Inhibition of corrosion using benzofuran in aqueous medium of 0.5M H_2SO_4

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Abstract

The corrosion rates of mild steel crystal plane have been determined in stirred 0.5M H_2SO_4 solution containing various concentrations (0.5M to 5.0M) of Benzofuran by weight loss and polarization techniques. The corrosion rate which was controlled by surface reaction, was found to be a function of crystallographic orientation, temperature and benzofuran concentrations. The stability of the mild steel crystal orientation in pure acid was found. The observed corrosion data indicated inhibition by surface adsorption of inhibitor molecules, following the Langmuir adsorption isotherm. The weight loss and polarization technique gave similar inhibitor efficiency values. The stability of the mild steel crystal plane was further confirmed by a thermodynamic study of inhibitor molecule adsorption.

Key words : Benzofuran, polarization, inhibitor, Langmuir,0.5MH_2S0_4

1. Introduction

The study of corrosion of mild steel in $0.5MH_2SO_4$ is a subject of practical significance since the acid is highly corrosive and extensively used in various industrial operations [1] and [2]. Hence the use of corrosion inhibitors is essential in order to restrain the corrosion attack of acids on metallic materials[3]. Organic compounds containing nitrogen, sulphure and oxygen have been found to function as very effective corrosion inhibitors. Inhibitors are often used in this process mainly to control the metal loss by dissolution and also acid consumption [4,5] . The corrosion inhibition of mild steel by different organic compounds has been studied in considerable detail [6,7,8,9,10,11].The effectiveness of these compounds as corrosion inhibitors can be attributed to the number of mobile election pairs present, the π- electron character of free electron and the electron density around the nitrogen atoms[12,13,14]. In the present work, a benzofurans ($IH_1 - IH_3$) used as a inhibitor on the corrosion of mild steel in $0.5MH_2SO_4$. The effect of these organic compounds on the corrosion rate of mild steel has been studied by weight loss method, electrochemical impedance and polarization measurements.

2. Experimental.

The metal analysis in mild steel was carried out by preparing 1ppm solution in 1:1 hydrochloric acid Thermo Jarrrl AAS corporation make Smith- Heieftjee- 1000 was used for analysis (composition: Mn= 0.0326%, Fe=5.248%, Ni = 1.158%, Cu=0.917%, Zn= 0.243%, Pb = 0.1697%). Mild steel metal having a surface area of 0.985 cm^2 were fixed in a Tygon tubing exposing only the desired plane. The metal plane was mechanically polished on 4/0 emery paper using ethanol as lubricant and subsequently electropolished in orthophosphoric acid (1:1) for 30 minutes at a cell potential of 12V. The metal was taken out without switching off the current and washed with 10% phosphoric acid followed by distilled water. The metal was immediately transferred to the corrosion cell through the central neck, such

that the desired surface was just below the surface of the solution. The metal surface was

dipped in $0.5MH_2SO_4$ solution, stirred without and with various concentrations of benzofuran

inhibitor for desired interval of time (1 to 6 hrs).

2.2. Methods

Mild steel crystal plane was dissolved under stirred and unstirred conditions in

areated $0.5MH_2SO_4$ without and with various concentrations (0.5M to 5.0M) of benzofuran

at 30^0C. The dissolution rates ($mgcm^{-2}h^{-1}$) were calculated by estimating the amount of mild

steel surface dissolved in corrosive medium spectrophotometrically very significant

inhibitory effect of inhibitors on the dissolution rate of mild steel was seen. Decrease in the

corrosion rate of mild steel was found to be a function of crystallographic orientation and

concentration of inhibitors. Inhibitor efficiency (I.E.), corrosion rate and surface coverage

ϑ were calculated from the weight losses of the specimens in the absence and presence of

the inhibitor using the equations.

$$IE\% = \frac{[\text{Weight loss without inhibitor - weight loss with inhibitor}]}{\text{Weight loss without inhibitor}} x100$$

The corrosion rate was calculated by measuring the amount of mild steel dissolved in the

solution spectrophotometrically.

$$\text{Surfacecoverage} \ (\theta) \ = \ \frac{\text{Weightloss without inhibitor} \ - \ \text{weight loss withinhibitor}}{\text{weight loss without inhibitor}}$$

3. Results and discussion.

3.1.Weight loss measurements

The measured corrosion rates in stirred $1MH_2SO_4$ and in presence of the three organic

compounds (IH_1 to IH_3) at 30^0C are given in Table 1, from which it can be seen that the

concentrations between 0.5M to 5.0M was determined after 5 hrs of immersion. The values

of I.E., corrosion rate, surface coverage (θ) obtained from weight loss measurement.
Inhibition efficiency is seen to increase with increasing inhibitor concentration. A maximum
inhibitor ($1H_1 – IH_3$) efficiency of 96- 98% was observed at 5M.

It is evident from fig 1 shows the I.E. for different concentrations of inhibitors in
$1MH_2SO_4$. All the compounds inhibit the corrosion of mild steel even at a very low
concentrations (0.5M). Mild steel crystal plane was immersed for different periods in
$1MH_2SO_4$ containing 0.5M to 5.0M benzofuran at 30^0C. The weight loss varied linearly with
immersion period with and without inhibitor on the mild steel crystal plane Fig. 2. These
compounds are contain very high I.E. is understandable from the electron donating properties
of the different nitrogen atoms present in the molecules. From the molecular structure of the
inhibitors it is clear that an extensively delocalized orbit covers all the molecular atoms and
the orbit is filled up with a number of π- electrons, they being contributed by different
anchoring atoms of the molecule. It is apparent from the molecular structure that these
molecules are able to absorb on the metal surface through

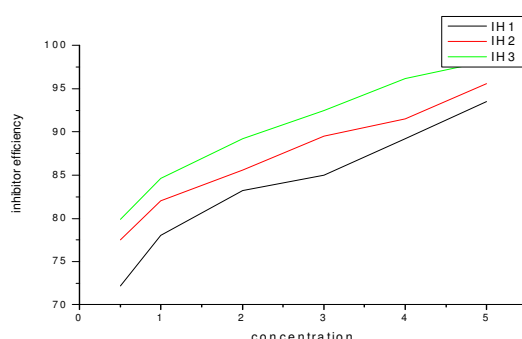nitrogen X-N groups and aromatic rings[15].

Fig. 1. Variation of inhibitor efficiency with concentration of inhibitor at 30 ^oC

Inhibitor	Concentration (M)	I.E. (%)	Corrosion rate $X10^3$ (mg m^{-2}h^{-1})	Surface coverage (θ)
IH1	0.5	72.2	25.10	0.782
	1.0	75.0	13.16	0.805
	2.0	80.5	20.00	0.861
	3.0	82.5	16.15	0.910
	4.0	88.6	13.50	0.948
	5.0	93.5	10.45	0.952
IH$_2$	0.5	77.5	23.85	0.795
	1.0	82.0	22.15	0.820
	2.0	85.6	18.26	0.856
	3.0	89.5	15.55	0.903
	4.0	91.5	13.21	0.950
	5.0	95.6	9.15	0.962
IH$_3$	0.5	79.9	19.15	0.835
	1.0	84.6	17.25	0.856
	2.0	89.2	13.31	0.905
	3.0	92.5	08.85	0.928
	4.0	96.2	04.31	0.982
	5.0	98.2	02.15	0.982

Table.1. Inhibition efficiencies at various concentration of inhibitors for corrosion of mild steel in 0.5MH_2SO_4 obtained by weight loss measurements at 303K

3.1.1. Adsorption Isotherm Process

The degree of surface coverage (θ) for different concentrations of the inhibitor was evaluated[16] from weight loss measurement (Table I). The data were tested graphically for fitting a suitable isotherm. The Langmuir isotherm was tested by plotting C/ θ versus C for all the compounds (Fig. 2). A straight line was obtained in all the compounds proving the fact that adsorption of these compounds adsorption on the mild steel surface obeys the Langmuir adsorption isotherm.
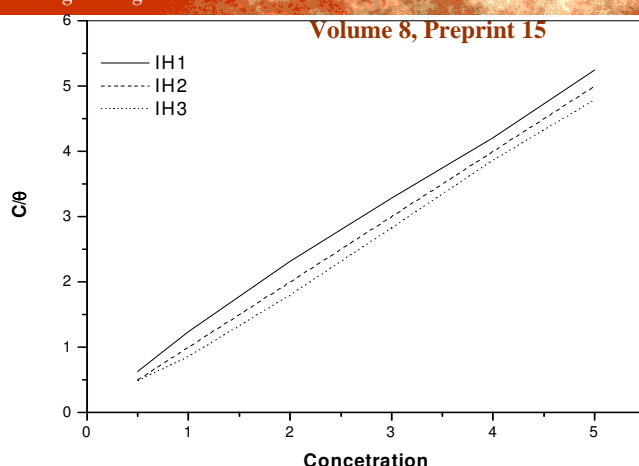
Fig. 2. Langmuir's plots for corrosion of mild steel in various concentrations of inhibitors

3.1.2. Effect of Temperature

To determine the effect of temperature on rate of corrosion, gravimetric measurements were carried out in the presence and absence of inhibitors at 303K and 318K in all the three organic compounds (IH$_1$ – IH$_3$) at 50M concentration. The corresponding results are green in Table II. The data in Table II clearly indicate an

increase in corrosion rate and decrease in I.E. with an increasing the temperature. The reduced IE on increasing temperature may be due to desorption of the inhibitor from the metal surface and thus exposing the fresh metal surface for attack by acids[17]. Values of Ea were calculated by plotting log corrosion rate versus 1000/T (Fig. 3)

$$E_a = \text{slope x } 8.314 \text{ x } 2.303 \text{ kJ}$$

Values of the free energy of adsorption (ΔG^0_{ads}) at various temperatures were calculated using the following equation.

$$\Delta G^0_{ads} = - RT \ln (55.5K)$$

Where K=θ/C (1-θ), θ = degree of coverage on the metal surface, and C= concentration of the inhibitor in M. Values of Ea and ΔG^0_{ads} are given in table III. The where K=θ/C (1-θ), θ = degree of coverage on the metal surface, and C= concentration of the

inhibitor in M. Values of Ea and ΔG^0_{ads} are given in table III. The less negative values of ΔG^0_{ads} with increase in temperature indicates physical adsorption of the benzofurans on the metal surface. The increase in Ea values for the inhibited solution in comparison to uninhibited solution may be due to the presence of reactive centers on the inhibitors that can block the active sites for corrosion[18].
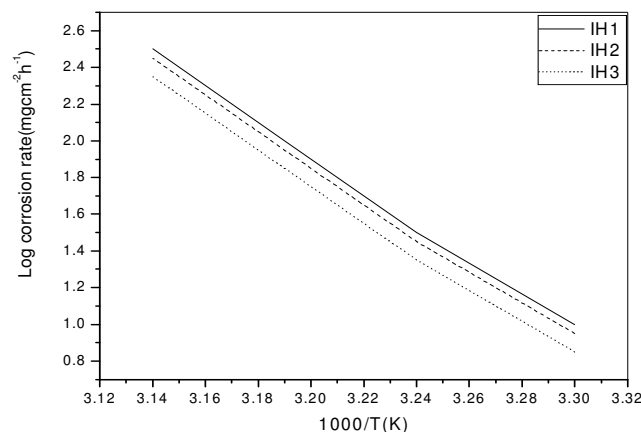

Fig. 3. Arrhenius Plotes of corrosion rate verses 1000/T for mild steel in $0.5MH_2SO_4$ solution in presence of inhibitors

Inhibitor	Temperature (K)	I.E (%)	Corrosion rate ($mgcm^{-2}h^{-1}$)
IH_1	303	95.2	10.45
	308	91.2	26.16
	313	87.5	92.21
	318	83.1	135.05
IH_2	303	96.2	9.15
	308	92.5	21.01
	313	88.2	65.00
	318	85.6	126.50
IH_3	303	98.2	02.15
	308	94.8	18.25
	313	92.5	61.20
	318	88.9	118.15

Table. 2.Inhibition efficiencies of the inhibitors at 5M concentration for the corrosion of mild steel in $0.5MH_2SO_2$ obtained by weight loss measurements.

Inhibitor	E_a (KJ)	ΔG^0_{ads} at various Temperature (KJ)			
		303K	308K	313K	318K
Blank	3.982	-	-	-	-
IH_1	33.25	-16.25	-14.45	-13.69	-11.12
IH_2	61.05	-15.62	-12.52	-11.72	-10.01
IH_3	94.60	-19.5	-15.55	-14.15	-12-72

Table. 3. Values of E_a and ΔG^0_{ads} for the corrosion of mild steel in $0.5MH_2SO_4$ containing 5M concentration of inhibitors.

3.2. Polarization Measurements

The cathodic and anodic polarization of mild steel surface was carried out Galvan statically in stirred $1MH_2SO_4$, and in the presence and absence of different concentrations of IH_1, between 0.5 and 15mA cm^{-2} at 30^0C is shown in fig. 4. Similar polarization studies were made for other inhibitors. Electrochemical parameters such as corrosion current density (i_{corr}) and corrosion potential (E_{corr}) calculated from Tafel plots are given in Table IV. The inhibitor efficiencies were also calculated from the polarization data by using the equation

$$\%P = \frac{i - i^*}{i}\ x100$$

Where i and i* are the corrosion currents in the absence and presence of the inhibitor. At any given concentration on the mild steel surface, the % P values from weight loss data are in good agreement with the values obtained from polarization studies.

Inhibitor	Inhibitor concentration cone (M)	Tafel scope ($\pm$ 5 mV decad^{-1}) anodic		Icorr (mA cm^{-2})	Inhibition Efficiency (%)
		Anodic	Catholic		
Blank	-	65.15	116.20	0.25	-
IH$_1$	0.5	46.85	105.06	0.12	83.5
	2.5	42.12	86.28	0.10	89.2
	5.0	51.50	109.15	0.11	96.0
IH$_2$	0.5	48.10	106.15	0.14	85.6
	2.5	41.56	92.86	0.10	91.1
	5.0	53.75	110.10	0.12	98.5
IH$_3$	0.5	50.68	108.15	0.14	84.5
	2.5	45.25	95.50	0.11	93.2
	5.0	52.00	111.85	0.13	98.9

Table. 4. Variation of percentage inhibitor efficiency (%P), corrosion current density [I$_{corr}$] and anodic and cathodic Tafel slope in stirred 0.5M H$_2$SO$_4$ containing different concentration of benzofuran at 30^{0}C.
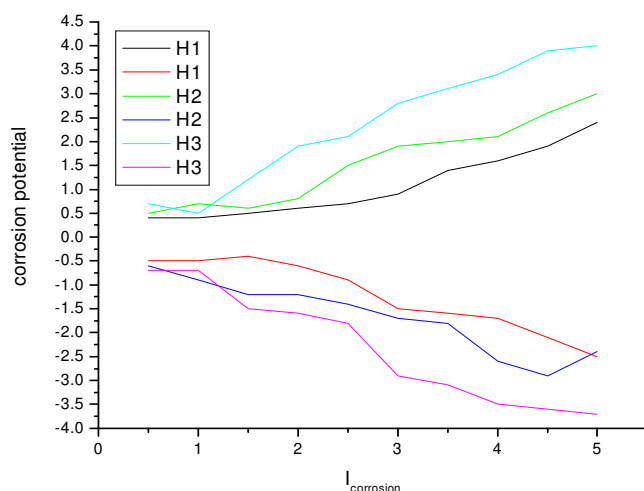

Fig. 4. Corrosion current density verses corrosion potential and anodic and cathodic Tafel slope in stirred 0.5M H$_2$SO$_4$ at 30 ^{0}C

4. Conclusions

The inhibitor efficiency of mild steel dissolution by the tested inhibitors follows by the order $IH_3 > IH_2 > IH_1$.T the higher inhibition efficiency of the inhibitors is due to the presence of electron releasing substitution groups. The inhibition efficiency increases with increase in inhibitor concentration, immersion time.

Benzofurans showed a maximum I.E. of 96-99%. The increase in cathodic Tafel scopes revealers that the inhibitors are controlling the cathodic reaction. The less negative values of ΔG^0_{ads} with increase in temparature indicate the physical adsorption of the inhibitors on the metal surface. The adsorption of the benzofarns on the metal surface obeys the Langmuir adsorption isotherm.

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