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Inhibiting effect of Tetra-n-butylammonium iodide on the corrosion of mild steel in acidic medium

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Abstract

The inhibition effect of tetra-N-butylammonium iodide (TBAI) on mild steel in 1N H_2SO_4 has been studied by using weight loss, electrochemical polarization, Fourier Transform Infrared (FTIR) and scanning electron microscopic (SEM) techniques. It has been concluded that percentage inhibition increases with increase in concentration of inhibition. The adsorption of TBAI on mild steel surface in 1N H_2SO_4 obeys Langumir adsorption isotherm, surface analysis and IR studies are also carried out to establish the mechanism of corrosion inhibition.

Keywords: Corrosion, mild steel, H_2SO_4, tetra-N-butylammonium iodide (TBAI)

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Introduction

Corrosion is destructive attack of metal by its environment. Inhibitors are generally used to protect materials against deterioration from corrosion. Many organic compounds containing oxygen, nitrogen and sulphur have been used as corrosion inhibitor for metal [1-10]. Amines are effective inhibitors for steel corrosion in acidic solution [11-13]. The present paper deals with the study of inhibiting action of TBAI on mild steel in acidic solution. The electrochemical behavior of mild steel in H_2SO_4 media in absence and presence of inhibitor has been studied by galvanostatic polarization, IR and SEM method.

Experimental

The mild steel coupons of composition(C=0.10-0.20%, Mn=0.40-0.50%, Si=0.05%, S=0.025-0.030%, P=0.30-0.80% and rest is Fe) and of size (i.e. 0.8×0.8×3.0 cms) have been used for weight loss measurements. These coupons are given mechanical polishing and then degreased before use. The inhibition efficiency for different concentrations of inhibitor is calculated from weight loss values.

For polarization studies a cylindrical mild steel rod of it composition embedded ion araldite is used. The electrodes are polished with emery papers and degreased. AR grade of H_2SO_4 acid is used for preparing solutions. Double distilled water is used to prepare all solutions. For accurate measurements of potential and current densities, galvanostatic polarization studies were carried out at different temperatures. A platinum foil and saturated calomel electrode are used as counter and reference electrode respectively. Polarization was carried out in H_2SO_4 in the absence and presence of inhibitor of various concentrations and temperatures.

The Fourier Transform Infrared Spectroscopic analysis (FTIR) Spectra of pure inhibitor as well as spectra of inhibitors adsorbed on silica gel are recorded by using Perkin Elmer Infrared Spectroscope IR 137. The pure saturated solutions of additive is prepared in solvent i.e. benzene in which the compound is soluble. Now silica gel, which is dried in oven to remove the moisture, is added in the additive. The dried solid pallet of the additive mixed in silica gel are used to record the FTIR spectra.

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To know the surface morphology of mild steel scanning electron microscopy technique using LEO 435 V.P. Scanning Electron Microscope is used. The polished specimens, which is used in this experiment are examined to find out any surface defects by optical microscope. Those specimens are taken which have smooth surface. After this the specimen are washed with double distilled water and dried in desiccators. These specimens are dipped in the solutions of 10^{-1}M and 10^{-7}M concentration for the inhibitor in 1N sulphuric acid for 24 hours at room temperature. These specimens are then washed with distilled water and dried in a desiccator. The SEM photographs are recorded of these corroded specimens as well as with out corrode mild steel specimen.

Result and Discussion

Weight loss Measurement

The corrosion inhibition efficiency of TBAI for corrosion of mild steel is calculated as follows

$$\%\,Efficiency = \frac{w_0 - w}{w_0} \times 100$$

where w_0 and w are the values of corrosion weight loss of steel without and with inhibitor respectively. Table I gives the value of inhibition efficiencies obtained from weight loss study for various concentrations and temperatures. It has been observed that the inhibition efficiencies slightly change as the temperature increases from 298 K to 328 K for 10^{-1}M concentration. The change in inhibition efficiencies are quite less for all concentrations viz. 10^{-1}M, 10^{-3}M, 10^{-5}M and 10^{-7}M at temperature 298 K. While changes in inhibition efficiencies are more as the temperature increases from 308 K to 328 K for all concentrations.

Polarization Measurement

Figures I to IV show the anodic and cathodic polarization curves(Tafel's plot) of mild steel in 1N H2SO4 solution with and without the addition of various concentration of TBAI at different temperatures i.e. 298 K, 308 K, 318 K and 328 K. The various electrochemical parameters corrosion current density (I_{corr}), corrosion potential E_{corr}, Tafel's value b_a and b_c for different concentrations are given in Table II. The corrosion current densities are calculated by extra plotting the tangents of anodic and

cathodic curves and their intersection with corrosion potential. These curves explain the corrosion current densities decreases with increase in concentration of inhibitor. The percentage inhibition of each inhibitor at various concentrations in 1N H_2SO_4 is shown in Table II after being calculated from the expression

$$\% \text{ Inhibition} = \frac{I_{(corr)\ uninh} - I_{(corr)\ inh} \times 100}{I_{(corr)\ uninh}}$$

The percentage inhibition of TBAI on mild steel in 1N H_2SO_4 shows that corrosion inhibition efficiency reaches about 95.2% with solution containing 10^{-1}M inhibitor concentration where as at low concentration (10^{-7}M) the percentage inhibition is about 87.41% at 298 K. While at 328K the corrosion inhibition efficiency reaches 94.8% with solution containing 10^{-1}M inhibitor. On the other hand the percentage inhibition efficiency is about 33.93% containing solution 10^{-7}M concentration. This effect could be attributed to the fact that inhibition increases due to large alkyl chain group, which cause enough coverage on the metal surface. In this way small area of electrode surface is left uncovered, which produces less corrosion on mild steel. The trend in the values of b_c and b_a suggest here that many inhibitor processes are participated in corrosion inhibition.

From the experimental method, it is concluded that inhibitor effect is anodic at temperature 298K rather than cathodic except 10^{-1}M. At higher temperature the inhibitor TBAI is anodic type.

Adsorption Kinetics

With high concentration of inhibitor a protective inhibitor layer formed on the mild steel surface which reduces the chemical attack of metal. The surface coverage θ values have been obtained from electrochemical measurements for various concentrations. There are many adsorption isotherms to study the adsorption process. Here Langumir adsorption isotherm is tested. Figure V shows the plot of log θ/1- θ v. log C graph, a straight line with approximately unit slope. The value of heat of adsorption can be calculated from the formula

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$$\log \frac{\theta}{1-\theta} = \log A + \log C - \frac{Q_{ads}}{2.3RT}$$

where A is Arrhenius constant, C is inhibitor concentration and Q is heat of adsorption.

The value of heat of adsorption for TBAI is 4.50 Kcal/mol.

To calculate the activation energy, the current densities are plotted against temperature in absence and presence of inhibitor (Fig. VI). The value of activation energy can be find out by Arrhenius equation.

$$\frac{\partial \log I_{corr}}{\partial \mathrm{T}} = \frac{\mathrm{E}_a}{RT^2}$$

where E_a is the activation energy. The value of activation energy of TBAI is 64.31 Kcal/mol.

FTIR Study of Inhibitor

To find out the types of bonding for organic molecule adsorbed on the surface of solid, FTIR study has been conducted. Silica gel has been chosen because of large surface area of adsorption of organic molecule and yields a spectrum of moderate intensity. The various peaks in spectra of pure and silica gel adsorbed additives are shown in Fig. VII and VIII and there vibrational modes are reported in Table III. The spectra of TBAI indicate the disappearance of N-C, N-H, -CH_2- and N-H_{wagg} and merging of two peaks for C-H_{str} bond into single peak. From the above observation it can be concluded that adsorption of this inhibitor over solid surface takes place through N-C bond, N-H bond and N-H_{wagg}.

Scanning Electron Microscopic Study

To study the surface morphology of mild steel coupons SEM technique has been used. Figure IX, X, XI and XII show the surface morphology of plain mild steel, in 1N H_2SO_4 and corroded surfaces after dipped in TBAI inhibitor at 10^{-7}M and 10^{-1}M. The micrograph obtained from different concentrations show that the surfaces are inhibited due to formation of insoluble stable film of mild steel surface. It proves that additive act as good inhibitor at higher concentration 10^{-1}M.

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Caption of Figures

Fig.I. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 298K.

Fig.II. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 308K.

Fig.III.Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 318K.

Fig.IV.Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 328K.

Fig.V. Variation of surface coverage vs. concentration at different temperatures of TBAI.

Fig. VI. Inhibition efficiency vs. concentration of TBAI at different temperatures

Fig. VII. FTIR Spectrum of Pure TBAI

Fig. VIII. FTIR Spectrum of TBAI adsorbed on Silica gel

Fig.IX. Scanning Electron Micrograph of plain Mild Steel at 2000 magnification

Fig.X. Scanning Electron Micrograph of Mild Steel in 1N H_2SO_4 at 2000 magnification.

Fig.XI. Scanning Electron Micrograph of Mild Steel in presence of 10^{-7} M TBAI in 1N H_2SO_4 at 2000 magnification.

Fig. XII. Scanning Electron Micrograph of Mild Steel in presence of 10^{-1} M TBAI in 1N H_2SO_4 at 2000 magnification.

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Table I

Inhibition Efficiency of tetra-N-butylammonium iodide (TBAI)

Temperature	Solution/mol (L^{-1})	Weight loss/gram	%I
298K	1N H_2SO_4	0.0786	-
	10^{-7}	0.0099	87.40
	10^{-5}	0.0073	90.71
	10^{-3}	0.0041	94.78
	10^{-1}	0.0035	95.54
308K	1N H_2SO_4	0.1568	-
	10^{-7}	0.0715	54.40
	10^{-5}	0.0598	61.86
	10^{-3}	0.0179	88.58
	10^{-1}	0.0071	95.47
318K	1N H_2SO_4	0.5468	-
	10^{-7}	0.3454	36.83
	10^{-5}	0.2374	56.58
	10^{-3}	0.1675	69.36
	10^{-1}	0.0260	95.24
328K	1N H_2SO_4	1.1891	-
	10^{-7}	0.8028	32.48
	10^{-5}	0.6849	42.40
	10^{-3}	0.2349	80.24
	10^{-1}	0.0683	94.25

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Table II

Corrosion Parameters of Mild Steel in 1N HNO_3 in presence of tetra-N-butylammonium iodide (TBAI)as additive:

Temp.	Solution/mol (L^{-1})	E_{corr} mV	Log i_{corr} $\mu A/cm^2$	b_c mV/dec	b_a mV/dec	%I
298K	0	512	3.45	99	141	-
	10^{-7}	482	2.55	91	161	87.41
	10^{-5}	463	2.43	81	179	90.45
	10^{-3}	485	2.20	100	168	94.30
	10^{-1}	541	2.13	241	349	95.20
308K	0	522	3.38	111	151	-
	10^{-7}	482	3.05	91	133	53.22
	10^{-5}	453	2.95	78	248	62.84
	10^{-3}	495	2.48	85	100	87.40
	10^{-1}	525	1.99	163	457	95.50
318K	0	500	3.35	75	73	-
	10^{-7}	485	3.15	40	98	36.90
	10^{-5}	455	2.99	93	204	56.34
	10^{-3}	482	2.83	81	159	80.80
	10^{-1}	480	2.03	168	432	95.21
328K	0	480	3.29	41	93	-
	10^{-7}	482	3.11	81	91	33.93
	10^{-5}	462	3.05	76	173	42.45
	10^{-3}	462	2.60	43	120	79.58
	10^{-1}	440	2.00	117	432	94.87

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Table III
Fourier Transform infrared bands pure and adsorbed tetra-N-butylammonium iodide (TBAI) inhibitor

TBAI	$TBAI^{ads}$	Peak
2987.1	2987.4	C-H
1472.5	1472.7	C-C
990.4	-	C-O
1257.0	-	N-C
1655.4	1620.0	N-H

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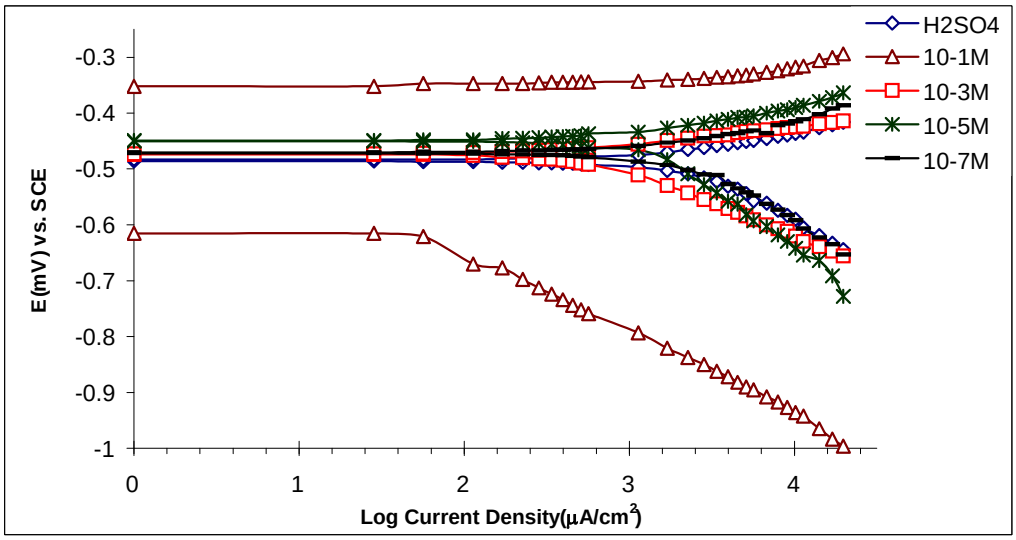

Fig. I. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 298K.

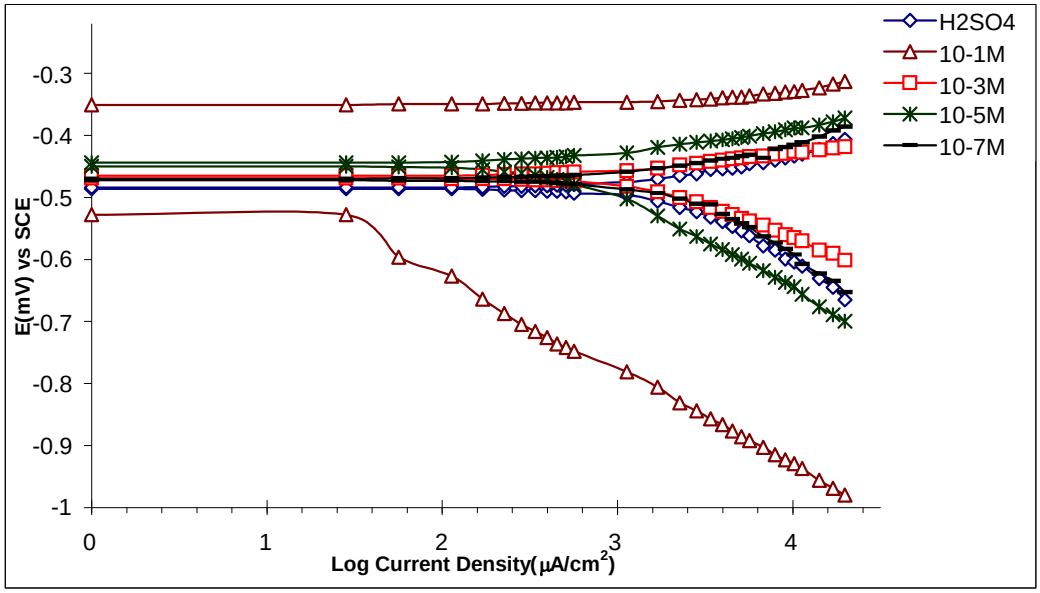

Fig. II. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 308K.

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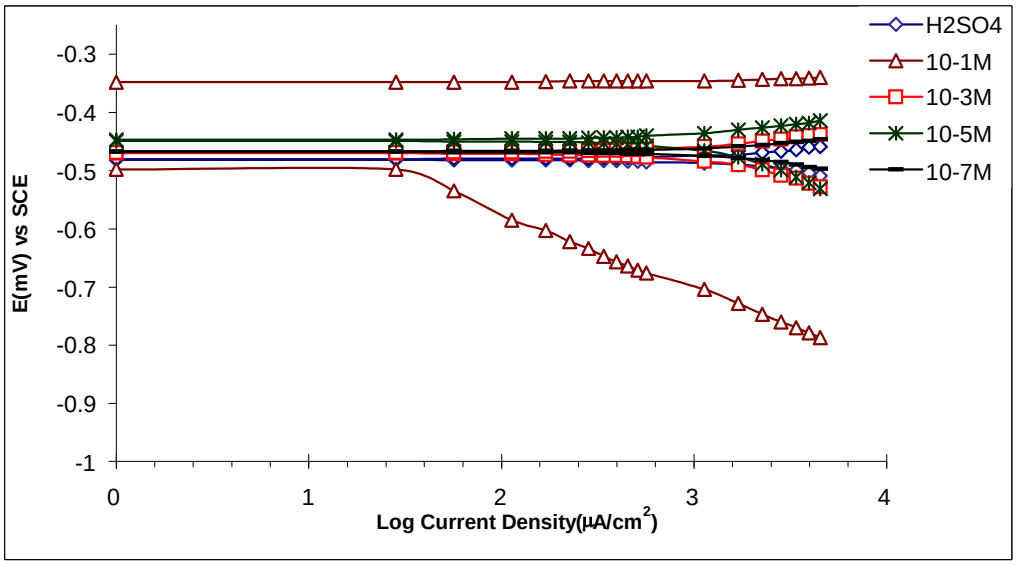

Fig. III. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 318K.

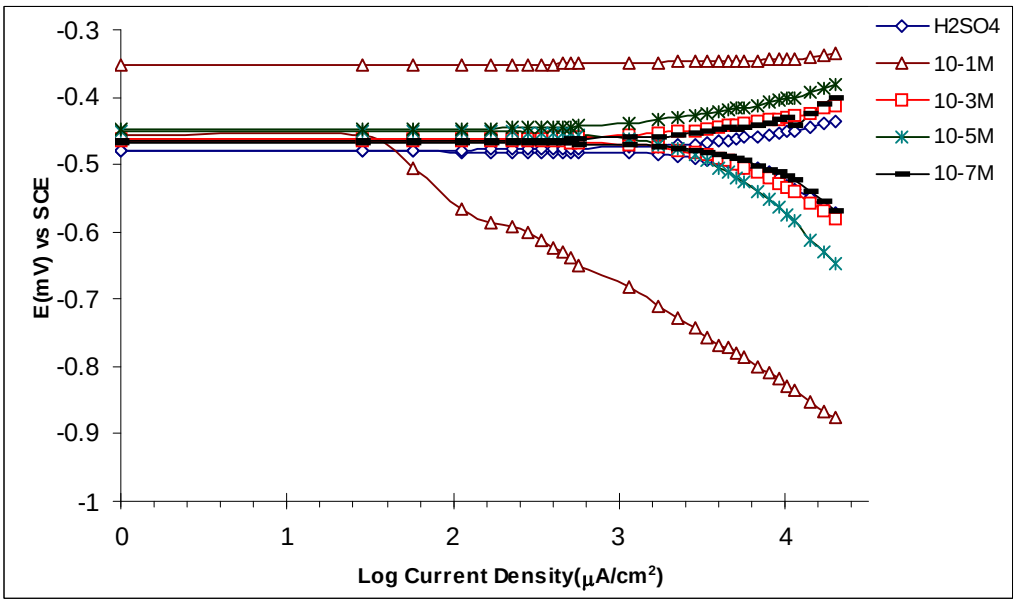

Fig. IV. Galvanostatic Polarization Curves of Mild Steel in 1N H_2SO_4 solution in presence of different concentrations of TBAI at 328K.

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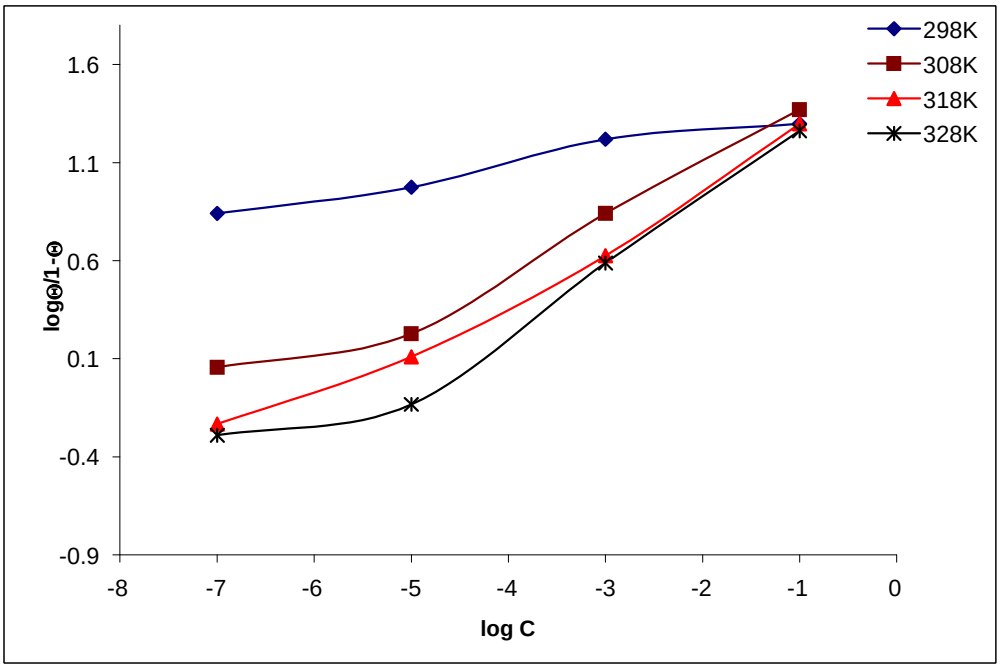

Fig. V. Variation of surface coverage vs. concentration at different temperature of TBAI.

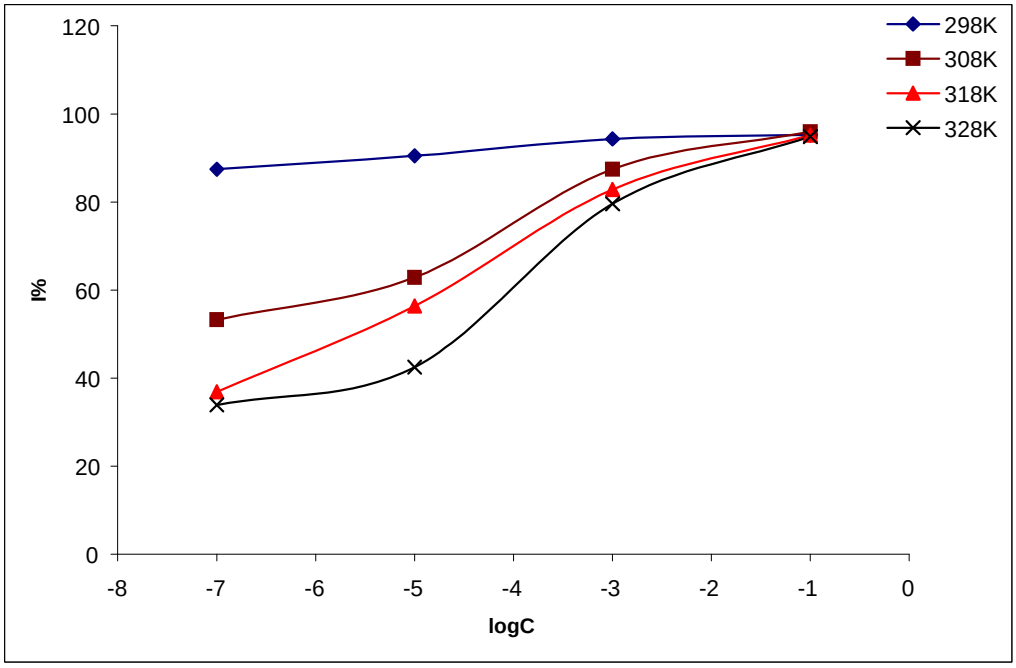

Fig. VI. Inhibition efficiency vs. concentration of TBAI at different temperatures

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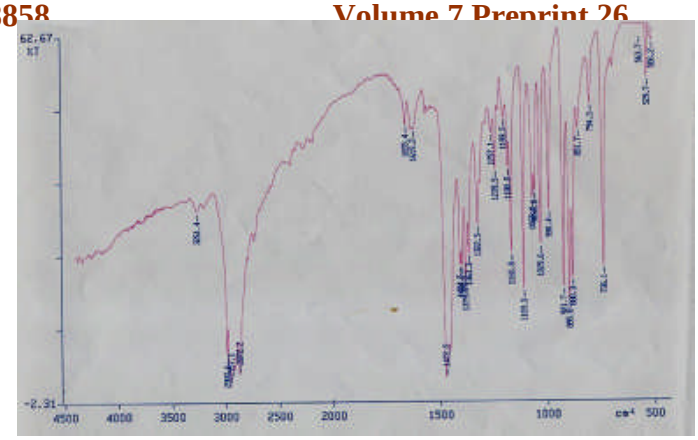

Fig. VII. FTIR Spectrum of Pure TBAI.

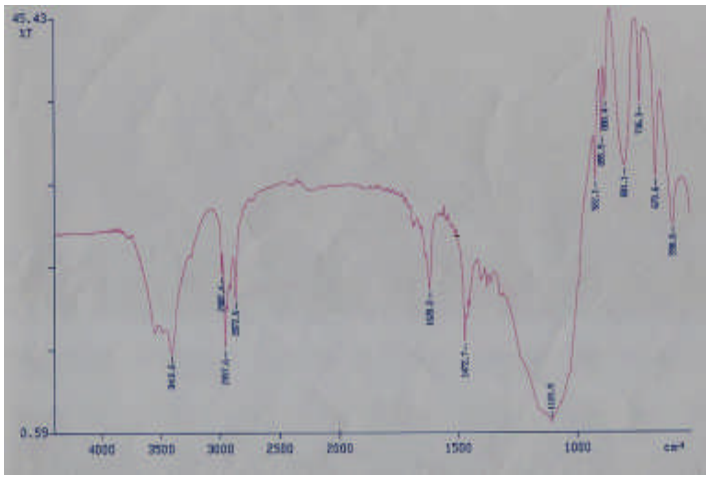

Fig. VIII. FTIR Spectrum of TBAI adsorbed on Silica gel

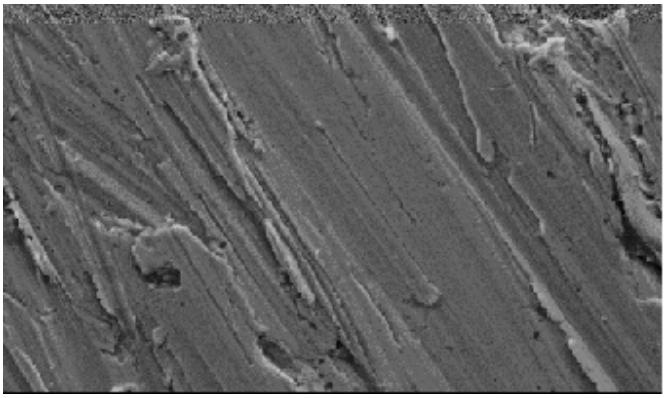

Fig. IX. Scanning Electron Micrograph of plain Mild Steel at 2000 magnification

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Fig. X. Scanning Electron Micrograph of Mild Steel in 1N H_2SO_4 at 2000 magnification

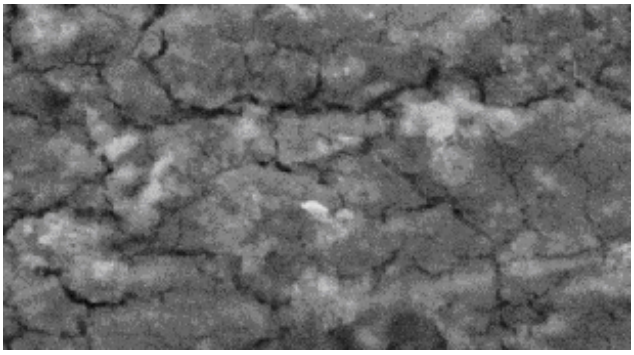

Fig.XI. Scanning Electron Micrograph of Mild Steel in presence of 10^{-7} M TBAI in 1N H_2SO_4 at 2000 magnification.

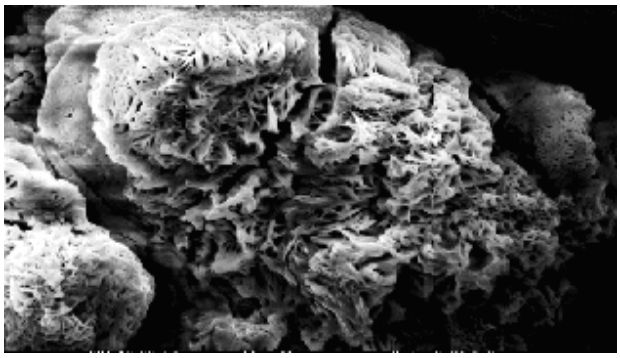

Fig. XII. Scanning Electron Micrograph of Mild Steel in presence of 10^{-1} M TBAI in 1N H_2SO_4 at 2000 magnification.