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Ketorol: New and Effective Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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The corrosion inhibition properties of Ketorol on mild steel corrosion in 1.0 M HCl solution was studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss methods. EIS data were interpreted using CPE in equivalent circuit. Adsorption of the inhibitor on the mild steel surface followed the Langmuir adsorption isotherm. The value of free energy of adsorption (ΔG°_{ads}) is -35.52 kJ mol^{-1} indicated that adsorption of Ketorol is a spontaneous process. Ketorol exhibited the highest inhibition efficiency 92.36 % at concentration 300 ppm.

Keywords: EIS; Ketorol; Acid solution; Adsorption

1. INTRODUCTION

The use of organic compounds as corrosion inhibitors to reduce the metallic dissolution is an attractive research field. The mineral acids are generally used for pickling in various industrial processes. The hydrochloric acid is one of the important picking acids. The organic compounds which contain heteroatoms such as N, O, S, and π electrons are most effective corrosion inhibitors. They are adsorbed on the metal surface by replacing water molecules from that surface. Their adsorption depends upon electron density at the donor atom, functional group, π bond character and electronic structure [1-6]. In recent years, there is a growing interest on the development of drugs as inhibitors for metallic corrosion due to their non toxic nature. In literature, several authors have reported that drugs are efficient inhibitors for the corrosion of metals in acid media [7-12]. In the present investigation Ketorol used as corrosion inhibitor is based on the following reasons, it contains N and O heteroatoms as active centres, π bond electrons, higher molecular weight and commercially available in market.

In continuation of our work on the development of drugs as corrosion inhibitors [13-16], the present work aims to investigate the inhibitive action of Ketorol on the corrosion of mild steel in 1.0 M HCl solution. Ketorol is used as an analgesic. It acts by inhibiting the synthesis of prostaglandins. The electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, linear polarization measurement and weight loss method has been used in the present investigation. The effect of temperature was also studied. Several isotherms were tested for their relevance to describe the adsorption behavior of the compound on mild steel surface.

2. EXPERIMENTAL

2.1 Material and Chemicals

The mild steel coupons of the rectangular size (2.5 × 2.0 × 0.025) cm having the composition (wt %): C 0.17%; Mn 0.46%; Si 0.026%; Cr 0.050%; P 0.012%; Cu 0.135%; Al 0.023%; Ni 0.05%; and balance Fe were used for weight loss study. Mild steel coupons were abraded with emery paper before use as described a method in our previous work [15]. Electrochemical experiments were carried out with mild steel coupons of the same composition having a exposed area 1.0 cm^2 rest being covered with epoxy resin. The Ketorol drug used as inhibitor is available in injection form which is manufactured by Dr Reddy’s laboratories Ltd. Hyderabad (India). The IUPAC name of Ketorol, is (±)-5-benzoyl-2,3-dihydro-1H-pyrrolizine-1-carboxylic acid,2-amino-2-(hydroxymethyl)-1,3-propanediol, and its molecular structure is shown in Fig. 1. These structural features favour interaction of Ketorol, with mild steel. The stock solution of drug was prepared by dissolving Ketorol in 1.0 M HCl. This stock solution was diluted to a different concentration for experimental purpose. The inhibitor concentration was taken in ppm.

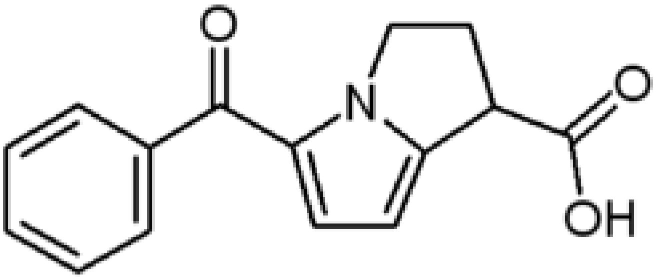

Figure 1. The molecular structure of Ketorol.

2.2 Electrochemical measurements

The electrochemical measurements were carried out by using Gamry Potentiostat/Galvanostat with a Gamry framework system based on ESA400. Gamry applications include software DC105 for corrosion, EIS300 for EIS measurements, and Echem Analyst version 5.50 software packages used for data fitting. A three-electrode cell employing a mild steel coupons as working electrode (WE), platinum as counter electrode, and saturated calomel electrode as a reference electrode (SCE). For the EIS measurements, measuring signal was a sine wave, range from 100,000 Hz to 0.01 Hz under potentiodynamic conditions, with amplitude of 10 mV peak-to-peak. Tafel polarization curves were obtained from anodic and cathodic potential from the range -250 to +250mV vs. OCP at a scan rate of 1 mVs^{-1} to study the effect the electrochemical nature of Ketorol.

2.3 Weight loss measurements

For weight loss experiments clean weighed mild steel rectangular coupons were immersed in 100 ml of 1.0 M HCl solution in absence and in the presence of different concentration of Ketorol. The coupons were taken out, washed, dried, and weighed accurately after the duration of 3 h at 303 K temperature. Triplicate experiments were performed in weight loss test for each concentration of inhibitor and without inhibitor and average of weight loss is reported.

3 RESULTS AND DISCUSSION

3.1 Electrochemical measurements

3.1.1 Electrochemical impedance spectroscopy (EIS) studies

The impedance spectra of mild steel in 1.0 M HCl without and with different concentration for Ketorol are presented as Nyquist plots in Fig 2 and Bode plots in Fig 3(a, b). As can be seen from the Fig. 2, depressed semicircles with the centre under real axis. These plots exhibit that the impedance spectra consists of one capacitive loop in high frequency (HF) zone. The capacitive loop arises from the time constant of the electrical double layer and charge transfer resistance [17-19]. The impedance response of mild steel has changed significantly after the addition of Ketorol and the diameter of semicircle of inhibited system increased with concentration. Fig. 3a presents the Bode diagrams for the same experimental data in /Z/ impedance vs log frequency in the presence of different concentrations of inhibitor. Figs.3a, there is no distinct diversification of impedance modulus, and the impedance modulus increase with inhibitor concentration. From the bode plots Fig. 3b phase angle at high frequencies provided a general idea of inhibition performance. Examining the phase angle vs. log freq. curves, Fig. 3b it is obvious that the most rapid relaxation process occurs at frequencies in the vicinity of 10^4 Hz. It is seen that the aforementioned relaxation process is associated with the double layer capacitance. At higher frequency greater the phase angle suggests the more capacitive electrochemical behaviour [20]. The phase angles with smaller values indicate higher surface roughness. The continuous increase in the phase angle shift Fig 3b correlating with the increase of inhibitor adsorbed on mild steel surface.

The equivalent circuit proposed to represent the corrosion of mild steel electrode in 1.0 M HCl solution, is shown in the Fig. 4. Where R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double-layer capacitance. A constant phase element (CPE) is substituted for the capacitive element to give a more accurate fit [21]. The introduction of such a CPE is often used to interpret data for rough solid electrodes. The Constant phase element (CPE) is a special element which exhibits more complicated frequency response than a simple undistributed RC time constant process [22]. Its impedance is expressed by the equation as:

$$Z_{\mathrm{CPE}} = Y_0^{-1}(i\omega)^{-n} \tag{1}$$

where Y_0 is the CPE constant, ω is the angular frequency ($= 2\pi f_{\max}$ in rad s^{-1}) and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface. The value of n parameter lies between 0.50 and 1.0 [23]. The double layer capacitance values C_{dl} derived from the CPE parameters according to:

$$C_{\mathrm{dl}} = (Y_0 R_{\mathrm{ct}}^{1-n})^{1/n}. \tag{2}$$

The electrochemical parameters are listed in Table 1. It can see from Table 1, the R_{ct} values increased with increasing the concentration of the inhibitor, indicated that a charge transfer process mainly controlling the corrosion process. The change of R_{ct} values can be related to the gradual replacement of water molecules by inhibitor molecules on the surface which decreases the number of actives sites necessary for corrosion reaction [24]. The inhibition efficiency $(\eta_{\%})$ of the inhibitor was calculated by the charge transfer resistance values using the following equation:

$$\eta_{\%} = \frac{R_{\mathrm{ct}}^{\mathrm{i}} - R_{\mathrm{ct}}^{0}}{R_{\mathrm{ct}}^{\mathrm{i}}} \times 100 \tag{3}$$

where, R_{ct}^{0} and $R_{\mathrm{ct}}^{\mathrm{i}}$ are the charge transfer resistance in absence and in the presence of inhibitor, respectively.

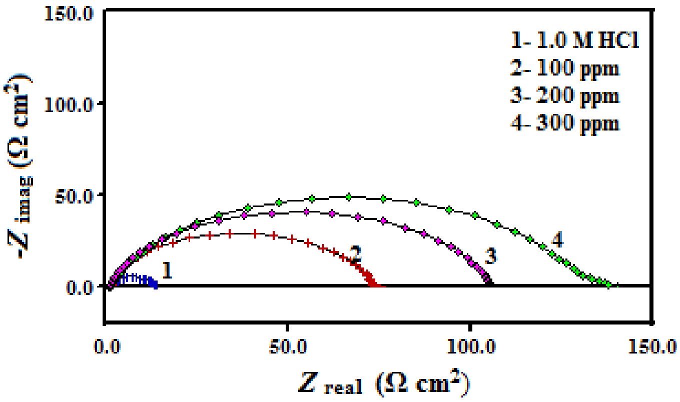

Figure 2. Nyquist plots for the mild steel in 1.0 M HCl with and without different concentrations of Ketorol

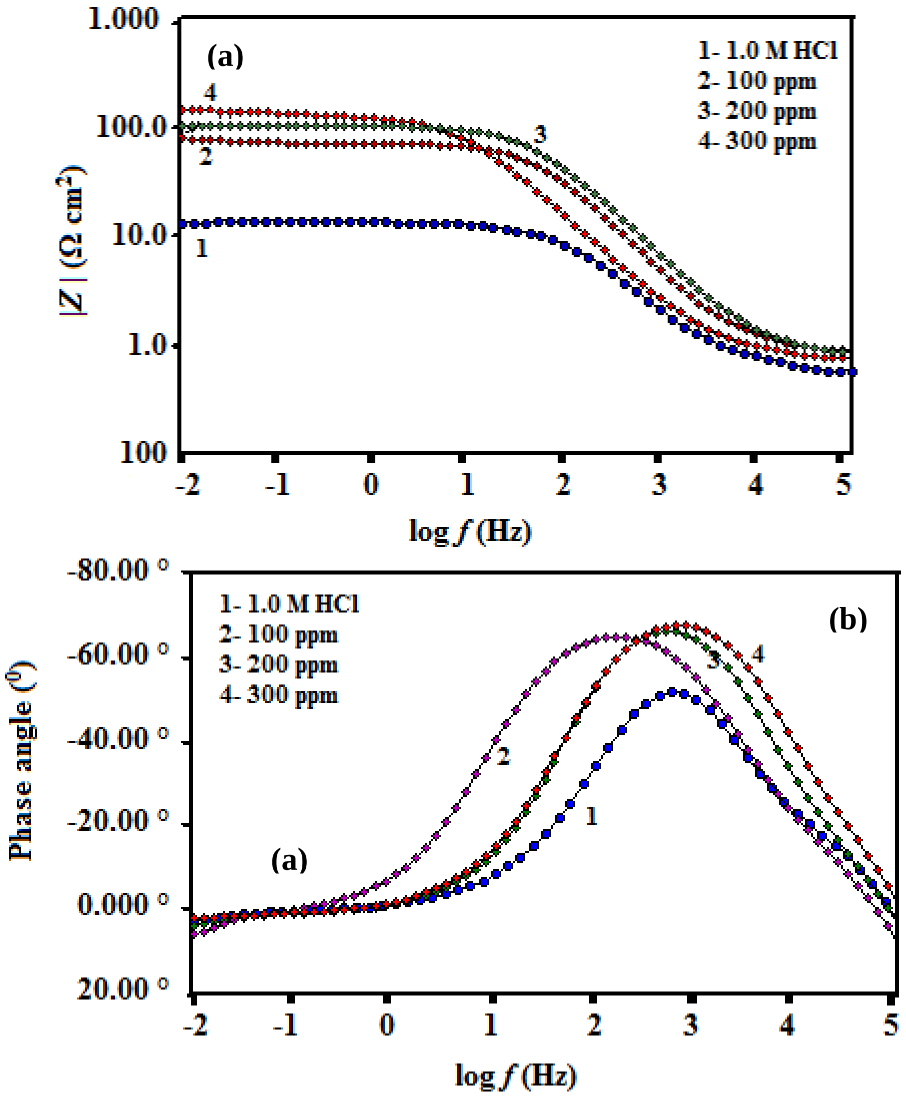

Figure 3. Bode plots of mild steel in absence and presence of different concentrations of Ketorol.

Table. 1. Calculated electrochemical parameters for mild steel in absence and presence of different concentrations of Ketorol.

Conc. of inhibitor	R_s (Ω)	N	R_{ct} (Ω cm^2)	C_{dl} (µF/Cm^2)	Inhibition efficiency ($\eta_{\%}$)
Blank	0.580	0.789	12.98	482.0	-
Ketorol					
100	0.774	0.820	73.42	320.4	83.32
200	0.855	0.860	104.2	104.7	88.25
300	0.905	0.870	132.9	81.96	90.78

On the other hand the values of C_{dl} decrease with an increase in the inhibitor concentration. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitors on the electrode surface mild steel may be attributed to the formation of a protective layer on the surface [25, 26].

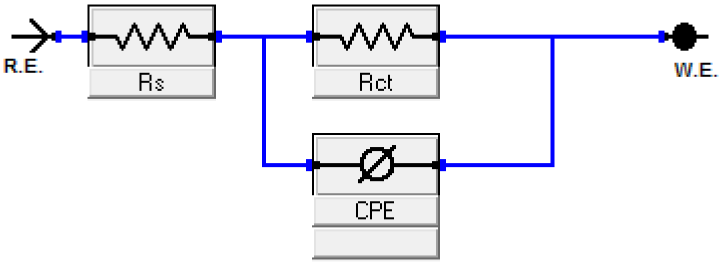

Figure 4. The equivalent circuit used to fit the impedance spectra.

3.1.2 Potentiodynamic polarization measurements

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions.

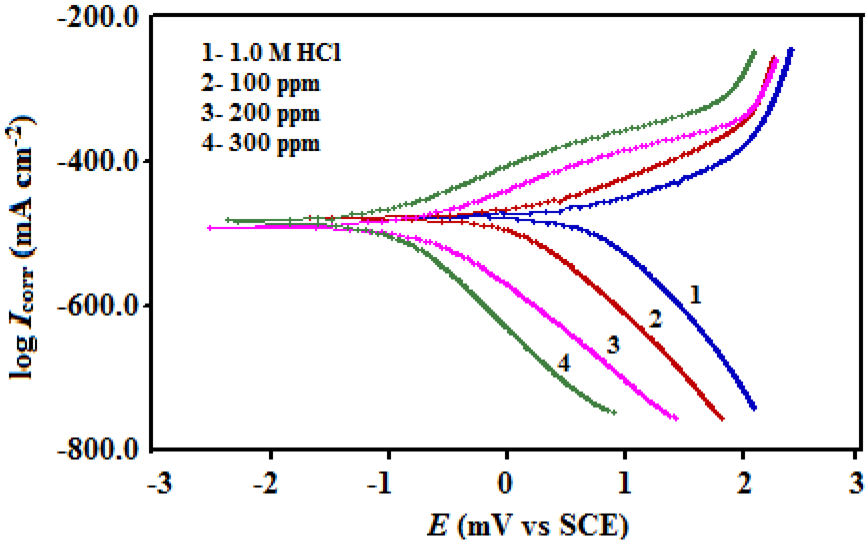

Figure 5. Polarization curves for corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentrations of Ketorol.

The of cathodic and anodic polarization curves recorded for mild steel in 1.0 M HCl solutions in absence and in the presence of various concentrations of Ketorol are shown in Fig 5. The electrochemical parameter such as corrosion potential (E_{corr}), corrosion current density (Icorr) cathodic Tafel slope (b_c), anodic Tafel slope (b_a) and inhibition efficiency are listed in Table 2. The inhibition efficiency ($\eta_{\%}$) was evaluated from the calculated (Icorr) values using the relationship:

$$\eta_{\%} = \frac{I^{0}_{\mathrm{corr}} - I^{\mathrm{i}}_{\mathrm{corr}}}{I^{0}_{\mathrm{corr}}} \times 100 \qquad (4)$$

where, I^{0}_{corr} and $I^{\mathrm{i}}_{\mathrm{corr}}$ are the corrosion current density in absence and in the presence of inhibitor, respectively. It is seen from the results that (*I*corr) shifted towards lower current density from 1780 µA cm^{-2} to136 µA cm^{-2} and give 92.36 % inhibition efficiency. It is also seen that addition of Ketorol did not cause any significant change in the value of E_{corr} [27-29]. The maximum displacement in E_{corr} value was 13 mV only. Both the slopes b_{c} and b_{a} change in presence of inhibitor this indicated that ketorol is a mixed type inhibitor.

Table. 2. Polarization parameters for mild steel in the absence and presence of Ketorol at different concentrations in 1.0 M HCl.

Inhibitor	Conc. of inhibitor	E_{corr} (mV vs. SCE)	β_{a} (mV dec^{-1})	β_{c} (mV dec^{-1})	I_{corr} (µA cm^{-2})	Inhibition efficiency ($\eta_{\%}$)
1.0 M HCl	-	-477.0	47.8	84.2	1780.0	-
Ketorol	100	-478.0	60.9	111.6	1000.0	57.87
	200	-490.0	72.5	123.7	221.0	87.58
	300	-483.0	95.5	172.1	136.0	92.36

3.2 Weight loss studies

3.2.1 Effect of inhibitor concentration

The effect of addition of different concentration of Ketorol on the dissolution of mild steel was studied by the weight loss method for three hour duration. The data are summarised in Table 3. The addition of concentration Ketorol lower the corrosion rate the maximum inhibition efficiency ($\eta_{\%}$) 95.71% is achieved at 300 ppm and further increase in concentration did not cause any appreciable change in the performance of the Ketorol. The inhibition efficiency ($\eta_{\%}$) is determined by following equation [30]:

$$\eta_{\%} = \frac{w_0 - w_{\mathrm{i}}}{w_0} \times 100 \qquad (5)$$

where w_0 and w_{i} is the weight loss value in the absence and presence of inhibitor, respectively. The corrosion rate (C_{r}) in (mg cm^{-2} h^{-1}) was determined using the following equation:

$$C_{\mathrm{r}} = \frac{w}{At} \qquad (6)$$

where *w* is a weight loss of coupons mild steel (mg), *A* the area of the coupon (cm^2), *t* is the exposure time (h).

Table 3. Parameters obtained from weight loss measurements of mild steel in 1.0 M HCl at different concentration of Ketorol at different 308 K.

Inhibitor	Conc. of inhibitor (ppm)	Corrosion rate (mg cm^{-2} h^{-1})	Surface coverage (θ)	Inhibition efficiency ($\eta_{\%}$)
1.0 M HCl	-	7.00	-	-
	100	1.83	0.7381	73.81
Ketorol	200	0.73	0.8905	89.05
	300	0.31	0.9571	95.71

3.2.2 Effect of temperature

The corrosion rate of mild steel was measured as a function of temperature in 1.0 M HCl in the absence and the presence of 300 ppm of Ketorol. The results are given in Table 4. From the Table 4 it is seen that inhibition efficiency decreases from 95 % to 70 % with increasing the temperature from 308 to 338 K. The decreased in inhibition efficiency may be attributed to desorption of Ketorol from the mild steel surface. However, without inhibitor corrosion rate increases more rapidly with temperature but in presence of higher concentration of inhibitor it increase in small amount, and lower the corrosion rate. Thus we concluded that Ketorol act as a good corrosion inhibitor for mild steel in 1.0 M HCl solution [31].

Table 4. Parameters obtained from weight loss measurements of mild steel in 1.0 M HCl containing optimum concentration of Ketorol at different temperatures.

Inhibitor	Temperature (K)	Corrosion rate (mg cm^{-2} h^{-1})	Inhibition efficiency ($\eta_{\%}$)
1.0 M HCl	308	7.00	-
	318	9.66	-
	328	14.60	-
	338	18.73	-
Ketorol (300 ppm)	308	0.31	95.71
	318	1.10	88.62
	328	3.00	79.45
	338	5.53	70.46

3.2.3 Thermodynamic parameters and adsorption isotherm

The Arrhenius equation is a simple, and accurate for temperature dependence corrosion rate equation [32]:

$$\log C_\mathrm{r} = -\frac{E_\mathrm{a}}{2.303RT} + \log \lambda \tag{7}$$

where E_a apparent activation energy, λ the pre-exponential factor, T absolute temperature, R is the universal gas constant and C_r is the corrosion rate. The Arrhenius plots of logC_r vs. 1/T for the blank and 300 ppm concentration of Ketorol are shown in Fig 6. From the results (Table 5) we can say that apparent activation energy of the inhibited system is higher 81.18 kJ mol^{-1} rather than uninhibited system 26.48 kJ mol^{-1}. The increase in activation energy can be attributed physical adsorption of the inhibitor on mild steel surface. To calculate enthalpy and entropy of activation for corrosion process transition state Eq. (6) was used

$$C_\mathrm{r} = \frac{RT}{Nh}\exp(-\frac{\Delta H^*}{RT})\exp(\frac{\Delta S^*}{R}) \tag{8}$$

where h is the Plank's constant, N is the Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation [33]. Fig. 7, shows a plot of log C_r/T vs 1/T gives a straight line the values of ΔH^* are calculated from their gradient (ΔH^* = -slope/2.303R) and ΔS^* from intercept [log(R/Nh) + (ΔS^*/2.303R)] and listed in Table 5.

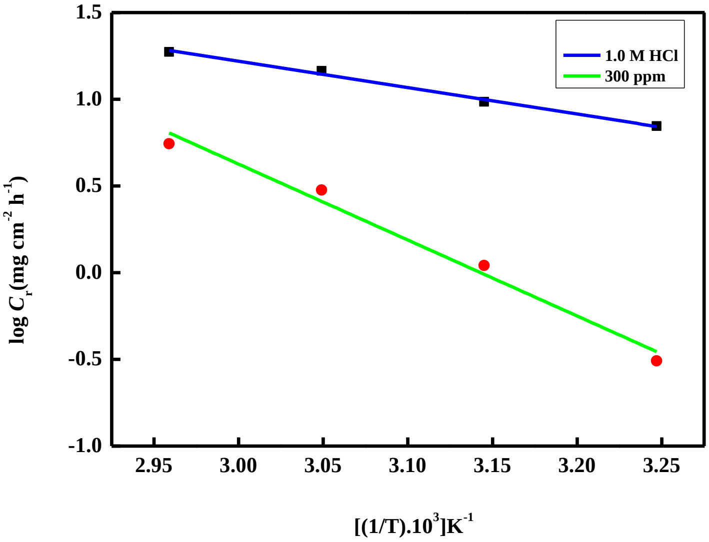

Figure 6. Arrhenius plots log (C_r) vs. 1,000 / T for the mild steel in 1.0 M HCl solution in the absence and presence of 300 ppm of Ketorol.

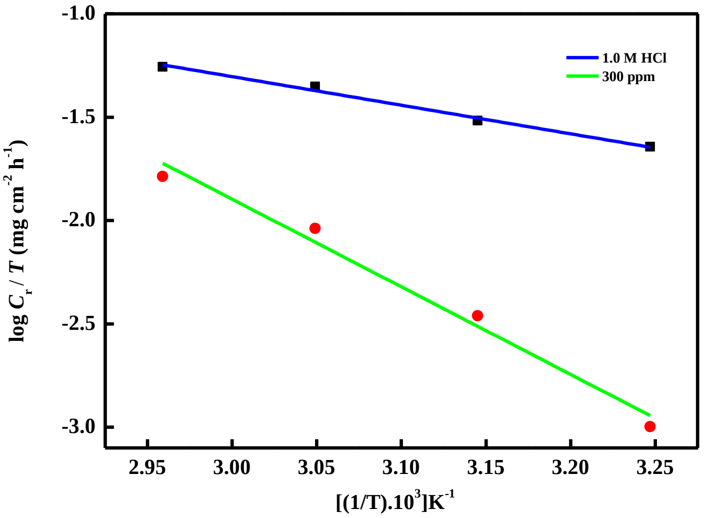

Figure 7. Arrhenius plots log (C_r / T) vs. 1,000 / T for the mild steel in 1.0 M HCl solution in the absence and presence of 300 ppm Ketorol.

Appraisal of Table 5 reveals that the thermodynamics parameters (ΔH^* and ΔS^*) of dissolution reaction of mild steel in 1.0 M HCl in the presence of inhibitor are higher than that absence of inhibitor. The positive signs of ΔH^* reflect the endothermic nature of mild steel dissolution process which suggests the slow dissolution of mild steel in presence of Ketorol. The values of ΔS^* 9.61 J mol^{-1}K^{-1} is higher for inhibited solutions than that for the uninhibited solution -143.09 J mol^{-1}K^{-1} suggesting an increase in randomness on going from reactants to the activated complex. In such condition, the adsorption of inhibitors molecules is followed by desorption of H_2O molecules from the electrode surface. Thus increase in entropy of activation is attributed to solvent (H_2O) entropy [34].

Table 5. Thermodynamic activation parameters for mild steel in 1.0 M HCl in absence and presence of 300 ppm Ketorol.

Inhibitor	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1}K^{-1})	K_{ads} (x10^4 M^{-1})	ΔG^o_{ads} (kJ mol^{-1})
1.0 M HCl	29.17	26.48	-143.09	-	-
Ketorol	83.86	81.18	9.61	1.89	-35.52

3.3 Adsorption isotherm

The adsorption isotherm provides the information about provide interaction energy between inhibitors and metal surface. In the present study, Langmuir adsorption isotherm was found to be the best fit. In Langmuir's adsorption isotherm the surface coverage (θ,) of the inhibitor on the mild steel surface is related to the concentration (C_{inh}) of the inhibitor in the bulk of the solution according to the following equation [35]:

$$\theta = \frac{K_{\mathrm{ads}} C_{\mathrm{inh}}}{1 + K_{\mathrm{ads}} C_{\mathrm{inh}}} \qquad (9)$$

where K_{ads} is the equilibrium constant for the adsorption/desorption process and C_{inh} is the inhibitor concentration in mol L^{-1}. This equation can be rearranged to

$$\frac{C_{\mathrm{inh}}}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C_{\mathrm{inh}} \qquad (10)$$

Plot of $C_{\mathrm{inh}}/\ \theta$ as function of C_{inh} yielded a straight line as shown in Fig. 8. The obtained plots of the triazoles are almost linear with correlation coefficient (R^2 = 0.9999) for Langmuir adsorption isotherm. K_{ads} can be calculated from the intercepts of the straight lines in Fig. 8.

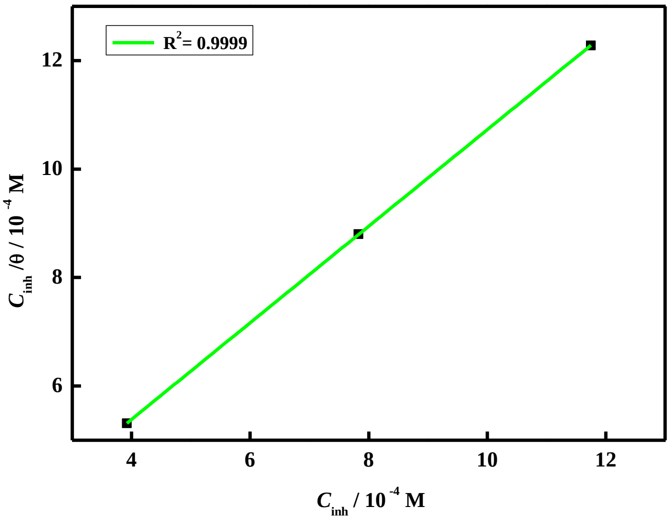

Figure 8. Langmuir adsorption isotherm plots for the adsorption of Ketorol on the mild steel surface in 1.0 M HCl solution

The standard free energy of adsorption ($\Delta G^0_{\mathrm{ads}}$) at different temperatures is calculated from the equation:

$$\ln K_{\mathrm{ads}} = \frac{-\Delta G^0_{\mathrm{ads}}}{RT} + \ln \frac{1}{55.5} \qquad (11)$$

where 55.5 is the concentration of water in solution in mol L^{-1} and R is the universal gas constant . The values of adsorption equilibrium constant and standard free energy for mild steel in 1.0 M HCl solution in the presence of 300ppm Ketorol is given in Table 5. The negative values of $\Delta G^0_{\mathrm{ads}}$ -

35.52 kJ mol^{-1} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. The large values of adsorption equilibrium constant 1.89x10^{4} M^{-1}also suggest the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, values of $\Delta G^0_{\rm ads}$, around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and charge metal, such as physisorption. When it is around -40 kJ mol^{-1} or higher values it involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond that is chemisorption [36, 37]. The calculated $\Delta G^0_{\rm ads}$ values is -35.52 kJ mol^{-1} Table 6. This indicates that the adsorption mechanism of the Ketorol on steel in 1.0 M HCl solution is typical of chemisorption. The unshared electron pairs of heteroatom may interact with d-orbital of iron atom of steel to provide a protective chemisorbed film.

4. CONCLUSION

The studied Ketorol was found to be good corrosion inhibitor for mild steel in 1.0 M HCl solution and the inhibition efficiency increases with concentration of inhibitor. It gave inhibition efficiency 92.36 % at 300 ppm. The results of potentiodynamic polarization showed that Ketorol is a mixed type inhibitor. The EIS study showed that Ketorol inhibit corrosion by adsorption mechanism. The adsorption of Ketorol on mild steel surface is found to obey the Langmuir adsorption.

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References

1. R. C. Ayers Jr., and N. Hackerman, *J. Electrochem. Soc.* 110 (1963) 507
2. E. Norr, *Corros. Sci.* 47 (2005) 33
3. M. Lagrenee, B. MernariM. , Bouanis, M. Traisnel, and F. Bentiss, *Corros. Sci.* 44 (2002) 573
4. F. Bentiss, M. Lagrenee, M. Traisnel, and J.C. Hornez, *Corros. Sci.* 41 (1999) 789
5. M. A. Quraishi, and R. Sardar, *Corrosion.* 58 (2002) 748
6. M. Abdallah, *Corros. Sci.* 46 (2004) 1981
7. N. O. Eddy, and S. A. Odoemelam, *Adv. Nat. Appl. Sci.* 2 (2008) 225
8. A. S. Fouda, A. A. Al-Sarawy, F. Sh. Ahmed, and H. M. El-Abbasy, *Corros. Sci.* 51 (2009) 485
9. S. M. Tamborim, S. L. P. Dias, S. N. Silva, L. F. P. Dick, and D. S. Azambuja, *Corros. Sci.* 53 (2011) 1571
10. I. Naqvi, A. R. Saleemi, and S. Naveed, *Int. J. Electrochem. Sci.* 6 (2011) 146
11. M. S. Morad, *Corros. Sci.* 50 (2008) 436
12. M. A. Quraishi, and S. K. Shukla, *Mater. Chem. Phys.* 113 (2009) 685
13. S. K. Shukla, and M. A. Quraishi, *J. Appl. Electrochem.* 39 (2009) 1517
14. S. K. Shukla, and M. A. Quraishi, *Corros. Sci.* 51 (2009) 1007
15. A. K. Singh, S.K. Shukla, M. Singh, and M. A. Quraishi, *Mater. Chem. Phys.* 129 (2011) 68
16. A. K. Singh, and M.A. Quraishi, *Corros. Sci.* 52 (2010) 152
17. I. Epelboin and M. Keddam, *Electrochim. Acta.* 17 (1972) 177

18. F. Mansfeld, *Electrochim. Acta.* 35 (1990) 1533
19. K. Jiittner, *Electrochim. Acta.* 35 (1990) 1501
20. A. Popova, and M. Christov, *Corros. Sci.* 48 (2005) 3208
21. M. W. Kendig, E. T. Allen and F. Mansfeld, *J. electrothem. Sot.* 131 (1984) 935
22. F. Mansfeld, S. L. Jeanjaquet and M. W. Kendig, *Corros. Sci*. 26 (1986) 735
23. W.J. Lorenz, and F. Mansfeld, *Corros. Sci.* 21 (1981) 647
24. T. Zhao, and G. Mu, *Corros. Sci.* 41 (1999) 1937
25. F. Bentiss, M. Traisnel, and M. Lagrenée, *Corros. Sci.* 42 (2000) 127
26. H.J. Flitt, and D. P. Schweinsberg, *Corros. Sci.* 47 (2005) 2125
27. M. A. Amin, K. F. Khaled, Q. Mohsen, and H. A. Arida, *Corros. Sci.* 52 (2010) 1684
28. W. H. Li, Q. He, C. L. Pei, and B. R. Hou, *J. Appl. Electrochem.* 38 (2008) 289
29. E. S. Ferreira, C. Giancomelli, F. C. Giacomelli, and A. Spinelli, *Mater. Chem. Phys.* 83 (2004) 129
30. I. Ahamad, R. Prasad, and M. A. Quraishi, *J. Solid State Electrochem.* 14 (2010) 2095
31. I. Ahamad, R. Prasad, and M. A. Quraishi, *Corros. Sci*. 52 (2010) 3033
32. A. K. Singh, M. A. Quraishi, and E. E. Ebenso, *Int. J. Electrochem. Sci.* 6 (2011) 5676
33. M. A. Quraishi, Sudheer, K. R. Ansari, and E. E. Ebenso, *Int. J. Electrochem. Sci.* 7 (2012) 7476
34. O. L. Riggs Jr., and R. M. Hurd, *Corrosion.* 23 (1967) 252
35. H. Keles, M. Kele, I. Dehri, and O. Serindag, *Colloids Surf. A.* 320 (2008) 138
36. G. Moretti, G. Quartarone, A. Tassan, and A. Zingales, *Electrochim. Acta* 41 (1996)1971
37. M. Sahin, S. Bilgic, and H. Yılmaz, *Appl. Surf. Sci.* 195 (2002) 1