Inhibition of Mild Steel Corrosion in Phosphoric Acid using Allyl Methyl Sulfide

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The effect of allyl methyl sulfide on the corrosion of mild steel in a solution of phosphoric acid has been investigated by weight loss method in relation to the concentration of the inhibitor and acid as well as the temperature. At room temperature, the efficiency of the inhibition increases with concentration of allyl methyl sulfide increases for mild steel. Corrosion rate is maximum for uninhibited solution as compared to the inhibited solution at all temperature. Corrosion rate is increases with increase of temperature. For 1×10^{-2} M of allyl methyl sulfide concentration, the percentage efficiency decreases with the temperature increases because of decreasing adsorption with increase in temperature. Low heat of adsorption indicates the adsorption is only physical in nature. By increasing the temperature, the free energy change values decreases. This shows that increase in temperature favours the corrosion process. As the concentration of the inhibitor decreases the free energy change increases. This shows that with decrease in concentration of allyl methyl sulfide the corrosion process becomes more and easier.

Key Words: Corrosion, Phosphoric acid, Adsorption isotherm, Mild steel, Allyl methyl sulfide.

INTRODUCTION

Corrosion may be defined as the process of gradual destruction of a metal by its environment. Corrosion is nothing but an exact reverse process of extraction of metals. According to Shreir[1] corrosion is the reaction of solid with environment. It is the common electrochemical phenomenon experienced in day to day life. Except noble metals almost all the metals undergo corrosion. Corrosion process caused a tremendous economic loss and every effort is now being taken to prevent it. Corrosion is probable the greatest consumer of metals known to man. In United States the cost of corrosion per year has been estimated to be over 20 billon dollars. The corrosion map of India shows that the amount works out to be roughly over 30,000 crores per year. Although the corrosion is inevitable its cost can be considerably reduced. It is thus quite important that crores of rupees are being spent on research to find out the means of preventing corrosion. So corrosion of carbon steel in phosphoric acid medium can be prevented by allyl methyl sulfide is discussed in this paper. The corrosion rate at different concentration of inhibitor was studied from that the maximum efficiency can be found out. At which the 1×10^{-2} M concentration of inhibitor the inhibition efficiency is 96.87 % (Table-1). When the concentration of the inhibitor decreases the % inhibition efficiency also get decreases. At the same time the % inhibition efficiency taken for different temperatures was given in Table-2. According to the connect the % inhibition efficiency is maximum at 303 K so the corrosion rate is low at this temperature.

TABLE-1
VALUES OF INHIBITION EFFICIENCIES CALCULATED FROM WEIGHT LOSS STUDIES FOR THE CORROSION OF MILD STEEL IN 1M H_3PO_4 IN PRESENCE OF DIFFERENT CONCENTRATIONS OF ALLYL METHYL SULFIDE

Concentration of the inhibitor (M)	Wt. loss (g)	Corrosion Rate (mmpy)	IE (%)
Blank	0.0984	53.46	–
0.00001	0.0729	39.25	25.89
0.00005	0.0594	31.98	39.57
0.00010	0.0474	25.52	51.74
0.00050	0.0301	16.20	69.36
0.00100	0.0105	5.660	89.29
0.00500	0.0074	4.010	92.41
0.01000	0.0030	1.650	96.87

EXPERIMENTAL

The experimental studies related to the inhibitive action of allyl methyl sulfides on mild steel in 1M H_3PO_4 have been presented here. Such studies include weight loss, polarization measurements, hydrogen permeation gasometric and impedance. Weight loss study is used to access the effectiveness of the inhibitor to be used in pickling baths.

TABLE-2
VALUES OF INHIBITION EFFICIENCIES CALCULATED FROM
WEIGHT LOSS STUDIES FOR THE CORROSION OF MILD
STEEL IN1M H_3PO_4 IN THE PRESENCE OF 10^{-2} M of ALLYL
METHYL SULFIDE (AMS) AT DIFFERENT TEMPERATURES

Temperature (K)	Weight loss (g)		Inhibition efficiency (%)	Corrosion rate (mmpy)	
	Blank	AMS		Blank	AMS
303	0.0984	0.0030	96.87	52.98	1.6081
308	0.1210	0.0064	93.49	65.15	3.4460
313	0.3124	0.0082	91.64	168.21	4.4152
328	0.4417	0.0196	90.19	237.83	5.1690
338	0.5723	0.0183	81.36	308.15	9.8749

Phosphoric acid and allyl methyl sulfide were procured from Sarabhai M. Chemicals and Fluka, respectively.

General procedure:

Weight loss method: Mild steel specimen of composition C - 0.07 %, Si - nil, Mn - 0.34 %, P - 0.008 %, S - nil, Fe-remainder are used in weight loss studies were in the form of rectangular pieces of surface area 4 cm^2 and thickness 0.02 cm. Before each run, the specimens were mechanically polished successively with 0/0, 1/0, 2/0, 3/0, 4/0 grade emery papers and finally degreased with acetone. The samples were stored in desiccators. The initials weights of the specimens were noted. Then each specimen was suspended through the hole punched at the top of the specimen in a beaker containing 100 mL of the 1M H_3PO_4 acid. The specimen was immersed in the acid used in each experiment for a stipulated interval of time. The temperature was maintained at 30 ± 2 ℃. At the end of 2 h the specimens were taken out, washed in running tap water and then in distilled water. They were dried and reweighed. The loss in weights was calculated. Each experiment was duplicated to get good reproducibility.

Effect of temperature: The same procedure adopted for weight loss studies at room temperature (30 ℃) was followed here, except that the temperature of the study was varied from 35 to 65 ℃. At the end of the each experiment, the specimens were taken out, washed both in running tap water and in distilled water. They were dried and their weights were measured. The loss in weights was calculated. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in1M H_3PO_4 with and without the addition to the inhibitor at their best inhibiting concentrations. Percentage inhibition of the inhibitor at various temperatures was calculated[2,3].

Detection method: The corrosion rate was found out by various concentration of the allyl methyl sulfide inhibitor and inhibition efficiency is also calculated by using different concentrations of allyl methyl sulfide at different temperatures. At which a 10^{-2} M allyl methyl sulfide the inhibition efficiency is maximum. The surface coverage and free energy change was found out by using 10^{-2} M allyl methyl sulfide concentration and different temperatures. From the Tables 3-5, values can predict the adsorption isotherm fits in straight line.

RESULTS AND DISCUSSION

Weight loss method: Corrosion behaviour of mild steel specimens at different concentrations of allyl methyl sulfide in 1M H_3PO_4 solution exposed for 2 h has been studied by the

TABLE-3
VALUES OF SURFACE COVERAGE CALCULATED FROM
WEIGHT LOSS STUDIES FOR THE CORROSION OF MILD
STEEL IN 1M H_3PO_4 IN THE PRESENCE OF 10^{-2} M OF ALLYL
METHYL SULFIDE AT DIFFERENT TEMPERATURES

θ	1-θ	Log θ/1-θ	1/T
0.9687	0.0313	1.4906	3.30×10^{-3}
0.9347	0.0653	1.1557	3.24×10^{-3}
0.9164	0.0836	1.0399	3.14×10^{-3}
0.9019	0.0981	0.9635	3.04×10^{-3}
0.8137	0.1863	0.6402	2.95×10^{-3}

TABLE–4
VALUES OF FREE ENERGY CHANGE CALCULATED FROM
WEIGHT LOSS STUDIES FOR THE CORROSION OF MILD
STEEL IN 1M H_3PO_4 IN THE PRESENCE OF DIFFERENT
CONCENTRATIONS OF ALLYL METHYL SULFIDE

Concentration (M)	θ	1- θ	Logθ/1-θ	ΔG (kJ/mol)
0.00001	0.2589	0.7411	-0.4567	-36.45
0.00005	0.3957	0.6043	-0.1839	-33.98
0.0001	0.5174	0.4826	0.0302	-33.47
0.0005	0.6936	0.3064	0.3548	-31.30
0.001	0.8929	0.1071	0.9210	-32.84
0.005	0.9241	0.0759	1.0855	-29.74
0.01	0.9687	0.0313	1.4906	-30.34

TABLE-5
VALUES OF FREE ENERGY CHANGES CALCULATED FROM
WEIGHT LOSS STUDIES FOR THE CORROSION OF MILD
STEEL IN 1M H_3PO_4 IN THE PRESENCE OF 10^{-2} M
CONCENTRATIONS OF ALLYL METHYL SULFIDE
AT DIFFERENT TEMPERATURES

Temperature (K)	θ	(1-θ)	log θ/(1-θ)	ΔG (kJ/mol)
303	0.9687	0.0313	1.4906	-30.34
308	0.9347	0.0653	1.1557	-28.87
313	0.9164	0.0836	1.0399	-29.10
328	0.9019	0.0981	0.9635	-29.53
338	0.8137	0.1863	0.6402	-28.34

weight loss method. The corrosion rates (mmpy), inhibitor efficiency and corrosion rate in different temperature are given in Tables 3-5. Corrosion rate in terms of millimeter per year (mmpy) has been calculated by the formula.

$$\text{Rate} = \frac{13.56\,W}{DAT}\ \text{mmpy}$$

where, W - weight loss in mg, D - density of the specimen in g/cc, A - area of the specimen in inch square, T - time of exposure in h.

The percentage inhibitor efficiency (IE) is calculated using the following formula.

$$\text{IE (\%)} = \frac{C_R - C_i}{C_R} \times 100$$

C_R = corrosion rate without inhibitor; C_i = corrosion rate with inhibitor.

From the experimental results the corrosion rate decreases with increasing concentrations of allyl methyl sulfide. But the corrosion rates are less than that of the uninhibited solution. The percentage efficiency increases with increase in concentration of allyl methyl sulfide. The same experiment was conducted also at higher temperature for 10^{-2} M concentration of allyl methyl sulfide. The corrosion rates and the percentage

efficiency are given in Table-2. From the experimental results, the corrosion efficiency of allyl methyl sulfide decreases with increase in temperature.

Temperature kinetic studies: Corrosion of mild steel in 1M H_3PO_4 increases with the raise of temperature. In the presence of adsorbing species (inhibitor) corrosion reaction become mere complicated because of; (a) The preferential adsorptions of inhibitors over the crowding surface and; (b) The tendency of the metal to enter into the complex formation with the inhibitors.

The effect of temperature on the acid corrosion of metal in the presence and in absence of organic inhibitor have been studied by a number of investigations[4-8] who have examined the kinetics of adsorption and corrosion rates on the basis of heat of adsorption. If it is assumed that the inhibitor form a mono layer at any instant a fraction θ of the metal surface in a uniform and random manner and that the uncovered fraction of the (1-θ) reacts with the acid in the absence of an inhibitor. The (1-θ) must equal to the ratio between the weight loss with inhibitor and weight loss without inhibitor and θ can be readily computed from the results within a certain range of inhibitor concentration and temperature, where mono layer adsorption is readily maintained. The isotherm may be written as:

$$θ/(1-θ) = Ac\ e^{-θ/RT}$$

where, A is the constant independent of temperature and dependent of the characteristic of the system; θ is the heat of adsorption.

The equation can be written to logarithmic form as follows:

$$\log θ/(1-θ) = \log A + \log (C-θ)/2.303\ RT$$

Heat of adsorption: A plot of log θ/(1-θ) against 1/T was a straight line and the results are shown in the Fig. 1. The slope of the straight line is equal to θ/2.303 RT from which the average heat of adsorption was calculated.

$$θ = -slope × 1.987 × 2.303\ cal/mol.$$

The low heat of adsorption values obtained indicates the adsorption process is only physical in nature.

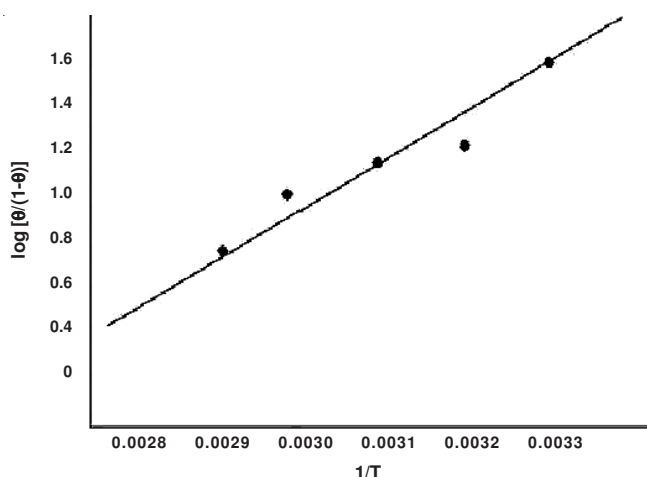Fig. 1. Adsorption isotherm

Free energy change:

$$\log C = \log θ/(1-θ)-\log B$$

where B = -1.74-(ΔG/2.303 RT) ΔG - 2.303 RT (log C - log [θ/(1-θ)] -1.74 J/mol.

The free energy changes for the solutions at room temperature and for 10^{-2} M concentration of solution at different temperature are shown in Table-4. The free energy values are different for various concentrations, which reveal the fact that there may not be any lateral interaction among the inhibitor molecules on the metal surface. It has been observed that as the concentration of the inhibitor decreases, the free energy change increases there by indicating that the corrosion process becomes more and easier with decrease in concentration of the inhibitor. As the temperature increases the free energy decreases[9-13], there by indicating that the corrosion process become more and easier with increase in temperature, which is shown in the Table-5.

Conclusion

(i) At room temperature, the inhibition efficiency increases as the concentrations of allyl methyl sulfide increases for the mild steel.

(ii) Corrosion rate is maximum for the uninhibited solution as compared to the inhibited solution at all temperatures.

(iii) Corrosion rate increases as the temperature increases.

(iv) For $1 × 10^{-2}$ M concentration, the percentage efficiency decreases as the temperature increases because of decreasing adsorption with increase in temperature.

(v) The low heat of adsorption values indicates the adsorption is only physical in nature.

(vi) The changes in free energy values differ for different concentrations indicating that there may not be any lateral interaction on the metal surface.

(vii) As the temperature increases, the free energy change values decreases. This show that increase in temperature favours the corrosion process.

(viii) As the concentration of the inhibitor decreases the free energy change increases. This shows that with decrease in concentration of allyl methyl sulfide the corrosion process becomes more and easier.

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