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Inhibiting effect of cytisine derivative on the corrosion of mild steel in acidic medium

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ABSTRACT

The inhibition effect of Cytisine derivative namely [N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] on mild steel in 1M H_2SO_4 has been studied by using weight loss, electrochemical polarization and scanning electron microscopic (SEM) techniques. It has been concluded that percentage inhibition increases with increase in concentration of inhibitor. The adsorption of [N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] on mild steel surface in 1M H_2SO_4 obeys Langumir adsorption isotherm, surface analysis studies are carried out to establish the mechanism of corrosion inhibition. The polarization data indicate that this compound act as very good cathodic inhibitors for mild steel in 1M H_2SO_4 and its inhibition efficiency increases with concentration and the highest value obtained is around 92%.

Key words: Corrosion, Inhibition, mild steel, H_2SO_4, [N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine].

INTRODUCTION

Corrosion is destructive attack of metal by its environment. One of the methods used to reduce the rate of metals corrosion is the addition of inhibitors. Many metals and alloys which used in different human activities are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media. Many studies have been carried out to find suitable compounds to be used as corrosion inhibitors for different metals and alloys in different aqueous solution. These studies reported that there are a number of organic and inorganic compounds which can do that for the corrosion of mild steel[1-3]. Many organic compounds containing oxygen, nitrogen and sulphur have been used as corrosion inhibitor for metal[4-10]. Amines are effective inhibitors for steel corrosion in acidic solution[11-14]. The present paper deals with the study of inhibiting action of [N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] on mild steel in acidic media. The electrochemical behavior of mild steel in H_2SO_4 media in absence and presence of different concentration of inhibitor has been studied by galvanostatic polarization and SEM method.

EXPERIMENTAL

Specimens

The mild steel coupons of composition(C=0.16%, Mn=0.035%, Si=0.05%, S=0.025%, P=0.25% and balance Fe) and have been used for weight loss measurements. These coupons were mechanically polished with emery papers of 1/0 , 2/0 ,3/0 and 4/0 grade and degreased with acetone before use.

Electrolyte

The aggressive solutions used were made of AR grade of H_2SO_4 acids. Appropriate concentrations of acid were prepared using double distilled water. The concentration range of inhibitor employed was 100 ppm to 1000 ppm in acidic solutions.

Weight loss studies

The mild steel strips of size i.e. (1cm × 1cm ×3 cm) were used for weight loss measurement studies. All the weight loss experiments were carried out at 298 to 328k temperatures and immersion time 6, 12 and 24 hour .The experiments were performed as per ASTM G31-72 method[15]. The percentage inhibition efficiency was calculated using the following equation:

where, Wo and Wi are weight losses in the absence and presence of inhibitor respectively.

Electrochemical studies

For potentiodynamic polarization studies, mild steel strips of above mentioned composition were used and the experiments were carried out at different temperatures and time period, up to 24 hours in the absence and presence of inhibitor. For polarization studies a cylindrical mild steel rod of the same composition, as that of weight loss, coated with araldite (exposed area of 1cm²) was used. The electrodes were polished with emery papers and degreased with acetone before used. For accurate measurements of potential and current densities, galvanostatic polarization studies were carried out at different temperatures. A platinum foil and saturated calomel electrode were used as counter and reference electrode respectively. Polarization studies were carried out in 1M H_2SO_4 in the absence and presence of inhibitor of varying concentrations and temperatures.

Scanning electron microscopy studies

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 are used in this experiment, are examined to find out any surface defects by optical microscope. The specimens selected for study were having smooth surfaces. After this the specimens were washed with double distilled water and dried in desiccators. These specimens were then dipped in the solutions of 1000 ppm and 100 ppm concentration for the inhibitor in 1M sulphuric acid for 24 hours at room temperature. These specimens were then washed with distilled water and dried in desiccators. The SEM photographs were recorded of these corroded as well as uncorrode mild steel specimens.

RESULTS AND DISCUSSION

Weight loss measurement

The corrosion inhibition efficiency (% I) of [N–(3– Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] for corrosion of mild steel is calculated using the above mentioned equation. Table 1 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 decrease at the temperature increases from 298 K to 328 K for all inhibitor concentrations. The changes in inhibition efficiencies are quite less for all concentrations viz. 1000 ppm, 500 ppm, 200 ppm and 100 ppm at temperature 298 K. While changes in inhibition efficiencies are more as the temperature increases from 308 K to 328 K for all concentrations.

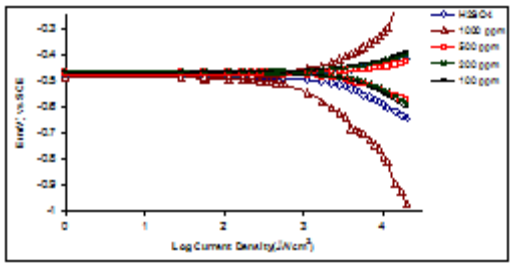

Fig. -1: Galvanostatic Polarization Curves of Mild Steel in 1M H_2SO_4 solution in presence of different concentrations of [N-(3- Methylthio- 5-acetamido-1,2,4-thiadiazolyl) cytisine] at 298K.

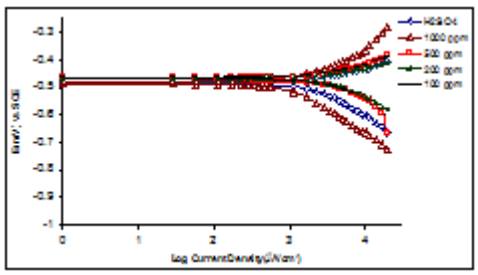

Fig. - 2: Galvanostatic Polarization Curves of Mild Steel in 1M H_2SO_4 solution in presence of different concentrations of [N-(3-Methylthio- 5-acetamido-1,2,4-thiadiazolyl) cytisine] I at 308K.

Galavonstatic polarization measurement

Figs. 1 to 4 show the anodic and cathodic polarization curves (Tafel's plot) of mild steel in 1M H_2SO_4 solution with and without the addition of various concentration of [N-(3-Methio-5-acetamido-1,2,4-thiadizoyl) cytisine] 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 2. 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 that the corrosion current densities decrease with increase in concentration of inhibitor. The percentage

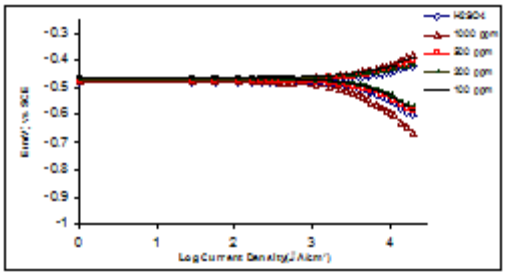

Fig. -3: Galvanostatic Polarization Curves of Mild Steel in 1M H_2SO_4solution in presence of different concentrations of [N-(3-methylthio- 5-acetamido-1,2,4-thiadiazolyl) cytisine] at 318K.

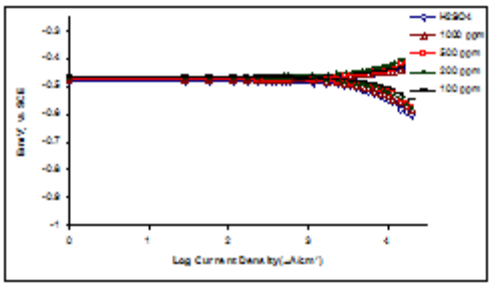

Fig. -4: Galvanostatic Polarization Curves of Mild Steel in 1M H_2SO_4 solution in presence of different concentrations of[N-(3-methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] at 328K.

Table -1: Inhibition Efficiency of [N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine]

Temperature	Solution in ppm	Weight loss/gram	%I
298K	1M H_2SO_4	0.0786	-
	100	0.0099	69.39
	200	0.0073	80.71
	500	0.0041	94.78
	1000	0.0035	92.54
308K	1M H_2SO_4	0.1568	-
1.	100	0.0715	54.40
1.	200	0.0598	61.86
1.	500	0.0179	88.58
1.	1000	0.0071	95.47
318K	1M H_2SO_4	0.5468	-
1.	100	0.3454	36.83
1.	200	0.2374	56.58
1.	500	0.1675	69.36
1.	1000	0.0260	95.24
328K	1M H_2SO_4	1.1891	-
1.	100	0.8028	32.48
1.	200	0.6849	42.40
1.	500	0.2349	80.24
1.	1000	0.0683	94.25

inhibition of each inhibitor at various concentrations in 1M H_2SO_4 is shown in Table 2 after being calculated from the expression:

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

The percentage inhibition of [N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] on mild steel in 1M H_2SO_4 shows that corrosion inhibition efficiency reaches about 92.5% with solution containing 1000 ppm inhibitor concentration where as at low concentration (100 ppm) the percentage inhibition is about 73.41% at 298 K. While at 328K the corrosion inhibition efficiency reaches 90.8% with solution containing 1000 ppm inhibitor. On the other hand the percentage inhibition efficiency is about 33.93% containing solution 100 ppm 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 that many inhibitor processes are participated in corrosion inhibition.

From the experimental method, it is concluded that inhibition effect is anodic at temperature 298K rather than cathodic except 1000 ppm. At higher temperature the inhibitor [N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] 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 on metal. The surface coverage θ values have been obtained from electrochemical measurements for various concentrations. There are many adsorption

Table - 2: Corrosion parameters of mild steel in 1M H_2SO_4 in presence of [N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] as additive

Temp.	Inhi. conc. in ppm.	E_{corr} mV	Log i_{corr} μA/cm²	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

isotherms to study the adsorption process. Here, Langumir adsorption isotherm is tested. Fig. 5 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

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

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

The value of heat of adsorption for[N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] is 4.50 Kcal/mol.

To calculate the activation energy, the current densities are plotted against temperature in absence and presence of inhibitor (Fig. 6). The value of activation energy can be finding 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 [N-(3- Methylthio-5-acetamido-1, 2, 4-thiadiazolyl) cytisine] is Kcal/mol.

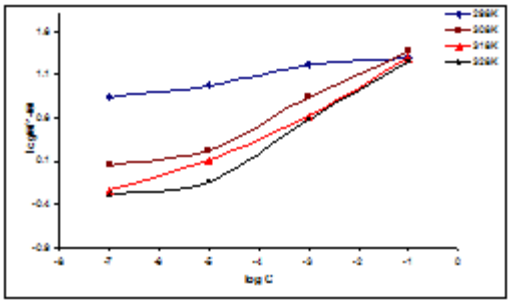

Fig. - 5: Variation of surface coverage vs. concentration at different temperature of [N-(3-Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] .

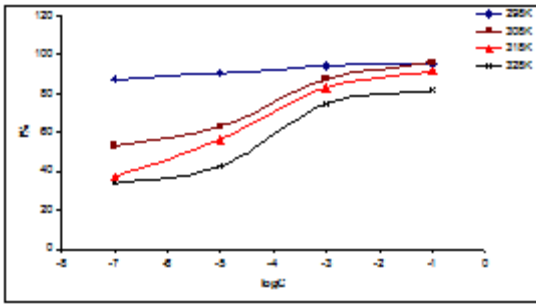

Fig. - 6: Inhibition efficiency vs. concentration of [N-(3- Methylthio- 5-acetamido-1,2,4-iadiazolyl) cytisine] at different temperatures

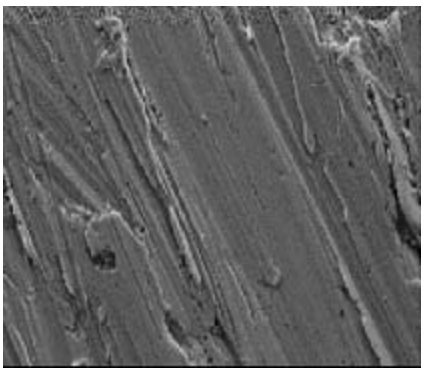

Fig. - 7: Scanning Electron Micrograph of plain Mild Steel at 2000 magnification

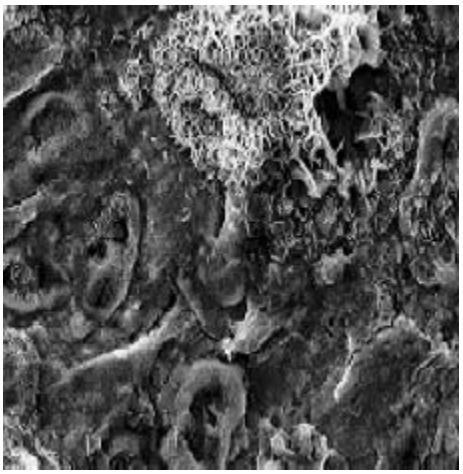

Fig. - 8: Scanning Electron Micrograph of Mild Steel in 1N H_2SO_4 at 2000 magnification

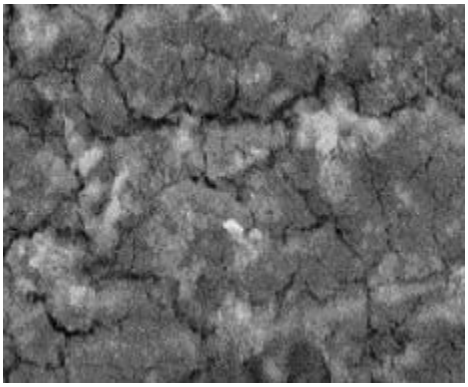

Fig. -9: Scanning Electron Micrograph of Mild Steel in presence of 100 ppm of [N-(3- Methylthio-5-acetamido- 1,2,4-thiadiazolyl) cytisine] in 1M H_2SO_4 at 2000 magnification.

Fig. -10: Scanning Electron Micrograph of Mild Steel in presence of 1000 ppm[N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] in 1M H_2SO_4 at 2000

Scanning electron microscopic study

To study the surface morphology of mild steel coupons SEM technique has been used. Figure VII,VIII, IX and X show the surface morphology of plain mild steel, in 1M H_2SO_4 and corroded surfaces after dipped in [N-(3- Methylthio-5-acetamido-1,2,4-thiadiazolyl) cytisine] inhibitor at 100 ppm and 1000 ppm. 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 1000 ppm.

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