Pavetta Indica Bark as Corrosion Inhibitor in Mild Steel Corrosion in HCl and H_2SO_4 Medium: Adsorption and Thermodynamic Study

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Abstract: Corrosion inhibition in the presence of *Pavetta indica* bark (PIB) extract in 1 M HCl and 1 M H_2SO_4 was studied using the weight loss technique at 303 to 353 K. The results obtained revealed that the inhibition efficiency increased with increase in temperature and showed maximum at 313 K. Inhibition occurred through adsorption of the molecules in PIB extract on the metal surface. The experimental data were best fit with Temkin isotherm model. The activation energies, enthalpies and entropies of the corrosion process and the free energies, enthalpies and entropies for the adsorption process were determined and discussed.

Introduction

Corrosion is one of the unavoidable problems in the world; it leads to a huge economic loss to every nation. It is necessary to direct more attention to metallic corrosion nowadays than earlier because of the increased pollution of atmosphere; the environment became more corrosive. Now a days different types of metals are used in all the technical areas like atomic energy field, boiler plants, oil industry, petroleum industry *etc*.

Mild steel is the most widely used material particularly in industry. In the presence of corrosive environment the metals becomes corroded even though slowly but creates loss to the industry. For cleaning the affected metals, mild acids like hydrochloric acid and sulphuric acids are generally used. But there requires the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials.

Like most chemical reactions, the corrosion rate of metals in aqueous acid solutions increases with increasing temperature, especially when evolution of hydrogen accompanied corrosion, *e.g*., during dissolution of metal in alkaline or acid media. If oxygen takes part in a cathodic reaction during corrosion, the relationship between corrosion rates and temperature becomes more complicated owing to the lower stability of oxygen at elevated temperature[1].

Pavetta indica Linn is an erect, nearly smooth or somewhat hairy shrub, growing to a height of 2 to 4 meters, in the family of Rubiaceae. Bark grey, smooth and irregularly scaly when mature; blaze greenish cream[2].Its Stems contain essential oil, resin, alkaloid, tannin and a pectic principle. Bark is used for visceral obstructions and arthritis. Wood is used as antirheumatic[3-7]. In the light of the available information, the present paper reported the result of our investigation on the anticorrosive performance of *Pavetta indica* bark extracts as green corrosion inhibitor on mild steel in different temperature (303-353 K) in 1 M HCl and 1 M H_2SO_4 solution using gravimetric method.

Experimental

Cold rolled mild steel sheet of composition (Table 1) was used. The composition estimated is presented in Table 1.

Table 1. Chemical composition of mild steel

Element	C	Mn	Si	P	S	Cr	Mo	Ni
Wt%	0.091	0.195	0.016	0.020	0.013	0.027	0.20	0.018

The sheet was mechanically pressed, cut into 5 cm x 1 cm coupons with 2 mm thickness, mechanically polished, a hole drilled at one end for free suspension and numbered by punching. Their edges were abraded with fine grade of emery papers, degreased with acetone, washed in double distilled water, dried, stored in a dessicator and used for the entire immersion studies. 1 M HCl and 1 M H_2SO_4 used in this study were prepared from analar HCl and Analar H_2SO_4 using distilled water.

Preparation of Pavetta Indica bark extracts

The bark of plant were collected from Chalavara, a village in Palakkad, Kerala, India. Cleaned and chopped into small pieces, shade dried, powdered and stored at room temperature prior to use. 25 g of the powder was transferred to a 1000 mL round bottomed flask, heated with 500 mL of 1 M HCl in a mantle with water condenser at about 40-50 °C for 3 h. The resulting solution was allowed to stand overnight and filtered through ordinary filter paper. The residue was repeatedly washed with small amount of 1 M HCl and the filtrate was made up to 500 mL and stored. From this 5% stock solution of *Pavetta indica* bark extract (PIB), different concentration of inhibitor solutions ranging from 0.05 to 0.5% were diluted. The same procedure was adopted for the preparation of extract in 1 M H_2SO_4 also.

Gravimetric measurements

The weight loss measurements were performed on the mild steel samples with rectangular steel specimens of size 5x1x0.2 cm in one molar solution of HCl and H_2SO_4 without and with addition of different concentrations (0.1 to 0.5%) of PIB. Every sample was weighed on Shimadzu analytical balance. The experiments were carried out in triplicate for a temperature range from 303 K to 353 K. After immersion, the surface of the specimen was cleaned by double distilled water followed by rinsing with acetone and the sample was weighed again in order to calculate inhibition efficiency (IE%) and corrosion rate (CR). For each experiment a freshly prepared solution was used and the solution temperature was thermostatically controlled at a desired value.

The inhibition efficiency (IE%),of the inhibitor ,degree of surface coverage (θ) and corrosion rate (CR) were determined from the weight loss results , using equations 1,2 and 3 respectively.

$$IE(\%) = \left(\frac{w_0 - w}{w_0} \right) x100 \qquad (1)$$

$$\theta = \frac{w_0 - w}{w_0} \qquad (2)$$

$$CR = \Delta W / At \qquad (3)$$

Were W_0 and W are the values of weight loss (g/dm^3) for mild steel after immersion in solutions with out and with inhibitor respectively, θ is the degree of surface coverage of the inhibitor, $\Delta W = W_0 - W$, A is the area of the mild steel coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of mild steel after the time, t.

Results and Discussion

Effect of temperature on mild steel corrosion

Hot acid solutions are generally used for removing mill scales (oxide scales) from the metal surface in various industries at elevated temperature such as 60 °C in HCl and up to 95 °C in H$_2$SO$_4$[8]. To evaluate the stability of adsorbed layer of inhibitor on mild steel surface at higher temperatures in both acidic media, weight loss measurements were carried out. The temperature studied were 303-353 K in the absence and presence of inhibitor of various concentrations in 0.1%,0.2%,0.3%,0.4%,0.45% and 0.5% for half an hour immersion time. The CR values were calculated from equation (3). From the plots of CR *versus* temperature (Figure 1), it can be understood that at higher temperature the corrosion rate increased. This signified that the dissolution of the metal coupons increased at higher temperatures. This observation was attributed to the general rule guiding the rate of chemical reaction, which says that chemical reaction increases with increasing temperatures. Also an increased temperature favors the formation of activated molecules, which may be doubled in number, with 10 ^{o}C rise in temperature, thereby increasing the reaction rate. This is because the reactant molecules gain more energy and are able to overcome the energy barrier more rapidly[9]. An increase in temperature may also increase the solubility of the adsorbed films on the metals, thus increasing the susceptibility of the metal to corrosion[10]. The blank solution showed maximum corrosion rate than in the presence of extract.
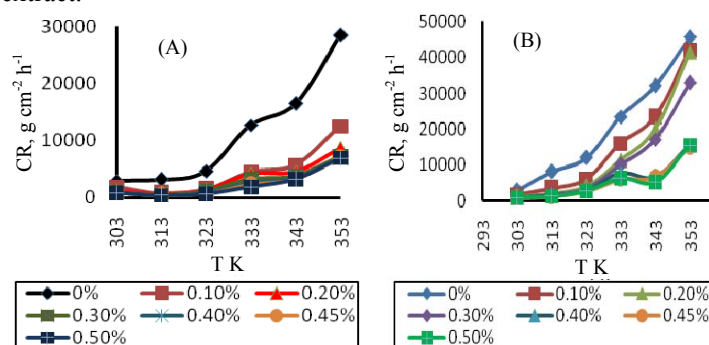

Figure 1. Corrosion rates CR (g.cm^{-2}.h^{-1}) of mild steel specimen in (A) 1 M HCl (B) 1M H$_2$SO$_4$ at different concentrations

Relationship of inhibition efficiency with temperature

From the Figure, in H_2SO_4 media, inhibition efficiency increased up to 313 K and then decreased at higher temperatures. The decrease in IE with the increase in temperature in H_2SO_4 media might be due to weakening of physical adsorption. As per Putilova's explanation, the decrease in the inhibition efficiency of the inhibitor with increase in temperature might be due to adsorption and desorption of inhibitor. Adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature[11]. With the increase of temperature the equilibrium between adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant[12]. But in the case of HCl media IE increased at higher temperature. For a physical adsorption mechanism, IE of an inhibitor decreases with temperature while for a chemical adsorption mechanism, values of inhibition efficiency increases with temperature[13-15].
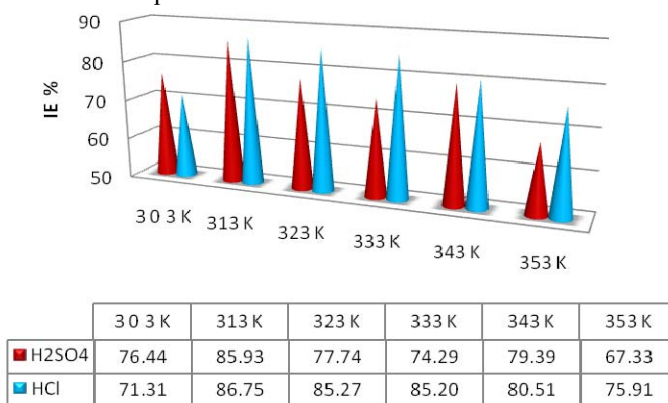

	303K	313K	323K	333K	343K	353K
■ H2SO4	76.44	85.93	77.74	74.29	79.39	67.33
■ HCl	71.31	86.75	85.27	85.20	80.51	75.91

Figure 2. Inhibition efficiency of PIB at optimum concentration in HCl and H_2SO_4 at different temperature

Adsorption parameters

Adsorption isotherm

The inhibition of the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 medium with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extracts on the metal surface. Inhibition efficiency was directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, the variation of θ with the extract concentration specifies the adsorption isotherm that describes the system. The isotherm gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The values of the degree of surface coverage were evaluated at different concentrations of the inhibitors in both acid solutions. Attempts were made to fit θ values to various adsorption isotherms. On examining, the adsorptions of different concentrations of PIB extracts on the surface of mild steel in both acids were found to obey Temkin isotherm. The Temkin adsorption isotherm plot for the adsorption of various concentrations of the plant extracts was shown in Figure 3.According to the Temkin isotherm model[16].

$$\exp^{(-2a\theta)} = KC \tag{4}$$

Where K is the adsorption equilibrium constant and, a designates as the Frumkin lateral interaction parameter[17]. Rearranging and taking logaritham of both sides of equation (4), Equation (5) is obtained.

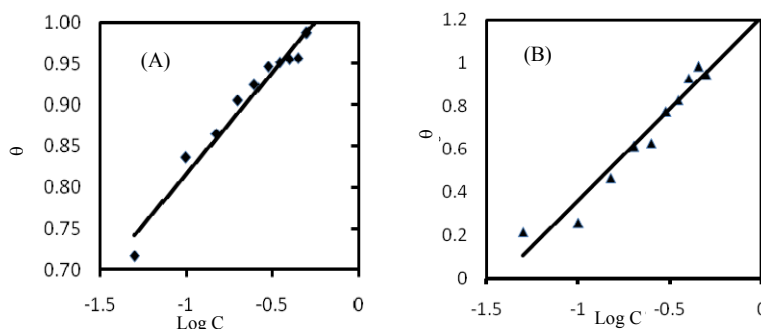$$\theta = \frac{-2.303 \log K}{2a} - \frac{2.303 \log C}{2a} \tag{5}$$

Figure 3. Temkin isotherm adsorption model of PIB on mild steel in (A) HCl (B) H_2SO_4 medium

Temkin adsorption parameters were recorded in Table 2. It indicated that the inhibitor obeys the Temkin model since the experimental data presents adequate curve fitting for the applied adsorption isotherms. The attractive parameter value (a), describes the molecular interaction in the adsorbed layer and is a measure for the steepness of the adsorption isotherm. It can have both positive and negative values. The positive 'a' value indicated the steepness of the adsorption isotherm[17]. K_{ads} represents the strength between adsorbate and adsorbent. Larger values of the K_{ads} imply more efficient adsorption and hence better inhibition efficiency[18,19]. K_{ads} value decreased in this study with increase in the temperature indicating that adsorption of PIB on the mild steel surface was unfavorable at higher temperature. The correlation coefficient (R^2) values in HCl and H_2SO_4 media were close to unity.

Table 2. Some parameters of the linear regression from Temkin Adsorption isotherm

	Temp, K	a	K_{ads}	R^2	ΔG_{ads}
HCl	303	2.45	75.86	0.88	-21.03
	313	6.40	12.59×10^4	0.91	-41.02
	323	4.48	34.67×10^2	0.83	-32.68
	333	3.90	$12.58 \times 10_2$	0.91	-30.89
	343	5.39	12.59×10^3	0.99	-38.38
	353	4.13	12.88×10^2	0.90	-32.81
H_2SO_4	303	2.52	81.28	0.93	-21.22
	313	2.88	295.12	0.95	-25.28
	323	2.82	177.83	0.97	-24.69
	333	1.92	33.88	0.98	-20.90
	343	1.32	16.60	0.87	-19.48
	353	1.16	9.12	0.81	-18.25

Thermodynamic Adsorption parameters

Theoretical fitting of the corrosion data to the kinetic - thermodynamic model was tested to show the nature of adsorption. The standard free energy of adsorption ΔG_{ads} is related to the equilibrium constant of adsorption K_{ads}, ΔG_{ads} can be calculated by the following equation

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ads}}{RT}\right) \qquad (6)$$

Where R is the gas constant and T is the temperature. This equation can also be expressed as:

$$\Delta G_{ads} = -2.303RT \log(55.5 K_{ads}) \qquad (7)$$

Where $K_{ads} = \dfrac{\theta}{c(1-\theta)}$ \qquad (8)

Where θ is the degree of surface coverage, C is the concentration of inhibitor, ΔG_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin and Kads is the equilibrium constant for the adsorption process and 55.5 is the molar concentration of water in solution. K_{ads} value was calculated from the intercept of the Temkin plot and listed in Table 2. The temperature study confirmed the spontaneous adsorption of PIB onto the mild steel surface[20] and strong interactions between inhibitor molecules and the metal surface[21]. The calculated values of ΔG were around -40 kJ mol^{-1} indicating that the adsorption mechanism of PIB on mild steel in 1 M HCl solution at higher temperatures was chemisorption[22]. The unshared electron pairs in electron rich molecule in extract may interact with *d*-orbitals of Fe to provide a protective chemisorbed film[23]; but in H_2SO_4 media, the values indicates physisorption. Thermodynamic parameters such as enthalpy of adsorption and entropy of adsorption can also be deduced from integrated version of the Van't Hoff equation expressed by[24].

$$\ln(K_{ads}) = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} + \ln\frac{1}{55.5} \qquad (9)$$

Figure 4 showed a plot of lnK$_{ads}$ *versus* 1/T which gave straight lines with slope of $\left(\dfrac{-\Delta S_{ads}}{R}\right)$ and intercepts of (ΔS_{ads} / R + ln 1/55.5). Calculated value of ΔH$_{ads}$ and ΔS$_{ads}$ using the Van't Hoff equation in HCl are18.56 kJ mol^{-1} and -33.39 J mol^{-1} K^{-1} and in H_2SO_4 media-53.03 kJ mol^{-1}and -95.7Jmol[-1]K[-1] respectively. The enthalpy and entropy for the adsorption of PIB on mild steel were also deduced from the thermodynamic basic equation[25].
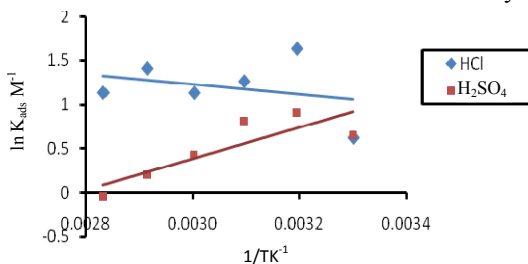

Figure 4. The relationship between ln K$_{ads}$ and 1/T

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (10)$$

Where ΔH$_{ads}$ and ΔS$_{ads}$ are the enthalpy and entropy changes of adsorption process, respectively. A plot of ΔG$_{ads}$ *versus* T is linear (Figure 5) with the slope equal to -ΔS $_{ads}$ and intercept of ΔH$_{ads}$. The enthalpy of adsorption and the entropy of adsorption, obtained in HCl was 13.34 kJ mol^{-1} and 0.1407 J mol^{-1} K^{-1} respectively and in H_2SO_4 enthalpy was -55.43 kJmol[-1] and entropy was -0.103 J mol^{-1}K[-1].
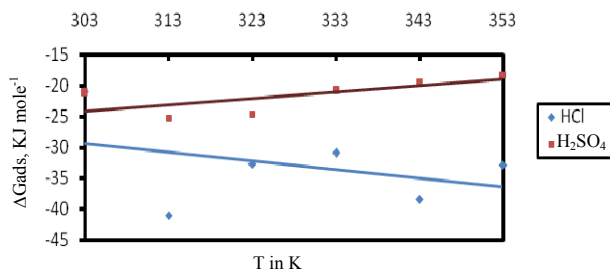
Figure 5. The variation of ΔG_{ads} *versus* T (K) in 1M HCl and 1 M H_2SO_4

The enthalpy for the adsorption of PIB on mild steel may be also evaluated by the Gibbs–Helmholtz equation, which is defined as follows:

$$\left[\frac{\delta \Delta G_{ads}/T}{\delta T}\right] = \frac{\Delta H_{ads}}{T^2} \tag{11}$$

Which can be arranged to give the following equation:

$$\frac{\Delta G_{ads}}{T} = \frac{\Delta H_{ads}}{T} + A \tag{12}$$

The variation of $\Delta G_{ads}/T$ with 1/T gave a straight line with a slope that equals ΔH_{ads} (Figure 6). It can be seen from Figure 6 that $\Delta G_{ads}/T$ increase slightly with 1/T in a linear fashion in HCl and decreases in a linear fashion in H_2SO_4 media. The values of ΔH_{ads} was positive (ΔH_{ads} =18.56 kJ mol^{-1}), reflecting the endothermic behaviour of adsorption on the steel surface in HCl and negative value (-53.03 kJ mol^{-1}) in H_2SO_4 media indicate the exothermic nature of reaction. The ΔH_{ads} values calculated from the different equations were in good agreement.

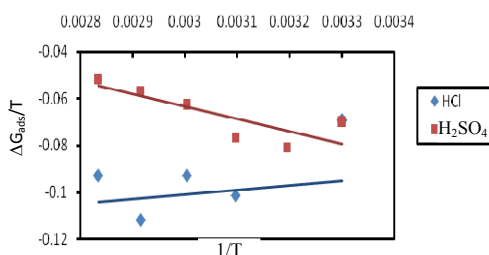**Figure 6.** Variation of $\Delta G_{ads}/T$ with 1/T for mild steel in 1.0 M HCl and 1 M H_2SO_4 in the presence of PIB

Table 3. Heat of adsorption and entropy of adsorption values calculated by different thermodynamic equations

Different thermodynamic equations	HCl		H_2SO_4	
	ΔH_{ads}	ΔS_{ads}	ΔH_{ads}	ΔS_{ads}
Van't Half Equation(eq 9)	18.56	-33.39	-53.03	-95.70
Gibbs- Helmholtz Equation (eq 11 & 12)	18.56	-	-53.03	-
Basic Thermodynamic equation (eq 10)	13.34	0.1407	-55.43	-0.10

Kinetic thermodynamic corrosion parameters

The Arrhenius equation is employed to study the effect of temperature on the rate of corrosion of mild steel in acid media containing various concentrations of acid extract of PIB as expressed by equation (13);

$$CR = A\exp(-Ea/RT) \tag{13}$$

Where CR is the corrosion rate of mild steel, A is Arrhenius pre-exponential factor,Ea is the activation energy,R is the gas constant and T is the temperature[26-28]. A plot of logrithemic variation of corrosion rate with reciprocal of absolute temperature gave a straight line as shown in Figure 7 and Figure 8 with a slope of –Ea/2.303 R. The obtained values were reported in Table 4. This showed that the adsorbed organic matter had provided a physical barrier to charge and mass transfer, leading to reduction in corrosion rate. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. Szauer and Brand explained the increase in activation energy due to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature. As adsorption decreases, more desorption of inhibitor molecules occurs because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of mild steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature[29].
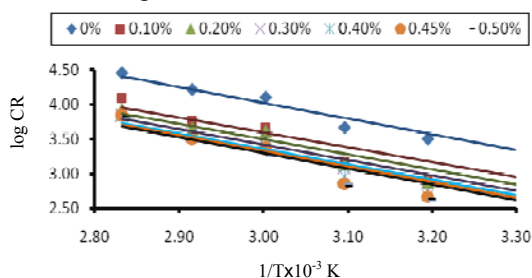

Figure 7. Arrhenius plots for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of PIB extract
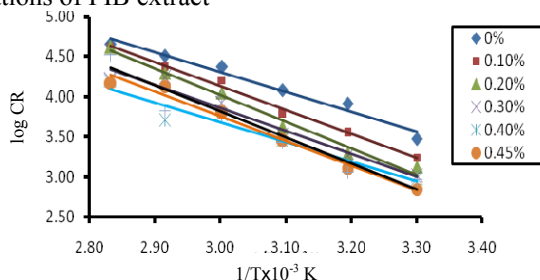

Figure 8. Arrhenius plots for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of PIB extract

Table 4. Activation energy in HCl and H_2SO_4 media at different concentrations of PIB extract

Con %	0.00	0.10	0.20	0.30	0.40	0.45	0.50
HCl	43.74	41.07	42.23	42.24	42.91	42.97	43.89
H_2SO_4	47.12	57.31	63.33	63.87	50.06	54.32	48.50

Experimental corrosion rate values evaluated from the weight loss data for mild steel in 1 M HCl and 1 M H_2SO_4 in the absence and presence of PIB was used to determine the enthalpy of activation (ΔH_{cor}) and apparent entropy of activation (ΔS_{cor}) for the formation of the activation complex in the Eyring transition state equation[30], which is an alternative formulation of Arrhenius equation is[31].

$$CR = \frac{RT}{Nh}\exp(\Delta S_{cor} / R)\exp(-\Delta H_{cor} / RT) \tag{14}$$

Where h is plank's constant, N is Avogadro's number, ΔS_{cor} is the entropy of activation, and ΔH_{cor} is the enthalpy of activation. A plot of Log (CR/T) *versus* 1/T gave a straight line (Figure 9 and Figure 10) with a slope of - ΔH_{cor}/2.303 R and an intercept of log R/Nh+ ΔS_{cor}/2.303 R, from which the values of ΔS_{cor} and ΔH_{cor} were calculated and listed in Table 5 and 6 for HCl and H$_2$SO$_4$ medium respectively. The change in activation free energy (ΔG_{cor}) of the corrosion process can be calculated at each temperature by applying the equation:

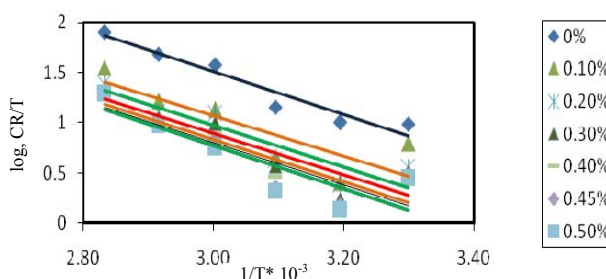$$\Delta G_{cor} = \Delta H_{cor} - T\Delta S_{cor} \tag{15}$$

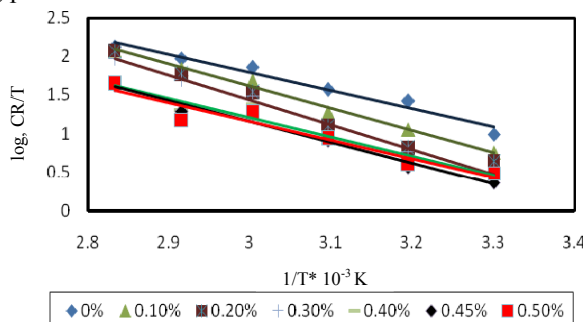**Figure 9.** Eyring plots for mild steel corrosion in 1 M HCl without and with PIB

Figure 10. Eyring plots for mild steel corrosion in 1 M H$_2$SO$_4$ without and with PIB

Table 5. Calculated values of free energy of activation, activation enthalpy and activation entropy for mild steel in 1 M HCl containing PIB extract

Con.	ΔG_{cor} in kJ/mole						ΔH_{cor} in	ΔS_{cor} in
%	303 K	313 K	323 K	333 K	343 K	353 K	kJ/mole	J/mole
0	-26.38	-28.60	-30.82	-33.05	-35.27	-37.50	41.03	0.22
0.1	-24.09	-26.15	-28.21	-30.27	-32.33	-34.39	38.35	0.21
0.2	-23.42	-25.50	-27.58	-29.66	-31.73	-33.81	39.52	0.21
0.3	-22.96	-25.03	-27.09	-29.15	-31.21	-33.28	39.52	0.21
0.4	-22.55	-24.62	-26.69	-28.76	-30.83	-32.90	40.19	0.21
0.45	-22.35	-24.41	-26.48	-28.55	-30.61	-32.68	40.25	0.21
0.5	-22.10	-24.19	-26.28	-28.37	-30.45	-32.54	41.17	0.21

The positive values of ΔH_{cor} both in absence and presence of inhibitor reflect the endothermic nature of the mild steel dissolution process meaning that dissolution of steel is

difficult[32]. The shift towards positive value of entropies(ΔS_{cor}) imply that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex[33].These values of ΔG_{cor} were negative in all temperatures (303 to 353K) indicating increased rate of corrosion.

It was evident from the table that the value of ΔH_{cor} increased in the presence of the inhibitor than the uninhibited solution indicating higher protection efficiency. This may be attributed to the presence of energy barrier for the reaction; hence the process of adsorption of inhibitor leads to rise in enthalpy of the corrosion process.

Table 6. Calculated values of free energy of activation, activation enthalpy and activation entropy for mild steel in 1 M H_2SO_4 containing PIB

Con.	ΔG_{cor} in kJ/mole						ΔH_{cor} in	ΔS_{cor} in
%	303	313	323	333	343	353	kJ/mole	J/mole
0	-27.67	-30.05	-32.43	-34.81	-37.19	-39.56	44.41	0.24
0.1	-25.74	-28.39	-31.04	-33.69	-36.34	-38.99	54.59	0.27
0.2	-24.56	-27.38	-30.19	-33.00	-35.81	-38.62	60.61	0.28
0.3	-24.08	-26.89	-29.70	-32.52	-35.33	-38.14	61.15	0.28
0.4	-24.05	-26.41	-28.77	-31.12	-33.48	-35.84	47.35	0.24
0.45	-23.38	-25.85	-28.32	-30.80	-33.27	-35.75	51.60	0.25
0.5	-23.91	-26.21	-28.51	-30.81	-33.11	-35.41	45.78	0.23

On comparing the values of entropy of activation (ΔS_{cor}) listed in Table 6, it was clear that entropy of activation increased in the presence of the studied inhibitor compared to free acid solution. In the free acid solution it can be explained as follows: the transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state, so a high value for the entropy of activation is obtained. In the presence of inhibitor, however, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. Since the surface is covered with inhibitor molecules, this will retard the discharge of hydrogen ions at the metal surface causing the system to pass from a random arrangement and hence entropy of activation is increased. Hence, increase in the entropy of activation (ΔS_{cor}) in the presence of inhibitor increases in the disordering on going from reactant to activated complex[34].

Conclusion

- PIB acts as a good inhibitor for the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4. The inhibition efficiency values increase with the inhibitor concentration and the solution temperature.
- The maximum IE reported in both media were at 313 K.
- The adsorption of PIB on the mild steel surface obeys the Temkin adsorption isotherm.
- The negative values of ΔG_{ads} emphasize the spontaneity of the adsorption process and the stability of the adsorbed layer on the steel surface.
- ΔG_{ads} values in both media indicated more tendency of physisorption,but some values showed a little tendency of chemisorption in HCl media.
- The estimated high, positive value of ΔH_{ads} in HCl ensures that PIB species was adsorbed chemically on mild steel surface and in H_2SO_4 media, negative value indicate physisorption.
- The values of ΔG_{ads} ΔH_{ads} and ΔS calculated from the different equations were in good agreement.

References

1. Quraishi M A and Wajid Khan, *Methods Meter.,* 1996, **43(2)**, 5.
2. Sasidharan, Biodiversity documentation for Kerala-Flowering Plants, Part 6, 2004, 229.
3. Kirtikar K R and Basu B D, Indian Medicinal Plants, 1987, **2**, 2nd Ed., Dehradun: International Book Distributors, 1290-1292.
4. The Wealth of India, A Dictionary of Indian Raw Material and Industrial Products, Raw Material, 1991, **7**, N-Pe, 282.
5. Husain Akhtar, Virmani O P, Popli S P, Mishra L N, Gupta M M, Shrivastava G N, Abraham Z and Singh A K, Dictionary of Medicinal Plant, 1992, 332-333.
6. Gamble J S, The flora of presidency of Madaras Aplard & Son Ltd, London, 1979, **2**, 633.
7. Bur Kill H M, The Useful Plants of West tropical, Africa, 1985, **4.**
8. Abd El-Maksoud S A, *Int J Electrochem Sci.,* 2008, **3**, 528-555.
9. James A O and Akaranta O, *Res J Chem Sci.,* 2011; **1(1),** 31-37.
10. James A O, Oforka N C and Abiola O K, *Int J Electrochem Sci.,* 2007, **2**, 278.
11. Putilova I N, Balezin S A and Barannik V P, Metallic Corrosion Inhibition; Pergamon Press, New York, 1960, 31.
12. Rawat N S and Singh A K, *Bull Electrochem.,* 1987, **3**, 7.
13. Ebbenso E E, *Mater Chem Phys.,* 2003a*,* **79(1)**, 58-70; DOI:10.1016/S0254-0584(02)00446-7
14. Ebbenso E E, *Bull Electrochem Part-1,* 2003b, **19(5)**, 209.
15. Ebbenso E E*, Bull Electrochem Part-2,* 2004, **20,** 551.
16. Ebenso E E, Eddy N O and Odiongenyi A O, *Portugaliae Ectrochimica Acta,* 2009, **27(1)**, 13-22.
17. Drazic D M, Vracar L J and Drazic V J, *Electrochim Acta*, 1994, **39(8-9),** 1165-1170; DOI:10.1016/0013-4686(94)E0032-U
18. Singh A K and Quraishi M A, *J Appl Electrochem.,* 2011, **4(1)1**, 7-18; DOI:10.1007/s10800-010-0202-y
19. Singh A K and Quraishi M A, *J Appl Electrochem.*, 2010, **40(7)**, 1293-1306; DOI:10.1007/s10800-010-0079-9
20. Ashassi-Sorkhabi H, Shaabani B and Seifzadeh D, *Appl Surf Sci.,* 2005, **239(2)**, 154-164; DOI:10.1016/j.apsusc.2004.05.143
21. Solomon M M, Umoren S A, Udousoro I I and Udoh A P, *Corros Sci.,* 2010, **52(4)**, 1317-1325; DOI:10.1016/j.corsci.2009.11.041
22. Li X, Deng S, Fu H and Li T, *Electrochim Acta,* 2009, **54(16)**, 4089-4098; DOI:10.1016/j.electacta.2009.02.084
23. Obot I B and Obi-Egbedi N O, *Corros Sci.,* 2010, **52(2)**, 657-660; DOI:10.1016/j.corsci.2009.10.017
24. Noor E A, *J Appl Electrochem.,* 2009, **39()9**, 1465-1475; DOI:10.1007/s10800-009-9826-1
25. Badiea A M and Mohana K N, *Corros Sci.,* 2009, **51(9)**, 2231-2241; DOI:10.1016/j.corsci.2009.06.011
26. Eddy N O and Ebenso E E, *African J Pure Appl Chem.,* 2008, **2(6)**, 046-054.
27. Eddy N O and Odoemelam S A, *J Surface Sci Technol.*, 2008a, **24(1-2)**, 1.
28. Umoren S A, Obot I B, Ebenso E E and Okafor P C, *Portugaliae Electrochim Acta*, 2008, **26(3),** 267-282.
29. Venkatachalam C S, Rajagopalan S R and Sastry M V C, *Electrochim Acta.* 1981, **26(9)**, 1219-1224; DOI:10.1016/0013-4686(81)85102-X

30.   Matai S, Bagchi D K, Granam A, Krishaswamy S I and Kaha J S, (Eds)., Proceedings International Symposium on Biological Applications of Solar Energy. Mandras: Macmillan Company of India.1980, 144-148.
31.   Bockris J O M and Reddy A K N, Modern Electrochemistry Plenum Press, New York, N.Y,USA,197 7.
32.   Ebenso E E and Obot I B, *Int J Electrochem Sci*., 2010, **5,** 2012-2035.
33.   Prabhu R A, Shanbhag A V and Venkatesha T V. *J Appl Electrochem.,* 2007, **37(4)**, 491-494\7; DOI:10.1007/s10800-006-9280-2
34.   Elachouri M, Hajji M S, Salem M, Kertit S, Aride J, Coudert R and Essassi E, *Corrosion*, 1996, **52(2)**, 103-108.