

## The electrochemical behaviour of zinc electrode corrosion in hydrochloric acid solution

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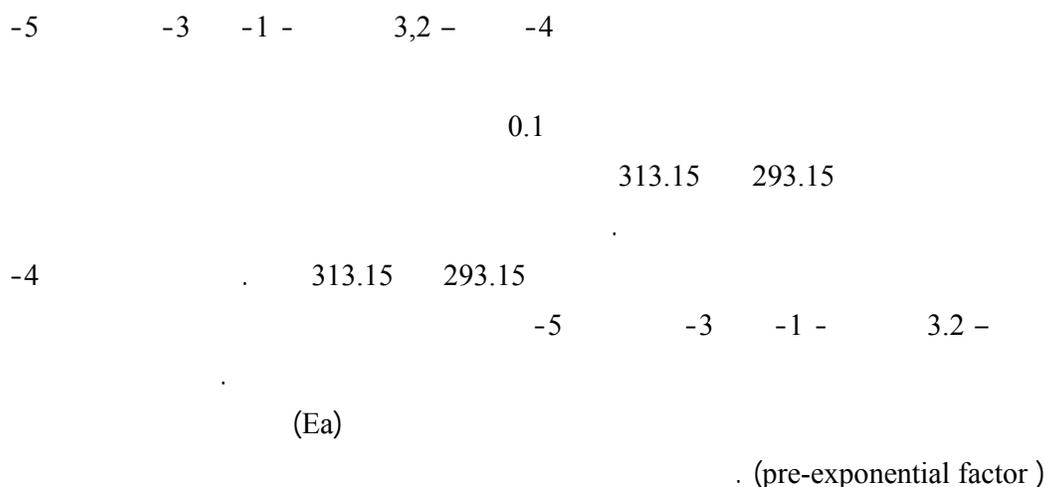
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### Abstract

The effect of 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one inhibitor at various concentration on the electrochemical corrosion of zinc electrode in 0.1 mol dm<sup>-3</sup> aerated hydrochloric acid solution at over temperatures range from 293.15 K to 313.15K was studied using Potentiostat technique . The percentage of protection efficiencies were decreased with increasing the various concentration of 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one inhibitor and with increased the temperatures . Thus , the accelerating effect of the extent of 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one inhibitor concentration was noticed when the corrosion current densities ( $i_{corr.}$ ) became higher as compared with corrosion current densities in the absence of inhibitor . The kinetics of the corrosion followed Arrhenius type rate equation . The compensation effect were discussed according to the linear relationship between the values of Log A and the corresponding values of  $E_a$  . Furthermore , The values of the thermodynamics quantities (  $\Delta G$  ,  $\Delta H$  ,  $\Delta S$  ) were estimated and discussed to enhanced the corrosion inhibition process .



## Introduction

The corrosion problems are translated in great economic losses for the industry and one of the most efficient alternatives to protect metals or alloys of this phenomenon, is the use of substances that being adsorbed on the metallic surfaces, slow down the cathodic reaction as well as the anodic process of dissolution of the metal<sup>(1)</sup>. Acid solutions are widely used for the removal of undesirable scale and rust in many industrial processes.

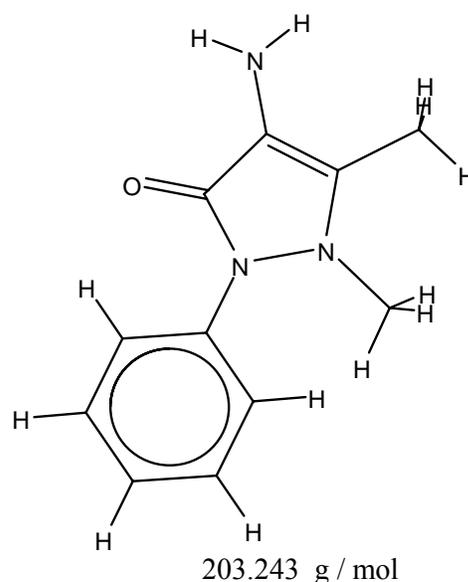
Examples of these are acid cleaning of boilers, pickling of metals and scale removal. Inhibitors are generally used in these processes to control metal dissolution as well as consumption of the acid<sup>(2-4)</sup>. Organic compounds are widely used in industry for preventing corrosion in acidic environments. The corrosion inhibiting property of these compounds is mainly decided by their molecular structure<sup>(5-8)</sup>. Because of the wide spread use of zinc, the study of its corrosion has turned to be an outstanding subject in corrosion with the industry of today<sup>(9)</sup>. One effective method to slow down the corrosion process of zinc is alloying with small amounts of mercury. However, from the ecological view the use of toxic mercury is harmful. Insignificant amounts of other metals such as Al, Pb, In, Bi can be used to prevent the corrosion of zinc<sup>(10)</sup>. Another effective method to solve the problem of zinc corrosion is to use organic inhibitors<sup>(11-13)</sup>. Fouda, Bianchi and Evans have explained the corrosion of zinc in HCl<sup>(9,14-15)</sup>. Among nitrogen containing compounds; quinoline, aniline and ephedrine, narcontire, brucine, strychnine<sup>(16-17)</sup> have shown good inhibition towards zinc in acidic medium. Quinine sulphate, piperazine, caffeine, barbitone and pyridine derivatives have been

investigated as corrosion inhibitors for aluminum and zinc in acidic medium<sup>(18-19)</sup>. In the present work, the influence of addition of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one inhibitor on the electrochemical behaviour of zinc electrode in 0.1 HCl mol dm<sup>-3</sup> was investigated by electrochemical technique such as potentiostatic polarization. The effects of temperature were also determined and the activation parameters that govern zinc electrode corrosion in acidic media were evaluated. Attention was extended to investigate their surface and thermodynamics properties.

## Experimental details

### Materials

The molecular structure and molecular weight of inhibitor for this study is given in following form:



The effects of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one or "Ampyrone" on the corrosion rate of zinc electrode in aerated 0.1 mol dm<sup>-3</sup> were studied to investigate the mechanism of inhibition. Hydrochloric acid, BDH analar grade was used for the preparation of the solutions. The 4-

amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one compound was analar grade chemicals which has been obtained from BDH .

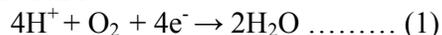
#### Method & Procedure.

Experiments were carried out using pure zinc plate (99.99 percent) which has obtained from BDH as the electrode material . The plate samples were mounted in Teflon , and had a surface area of  $1\text{cm}^2$  . The exposed surface was polished with a sequence of emery papers of different grads , polished to mirror finish by aqueous alumina suspensions with particles size decreasing down to  $0.05\ \mu\text{m}$  on the soft cloth and washed with double distilled water . After that , degreased by hot benzene and acetone . A 1000 ml of the test solution was transferred to the clean corrosion cell . the electrode was immersed 20 min in the electrolyte solution until a steady free corrosion potential as reached ( steady state open – circuit potential  $E_{ocp}$  ) . The potentials were with measured with reference to a saturated calomel electrode (SCE) , which a luggin probe positioned close to the electrode surface to minimize the Ohmic potential drop <sup>(20)</sup> connected to a potentiostatic ( type : MLab 2 – channel : Max. current per channel  $\pm 100\text{mA}$  ; Max. CE voltage  $\pm 20\ \text{V}$  ; current ranges 7 ; current resolution  $100\text{pA}$  ; interfaces ; IRs 232 ; potential accuracy  $\pm 1\text{mV}$  , Made in Germany . which has obtained from the BANK company , with software MLab Sci . The platinum electrode was used as an auxiliary electrode . Platinum auxiliary electrode was used in the experiments due to its large surface area and high catalytic activity <sup>(21,22)</sup> . The temperature of the solution was brought to the desired value by immersing the test cell in a controlled temperature water bath with a precision of  $\pm 1^\circ\text{C}$  , a temperature regular called Temp-unit , type

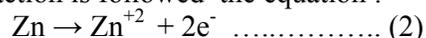
HAAKE , was used . Details of the polarization cell , techniques procedure and electrodes are found in elsewhere <sup>(23,24)</sup> . inhibitor

#### **Results and discussion**

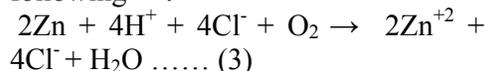
Figures (1-3) show the anodic and cathodic polarization curves recorded on zinc electrode in  $0.1\ \text{mol dm}^{-3}$  aerated HCl without and with at various concentrations of 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one inhibitor or " inhibitor I " at 20 , 30 and 40 K , respectively . The cathodic polarization curves display a current plateau from  $-650\text{mV}$  to  $-500\text{mV}$  which may be attributed to the diffusion controlled reduction of dissolved oxygen . According to Zhang<sup>(25)</sup> , the cathodic corrosion reaction in an aerated acidic chloride solution is :



The anodic process of corrosion reaction is followed the equation :



Thus , the total corrosion reaction of zinc in acidic chloride solution is as following<sup>(25)</sup> :



In the case of inhibitor I at concentration  $7.87 \times 10^{-5}\ \text{mol dm}^{-3}$  , not negligible difference were found between the curves of uninhibited and inhibited aerated solutions . it's cathodic currents were about one order of magnitude higher than these for the inhibitor – free solutions , figure (3) . At higher concentrations accelerated both cathodic and anodic reactions , and consequently stimulated corrosion . On the contrary , the inhibitor I at initial concentration hindered the acid attack at the zinc electrode . It's presence caused the anodic and cathodic polarization curves gave rise to parallel Tafel lines indicating that the cathodic and anodic reaction is activation controlled .

Thus, the electrical field of double layer increases the polarization. This result indicated that exhibited both cathodic and anodic inhibition effect (figure 2). This observation was indicative of the mixed – type control and refer to act as a mixed – type inhibition in 0.1 mol dm<sup>-3</sup> aerated HCl solution. Tafel lines not equal slopes were obtained as can be seen from table (1),  $b_c > b_a$ . This indicates that adsorbed molecules of inhibitor effect on the mechanism of either zinc electrode dissolution or cathodic corrosion reaction<sup>(26,27,28)</sup>. The corrosion current density ( $i_{corr}$ ) were determined by extrapolation of the cathodic Tafel lines and anodic Tafel lines to the corrosion potential ( $E_{corr}$ ). The calculated percentage inhibition efficiencies<sup>(29)</sup> (%P) is defined as:

$$\% P = i_{corr} - i_{corr (inh.)} / i_{corr} \dots\dots(4)$$

where  $i_{corr}$  and  $i_{corr (inh.)}$  are the corrosion current density values without and with inhibitor, respectively. Positive values of P% indicate corrosion inhibition while a negative values indicate increased corrosion. The analysis of these data shows that under cathodic and anodic polarization, the extent of concentration inhibitor I increased the corrosion current density. An increase in the cathodic and anodic currents without noticeable change in the corrosion potential with respect to the uninhibited solution was observed; table (1). Thus, %P values were found to negative, showing that the corrosion of the zinc electrode is accelerated in 0.1 mol dm<sup>-3</sup> aerated HCl. These results indicated that extent of concentration have a catalytic effect, both on the cathodic reaction rate as well as on zinc electrode dissolution, as this behaviour is documented in literatures<sup>(23,30-31)</sup>. On the contrary, the addition of inhibitor I in at 3.93×10<sup>-6</sup> mol dm<sup>-3</sup> decreased corrosion current density, table (1).

Consequently, inhibitor I inhibit the corrosion of zinc electrode in 0.1 mol dm<sup>-3</sup> aerated HCl and reaches a maximum value of protection efficiency p%, at 25<sup>o</sup>C in concentration 3.93×10<sup>-6</sup> mol dm<sup>-3</sup>; the corresponding efficiency value is 85%. The acceleration of corrosion process by inhibitor I at extent of concentration may be attributed to the following factors: the lowering of overpotential for the cathodic process, stimulation through preferential paths of partial electrochemical reactions in corrosion processes and stimulation caused by inhibitor participation in the metal dissolution process<sup>(32)</sup>. Furthermore, the acceleration of corrosion in the presence of organic compounds is related to the oxidative propensity of the surface chelates. It take place until the chelate is adsorbed. If charge transfer comes about with desorption of the complex ion and the additive will undoubtedly act as stimulator or accelerator<sup>(31)</sup>. Unlike the inhibitor I at 3.93×10<sup>-6</sup> mol dm<sup>-3</sup>, the adsorption on the zinc electrode surface can occur either directly on the basis of donor-acceptor interactions between the 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one inhibitor and the vacant d-orbitals of zinc surface atom or interaction of inhibitor with already adsorbed chloride ions as proposed by Lebrini and Lagrenee<sup>(31,32)</sup>.

Temperature can affect on the zinc electrode corrosion in the acidic media in the presence and absence of inhibitor I. Generally, the corrosion rate increases with the rise of the temperature. To determine the activation energy of the corrosion process, electrochemical measurements are taken at various temperature (293.15-313.15)K in the absence and presence of inhibitor I at various concentrations. The corresponding results are given in

table (1) . It is clear that the increase of corrosion current density is more pronounced with the rise of temperature for the uninhibited solution . In the presence of the 4-amino-2,3dimethyl-1-phenyl 3-pyrazoline 5-one molecules , P% is reduced even at high temperature . P% passed from (85 to -84)% when temperature rises from (293.15-313.15)K at various concentrations . It is clear that the efficiency of the inhibitor I depends on the temperature and decreases with the rise of temperature from (293.15-313.15)K . This effect is due to desorption of some adsorbed inhibitor molecules from the zinc electrode surface<sup>(36-40)</sup> . The rate of the zinc electrode corrosion increased with increasing temperatures from (293.15-313.15)K , the behaviour may be described by Arrhenius equation<sup>(23)</sup>

$$\text{rate} = A \exp^{-E_a/RT} \dots\dots\dots (5)$$

where A and  $E_a$  are the pre-exponential factor and energy of activation , respectively . The value of rate at any temperature was taken to be proportional to the corrosion current density ( $i_{\text{corr}}$ ) . The values of  $E_a$  were derived from the slopes of the  $\log i_{\text{corr}}$  versus  $1/T$  plots of figure (4) , while those A were obtained from intercepts of the such plots at  $1/T = 0$  ; values of A , expressed in term of  $\text{Acm}^{-2}$  , and have then converted into molecules per  $\text{cm}^{-2}$  per second<sup>(41)</sup> . Table (2) show the resulting values of  $E_a$  and A for the corrosion of the zinc electrode in aerated acidic solution in the absence and the presence of inhibitor I . The calculated values of  $E_a$  are  $82.86 \text{ kJ mol}^{-1}$  in uninhibited solution and  $25.9 \text{ kJ mol}^{-1}$  at  $3.93 \times 10^{-6} \text{ mol dm}^{-3}$  concentration . thus , the  $E_a$  values are practically changed in the absence and the presence of inhibitor I . According to Oguzie and another authors<sup>(42,43)</sup> , lowered activation energy in inhibited system compared to

the uninhibited is indicative of chemisorption possibly , because some energy is used up in chemical reaction . Also , the value of  $E_a$  in the presence of inhibitor I at  $7.87 \times 10^{-5} \text{ mol dm}^{-3}$  is higher than from the uninhibited acid solution . The result agreed with of previous studies in acidic solution<sup>(44,45)</sup> . The increase of  $E_a$  indicates the physical adsorption or weak chemical bonding between inhibitor I molecules and the zinc electrode surface<sup>(44)</sup> . According to equation (5) , it can be seen that the lower A lead to the lower corrosion current density . For the present study , the results of pre-exponential factor are good agreement . Furthermore , The result of figure (5) indicate the existence of a linear relationship between the values of Log A and the corresponding values of  $E_a$  with  $R^2 = 0.99$  which may be expressed as<sup>(46)</sup>  $\log A = mE_a + I \dots\dots (6)$  , where m and I are respectively the slope and intercept of the plot in figure (5) . such a behaviour is referred to as compensation effect , which describes the kinetics of a great number of catalytic and tarnishing reactions on the metal<sup>(23)</sup> . Equation (6) indicates the simultaneous increase or decrease  $E_a$  and Log A for a system tend to compensate from the standpoint of the reaction rate . A number of interpretations<sup>(47)</sup> have been offered for the phenomenon of the compensation effect in surface reaction , among which the effect could be ascribed to the presence of energetically heterogeneous reaction sites on the electrode surface , which suffered corrosion in the electrolytic solution . Thus , an increase in the Log A at constant  $E_a$  implies a higher rate , while simultaneous increase in  $E_a$  and Log A therefore tend to compensate from the standpoint of the corrosion rate . when such a compensation operates , it is possible for striking

variations in  $E_a$  and  $\log A$  through a series of surface sites on the electrode surface of zinc to yield a small variation in reactivity.

When a zinc electrode undergoes corrosion, the work done " the free energy change of the corrosion process " is expressed in terms of the potential difference " corrosion potential,  $E_{\text{corr}}$ " and the charge transported by the well-known equation<sup>(23)</sup>

$$\Delta G = -nFE_{\text{corr}} \dots (7)$$

where  $F$  is the Faraday constant which represents the charge transported by one mole of electrode and has the value of 96494 Coulombs per mole. The potential  $E$  is converted to Volt and  $n$  is the number of electrodes transferred in the corrosion reaction. A negative sign is necessary to indicate the conventional assignment of negative charge of electrons and since  $n$  and  $F$  are positive quantities, this leads to positive measured potential when the reaction is spontaneous. Furthermore, the equation (7) showed the energy change is directly measurable from electrochemical potential determination. From the value of  $\Delta G$  at a range of temperature (293.15-313.15)K, the change in the entropy  $\Delta S$  of corrosion process and change in the enthalpy of corrosion zinc electrode reaction could be derived according to the well-known thermodynamic relation by fitting method<sup>(48)</sup>

$$\Delta G = \Delta H - T\Delta S \dots (8)$$

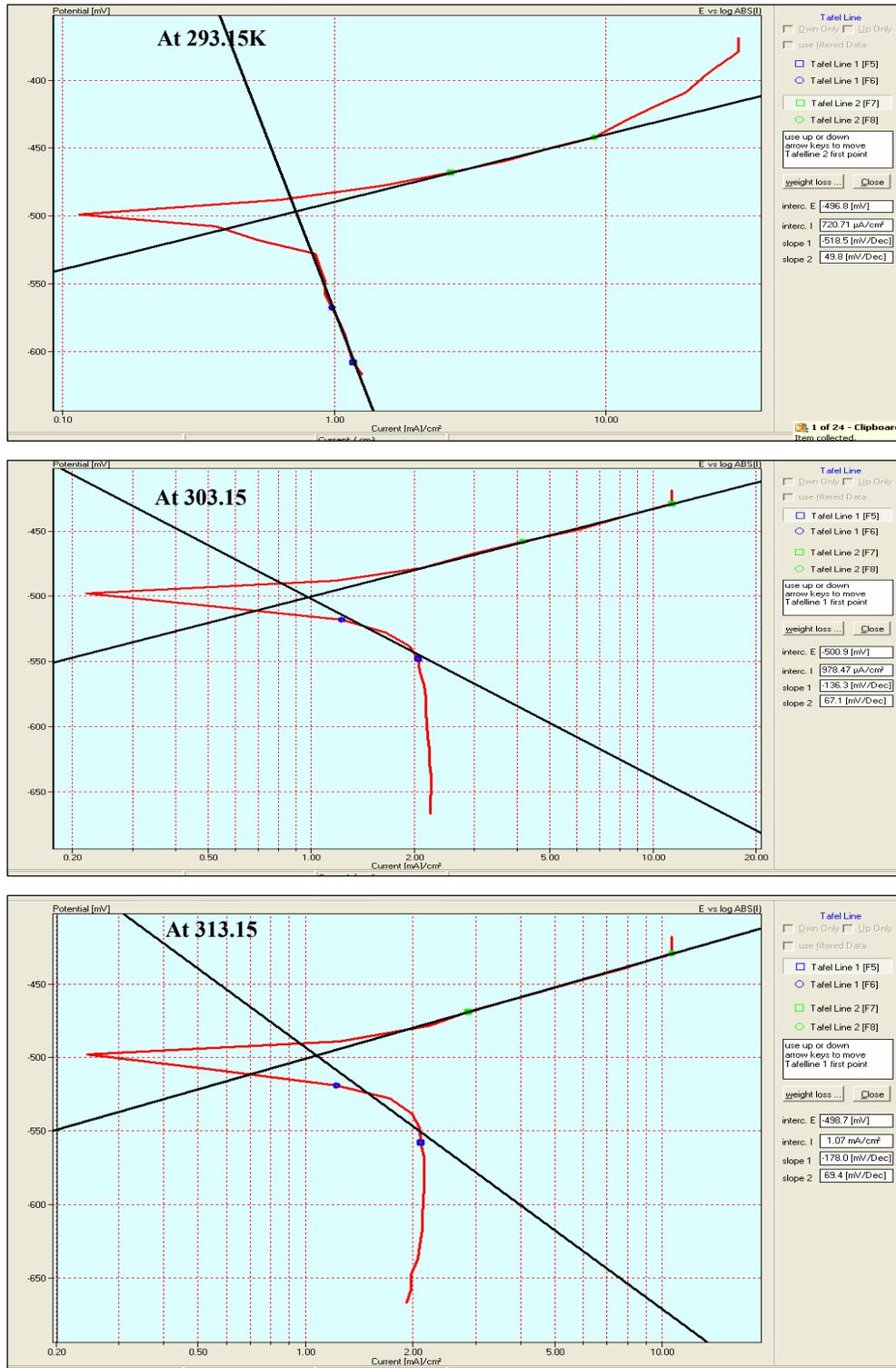
All calculated thermodynamic parameters  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  for the corrosion of zinc electrode in aerated acidic solution of 0.1 mol dm<sup>-3</sup> hydrochloric acid are listed in table (3). The values of  $\Delta G$  of table (3) in the uninhibited and inhibited acidic solution at various concentrations were generally slightly changed about the value (-96±1kJ mol<sup>-1</sup>), this refers to retard of corrosion feasibility somewhat on thermodynamic ground.

The magnitude of  $\Delta H$  in table (3) shows that comprehensive adsorption (physical and chemical adsorption) might occur<sup>(43)</sup>. The negative sign of  $\Delta H$  also shows that the adsorption of inhibitor I is an exothermic process, which indicates that P% decrease with temperature, such behaviour can be interpreted on the basis that increasing temperature resulted in desorption of the some inhibitor molecules from the zinc electrode surface. The important values of  $\Delta S$  reflects the change in order and orientation of the solvent molecules around the ions in the corrosion medium when the atoms were corroded in acidic aerated solution<sup>(23)</sup> and the negative values suggest some loss in the degree of freedom throughout the presence of inhibitor I on the electrode zinc surface. Furthermore, on the basis of the complex activation theory<sup>(48,49)</sup>, the more negative value of  $\Delta S$  imply that the activated complex in the rate determining step represents association rather than dissociation meaning that a decrease in the disordering which take place on going from reactants to activated complex.

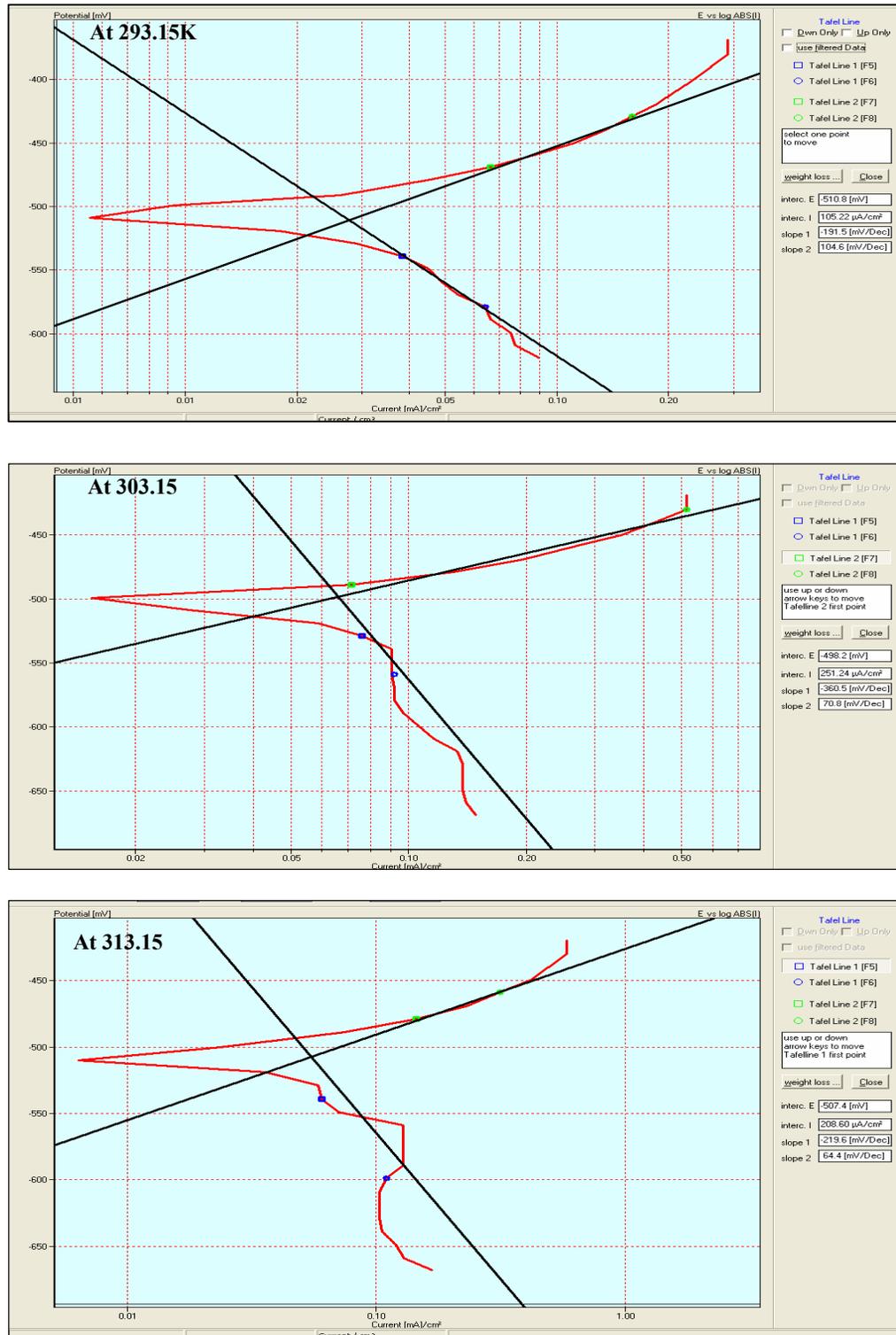
### Conclusion

The study of the inhibition of the corrosion of zinc electrode in 0.1 mol dm<sup>-3</sup> hydrochloric acid aerated solution at over temperatures range from 293.15 K to 313.15K by inhibitor I by technique of three electrodes the polarization curves at 3.93×10<sup>-6</sup> mol dm<sup>-3</sup> appears the Tafel behaviour indicates that inhibitor is a mixed-type inhibitor. Thus, the values of P% is positive. But, at extent the concentration of inhibitor I appears the acceleration action. The protection efficiencies are decreased with increasing temperatures from 293.15 K to 313.15K. Furthermore, The values of activation energy and pre-exponential factor are enhanced the results of polarization curves. The

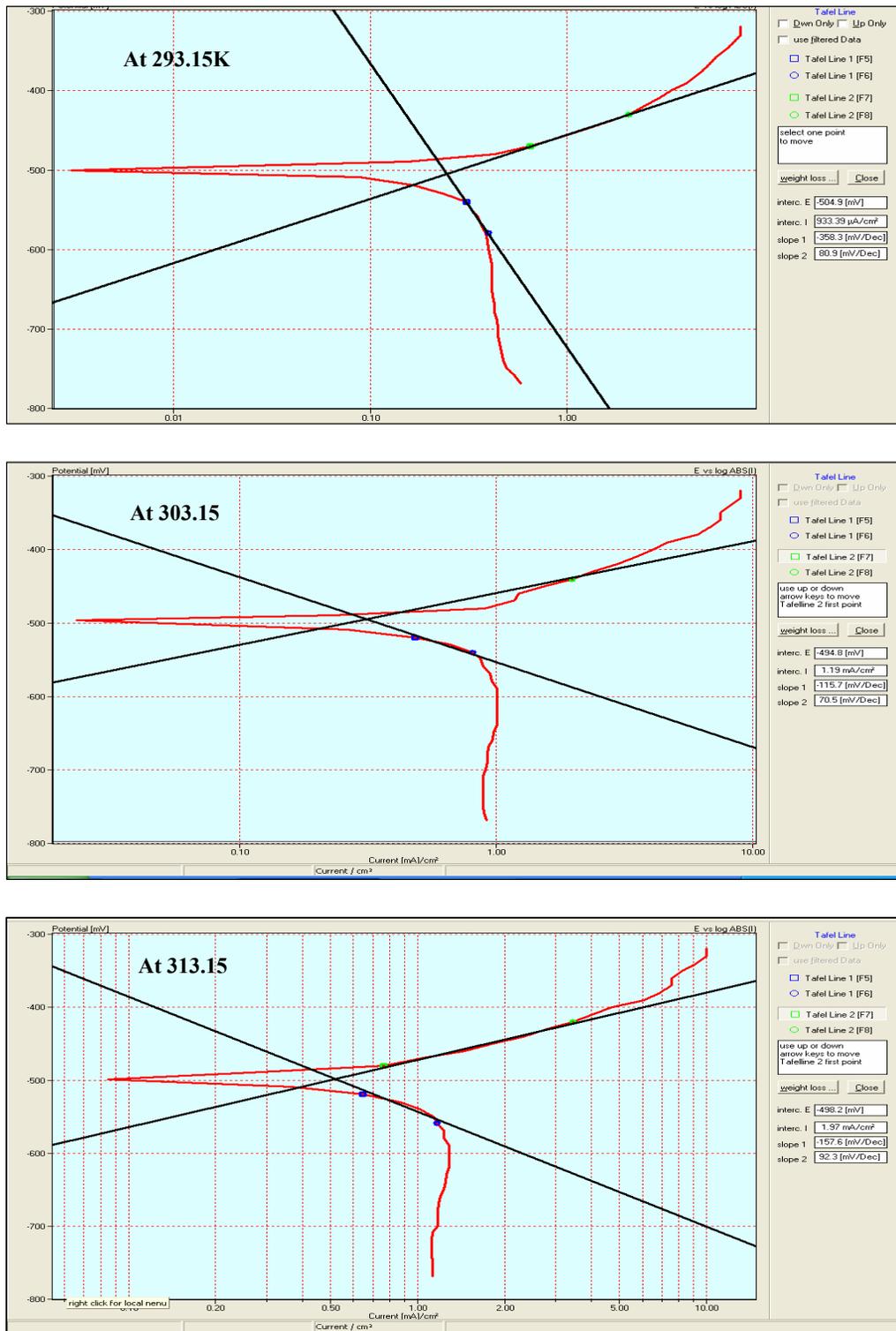
compensation effect have been discussed according to the linear relationship between the values of Log A and the corresponding values of  $E_a$ . The free energy change of the corrosion process have been calculated with related to the corrosion of potential and have been shown the slightly change of  $\Delta G$  in the uninhibited and inhibited acidic aerated solution. Also, The values of  $\Delta S$  have been reflected the change of order and orientation of the solvent molecules around the zinc ions. The values of  $\Delta H$  have been cleared the exothermic process for the systematic zinc metal corroded / inhibitor I.



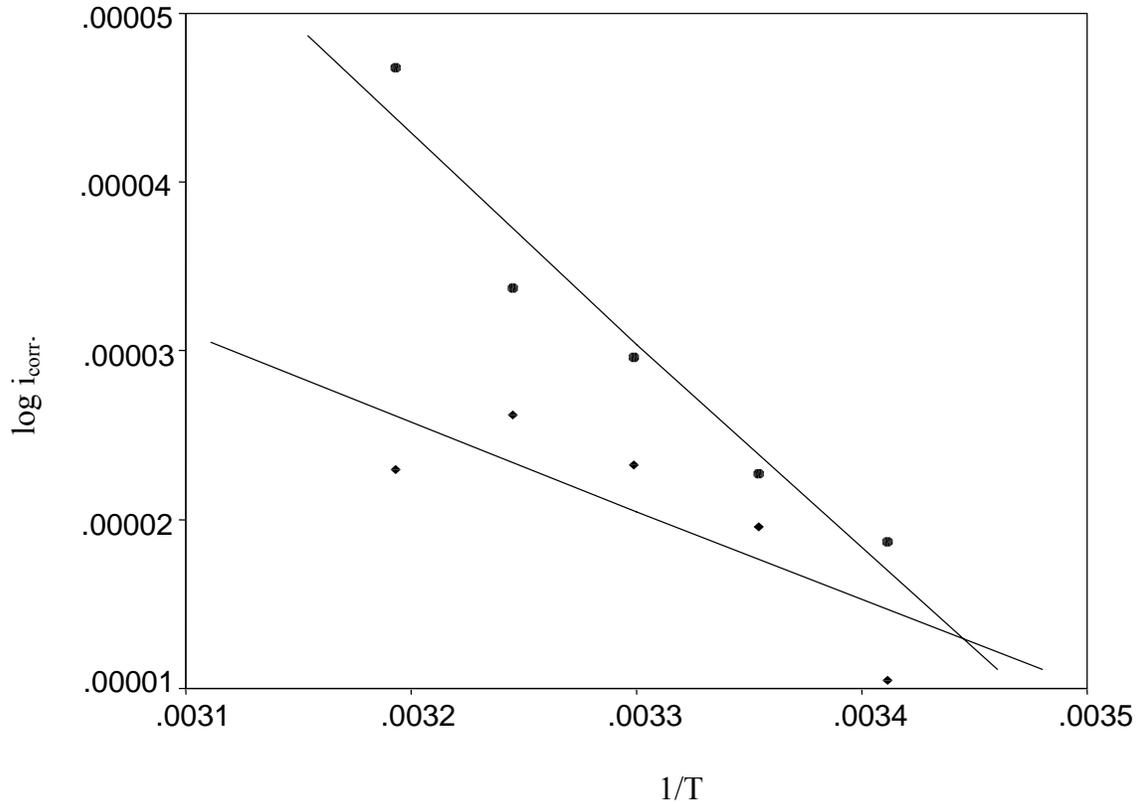
**Figure (1) :** The anodic and cathodic polarization curves in  $0.1 \text{ mol dm}^{-3}$  aerated hydrochloric acid solution in the absence the inhibitor I at 293.15 K , 303.15K and 313.15K , respectively .



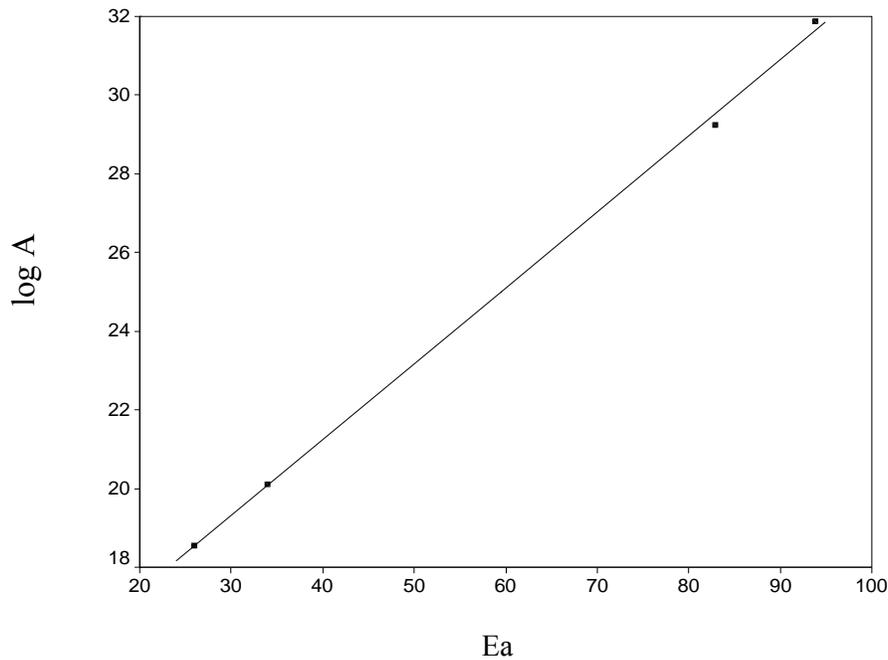
**Figure (2) : The anodic and cathodic polarization curves in 0.1 mol dm<sup>-3</sup> aerated hydrochloric acid solution in the presence of 3.93×10<sup>-6</sup> mol dm<sup>-3</sup> of inhibitor I at 293.15 K , 303.15K and 313.15K , respectively .**



**Figure (3) :** The anodic and cathodic polarization curves in 0.1 mol dm<sup>-3</sup> aerated hydrochloric acid solution in the presence of 7.87 × 10<sup>-5</sup> mol dm<sup>-3</sup> of inhibitor I at 293.15 K , 303.15K and 313.15K , respectively .



**Figure (4) :** Arrhenius plots , relating  $\log i_{\text{corr}}$  values to  $1/T$  for the corrosion of the zinc electrode in  $0.1 \text{ mol dm}^{-3}$  aerated hydrochloric acid solution in the presence of (●)  $3.93 \times 10^{-6} \text{ mol dm}^{-3}$  and (◆)  $2.36 \times 10^{-5} \text{ mol dm}^{-3}$  of inhibitor I .



**Figure (5):** Log A values plotted against  $E_a$  (kJ/mol-1 ) for the zinc electrode in uninhibited and inhibited of  $0.1 \text{ mol dm}^{-3}$  aerated hydrochloric acid solution .

**Table (1) : Polarization parameters and the corresponding inhibition efficiencies for zinc electrode in uninhibited and containing different concentration of inhibitor I of  $0.1 \text{ mol dm}^{-3}$  aerated hydrochloric acid solution at over temperatures range (293.15 -313.15)K .**

Temp. K	Concentration $\text{mol dm}^{-3}$	$i_{\text{corr.}}$ ( $\mu\text{A cm}^{-2}$ )	$-E_{\text{corr}}$ (mV/SCE)	$-B_c$ $\text{mV dec}^{-1}$	$B_a$ $\text{mV dec}^{-1}$	P%
293.15	Uninhibited	720.7	496.8	518.5	49.8	-
	$3.93 \times 10^{-6}$	105.22	510.8	191.5	104.6	85.4
	$2.36 \times 10^{-5}$	187.11	504.2	410.3	48.5	74.05
	$7.87 \times 10^{-5}$	933.39	504.9	358.3	80.9	-29.50
298.15	Uninhibited	889.86	497.9	216.6	60.8	-
	$3.93 \times 10^{-6}$	196.39	510.6	387.39	74.5	77.93
	$2.36 \times 10^{-5}$	227.26	506.0	420.2	49.9	74.46
	$7.87 \times 10^{-5}$	1.19 mA	497.8	105.3	65.9	-33.72
303.15	Uninhibited	978.47	500.9	136.3	67.1	-
	$3.93 \times 10^{-6}$	251.24	498.2	360.5	70.9	74.32
	$2.36 \times 10^{-5}$	295.59	507.2	443.3	100.1	69.79
	$7.87 \times 10^{-5}$	1.19 mA	494.8	115.7	70.5	-21.61
308.15	Uninhibited	987.23	502.7	122.5	67.5	-
	$3.93 \times 10^{-6}$	262.21	472.8	350.22	69.5	73.41
	$2.36 \times 10^{-5}$	336.63	501.4	319.2	89.7	65.90
	$7.87 \times 10^{-5}$	1.17 mA	497.1	119	60.8	-18.51
313.15	Uninhibited	1.07 mA	498.7	178	69.4	-
	$3.93 \times 10^{-6}$	208.6	507.4	219.6	80.5	80.50
	$2.36 \times 10^{-5}$	467.99	510.1	324.8	125.5	56.26
	$7.87 \times 10^{-5}$	1.97 mA	498.2	92.3	92.3	-84.11

**Table (2) : Values of the activation energies  $E_a$  ( $\text{kJmol}^{-1}$ ) and pre-exponential factors  $A$  ( $\text{molecules cm}^{-2} \text{s}^{-1}$ ), for the corrosion of the zinc electrode in  $0.1 \text{ mol dm}^{-3}$  aerated hydrochloric acid solution at over temperatures range (293.15 - 313.15)K.**

Concentration $\text{mol dm}^{-3}$	Kinetic Parameters Model	
	$E_a$ ( $\text{kJmol}^{-1}$ )	$A$ ( $\text{molecules cm}^{-2} \text{s}^{-1}$ )
Uninhibited	82.86	$1.7508 \times 10^{29}$
$3.93 \times 10^{-6}$	25.92	$3.5838 \times 10^{18}$
$2.36 \times 10^{-5}$	33.98	$1.3060 \times 10^{20}$
$7.87 \times 10^{-5}$	93.87	$7.5034 \times 10^{31}$

**Table (3) : Values of the thermodynamics quantities ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ), for the corrosion of the zinc electrode in 0.1 mol dm<sup>-3</sup> aerated hydrochloric acid solution at different concentration of inhibitor I in over temperatures range (293.15 - 313.15)K.**

Concentration mol dm <sup>-3</sup>	Thermodynamics Quantities		
	$-\Delta G$ (kJmol <sup>-1</sup> )	$\Delta H$ (kJmol <sup>-1</sup> )	$\Delta S$ (Jmol <sup>-1</sup> K <sup>-1</sup> )
Uninhibited	96.3782	-86.32	0.0331
$3.93 \times 10^{-6}$	96.4863	-148.70	-0.1721
$2.36 \times 10^{-5}$	97.6095	-89.18	0.0277
$7.87 \times 10^{-5}$	96.2161	-112.7	-0.0544

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