Thermodynamic properties of Amino melamine Formaldehyde as corrosion inhibitor for steel in sulfuric acid solution

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Received in 1 Fev 2011, Revised 29 Mar 2011, Accepted 29 Mar 2011.
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Abstract

The corrosion inhibition of steel by amine melamine formaldehyde resin in different pH 4 and 6 from H_2SO_4 solution was studied at various temperatures (30,40,50) °C using electrochemical technique. The thermodynamic functions of dissolution and adsorption processes were calculated from experimental polarization data and the interpretation of the results are given. The apparent activation energies, enthalpy and entropy of the dissolution, process were determined and discussed.

Keywords: Melamine formaldehyde, Sulfuric acid; Corrosion inhibitors; Thermodynamics

Introduction

The use of organic inhibitor is one of the most practical methods for protecting metals against corrosion especially in acidic media [1-4].

The efficiency of an organic compound as an inhibitor is mainly dependent on its ability to get adsorbed on metal surface which consists of a replacement of water molecule at a corroding interface as:

$$\mathrm{Org_{(Sol)}} + n\mathrm{H_2O_{(ads)}} \rightarrow \mathrm{Org_{(ads)}} + n\mathrm{H_2O_{(Sol)}}$$

The adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, and electron density at donor site, presence of functional group such as –CHO, –N, R–OH, etc., molecular area and molecular weight of the inhibitor molecule [5–7].

Most studies concern inhibitor were concentrated on the structural properties of chemical substances which showed that the efficiency of inhibitor is well depends on molecular structure as well as the polar groups in the molecules [8-10]. It is known that the structure of the inhibitor molecule is not the only factor affecting the efficiency of the organic inhibitor but also the parameters of the system such as temperature, pH, time duration and metal compositions [11,12].

Under certain conditions of the experiment the electronic structure of the organic inhibitor is an effective characteristic on the corrosion inhibition efficiency [13].

The inhibition of the corrosion in acid solutions can be effected by the addition of variety organic compounds which has been investigated by several workers [14-16]. The unsaturated bonds or aromatic rings in the molecular structure of the inhibitor could favor its adsorption on the metal surface [17].

An earlier study [18] has shown that the introduction of formaldehyde performs so much the inhibitive properties of polyaniline on corrosion of iron in acid chloride solution due to the presence of π-electrons, quaternary nitrogen atom and large molecular size which ensures greater coverage of the metallic surface. So the adsorption of polymer molecules on the iron electrode surface is more, which leads to more inhibition efficiency [18]. Also Dense adherent and homogeneous waterborne resorcinol formaldehyde (RF)-cured composite coatings of poly(1-naphthylamine) (PNA)/poly(vinylalcohol) (PVA) coatings on mild steel were evaluated for their corrosion protective performance. The OCP curves, showed that PNA/PVA:RF composite coatings act as a barrier to the permeation of corrosive ions owing to the presence of a compact morphology. These coatings were found to be more adherent allowing a better passivation of steel substrates against corrosion. In corrosive medium conducting polymer film is in partially oxidized conducting state, which is able to maintain steel in passive state for several hours to several days [19].

The fire retardant characteristics of additives based on mixtures of melamine hydrobromide-free radical initiator-basic bismuth carbonate (or antimony trioxide) are discussed on the basis of the dependence of oxygen index on composition in the case of polypropylene [20].

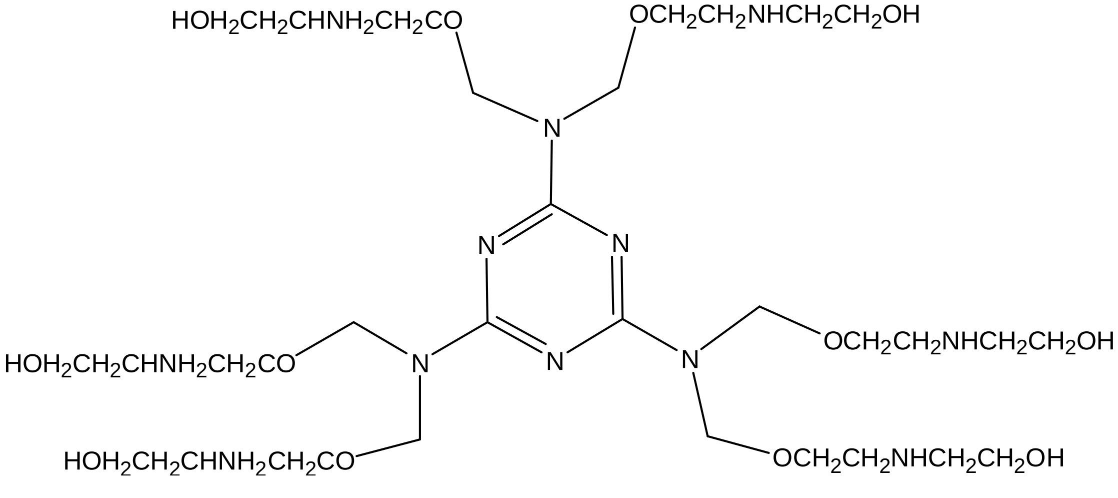
The aim of this work is to investigate the role played by amine Melamine formaldehyde resin on the corrosion behavior of mild steel at different pH employing electrochemical methods. The thermodynamic parameters for both dissolution and adsorption process were calculated and discussed.

Experimental

1- chemicals

Melamine, formaldehyde, diethanol amine and sulfuric acid were supplied by B.D.H. Company.

Amine melamine formaldehyde resin (molecular weight 744 g/mole) was prepared according to the procedure explained in reference [21] to obtain the following structure:



Scheme 1: *Amine melamine formaldehyde resin*

2- Apparatus

Electrochemical measurements were carried out using ACM Gill 8 with soft war 5-13, Arab Emirate University / central laboratories unit

3- Corrosion test

Corrosion tests were carried out on electrodes cut from sheets of mild steel strips containing 0.0 % P, 0. % Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and the remaining is iron were used for the measurement.

The surface preparation of the specimens was carried out using emery paper (No. 600 and 1200). These were degreased with ethanol and then dried at room temperature before used. Electrochemical experiments were performed in a conventional three electrodes cell consisting of a steel working electrode (WE), platinum counter electrode (CE) and a saturated calomel reference electrode (SCE).

Results and Discussion

The polarization behavior of mild steel at pH 4 and pH 6 with and without addition of amine melamine formaldehyde resin at concentration (50 and 100 ppm) at different temperature are given in Figs. (1-5).The current density (I_{corr}) obtained by extrapolation of the Tafel lines. The protection efficiency (%E) can also be calculated from the electrochemical relation as:

$$E\% = (1 - \frac{I'_{corr}}{I_{corr}})x100 \quad (1)$$

where I_{corr} and I'_{corr} are the corrosion density values without and with inhibitor respectively as listed in Table (1). These data shows that amine melamine formaldehyde resin is good inhibitor for mild steel at pH 6 and better performance is seen in the case of 100 ppm. The addition of resin modifies slightly the cathodic and anodic slopes.

At anodic we notice that the presence of resin results in reduction of anodic current density. This result indicates that this inhibitor exhibited cathodic and anodic inhibition effects and then the resin is classified as a mixed type inhibitor.

The change of the corrosion process rate with the temperature was studied in and out the presence of inhibitors. Generally the corrosion rate increase with the rise of temperature. The activation energies for the corrosion process were calculated from Arrhenius type plot according to the following equation:

$$I_{corr} = A\exp(-\frac{E_a}{R.T}) \quad (2)$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant.

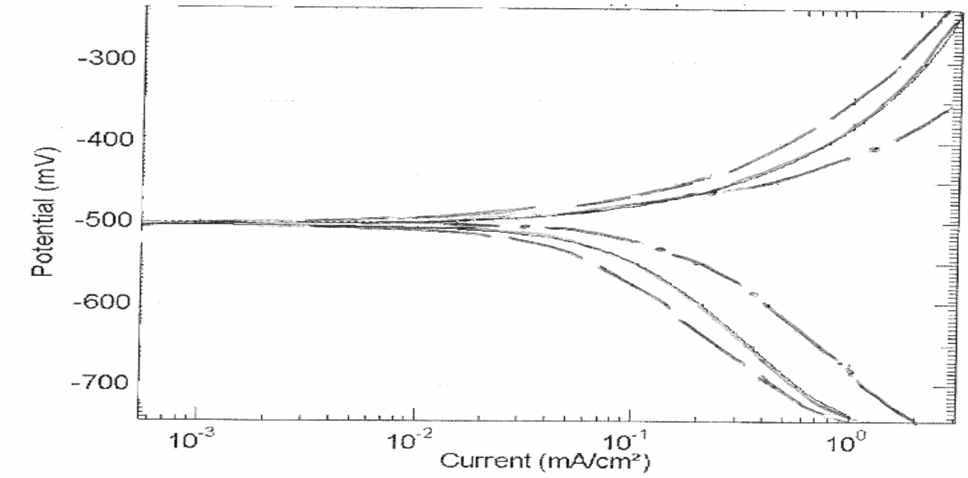


Fig. 1. Polarization curves for mild steel at pH 6 at different temperature (—•—) 30 °C, (——)40 °C, (----) 50 °C

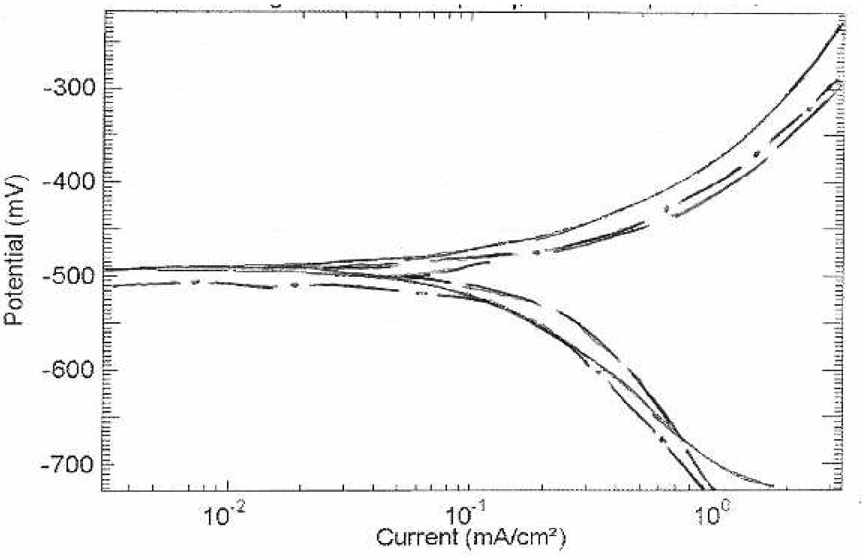


Fig. 2. Polarization curves for mild steel at pH 4 at different temperature (——) 30 °C,(— —) 40 °C, (—•—) 50 °C

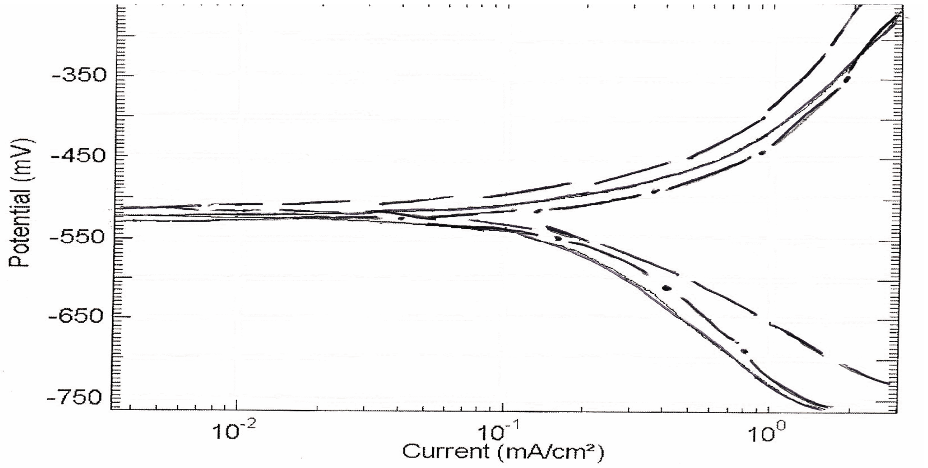


Fig. 3. Polarization curves for mild steel at pH 6 containing 50 ppm amine melamine formaldehyde resin at different temperature (— —)) 30 ˚C, (——)40 ˚C, (—•—) 50 ˚C

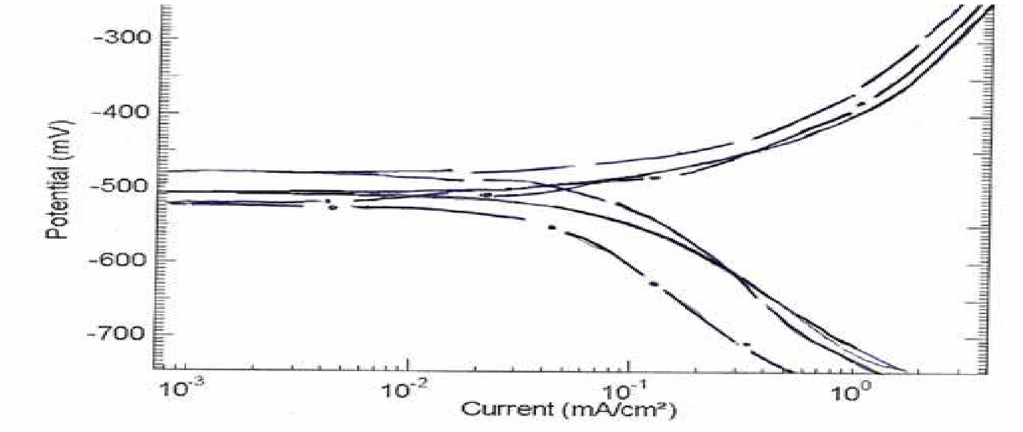


Fig. 4. Polarization curves for mild steel at pH 4 containing 50 ppm amine melamine formaldehyde resin at different temperature (— —)) 30 ˚C, (——)40 ˚C, (—•—) 50 ˚C

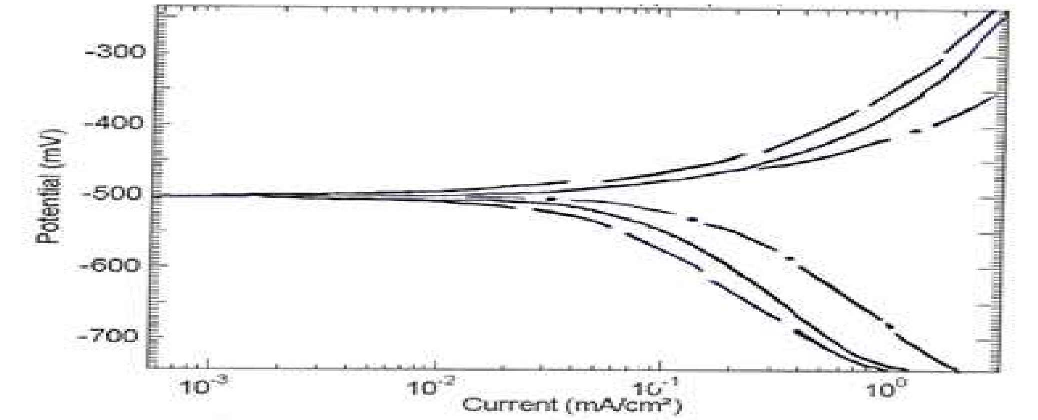


Fig. 5. Polarization curves for mild steel at pH 4 containing 100 ppm amine melamine formaldehyde resin at different temperature (— —)) 30 ˚C, (——)40 ˚C, (—•—) 50 ˚C

ΔH*and ΔS* may be evaluated using the alternative formulation of the Arrhenius equation called also the transition state equation:

$$I = \frac{RT}{Nh}.\exp(\frac{\Delta S *}{R}).\exp(-\frac{\Delta H *}{RT}) \qquad (3)$$

where h is Plank’s constant, N is the Avogadro number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation.

Table 1 : Electrochemical parameters of mild steel

C ppm	pH	Temperature K	$I_{corr.}$ mA/ cm^2	Corrosion rate MPY	% E
0	4	303	0.194	0.089	-
		313	0.655	0.302	-
		323	0.698	0.322	-
0	6	302	0.172	0.794	-
		313	0.228	0.105	-
		323	0.276	0.127	-
50	4	303	0.112	0.052	42.3
		313	0.402	0.185	38.7
		323	0.445	0.205	36.3
50	6	303	0.118	0.054	31.6
		313	0.163	0.076	28.4
		323	0.204	0.094	25.8
100	4	303	0.104	0.43	46.4
		313	0.366	0.169	44.0
		323	0.398	0.183	43.2
100	6	303	0.108	0.049	38.3
		313	0.149	0.068	35.2
		323	0.185	0.085	33.1

Figs. (6-11) shows a plot of In (I_{corr} / T) against 1/T where a straight lines are obtained with slope of ($-\Delta H^*/R$) and an intercept of In R/Nh + $\Delta S/R$ from which the values of ΔH^* and ΔS^* are calculated and listed in Table (2).

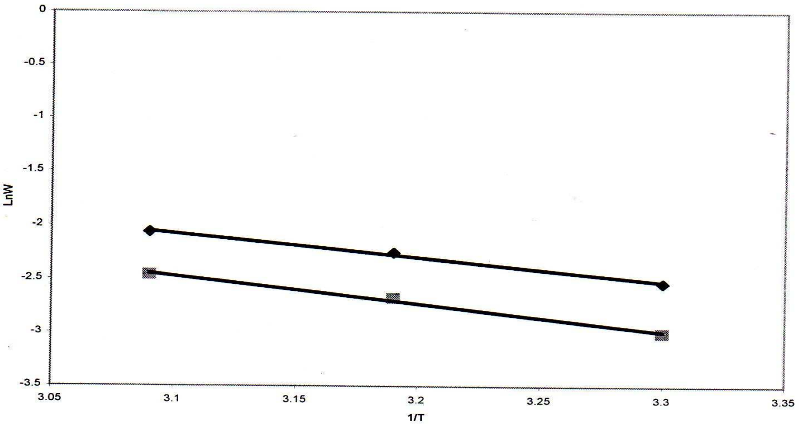


Fig. 6: Arrhenius plots of In w Vs 1/T at pH 6 ♦ without inhibitor ■ with 100ppm inhibitor

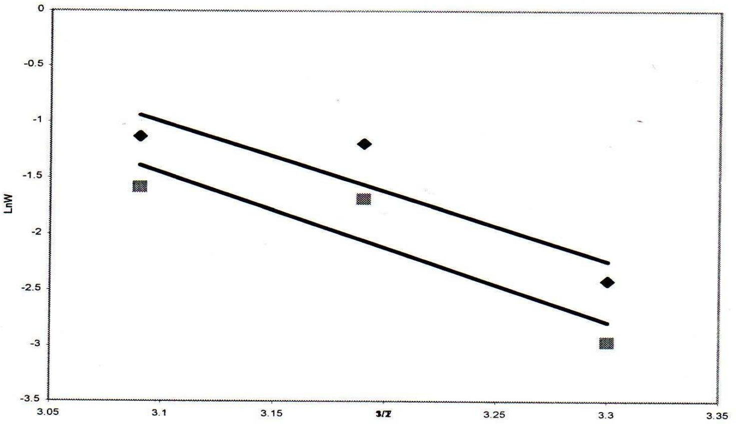


Fig. 7: Arrhenius plots of In w Vs 1/T at pH ♦ without inhibitor ■ with 50 ppm inhibitor

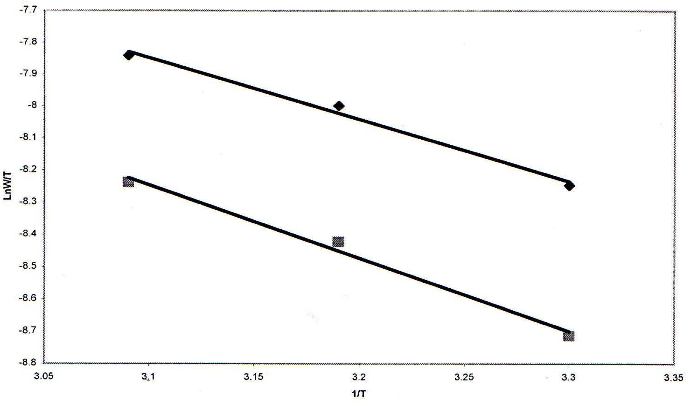


Fig. 8: Arrhenius plots of In w/T Vs 1/T at pH 6 ♦ without inhibitor ■ with 100ppm inhibitor

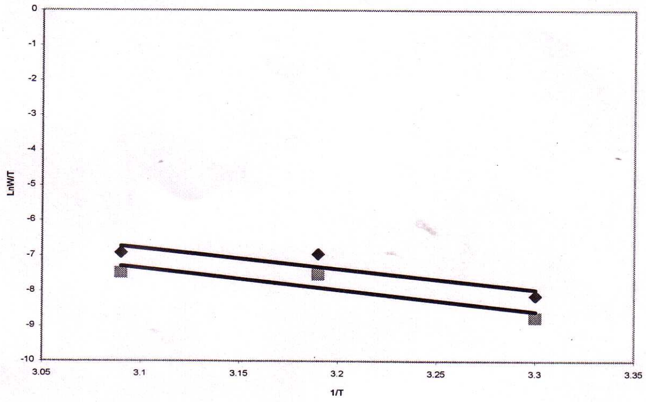


Fig. 9: Arrhenius plots of In w/T Vs 1/T at pH 4 ♦ without inhibitor ■ with 100 ppm inhibitor

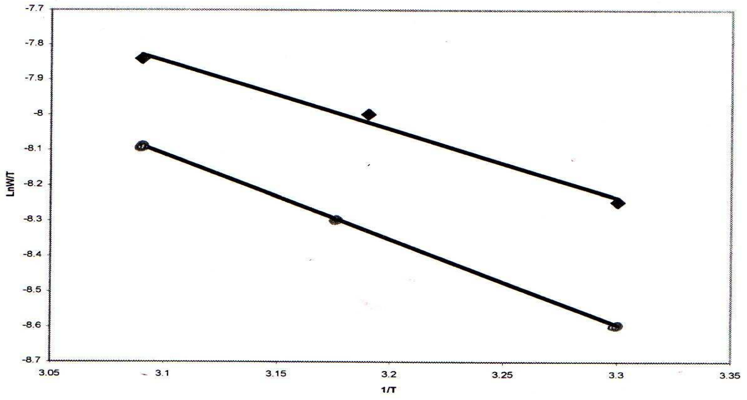


Fig. 10: Arrhenius plots of Ln w/T Vs 1/T at pH 6 ♦ without inhibitor ■ with 50 ppm inhibitor

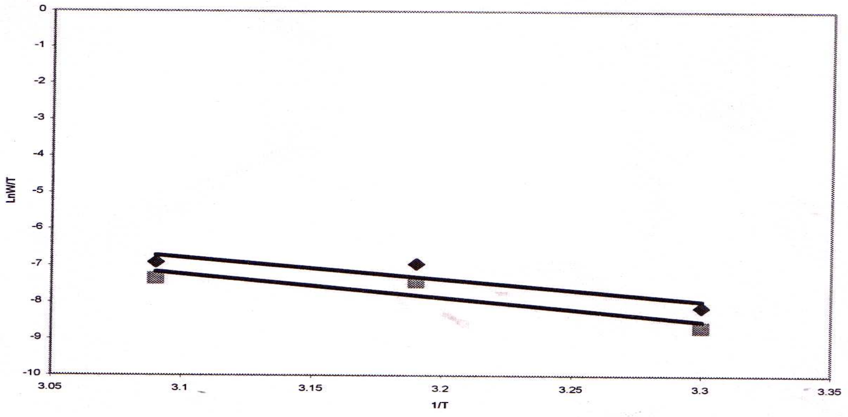


Fig. 11: Arrhenius plots of In w/T Vs 1/T at pH 4 ♦ without inhibitor ■ with 50 ppm inhibitor

Table 2 : The values of thermodynamic parameters ΔE, ΔH*, and ΔS* For mild steel in the absence and presence of inhibitor

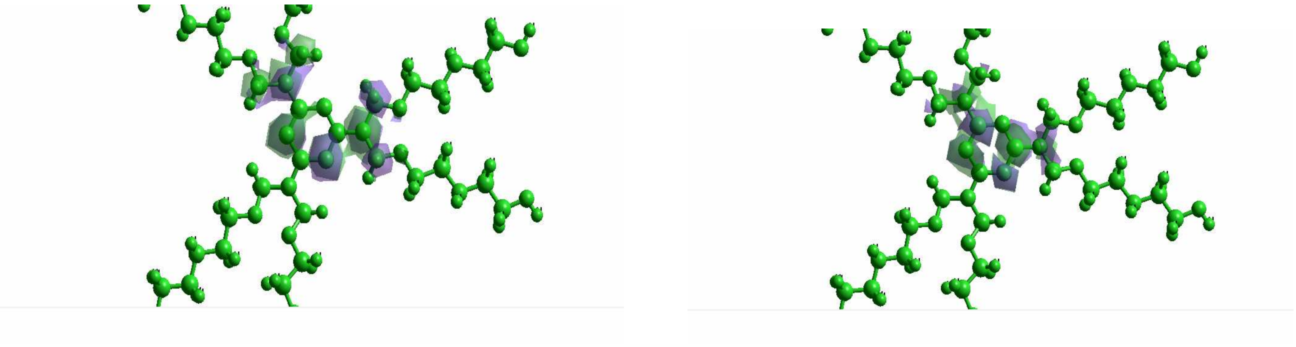
Inhibitor Conc. ppm	pH	ΔE kJ mole^{-1}	ΔH* kJ mole^{-1}	ΔS* J mole^{-1} K^{-1}
0	4	49.884	47.506	-249.07
50		52.555	51.021	-252.40
100		55.652	52.546	-260.72
0	6	18.204	16.034	-260.72
50		20.655	18.161	-261.83
100		21.785	19.997	-264.21

The higher values of E_a and ΔH* in the presence of resin rather than without resin indicated that as the temperature is raised a decrease in protection efficiency is obtained [22]. The negative value of ΔS* implies that the activation complex represents an association rather than a disordering take place going from reactants to the activated complex.

The positive sign of the enthalpy (ΔH*) is an endothermic nature of the steel dissolution in HCl solution. The entropy of activation (ΔS^*) in the absence of inhibitor is negative and increasing with increase concentration of inhibitor. Values of ΔE_a obtained in the presence of inhibitor are higher than that for the uninhibited one, indicating a strong inhibitive action for the studied compounds by increasing the energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on mild steel surface [23].

The increase of E_a and ΔH* accompanying the increase in the inhibitor concentration is explained by an increase of the energy barrier of corrosion reaction. In case of endothermic H adsorption, with a high activation energy barrier for the transition between strongly bonded H_{ads} and H_{diss} [24]. The higher activation energy in the inhibitor's presence further supports the proposed physisorption mechanism. Unchanged or lower values of E_a in inhibited systems compared to the blank to be indicative of chemisorption mechanism, while higher values of E_a suggest a physical adsorption mechanism.

Theoretical studies of the inhibitor were calculated by optimization of their bond lengths and bond angles using geometry optimization PM3.HOMO energy, LUMO energy, LUMO-HOMO energy gap and total energy are given in table 3 fig. 12. E_{HOMO} often is associated with electron donating ability of the molecule. High values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbital .Therefore the energy of the lowest unoccupied molecular orbitals indicates the ability of the molecule to accept electrons. The lower is the value of E_{LUMO} , the more probable it is that the molecule except electron [25].



HOMO LUMO

Fig. 12. HOMO and LUMO orbitals of amine melamine formaldehyde

Table 5. Quantum indices of amine melamine formaldehyde

E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Total energy (kCal mol^{-1})
-9.0003	-0.0634	8.9369	-24193680

Conclusion

The E(%) of amino melamine formaldehyde resin is found to increase with increasing the concentration and found it at pH= 4 more than at pH = 6 , on the other hand the E(%) of the inhibitor is decrease with increasing temperature.

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