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Corrosion Inhibition of Mild Steel in 1M HCl Medium using 2-Dimethyl Amino Ethanol

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Abstract: The efficiency of 2-Dimethyl amino ethanol investigated as corrosion inhibitor of mild steel in 1M HCl using weight loss, potentiodynamic polarization and electrochemical impedance studies. The inhibition efficiency increased with increasing inhibitor's concentration, but decreased with the increase in temperature. The adsorption of studied compounds on mild steel surface was found to follow the Langmuir isotherm. Thermodynamic calculations reveal physicochemical interactions and spontaneous adsorption mechanism. Potentiodynamic polarization results show that the inhibitor acts as mixed type in 1M HCl.

Keywords: 2-Dimethyl amino ethanol, mild steel, weight loss, Langmuir isotherm, impedance, potentiodynamic polarization.

1. INTRODUCTION

Corrosion is described as the deterioration of metal by an electrochemical process or the steady eating away of metal by the action of the environment. Hydrochloric acid is generally used for the removal of undesirable scale and rust in several industrial processes. Thus, inhibitors are one of the most convenient methods for protection against corrosion, particularly in acid solutions to prevent unexpected metal dissolution and acid consumption^[1]. The majority of the well-known acid corrosion inhibitors are organic compounds that contain nitrogen, sulfur or oxygen atoms^[2]. Organic inhibitors can adsorb onto the metal/solution interface via four distinct mechanisms: (a) electrostatic attraction between charged molecules and the metal; (b) interaction between uncharged electron pairs in the molecule and the metal; (c) interaction between p-electrons and the metal and (d) a combination of mechanism (a) and (c)^[3]. Generally, the tendency to form stronger coordination bonds and, as a result, the inhibition efficiency increases according to the following trend: O < N < S < P^[4]. The planarity (p) and lone pairs of electrons present on N, O and S atoms are important structural features that control the adsorption of these molecules onto the surface of the metal^[5].

In this work, the inhibition ability of DMAE for mild steel corrosion in HCl solution was evaluated. The inhibitory mechanism of this organic compound was discussed based on the analysis of the Langmuir adsorption isotherm, weight loss, thermodynamic and potentiodynamic polarization and EIS. The effect of temperature on the corrosion behavior was also investigated studies.

2. Experimental Method

Mild steel coupons with the composition of C–0.07%, P–0.008%, Mn–0.34%, S–Nil, Si–Nil, Fe – Bal and size 3cm x 1cm x 0.1cm were used for weight loss investigation. The mild steel rod was used for potentiodynamic polarization and impedance techniques. 1M HCl solutions were prepared by the dilution of analytical grade HCl with distilled water respectively. The concentration of the inhibitor was used 2.5ppm, 7.5ppm and 10ppm. The loss of weights in different temperatures (298K, 303K, 308K and 318K) was used to study the inhibition efficiency of inhibitor at higher temperature.

EIS and Tafel polarization were conducted in an electrochemical measurements units (Model Stat [10V, 30mA] IVIUM). The EIS

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measurements were made at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV. The Tafel polarization measurements were made after EIS for a potential range of -200 mV to +200 mV with respect to open circuit potential at a scan rate of 1 mV/sec. From the Nyquist plot (Z_{real} vs $Z_{\text{imaginary}}$), electrochemical resistance R_{ct} and double layer capacitance C_{dl} was calculated. From the plot of potential E Vs $\log I$, the corrosion potential (E_{corr}), the corrosion current (I_{corr}) b_c and b_a were obtained.

3. Result and Discussion

3.1 Weight Loss Method

The inhibition efficiency with different concentrations (2.5 ppm, 7.5 ppm, 10 ppm) of the inhibitor (2-DMAE) on mild steel has been evaluated by weight loss measurements and the results are given in Table 1. It shows that the corrosion rate decreases with the increase of inhibitor concentration at 298 K the inhibitive efficiency increases with the presence of higher concentration of inhibitor. The maximum inhibitive efficiency is 91.6% at 10 ppm for 5 hrs, which suggests the 2-DMAE effectively inhibited the corrosion of MS in acidic solution. This behaviour is due to the extent of adsorption and surface coverage of the inhibitor on the MS surface increased with the concentration [6].

3.2 Effect of Temperature

The effect of temperature on corrosion rate and inhibition efficiency was evaluated by the weight loss method in the temperature range 298-313 K, in the absence and presence of the inhibitor in 1 M HCl solution and the results given in Table 1. The higher corrosion rate observed at elevated temperature can be attributed to an appreciable increase in desorption of the inhibitor on the MS surface with rise in the temperature. Because of more adsorption of inhibitor molecules at higher temperatures, the greater surface area of MS comes into contact with acid environment, resulting in increased corrosion rates with increasing temperature [7]. According to Obot et al. [8] and Umoren [9], decrease in IE with increase in temperature is an indication that the adsorption of DMAE on MS surface is physical in nature.

3.3 Adsorption Isotherm

The correlation between surface coverage (θ) and the amount of inhibitor in the corroding medium was by Langmuir adsorption isotherm which can be expressed as $C/\theta = 1/K_{\text{ads}} + C$

Where C is the inhibitor concentration, θ is the surface coverage and K_{ads} is the equilibrium constant of the inhibitor adsorption process. The straight line was observed upon plotting C/θ against C with correlation coefficient higher than 0.99 and suggest that the Langmuir adsorption isotherm fits very well with the experimental data. The slope value being very near to unity further confirms the validity of Langmuir adsorption isotherm.

The K_{ads} can be calculated from the intercepts on the C/θ axis. This value is related to the standard free energy of adsorption (ΔG_{ads}) by the equation [10]

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}})$$

Where R is the gas constant and T is the absolute temperature. The value of 55.5 is the concentration of water in solution in mol L^{-1} . The negative sign of ΔG_{ads} indicates that the inhibitor is spontaneously adsorbed on the metal surface [11]. Generally the magnitude of ΔG_{ads} around -20 kJ mol^{-1} or less negative is assumed to be due to electrostatic interaction between the inhibitor and the charged metal surface (ie) physisorption. The values of ΔG_{ads} around -40 kJ mol^{-1} are more negative indicates that a charge sharing or transferring from organic species to the metal surface occurs to form coordinate type of bond (ie) chemisorption [12]. Hence this process can be considered as physisorption the change in free energy was also found to decrease with increase in temperature.

To accumulate supporting information about the mechanism of corrosion inhibition, other thermodynamic parameters such as enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) were calculated by using the following equation [13]

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$$

$$\ln K_{\text{ads}} = (-\Delta H_{\text{ads}} / RT) + (\Delta S_{\text{ads}} / R) - \ln (55.5)$$

From the plots of $\ln K_{\text{ads}}$ Vs T^{-1} for adsorption of 2-DMAE in HCl, the lines obtained represent a slope of $-\Delta H_{\text{ads}} / R$ and intercept of $(\Delta S_{\text{ads}} / R) - \ln (55.5)$. It indicates that an endothermic adsorption process ($\Delta H_{\text{ads}} > 0$) refers to chemisorption. Whereas exothermic adsorption process ($\Delta H_{\text{ads}} < 0$) may involve either physisorption / chemisorption / both of the process occurring together. In an exothermic process the distinction between physisorption & chemisorptions is based upon the absolute value of ΔH_{ads} [13].

Table 2 shows the ΔG_{ads} , ΔS_{ads} , ΔH_{ads} and E_a values for 2-DMAE in 1 M HCl. The calculated values of ΔH_{ads} in HCl for 5 hrs is 125.8 low confirming that the inhibitors were physically adsorbed onto the mild steel surface. The values of ΔS_{ads} for 2 DMAE negative since the adsorbed molecule lose their translation freedom when they are attached onto the surface of a material [14]. The increasing activation energy in the presence of inhibitor indicates that physical adsorption occurs in the first stage [15, 16]. The values of ΔH and E_a are nearly

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the same and are higher in the presence of the inhibitor. This indicates that the energy barrier of the corrosion reaction increases in the presence of the inhibition without changing the mechanism of dissolution.

3.4. Electrochemical Impedance Spectroscopy

Inhibition efficiencies and other calculated impedance parameters for 2-DMAE in 1M HCl were represented in Table 3. Fig.1 show the Nyquist plots for mild steel in 1M HCl with and without inhibitor at various concentration of 2-DMAE. The increase in R_{ct} values are attributed to the formation of the protective film of the inhibitor on the metal/solution interface^[17]. The decrease in Cdl values can be attributed to decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor molecules inhibit the corrosion rate by adsorption at the metal/ solution interface^[18].

3.5. Polarization Measurements

The values of electrochemical parameters associated with polarization measurements such as corrosion potential (E_{corr}), corrosion current densities (I_{corr}), Tafel slopes (b_a and b_c) and calculated IE% were listed in Table.3. Polarization curves for mild steel in 1M HCl without and with inhibitor at different concentrations are shown in Fig 2. It has been reported that when the change in E_{corr} values are not less than 80mV, a compound can be recognized as an anodic / a cathodic type of inhibitor^[19]. The values of b_a and b_c are both influenced by the presence of inhibitor which suggest that these are mixed type of inhibitor. I_{corr} was found to decrease as the concentration of the inhibitor increases. This confirms the inhibitory action of the 2-DMAE on metal surface.

4. Conclusion

From experimental analysis of 2-dimethyl amino ethanol showed that the compound to be an efficient inhibitor in the acid environment, giving a maximum inhibition efficiency from weight loss analysis. Inhibition efficiency values increased with increase in inhibitor concentration and decrease with temperature. Adsorption of 2-DMAE on the mild steel surface in 1M HCL obeys Langmuir adsorption isotherm. Thermodynamic variables of adsorption deduced revealed a physisorption with the steel surface and spontaneous adsorption of DMAE.

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Table 1 Corrosion parameters obtained from weight loss measurements for mild steel in 1M HCl solution without and with different concentrations of inhibitors for 5 Hrs at different temperatures

Temperature	Concentration (ppm)	Weight loss (mg)	Corrosion rate (mY)	% IE	θ
298	Blank	0.06	217.18		
	2.5	0.025	90.40	58.33	0.5833
	7.5	0.0105	54.29	75	0.75
	10	0.005	18.10	91.67	0.9167
303	Blank	0.06	217.18		
	2.5	0.03	108.59	50	0.5000
	7.5	0.02	72.39	60.67	0.6067
	10	0.01	36.20	83.33	0.8333
308	Blank	0.12	434.35		
	2.5	0.085	307.67	29.17	0.2917
	7.5	0.055	199.08	54.17	0.5417
	10	0.04	144.78	66.67	0.6667
313	Blank	0.120	434.35		
	2.5	0.09	325.76	25	0.25
	7.5	0.08	289.57	33.33	0.3333
	10	0.06	217.18	50	0.5000

Table 2 Thermodynamic parameters for 2-DMAE in 1M HCl

Concentration in ppm	$-\Delta G_{ads}$ (KJ/mol)	$-\Delta S_{ads}$ (J/mol/K)	ΔH_{ads} (KJ/mol)	E_a
2.5	8.5	241	80	75.81
7.5	10.4	272	91	95.53
10	13.6	376	125	137.26

Table 3 Electrochemical parameters for the corrosion of mild steel in 1M HCl with and without 2-DMAE

Concentration in ppm		Blank	2.5	7.5	10
Impedance Studies	R_{ct} Ohm	10.4	47.65	56.24	61.84
	C_{dl} F x10 ⁻⁵	5.45	5.31	5.19	5.15
	IE%	-	78.17	81.51	83.18
Potentiodynamic polarization studies	I_{corr} μ A/cm ²	0.000414	0.000225	0.000121	0.000109
	E_{corr} V	-0.4739	-0.4505	-0.4575	-0.4580
	b_a V/dec	0.101	0.072	0.069	0.069
	b_c V/dec	0.107	0.099	0.11	0.11
	IE%	-	45.65	70.77	73.67

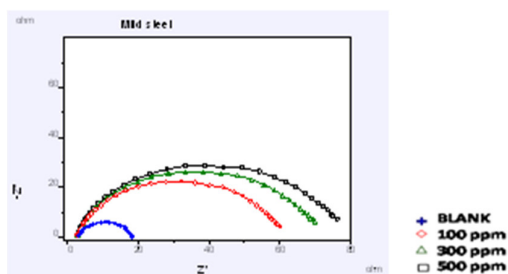


Fig. 1 Nyquist plot of 2-DMAE in 1M HCl

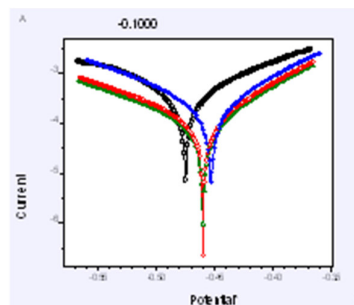


Fig. 2 Polarization curves of 2-DMAE in 1M HCl

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