  : measured surface coverage by both the anion and cation.

Synergism parameter, ( $S_\theta$ ) was calculated from the above equation. All the ( $S_\theta$ ) values are shown in Tables (5-7). Since most of these values nearly equal to unity, which suggests that the enhanced inhibition efficiencies caused by the addition of these anions to thiazolidinone derivatives is due mainly to the synergistic effect.

Table(5): Synergism parameter ( $S_\theta$ ) for different concentrations of thiazolidinone for aluminum dissolution in 3M  $H_3PO_4$  with addition of 0.01 M KI at 30°C.

Concentration M	Synergism parameter ( $S_\theta$ )				
	(a)	(b)	(c)	(d)	(e)
$5 \times 10^{-7}$	1.053	1.106	1.129	1.155	1.180
$7 \times 10^{-7}$	1.082	1.113	1.131	1.173	1.193
$9 \times 10^{-7}$	1.098	1.128	1.143	1.218	1.231
$11 \times 10^{-7}$	1.103	1.130	1.162	1.238	1.262
$13 \times 10^{-7}$	1.110	1.137	1.189	1.253	1.293
$15 \times 10^{-7}$	1.125	1.139	1.206	1.271	1.334

Table( 6): Synergism parameter ( $S_\theta$ ) for different concentrations of thiazolidinone for aluminum dissolution in 3M  $H_3PO_4$  with addition of 0.01M KSCN at 30°C.

Concentration M	Synergism parameter ( $S_\theta$ )				
	(a)	(b)	(c)	(d)	(e)
$5 \times 10^{-7}$	1.030	1.081	1.091	1.114	1.169
$7 \times 10^{-7}$	1.057	1.090	1.096	1.130	1.189
$9 \times 10^{-7}$	1.070	1.102	1.120	1.173	1.217
$11 \times 10^{-7}$	1.082	1.107	1.132	1.197	1.255
$13 \times 10^{-7}$	1.094	1.125	1.148	1.204	1.280
$15 \times 10^{-7}$	1.103	1.121	1.191	1.224	1.296

Table( 7): Synergism parameter ( $S_\theta$ ) for different concentrations of thiazolidinone for aluminum dissolution in 3M  $H_3PO_4$  with addition of 0.01M KBr at 30°C.

Concentration M	Synergism parameter ( $S_\theta$ )				
	(a)	(b)	(c)	(d)	(e)
$5 \times 10^{-7}$	0.977	0.988	1.024	1.035	1.051
$7 \times 10^{-7}$	0.988	0.996	1.031	1.052	1.064
$9 \times 10^{-7}$	0.993	1.003	1.046	1.072	1.096
$11 \times 10^{-7}$	1.001	1.023	1.048	1.084	1.104
$13 \times 10^{-7}$	1.019	1.039	1.066	1.090	1.118
$15 \times 10^{-7}$	1.051	1.077	1.095	1.108	1.134

From previous results it is known that KI would be considered as one of the effective anions for synergistic action within the investigated salts. The net increment of inhibition efficiency shows a synergistic effect of KBr, KI, KSCN with thiazolidinone derivatives. The synergistic effect depends on the type and concentration of anions. The adsorption ability on the aluminum surface was in the order  $KI > KSCN > KBr$ , this order was parallel to their ionic radii.

### 3. 3.Adsorption Isotherm

Figure 5 demonstrates the variation of the degree of surface coverage ( $\theta$ ) with the logarithmic of concentrations of the additives from weight loss technique.

The adsorption isotherms follow that of Temkin's adsorption isotherm [38]. For such an isotherm ( $\theta_{inh}$ ) is a linear function of ( $\log C$ ) according to the equation:

$$\ln K C = a \theta \quad (8)$$

Where ( $K$ ) is the equilibrium constant of the adsorption reaction, ( $C$ ) is the inhibitor concentration in the bulk of the solution, ( $a$ ) is the interaction parameter and ( $\theta$ ) is the surface coverage. The surface coverage, i.e., the fraction of the surface covered by the inhibitor molecules. On the other hand, it was found that the kinetic-thermodynamic model of El Awady *et al.*, [39] is valid to operate the present adsorption data (equation 9).

$$\frac{\log \theta}{1-\theta} = \log K' + y \log C \quad (9)$$

The equilibrium constant of adsorption ( $K=K'^{(1/y)}$ ), where ( $1/y$ ) is the number of the surface active sites occupied by one thiazolidinone molecule and ( $C$ ) is the bulk concentration of the inhibitor. The plotting ( $\log \theta/(1-\theta)$ ) against  $\log C$  at  $30^\circ\text{C}$  is given in Fig.(6), where straight line relationships were obtained suggesting the validity of this model for all cases studied. The calculated values of ( $1/y$ ), ( $K$ ) and ( $\Delta G^\circ_{ads}$ ) are given in Table (8). Inspection of the data of this Table shows that the



large values of ( $\Delta G^{\circ}_{ads.}$ ) and its negative sign, indicate that the adsorption of thiazolidinone compounds on the aluminum surface is proceeding spontaneously and is accompanied by a highly-efficient adsorption. It is worth noting that the value of ( $1/y$ ) is more than unity. This means that the given inhibitor molecules will occupy more than one active site. In general, the values of ( $\Delta G^{\circ}_{ads.}$ ) obtained from El-Awady et al model are comparable with those obtained from Temkin's isotherm. From these results it may be generalized that the more efficient inhibitor has more negative ( $\Delta G^{\circ}_{ads.}$ ) value, So that from the tabulated values of ( $\Delta G^{\circ}_{ads.}$ ) the order of inhibition efficiencies is as following:

*Compound (e) > compound (d) > compound (c) > compound (b) > compound (a).*

Table ( 8 ): Inhibitor binding constant ( K ), free energy of binding ( $\Delta G_{ads.}$ ), number of active sites ( $1/y$ ) and later interaction parameter ( a ) for thiazolidine derivatives at 30 °C.

Inhibitors	Kinetic model			Temkin		
	$1/y$	$K, 10^5$	$-\Delta G_{ads.}$ $\text{kJ mol}^{-1}$	a	$K, 10^6$	$-\Delta G_{ads.}$ $\text{kJ mol}^{-1}$
(a)	0.745	4.7988	43.059	4.05	31.3660	47.786
(b)	0.849	4.9784	43.151	4.24	37.7252	48.251
(c)	0.972	5.8745	43.568	4.36	50.3155	48.977
(d)	1.157	6.7442	43.915	4.90	77.4179	50.062
(e)	1.248	7.5966	44.215	5.15	99.6197	50.697

### 3.4. Effect of Temperature and Activation Parameters

The effect of temperature (30-60 °C) on the performance of the inhibitors at concentration of  $9 \times 10^{-7} \text{M}$  for 6163 aluminum in 3M  $\text{H}_3\text{PO}_4$  was studied using weight loss measurements. The percentage efficiency was found to decrease with increasing temperature ( Fig. 7 ),, this behavior can be explained on the basis that the increase of the temperature leads to desorption of the adsorbed molecules of the inhibitors from the metal surface. Table (9 ) shows the effect of temperature on the % inhibition of

aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of 9x10<sup>-7</sup>M of thiazolidinone derivatives. The apparent activation energy (E<sub>a</sub><sup>\*</sup>), enthalpy and entropy of activation (ΔH<sup>\*</sup>, ΔS<sup>\*</sup>) for the corrosion of 6163 aluminum in 3M H<sub>3</sub>PO<sub>4</sub> solutions in the absence and presence of 9X10<sup>-7</sup>M of thiazolidinone derivatives at 30, 40,50, 60°C were calculated from Arrhenius-type equation:

$$\text{Rate} = A \exp (-E_a^*/RT) \quad (10)$$

and transition-state equation:

$$\text{Rate} = RT/Nh \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \quad (11)$$

Where (A) is the frequency factor, (h) is the Planck's constant, (N) is Avogadro's number and (R) is the universal gas constant. A plot of log Rate vs. 1/T and log (Rate/T) vs. 1/T (Figures 8 ,9 ) give straight lines with slope of - E<sub>a</sub><sup>\*</sup>/2.303R, and - ΔH<sup>\*</sup>/2.303R, respectively. The intercepts will be (A) and (log R/Nh + ΔS<sup>\*</sup>/2.303R) for Arrhenius and transition state equations respectively. The calculated values of( E<sub>a</sub><sup>\*</sup>), (ΔS<sup>\*</sup>) and (ΔH<sup>\*</sup>) are given in Table (10). The almost similar values of E<sub>a</sub><sup>\*</sup> suggest that the inhibitors are similar in the mechanism of action and the order of efficiency may be related to the preexponential factor (A) in equation (10). This is further related to concentration, steric effects, metal surface characters. The order of the inhibition efficiency of thiazolidinone derivative as gathered from the increase in (E<sub>a</sub><sup>\*</sup>) and (ΔH<sup>\*</sup>) values and decrease in (ΔS<sup>\*</sup>) values is:

*Compound (e) > compound (d) > compound (c) > compound (b) > compound (a).*

Table (9): % Inhibition of aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in presence of 9x10<sup>-7</sup>M of thiazolidinone derivatives at different temperatures and at 210 min. immersion.

Temperature, °C	%Inhibition (%I)				
	(a)	(b)	(c)	(d)	(e)
30	23.8	25.7	31.6	38.7	41.1
40	19.8	23.6	27.7	32.3	34.4
50	16.9	21.2	24.6	27.9	30.6
60	14.6	18	20	24.8	26.7

Table ( 10 ): Activation parameters of aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of 9x10<sup>-7</sup> M thiazolidinone derivatives.

Inhibitors	Activation parameters		
	E <sub>a</sub> <sup>*</sup> , kJ mol <sup>-1</sup>	ΔH <sup>*</sup> , kJ mol <sup>-1</sup>	-ΔS <sup>*</sup> , J mol <sup>-1</sup> K <sup>-1</sup>
Free acid	57.84	55.21	99.30
(a)	61.06	57.96	92.35
(b)	61.12	58.45	91.15
(c)	61.93	59.29	89.00
(d)	63.58	60.94	84.35
(e)	63.96	61.32	83.43

### 3.5. Galvanostatic Polarization Measurements

Figure (10) shows the galvanostatic polarization curves (E vs. log I) of 6163 aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of different concentrations of inhibitor (e) at 30 °C. Similar curves were obtained for other inhibitors (not shown). The numerical values of the variation of the corrosion current density (i<sub>corr.</sub>), the corrosion potential (E<sub>corr.</sub>), Tafel slopes (β<sub>a</sub> and β<sub>c</sub>) degree of surface coverage (θ) and the inhibition efficiency (% I) with the concentration of inhibitor (e) is given in Table (11). The results indicate that:

1. The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of thiazolidinone derivatives increased both the cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively.
2. The corrosion current density (i<sub>corr.</sub>) decreases with increasing the concentration of the thiazolidinone derivatives which indicates that these compounds act as inhibitors, and the degree of inhibition depends on the concentration and type of the inhibitor present.
3. The order of increased inhibition efficiency for the additives is as following: (e) > (d) > (c) > (b) > (a).

This is also in agreement with the observed order of corrosion inhibition determined from weight-loss method.

4. The data suggested that these compounds act as mixed-type inhibitors because they enhance both the anodic and cathodic processes but the anode is more

polarized when an external current was applied.

5. The values of corrosion potential ( $E_{corr.}$ ) values shifted to less negative values by increasing the concentration of thiazolidinone derivatives

Table (11): The effect of concentration of compound (e) on the corrosion potential ( $E_{corr.}$ ), corrosion current density ( $i_{corr.}$ ), Tafel slopes ( $\beta_a$  &  $\beta_c$ ), inhibition efficiency (%I) and degree of surface coverage ( $\theta$ ) in presence of 3M  $H_3PO_4$  at 30°C.

Concentration, M	$-E_{corr.}$ mV.	$i_{corr.}$ $\mu A\ cm^{-2}$	$\beta_a$ mV dec <sup>-1</sup>	$\beta_c$ mV dec <sup>-1</sup>	$\theta$	%I
0	942	62.0	217	89	-----	-----
$5 \times 10^{-7}$	939	41.0	206	111	0.34	33.8
$7 \times 10^{-7}$	938	38.8	208	113	0.37	37.4
$9 \times 10^{-7}$	937	36.3	210	115	0.41	41.5
$11 \times 10^{-7}$	936	33.9	211	117	0.45	45.4
$13 \times 10^{-7}$	935	31.6	213	119	0.49	49.0
$15 \times 10^{-7}$	934	27.7	214	121	0.55	55.4

### 3.6. Chemical structure and corrosion inhibition

Skeletal representation of the mode of adsorption of the thiazolidinone derivatives is shown in Fig.(11), and clearly indicates the active adsorption centers. The order of decreasing inhibition efficiency of the investigated thiazolidinone derivatives in 3M  $H_3PO_4$  is :

*Compound (e) > compound (d) > compound (c) > compound (b) > compound (a).*

The inhibition efficiency of the compounds depends on many factors [39], which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes.

Compound (e) comes on the top in the inhibition efficiency because: (i) It has two active centers (one sulphur atom and one oxygen atom) and high molecular size, so it covers larger area of the aluminum surface and (ii) The presence of highly electron releasing group ( $-OCH_3$ ) with  $\sigma = -0.27$  (Hammett constant), which enhances the delocalized  $\pi$ - electrons on the active centers of the compound.

Compound (d) comes after compound (e) in the sequence of decreasing inhibition efficiency. This due to: (i) It has only one active center (one sulphur atom), (ii) It has lower molecular size than compound (e), so it covers lesser surface area of aluminum and (iii) It has lesser  $\sigma$  ( $\sigma_{\text{CH}_3} = -0.17$ ).

Compound (c) comes after compound (d) in decreasing inhibition efficiency this may be due to: (i) It has lower molecular size than compound (d) and (ii) It has ( $\sigma_{\text{H}} = 0.0$ ) which contributes no electron charge density to the molecule and hence lower inhibition efficiency .

Compound (b) and compound (a) come after compound (c) in decreasing inhibition efficiency because they have positive  $\sigma$  values ( $\sigma_{\text{CL}} = +0.23$  and  $\sigma_{\text{NO}_2} = +0.78$ ) and hence lower electron sharing to their molecules. The inhibition efficiency of these molecules are parallel to the increased order of electron withdrawing (electrophilic) character of these groups.

#### 4. Conclusions

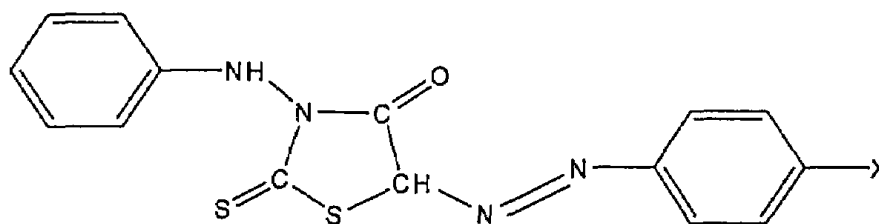
1. All the derivatives studied were found to perform well as a corrosion inhibitors for 6163 aluminum dissolution in 3M  $\text{H}_3\text{PO}_4$  and the inhibiting efficiency values of examined compounds follow the order: compound (e) > compound (d) > compound (c) > compound (b) > compound (a) at all the studied conditions.
2. The adsorption of these compounds on 6163 aluminum surface was found to obey Temkin's adsorption isotherm.
3. The protection efficiency increases with a decrease in temperature or an increase in the concentration of the studied compounds.
4. The compounds studied were found to act as mixed-type inhibitors.
5. The addition of KI, KSCN and KBr was found to increase the percentage inhibition due the synergistic effect.
6. The order of inhibition efficiency of all inhibitors as given by polarization measurements is in good agreement with that obtained from weight-loss measurements. This indicates the validity of the results obtained.
7. The order was explained on the basis of the chemical structure and adsorption active centers of the investigated compounds.

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Where,

Compound	X
a	Nitro, - NO <sub>2</sub>
b	Chloro, - Cl
c	Hydrogen, - H
d	Methyl, - CH <sub>3</sub>
e	Methoxy, - OCH <sub>3</sub>

Fig.1: Chemical structure of thiazolidinone derivatives

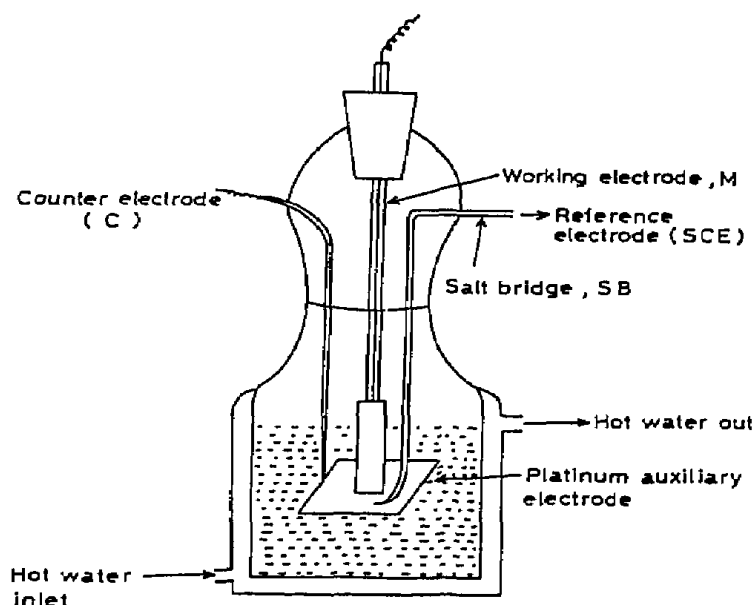


Fig.2: Polarization cell

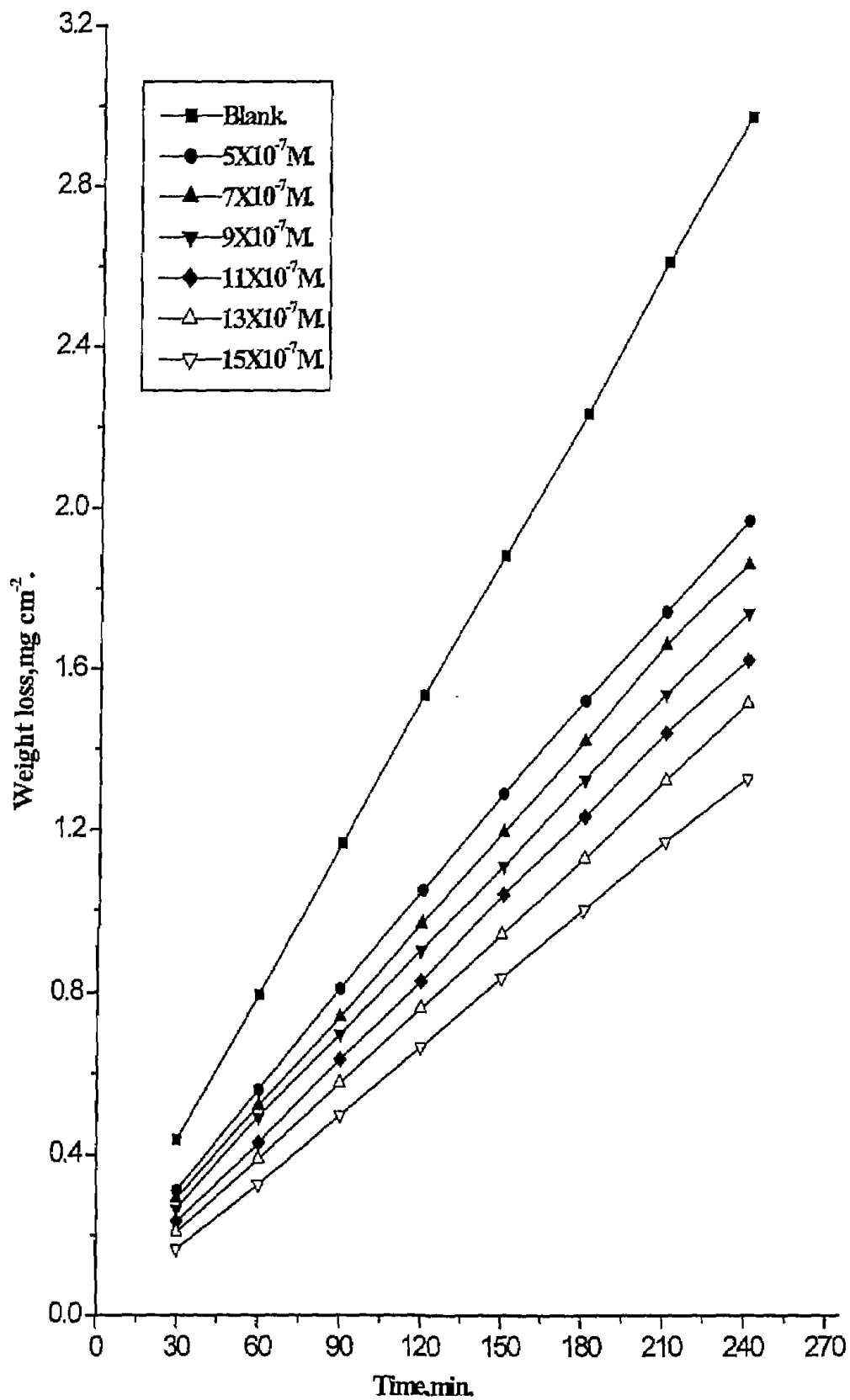


Fig. (3): Weight loss-time curves for the corrosion of 6163 aluminum in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of different concentrations of compound (e) at 30°C.



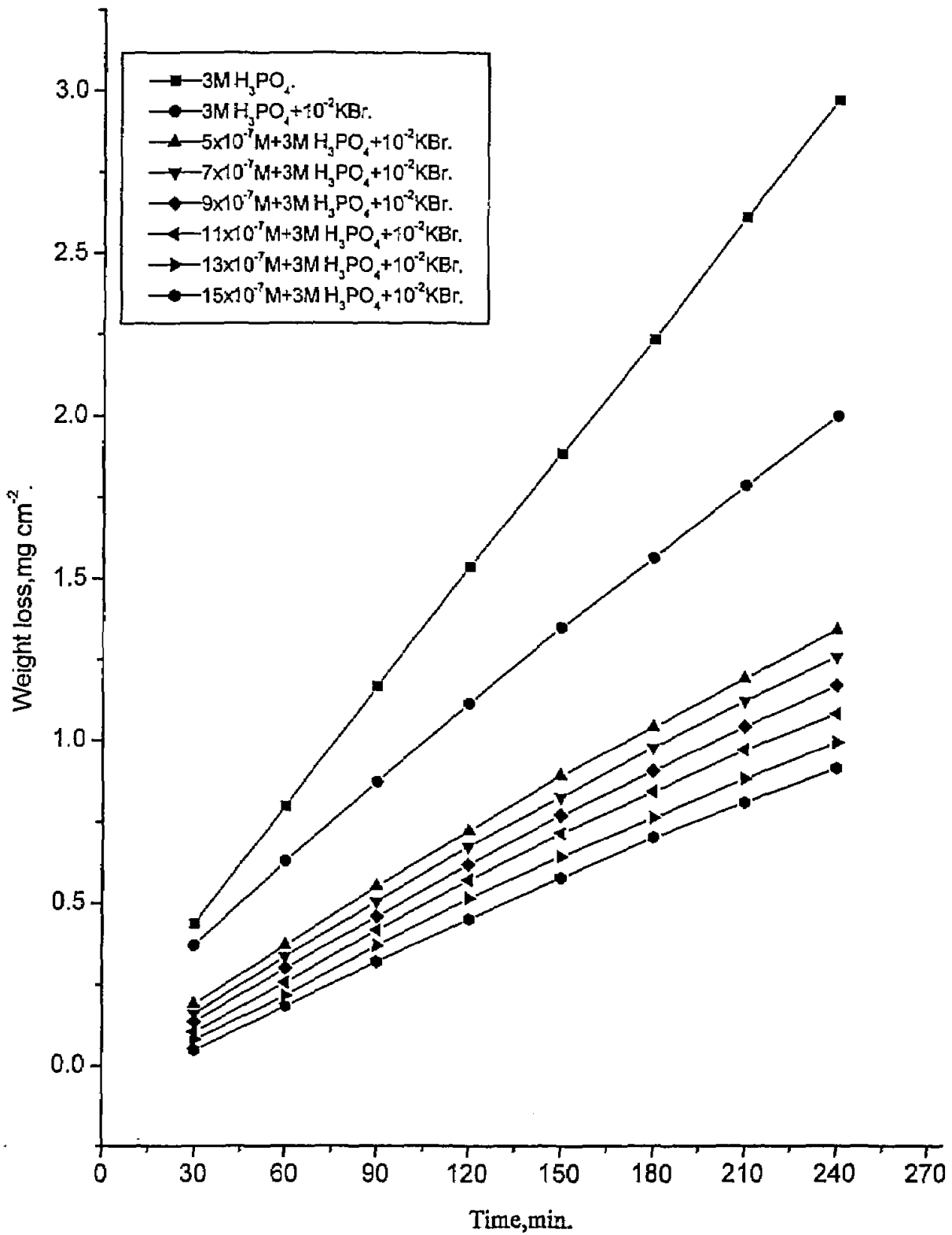


Fig. (4): Weight loss-time curves for 6163 aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of different concentrations of compound (e) without and with addition of 1x10<sup>-2</sup> M KBr at 30 °C.

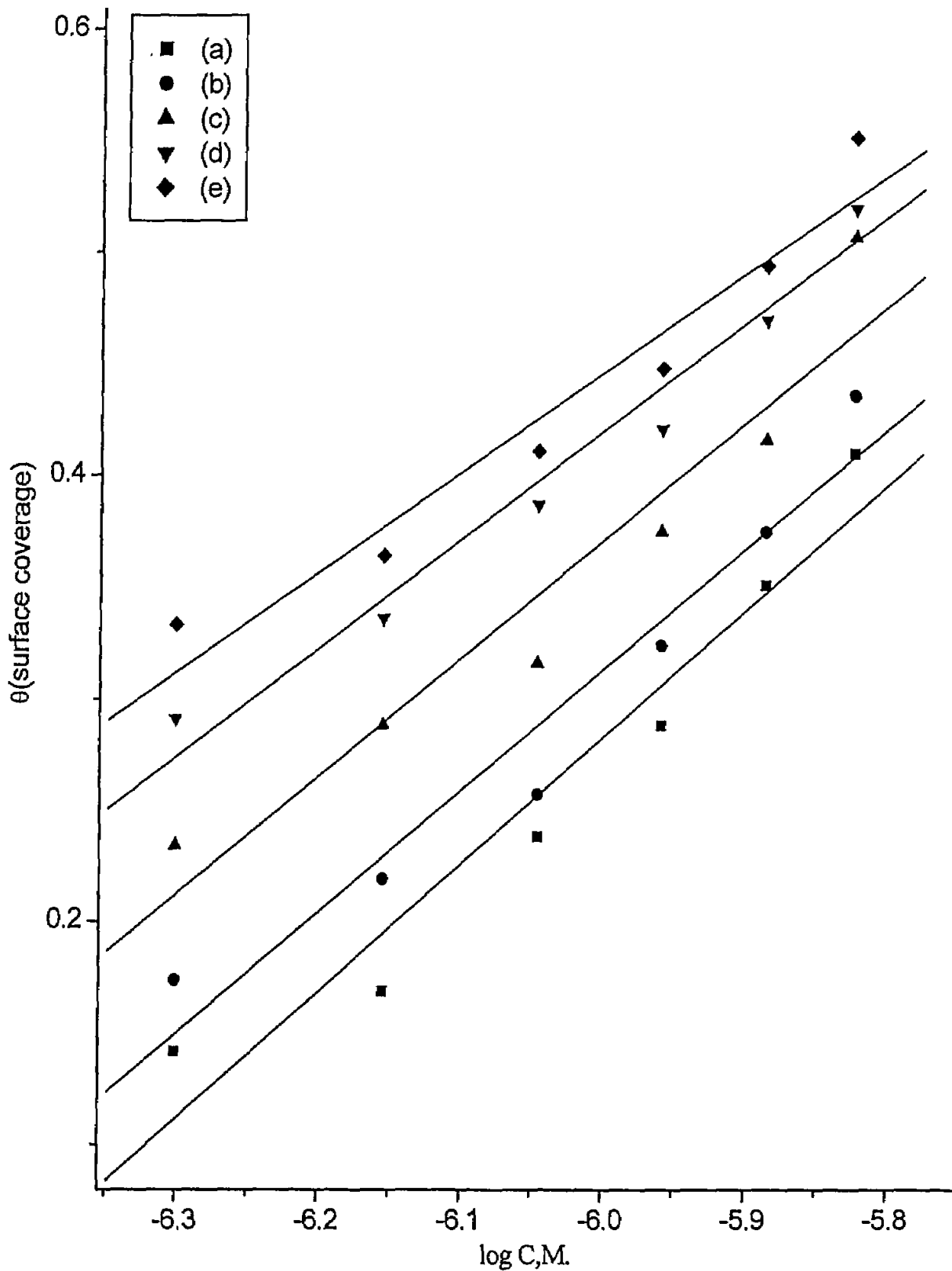


Fig. (5): Curve fitting of corrosion data for 6163 aluminum in 3M H<sub>3</sub>PO<sub>4</sub> in presence of 9x10<sup>-7</sup> M of thiazolidine derivatives to the Temkin' isotherm at 30°C.

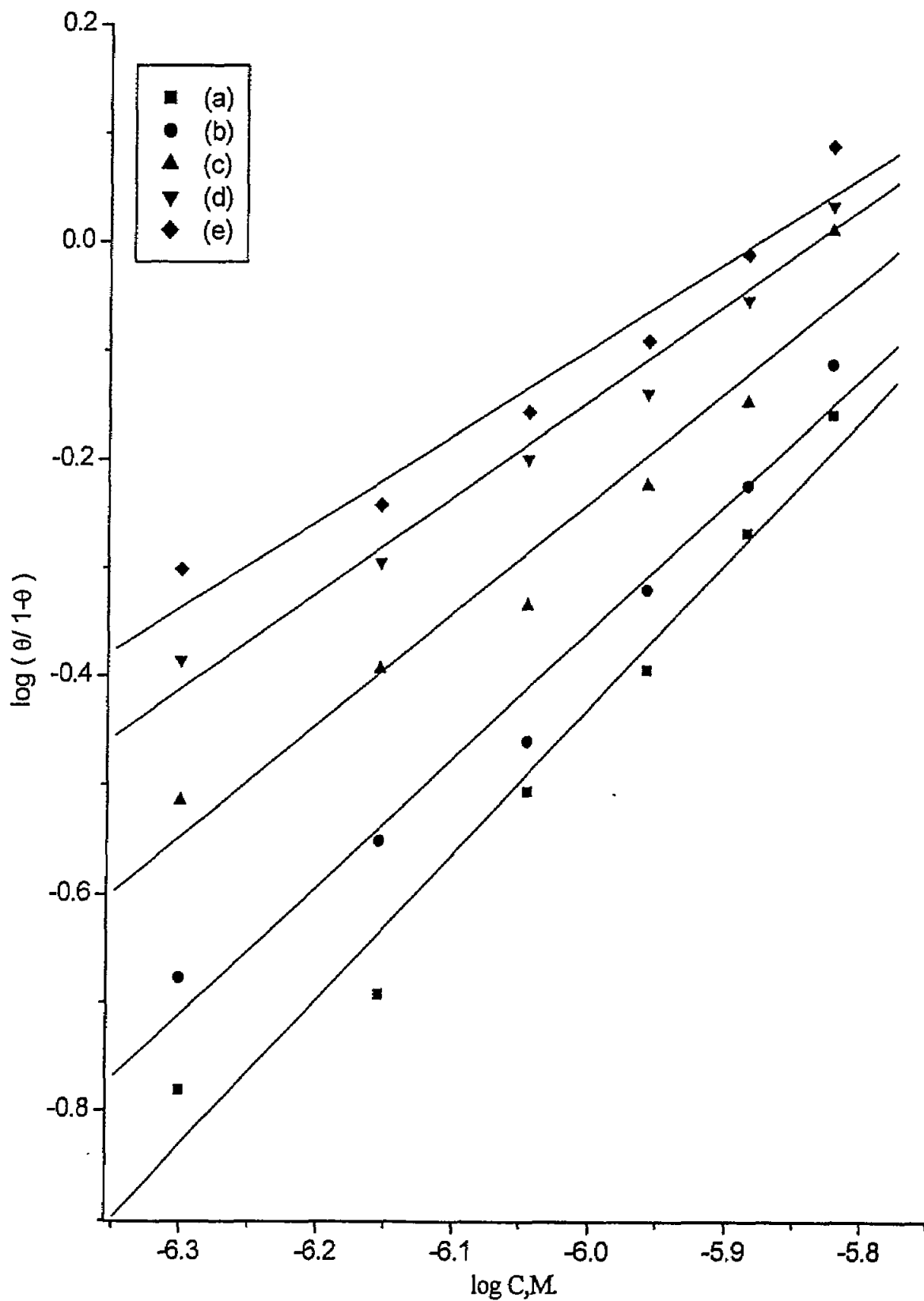


Fig. (6): Curves fitting of corrosion data for 6163 aluminum dissolution in 3M  $H_3PO_4$  in presence of  $9 \times 10^{-7} M$  of thiazolidine derivatives to the kinetic model at  $30^\circ C$ .

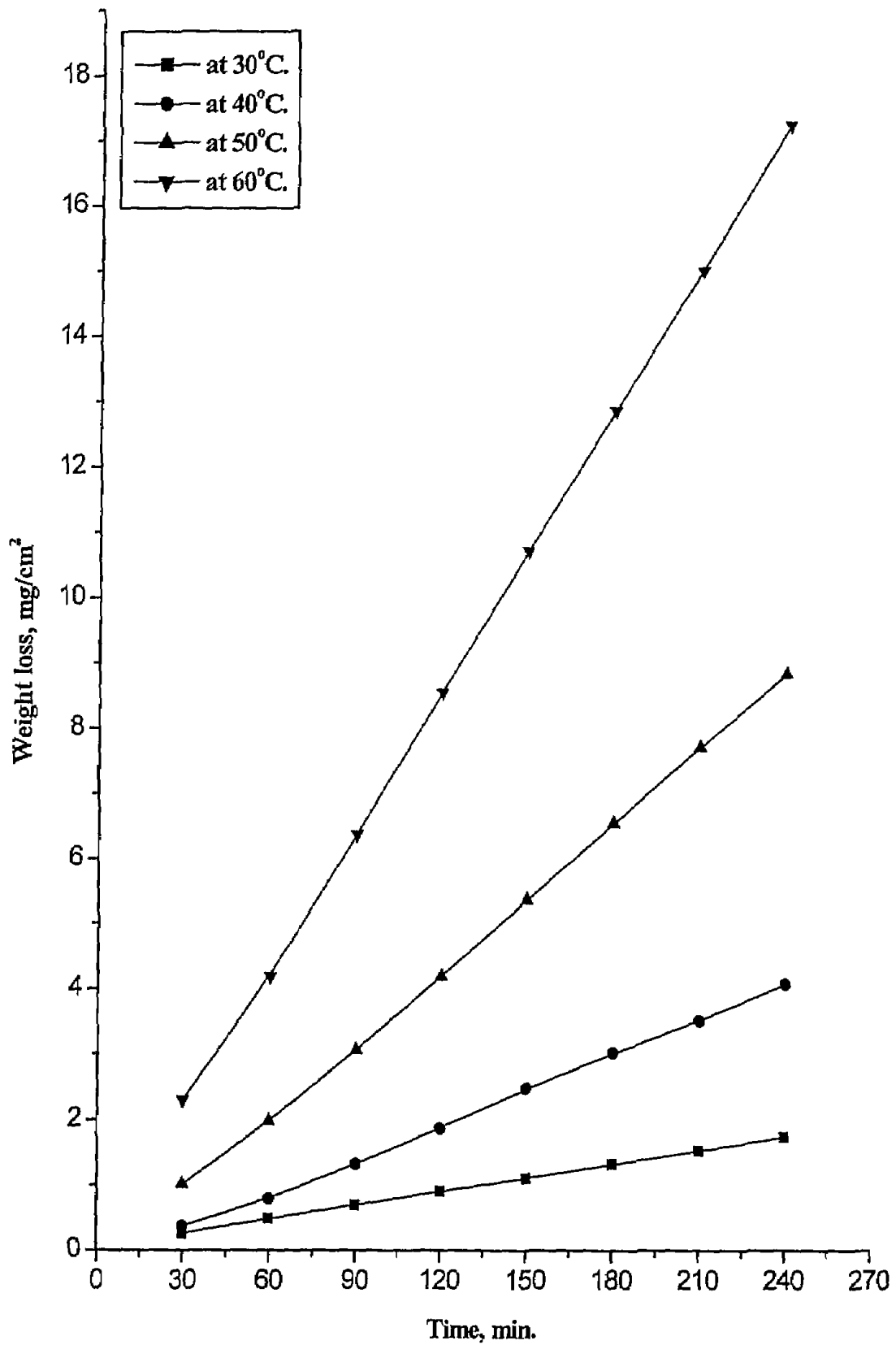


Fig. (7): Weight loss-time curves for the corrosion of 6163 aluminum in 3M H<sub>3</sub>PO<sub>4</sub> in the presence of 9x10<sup>-7</sup>M of compound (e) at different temperatures.

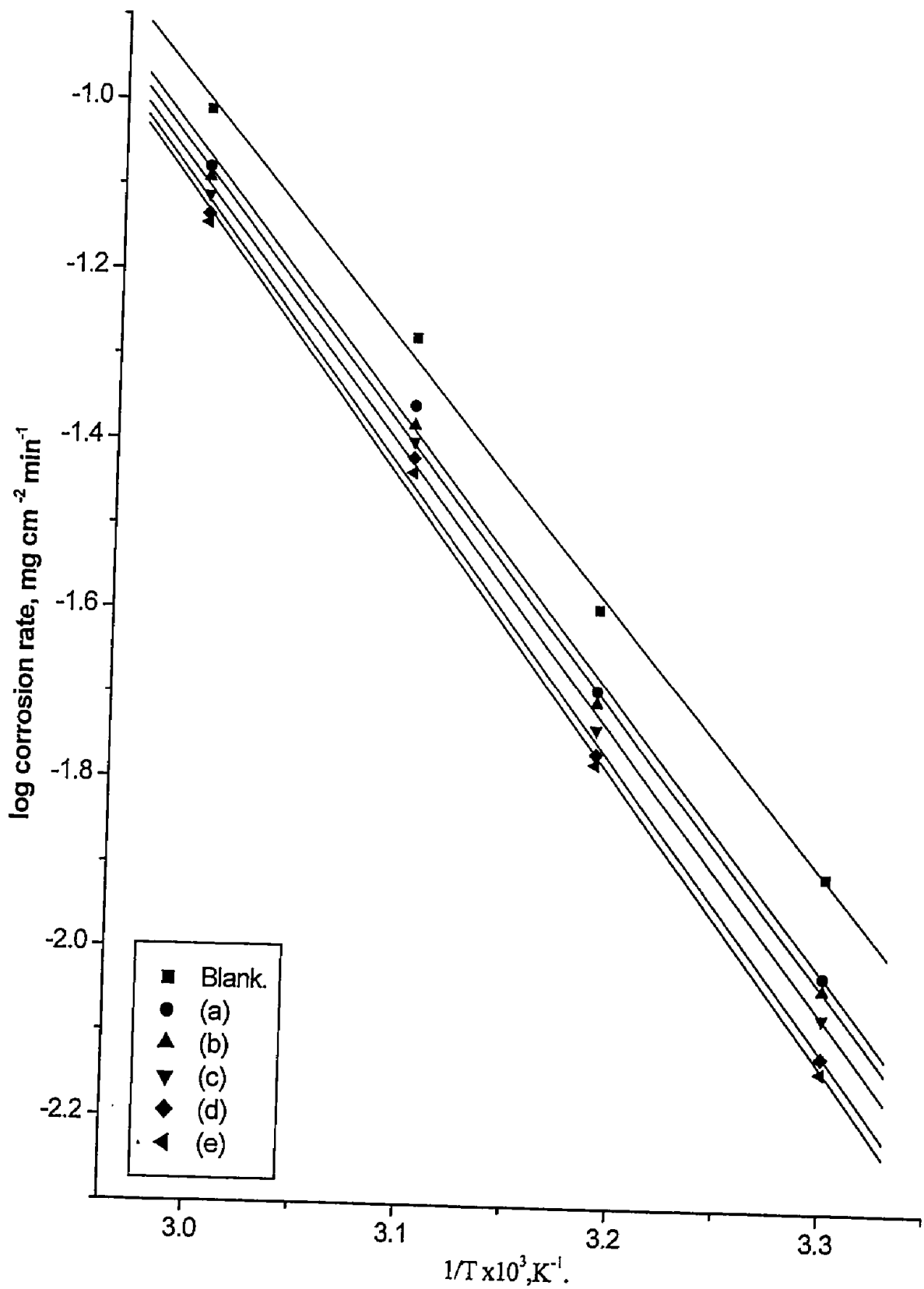


Fig. (8): Log corrosion rate-1/T curves for 6163 aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of 9x10<sup>-7</sup>M of thiazolidine derivatives.

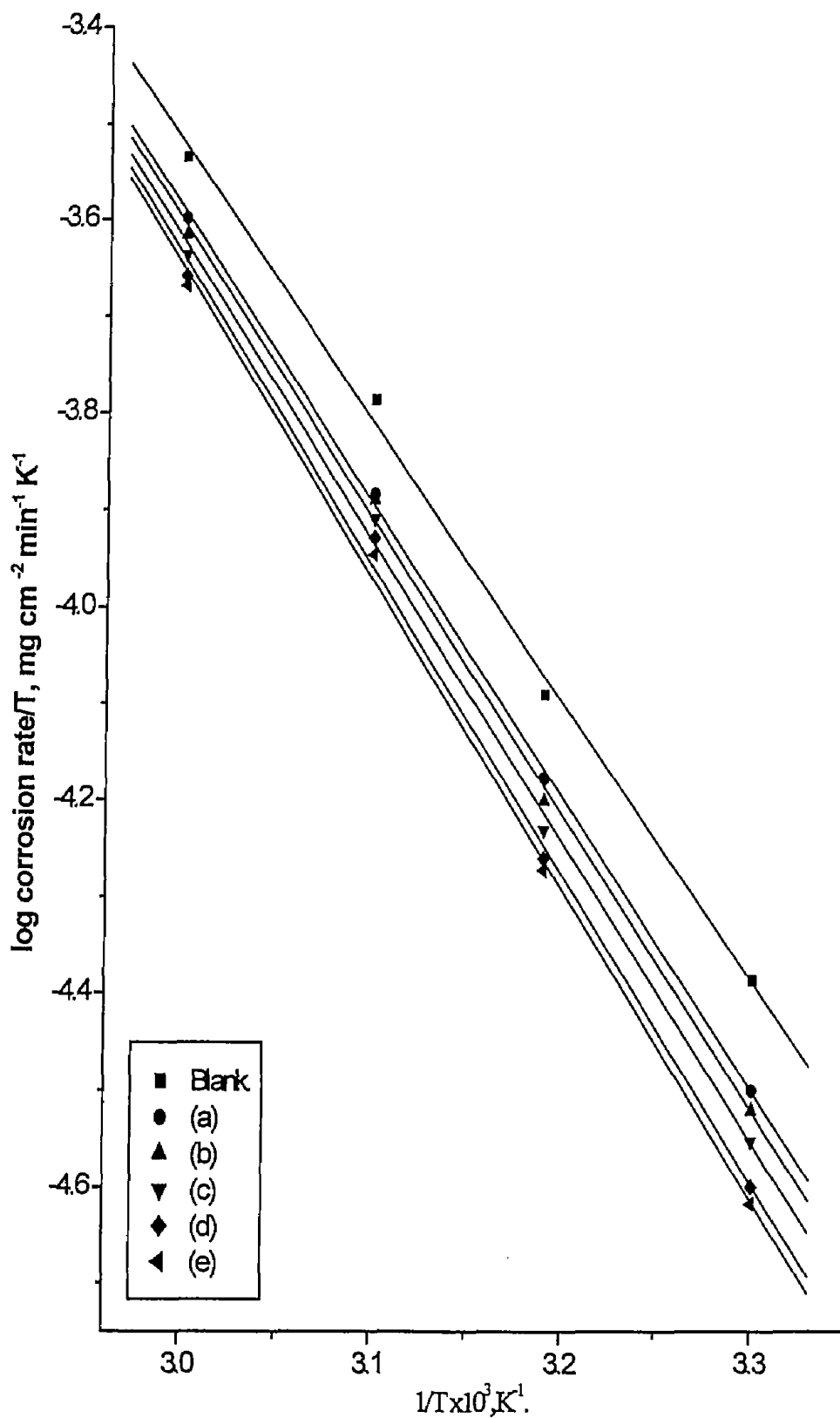


Fig. (9): Log (corrosion rate/T) -1/T curves for 6163 aluminum dissolution in 3M H<sub>3</sub>PO<sub>4</sub> in absence and presence of 9x10<sup>-7</sup>M of thiazolidine derivatives.

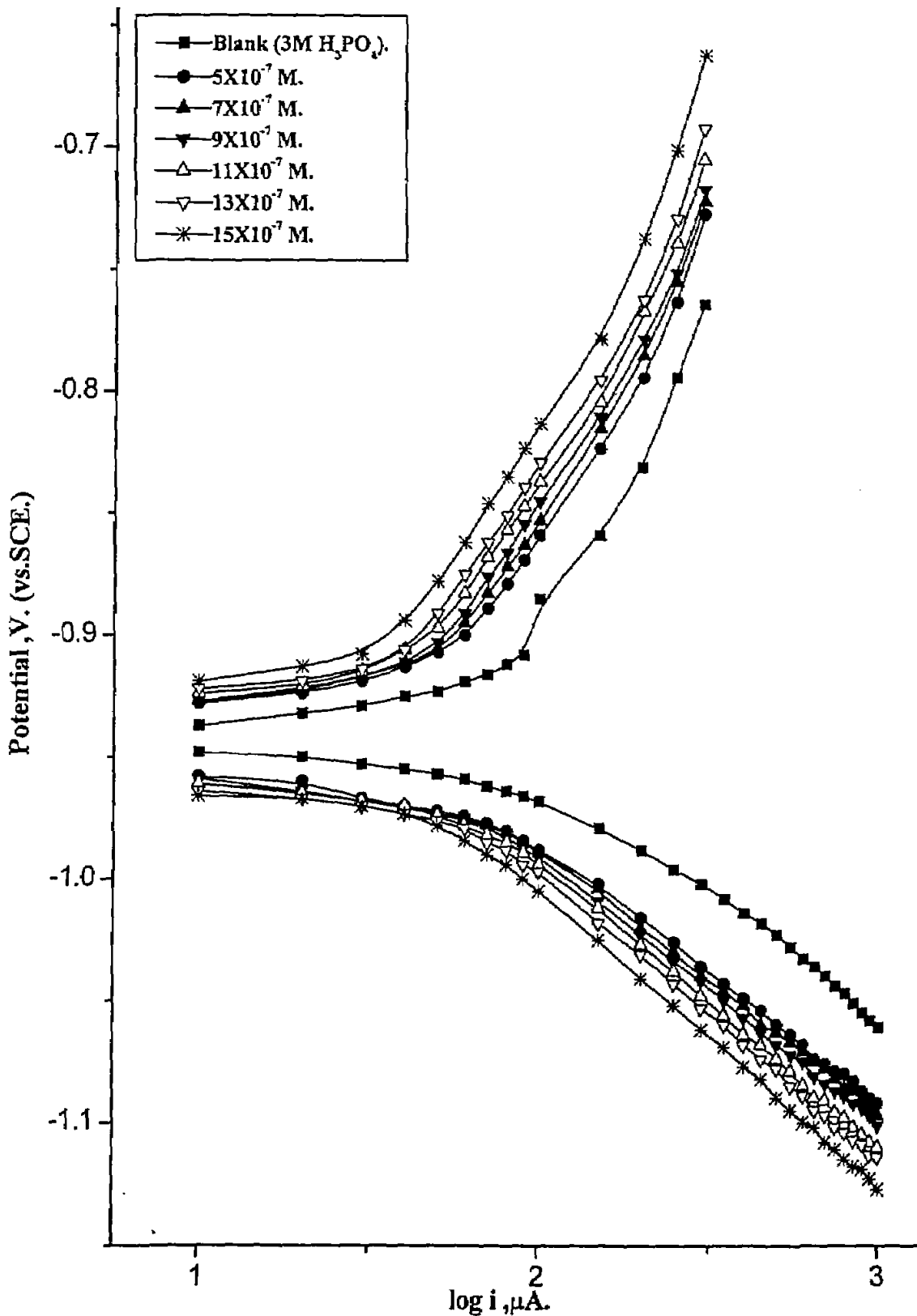


Fig. (10): Polarization curves for 6163 aluminum dissolution in 3M  $\text{H}_3\text{PO}_4$  in presence of different concentrations of compound (e) at 30 °C.

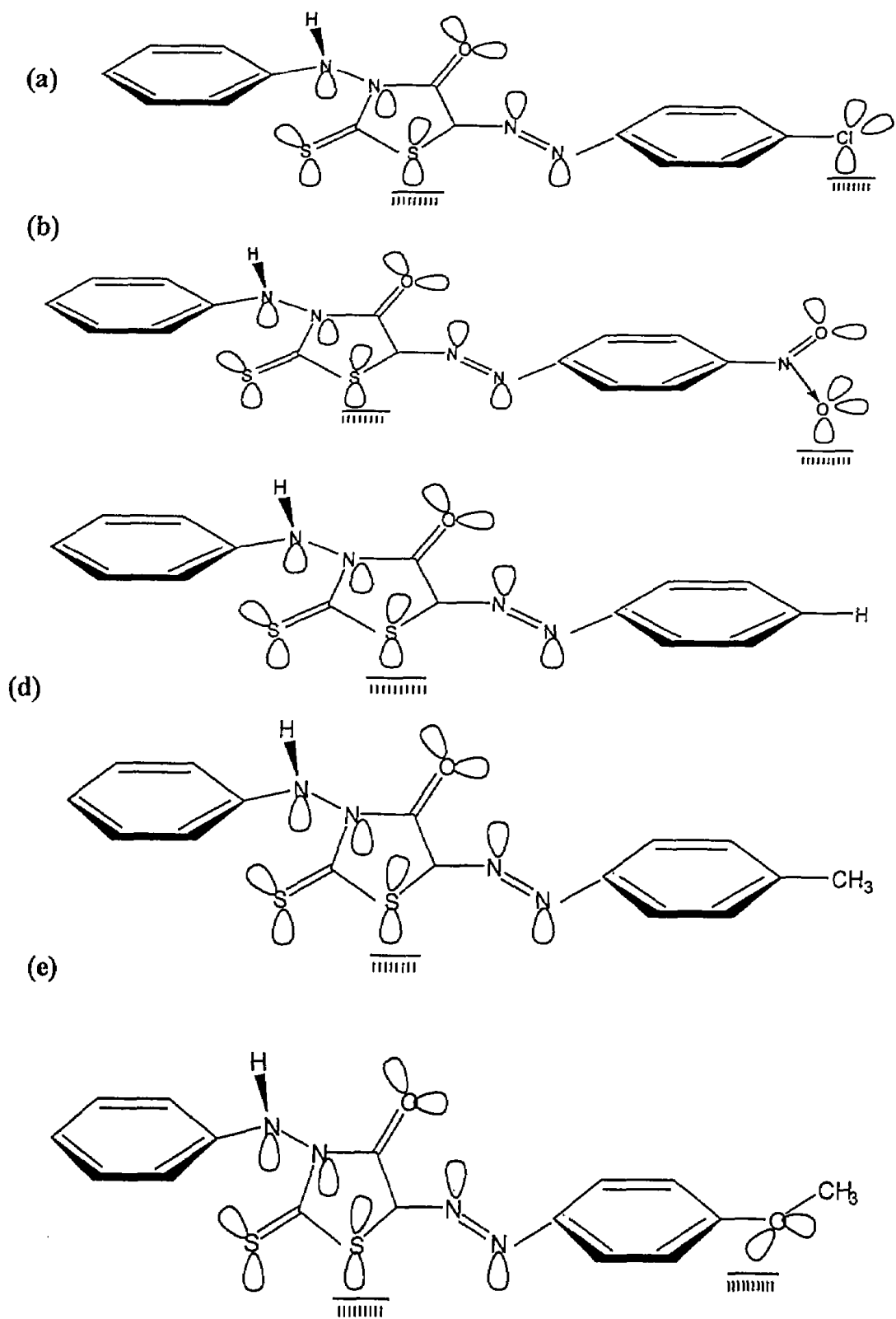


Fig.(11); Skeletal representation of the mode of adsorption of thiazolidinone derivatives.