J Appl Electrochem (2007) 37:491–497
DOI 10.1007/s10800-006-9280-2

ORIGINAL PAPER

Influence of tramadol [2-[(dimethylamino)methyl]-1-(3-methoxyphenyl) cyclohexanol hydrate] on corrosion inhibition of mild steel in acidic media

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Received: 18 August 2006 / Accepted: 20 November 2006 / Published online: 5 January 2007

Abstract Tramadol[2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexanol hydrate], a drug, was tested as a corrosion inhibitor for mild steel in 0.5 M HCl and 0.25 M H_2SO_4 separately at 300, 310 and 320 K using mass loss and galvanostatic polarization techniques. The percentage protection efficiencies were evaluated at different concentrations of the inhibitor at different temperatures. The protection efficiency increased with increase in inhibitor concentration and decreased with increase in temperature in both the acid solutions. Galvanostatic polarization studies showed that the inhibitor is of mixed type with a slight predominance of cathodic character. The inhibitor was more active in HCl than in H_2SO_4. The maximum protection efficiency approached 82.6% in the presence of 2.16×10^{-3} M inhibitor. Some samples of mild steel were examined by scanning electron microscopy. The inhibitor was found to adsorb on the mild steel surface according to the Langmuir adsorption isotherm. The thermodynamic functions of dissolution and adsorption processes were evaluated.

Keywords Acidic media · Adsorption · Corrosion · Inhibition · Mild steel · Tramadol

1 Introduction

Organic compounds containing N, S and O atoms have been found to be good corrosion inhibitors of metals particularly for active metals like Fe, Zn, Mg etc. The power of inhibition of such compounds has been interpreted in terms of their molecular size, molecular mass, internal structure, nature of heteroatoms present and adsorptive tendencies [1]. The influence of organic compounds containing nitrogen on the corrosion of the steel in acidic solutions has been investigated by several authors [2–6]. Such compounds can adsorb on the surface of the metal, block the active centres on the surface and thus reduce the corrosion rate. It has been observed that the adsorption behaviour of corrosion inhibitors depends mainly on physico-chemical characters of the molecule like functional groups, steric factors, aromaticity, π orbital character of donating electrons, electron density at the donor atoms [7–9].

The present paper describes a study of the corrosion protection action of Tramadol on mild steel in HCl and H_2SO_4 solutions using mass loss and galvanostatic polarization measurements. Tramadol is a synthetic analgesic drug. The molecule is made up of a benzene ring of planar structure with delocalized π electrons (aromaticity), a methoxy group ($-OCH_3$) of pronounced +M effect which makes benzene ring more active, a dimethylamino methyl group ($-CH_2N(CH_3)_2$) in which the nitrogen (N) atom is electron rich with its lone pair of electrons as well as the +I effect of two methyl groups and a cyclohexanol ring with electron

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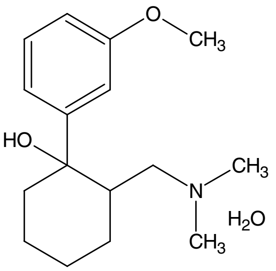
rich oxygen (O) atom. These factors favour the interaction of Tramadol with metal. Further the molecule is big enough (molecular mass—281.4) and sufficiently planar to block more surface area (due to adsorption) of the mild steel. In view of these favourable characteristics Tramadol was chosen for the corrosion studies. The structure of Tramadol is shown in Fig. 1. The effect of the inhibitor in different concentrations at different temperatures on corrosion rate in acidic media was investigated. The thermodynamic parameters of dissolution and adsorption processes were calculated.

2 Experimental details

Mild steel specimens having compositions 0.04% C, 0.35% Mn, 0.022% P, 0.036% S and the remainder being Fe were used. Specimens of size 5 cm × 1 cm × 0.1 cm were used for the mass loss method and of 1 cm × 1 cm (exposed) with a 5 cm long stem (isolated with araldite resin) were used for polarization method. These samples were polished with emery papers of grades 220, 320, 400, 800 and 1,000, degreased with trichloroethylene, washed thoroughly with triply distilled water and finally dried.

For the mass loss method, the cleaned and dried specimens were weighed before and after immersion in 0.5 M HCl for 4 h in the absence and presence of the inhibitor at different temperatures (300, 310 and 320 K) for each concentration (3.6×10^{-4}–21.6×10^{-4} M) of the inhibitor. The same procedure was repeated by taking fresh specimens in 0.25 M H_2SO_4. Duplicate experiments were conducted and the average mass loss was noted. The mass loss was expressed in mg cm^{-2} h^{-1}. A. R. grade chemicals and triply distilled water were used in the preparation of the test solutions. A very pure sample of Tramadol was obtained from "Jubilant Organosis" Max India Ltd., Mysore.



2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexanol hydrate

(Tramadol)

Fig. 1 Structure of Tramadol

The polarization measurements were performed at 300 K in the absence and presence of various concentrations of the inhibitor as used in mass loss method. The influence of temperature at 300, 310 and 320 K, was studied by polarization measurements in both acids using 21.6×10^{-4} M inhibitor. For the polarization measurements, a conventional three electrode Pyrex glass cell consisting of a saturated calomel electrode (SCE), the mild steel specimen and a platinum foil as reference, working and counter electrodes, respectively, was used. All electrodes were dipped in the same test solutions with a Luggin capillary bridge arrangement to minimize ohmic polarization.

The anodic and cathodic polarization values were measured under galvanostatic conditions. The potential of the working electrode varied from the open circuit potential at the rate of 20 mV per min and steady values were noted using an ELICO Potentiostat/Galvanostat (Model CL-95). Anodic and cathodic Tafel lines were constructed and corrosion rates and percentage protection efficiencies were calculated.

All experiments were carried out at constant temperature ±0.5 °C using a thermostatic controlled METZER water bath (Model METZ-4019).

The scanning electron microscope (SEM) images of the corroded surface of some samples in the absence and presence of the inhibitor were taken using a SEM-Model HITACHI S-3000 N.

3 Results and discussion

3.1 Mass loss studies

The percentage protection efficiency (P) of Tramadol obtained by the mass loss method at different inhibitor concentrations for mild steel in 0.5 M HCl and 0.25 M H_2SO_4 at 300, 310 and 320 K are given in Table 1. The percentage protection efficiency was calculated from [10]

$$P = \frac{w_0 - w}{w_0} \times 100 \qquad (1)$$

where w_0 and w are mass loss in the absence and presence of the inhibitor, respectively. The protection efficiency increases with increase in inhibitor concentration and decreases with increase in temperature in both acid media. Further P is comparatively higher in HCl than in H_2SO_4 under similar experimental conditions. This is probably due to the lesser surface coverage in H_2SO_4 solution. Again chloride (Cl^{-1}) ions have a greater adsorption tendency than sulfate (SO_4^{-2}) ions on steel [11].

Table 1 Percentage protection efficiency (*P*) of Tramadol for mild steel in 0.5 M HCl and 0.25 M H_2SO_4 at its different concentrations and at different temperatures by mass loss method

Concentration of the inhibitor × 10^{-4} M	*P* in 0.5 M HCl			*P* in 0.25 M H_2SO_4		
	300 K	310 K	320 K	300 K	310 K	320 K
3.6	47.2	36.5	30.0	37.5	30.0	24.7
5.4	57.3	46.4	37.8	49.5	41.0	36.0
10.8	71.7	62.0	52.0	63.0	59.0	47.9
14.4	76.5	68.0	59.0	68.8	61.0	53.0
18.0	81.8	72.0	63.5	74.2	66.2	57.0
21.6	82.6	75.0	68.0	76.0	70.2	62.0

To establish whether inhibition is due to the formation of an organic film due to adsorption on the metal surface, scanning electron microscope images were taken (Fig. 2a–d). SEM Fig. 2a and b show the surface features when immersed in 0.5 M HCl in the absence and presence of inhibitor, respectively. In contrast, Fig. 2c and d show the features of similar specimens immersed in 0.25 M H_2SO_4. Close examination of Fig. 2b and d reveals that the specimens immersed in 0.5 M HCl and 0.25 M H_2SO_4 containing the inhibitor are in better condition, having smooth surfaces. This indicates that inhibitor molecules are adsorbed on the mild steel surface and reduce the corrosion. The comparative study of SEM images of mild steel in both acids indicates that the extent of adsorption was higher in HCl than in H_2SO_4 (Fig. 2b, d). This is in good agreement with the experimental observations that the protection efficiency of the Tramadol is higher in HCl than in H_2SO_4.

3.2 Galvanostatic polarization studies

Figure 3 shows anodic and cathodic polarization curves in 0.5 M HCl without and with various concentrations of Tramadol at 300 K. The cathodic curves are more polarized than anodic curves and Tramadol is comparatively more effective on cathodic sites. The decrease in anodic and cathodic current densities indicates that the inhibitor suppresses both the anodic and cathodic reactions. Similar trends were obtained in 0.25 M H_2SO_4. The percentage protection efficiencies (*P*) were determined from the equation:

$$P = \frac{i^0_{corr} - i_{corr}}{i_{corr}} \times 100 \qquad (2)$$

where i^0_{corr} and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively. Calculated polarization results like corrosion potential (E_{corr}), corrosion current density (I_{corr}) and percentage protection efficiency (*P*) in both acidic media at 300 K obtained by extrapolation of Tafel lines are listed in Table 2. These data show that corrosion current density (I_{corr}) decreased and the protection efficiency (*P*) increased with increase in Tramadol concentration in both acids. Figure 4 shows the effect of temperature (300, 310 and 320 K) on the anodic and cathodic potentials for the mild steel in 0.5 M HCl containing 21.6 × 10^{-4} M Tramadol. Similar results were obtained in 0.25 M H_2SO_4. This shows that the protection

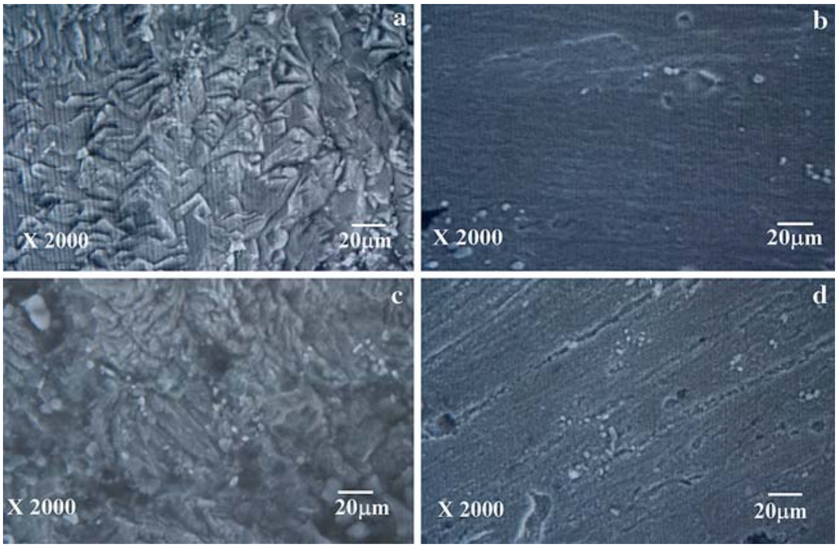


Fig. 2 Scanning electron micrographs of the steel surface after 4h immersed at 300 K in: (**a**)0.5 M HCl (**b**) 0.5 M HCl + 21.6 x 10^{-4} M Tramadol and (**c**) 0.25 MH_2SO_4 (**d**) 0.25 M H_2SO_4 + 21.6 x 10^{-4} M Tramadol

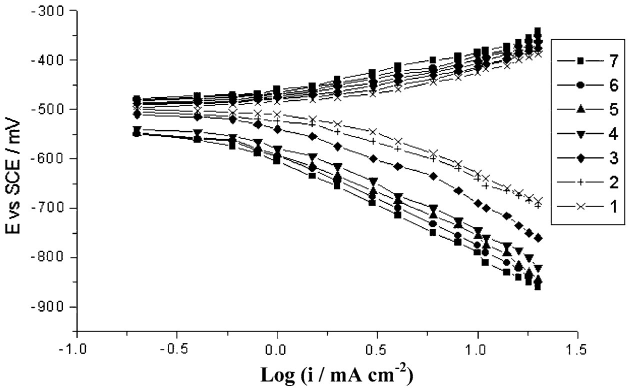


Fig. 3 Galvanostatic polarization curves for the mild steel in 0.5 M HCl in the presence of different concentrations of Tramadol at 300 K: (1) 0.00, (2) 3.6×10^{-4} M, (3) 5.4×10^{-4} M, (4) 10.8×10^{-4}, (5) 14.4×10^{-4}, (6) 18.0×10^{-4} and (7) 21.6×10^{-4} M

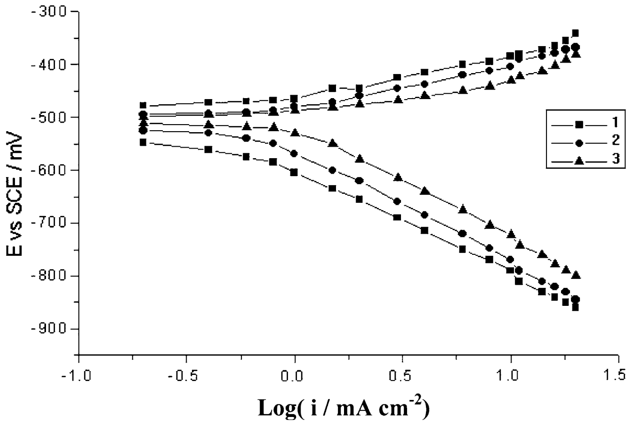


Fig. 4 Effect of temperature on the cathodic and anodic potentials for the mild steel in 0.5 M HCl containing 21.6×10^{-4} M Tramadol: (1) 300, (2) 310 and (3) 320 K

efficiency (P) decreased with increase in temperature in both acids. Further, the percentage protection efficiencies obtained from Tafel line extrapolations approximately match with those calculated from mass loss measurements.

Activation parameters like activation energy (E_a^0), enthalpy (ΔH^0) and entropy (ΔS^0) for the dissolution of mild steel in both acid media in the absence and presence of various concentrations of Tramadol were calculated from the Arrhenius equation (Eq. 3) and the transition state equation (Eq. 4) [10]

$$\log R' = -\frac{E_a^0}{2.303RT} + \log A \quad (3)$$

$$R' = \frac{RT}{N_A h} \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(\frac{-\Delta H^0}{RT}\right) \quad (4)$$

where R' represents corrosion rate, E_a^0 is the apparent activation energy, A is the pre-exponential factor, h is Planck's constant, N_A is the Avogadro number, R is the universal gas constant, ΔH^0 is the enthalpy of activation and ΔS^0 is the entropy of activation. The Arrhenius plot of log R' against $1/T$ (Eq. 3) for the mild steel sample in 0.5 M HCl in the presence of different concentrations of Tramadol gave straight lines with slopes of $E_a^0/2.303R$ as shown in Fig. 5. Similar results were obtained in 0.25 M H_2SO_4. E_a^0 values for the corrosion dissolution reactions were calculated in the absence and presence of Tramadol of different concentrations in both acids. Again the plots of log R'/T against $1/T$ also gave straight lines with slope $-\Delta H^0/2.303\ R$ and intercept (log $R/N_A h$ + $\Delta S^0/2.303\ R$) from which ΔH^0 and ΔS^0 values were calculated. The activation parameters are given in Table 3. The apparent activation energy E_a^0 and entropy ΔH^0 in both acid solutions increased and the extent of the increase is proportional to the inhibitor concentration indicating that the energy barrier for the corrosion reaction increases with Tramadol concentration. The entropy of activation ΔS^0 in the absence and presence of Tramadol is large and negative. This implies that the activated complex in the rate-determining step represents association rather than dissociation, indicating that a decrease in randomness takes place on going from reactants to the activated complex direction.

3.3 Adsorption isotherm

Figure 6 shows a plot of $\theta/1–\theta$ against C for the inhibitor at temperatures of 300, 310 and 320 K in HCl medium, which gives straight lines with almost unit

Table 2 Polarization results obtained for the corrosion of mild steel in 0.5 M HCl and 0.25 M H_2SO_4 containing different concentrations of Tramadol at 300 K

Polarization parameters	0.5 M HCl							0.25 M H_2SO_4						
Conc 10^{-4} (M)	0	3.6	5.4	10.8	14.4	18.0	21.6	0	3.6	5.4	10.8	14.4	18.0	21.6
E_{corr} (mV)	–500	–495	–487	–480	–475	–470	–460	–510	–505	–500	–494	–490	–475	–465
I_{corr} (mA cm^{-2})	1.5	0.86	0.7	0.48	0.42	0.33	0.3	1.6	1.02	0.86	0.62	0.54	0.48	0.43
P	–	43.0	53.5	68.0	73.3	78.0	80.0	–	36.3	46.2	61.0	66.0	70.0	73.0

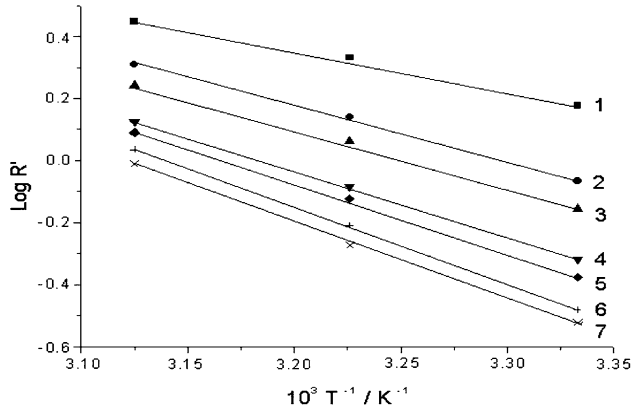


Fig. 5 Arrhenius plot of the corrosion rate for the mild steel in 0.5 M HCl in the presence of different concentrations of Tramadol: (1) 0.00, (2) 3.6 × 10^{-4} M, (3) 5.4 × 10^{-4} M, (4) 10.8 × 10^{-4}, (5) 14.4 × 10^{-4}, (6) 18.0 × 10^{-4} and (7) 21.6 × 10^{-4} M

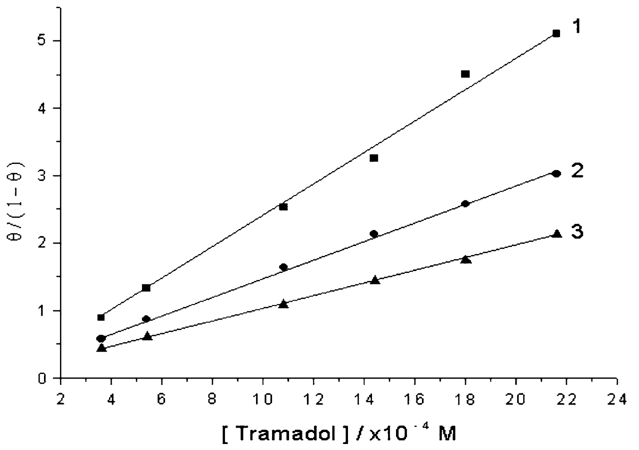


Fig. 6 Langmuir adsorption isotherm for the mild steel in 0.5 M HCl containing different concentrations of Tramadol at different temperatures: (1) 300, (2) 310 and (3) 320 K

Table 3 Activation parameters of the dissolution of mild steel in 0.5 M HCl and 0.25 M H_2SO_4 in the absence and presence of different concentrations of Tramadol

Acids	0.5 M HCl			0.25 M H_2SO_4		
Conc × 10^{-4} (M)	E_a^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	E_a^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})
0.0	29.1	27.4	–234.7	27.4	25.46	–234.3
3.6	32.5	30.7	–237.2	30.6	28.72	–236.8
5.4	38.3	36.6	–236.6	33.7	30.8	–237.2
10.8	42.1	39.4	–240.0	36.4	31.9	–239.7
14.4	43.5	41.9	–240.8	38.3	34.5	–240.4
18.0	46.0	44.5	–241.4	40.2	36.55	–240.6
21.6	49.8	46.7	–241.8	42.1	38.3	–241.2

slope indicating that the inhibitor obeys the Langmuir adsorption isotherm. Similar trends were observed in H_2SO_4. According to this isotherm θ is related to concentration of inhibitor C via

$$\frac{\theta}{1-\theta} = KC \tag{5}$$

where K is the equilibrium constant of the adsorption process, C is the inhibitor concentration and θ is the surface coverage. The values of surface coverage θ were evaluated by mass loss measurements using the equation

$$\theta = \frac{w_0 - w}{w_0} \tag{6}$$

where w_0 and w are mass loss in the absence and presence of the inhibitor, respectively. The slopes of the straight lines give values of K at different temperatures. The standard free energy of adsorption (ΔG^0_{ads}) can be calculated from the equation [10, 12]

$$K = \frac{1}{55.5}\exp\left(\frac{-{}^{0}_{\mathrm{ads}}}{RT}\right) \tag{7}$$

where 55.5 is the concentration of water in the solution in M. The thermodynamic data: $\Delta H^0_{\mathrm{ads}}, \Delta S^0_{\mathrm{ads}}and\Delta G^0_{\mathrm{ads}}$ were calculated from the equations [13]

$$\log K = \frac{-\Delta H^0_{\mathrm{ads}}}{2.303RT} + \frac{\Delta S^0_{\mathrm{ads}}}{2.303R} \tag{8}$$

$$\Delta G^0_{\mathrm{ads}} = \Delta H^0_{\mathrm{ads}} - T\Delta S^0 \tag{9}$$

Figure 7 shows a plot of log K against $1/T$ which gives straight lines with slopes of ($-\Delta H^0_{\mathrm{ads}}/2.303R$) and intercepts of ($\Delta S^0_{\mathrm{ads}}/2.303R$) given in Table 4. The $\Delta G^0_{\mathrm{ads}}$ values have a negative sign indicating that the adsorption process takes place spontaneously. This supports the observed good protection efficiency of Tramadol. Increase in $\Delta G^0_{\mathrm{ads}}$ values with increase in temperature indicates a decrease in adsorption and a relative decrease in protection efficiency.

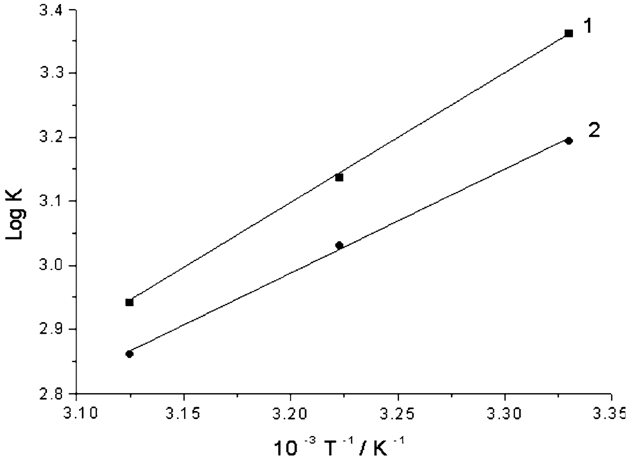


Fig. 7 Plot of log K against $1/T$ for Tramadol derived from experimental adsorption isotherm for mild steel at different temperatures 300, 310 and 320 K in acids: (1) 0.5 M HCl and (2) 0.25 M H_2SO_4

These observations show that the inhibitor is adsorbed on mild steel. It is generally assumed that adsorption at the metal–solution interface is the first step in the inhibition mechanism in aggressive acidic media. Four mechanisms have been suggested for the adsorption of organic molecules at the metal–solution interface [14, 15]. These are:

(i) electrostatic attraction between charged molecules and charged metal,
(ii) interaction of unshared electron pairs in the molecule with the metal,
(iii) interaction of π electrons with the metal and
(iv) a combination of the above.

It is postulated that chemisorption involves sharing or charge transfer from the inhibitor molecules to the metal surface to form co-ordination or similar bonds. Transition metals, most of which have half filled vacant *d* orbitals, can easily accept electrons and participate in adsorption processes. Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or oxygen; each might be a chemisorption centre. The inhibitive action depends on the electron densities around the chemisorption centre; the higher the electron density at the centre, the more efficient is inhibitor. Protection efficiency depends on several factors such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and extent of formation of metallic complexes [16].

The adsorption of Tramadol at mild steel can take place through its three active centres; two oxygen and one nitrogen polar atoms in addition to a π electron interaction of the benzene nucleus with unshared d electrons of iron atoms [17–19]. As chloride ions from HCl medium are more strongly adsorbed on the iron surface than sulphate ions (H_2SO_4 medium), the cationic form of the Tramadol molecule can jointly adsorb on the metal surface without much difficulty in HCl compared with H_2SO_4 [20]. Hence, adsorption in HCl is higher than in H_2SO_4. This is revealed by the higher *P* of the inhibitor in HCl than in H_2SO_4.

4 Conclusion

Tramadol reduces the rate of corrosion of mild steel in both acids but is more efficient in HCl than in H_2SO_4. The protection action of Tramadol is due to adsorption as revealed by scanning electron micrographs. Adsorption of Tramadol on the mild steel surface in both acids follows the Langmuir adsorption isotherm. The adsorbed Tramadol molecules are assumed to inhibit the corrosion reactions by decreasing the number of available vacant surface sites for corrosion. Inhibition tendencies of Tramadol determined from both mass loss and polarization methods agree. The inhibitive action of Tramadol is predominantly cathodic in nature. Percentage protection efficiency decreases with increase in temperature and increases with increase in concentration. These results show that the Tramadol is a good corrosion inhibitor for mild steel in acidic media.

Table 4 Thermodynamic parameters for the adsorption of Tramadol on mild steel surface in 0.05, 0.5 M HCl and 0.25 M H_2SO_4

Acids (mol^{-1})	Thermodynamic data				
	Temp.	10^3 K (mol^{-1})	($-\Delta G^0_{ads}$) (kJ mol^{-1})	($-\Delta H^0_{ads}$) (kJ mol^{-1})	(ΔS^0_{ads}) (J K^{-1} mol^{-1})
0.5 M HCl	300 K	2.3	29.33	38.3	53.6
	310 K	1.37	28.97		
	320 K	0.875	28.71		
0.25 M H_2SO_4	300 K	1.425	28.37	30.64	52.65
	310 K	1.07	28.34		
	320 K	0.725	28.21		

Acknowledgements The authors thank Jubilant Organosis Max India Ltd., Nanjangud, Mysore, for providing the pure sample of Tramadol and also Mr. Uday Bhat for valuable suggestions during this work.

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