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Coumarin Derivatives as Corrosion Inhibitors for Zinc in HCl Solutions

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Keywords: Coumarin, zinc, adsorption, corrosion inhibitors

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1. Introduction

Zinc and their alloys are exposed to attack by acids especially hydrochloric acid. For scale removal and cleaning surfaces with acidic solutions, it is become necessary to added corrosion inhibitors to minimize metal loss and reduce acid consumption. Several organic compounds containing nitrogen, oxygen and sulphur atoms are used to inhibit the corrosion of zinc in acidic solutions [1-10]. The inhibiting power of these compounds is attributed to the interaction between zinc surface and inhibitors molecules through their adsorption on the metal surface. The adsorption influenced by factors such as nature and surface charge on the metal, the type of aggressive media, the structure of the inhibitor, and the nature of its interaction with the metal surface [11].

The aim of this study is to investigate the effect of 4-coumarin derivatives inhibitors on the corrosion of zinc in HCl solution using weight loss method (chemical method) and galvanostatic polarization method (electrochemical method) at 303 K. Investigate the synergistic effect by addition of KI to the investigated 4-coumarin derivatives in 0.1M HCl solution. The effect of the temperature on the corrosion of Zn in free and inhibited acid solution was studied. Adsorption and activated thermodynamic parameters were computed.

2. Experimental methods

The zinc (BDH grade) used in this investigation has chemical composition listed in Table 1. For weight loss measurements, the reaction basin used in this method was a graduated glass vessel having a total volume of 100 ml. 100 ml of the test solution was employed in each experiment. The test pieces were 20 x 20 x 2 mm. 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.

Weight loss measurements were carried out as described elsewhere [12]. The percentage inhibition efficiency (% IE) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated using the following equations:

$$\%IE = [\frac{W_{add}}{1 - W_{free}}]x100 \quad (1)$$

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

where, W_{free} and W_{add} are the weight losses of Zn sample in free and inhibited acid solution, respectively.

For galvanostatic polarization measurements, a cylindrical rod embedded in araldite with exposed surface of 0.5 cm^2 was used. The electrode was polished with different grades emery paper, degreased with acetone and rinsed by distilled water. Galvanostatic polarization studies were carried out using zinc rod of the same compositions used in weight loss. E vs. log I curves were recorded at temperature 30 °C. A constant quantity of the test solution (100 ml) was taken in the polarization cell. Galvanostatic polarization studies were carried out using EG&G model 173 potentiostat/galvanostat. for accurate measurements of potential and current density. Three compartment cell with a saturated reference calomel electrode and a 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±1 °C by using ultra circulating thermostat.

Tab. 1: Chemical composition of zinc alloy.

Element	Pb	Fe	Cd	Cu	Zn
Weight %	0.001	0.002	0.001	0.003	rest

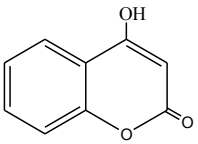
The percentage inhibition efficiency (% IE) was calculated from corrosion current density values using the equation

$$\%IE = [\frac{1 - I_{add}}{I_{free}}]x100 \quad (3)$$

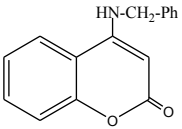
where, I_{free} and I_{add} are the corrosion current densities in absence and presence of inhibitors, respectively.

Chemical structure of coumarin derivatives

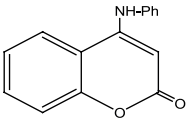
(a) 4-hydroxy - coumarin



(b) 4-benzyl amino-coumarin



(c) 4-phenyl amino-coumarin



3. Results and discussion

3.1. Weight - loss measurements

Figure 1 show the weight loss-time curves for zinc in 0.1M HCl solution in absence and presence of different concentrations of compound (b) as an example. Similar curves were also obtained for other two compounds. As shown from Figure 1, it is clear that, as the concentration of these derivatives increase, the weight loss of zinc samples are decreased. This means that the presences of these derivatives retard the corrosion of zinc in 0.1M HCl solution or in other words, these compounds act as inhibitors. The linear variation of weight loss with time in uninhibited and inhibited 0.1M HCl solution indicates that the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed on to the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

The percentage inhibition efficiencies (% IE) of these compounds were determined using the equation (1). The calculated values of % IE are given in Table 2, from the values of % IE, the order of the inhibition efficiencies of 4-coumarin derivatives decreased as following: (b) > (c) > (a). This order will be discussed later.

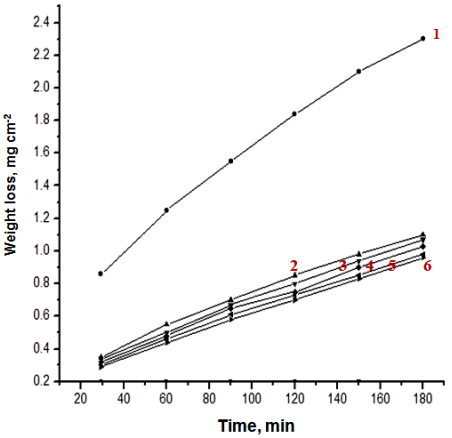


Fig. 1: Weight-loss vs. time curves for the dissolution of zinc in 0.1 M HCl in absence and presence of different concentrations of compound (b) at 30 °C.
1) Blank, 2) $3x10^{-6}$ M, 3) $5x10^{-6}$ M, 4) $7x10^{-6}$ M, 5) $9x10^{-6}$ M, 6) $11x10^{-6}$ M

Tab. 2: Inhibition efficiency obtained from weight loss of zinc in 0.1M HCl at different concentrations of the 4-coumarin derivatives after 180 min immersion at 30°C.

Conc., M	% Inhibition efficiency (% IE)		
	(a)	(b)	(c)
$1x10^{-6}$	54.0	56.0	52.6
$3x10^{-6}$	58.8	60.0	59.4
$5x10^{-6}$	60.6	68.6	62.0
$7x10^{-6}$	63.2	71.2	66.8
$9x10^{-6}$	65.8	74.8	69.6
$11x10^{-6}$	67.6	76.4	71.4

3.2. Synergistic effect of KI

The effect of KI, on the corrosion inhibition of zinc in 0.1M HCl solution in absence and presence

Tab. 3: Inhibition efficiency obtained from weight loss of zinc dissolution in 0.1 M HCl at different concentrations of the 4-coumarin derivatives with addtion of $1X10^{-2}$ M KI after 180 min immersion at 30°C.

Conc., M	% Inhibition efficiency (% IE)		
	(a)	(b)	(c)
$1x10^{-6}$	77.52	85.82	82.58
$3x10^{-6}$	80.92	87.28	85.79
$5x10^{-6}$	85.45	89.85	87.41
$7x10^{-6}$	97.78	91.55	89.54
$9x10^{-6}$	89.45	92.40	90.85
$9x10^{-6}$	90.57	94.12	92.28

of different concentrations of these additives was studied by the weight loss method. Similar curves were obtained to Figure 1 not shown. The percentage inhibition efficiency (% IE) for specific concentrations of KI ($1x10^{-2}$ M) in the presence of various concentrations of 4-coumarin derivatives is given in Table 3.

It is observed that % IE of the inhibitors increases by increasing the concentrations of 4-coumarin derivatives, also the order of inhibition efficiency increased as following: (b) > (c) > (a). The strong chemisorption of iodide ion on the metal surface is responsible for the synergistic effect of this ion leads to greater surface coverage and, therefore, greater inhibition.

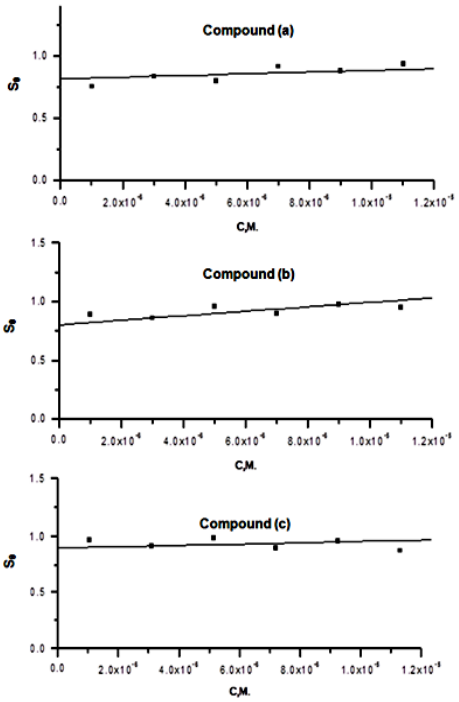


Fig. 2: Plots of synergism parameter (Sθ) vs. the concentration of 4-coumain derivatives for dissolution of zinc in 0.1 M HCl in presence of $1x10^{-2}$ M KI at 30 °C.

The synergistic inhibition effect was evaluated using a parameter, S_ϑ, obtained from the surface coverage values (θ) of the anion, cation and both.

Tab. 4: Synergism parameter (S_θ) for different concentrations of the 4-coumarin derivatives with addition of $1x10^{-2}$ M KI.

Corrosive medium	Synergism parameter (S_θ)						
	Conc., M	1×10^{-6}	3×10^{-6}	5×10^{-6}	7×10^{-6}	9×10^{-6}	11×10^{-6}
0.1M HCl	(a)	0.896	0.835	0.847	0.856	0.864	0.874
	(b)	0.955	0.868	0.902	0.915	0.926	0.950
	(c)	0.995	0.910	0.927	0.948	0.951	0.962

Aramaki and Hackerman [13] calculated the synergism parameter S_ϑ using the following equation

$$S_\vartheta = [\frac{1-\theta_{1+2}}{1-\theta'_{1+2}}] \quad (4)$$

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

θ1 = surface coverage by anion;

θ2 = surface coverage by cation;

θ'1+2 = measured surface coverage by both the anion and cation;

The synergism parameters was calculated from equation (4). The plot of the synergism parameter (Sθ) against various concentrations of 4-coumarin derivatives given in Figure 2 and the corresponding values are shown in Table 4. As can be seen from this Table, the values of Sθ are nearly equal to unity, which suggests that the enhanced inhibition efficiencies caused by the addition of KI to 4-coumarin derivatives is due mainly to the synergistic effect.

Synergistic adsorption is classified into two types plus a mixture of the two:

(i) specific co-adsorption of anions and cations, and

ii) ionic or physical overlap adsorption of cations over the anion covered zinc surface.

3.3. Adsorption Isotherm

Organic molecules like 4-coumarin molecules inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitution process between the inhibitor molecule in the aqueous phase I(aq) and the water molecules

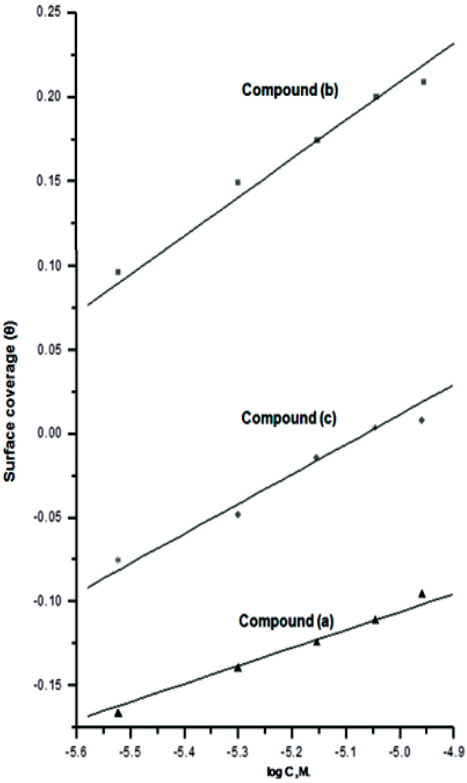


Fig. 3: Curve fitting of the corrosion data for zinc in 0.1 M HCl in presence of different concentrations of 4-coumain derivatives to the Temkin adsorption isotherm at 30 oC

adsorbed on the metal surface $H_2O(ads)$ [14, 15] according to the following equation

$$I_{(aq)} + xH_2O_{(ads)} \rightarrow I_{(ads)} + xH_2O_{(aq)} \quad (5)$$

where, x is 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.

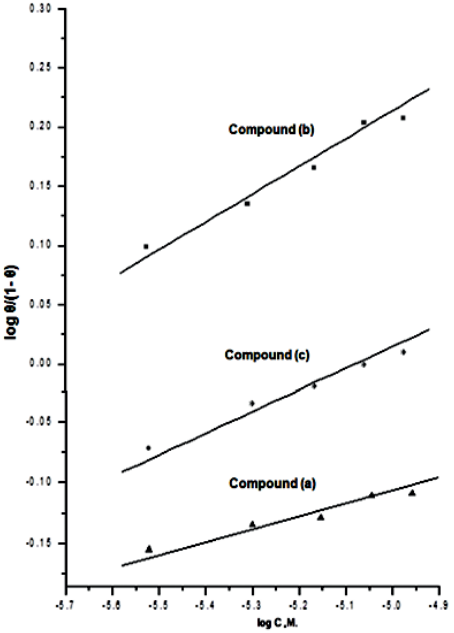


Fig. 4: Curve fitting of the corrosion data for zinc in 0.1 M HCl in presence of different concentrations of 4-coumarin derivatives to the kinetic model at 30 °C

Attempt were made to fit surface coverage (θ) values to various adsorption isotherms including Langmuir, Freundlich, Frumkin and Temkin. By far, the best results were obtained fitted Temkin isotherm according the following equation:

$$\ln K C = a\,\theta \qquad (6)$$

where, C is the inhibitor concentration in the bulk of the solution, a is the interaction parameter and K is the equilibrium constant of the adsorption process which is related to the standard free energy of adsorption ($\Delta G°_{ads.}$) by:

$$K = \frac{1}{55.5}\exp^{\frac{-\Delta G^0_{ads}}{RT}} \qquad (7)$$

where, R is the universal gas constant and T is the absolute temperature.

Plots of θ vs. log C (Temkin adsorption plots) for adsorption of 4-coumarin derivatives on the surface of zinc in 0.1M HCl acid at 30 °C is shown in Figure 3. The data gave straight lines indicating that Temkin's isotherm is valid for these systems. Temkin's isotherm is applied for ideal case

Tab. 5: Inhibitor binding constant(K), Free energy of binding ΔG_{ads}, number of active sites(1/y) and later interaction parameter (a) for 4-coumarin derivatives at 30°C.

Corrosive medium		Kinetic model			Temkin		
		1/y	K	$-\Delta G_{ads.}$, kJmol^{-1}	a	K	$-\Delta G_{ads.}$, kJmol^{-1}
0.1 M HCl	(a)	8.21	10144.70	30.24	20.70	101105.82	33.31
	(b)	4.25	798063.94	41.90	9.40	751790.95	42.25
	(C)	5.33	11663.54	38.80	17.50	115106.68	39.66

Tab. 6: Thermodynamic parameters for the adsorption of 4-coumarin derivatives in 0.1 M HCl on zinc surface.

Corrosive medium	inhibitors	Thermodynamic parameters		
		$-\Delta G_{ads.}$, kJmol $^{-1}$	$-\Delta S_{ads.}$, $Jmol^{-1}K^{-1}$	-Q, $kJmol^{-1}$
0.1 M HCl	(a)	33.31	29.86	22.61
	(b)	42.25	19.76	19.30
	(c)	39.66	22.09	19.65

of physical and chemical adsorption on a smooth surface with no interaction between the adsorbed molecules.

On the other hand, it is found that the kinetic-thermodynamic model of El Awady et al [16].

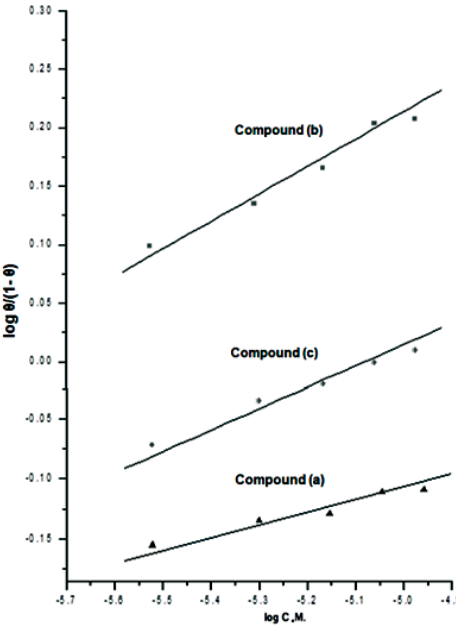


Fig. 5: Log θ/(1- θ) vs. 1/T plots of for the dissolution of zinc in 0.1 M HCl in presence of $11x10^{-6}$ M of 4-coumarin derivatives at 30 °C.

$$\log\frac{\theta}{1-\theta} = \log K' + y\log C \qquad (8)$$

is valid to operate the present adsorption data. The equilibrium constant of adsorption $K = K'^{(1/y)}$, where 1/y is the number of the surface active sites occupied by one 4-coumarin molecule and C is the bulk concentration of the inhibitor. Plotting log θ/(1-θ) against log C at 30 °C is given in Figure 4. Straight line relationships were obtained suggesting the validity of this model for all cases studied. The calculated values of 1/y, K and $\Delta G°_{ads.}$ are given in Table 5. Inspection of the data of these Tables shows that the large values of $\Delta G°_{ads.}$ and its negative sign, indicate that the adsorption of 4-coumarin compounds on the zinc 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 $\Delta G°_{ads.}$ obtained from El-Awady et al., model are comparable with those obtained from Temkin isotherms.

The entropies of adsorption $\Delta S°_{ads.}$ were calculated from the relation between $\Delta G°_{ads.}$ and T:

$$-\Delta S^0_{ads.} = \left(\frac{\partial \Delta G^0_{ads}}{\partial T}\right)p \qquad (9)$$

For calculating the values of heat of adsorption of the various inhibitors, plots of log (θ/1-θ) vs. 1/T. Figure 5. The heat of adsorption (Q) are cal-

culated from the slopes of these plots. The values of $\Delta S^\circ_{ads.}$ and Q are given in Table 6. From these results it may be generalized that the more efficient inhibitor has more negative $\Delta G^\circ_{ads.}$ value and less values of $\Delta S^\circ_{ads.}$ and Q. So that from the tabulated values of $\Delta G^\circ_{ads.}$ $\Delta S^\circ_{ads.}$ and Q the order of inhibition efficiencies is as following: (b) > (c) > (a). This trend will be interpreted latter.

3.4. Effect of Temperature

The effect of rising temperature from 30° to 55°C on the corrosion of zinc electrode in 0.1M HCl solution in the presence of $11x10^{-6}$ M of 4-coumarin derivatives was studied using weight-loss measurements. Similar curves to Figure 1 were obtained (not shown). As the temperature rises the dissolution rate of zinc increase and the percentage inhibition efficiency decrease. This behavior indicated that the adsorption of 4-coumarin derivatives on the zinc surface is physically adsorption.

Activation parameters for corrosion of zinc were calculated from Arrhenius-type equation [17, 18]

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

and transition-state equation:

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

where, A is the frequency factor, h is the Plank's constant, N is Avogadro's number and R is the universal gas constant. E_a is the apparent activation energy, ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation.

Figure 6 represents the relation between the logarithm of corrosion rate ($\log_{Rate}$) versus 1/T. The values of activation energy E_a can be calculated

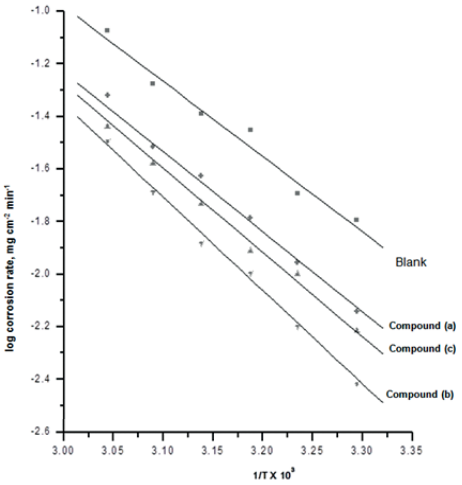


Fig. 6: Log corrosion rate vs. 1/T plots of for the dissolution of zinc in 0.1 M HCl in presence of $11x10^{-6}$ M of 4-coumarin derivatives at 30 °C.

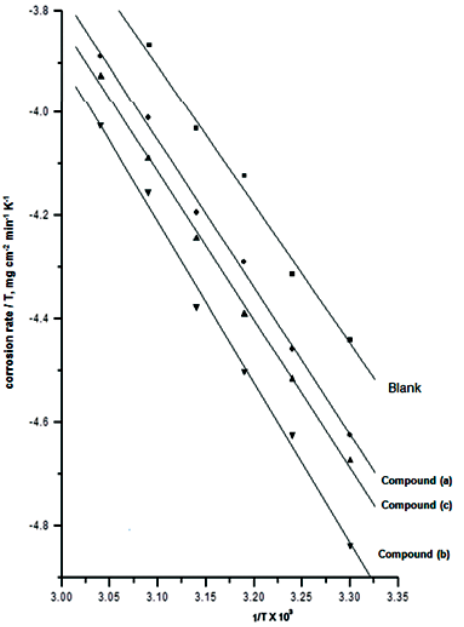


Fig.7: Log corrosion rate / T vs. 1/T plots of for the dissolution of zinc in 0.1 M HCl in presence of $11x10^{-6}$ M of 4-coumarin derivatives at 30 °C.

Tab. 7: Activation parameters of the dissolution of zinc in 0.1M HCl in the absence and presence of $11x10^{-6}$ M 4-coumarin derivatives.

Corrosive medium	inhibitors	Activation parameters		
		E_a, kJmol $^{-1}$	ΔH^*, kJmol^{-1}	$-\Delta S^*$, Jmol^{-1}k^{-1}
0.1 M HCl	Free acid	5.00	5.39	78.01
	(a)	7.17	5.08	67.80
	(b)	11.30	5. 22	53.21
	(c)	9.82	4.84	65.63

from the slope of the straight line in Figure 6. The values of E_a are listed in Table 7. It obvious that the presence of the studied compounds increased the values of E_a This indicate that the 4-coumarin derivatives acted as inhibitors through increasing the activation energy of metal dissolution by making a barrier to mass and charge transfer by their adsorption on metal surface [19].

Figure 7 shows a plot of log (Rate/T) vs. 1/T. A straight lines are obtained with slope equal to (-ΔH*/2.303R) and an intercepts of (log R/Nh + ΔS*/2.303R) from which the values of ΔH* and ΔS* are calculated and listed in Table 7.

The increasing in the temperature has a reverse relationship with the percentage efficiency this means that the adsorption of 4-coumarin derivatives on the metal surface is physically. 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.

The calculated values of the apparent activation energy, E_a, activation entropies, ΔS* and activation enthalpies, ΔH* are given in Table 7. The almost similar values of E_a 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 (11). This is further related to concentration, steric effects, metal surface characters. The order of the inhibition efficiencies of 4-coumarin derivative as gathered from the increase in E_a* and ΔH* values and decrease in ΔS* values is as following: (b) > (c) > (a)

3.5. Galvanostatic Polarization

The effect of 4-coumarin derivatives on the anodic and cathodic polarization curves of zinc electrode in 0.1M HCl solution at 30 °C was studied. The effect of increased concentrations

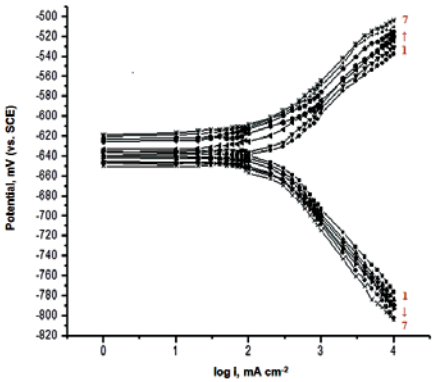


Fig. 8: Galvanostatic polarization curves for dissolution of zinc in 0.1 M HCl in absence and presence of different concentrations of compound (b) at 30 °C.
1) Blank, 2) $1x10^{-6}$ M, 3) $3x10^{-6}$ M, 4) $5x10^{-6}$ M, 5) $7x10^{-6}$ M, 6) $9x10^{-6}$ M, 7) $11x10^{-6}$ M

Tab. 8: Electrochemical parameters obtained from galvanostatic polarization of Zn in 0.1M HCl solution containing different concentrations of inhibitors at 30 ˚C.

Conc., M	$-E_{corr}$, mV, (SCE)	I_{corr}, uA cm^{-2}	β_a mV dec^{-1}	β_c mV dec^{-1}	% Inhibition
Compound (a)					
0.00 M	638	270	87	98	--
$1x10^{-6}$	626	118	75	92	56.29
$3x10^{-6}$	630	105	77	90	61.11
$5x10^{-6}$	632	95	73	89	64.81
$7x10^{-6}$	628	88	74	90	67.41
$9x10^{-6}$	625	80	72	88	70.37
$11x10^{-6}$	622	75	73	87	72.22
Compound (b)					
$1x10^{-6}$	648	98	60	80	63.70
$3x10^{-6}$	648	81	65	83	70.00
$5x10^{-6}$	631	76	66	77	71.85
$7x10^{-6}$	632	70	65	74	74.07
$9x10^{-6}$	623	63	61	73	76.66
$11x10^{-6}$	621	59	68	72	78.15
Compound (c)					
$1x10^{-6}$	630	73	73	85	60.00
$3x10^{-6}$	632	70	70	82	64.44
$5x10^{-6}$	633	71	71	83	67.41
$7x10^{-6}$	630	69	69	80	70.37
$9x10^{-6}$	628	68	68	78	72.22
$11x10^{-6}$	626	67	67	76	74.44

of compound (b) Figure 8 as an example. Similar curves were also obtained for other two compounds (not shown). The corrosion parameters such as the corrosion current density ($I_{corr.}$), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c) and inhibition efficiency (% IE) are calculated and given in Table 8.
Inspection of Table 8, it is clear that, the corrosion current density (I_{corr}) was determined by the intersection of the extrapolation anodic and cathodic Tafel lines with the steady state (corrosion) potential E_{corr}.

Inspection of Table 8 reveals that:

i) The increase in concentration of the additives showed that, the cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of 4-coumarin derivatives increased both cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively.

ii) E_{corr} was almost constant and the values of the corrosion current density ($I_{corr.}$) decreases with increasing the concentration of 4-coumarin derivatives indicating that the presence of these derivatives retards the dissolution of zinc in 0.1M HCl and the degree of inhibition depends on the concentration and type of the inhibitor present.

iii) The values of anodic (β_a) and cathodic (β_c) Tafel slopes are nearly constant indicating the inhibitor acted by blocking the reaction sites of the metal surface without changing the anodic and cathodic reaction mechanism [20]. However, the data suggested that these compounds act mainly as mixed-type inhibitors.

iv) The inhibition efficiencies of the three tested compounds increased in the following order (b) > (c) > (a).

3.6. Chemical Structure of Inhibitors and Corrosion Inhibition

Inhibition of corrosion of zinc in 0.1M HCl solution by the investigated 4-coumarin derivatives as measured by chemical and electrochemical measurements was found to depend on both the concentration and the nature of the inhibitor. The observed corrosion date in presence of the inhibitors, namely. The decrease of corrosion rate with increasing the concentration of the inhibitors. The linear variation of weight loss with time. The parallel shift in Tafel lines to higher potential values, and the decrease in corrosion inhibition efficiency with increasing temperature.

These observations indicate that the corrosion inhibition is due to adsorption of the inhibitors at the solution/interface [21, 22]. The nature of inhibitor interaction on the metal surface during corrosion inhibition can be explained in terms of its adsorption characteristics. However, inhibition efficiency of additive compounds depends on many factors, 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.

The inhibition efficiency of the three studied derivatives: (a), 4-hydroxy coumarin, (b), 4-benzyl amino coumarin, and (c), 4-phenyl amino coumarin, for zinc in 0.1M HCl solution decreases in the order: (b) > (c) > (a). The extent of inhibition depends on the molecular size of the molecule and the electron density (donating or with drawing) of the subsistent groups. Skeletal representation of the mode of adsorption of the tested derivatives is shown in Figure 9. Compound (b) exhibits excellent inhibition power due to: (i) its larger molecular size that may facilitate better surface coverage, (ii) its adsorption through two

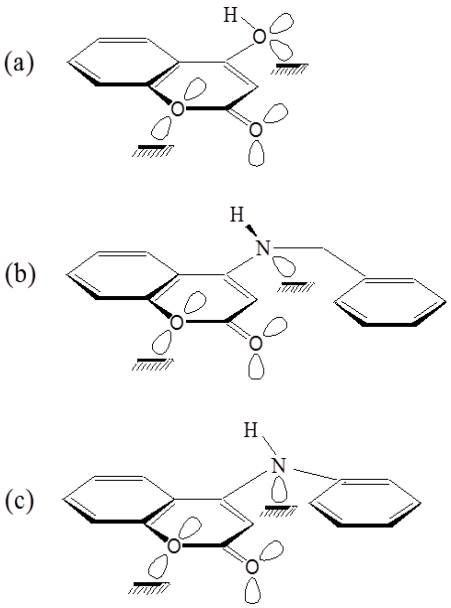


Fig. 9: Selected representation of the mode of adsorption of the tested derivatives.

active centers as shown from Figure 9, and (iii) the benzyl group which is highly electron releasing group which enhance the delocalized π-electrons on the active centers of the compound. Compound (c) comes after compound (b) in inhibition efficiency in spite of it has two active centers, because it has lesser molecular size. Compound (a) has the lowest inhibition efficiency; in spite of it has two active centers. This is because it has the lowest molecular size.

4. Conclusions

1. 4-coumarin derivatives act as inhibitors for the corrosion of zinc in 0.1M HCl solution.
2. The inhibition efficiencies of 4-coumarin derivatives is increase in concentration of these inhibitors but decreases with increase temperature as following (b) > (c) > (a).
3. Investigate the synergistic effect of some anions such as KI improve the values of the inhibition efficiency due to synergistic effect.
4. 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 zinc surface.
5. The desorption of the adsorbed molecules of the inhibitors from the zinc surface followed Temkin desorption isotherm.

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