THE COMPARATIVE STUDY OF INHIBITORY EFFECT OF TWO SUBSTITUTED AMINES ON CORROSION OF MILD STEEL IN ACIDIC MEDIUM

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Abstract

The inhibitory effect of two substituted amines, diethanolamine (DEA) and triethanolamine (TEA) on corrosion of mild steel in 0.5M H_2SO_4 have been investigated by weight loss and polarization techniques. The percentage inhibition efficiency was found to increase with increasing concentration of amines. Galvanostatic polarization measurements indicate that both DEA and TEA are mixed type of inhibitor. The adsorption of DEA on the mild steel surface was well described by Frumkin adsorption isotherm in acidic media and TEA adsorbed on mild steel surface according to Freundlich adsorption isotherm. Among the two compounds, DEA exhibits better inhibition efficiency than TEA.

Keywords: Corrosion inhibition; Inhibitor; Adsorption and Substituted Amines

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1. Introduction

Mild steel is widely used as constructional material in many industries due to its excellent mechanical properties. The use of inhibitor remains one of the necessary methods to protect the metal against acidic corrosion [1, 3, 4, 5, 9]. Organic compounds containing nitrogen and oxygen atom are commonly used to reduce corrosion attack on mild steel in acidic medium [1-5, 9]. The inhibition efficiencies of organic compounds are generally dependent on their tendency and nature of adsorption on metal surface. Inhibition may also involve either physiorption or chemisorption of inhibitors onto the metal surface. The adsorption of inhibitors may blocks either cathodic, anodic or both reactions.

The aim of this work is to study the effect of two substituted amines (DEA and TEA) on corrosion of mild steel in 0.5 M sulphuric acid using weight loss and galvanostatic polarization measurements.

2. Experimental methods

Sulphuric acid (E Merck, India, AR Grade) was used directly for the preparation of solutions. Sulphuric acid solution of 0.5 M was prepared in double distilled water and was used throughout the studies. The solutions of 10^{-3}, 10^{-5} and 10^{-7} M DEA and TEA were prepared in 0.5 M sulphuric acid by dilution method. These different concentrations of the solutions were used for experiment at different temperatures.

The experiments were conducted using mild steel (C = 0.15%, Mn = 1.02%, Si = 0.025%, P = 0.025%). They were abraded into uniform surfaces with the help of grinding machine by using 150, 320, 400 and 600 grade emery papers. Weight loss measurements were carried out by using coupons of the dimensions 2.0 x 2.0 x 2.0 cm and taking 100 ml of solutions. The coupons were dipped in solutions for 5 hours. Inhibition efficiency (I %) was calculated by using the following equation [7, 9] :

$$I\% = [1 - W_{add} / W_{free}] \times 100$$

Where W_{free} and W_{add} are the weight loss of mild steel coupon in absence and presence of inhibitors in 0.5 M sulphuric acid solution respectively.

An electrochemical cell assembly of three electrodes was used for galvanostatic polarization measurements. Calomel electrode was used as the reference electrode and Platinum wire was used as auxiliary electrode. Polarization measurements were made under thermostatic conditions at 303K, 313K, 323K and 333K. The electrode was held in the test environment for 3 h prior to each experiment, which was sufficient for open circuit potential (OCP) to attain stable value. The current was then passed through the cell at different predetermined values from galvanostat through the counter electrode and the equilibrium potential between the working and reference electrodes was measured. The cathodic polarization curve was determined first and then after the reestablishment of open circuit potential, anodic curve was traced. Potential values at a given current were found to be generally constant within 1 min. The inhibition efficiency (I %) was calculated using the following equation [7, 9]:

$$I\% = [1 - i_{add}/i_{frer}] \times 100$$

Where i_{add} and i_{free} is the corrosion current densities in absence and presence of inhibitors in 0.5 M sulphuric acid solution respectively.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurement

The corrosion behavior of mild steel in 0.5 M sulphuric acid in the presence and absence of substituted amines at the different concentrations was studied by weight loss at 303 K. The influence of inhibitors concentrations on the inhibitor efficiency (I %) is shown in fig.1. The results of weight loss measurement were summarized in table 1. It was found that these inhibitors give inhibition efficiency of more than 90% in 10^{-3} M inhibitor

solution in 0.5 M sulfuric acid. The inhibition efficiency increases with increase in concentration of the inhibitors, i.e. inhibition efficiency is directly proportional to concentration. The highest inhibition of 94.4% was obtained by DEA as compared to that of TEA (91.5%) at 10^{-3} M concentration.
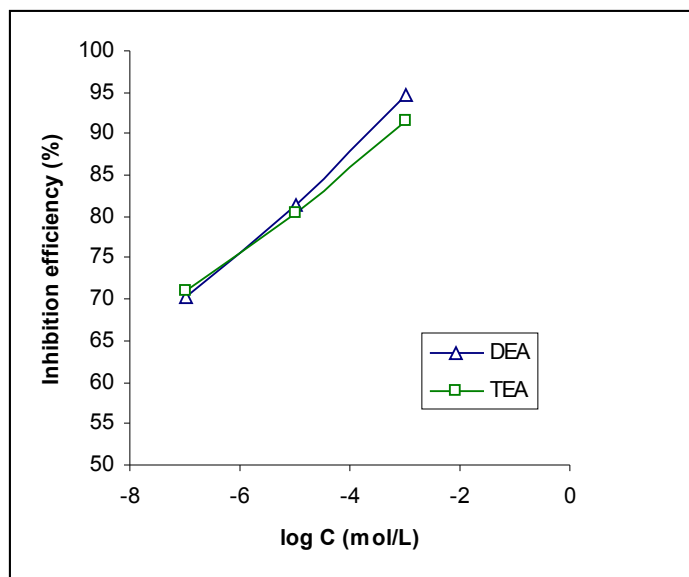

Fig.1. Change of inhibition efficiency with change in inhibitors concentration by weight loss measurement.

Table 1: Inhibition efficiency of DEA and TEA at different concentrations as determined by weight loss at 303 K

Conc. of inhibitor (M)	Inhibition efficiency (I %)	
	DEA	TEA
10^{-3}	94.4	91.5
10^{-5}	81.5	78.5
10^{-7}	70.3	68.0

3.2. Galvanostatic Polarization measurement

Figs.2-3 represents galvanostatic polarization curves of mild steel in 0.5 M H_2SO_4 in the absence and presence of various concentrations of the two compounds under study at 303K. The effect of concentration of inhibitor on the corrosion parameters of mild steel in 0.5M sulphuric acid are given in table 2 and 3. The corrosion currents densities have been determined by linear extrapolation of the anodic and cathodic Tafel line upto open circuit potential. The addition of the compounds decreases both the cathodic and anodic current densities to almost equal extent. These results indicate that these compounds are able to suppress both anodic and cathodic partial processes to an equal extent [6]. There is no appreciable shift of E_{corr} towards any direction in both the case. It indicates that these inhibitors act as mixed type of inhibitor by blocking both cathodic and anodic sites [1, 4, 5, 13].

The decrease in current density in case of DEA is found to be more than that of TEA which indicates that DEA is better inhibitor than TEA. The inhibition efficiency is found to increase with increase in concentrations of both the inhibitors.

Table 2: Corrosion parameters of Mild Steel in 0.5 M H_2SO_4 in presence of various concentrations of DEA at 303K.

Conc. (M)	$-E_{corr}$ (mV)	i_{corr} (mA/cm^2)	b_c (mV/dec)	b_a (mV/dec)	θ	(I %)
0	515	3.85	45	35	-	-
10^{-3}	510	2.90	120	80	0.887	88.7
10^{-5}	505	3.30	100	65	0.718	71.8
10^{-7}	535	3.50	85	50	0.553	55.3

Table 3: Corrosion parameters of Mild Steel in 0.5 M H_2SO_4 in presence of various concentrations of TEA at 303K.

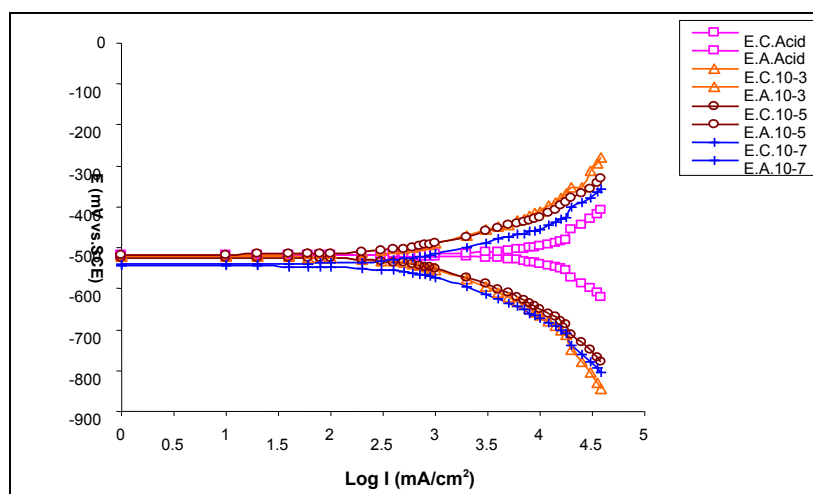| Conc. (M)	$-E_{corr}$ (mV)	I_{corr} (mA/cm^2)	b_c (mV/dec)	b_a (mV/dec)	θ	I%
0	515	3.85	45	35	-	-
10^{-3}	519	3.14	90	65	0.805	80.5
10^{-5}	510	3.35	85	50	0.683	68.3
10^{-7}	515	3.43	70	45	0.619	61.9

Fig.2: Galvanostatic polarization curve for the corrosion of mild steel in 0.5 M H_2SO_4 solution and in the presence of various concentrations of DEA at 303K.
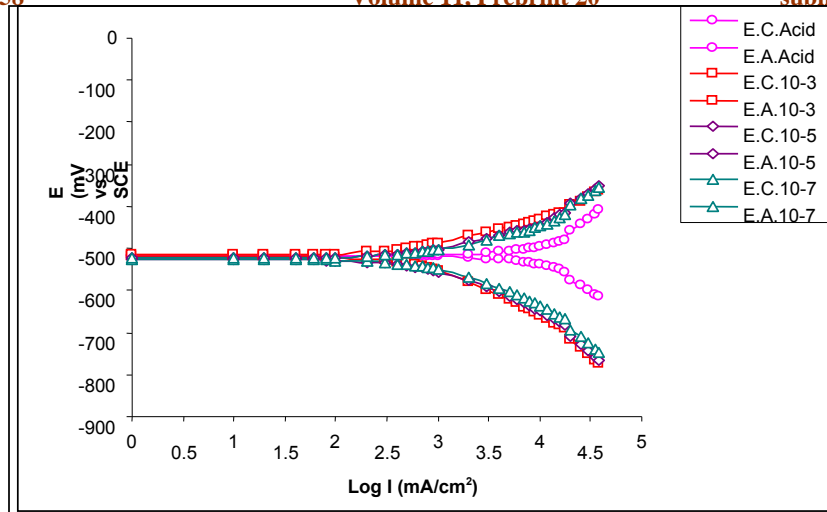
Fig. 3: Galvanostatic polarization curve for the corrosion of mild steel in 0.5 M H_2SO_4 solution and in the presence of various concentrations of TEA at 303K.

3.3. Adsorption isotherms

Two main types of interaction can describe adsorption of the organic compounds on the electrode surface: physical adsorption and chemisorption. Both types of adsorption are influenced by the nature and charge of the metal, the chemical structure of the inhibitor as well as the type of the corrosive electrolytes. However, the basic information on the interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm which depends on the degree of electrode surface coverage. The surface coverage (θ) has been determined using the equation [10],

$$\theta = [\ I \ \% \ / \ 100 \ ]$$

Where I % is inhibition efficiency.

Table 4: Thermodynamic parameters for DEA at 303K

a	K	R^2	ΔG_{ads} (kJ/mol)
-4.415	2.394×10^5	0.9988	-41.32

Table 5: Thermodynamic parameters for TEA at 303K

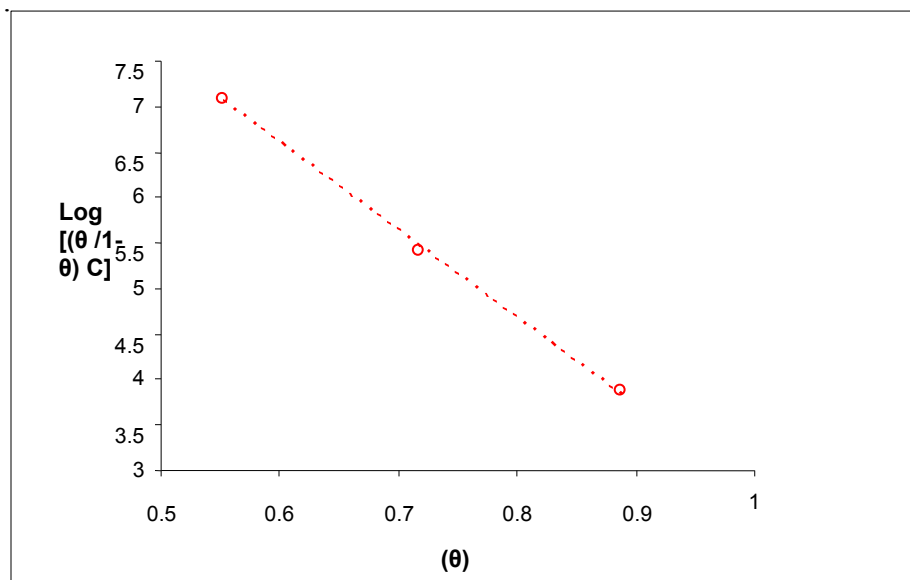| K	n	R^2	ΔG_{ads} (kJ/mol)
1.0313	35.087 7	0.9793	-10.20

Fig.4. Curve fitting of the plot of Log $\{\theta/(1-\theta)C\}$ Vs. θ for mild steel in 0.5 M H_2SO_4 in the presence of DEA at 303K.

The best-fit adsorption isotherm is Frumkin isotherm for adsorption of DEA on mild steel surface with the mean R^2 value 0.9989. The plots of Log $\{\theta/(1-\theta)C\}$ vs. θ is shown in fig.4 and the values of K and "a" have been calculated from intercept and slope respectively. The negative values of 'a' (the interaction parameter) suggest that there is the presence of the lateral force of repulsion between the molecules in the adsorbed layer.

This means that the inhibitory effect of DEA through adsorption of amine (NH-) and the hydroxyl groups (OH-) on the metal surface may be weaken due to its repulsive interaction among branched hydroxyl groups (OH-) on the metal surface [11].

Whereas Freundlich adsorption isotherm is the best-fit adsorption isotherm for TEA with the mean R^2 value 0.9895. This means that adsorption is non linear or non-specific and adsorbed molecules interact with each other on the surface [5, 12]. This means that the inhibitory effect of TEA through adsorption of amine (NH-) and the hydroxyl groups (OH-) on the metal surface is weaken due to its repulsive interaction among the hydroxyl groups (OH-) on the metal surface [11]. The plots of log θ vs. log C (shown in Fig. 5) gives, the values of K and n from intercept and slope respectively. The adsorption intensity (n) is more than 2 which shows good adsorption.

The values of free energy of adsorption $(\Delta G)_{ads}$ have been determined by using the following equation [5, 6, 8, 9]:

$$\Delta G_{ads} = - RT \ln 55.5 K$$

The various values are tabulated in the table 4 and 5. The negative value of ΔG_{ads} indicates the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [6, 8]. The mean value of ΔG_{ads} for DEA is -41.32 kJ/mol obtained in case of DEA indicates that DEA is strongly adsorbed on the metal surface. This kind of isotherm is generally regarded to indicate chemisorption whereas the mean value of ΔG_{ads} for TEA is -10.20 kJ/mol. This low value of ΔG_{ads} suggested the physical adsorption of TEA on the metal surface [3, 14]. This result supplement the proposal that DEA is better inhibitor than TEA because repulsive interaction among NH- and –OH groups are minimum in case of DEA due to less hindered structure of the molecule and nature of linearity as compared to that of TEA.
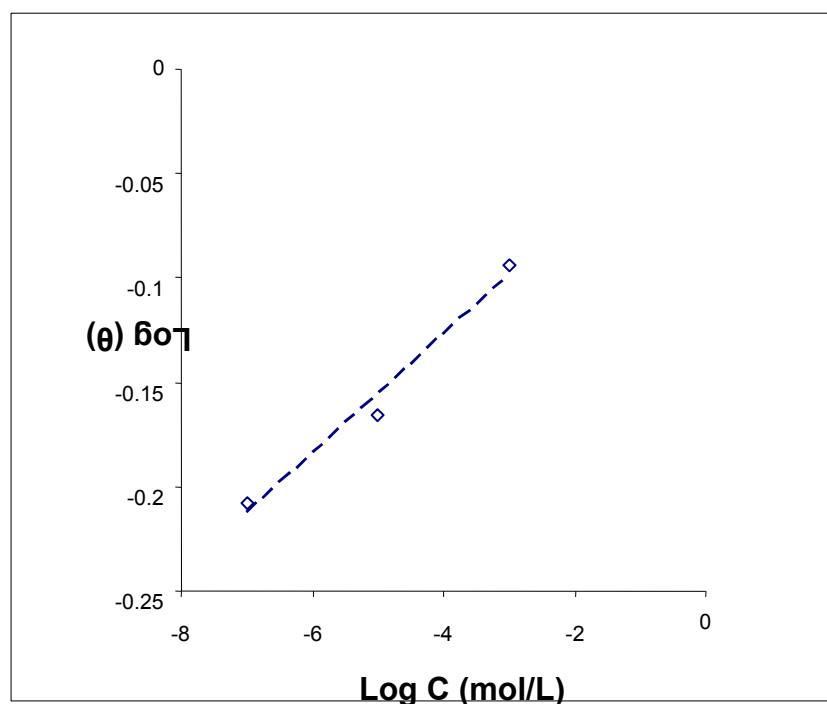
Fig. 5: The plot of Log θ Vs. Log Conc. for mild steel in 1N H_2SO_4 in the presence of TEA at 303K.

4. Conclusions

The following conclusions have been drawn from the present study:

(i) Both DEA and TEA act as corrosion inhibitors for mild steel in acid solutions at 303K. The inhibition efficiency increases with increase in concentrations.

(ii) Frumkin adsorption isotherm is closest to the description of the adsorption of DEA on the mild steel surface. DEA inhibits the corrosion by chemisorption as suggested by higher values of ΔG_{ads}.

(iii) The adsorption of TEA on mild steel in sulphuric acid solution follows Fruendlich adsorption isotherm and its inhibition is due to physical adsorption as indicated by low value of ΔG_{ads}.

(iv) Inhibition efficiency of DEA is more than that of TEA because DEA is less hindered molecule which helps in stronger adsorption on metal surface as compared to that of TEA.

(v) DEA and TEA are mixed type inhibitors inhibiting both cathodic and anodic process to almost equal extent.

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