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# Cephalexin as Efficient Corrosion Inhibitor for Mild Steel in Acidic Media Chemical, Electrochemical and Thermodynamic Studies

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*The polarization data showed that this drug is mixed-type inhibitor. The percentage inhibition efficiency was found to increase with increasing the concentration of the drug and with decreasing temperature. The Langmuir's isotherm was found to provide an accurate description of adsorption behavior of this drug. Some thermodynamic parameters were computed and discussed. The correlations between advanced quantum chemical concepts and inhibition efficiency was found and discussed. The data obtained from different methods are in good agreement.*

**Keywords:** Mild steel, Cephalexin drug, H<sub>2</sub>SO<sub>4</sub>, Corrosion inhibition, Quantum chemical calculation

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## 1. Introduction

Mild steel is the major structural material in industry, the protection of steel against corrosion has attracted much attention. As most steels are generally stable in neutral and alkaline media, acidic environments are the major concern [1]. Acid solutions are generally used for the removal of undesirable scale and rust in several petroleum processes. Inhibitors are used in this process to control metal dissolution. Most of the well-known acid inhibitors are organic compounds containing O, S, and /or N atoms [2-5].

However, there are several studies on the corrosion inhibition of organic compounds in acidic solutions [6-15]. The inhibitive action is connected with several factors including the structure and the charge distribution on the molecule, the number and the types of adsorption sites, and the nature of interaction between the molecule and the metal surface [16]. Corrosion inhibition occurs via adsorption of the organic molecule on the corroding metal surface following some known adsorption isotherms with the polar groups acting as active centers in the molecules. The resulting adsorption film acts as

a barrier that isolates the metal from the corroding solution and inhibition efficiency depends on the mechanical, structural and chemical characteristics of the adsorption layer formed under particular conditions [17, 18].

The aim of this work is to study the effect of (7R)-3-Methyl-7-( $\alpha$ -D-phenylglycylamino)-3-cephem-4-carboxylic acid monohydrate (Cephalexin drug) as inhibitor for the corrosion of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solutions using chemical and electrochemical measurements. The use of EFM technique. Yes this is the first time to use this drug as corrosion inhibitor for mild steel in 0.5 M sulfuric acid. I think so. Because it contains different hetero atoms, high molecular weight, soluble in water and so on

## 2. Experimental methods

### 2.1. Materials and solutions

The mild steel coupons with dimensions 2 × 2 × 0.1 cm were cut from a sheet. The chemical composition (weight %) of mild steel: 0.2 C, 0.35 Mn, 0.024 P, 0.003 Si and Fe rest. The acid solutions were made from AR grade H<sub>2</sub>SO<sub>4</sub>. An appropriate concentration of acid was prepared using distilled water. Cephalexin in pure form was purchased from Al-Gomhoria Company, Egypt.

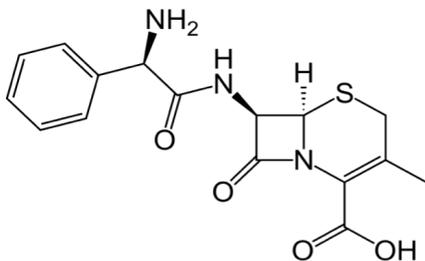


Fig. 1: Molecular structure of Cephalexin Molecular formula: C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>S, Molecular weight: 347.39

The various concentrations of the drug was prepared using bidistilled water. Its chemical structure is shown in Figure 1.

### 2.2. Weight loss method

The mild steel coupons with dimensions 2 × 2 × 0.2 cm were abraded with different grades of emery paper up to 1200 grit size, washed with bi-distilled water and acetone. After weighing accurately, the specimens were immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with and without addition of different concentrations of drug. After 3 hours the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of the three parallel mild steel sheets could be obtained at required temperature at 25°C. The inhibition efficiency (IE) and the degree of surface coverage ( $\theta$ ) of the investigated drug on the corrosion of C-steel were calculated as follows [19]:

$$\%IE = \theta \times 100 = [(W_0 - W) / W_0] \times 100 \quad (1)$$

where W<sub>0</sub> and W are the values of the average weight loss in the absence and presence of the inhibitor, respectively.

### 2.3. Electrochemical measurements

A three electrode cell assembly at room temperature [20, 21] was used for all electrochemical measurements. The working electrode was mild steel of above composition of 1 cm<sup>2</sup> area and the rest being covered by using commercially available lacquer. A rectangular Pt foil of 1 cm<sup>2</sup> was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode was abraded with different grades of emery papers up to 1200 grit size, washed with bi-distilled water and degreased with acetone. All electrochemical measurements were carried out using Gamry Potentiostat/Gal-

vanostat (model PCI 300/4) Gamry-Instruments Inc., USA with EIS300 software for EIS, DC105 software for polarization and EFM140 software for EFM measurements. Data was analyzed by Echem Analyst 5.21. All the experiments were carried out after the stabilization of the system for 30 min. i.e. open circuit potential (OCP).

### 2.3.1. The potentiodynamic polarization tests

The potentials were recorded by changing the electrode potential from -1.0 to 0.0 V versus SCE with scan rate of 1 mV/s. All experiments were carried out in freshly prepared solutions at constant temperature (25-55°C) using a thermostat. %IE and [22] the degree of surface coverage ( $\theta$ ) were defined as:

$$\%IE = \theta \times 100 = [(i_{\text{corr}} - i_{\text{corr(inh)}}) / i_{\text{corr}}] \times 100 \quad (2)$$

where  $i_{\text{corr(blank)}}$  and  $i_{\text{corr(inh)}}$  are the uninhibited and inhibited corrosion current density values, respectively, determined by extrapolation of Tafel lines.

### 2.3.2. The electrochemical impedance spectroscopy (EIS) tests

The spectra of EIS were recorded at open circuit potential (OCP) after immersing the electrode for 30 min. in the test solution. The signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz. The inhibition efficiency (%IE) and the surface coverage ( $\theta$ ) of the used drug were calculated by applying the following relation [22]:

$$\%IE = \theta \times 100 = [1 - (R_{\text{ct}}^{\circ} / R_{\text{ct}})] \times 100 \quad (3)$$

Where,  $R_{\text{ct}}^{\circ}$  and  $R_{\text{ct}}$  are the charge transfer resistance in the absence and presence of inhibitor, respectively.

### 2.3.3 The electrochemical frequency modulation (EFM) tests

EFM is a new technique which provides a new tool for electrochemical corrosion monitoring. With the electrochemical modulation technique (EFM), a potential perturbation by two sine waves of different frequencies is applied to the system. As a corrosion process is non-linear in nature, responses are generated at more frequencies than the frequencies of the applied signal. The current responses can be measured at zero, harmonic, and intermodulation frequencies. Analysis of these current responses can result in the corrosion current density and Tafel parameters. The inhibition efficiency (%IE<sub>EFM</sub>) and the surface coverage ( $\theta$ ) of the used drug were calculated by applying the following relation:

$$IE_{\text{EFM}} \% = \theta \times 100 = [(i_{\text{corr}} - i_{\text{corr(inh)}}) / i_{\text{corr}}] \times 100 \quad (4)$$

where  $i_{\text{corr(blank)}}$  and  $i_{\text{corr(inh)}}$  are the corrosion currents in the absence and presence of inhibitor, respectively.

## 3. Results and Discussion

Figure 2 shows the weight loss-time curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C in the absence and presence of different concentrations of used drug. As shown from these Figures, by increasing the concentration of this drug, the weight loss of mild steel samples is decreased. This means that the presence of this additive retards the corrosion of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> or, this additive acts as inhibitor [23]. The linear variation of weight loss with time in uninhibited and inhibited 0.5M H<sub>2</sub>SO<sub>4</sub> indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitor is first adsorbed onto the metal surface and thereafter affects the corrosion behaviour either by merely blocking the reaction sites (anodic and cathodic) or by altering the mech-

anism of the anodic and cathodic partial processes. The inhibition efficiency (%IE) of inhibitor was calculated and also corrosion rate (CR) [Table 1].

### 3.1.1. Role of anion in corrosion-inhibition of mild steel in $H_2SO_4$ solutions and its synergistic effect

The effect of potassium iodide (KI) on the corrosion of mild steel in 0.5 M  $H_2SO_4$  solution in the absence and presence of different concentrations of Cephalexin was studied by weight loss method. Figure 3 shows the weight loss-time curves for C-steel in

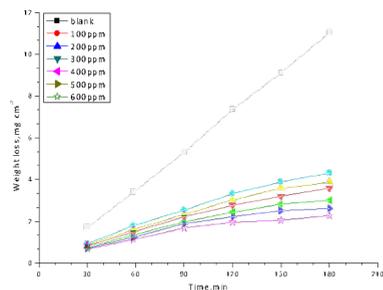


Fig. 2: Weight loss-time curves for mild steel dissolution in 0.5M  $H_2SO_4$  in the absence and presence of different concentrations of investigated drug at 25°C

Tab. 1: Inhibition efficiency (%IE) and corrosion rate (C.R.) of mild steel in 0.5 M  $H_2SO_4$  at different concentrations of the drug as determined by weight loss method after 90 min. immersion at 25°C

[Inhibitor] ppm	Inhibition efficiency %IE	C.R. x 10 <sup>-3</sup> mg cm <sup>-2</sup> min <sup>-1</sup>
100	52.3	28.0
200	56.1	26.0
300	58.6	25.0
400	62.8	22.0
500	64.5	21.0
600	68.5	19.0

0.5 M  $H_2SO_4$  solution in the absence and presence of different concentrations of the drug beside the presence of 0.01M KI. The inhibition efficiency (%IE), Corrosion rate (CR) and the  $S_\Theta$  values in the presence of 0.01M of KI is shown in Table 2. The synergism parameter ( $S_\Theta$ ) was calculated using the relationship given by Aranmki and Hackerman [24].

$$S_\Theta = (1 - \theta_{1+2}) / (1 - \theta'_{1+2}) \quad (5)$$

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 anion and cation.

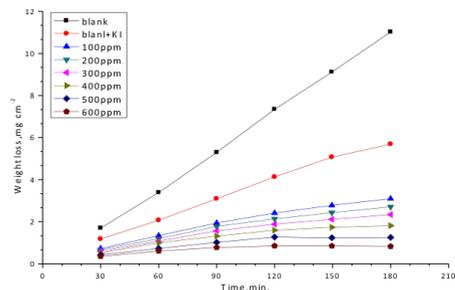


Fig. 3: Weight loss-time curves for mild steel dissolution in 0.5M  $H_2SO_4$  and 0.01M KI in absence and presence of different concentrations of the drug at 25°C

Tab. 2: Inhibition efficiency (%IE), corrosion rate (CR) and synergistic parameter ( $S_\Theta$ ) of drug at different concentrations of drug for mild steel in 0.5M  $H_2SO_4$  and 0.01M KI as determined from weight loss method after 90 min. immersion at 25°C

[Inhibitor] ppm	Inhibition efficiency %IE	CR mg cm <sup>-2</sup> min <sup>-1</sup> x 10 <sup>3</sup>	$S_\Theta$
100	63.5	22.0	1.362
200	66.5	20.0	1.364
300	70.4	17.0	1.121
400	75.3	15.0	1.078
500	80.8	11.0	1.078
600	85.5	9.0	1.267

This equation actually compares the corrosion rate of either anion or cation and of the inhibitor mixture (anion + cation). If anions and cations have no effect on each other and adsorbed at metal surface independently, the  $S_0$  value should be equal to 1. Furthermore, synergistic effects are observed if  $S_0 > 1$  and activation of corrosion is observed if  $S_0 < 1$ . It can be seen from Table 2 that the addition of KI inhibits the corrosion of mild steel to a large extent. This can be interpreted according to Schmitt and Bedbur [24], which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption the anions and cations are adsorbed at different sites on the electrode surface, and in cooperative adsorption, the anions are chemisorbed on the surface and the cations are adsorbed on a layer of the anions, apart from the adsorption on the surface directly. These two types are illustrated in Figure 4 [25].

Since  $S_0 > 1$  synergistic effect takes place i.e. competitive adsorption occurs

### 3.2.1. Potentiodynamic polarization measurements

Figure 5 shows the potentiodynamic polarization curves for mild steel without and with different concentrations of Cephalexin at 25°C. The obtained electrochemical parameters; cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel slopes, corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), and polarization resistance ( $R_p$ ) were obtained and listed in Table 3. Table 3 and Figure 5:

1. Clearly shows that both anodic and cathodic reactions are inhibited, in addition,  $E_{corr}$  does not change obviously, the value at 100 ppm is 468 these indicate that investigated drug acts as a mixed-type inhibitor [26-27],

- $i_{corr}$  decreases by increasing the concentration of the drug and
- The curves of  $\beta_a$  and  $\beta_c$  are parallel, this indicates that the mechanism of the corrosion reaction of C-steel does not change.

#### 3.2.1.1. Adsorption isotherms

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/

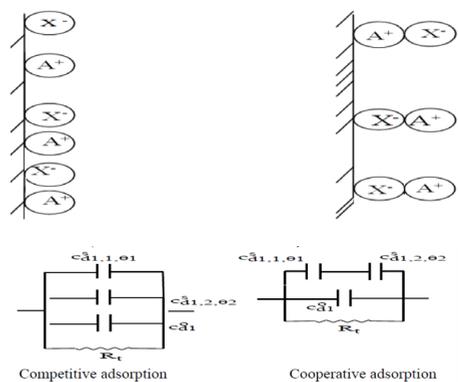


Fig. 4: Schematic diagrams and equivalent circuits of competitive and cooperative adsorption of anion and cation (Please enlarge the Fig in order to modify the diagram)

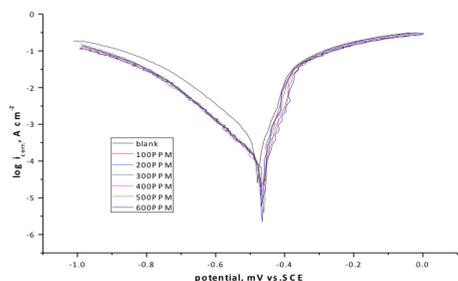


Fig. 5: Potentiodynamic polarization curves for the dissolution of mild steel in 0.5 M  $H_2SO_4$  in the absence and presence of different concentrations of investigated drug at 25°C

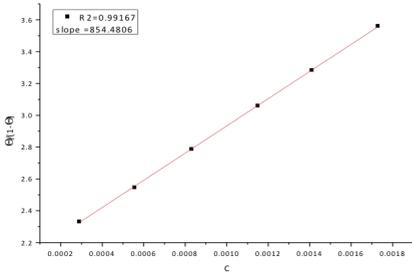


Fig. 6: Langmuir adsorption isotherm plotted as  $\theta/(1-\theta)$  vs. C of the investigated drug for corrosion of mild steel in 0.5M  $H_2SO_4$  solution at 25°C

inhibitor/ environment system [28]. The surface coverage ( $\theta$ ) values were tested graphically to allow fitting of a suitable adsorption isotherm. The plot of  $\theta/(1-\theta)$  versus C (Figure 6) yielded a straight line, this proving that the adsorption of

this drug from 0.5 M  $H_2SO_4$  solution on C-steel surface obeys Langmuir adsorption isotherm according to equation (6):

$$\theta/(1-\theta) = K_{ads}C \quad (6)$$

Where,  $K_{ads}$  is equilibrium constant of adsorption process,  $\theta$  is the surface coverage, C is concentration of the drug.

It is well know that the equilibrium constant for adsorption process,  $K_{ads}$  is related to the standard free energy of adsorption ( $\Delta G_{ads}^0$ ) by the following equation [29]:

$$K_{ads} = 1/ 55.5 \exp (-\Delta G_{ads}^0 / RT) \quad (7)$$

Inspection of the data of Table 4, the large values of  $\Delta G_{ads}^0$  and its negative sign, indicates that the

Tab. 3: The effect of concentrations of investigated drug on the free corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), Tafel slopes ( $\beta_c$ ,  $\beta_a$ ), corrosion rate(C.R.), inhibition efficiency (%IE) and degree of surface coverage ( $\theta$ ) of mild steel in 0.5M  $H_2SO_4$  at 25°C

[Inh.] Ppm	$-E_{corr}$ mV vs.SCE	$i_{corr}$ $\mu A$ $cm^{-2}$	$\beta_c$ mV $dec^{-1}$	$\beta_a$ mV $dec^{-1}$	$R_p \times 10^{-2}$ $\Omega$ $cm^2$	CR $mm^{-1}$	$\theta$	% IE
0.0	487	896.1	214	165	0.33931	10.402	----	----
100	468	265.7	180	142	130.1	3.077	0.704	70.4
200	466	253.3	178	140	1.344	2.940	0.717	71.7
300	466	240.1	175	134	1.373	2.788	0.732	73.2
400	469	218.9	177	138	1.542	2.541	0.756	75.6
500	462	209.1	174	132	1.561	2.427	0.767	76.7
600	466	196.1	175	137	1.700	2.276	0.781	78.1

Tab. 4: dsorption equilibrium constant of ( $K_{ads}$ ), free energy of adsorption ( $\Delta G_{ads}^0$ ), enthalpy of adsorption ( $\Delta H_{ads}^0$ ) and entropy of adsorption ( $\Delta S_{ads}^0$ ) of drug on C-steel surface in 0.5 M  $H_2SO_4$  at different temperatures

temperature	$K_{ads} M^{-1}$	$-\Delta G_{ads}^0$ , kJ $mol^{-1}$	$-\Delta H_{ads}^0$ kJ $mol^{-1}$	$-\Delta S_{ads}^0$ J $mol^{-1}K^{-1}$
25	854.48	26.7	23.4	11.0
35	1014.77	28.0		15.0
45	623.01	27.6		13.3
55	379.50	27.2		11.5

adsorption of the drug on C-steel surface is proceeding spontaneously and accompanied by highly efficient adsorption. The enthalpy of adsorption can be calculated from the Van't Hoff equation [30]:

$$(\Delta G_{\text{ads}}^{\circ} / T) = (\Delta H_{\text{ads}}^{\circ} / T) + \text{constant} \quad (8)$$

The variation of  $(\Delta G_{\text{ads}}^{\circ} / T)$  with  $1/T$  gives a straight line with a slope which is equal to  $\Delta H_{\text{ads}}^{\circ}$  Figure 7. It can be seen from the Figure that  $(\Delta G_{\text{ads}}^{\circ} / T)$  decreases with  $1/T$  in a linear fashion. The enthalpy and entropy for the adsorption of steel were also deduced from the thermodynamic basic equation [31]:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}} \quad (9)$$

where  $\Delta H_{\text{ads}}^{\circ}$  and  $\Delta S_{\text{ads}}^{\circ}$  are the enthalpy and entropy changes of adsorption process, respectively. A plot of  $\Delta G_{\text{ads}}^{\circ}$  versus  $T$  was linear (Figure 10) with the slope equal to  $-\Delta S_{\text{ads}}^{\circ}$  and intercept of  $\Delta H_{\text{ads}}^{\circ}$ . The enthalpy of adsorption  $\Delta H_{\text{ads}}^{\circ}$  and the entropy of adsorption  $\Delta S_{\text{ads}}^{\circ}$  obtained are negative. The negative sign of  $\Delta H_{\text{ads}}^{\circ}$  indicates that the adsorption of Cephalexin molecules is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of  $\Delta H_{\text{ads}}^{\circ}$ . For physisorption process, the enthalpy of adsorption is lower than  $40 \text{ kJ mol}^{-1}$  while that for chemisorption approaches  $100 \text{ kJ mol}^{-1}$  [32]. In the present study, the absolute value of enthalpy of adsorption obtained is typical of physisorption. Values of  $\Delta H_{\text{ads}}^{\circ}$  obtained by the two methods are in good agreement. The entropy of adsorption obtained from Equation (9) was negative because the inhibitor molecules freely moving in the bulk solution were adsorbed in an orderly fashion onto the mild steel, resulting in a decrease in entropy [30]. Moreover, from thermodynamic principles, since the adsorption was an exothermic process, it must be accompanied by a decrease in entropy [33].

### 3.2.1.2. Effect of temperature

To investigate the mechanism of inhibition and to determine the activation energy of corrosion process, potentiodynamic curves of C-steel in  $0.5 \text{ M H}_2\text{SO}_4$  were studied at various temperatures ( $25\text{--}55^{\circ}\text{C}$ ) in the absence and presence of different concentrations of investigated drug. This drug retards the corrosion process at lower temperatures [34] whereas the inhibition is considerably decreased at elevated temperatures. The increasing of the corrosion rate with increasing temperature is suggestive of physical adsorption of the investigated drug on the C-steel surface. The obtained electrochemical parameters; cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel slopes, corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), and

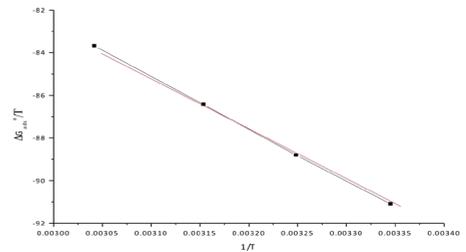


Fig. 7: Relationship between  $\Delta G_{\text{ads}}^{\circ}/T$  and  $1/T$  for the drug

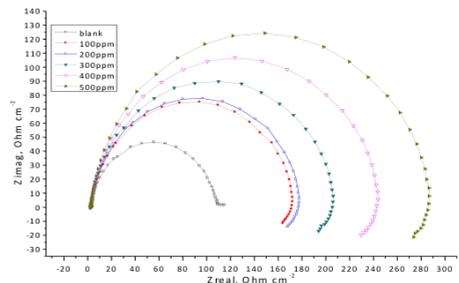


Fig. 8: The Nyquist plot for mild steel in  $0.5 \text{ M H}_2\text{SO}_4$  solution in the absence and presence of different concentrations of investigated inhibitor at  $25^{\circ}\text{C}$

polarization resistance ( $R_p$ ) at different concentrations were obtained and listed in Table 5. Table 5 shows that  $i_{corr}$  increases by increasing temperature and hence % IE decreases by increasing the temperature. Figure 5 represents the Arrhenius plots of natural logarithm of corrosion rate versus  $1/T$ , for C- steel in 0.5M  $H_2SO_4$  solution, in the absent and presence of different concentrations of Cephalexin. The values of slopes of these straight lines permit the calculation of the activation energy,  $E_a^*$ , according to:

$$k = A \exp(-E_a^*/RT) \quad (10)$$

Where  $k$  is the corrosion rate,  $A$  is the pre-exponential factor,  $E_a^*$  is the apparent activation energy,  $R$  is the universal gas constant and  $T$  is the absolute temperature.

The values of  $E_a^*$  are given in Table 6. The results of Table 6 revealed that, the values of  $E_a^*$  were increased by increasing the concentration of the investigated inhibitor indicating that the dissolution of C-steel under these conditions is activation controlled and also indicates the energy barrier of the corrosion reaction increases in the presence of these additives. Other authors [35-37]

Tab. 5: The effect of concentrations of investigated compound on the free corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), Tafel slopes ( $\beta_c$ ,  $\beta_a$ ), corrosion rate (CR), inhibition efficiency (%IE) and degree of surface coverage ( $\theta$ ) of mild steel alloy in 0.5M  $H_2SO_4$  at different temperatures

Temp. °C	[Inh] ppm	$-E_{corr}$ mV vs SCE	$i_{corr}$ $\mu A cm^{-2}$	$\beta_c$ mV dec <sup>-1</sup>	$\beta_a$ mV dec <sup>-1</sup>	$R_p$ $\times 10^{-2}$ $\Omega cm^2$	CR $mm y^{-1}$	$\theta$	% IE
35	0.0	474	1172	236	187	38.68	13.60	----	----
	100	467	520.0	206	163	75.93	6.036	0.556	55.6
	200	461	479.9	201	160	181.8	5.571	0.591	59.1
	300	465	417.8	198	156	90.82	4.850	0.644	64.4
	400	464	397.1	192	150	92.15	4.610	0.661	66.1
	500	465	333.4	191	149	108.8	3.870	0.716	71.6
	600	467	324.0	194	152	114.5	3.760	0.724	72.4
45	0.0	489	2543	284	227	21.52	29.52	----	----
	100	489	2499	249	202	19.39	29.00	0.017	1.7
	200	491	2067	238	192	22.33	23.99	0.187	18.7
	300	491	1879	256	207	26.48	21.81	0.261	26.1
	400	484	1554	221	159	25.81	18.03	0.389	38.9
	500	482	1480	223	170	28.32	17.18	0.418	41.8
	600	482	1323	225	181	73.97	15.35	0.480	48.0
55	0.0	473	3807	249	162	11.18	44.19	----	----
	100	477	3548	269	204	14.20	41.18	0.068	6.8
	200	484	3356	253	183	13.75	38.95	0.118	11.8
	300	478	2816	242	170	15.41	32.69	0.260	26.0
	400	481	2623	234	147	14.93	30.45	0.311	31.1
	500	478	2567	244	174	17.18	29.80	0.326	32.6
	600	482	2369	225	147	16.31	27.49	0.378	37.8

obtained similar results. The higher values of  $E_a^*$  are good evidence for the strong adsorption of Cephalixin on C-steel surface.

An alternative formulation of Arrhenius equation is the transition state equation [38], Figure 6 represents the transition state:

$$\log k/T = \log (R/ Nh) + \Delta S^*/ 2.303R + (-\Delta H^*/ 2.303R) 1/T \tag{11}$$

By plotting  $\log k/T$  against  $1/T$  we obtain  $\Delta H^*$  from the slope and  $\Delta S^*$  from the intercept where slope =  $-\Delta H^*/ 2.303R$ , Intercept =  $\log (R/ Nh) + \Delta S^*/ 2.303R$

Where  $h$  is Plank's constant,  $N$  is Avogadro's number,  $\Delta H^*$  is the activation enthalpy and  $\Delta S^*$  is the activation entropy. The values of  $(\Delta H^*)$  are positive and higher in the presence of the drug than in its absence. This implies that the energy barrier of the corrosion reaction in the presence of the investigated compound increases and indicates the endothermic behavior of the corrosion process. On the other hand  $\Delta S^*$  values are lower and have negative values in presence of the additives, this means that addition of these compounds cause a decrease in the disordering in going from reactants to the activated complexes [39,40].

Tab. 6: Thermodynamic activation parameters for the dissolution of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentration of investigated drug

Conc. ppm	$\Delta E_a^*$ kJmol <sup>-1</sup>	$\Delta H^*$ kJmol <sup>-1</sup>	$-\Delta S^*$ Jmol <sup>-1</sup> K <sup>-1</sup>
0.0	38.01	35.41	106.59
100	76.12	73.53	10.66
200	74.90	72.30	5.98
300	72.27	69.67	3.40
400	71.63	69.03	6.28
500	73.17	70.57	1.97
600	72.10	69.50	6.00

### 3.2.2. Electrochemical Impedance Spectroscopy (EIS) measurements

The corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of the investigated compound was investigated by EIS method at 25 °C after 20 min

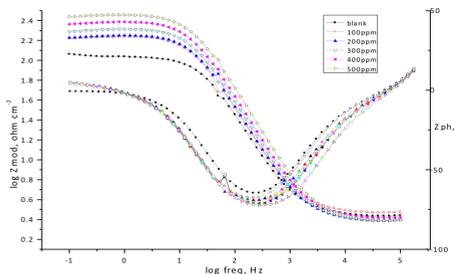


Fig. 9: The bode plot for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of different concentrations of the investigated drug

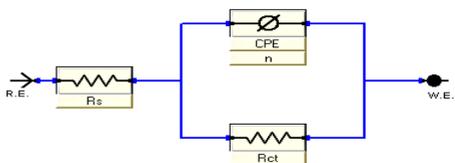


Fig. 10: Equivalent circuit model used to fit the impedance spectra

Tab. 7: Electrochemical kinetic parameters obtained by EIS technique for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different concentrations of investigated drug at 25°C

Conc. ppm	$C_{dl}$ μFcm <sup>-2</sup>	$R_{ct}$ Ω cm <sup>2</sup>	$\theta$	%IE
0	62.57	107.4	---	---
100	56.06	168.9	0.364	36.4
200	51.78	174.4	0.384	38.4
300	47.09	201.9	0.468	46.8
400	41.46	238.8	0.550	55.0
500	33.86	281.6	0.619	61.9

immersion. Nyquist plot in the absence and presence of the investigated compound is presented in Figure 8 and also the Bode plot is presented in Figure 9. It is apparent that Nyquist plots show a single capacitive loop, both in uninhibited and inhibited solutions. The impedance data of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> are analyzed in terms of an equivalent circuit model (Figure 10) which includes the solution resistance  $R_s$  and the double layer capacitance  $C_{dl}$  which is placed in parallel to the charge transfer resistance  $R_{ct}$  [41] due to the charge transfer resistance. For the Nyquist plots, it is obvious that low frequency data are on the right side of the plot and higher frequency data are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true for all circuits). The capacity of double layer ( $C_{dl}$ ) can be calculated from the following equation:

$$C_{dl} = [1/2\pi f_{max} R_{ct}] \quad (12)$$

Where  $f_{max}$  is maximum frequency used. The parameters obtained from impedance measurements are given in Table 7. It can be seen from Table 7 that the values of charge transfer resistance  $R_{ct}$  increase with inhibitor concentration [42]. In the case of impedance studies, % IE increases with inhibitor concentration in the

presence of investigated inhibitor. The impedance study confirms the inhibiting character of these compounds obtained from potentiodynamic polarization and weight loss methods. It is also noted that the ( $C_{dl}$ ) values tend to decrease when the concentration of these compounds increases. This decrease in ( $C_{dl}$ ), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that these compounds function by adsorption at the metal/solution interface [43]. The inhibiting effect of these compounds can be attributed to their parallel adsorption at the metal solution interface. The parallel adsorption is owing to the presence of one or more active center for adsorption.

### 3.2.3. Electrochemical frequency modulation (EFM) measurement

Electrochemical frequency modulation (EFM) is a non-destructive corrosion measurement technique that can directly give values of corrosion current without prior knowledge of Tafel constants. In this technique current responses due to a potential perturbation by one or more sine waves are measured at more frequencies than the frequency of the applied signal, for exam-

Tab. 8: Electrochemical kinetic parameters obtained by EFM technique for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with different concentration of investigated drug

[Inh] ppm	$i_{corr}$ $\mu A\ cm^{-2}$	$\beta_{an}$ $mV\ dec^{-1}$	$\beta_{c}$ $mV\ dec^{-1}$	CF-2	CF-3	CR, mpy	$\theta$	% IE
0.0	190.8	83	112	2.030	2.919	85.08	---	---
100	124.1	77	119	1.986	2.998	55.33	0.350	35.0
200	116.4	78	109	2.013	2.888	51.91	0.390	39.0
300	101.0	81	106	1.975	2.297	45.06	0.471	47.1
400	84.47	81	102	1.991	2.201	37.67	0.557	55.7
500	71.44	84	97	2.038	2.710	31.86	0.626	62.6

ple at zero harmonic and intermodulation frequencies [44]. The great strength of the EFM is the causality factors, which serve as an internal check on the validity of the EFM measurement [45]. The results of EFM experiments are a spectrum of current response as a function of frequency. Figures 11, 12 represent the intermodulation spectrum in absence and in presence of 600 ppm of drug as an example. The larger peaks were used to calculate the corrosion current

density ( $i_{corr}$ ), the Tafel slopes ( $\beta_c$  and  $\beta_a$ ) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined and listed in Table 8. As can be seen from this Table, the corrosion current densities increase in the presence of different concentrations of the drug than in the presence of 0.5 M  $H_2SO_4$  solution alone in case of C-steel. The causality factors also indicate that the measured data are of good quality.

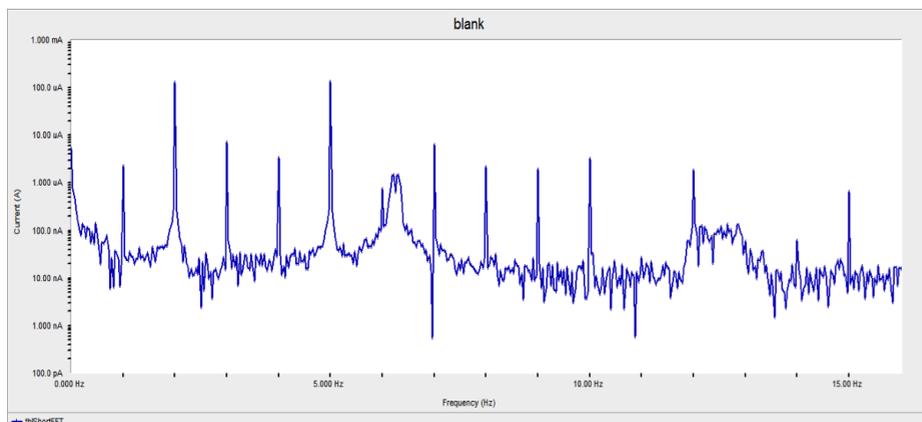


Fig. 11: Intermodulation spectrum for mild steel in 0.5 M  $H_2SO_4$  solutions without investigated compound at 25 °C.

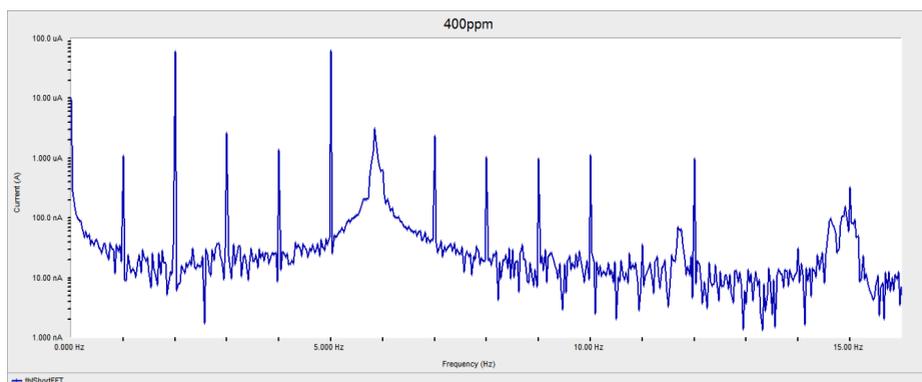


Fig. 12: Intermodulation spectrum for mild steel in 0.5 M  $H_2SO_4$  solutions with 600 ppm of investigated compound at 25 °C

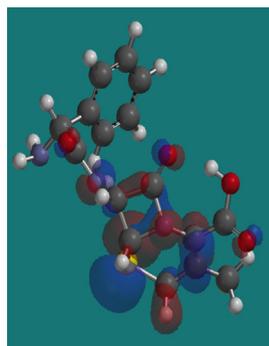
### 3.3. Quantum chemical studies

Quantum-chemical calculations have been widely used to study the reaction mechanism and to interpret the experimental results as well as to resolve chemical ambiguities. They have also proved to be a very important tool for studying corrosion inhibition mechanism. The energy of the highest occupied molecular orbitals ( $E_{\text{HOMO}}$ ) indicates the ability of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals and the energy of the lowest unoccupied molecular orbitals ( $E_{\text{LUMO}}$ ) indicates its ability to accept electrons. Figure 13 represents the optimized molecular structures, HOMO, LUMO of the investigated drug. The lower the value

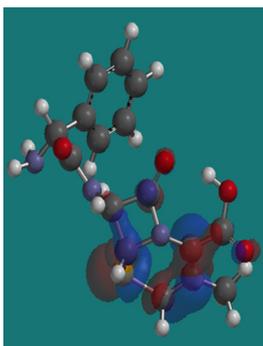
of  $E_{\text{LUMO}}$ , the more ability of the molecule is to accept electrons [46]. While, the higher is the value of  $E_{\text{HOMO}}$  of the inhibitor, the easier is its offering electrons to the unoccupied d-orbital of C-steel surface and the greater is its inhibition efficiency. The calculations listed in Table 9 showed that the highest energy  $E_{\text{HOMO}}$  is assigned for the compound Cephalexin, which is expected to have corrosion inhibition. Therefore, it has the greatest tendency to adsorb on the metal surface and accordingly has the highest inhibition efficiency. This expectation is in a good agreement with the experimental. ( $E_{\text{LUMO}} - E_{\text{HOMO}}$ ) energy gap,  $\Delta E$ , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller is the value of  $\Delta E$ , the more is the probable inhibition efficiency that the compound has [47-49]. It was shown from Table 9 that Cephalexin molecule has the smaller  $\Delta E$ . Accordingly, it could be expected that Cephalexin molecule has more inclination to adsorb on the metal surface. The dipole moment  $\mu$  was used to discuss and rationalize the structure [50]. The higher is the value of  $\mu$ , the more is the probable inhibition efficiency.

Tab. 9: The calculated quantum chemical parameters for Cephalexin compound using PM3.

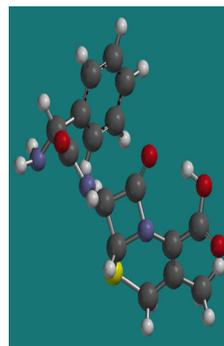
Parameter	Cephalexin
$-E_{\text{HOMO}}$ , eV	9.70
$-E_{\text{LUMO}}$ , eV	0.72
$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ , eV	8.98
Dipole Moment, debye	5.83
Molecular Area, $\text{\AA}^2$	347.43



Homo



Lumo



Optimized

Fig. 13: The optimized molecular structures, HOMO, LUMO

#### 4. Mechanism of Corrosion Inhibition

An elucidation of inhibition mechanism requires elaborated knowledge of the fundamental interaction amongst the protective compound and the metal surface. Many of the organic corrosion inhibitors have at least one polar unit with atoms of N, S, O and in some cases phosphorous. It has been reported that the inhibition efficiency decreases in the order  $O < N < S < P$ . The polar unit is considered as the reaction center for the chemisorption process. Moreover; the size, orientation, shape and electric charge on the molecule determine the degree of adsorption and therefore; the effectiveness of the inhibitor. An increase in inhibition efficiency with an increase in concentration of Cephalexin showed that the inhibition action is due to adsorption on the steel surface, following the types of adsorption that may take place at metal/solution interface: (a) Electrostatic attraction between the charged molecules and charged metal (b) Interaction of unshared electron pairs in the molecule with the metal (c) Interaction of p-electrons with the metal and (d) Combination of (a) and (c) [51]. In acidic solution, Cephalexin is present in its protonated form and it is well known that the steel surface bears a positive charge [52,53], so it is difficult for the protonated molecules to approach the positively charged mild steel surface due to the

electrostatic repulsion. Since  $SO_4^{--}$  ions could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged Cephalexin molecules, the protonated Cephalexin adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed  $SO_4^{--}$  ions and protonated Cephalexin. Thus, we can conclude that inhibition of mild steel corrosion in 0.5 M  $H_2SO_4$  is mainly due to electrostatic interaction. The decrease in inhibition efficiency with an increase in temperature supports electrostatic interaction.

#### 5. Conclusions

Cephalexin acts as a good inhibitor for the corrosion of mild steel in 0.5 M  $H_2SO_4$ . The inhibition efficiency of Cephalexin decreased with temperature, which leads to an increase in activation energy of corrosion process. The adsorption of Cephalexin follows Langmuir's adsorption isotherm. The adsorption process is spontaneous and exothermic, accompanied by an increase of entropy. Potentiodynamic polarization curves reveals that Cephalexin is a mixed-type but predominantly cathodic inhibitor. The results obtained from different experimental studies are in good agreement.

## References

- [1] R.H.Perry, D.W.Green(Eds.) and J.O.Maloney Perry's Chemical Engineer's Handbook, 7th ed., McGraw-Hill Publishing, (1997).
- [2] A.Chetouani, B.Hammouti, A.Aouniti, N.Benchat and T.Benhadda, *Prog.Org.Coat.* 45(2002) 373.
- [3] K.Bekkouch, A.Aouniti, B.Hammouti and S.Kertit, *J.Chim. Phys.* 96(1999)838.
- [4] S.Kertit, B.Hammouti, M.Taleb and M.Brighli, *Bull.Electrochem.* 13(1997)241.
- [5] M.Bouklah, N.Benchat, A.Aouniti, B.Hammouti, M.Benkaddaddour, M.Lagrene, H.Vezine and F. Bentiss, *Prog.Org.Coat.* 51(2004)118.
- [6] F. Bentiss, M. Lagrene and M. Traisnel, *Corrosion* 56(7) (2000) 733.
- [7] A. Popova, E. Sokolova, S. Raicheva and M. Christov, *Corros. Sci.* 45 (2003) 33.
- [8] M. Abdallah and M. M. El-Naggar, *Mater. Chem. Phys.* 71 (2001)291.
- [9] J. De Damborenea, J. M. Bastidas and A. J. Vazquez, *Electrochim. Acta* 42 (3) (1996)455.
- [10] S. S. Mahmoud and M. M. Ahmed; *Port. Electrochim. Acta*, 24 (2006)37.
- [11] S. Ramesh and S. Rajeswari; *Electrochim. Acta*, 49 (2004)811.
- [12] M. S. Abdel Aal and M. S. Morad, *Br. Corros. J.* 36 (4) (2001) 253.
- [13] A. K. Mohamed, H. A. Mostafa, G. Y. El-Ewady and A. S. Fouda, *Port. Electrochim. Acta* 18 (2000) 99
- [14] S. S. Abd El-Rehim, M. A. M. Ibrahim and K. F. Khaled, *J. Appl., Electrochem.* 29 (1999) 593.
- [15] F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin and M. Lagrene, *Corros. Sci.* 44(2002) 2271.
- [16] E. E. Ebenso, *Mater. Chem. Phys.* 71 (2002)62.
- [17] A.S.Fouda, M.N.Moussa, F.I.Taha and A.I.Elnanaa, *Corros. Sci.* 26(9) (1986)719.
- [18] M. Abdallah, E. A. Helal and A. S. Fouda: *Corros. Sci.*, 48 (2006) 1639.
- [19] E. E. Oguzie; *Mater. Letters*, 59 (2005) 1076.
- [20] Pandey, P. C.; Prakash R. Characterization of electropolymerized polyindole; application in the construction of a solid-state ion-selective electrode. *J. Electrochem. Soc.*, 145(12) (1998) 4103-4107.
- [21] M. Abdallah, H.MAI-Tass, B.A.ALJahdaly, A.S. Fouda, *Journal of Molecular Liquids* 216 (2016) 590-597
- [22] A. S. Fouda, M. Morsi, H. A. Mosallam, *ZASTITA MATERIJALA* 57 (2016) broj, 33-45
- [23] Mohan, J.; Joshi, S.; Prakash, R.; Srivastava, R. C. Novel Ni(II) mixed ligand complex modified electrode: catalytic effect on anodic oxidation of phenol. *Electroanalysis*, 16(7) (2004)572-576.
- [24] Schmitt, G., Bedbur, K., and Werkst, Ü. *Korros.*, 36 (1985)273
- [25] Kunitsugn, A. M., Hagiwara and Hiroshi Nishihara., *Corros. Sci.* 27 (5)(1987)487
- [26] H. Fisher, *Ann. Univ. Ferrara. Sez. 3 (Suppl. 3) (1960) 1.*
- [27] G.N.Mu,X.H.L and Q.Quand J.Zhou, *Corros.Sci.*, 48(2006)445.
- [28] Z.Szkarska-Smiałowska; *Electrochemical and Optical Techniques for the Study of Metallic Corrosion*, Kluwer Academic, the Netherlands; (1991) 545.
- [29] M.Kliskic,j.Radosevic and S.Gndic,j.*Appl.Elelectrochem.*;27(1997) 200 .
- [30] Singh, A.K., Quraishi, M.A., *Corros. Sci.* 52(2010) 152.
- [31] Bouklah, M., Hammouti, B., Lagrene, M., Bentiss, F.*Corros. Sci.* 48(2006), 2831.
- [32] Li, X., Deng, S., Fu, H., *Prog. Org. Coat.* 67(2010) 420.
- [33] Noor, E.A., Al-Moubaraki, A.H., *Mater. Chem. Phys.* 110(2008) 145.
- [34] F. L. Laque and H. R. Gapson; *Corrosion resistance of metals and alloys*; 2nd ed. Reinhold Publishing Corporation, New York, (1963).
- [35] A. S. Fouda, H. A. Mostafa, F. El-Taib and G. Y. El-Ewady, *Corros. Sci.*, 47(2005)1988-2004.
- [36] A.S.Fouda, A.A. Al-Sawary, F.Sh. Ahmed and H.M. El-Abbasy; *Corros. Sci.*; 51(2009)485.
- [37] L. Riggs and R. M. Hurd; *Corrosion*; 23 (1967) 252.
- [38] M.Bouklah, B.Hammouti, M.Lagrene, F.Bentiss; *Corros. Sci.*48 (2006)2831.
- [39] M. K. Gomma and M. H. Wahdan; *Mater. Chem. Phys.* 39 (1995) 209.
- [40] N. Cahskan and S. Bilgic, *Appl. Suref. Sci.*, 153 (2000) 128.
- [41] I. Sekine, M. Sabongi, H. Hagiuda, T. Oshibe, M. Yuasa, T.Imahc, Y. Shibata, and T. Wake; *J. Electrochem. Soc.*; 139 (1992) 3167.
- [42] M.Lagrene, B.Mernari, B.Bouanis, M.Traisnel and F.Bentiss, *Corros.Sci.* 44 (2002) 573.
- [43] M. Bethencourt, F.J. Botana, J.J. Calvino, M. Marcos; *Corros. Sci.*, 40 (1998) 1803.
- [44] Kus. E, Mansfeld. F; *Corros. Sci.*, 48 (2006) 965.
- [45] A.M.Abdel-Gaber; *Inter.J.of Appl.Chem.*;3(3)(2007)161.
- [46] G. Gece, *Corros. Sci.*, 50 (2008) 2981.
- [47] D.Q. Zhang, L.W. Gao and G.D. Zhou, *Corros. Sci.* 46 (2004) 3031.
- [48] G. Gao and C. Liang, *Electrochim. Acta*, 52 (2007) 4554.
- [49] Y. Feng, S. Chen, Q. Guo, Y. Zhang and G. Liu, *J. Electroanal. Chem.*, 602 (2007)115.
- [50] N. Khalil, *Electrochim. Acta*, 48 (2003) 2635.
- [51] H. Shorky, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie, G.K. Gomma, *Corros. Sci.* 40 (1998)2173.
- [52] G.N. Mu, T.P. Zhao, M. Liu and T. GU, *Corrosion* 52 (1996) 853.
- [53] Ashish Kumar Singh and M.A. Quraishi, *Corros. Sci.*, 52 (2010) 1529.

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