

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 1 N H₂SO₄ has been studied by using weight loss, electrochemical polarization, Fourier Transform Infrared (FTIR) and scanning electron microscopic (SEM) techniques. It has been concluded that the percentage inhibition increases with increasing the concentration of the inhibitor. The adsorption of TBAI on mild steel surface in 1 N H₂SO₄ obeys Langmuir adsorption isotherm; surface analysis and IR studies are also carried out to establish the mechanism of corrosion inhibition.

Keywords: corrosion, mild steel, H₂SO₄, tetra-N-butylammonium iodide (TBAI).

Introduction

Corrosion is a 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 inhibitors 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 H₂SO₄ media in absence and presence of the 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 the rest being Fe) and of size (i.e., 0.8×0.8×3.0 cm) have been used for weight loss measurements. These coupons have been given mechanical polishing and then degreased before use.

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The inhibition efficiency for different concentrations of the inhibitor is calculated from weight loss values.

The electrodes are polished with emery papers and degreased. AR grade of H₂SO₄ is used for preparing solutions, as well as double distilled water. 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 electrodes, respectively. Polarization was carried out in H₂SO₄ in the absence and presence of the inhibitor at 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 a Perkin Elmer Infrared Spectroscope IR 137. The pure saturated solutions of additive are prepared in solvent, i.e., benzene, in which the compound is soluble. Now silica gel, which is dried in an oven to remove the moisture, is added in the additive. The dried solid pallet of the additive mixed in silica gel is used to record the FTIR spectra.

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

Results 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 1 gives the values 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 is quite less for all concentrations viz. 10⁻¹ M, 10⁻³ M, 10⁻⁵ M and 10⁻⁷ M at 298 K, while changes in inhibition efficiencies are stronger as the temperature increases from 308 K to 328 K for all concentrations.

Table 1. Inhibition efficiency of tetra-N-butylammonium iodide (TBAI).

Temperature	Solution/mol (L ⁻¹)	Weight loss/gram	%I
298 K	1 N H ₂ SO 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
308 K	1 N H ₂ SO 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
318 K	1 N H ₂ SO 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
328 K	1 N H ₂ SO 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

Polarization measurement

Fig. 1 to 4 show the anodic and cathodic polarization curves (Tafel's plot) of mild steel in 1 N 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. Various electrochemical parameters are given in Table 2: corrosion current density (I_{corr}), corrosion potential E_{corr} , Tafel's values b_a and b_c for different concentrations. The corrosion current densities are calculated by intersection method, i.e., by extra plotting the tangents of anodic and cathodic curves and their intersection with corrosion potential. These curves explain the corrosion current densities decrease with increasing the concentration of the inhibitor. The percentage inhibition of each inhibitor at various concentrations in 1 N H₂SO₄ is shown in Table 2 after being calculated from the expression

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

The percentage inhibition of TBAI on mild steel in 1 N H₂SO₄ shows that the corrosion inhibition efficiency reaches about 95.2% with solution containing 10⁻¹ M inhibitor concentration, whereas at low concentration (10⁻⁷ M) the percentage inhibition is about 87.41% at 298 K, while at 328 K 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 the inhibition increases due to large alkyl chain group, which causes enough coverage on the

metal surface. 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 suggests here that many inhibitor processes are participating in corrosion inhibition.

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

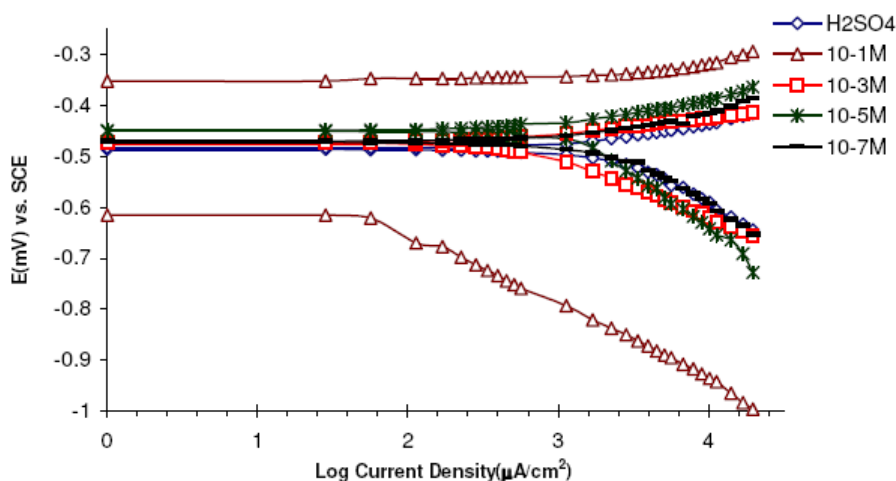


Figure 1. Galvanostatic polarization curves of mild steel in 1 N H_2SO_4 solution in the presence of different concentrations of TBAI at 298 K.

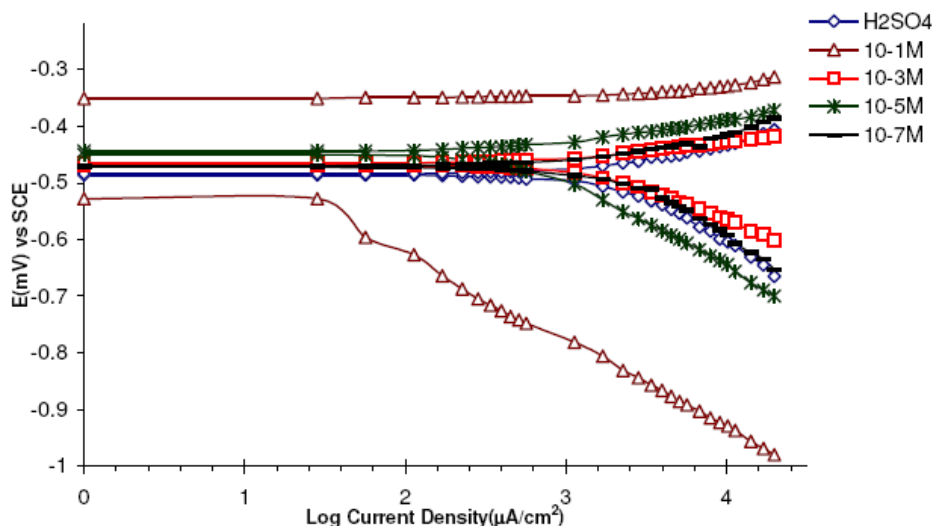


Figure 2. Galvanostatic polarization curves of mild steel in 1 N H_2SO_4 solution in the presence of different concentrations of TBAI at 308 K.

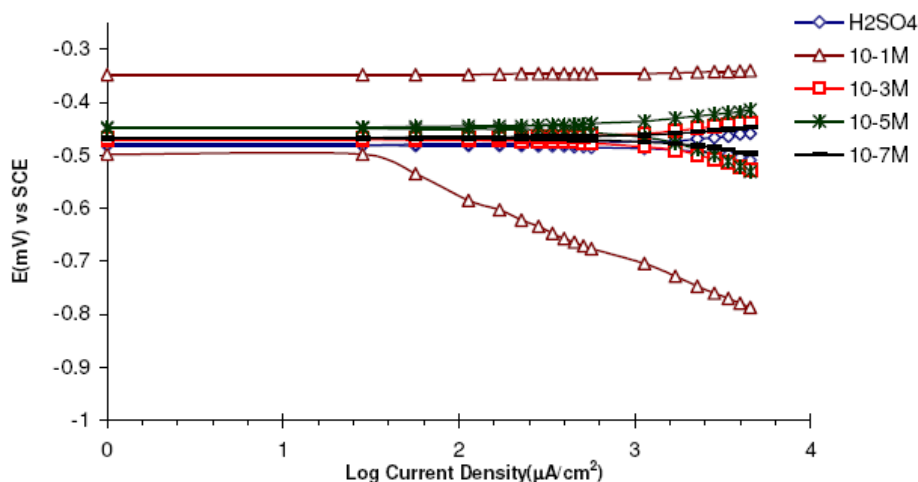


Figure 3. Galvanostatic polarization curves of mild steel in 1 N H₂SO₄ solution in the presence of different concentrations of TBAI at 318 K.

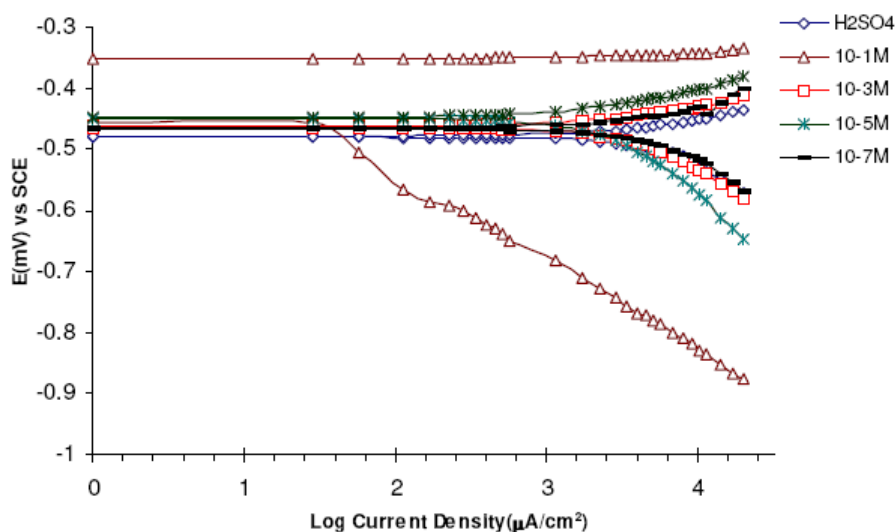


Figure 4. Galvanostatic polarization curves of mild steel in 1 N H₂SO₄ solution in the presence of different concentrations of TBAI at 328 K.

Adsorption kinetics

With high concentration of the 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 Langmuir adsorption isotherm is tested. Fig. 5 shows the plot of $\log \frac{\theta}{1-\theta}$ vs. $\log C$ graph, a straight line with approximately unit slope. The value of heat of adsorption can be calculated from the formula

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

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

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

Table 2. Corrosion parameters of mild steel in 1 N HNO₃ in the presence of tetra-N-butylammonium iodide (TBAI) as additive.

Temp.	Solution/mol (L ⁻¹)	E _{corr} mV	Log i _{corr} μA/cm ²	b _c mV/dec	b _a mV/dec	%I
298 K	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
308 K	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
318 K	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
328 K	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

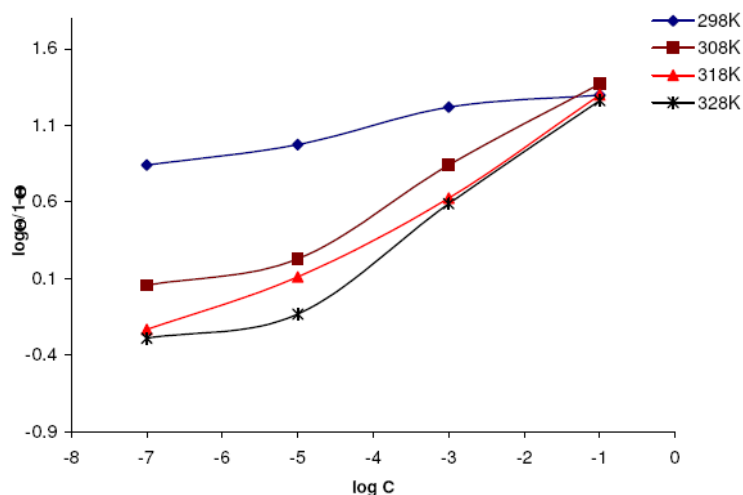


Figure 5. Variation of the surface coverage vs. concentration at different temperatures of TBAI.

To calculate the activation energy, the current densities are plotted against temperature in absence and presence of the inhibitor (Fig. 6). The value of activation energy can be found out by Arrhenius equation

$$\frac{\partial \log I_{corr}}{\partial T} = \frac{E_a}{RT^2}$$

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

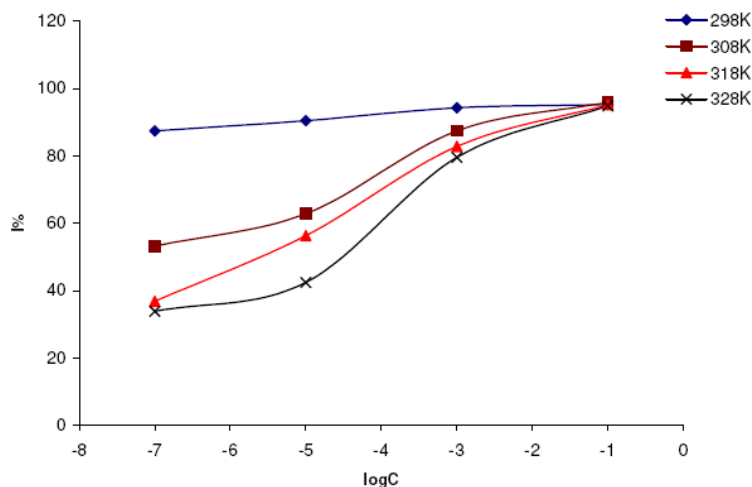


Figure 6. Inhibition efficiency vs. concentration of TBAI at different temperatures.

FTIR study of the inhibitor

To find out the types of bonding for organic molecules adsorbed on the surface of the solid, FTIR study has been conducted. Silica gel has been chosen because of large surface area of adsorption of organic molecules and yields a spectrum of moderate intensity. The various peaks in spectra of pure and silica gel adsorbed additives are shown in Fig. 7 and 8 and their vibrational modes are reported in Table 3. The spectra of TBAI indicate the disappearance of N-C, N-H, -CH₂- and N-H_{wagg} and merging of two peaks for C-H_{str} bond into a single peak. From the above observation it can be concluded that the adsorption of this inhibitor over solid surface takes place through N-C bond, N-H bond and N-H_{wagg}.

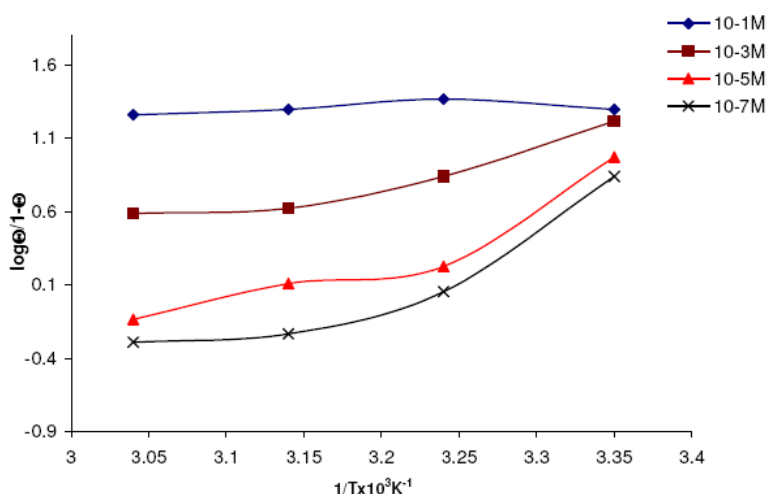


Figure 7. Variation of surface coverage vs. reciprocal of temperature at different concentrations of TBAI.

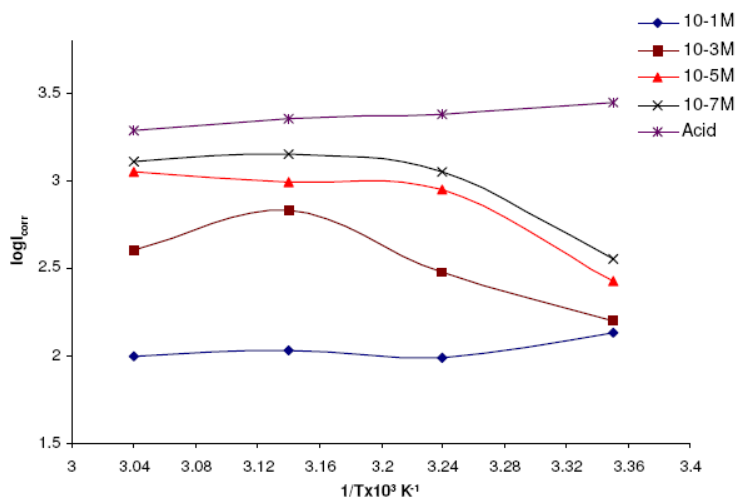


Figure 8. Variation of corrosion current vs. reciprocal of temperature at different concentrations of TBAI.

Table 3. Fourier transform infrared bands of 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

Scanning electron microscopic study

To study the surface morphology of mild steel coupons, SEM technique has been used. Fig. 9, 10, 11 and 12 show the surface morphology of plain mild steel, in 1 N H₂SO₄ and corroded surfaces after dipped in TBAI inhibitor at 10⁻⁷ M and 10⁻¹ M. The micrographs obtained from different concentrations show that the surfaces are inhibited due to the formation of insoluble stable film of mild steel surface. It proves that the additive acts as good inhibitor at higher concentration 10⁻¹ M.

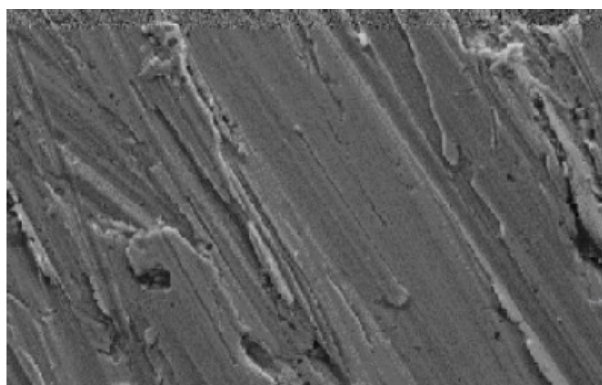


Figure 9. Scanning electron micrograph of plain mild steel at 2000 magnification.



Figure 10. Scanning electron micrograph of mild steel in 1 N H₂SO₄ at 2000 magnification.

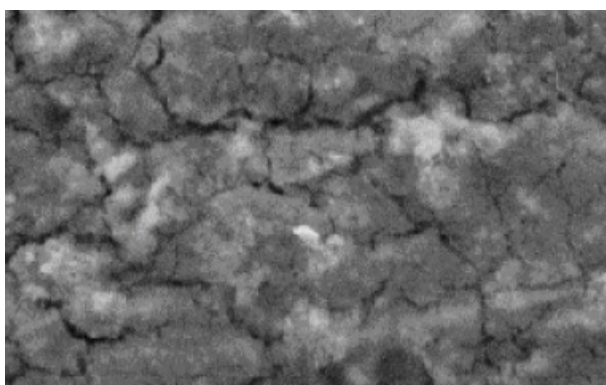


Figure 11. Scanning electron micrograph of mild steel in the presence of 10⁻⁷ M TBAI in 1 N H₂SO₄ at 2000 magnification.

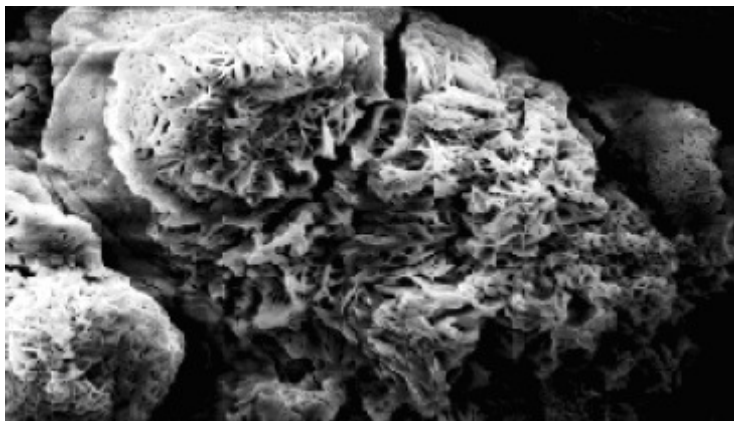


Figure 12. Scanning electron micrograph of mild steel in the presence of 10⁻¹ M TBAI in 1 N H₂SO₄ at 2000 magnification.

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