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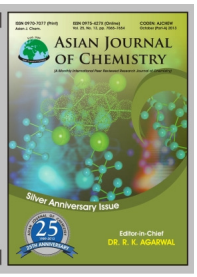

Phenobarbital: A New and Effective Corrosion Inhibitor for Mild Steel in 1 M HCl Solution

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Phenobarbital was investigated as corrosion inhibitor for mild steel in 1 M HCl solution by weight loss and quantum chemical calculations. Phenobarbital showed 95 % inhibition efficiency at concentration of 200 ppm. The adsorption of the inhibitor followed Langmuir adsorption isotherm. The quantum chemical calculations were applied to elucidate adsorption pattern of inhibitor molecules on steel surface.

Key Words: Phenobarbital, Mild steel, Weight loss, Adsorption, Quantum chemical calculations.

INTRODUCTION

Steel is widely used in industries and machinery and many other fields. Acids are used in industries during pickling, cleaning, descaling, *etc*.[1]. Inhibitors are used in acid solution to prevent metal dissolution. The use of organic inhibitors is most effective and most economic method for protection of metallic corrosion. The efficiency of an organic compound as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface[2].

The adsorption of an inhibitor is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, electron density at donor site, presence of functional groups, molecular area and molecular weight of the inhibitor molecule[3,4]. The adsorption requires the existence of attractive forces between the adsorbate and the metal[5]. Adsorption can be physisorption, chemisorption or a combination of both[6]. Most of the commercially available inhibitors are toxic in nature Thus, the development of non-toxic corrosion inhibitors of natural source and non-toxic type, has been considered to be more important and desirable[7]. In recent years researchers have paid attention on the use of drugs as inhibitors for metallic corrosion due to their non-toxic nature, namely cefatrexyl, metformin, ciprofloxacin, norfloxacin, ofloxacin drugs, Tacrine[8-10]. Recently, we have studied the inhibiting action of drugs such as cetirizine, cefotaxime sodium, cefazolin, doxycycline, pheniramine, streptomycin, cefalexin, fexofenadine, mebendazole, dapsone, on corrosion of metals in acid media[11-19]. We observed that the drugs act as efficient corrosion inhibitors due to the presence of π electrons, hetero atoms in their molecules through which they are either adsorbed or form insoluble metal complex at the metal surface and inhibit metal corrosion[20,21]. Phenobarbital drugs are nonselective central nervous system depressant which is primarily used as a sedative hypnotic and also as an anticonvulsant in subhypnotic doses. In present work we have investigated the inhibition action of phenobarbital drug as corrosion inhibitor of mild steel in 1 M HCl using weight loss and quantum chemical calculations.

EXPERIMENTAL

All the tests were performed on mild steel of following composition (wt. %): 0.076 % C, 0.192 % Mn, 0.012 % P, 0.026 % Si, 0.050 % Cr, 0.023 % Al, 0.123 % Cu and bal. Fe. Specimens with dimensions of 2.5 cm × 2 cm × 0.025 cm were used for weight loss studies.

Inhibitor: Phenobarbital tablets were commercially obtained from the medical shop as a trade name Barbee manufactured by the Indian Drugs and Pharmaceutical Ltd. (IDPL). The compound in its purest state has molecular formula ($C_{12}H_{12}N_2O_3$) and melting point (174-178 ºC). Its chemical structure is shown in Fig. 1. All the concentrations of the inhibitor in acid solution, were taken in ppm.

Weight loss measurements: The mild steel specimens used had a rectangular shape of (2.5 cm × 2.0 cm × 0.025 cm) were abraded with series of emery paper (600-1200 grades) then washed with distilled water and finally with acetone. After weighing accurately, the specimens were immersed in conical flask which contained 100 mL of 1 M HCl in the absence and presence of different concentration of inhibitor. All the test solutions were kept in a thermostated water bath. After 3 h, the specimens were taken out, washed, dried and weighed accurately. The mean corrosion rate (expressed in mg cm^{-2}) with respect to acid and inhibitor was calculated. The corrosion rate (C_R) was calculated from the following equation:

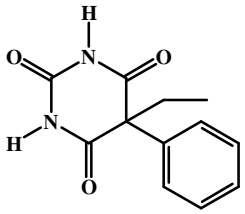

Fig. 1. Molecular structure of phenobarbital [5-ethyl-5-phenylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione]

$$C_R\ (mm/y) = \frac{87.6W}{at\ D} \quad (1)$$

where W is the average weight loss of mild steel specimens, a total area of one mild steel specimen, t is the immersion time (3 h) and D is density of mild steel in (g cm^{-3}). The inhibition efficiency (η %) of inhibitor on the corrosion of mild steel was calculated as follows,

$$\eta\ (\%) = \frac{C_R - C_{R\,inh}}{C_R} \times 100 \quad (2)$$

where C_R and $C_{R\,inh}$ are the corrosion rates of mild steel in the absence and presence of the inhibitors, respectively.

Quantum chemical calculations: Quantum chemical calculations were performed using density function theory (DFT) method, B3LYP with electron basis set 6-31G* (d, p) for all atoms. All the calculations were executed with Gaussian 03, E .01[22].

RESULTS AND DISCUSSION

Weight loss measurements: The weight loss results obtained for mild steel in 1 M HCl in the presence and absence of different concentration of phenobarbital are summarized in Table-1. The corrosion rate (mg cm^{-2}) values of mild steel in 1 M HCl decreases as the concentration of inhibitor increases *i.e.*, the inhibition efficiency increases as the concentration of inhibitor is raised. The tests were repeated at different temperatures and immersion time. Inhibition efficiency (h %) decreases with increase in temperature from 308-338 K. Inhibition efficiency increases with increase in immersion time. The results are shown in Fig. 2(A-C).

TABLE-1
WEIGHT LOSS MEASUREMENTS FOR MS IN 1 M HCl AT DIFFERENT CONCENTRATIONS OF PHENOBARBITAL

Inhibitor concentration (ppm)	Weight loss (mg cm^{-2})	η (%)	C_R (mm/y)	θ
Blank 1 M HCl	20	–	74	–
25	5	75	18	0.75
50	3	85	11	0.85
100	1	94	6	0.94
200	0.9	95	3	0.95

Adsorption isotherm: The adsorption isotherms provide useful information for the mechanism of corrosion inhibition. The surface coverage, θ, was calculated from the following equation:

$$\theta = \frac{C_R - {}^{inh}C_R}{C_R} \quad (3)$$

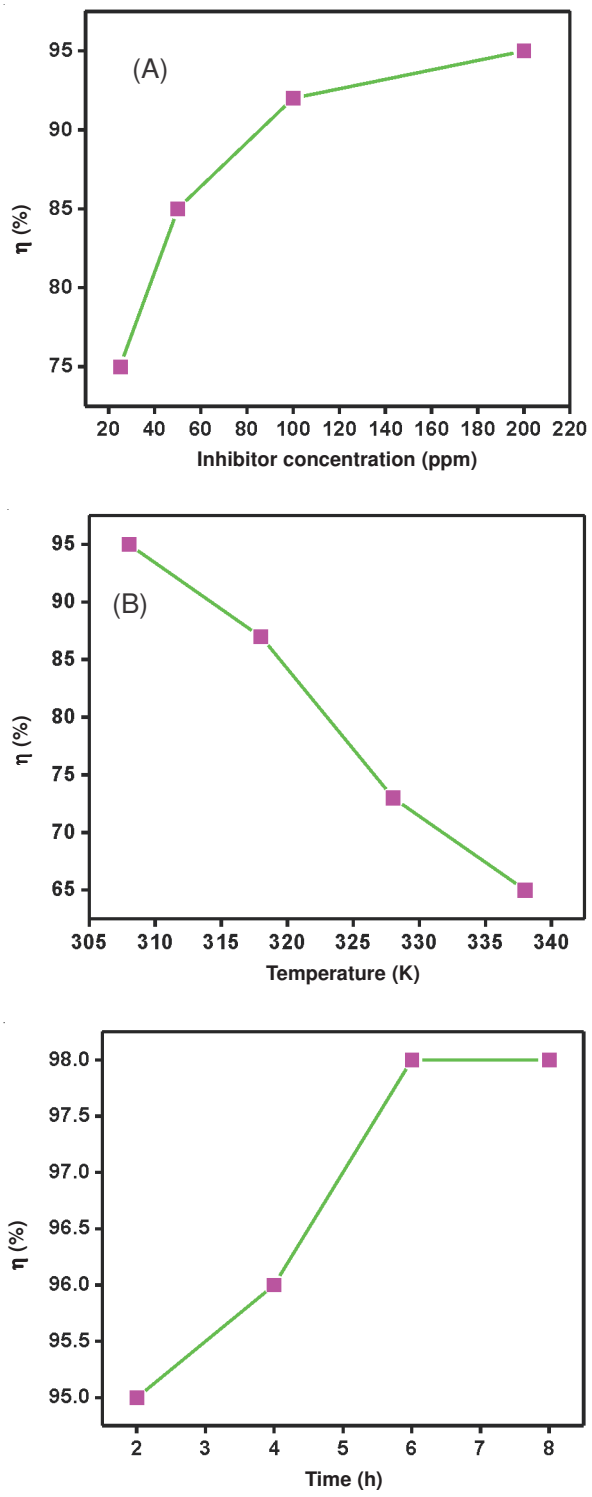

Fig. 2. Variation of inhibition efficiency in 1 M HCl on mild steel with (A) different concentrations of phenobarbital; (B) different temperatures from the weight loss data, (C) different immersion time

where, C_R and $^{inh}C_R$ are the corrosion rates of mild steel in the absence and presence of phenobarbital, respectively. By fitting the θ values obtained from weight loss data to various isotherms namely Langmuir, Temkin and Frumkin, the best fit was obtained with the Langmuir isotherm as shown in Fig. 3[23]. A straight line was obtained on plotting log C_{inh} *versus* log (θ/1– θ) for Langmuir isotherm with regression coefficient (R^2 = 0.9995) confirm this approach for all the techniques used.

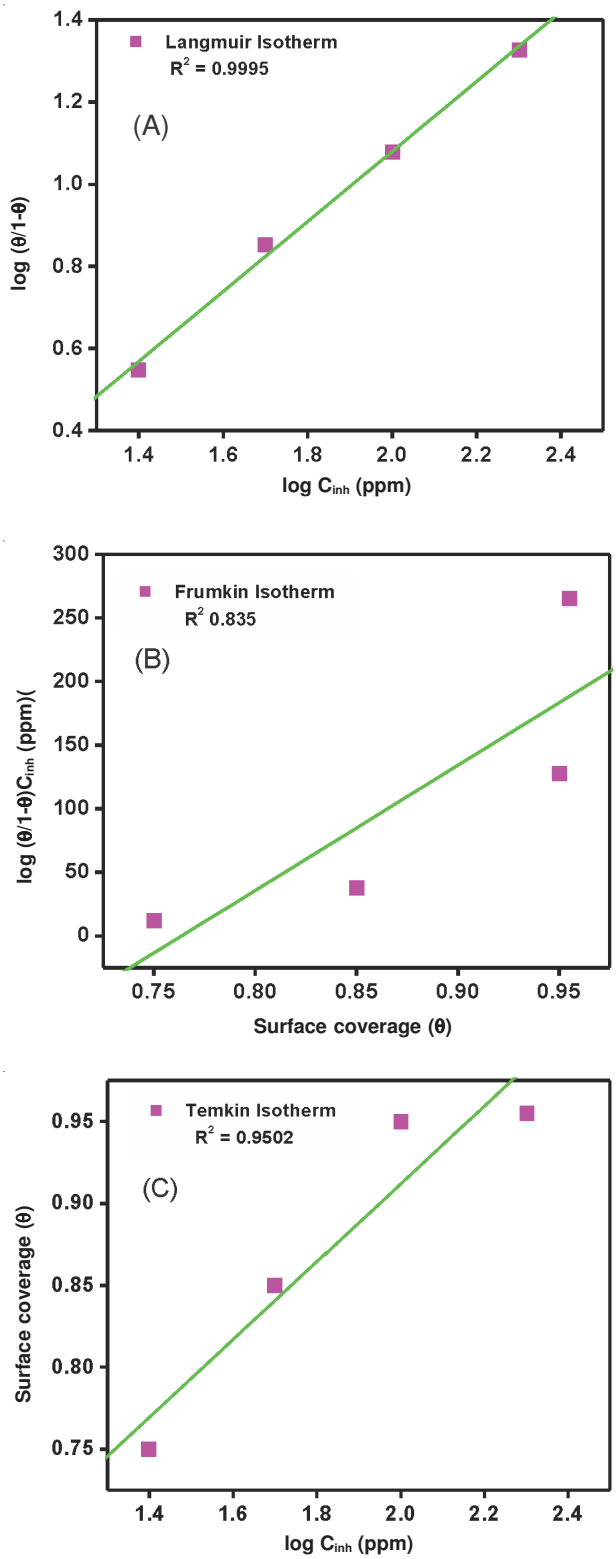

Fig. 3. Adsorption isotherms with regression coefficients (R^2) (A) Langmuir (B) Frumkin and (C) Temkin

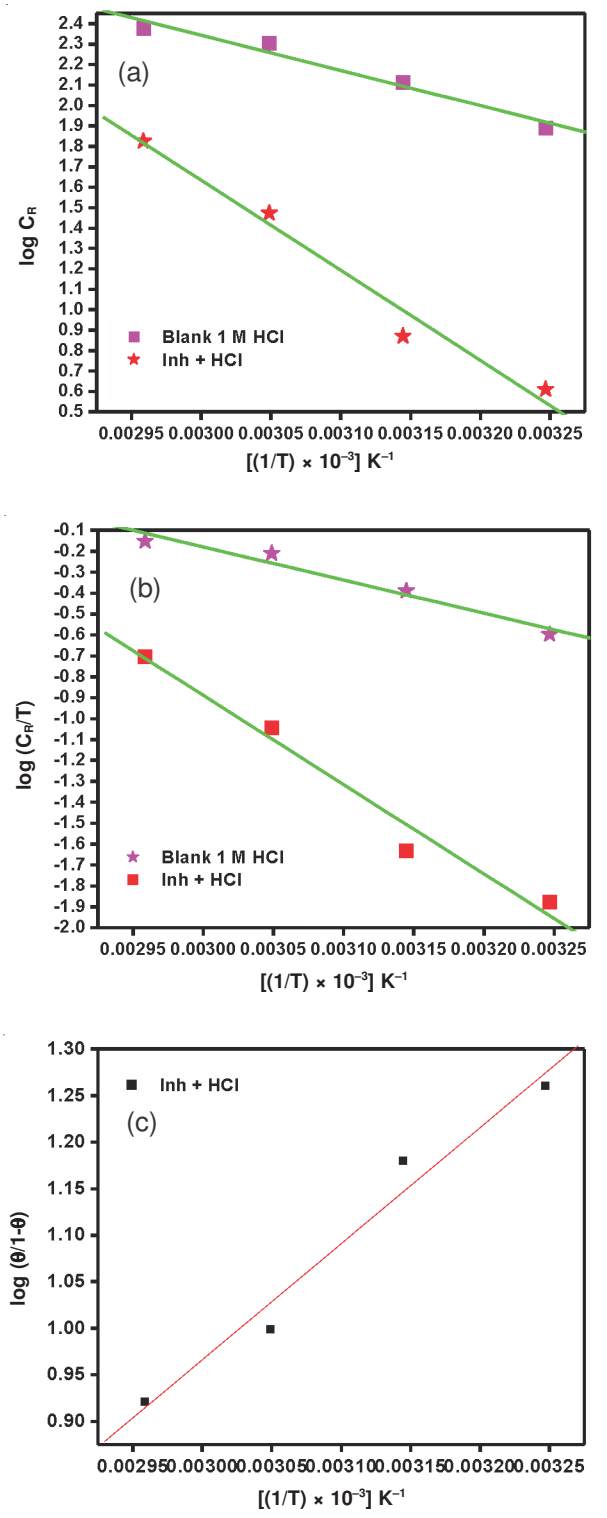

Fig. 4. (a) Arrhenius plot of log C_R *vs.* 1000/T (b) transition state plot of log C_R/T *vs.* 1000/T (c) $\log = \left(\frac{\theta}{1-\theta}\right)$ *versus* 1/T for mild steel in 1 M HCl in the absence and the presence phenobarbital

Thermodynamic activation parameters: A plot of the logarithm of corrosion rate *vs.* 1000/T gives a straight line as shown in Fig. 4(a). The apparent activation energy (E_a) was calculated by using following equation[24]:

$$\ln(C_R) = \frac{-E_a}{RT} + A \quad (4)$$

where E_a is activation energy for the corrosion of mild steel in 1 M HCl, R is the molar gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of E_a in 1 M HCl in absence and presence of phenobarbital were determined from the slope by plotting the values obtained (Table-2).

TABLE-2
THERMODYNAMIC PARAMETERS FOR MILD STEEL IN 1 M HCl IN ABSENCE AND PRESENCE OF PHENOBARBITAL

Inhibitor conc. (ppm)	E_a (kJ mol^{-1})	ΔH* (kJ mol^{-1})	ΔS* (J mol^{-1} K^{-1})	ΔQ_{ads} (kJ mol^{-1})
Blank	38	35	-93	–
100	58	61	-33	-26

The addition of phenobarbital changed the values of E_a and may be attributed to the adsorption of inhibitor on mild steel surface causing an energy barrier. The enthalpy of activation (ΔH*) and the entropy of activation (ΔS*) were calculated from the equation;

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (5)$$

where h is Planck constant, N is Avogadro's number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation. Fig. 4(b) shows a plot of log (C_R /T) against 1000/T which gave straight lines with slope of (-ΔH*/R) and intercept of [(ln (R/Nh)) + (ΔS*/R)] from which the values of ΔH* and ΔS* were calculated and are given in Table-2. Positive sign of ΔH* reflects the endothermic nature of dissolution of steel. The values of ΔS* were higher in presence of inhibitors than in its absence suggesting that the randomness increases on going from reactants to activated complex[25]. The heat of adsorption (ΔQ_{ads}) was obtained from the surface coverage and temperature by using following equation:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C_{inh} - \left(\frac{\Delta Q_{ads}}{2.303RT}\right) \quad (6)$$

A plot of $\log\left(\frac{\theta}{1-\theta}\right)$ *vs.* 1/T is given in Fig. 4C. The value of heat of adsorption was determined from the slope $\left(\frac{-\Delta Q_{ads}}{2.303RT}\right)$ of the graph and shown in Table-2. It is also evident from Table-2 that (ΔQ_{ads}) has negative value which indicates that inhibitor adsorption decreases with increase in the temperature hence decrease in inhibitor efficiency. The negative value of (ΔQ_{ads}) also suggested that the adsorption of inhibitor is an exothermic process[23].

The standard free energy of adsorption, ΔG°_{ads} and the values of equilibrium constant, K_{ads} at different temperatures were calculated from the equation:

$$K = \frac{\theta}{C(1-\theta)} \quad (7)$$

$$\Delta G^\circ_{ads} = -RT\ln(55.5K_{ads}) \quad (8)$$

The value 55.5 in the above equation is the concentration of water in solution in mol/L. The values of ΔG_{ads} are given in Table-3. The negative values of ΔG_{ads} indicate the spontaneity of the adsorption of inhibitor molecules on the metal surface. Generally, the values of ΔG_{ads} up to -20 KJ mol^{-1} are consistent with the electrostatic interaction (physisorption) of charged molecules and the charged metal, while those around -40 KJ mol^{-1} or more negative are associated with sharing or transfer of electrons from inhibitor molecules to the metal surface forming

TABLE-3
STANDARD FREE ENERGY OF ADSORPTION OF MILD STEEL IN 1 M HCl IN ABSENCE AND PRESENCE OF PHENOBARBITAL AT DIFFERENT TEMPERATURES

Temperature (K)	$-\Delta G_{ads}$ (kJ mol^{-1})	Temperature (K)	$-\Delta G_{ads}$ (kJ mol^{-1})
308	39	328	40
318	39	338	40

coordinate type bond (chemisorption)[26]. The calculated values of ΔG_{ads} from -39 to -40 KJ mol^{-1} indicated that the adsorption of the inhibitor on mild steel surface is by chemical adsorption[27].

Quantum chemical calculations: The structure and electronic parameters were obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The optimized molecular structures and frontier molecular orbital density distribution of the studied molecule are shown in Fig. 5. The calculated quantum chemical parameters such as E_{HOMO}, E_{LUMO}, $\Delta E_{LUMO-HOMO}$, dipole moments (μ) are listed in Table-4. The molecular structure of phenobarbital showed that the molecules seem to adsorb on mild steel surface by sharing of electrons of the nitrogen atoms with iron to form coordinated bonds and π-electron interactions of the aromatic rings.

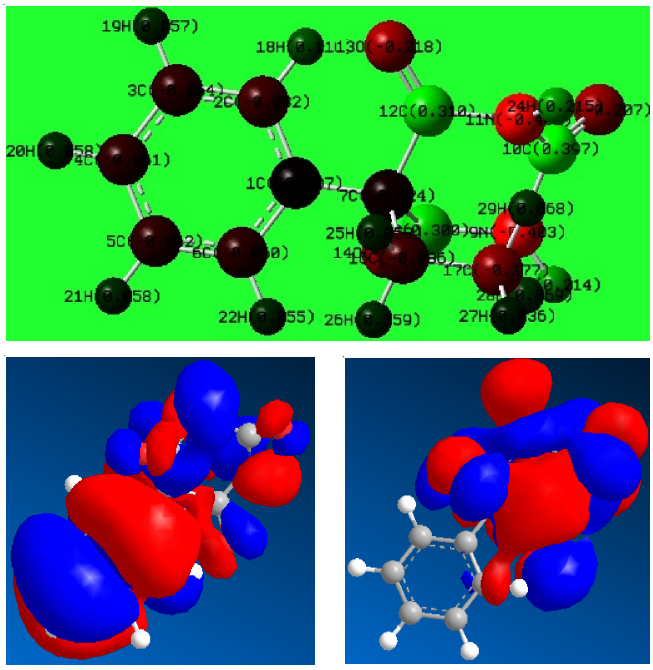

Fig. 5. Optimized molecular structure and frontier molecular orbital (HOMO, LUMO) density distribution of phenobarbital

TABLE-4
CALCULATED QUANTUM CHEMICAL PARAMETERS OF PHENOBARBITAL

Quantum parameters	Phenobarbital
HOMO (hartree)	-0.24001
LUMO (hartree)	0.00914
ΔE LUMO-HOMO (hartree)	0.23087
Dipole Moment (μ)	4.9868

The high value of highest occupied molecular orbital, E_{HOMO} indicates the tendency of the molecule to donate electrons

to acceptor molecule with empty and low energy orbital. Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO} indicates the tendency of the molecule to accept electrons. The lower the value of E_{LUMO}, the more probably the molecule would accept electrons[28]. The energy gap ΔE is an important parameter which is related to reactivity of the inhibitor molecule towards the metal surface. The interaction of inhibitor molecule to the metal surface is related to transfer of electrons from inhibitor to metal surface[29].

Mechanism of adsorption and inhibition: The data obtained from the different methods conclude that the inhibition by phenobarbital is due to adsorption at the metal/solution interface. The essential effect of phenobarbital used as corrosion inhibitor is due to the presence of free electron pairs in the oxygen and the nitrogen atoms, π-electrons on the aromatic rings, molecular size and mode of interaction with the metal surface and the formation of metallic complexes. The unshared and π-electrons interact with *d*-orbital of Fe to provide a protective film. The inhibitive properties of such compounds depend on the electron densities around the active centre; the inhibition mechanism of the inhibitor is a combination of surface blockage and electrostatic repulsion between adsorbed surfactant layer and chloride ions[30]. The adsorption density of inhibitor depends on the inhibitor concentration. The inhibition of these reactions would obviously depend on the degree of the surface coverage of the metal with the adsorbate. Adsorption is assumed to occur on the surface of the metal between the aggressive Cl^- and the inhibitor molecules, on the other. The order of the increasing inhibition, the molecular size of the inhibitor and consequently the number of adsorption centres plays an important role in the enhancement of the protection of carbon steel against corrosion[31].

Conclusion

Phenobarbital is good inhibitor for mild steel in 1 M HCl. The inhibition efficiency increased with increasing the concentration of the inhibitor up to a maximum of 95 % at 200 ppm. The adsorption of inhibitor molecules on the mild steel surface in 1 M HCl solution followed Langmuir adsorption isotherm. The negative values of ΔG_{ads} showed the spontaneity of the reaction.

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