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The Anticorrosive effect of Ethylene-1,1′-dimethyl-4,4′-bipyridinium iodide on Corrosion of Mild Steel in Acid Solution

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The electrochemical investigations of corrosion behavior of mild steel in sulfuric acid solution in presence and absence of different concentration of Ethylene-1,1′-dimethyl-4,4′-bipyridinium iodide (Edpi) at different temperatures were performed. The measurement of potentiodynamic polarization revealed that (Edpi) act as mixed type inhibitor with predominated of anodic effect. It was shown the adsorption process obeyed Langmuir adsorption isotherm and the inhibition efficiency increased with increased (Edpi) concentration and decreased with rise of temperatures. The effect of immersion time in R_p was studied, and the decreased of R_p with time suggest a deficiency in adsorbed film with long immersion time.

Keywords: Corrosion, Mild steel, Pyridinum, Immersion time.

1. INTRODUCTION

Corrosion of the metals is a major public health problem affecting the economic and human live. The mild steel has been one of the most important metal used as construction material in a lot of industries process[1]. It is consider a basic materials for metallurgical industries[2]. The main problem of using mild steel is its failure from corrosion in acidic solution.

In general acid solution such as sulfuric acid is widely used in many industrial application such as removal undesirable rust, acid pickling, acid cleaning and acid descaling [3]. The side effect of use acid in cleaning process, is causes corrosion of the metal on the cleaned surfaces even after removal of the corrosion products[4].

Therefore, many studies were afforded to protect metals from corrosion. Inhibitors are the most application where used to control corrosion of the metals. Corrosion inhibitors efficiently reduce the undesirable destructive effect and prevent metal dissolution. The use of inhibitors for the control of corrosion of metals and alloys, which are in contact with the aggressive environment, is therefore essential[4]. Organic compounds bearing hetero atoms with high electron density such as phosphorous, sulfur, nitrogen, oxygen or those containing multiple bonds which are considered as adsorption centers, are effective as the corrosion inhibitor[5–9].

In general, Such compound were added in tiny quantity and it is able to adsorpe on the metal surface and forming thin film which isolate metal surface from corrosive solution. The inhibitor molecules are bonded to the metal surface by chemisorption, physical adsorption or complexation, with the polar groups acting as the reactive centers in the molecules[9]. Many factors can affect the adsorption process such as nature of metals, inhibitors and aggressive environment [10].

The determination of type of adsorption is very important to know different parameter such as degree of surface converge and free energy of adsorption process[11].

Numerous studies have been reported on the topic of corrosion protection of mild steel in different acid environment. It has been reported by Avci that the presence of *N,N*_-Methylenediacrylamide[12] and indole-3-acetic acid[10] able to protect mild steel in acidic medium (0.5 M HCl). Doner et al[4] carried out a number of investigations into the effect of N-aminorhodanine on mild steel protection in 0.5 M H_2SO_4 and they found the inhibition efficiency increase with increasing inhibitor concentration. Resent evidence suggested heterocyclic containing nitrogen atom provided superior corrosion properties compare with the alkyl substituted quaternary ammonium compounds[13]. In another major study, Zhang et al [14] found that triazole derivatives provided excellent inhibition action against corrosion of carbon steel in HCl acid. Some quaternary N-heterocyclic compounds have been reported as good corrosion inhibitors for mild steel in HCl[15] and H_3PO_4[13]. Four quaternary ammonium bromides of different heterocyclic compounds were investigated as corrosion inhibitors of mild steel in 1 M HCl and 1 M H_2SO_4[16].

This paper attempts to show the corrosion kinetic parameters of mild steel and the adsorption thermodynamic parameters of Ethylene-1,1′-dimethyl-4,4′-bipyridinium iodide (Edpi) inhibitors (Fig. 1) on mild steel in 0.5M H_2SO_4 solution by using electrochemical technique such as potentiodynamic polarization and electrochemical impedance spectroscopy.

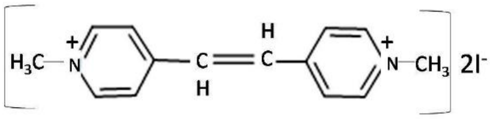

Figure 1. structures of the Ethylene-1,1′-dimethyl-4,4′-bipyridinium iodide (Edpi)

2. EXPERIMENTAL DETAILS

2.1. Materials and electrochemical cell

Sulfuric acid (> 98%, Fluka) and absolute ethanol (99.9%, Merck) were used as received. Ethylene-1,1′-dimethyl-4,4′-bipyridinium iodide (Edpi) inhibitors was synthesized as described before[17]. 0.5 M H_2SO_4 solution was prepared using bi-distilled water. The inhibitor solution was prepared by dissolving the appropriate weight in bi-distilled water, the solutions test were prepared at open atmosphere and constant temperature at 25^oC.

An electrochemical cell with a three-electrode was used for electrochemical measurements; mild steel rod (10 mm in diameter) coated with epoxy leaving the bottom working area of 0.79 cm^2, a platinum sheet, and a Metrohm Ag/AgCl electrode (in 3 M KCl) were used as a working, counter, and reference electrodes, respectively. The chemical composition (Wt. %) of the mild steel used in this study was: 0.055C, 0.010S, 0.008P, 0.007Si, 0.179Mn and the rest is Fe. Mild steel electrode was polished by a series of sand papers up to 1200, rinsed with ethanol and double distilled water and dried in air. Prior to any experiment, the working electrode was treated as described and freshly used with no further storage.

2.2. Electrochemical Corrosion test

ptentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurement were carried out in different temperatures and range of inhibitor concentration using Potentiostate/glvanostate ACM Gill AC instrument.

The polarization curves were recorded with a scan rate of 60 mV/min, where the initial potential was the corrosion potential value reached after 15 minutes of exposure time. The polarization curves were obtained starting from the open circuit potential (OCP) and varying the potential up to 200 mV in anodic branch of the Tafel plot and down to −800 mV cathodic branch of the Tafel plot. Electrochemical impedance spectroscopy data were obtained at corrosion potential over a frequency range from $1x10^4$ Hz to 0.1 Hz using AC amplitude of 30 mV around the open circuit potential.

3. RESULT AND DISCUSSION

3.1 Potentiodynamic polarization

Fig. 2 show the potentiodynamic polarization curves of mild steel in 0.5M H_2SO_4 at 25^o C in absence and presences of different concentration of inhibitor. It is noticeable from the figure that increasing inhibitor concentration leads to decrease the cathodic and anodic current density. In spite of, the corrosion potential shift to anodic direction with increasing the inhibitor concentration, this type of inhibitor can be classified as mixed type inhibitor with main anodic effective. Ferreira et al [18] assumed that the inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank. In this study, the maximum shift was about 54 mV. This indicate the presences of inhibitor adsorbed on the metal surface and working by simple blocking mechanism of reactive site on the mild steel surface and reduce both anodic metal dissolution and hydrogen evolution reaction.

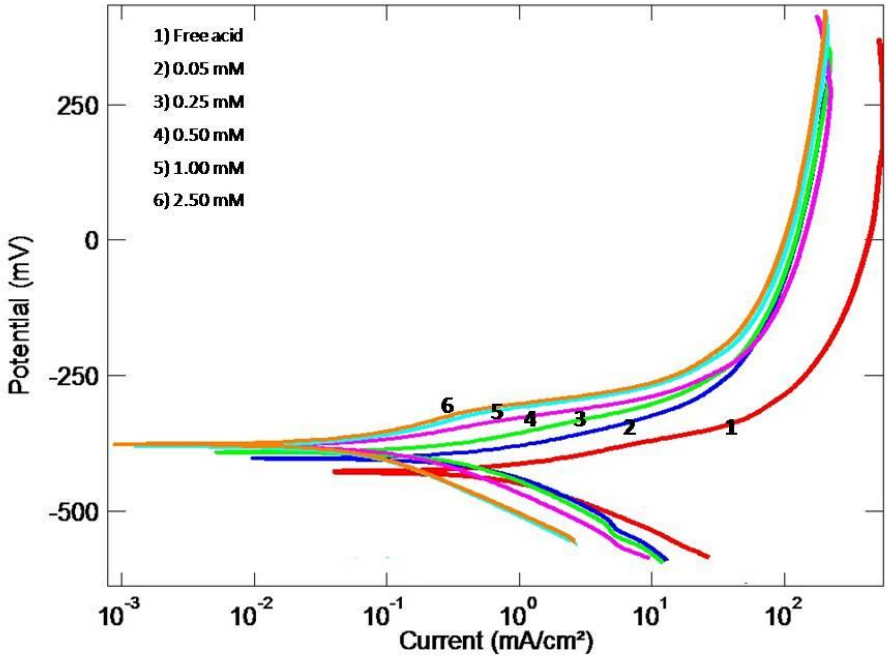

Figure 2. potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 in absence and presence of various concentrations of Edpi

The different polarization parameter such as corrosion potential (E_{corr}), corrosion current (i_{corr}), anodic and cathodic tafel slop (βa and βc) and inhibition efficiency IE_i% were tabulated in table 1.

The IE_i% can be calculated from the following relation:

$$IE_i\% = \left(1 - \frac{i_{corr}}{i^{o}_{corr}}\right) \times 100$$ **eq. 1**

where i_{corr} and i^o_{corr} are the inhibited and the uninhibited corrosion current densities, respectively. The corrosion current densities were obtained by the extrapolation of the cathodic current–potential lines to the corresponding corrosion potentials. It is useful to note that the numerical value for βa and βc not change extremely in presences of inhibitor suggesting the mechanisms of anodic and cathodic reaction not change by adding the Edpi. The value of both of βa and βc is consider as measurement of the symmetry of activation barrier for anodic and cathodic process, as observed from Fig.2 the shape of anodic and cathodic curve not change considerably with addition of inhibitor. In addition, the data in table 1 revealed the corrosion current decrease from 20.21 mAcm^{-2} of blank solution to 1.88 with addition of 2.5 mM of Edpi inhibitor. In contrary the inhibition efficiency increase with increasing Edpi concentration. It can be said that Edpi form a thin protective film act as barrier layer isolate metal surface from contact with acid solution.

3.2 Electrochemical impedance spectroscopy study

EIS spectra measurement is useful technique to evaluate the kinetic parameter. The Nyquist (fig. 3a) and Bode plot (fig. 3b) show the EIS spectra of inhibited and uninhibited system respectively. As can see from fig 3a, the Nyquist plot is depressed semicircles with capacitive loop, the deviation from an ideal semicircle is generally attributed to the frequency dispersion as well as to the inhomogeneities of surface and mass transport resistant[19]. In the current study, comparing inhibited solution with blank showed that the diameter of semicircle of blank solution has considerably changed after addition of different concentration of Edpi to the solution. From the data in Bode plot (Fig. 3b); it is apparent that the Area under |Z|-frequency curves can be used for Predicts of protection performances of the inhibitor. In the figure, there is a clear trend of increase the area under |Z|-frequency plots with increasing of inhibitor concentration. Increase of area under these curves with increasing concentration is strong evidence of the enhancement of corrosion resistance of steel metal. This result can be explained by increasing the number of adsorbed molecules with higher concentration that leads to decrease the contact of free metal area with corrosive media.

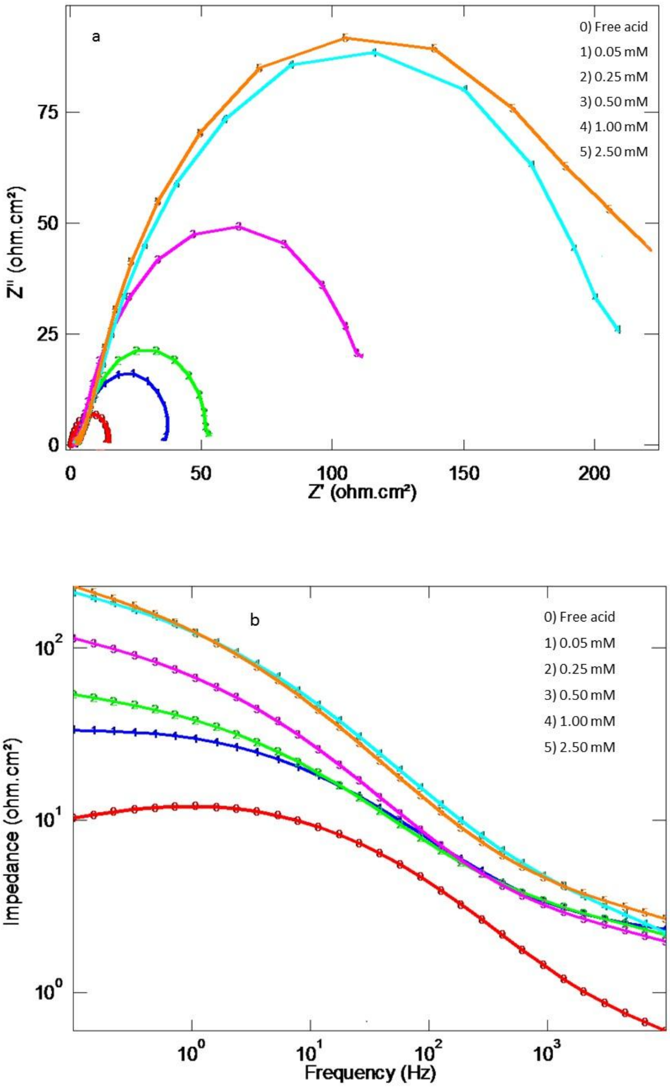

Figure 3. Nyquist(a) and Bode(b) plots for mild steel in 0.5M H_2SO_4 in absence and presence of various concentrations of Edpi

Table 1. Electrochemical parameters obtained from PDP and ES measurements on mild steel in 0.5M H_2SO_4 in absence and presence of various concentrations of Edpi

C_{inh} (mM)	E_{corr} (mV)	I_{corr} ($mAcm^{-2}$)	b_a ($mVdec^{-1}$)	b_c ($mVdec^{-1}$)	θ	IE_i%	Q_t10^3 (Fcm^{-2})	n	R_p (Ωcm^2)	IE_R%
Free acid	-429	20.21	79.12	135.82		-------	1.81	0.91	14.90	-------
0.05	-401	8.76	81.38	134.60	0.57	56.66	1.59	0.87	38.74	60.71
0.25	-390	6.34	74.17	122.82	0.69	68.62	1.38	0.87	54.08	71.40
0.50	-382	4.01	57.81	117.16	0.80	80.16	1.35	0.88	114.28	86.77
1.00	-379	3.13	52.29	126.68	0.89	88.63	1.34	0.85	209.66	92.87
2.50	-375	1.88	50.99	131.25	0.91	91.37	0.50	0.86	226.51	93.30

The kinetic parameter determined by fitting with the most proper equivalent circuit (Fig. 4) and tabulated in table 1. Where, Rs represents the solution resistance, the constant phase elements (CPE), and R_p the polarization resistance and can be defined also as the charge transfer resistance[20]. The summation of the film capacitance and double-layer capacitance represents the total capacitance of capacitor.

The IE_R% values can be calculated from R_p data as follows:

$$IE_R\% = \left(1 - \frac{R^{-1}{}_p}{R_p^{o-1}}\right) \times 100 \qquad \textbf{eq. 2}$$

Inspection of data in table 1 revealed that the value of R_p and IE_R% increase, while the value of CPE decreased with increasing of Edpi concentration. This result gives significant indication that Edpi molecules inhibit the corrosion of mild steel in acid solution by adsorption mechanism[21].

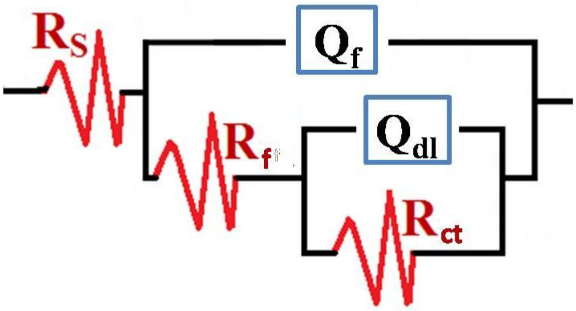

Figure 4. The equivalent circuit model used to fit the experimental impedance data

3.3 Adsorption isotherm

Evaluation of inhibition efficiency of Edpi molecule is determined by its ability of adsorption on the metal surface. However, isotherm diagram is often obtained by plotting of the degree of coverage (θ) of the metal surface versus different concentration of inhibitor. The values of θ which calculated from the following equation [22] were inserted in table2

$$\theta = \left(1 - \frac{i_{corr}}{i^{o}_{corr}}\right) \qquad \textbf{eq. 3}$$

where i_{corr} and i^{o}_{corr} are the inhibited and the uninhibited corrosion current densities, respectively. As Table 2 shows, there is a significant increased with increasing inhibitor concentration and decreased with rising of temperatures. According to θ values, Langmuir adsorption isotherm which given in equation (4) is the best fitted of the result

$$C_{inh}\theta^{-1} = \frac{1}{K_{ads}} + C_{inh} \qquad \textbf{eq. 4}$$

Plotting of C_{inh} θ^{-1} vs. concentration of inhibitor C_{inh} was shown in Fig.5 and gives straight line with intercept equal to reciprocal of adsorption equilibrium constant $K_{ads.}$ This isotherm assumes that the adsorbed molecules occupy only one site, and there are no interactions with other molecules adsorbed[10].

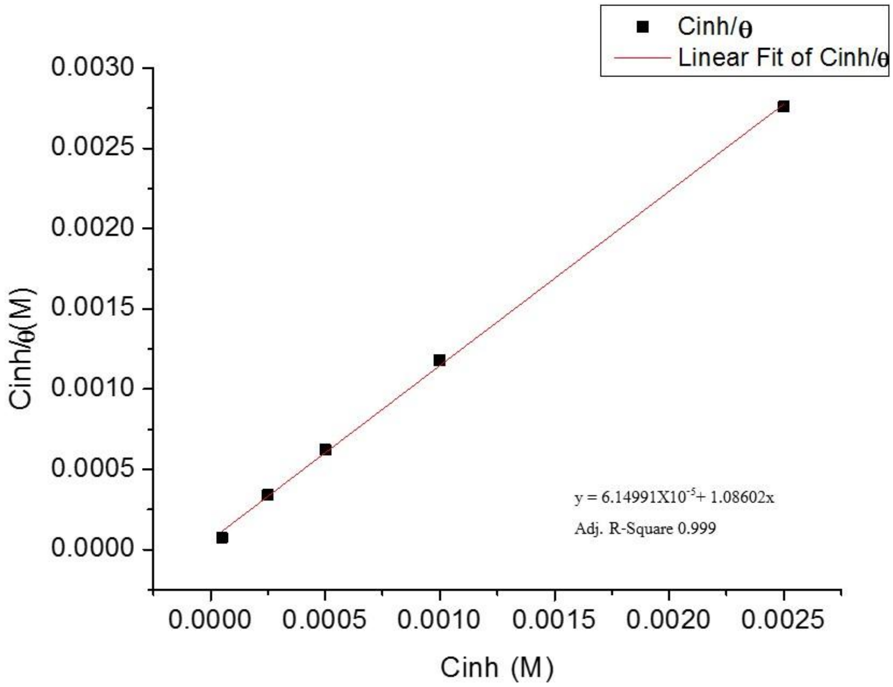

Figure 5. Langmuir Isotherm plot for mild steel in 0.5M H_2SO_4

The heat of adsorption (ΔH_{ads}) was obtained from the slope of straight line produced from the following equation[22]:

$$\frac{\theta}{1-\theta} = AC \exp\left(\frac{-\Delta H_{ads}}{RT}\right) \qquad \textbf{eq. 5}$$

Where R is gas constant, A is independent constant, T is temperatures and C is concentration of inhibitor. The correlation between adsorption constant (K_{ads}) and the free energy of adsorption (ΔG_{ads}) are shown in the following equation[10]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad \textbf{eq. 6}$$

The calculated value of ΔG_{ads} was about (-23.78KJ/mol), however, the negative value of ΔG_{ads} provided the spontaneously of adsorption of Edpi molecule on metal surface. Some authors have speculated [23,24] that negative values of ΔG_{ads} 20 kJ/mol or lower are endorsed the electrostatic interaction between the charged molecules and the charged metal (physisorption), while that negative values of ΔG_{ads} 40 kJ/mol or higher indicate of interaction of lone pair of electron in the adsorbed molecules with metal to form coordination bond (chemisorotion). This indicates that value of ΔG_{ads} (-23.78KJ/mol) is associated with physisorption type.

Table 2. Adsorption parameters and Corrosion activation parameters in presence of 0.50 mM Edpi on mild steel in 0.5M H_2SO_4

Sample	$K_{ads}10^{-4}$ (M^{-1})	ΔH_{ads} KJ/mol	ΔG_{ads} KJ/mol	E* KJ/mol	ΔH* KJ/mol	ΔS* J/Kmol	ΔG* KJ/mol				
							25°C	30 °C	35 °C	40 °C	45 °C
Free acid	-----	-----	-----	34.47	30.91	-122.87	67.53	68.14	68.76	69.37	69.99
inhibitor	1.60	83.21	23.78	47.44	46.88	-81.96	71.30	71.71	72.12	72.53	72.94

3.4 Effect of temperature

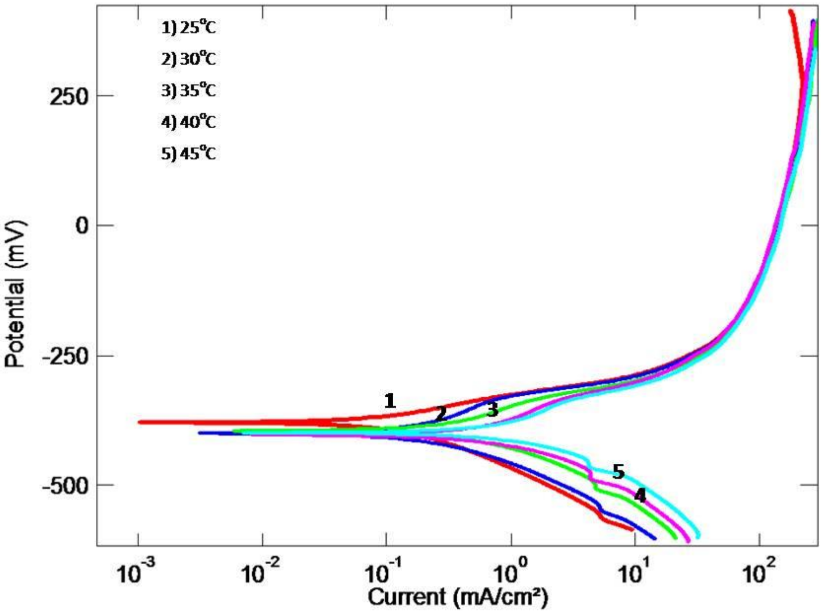

Figure 6. potentiodynamic polarization curves for mild steel in presence of 0.50 mM Edpi in 0.5M H_2SO_4 at different temperatures.

In this part, the electrochemical measurements were carried out in 0.5 H_2SO_4in absence and presence of 0.50 mM of Edpi at range of temperatures. The potentiodynamic polarization in fig.6 and the EIS measurement in fig.7 were performed in temperatures rang (25-45^{o}C) to evaluate the effect of change of temperature on inhibition efficiency. The effect of change the temperatures on corrosion parameters were estimated and presented in table 3, in table 3 there is a clear trend of decreasing of corrosion rate, surface coverage (θ) and the value IEi% with higher temperature. This result may be explained by the fact that Edpi molecules are adsorbed physically on metal surface[1].

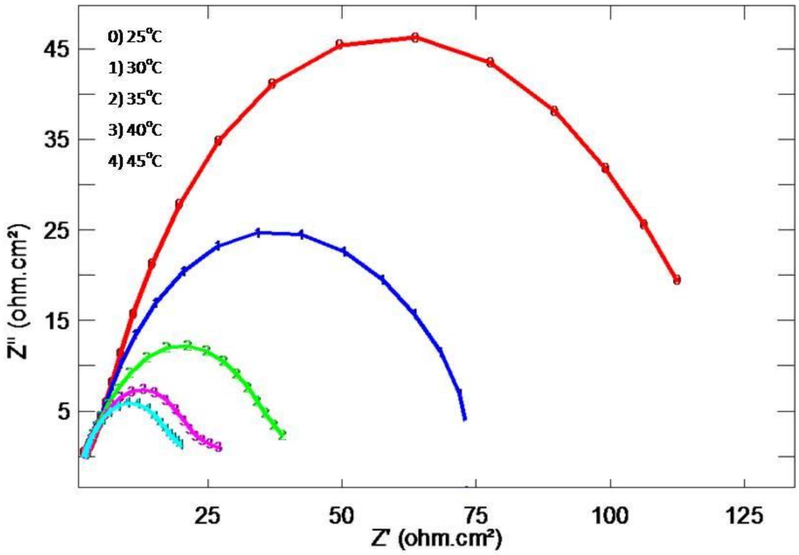

Figure 7. Nyquist plots for mild steel in presence of 0.50 mM Edpi in 0.5M H_2SO_4 at different temperatures.

Table 3. The effect of temperature on corrosion parameter in presence of 0.50 mM Edpi on mild steel in 0.5M H_2SO_4

T (^{o}C)	E_{corr} (mV)	i_{corr} ($mAcm^{-2}$)	Ba ($mVdec^{-1}$)	Bc ($mVdec^{-1}$)	θ	IE_i%	Q_t10^3 (Fcm^{-2})	n	R_p (Ωcm^2)	IE_R%
25	-382	4.01	57.81	117.16	0.80	80.16	2.34	0.88	114.28	86.96
30	-386.19	6.60	63.46	111.23	0.67	67.32	1.42	0.81	71.18	79.07
35	-394.18	8.73	78.94	122.76	0.57	56.79	3.13	0.84	37.70	60.48
40	-390.17	11.10	70.28	111.82	0.45	45.06	5.76	0.87	25.97	42.63
45	-394.89	13.87	91.38	144.62	0.31	31.37	12.9	0.90	23.31	36.08

Noor investigated the effect of temperature on inhibition action of N-hetrocyclic on corrosion of mild steel in phosphoric acid and she explained this result as decreased of time lag between adsorption-desorption process of inhibitor molecules above the metal surface with increasing of temperature[13]. The activation energy of corrosion process can be found from slope of Arrhenius equation[10]:

$$i_{corr} = Aexp\frac{-E_a}{RT} \qquad \textbf{eq. 7}$$

where A is Arrhenius factor, E_a is the apparent activation corrosion energy, this equation is represented in fig 8. As reported before the lower value of activation energy of corrosion process in the presence of inhibitor compare with blank solution is attributed to its chemisorption, opposite behavior is found in the case with physical adsorption[23]. Comparisons between the activation energy of uninhibited and inhibited system shows the inhibited systems have higher value (40.54 KJ/mol) than uninhibited solution (34.47 KJ/mol). These findings suggest that the reduction of corrosion process attributed to that adsorbed inhibitor formed physical barrier on metal surface.

The other kinetic parameter such as enthalpy, entropy and free energy of activation (ΔH*,ΔS* and ΔG*) of corrosion process for uninhibited and inhibited system can be calculated from the following equations[1]:

$$i_{corr} = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \qquad \textbf{eq. 8}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \textbf{eq. 9}$$

where h is the Plank constant, N is the Avogadros number. All activation parameters were calculated in presence and absence of 0.50 mM of inhibitor and presented in table 2

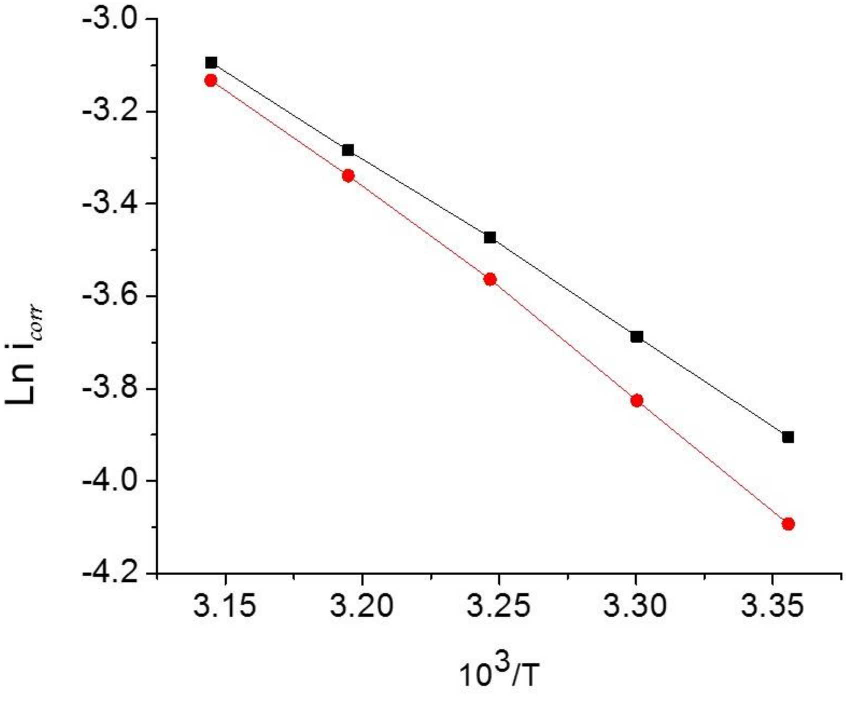

Figure 8. Arrhenius plots for the corrosion for mild steel in absence (■) and presence (•) of 0.50 mM Edpi in 0.5M H_2SO_4

The results, as shown in Table 2, show the higher values of these parameters for the inhibited solution compare with the uninhibited one. The positive value of enthalpy of activation is strong evidence for the endothermic reaction. As describe elsewhere[25], the negative singe of entropy of activation specify that the order of the system increase throughout activation process, this result is good indication of formation of activated complex which related to gradual decrease of degree of freedom of system during the corrosion process. The present findings seem to be consistent with other research[26], which found the similar result when used cyclic amine compound as inhibitor for mild steel in HCl solution.

In case of ΔG*, It is apparent from table 2 that very few increscent with rising temperatures, which be a sign of instability of formed activated complex and its formation decrease in higher temperature. A comparison of the ΔG* values with and without inhibitor reveals a higher value with presence of inhibitor which indicate the decrease of stability of activated complex with inhibitor.

3.5 Effect of immersion time

Fig.9 presents EIS spectra measurement at different immersion time(15min,1, 4, 10, 16 and 24 h) in 0.5 M H_2SO_4 containing 0.50 mM of Edpi.

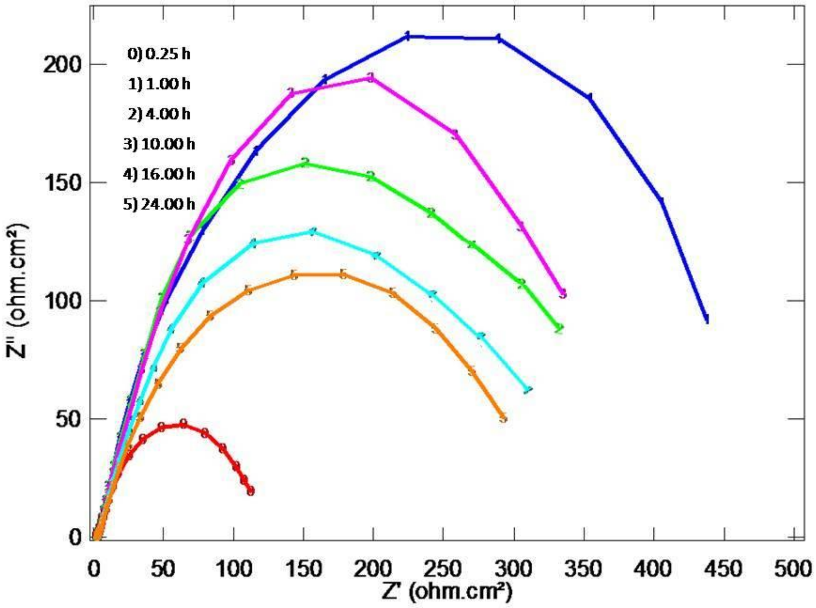

Figure 9. Nyquist plots for mild steel in presence of 0.50 mM Edpi in 0.5M H_2SO_4 at different immersion time.

The impedance spectra show a capacitive loop at both frequency region and the results obtained from the analysis of fig.9 can be compared in table 4. What is interesting in the table 4 is that diameter of semicircle (Rp) change with the immersion time, the maximum Rp occurs at one-hour exposure time. However, after a period, Rp is decreased with long immersion time. This suggest a deficiency in adsorbed film with long immersion time due to the interaction between metal and electrolyte which leads to dissolution of metal and hydrogen evolution at pores [27] , which allow of penetration of corrosive ions during the film microspores. The increasing of Rp after 10-hours may explained of accumulation of corrosion product in film pores which provides weak protection, however this protection filed with higher time and Rp decreased again[28].

Table 4. The EIS parameter of 0.50 mM Edpi on mild steel in 0.5M H_2SO_4

Time (h)	Rs (Ωcm^2)	n	Q_t10^3 (Fcm^{-2})	Rp(Ωcm^2)
0.25	1.71	0.85	24.99	132.86
1.00	2.04	1.00	7.28	448.31
4.00	2.08	0.84	6.48	402.98
10.00	2.56	0.84	6.77	427.93
16.00	2.38	0.81	8.81	354.35
24.00	2.07	0.77	11.46	328.14

Fig.10 gives a clear vision of vibration of of Rp and Qdl with different immersion time. From the graph, we can see that Rp decrease with time except at 10-houres as explained before. In contrast, Qdl increased resulting from increase of solution uptake with long period time[29]

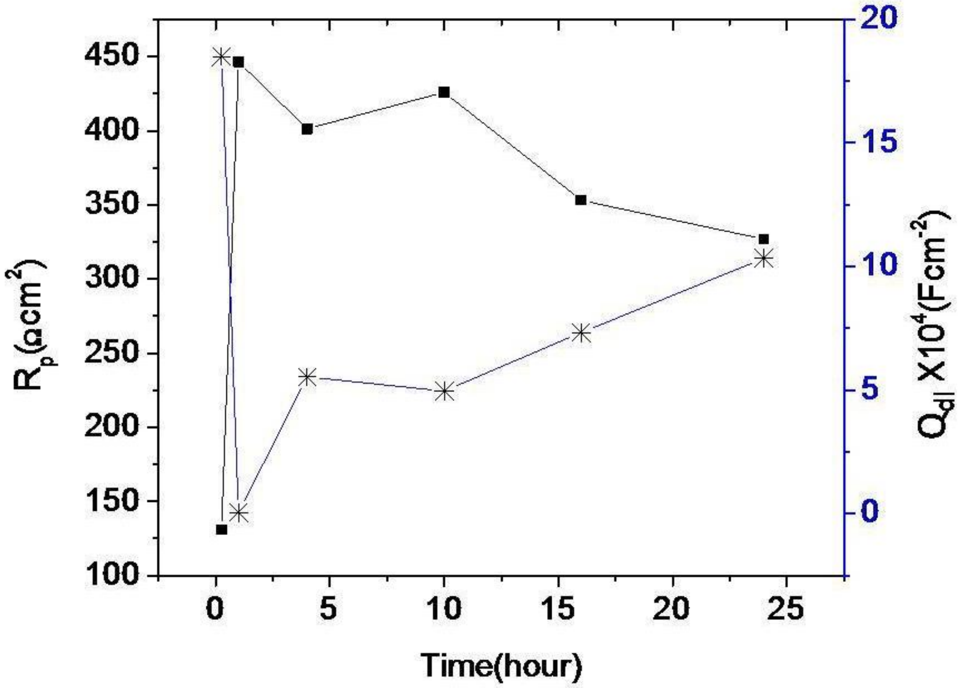

Figure 10. plots of R_p and Q_{dl} for mild steel in presence of 0.50 mM Edpi in 0.5M H_2SO_4 as function of immersion time.

3.6 Mechanism of inhibition

In view of the fact that the mild steel acquires a positive charge in H_2SO_4 as reported before, the inhibition of anodic and cathodic reaction in presence of Edpi depend on adsorption. It was suggested adsorption of Iodide ions, which present in the solution in first step, followed by electrostatic attraction between ionic charges on the adsorbed species and the electric charge at the metal (physical adsorption). The cathodic site on the metal is blocked by adsorption of bi-pyridinium cations which slow down hydrogen evaluation process (cathodic reaction), while the anodic reaction (dissolution of metal) can be hindered by adsorption of aromatic ring on anodic site on metal surface (planar adsorption) and the methyl group tail extended away in the solution[17]

4. CONCLUSION

The most obvious finding to emerge from this study is that Edpi provided inhibition of mild steel in 0.5M H_2SO_4. The inhibition efficiency increased with increased of Edpi concentration and decreased with rise of temperatures. The results of potentiodynamic polarization revealed that Edpi worked as mix type inhibitor. The adsorption was followed the Langmuir isotherm and the large values of adsorption parameter show strong adsorption of inhibitor molecules on surface of mild steel. The increase of value of activation parameters with inhibitor rather than without inhibitor emphasized the physical adsorbed of this compound on metal surface.

References

1. A.S. Fouda, Al-sarawy A A, E.E. El-katori, *Desalination,* 201 (2006) 1.
2. E.M. Sherif,A. A. Almajid , A. K. Bairamov , Eissa Al-Zahrani, *Int. J. Electrochem. Sci.*, 6 (2011) 5372.
3. K.C. Emregül, M. Hayvalí, *Corrosion Science,* 48 (2006) 797.
4. A. Döner, G. Kardaş, *Corrosion Science*, 53 (2011) 4223.
5. H. Hamani, T. Douadi, M. Al-Noaimi, S. Issaadi, D. Daoud, S. Chafaa, *Corrosion Science,* 88 (2014) 234.
6. J. Hu, D. Zeng, Z. Zhang, T. Shi, G.-L. Song, X. Guo, *Corrosion Science*, 74 (2013) 35.
7. N.O. Obi-Egbedi, I.B. Obot, *Arabian Journal of Chemistry*, 6 (2013) 211.
8. B. Xu, Y. Liu, X. Yin, W. Yang, Y. Chen, *Corrosion Science,* 74 (2013) 206.
9. I. Lukovits, E. Kálmán, F. Zucchi, *Corrosion,* 57 (2001) 3.
10. G. Avci, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 317 (2008) 730.
11. E.A. Noor, *Materials Chemistry and Physics,* 114 (2009) 533.
12. G. Avci, *Materials Chemistry and Physics*, 112 (2008) 234.
13. E.A. Noor, *Corrosion Science,* 47 (2005) 33.
14. S. Zhang, Z. Tao, W. Li, B. Hou, *Applied Surface Science*, 255 (2009) 6757.
15. E.A. Noor, A.H. Al-Moubaraki, *Materials Chemistry and Physics,* 110 (2008) 145.
16. A. Popova, M. Christov, A. Vasilev, *Corrosion Science,* 49 (2007) 3276.
17. M.S. Morad, A.A. Hermas, A.Y. Obaid, A.H. Qusti, *J Appl Electrochem.,* 38 (2008) 1301.
18. E.S. Ferreira, C. Giacomelli, F.C. Giacomelli, A. Spinelli, *Materials Chemistry and Physics,* 83 (2004) 129.
19. M. Behpour, S.M. Ghoreishi, N. Mohammadi, N. Soltani, M. Salavati-Niasari, *Corrosion Science,* 52 (2010) 4046.
20. E.M. Sherif, *Materials Chemistry and Physics,* 129 (2011) 961.
21. M.A. Migahed, *Materials Chemistry and Physics,* 93 (2005) 48.
22. M. Abdallah, *Corrosion Science,* 44 (2002) 717.

23. L. Larabi, Y. Harek, O. Benali, S. Ghalem, *Progress in Organic Coatings*, 54 (2005) 256.
24. F.M. Donahue, K. Nobe, *J. Electrochem. Soc.*, 112 (1965) 886.
25. G. Samuel,Textbook of Physical Chemistry.D. Van Nostrand company, inc.,New York (1940).
26. A.A. El-Awady, B.A. Abd-El-Nabey, S.G. Aziz, *J. Electrochem. Soc*., 139 (1992) 2149.
27. M. Kraljić, Z. Mandić, L. Duić, *Corrosion Science*, 45 (2003) 181.
28. M.R. Mahmoudian, Y. Alias, W.J. Basirum, M. Ebadi, *Current Applied Physics*, 11 (2011) 368.
29. B.S. Skerry, C.-T. Chen, C.J. Ray, *The Journal of Coatings Technology*, 64 (1992)77.