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Corrosion Inhibition Study of Dodecylamine as long Chain Amine Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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ABSTRACT

The corrosion inhibition study by using various concentrations of dodecylamine on mild steel in 1.0 M HCl solution at different temperature i.e. 298, 308 and 318K for immersion time periods of 24.0 hrs were carried out by Weight loss measurement, Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization measurement, SEM (Scanning Electron Microscope). The results from the weight loss measurement show that corrosion inhibition efficiency increases with increasing the inhibitors concentration but decreases with increasing in temperature range, the maximum percentage corrosion inhibition efficiency were found 88.67% for dodecylamine for 1000ppm concentration at 298 K temperature for 24.0 hours. By electrochemical impedance study it observed that charge transfer resistance (R_{ct}) value increases and double layer capacitance (C_{dl}) value decreases with increasing the inhibitior concentration hence inhibition efficiency increases which also related to the charge transfer resistance. Potentiodynamic polarization curves show that dodecylamine behave as mixed type corrosion inhibitor. Adsorption of studied inhibitor on the mild steel surface obeyed the Langmuir adsorption isotherm. SEM study also analysis that there is formation of protective layer on the surface of mild steel to protect the surface against corrosion and surface become smooth and more clean and clear with increasing the inhibitor concentrations. Hence all these techniques study shows that dodecylamine is performed as good corrosion inhibitor for Mild Steel in 1.0 M HCl solution.

Keywords: Mild Steel, Dodecylamine, HClSolution, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy, SEM.

I. INTRODUCTION

Corrosion of iron and mainly its alloys has been a subject of numerous studies due to their wide range of industrial applications especially in petroleum industries and power plants [1]. Acid solutions are extensively used in many industrial processes, the most important of which are acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [2-5].

The commonly used acids are hydrochloric acid, sulfuric acid, nitric acid, etc. Iron and its alloys are reactive materials and are prone to corrode in these acid solutions. The addition of inhibitors secures the iron and its alloys against an acid attack effectively. Mild steel is widely used in most of industries, mainly petroleum, power production and machinery due to its excellent ductile strength, low cost and easily availability [6-8]. However, the mild steel is easily corroded when it come in contact with different acidic medium [9-13].

Corrosion decreases the valuable properties of mild steel. Now a day, metal protections against corrosion is a very serious problem in research work. Hence, many researchers work in this field and found that the use of different types of corrosion inhibitors in one of the most practical method for protecting the mild steel against corrosion especially in hydrochloric acidic solution [14]. The role of corrosion inhibitors is that it reduces the corrosion rates on the surface of metal and also decreases the reaction of metal with acidic environment.

The corrosion inhibition of in acidic medium can be affected by different types of organic, inorganic and pharmaceutical compounds etc. In literature survey, it has been seen that among different types of organic and inorganic corrosion inhibitors, the use of organic compounds are the best approach and effective corrosion inhibitor for mild steel in acidic medium.

Generally, the organic compounds containing hetero atom such as nitrogen, oxygen or sulphur and π electron in multiple bonds in their aromatic ring type structure [15- 21] are considered as main adsorption centers due to which these compounds are considered more effective corrosion inhibitors. The corrosion inhibitive properties of these types of corrosion inhibitors mainly attributes to their molecular structure, steric factor, electron density and lone pair present on the heteroatom [22-24].

These compounds form a coordination covalent bond between metal surface and used corrosion inhibitors called chemical adsorption (Chemisorption) and electrostatic interaction between metal and corrosion inhibitors called physical adsorption (Physiorption) or combination of both type interactions [25, 26]. Among different organic compounds, compounds containing nitrogen such as amines and heterocyclic compounds are found to be most effective corrosion inhibitors [27–31].

The objective of present chapter is to discuss the effect of Dodecylamine as corrosion inhibitor on corrosion of mild steel in 1.0 M HCl solution at 25.0 , 35.0 and 45.0°C temperatures for 24 hrs immersion time periods using different corrosion techniques like weight loss measurement, electrochemical impedance spectroscopy, potentiodynamic polarization measurement and adsorption isotherm. Scanning electron micrographs of corroded mild steel surface have been taken in absence and presence different concentrations of these corrosion inhibitors in 1.0 M HCl solution.

II. METHODS AND MATERIAL

Preparation of material

Mild steel specimens used for corrosion study were purchased from local market having following composition, C 0.054, Mn 0.26, Cr 0.056, Cu 0.010, Ti 0.002, S 0.017, P 0.019, Mo 0.018, Si 0.015, Ni 0.009 and remained iron. First of all the mild steel specimens were cut into 1X3 cm^2 dimensions for weight loss measurement and 1X5 cm^2 for electrochemical and polarization measurements and then polished with different grades emery papers (100 - 1000). That after specimens were rinsed with double distilled water, degreased with acetone and dried with help of hot air dryer and then used for experiment study.

Inhibitor

Dodecylamine purchased from Sigma-Aldrich (99%) was used as corrosion inhibitor for corrosion study in acidic medium. The molecular mass and molecular formula of doecylamine is $C_{12}H_{27}N$ and 185.355 g/mol respectively.

Preparation of Solutions

The acidic media of 1.0 M HCl was prepared by dilution of concentration HCl analytical grade 37% with double distilled water. The corrosion inhibitor solution which have been used for experiment purposes were made up by dilution of 0.5ml dodecylamine with 500ml of 1.0 M HCl solution to make 1000 ppm solution (stock solution).The corrosion inhibitor used without any further purification. The concentrations range was used for experimentation from 0 ppm to 1000 ppm with a difference of 200 ppm.

Weight loss measurement

It is such type of technique that forms the baseline method of measurement in many corrosion monitoring programmers. First of all Mild steel samples were cut in to 1×3 cm^2 then abraded with emery paper of different grade (100-1000) and rinsed with double distilled water, cleaned with acetone and finally dried between filter paper then weighted. The weight loss study carried out at on previously weight sample in 30ml of 1.0 M HCl solution filled in 50ml beaker in presence and absence of different concentrations of corrosion inhibitor for immersion time period of 24 hrs at different temperature ranges i.e. 298, 308 and 318 K in test solution and then after sample put out side from the test solution after completion of time period and cleaned with double distilled water followed by acetone, dried then weighted again. The experiment was performed in triplicate and then average weight loss was recorded by this weight loss study. The percentage corrosion inhibition efficiency and surface coverage are calculated by using following equations.

$$\eta_{\mathrm{w}}\% = \frac{\mathrm{w_o} - \mathrm{w_i}}{\mathrm{w_o}}\ \mathrm{X}100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\theta = \frac{w_o - w_i}{w_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where, w_o and w_i are the weight loss value of mild steel in absenceand presence of inhibitor respectively.The corrosion rate of mild steel was calculated by using equation,-

$$C_R(\mathrm{mmy}^{-1}) = \frac{87.6\ \times\ W}{AtD} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where w is weight loss of mild steel in mg, A is area of sample (cm^2), t is exposure time (hours) and D is density of mild steel (g cm^{-3}).

Electrochemical Measurement

Mild Steel specimen sizes of 1x5cm^2 dimensions are used for electrochemical measurement. The specimens were rubbed with (100-1000) grades of emery papers, cleaned with double distilled water followed by acetone & dried with hot air dryer put into desiccators then after used for experimental study. The sample surface area 1.0 × 1.0 cm^{2}has been selected for the electrochemical study.

Electrochemical impedance and Potentiodynamic polarization were carried out by AUTOLAB Salatron model 1280B Potentiostat. Electrochemical process were carried out with help of three electrodes, one of them is mild steel as working electrode, platinum as counter electrode and saturated calomel electrode as reference electrode are suspended in 50 ml beaker with different concentrations (200-1000ppm) of dodecylamine prepared by 1.0 M HCl solution. Before starting each experiments first of all the electrodes were immersed in test solution at open circuit potential (OCP) for 30 minutes at 298 K temperature to attained a stabilized value of OCP and then after proceeds the measurement.

Electrochemical impedance spectroscopy

The electrochemical impedance measurements were carried out in frequency range of 10 kHz to 0.01Hz with signal amplitude of 10 mV at the corrosion potential (-E_{corr}) at different concentration of used corrosion inhibitor. The impedance measurements were automatically controlled by Z-view software and the impedance diagrams were given in the Nyquist representation. Electrochemical impedance parameters such as Charge Transfer Resistance (R_{ct}) and Double Layer Capacitance (C_{dl}) were calculated from EIS data.

Potentiodynamic Polarization

The polarizations behavior of mild steel specimens in presence and absence of different concentrations of inhibitor in 1.0 M HCl solution at 298 K was carried out by the Potentiodynamic polarization curves. The potentiodynamic polarization study was taken after impedance measurement at same cell setup and potential range were taken -200 mV to +200 mV with respect to open circuit potential, at a scan rate of 1.0 mV/ sec. The different corrosion parameters such as corrosion potential (-E_{corr}), corrosion current density (I_{corr}), cathodic (β_c) and anodic (β_a) Tafel constant were obtained by the plot of polarization curve.

SEM analysis

The surface mild steel specimens after it exposure to 1.0 M HCl in the absence and presence of dodecylamine as corrosion inhibitor at different temperatures for 24.0 hrs were analyzed by ZEISS Scanning Electronic Microscope (AIIMS, DELHI).

III. RESULTS AND DISCUSSION

Weight loss measurements,

Weight loss measurements widely used by many researchers in earlier works [32-35]. In present work, dodecylamine tested as corrosion inhibitor for mild steel in acidic medium by using weight loss techniques in absence and presence of different concentrations inhibitors in 1.0 M HCl solution at different temperatures for 24.0 hrs immersion time.

Effect of concentration,

The calculated experimental values of corrosion inhibition efficiency and corrosion rate without and with different concentrations of Dodecylamine in 1.0 M HCl solutions are summarized in Tables 1.

Table 1.Inhibition Efficiency and Corrosion Rate values for the Corrosion of mild steel in acid solution of 1.0 M HCl in the absence and in the presence of different concentrations of Dodecylamine from weight loss measurements at different temperature i.e. 298, 308 and 318 K for 24.0 hours of immersion time

Corrosion Inhibitor Name	Immersion Time Periods (hrs)	Concentrations (ppm)	Weight Loss (mg)	Corrosion Rates (mmy^{-1})	Percentage Inhibition Efficiencies (% I. Ew)	Surface Coverage (θ)
Dodecyl amine (24.0 hrs)	298 K	0	0.212	33.58	-	-
		200	0.050	7.92	76.41	0.76
		400	0.044	6.97	79.24	0.79
		600	0.039	6.17	81.60	0.81
		800	0.029	4.59	86.32	0.86
		1000	0.024	3.80	88.67	0.88
	308 K	0	0.212	0.237	37.54	-
		200	0.050	0.074	11.72	68.77
		400	0.044	0.066	10.45	72.15
		600	0.039	0.054	8.55	77.21
		800	0.029	0.046	7.28	80.59
		1000	0.024	0.037	5.86	84.38
	318 K	0	0.313	49.58	-	-
		200	0.111	17.58	64.53	0.64
		400	0.098	15.52	68.69	0.68
		600	0.084	13.30	73.16	0.73
		800	0.078	12.35	75.07	0.75
		1000	0.067	10.61	78.59	0.78

Data from these Tables revealed that the percentage corrosion inhibition efficiency increases and corrosion rates decreases with increase in the concentration corrosion inhibitors in acidic solution i.e. from 200 to 1000 ppm that might be due to the increased adsorption of inhibitor on the metal surface with the increase in the concentration of corrosion inhibitors.

Effect of Temperature,

Theeffects of temperatures on the corrosion rates and corrosion inhibition efficiency of mild steel samples in 1.0 M HCl solution at different concentrations of dodecylamine is shown in figures 1 and 2. It can be seen from the inspection of Tables 1 that with rise in temperature from 298 to 318 K the weight loss of mild steel increased hence the corrosion rates value increased but corrosion inhibition efficiency value decreased at same concentration of corrosion inhibitor.

This behaviour could attributes to decrease in the strength of the adsorption process and it also indicates desorption of inhibitor from the surface of mild steel at higher temperature [36].

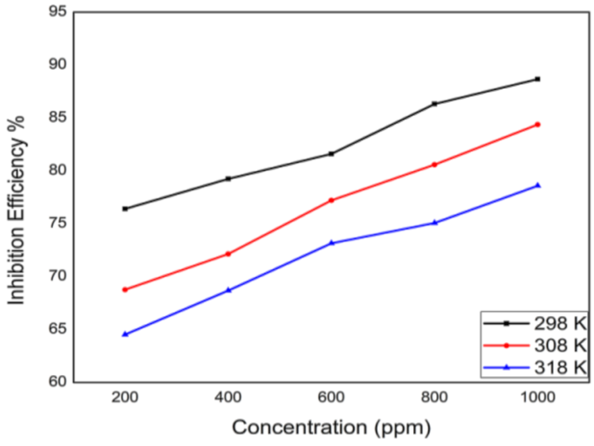

Figure 1. Variation of Inhibition Efficiency with Different Concentrations of Dodecylamine at Different Temperatures (298, 308 and 318 K) for Immersion Time Period 24.0 hours.

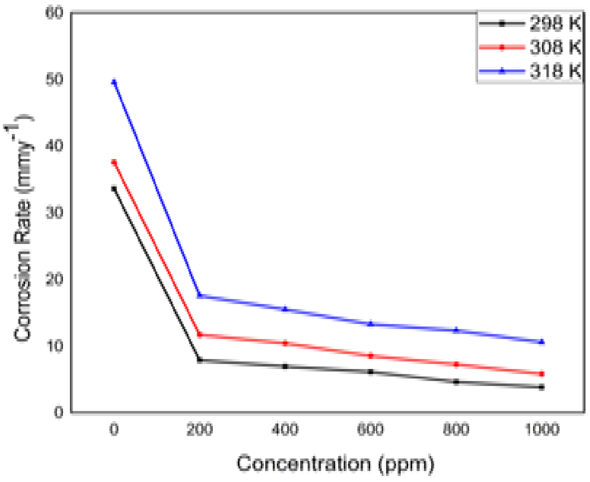

Figure 2. Variation of Corrosion Rates with Various Concentration of dodecylamine at Different Temperatures (298 , 308 and 318 K) for Immersion Time Period 24.0 hour.

According to Oguzie et al. [37], a decrease of corrosion inhibition efficiency with rise in temperature suggests that inhibitor molecules are physically adsorbed on the metal surface, While the reverse behavior suggests the molecules absorbed surface by the action of Chemisorptions Thus, the results signify that the adsorption of dodecylamine is mainly due to the physical adsorption. The increase in temperature usually accelerates the evolution of hydrogen, which results in a higher dissolution rate of the mild steel.

The maximum corrosion inhibition efficiency were found 88.67% and corrosion rate decreases 3.80 mmy^{-1} for dodecylamine with increasing the time periods from 24 hrs at temperatures 298 K for 1000 ppm concentration.

Adsorption Isotherm

For determining and understanding the mechanism of corrosion inhibitor and adsorption behavior, the study of absorption isotherm is most important. The isotherm can provide additional information about the corrosion inhibition properties. Different isotherm can be used to evaluate the adsorption behavior of corrosion inhibitor on the surface of mild steel such as Frumkin, Langmuir isotherm, Temkin, Freundlich and Flory - Huggins etc.

Among these several types of adsorption isotherms, In the Langmuir adsorption isotherm straight line was found to best fit for that experimental data measurement. A straight line curves with strong correlation coefficient nearly equal to 1.0 was obtained on plotting C_{inh}/θ against C_{inh} as at different temperatures i.e. 298, 308, 318 K for 24.0 hrs immersion time are shown in Figures 3.

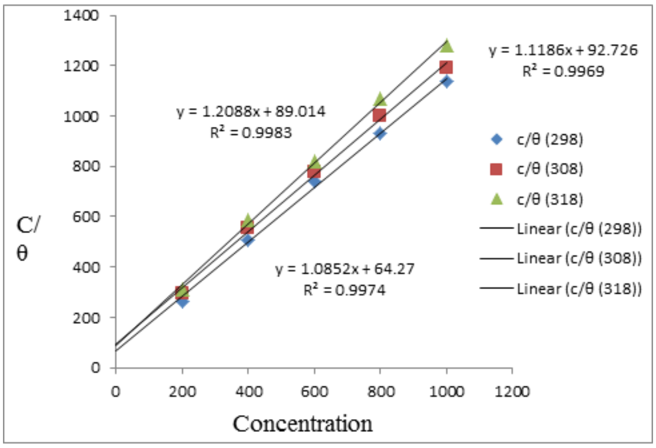

Figure 3. Langmuir adsorption isotherm plot for the mild steel in 1.0M HCl solution with different concentration of dodecylamine at different temperatures for immersion time 24.0 hours.

Figures suggest that adsorption of the Dodecylamine on the mild steel surface followed langmuir adsorption isotherm. The straight line relationship between surface coverage θ and the inhibitor concentrations which are characteristics of Langmuir adsorption isotherm are given by equation [38-40].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C \;\ldots\ldots\ldots\; (4)$$

Where, C_{inh} is the concentration of inhibitor, θ is the surface coverage which is obtained from the weight loss by using equation $\theta = \frac{w_o - w_i}{w_o}$ and K_{ads} could be calculated from the intercepts of the straight lines on the $\frac{C_{inh}}{\theta}$ axis, the equilibrium constant of the adsorption relation to the standard free adsorption energy is calculated from the equilibrium constant using following equation [41],

$$\Delta G^0{}_{ads} = -\,\mathrm{RT}\;(\ln 55.5 K_{ads}) \;\ldots\ldots\ldots\ldots\ldots\; (5)$$

Where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature and 55.5 is the concentration of water [42, 43] in solution (mol/lit.). The linear correlation coefficient adsorption parameters K_{ads} and ΔG^0_{ads} values are illustrate in Tables 2.

Table 2. Thermodynamic adsorption parameters for mild steel in 1.0 M HCl in the presence of various concentrations of Dodecylamine at different temperatures for 24 hrs time periods.

Corrosion Inhibitor Name	**Immersion Time (hrs)**	**Temperature (Kelvin)**	**Log 55.5 K_{ads}**	**$-\Delta G^0_{ads}$ (kJ mol^{-1})**
Dodecylamine	24.0	298	4.325	-24.680
		308	4.166	-24.569
		318	4.184	-24.475

The table reveals that with increase in temperature the K_{ads} decreases gradually, which indicates that the corrosion inhibitor strongly adsorbed on to the mild steel surface at a lower temperature. But when the temperature is high, the adsorbed corrosion inhibitor tends to desorbed from the steel surface.

Mainly, the absolute value of ΔG^0_{ads} is -20 kJ/mol or lower than -20 kJ/mol, they are consistent with the electrostatic interaction between the charged molecules and the charged metal called physical adsorption (physisorption) [44] and those that are -40 kJ/mol or more negative than -40 kJ/mol, which involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate bond called chemical adsorption (chemisorption) [45-48].

Here, from the Table 2 calculated value of ΔG^0_{ads} for dodecylamine are found to be ranged from -24.68 to -24.47, respectively for 24 hrs immersion time at different temperatures which lies between -20 kJ/mol and -40 kJ/mol that indicates the adsorption process of corrosion inhibitor on metal surface is mixed physical and chemical adsorption called physiochemical adsorption [49-52]. Also the negative values of ΔG^0_{ads} revealed that the adsorption of inhibitor on the mild steel is a spontaneous process usually shows the strong interaction on the surface.

Electrochemical Impedance Measurement, Electrochemical Impedance Spectroscopy Technique

The Electrochemical impedance spectra of mild steel for corrosion inhibitor present in the form of Nyquist plots are shown in Figures 4.

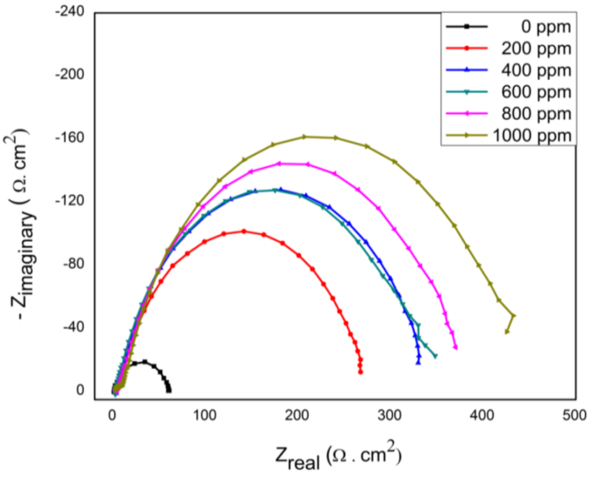

Figure 4. Nyquist Plots for Mild Steel Samples in 1.0 M HCl Solution with Presence and Absence of Different concentrations of Dodecylamine as Corrosion Inhibitor at 298 K Temperature.

It is clear from the graph that the Nyquist plots are semicircles in nature and it can be seen from the diagram that diameter of semicircle increases with increase in the concentration of corrosion inhibitor in 1.0 M HCl solution. Figure 4 shows that the impedance value in presence of inhibitor is larger than in the absence of inhibitor. It shows adsorption of inhibitor on surface of mild steel.

The impedance spectra show the one single capacitive loop which suggest that the corrosion of mild steel surface is mainly controlled by the charge transfer process and generally related to charge transfer and double layer behavior [53, 54].

Noticeably, these impedances are not perfectly semicircle which can be attributed to frequency dispersion as a result of non homogeneity or roughness of metal steel surface [55]. The corrosion of mild steel is usually related to charge transfer resistance and double layer capacitance behavior of corrosion process. The experimental calculated values of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and percentage corrosion inhibition efficiency (IE %) are listed in Table 3.

Table 3. Impedance parameters and their corresponding inhibition efficiency in presence and absence of different concentrations of Dodecylamine at 25.0°C temperature.

Corrosion Inhibitor Name	Temperature	Concentrations (ppm)	R_{ct}(Ω.cm^2)	C_{dl}(μF.cm^{-2})	PercentageCorrosion Inhibition Efficiencies (%I.E_R)
Dodecylamine	25.0°C	0	58.82	827.88	-
		200	265.29	183.55	77.82
		400	328.15	148.39	82.07
		600	346.01	140.13	83.00
		800	368.60	136.11	84.04
		1000	430.40	113.14	86.33

It is observed from the Table 5 that by increasing the concentration of inhibitor the double layer capacitance (C_{dl}) values decreases and charge transfer resistance values increases, which shows the adsorption of inhibitor on the metal/solution interface surface leading to the formation of thin layer film [56]. The decreases in the (C_{dl}) values with concentration the situation were the result from a decrease in dielectric constant [57, 58] and increase in the thickness of the electric double layer which denote the inhibitor molecule function by adsorption at the metal/ solution interface [59].

The charge transfer resistance value calculated from the difference in impedance (Z_{real}) at lower to higher frequencies [60-62]. The value of double layer capacitance are obtained from the frequency at which the imaginary component of impedance is ($-Z_{max}$) maximal and calculated from following equation [63].

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where, f_{max} is the frequency value at the top of semicircle and it is mid way of Z_{real}& also at which Z_{image}. Component is maximal.

The percentage corrosion inhibition efficiency is calculated from using charge transfer resistance value by following equation [64].

$$I.E.\% = \frac{R_{ct\,(inh)} - R_{ct}}{R_{ct\,(inh)}} \text{x } 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where R_{ct} and $R_{ct\ (inh)}$ are the charge transfer resistance in absence and presence of different concentrations of inhibitor. The maximum percentage corrosion inhibition efficiency (IE_R%) were found by EIS measurement was 86.33 % at 1000 ppm concentrations for dodecylamine

The Bode impedance diagram of log Z vs. frequency obtained for the mild steel in the absence and presence of 200 to 1000 ppm concentrations of dodecylamine in 1.0 M HCl solution at 298 K temperature are shown in Figures 5.

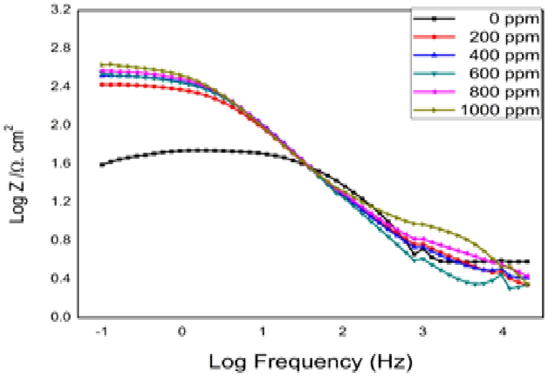

Figure 5. Bode digramme for Mild Steel Samples in 1.0 M HCl Solution with Presence and Absence of Different Concentrations of Dodecylamine as Corrosion Inhibitor at 298 K Temperature.

From these Figures, it was found that, in the higher frequency region, the Log Z tends to be very low. It also shows that the value of impedance increases on increasing the concentration of inhibitor in 1.0 M HCl solution.

Potentiodynamic Polarization Measurement

The corrosion behavior of dodecylamine on the cathodic and anodic polarization curve for mild steel in 1.0 M HCl solution with and without corrosion inhibitor is shown in Figures 6 as Tafel plots.

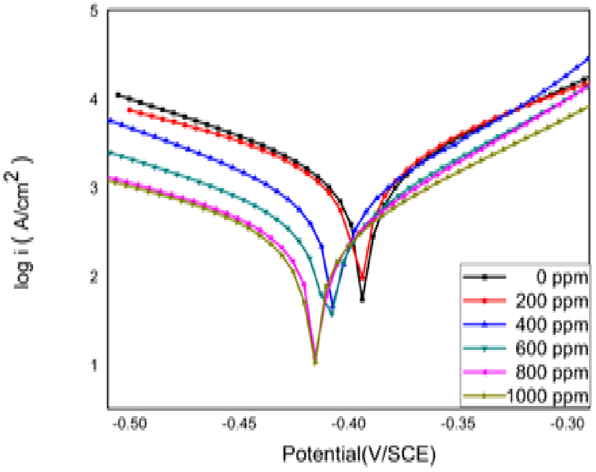

Figure 6. Potentiodynamic Polarization Curves for the Corrosion of Mild Steel in 1.0 M HCl Solution with and without different concentrations of Dodecylamine as Corrosion Inhibitor at 25.0°C Temperature.

It could be observed from the Figure that the with addition of corrosion inhibitor in acidic solution the cathodic and anodic reaction were suppressed, which suggested that both cathodic and anodic branches of Tafel curve to lower value of current density. It also shows that the inhibitor compound retard the corrosion process on the surface of mild steel. These results show the reduction of the anodic dissolution and retard the process of hydrogen evolution at cathode or controlled the cathodic and anodic reactions on the mild steel surface [65, 66]. This is due to the effect of inhibitor, which adsorb strongly on the surface at higher concentration. The different electrochemical corrosion parameters like i.e. corrosion potential ($-E_{corr}$), corrosion current density

(I_{corr}), cathodic (β_c) and anodic (β_a) Tafel constant obtained from extraplotation of polarization curves [67] and percentage corrosion inhibition efficiency are given in Tables 4.

Table 4. Potentiodynamic polarization measurements for mild steel samples in 1.0 M HCl with and without different concentration of Dodecylamine at 25.0^{0}C Temperature.

Corrosion Inhibitor Name	**Concentrations (ppm)**	**β_a(mVd^{-1})**	**β_c(mVd^{-1})**	**Rp(Ω.cm^2)**	**-E_{corr}(mV vs.SCE)**	**i_{corr}(μA cm^{-2})**	**Percentage Corrosion Inhibition Efficiencies (%I.E$_P$)**
Dodecyl Amine (25.0 °C)	0	426	1479	27.92	-450	5.14	-
	200	322	1261	63.50	-466	1.75	65.95
	400	352	1452	87.63	-485	1.40	72.76
	600	392	1159	102.17	-473	1.24	75.87
	800	292	1513	113.52	-493	0.93	81.90
	1000	281	1443	121.34	-507	0.84	83.65

In addition, from the Tables 4 that the anodic Tafel constant (β_a) and cathodic Tafel constant (β_c) values were slightly changed with addition inhibitor, this also indicates that these corrosion inhibitors affected both the anodic and cathodic reactions. But the values of cathodicTafel constant are higher than anodic which show the inhibitor effect on the cathodic hydrogen evolution reactions is more than on the anodic dissolution reactions.

The values of polarization resistance, cathodic& anodic Tafel constant were used to calculate the corrosion current density (I_{corr}). The corrosion current density (I_{corr}) calculated by using equation (8) (Stern-Geary equation).

$$I_{corr} = \frac{\beta_a X \beta_c}{2.303(\beta_a+\beta_c)} X \frac{1}{R_p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(8)}$$

Where, R_p is the polarization resistance, β_a and β_c are the cathodic and anodic Tafel constant, respectively.

There was no significant change in the E_{corr} values in the presence and absence of inhibitor in 1.0 M HClsolution which suggest that it is mixed type inhibitor [68, 69].

The inhibition efficiency (IE $_p$ %) for each concentrations of inhibitor are calculated from I_{corr} values by using following equation [83],

$$IE_p\% = (1 - \frac{I_{corr^i}}{I_{corr^0}}) \text{ x } 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(9)}$$

Where, I_{corr^0} and I_{corr^i} are the corrosion current density without and with different concentrations of inhibitor, respectively.

The maximum percentage corrosion inhibition efficiency that based on I_{corr} value was found to be 83.65% and the maximum reduction of corrosion current density I_{corr} value were found to be 0.84 μA cm^{-2} for dodecylamine at 1000 ppm concentration. It also confirms that the inhibitor is good corrosion inhibitor in 1.0 M HCl solution.

According to Ferreira and others [70, 71], if the value of displacement in corrosion potential -E_{corr} is higher than 85 mV with respect to blank solution, the inhibitor can be seen as a anodic or cathodic type corrosion inhibitor but if value of displacement in corrosion potential -E_{corr} is lower than 85 mV with respect to corrosion potential of blank solution, the inhibitor can be acts as mixed type inhibitor. In the present study, the maximum displacement in corrosion potential -E_{corr}values were found to be 57 mV for dodecylamine respectively, which are lower than 85 mV this implies that corrosion inhibitor act as mixed type of inhibitor and affects on both cathodic and anodic reactions [72]. Hence, overall result shows that there is formation of protective layers by corrosion inhibitors on mild steel surface [73].

Surface Study,

Scanning Electron Microscopy (SEM) Technique,

Surface analysis is carried out before and after immersion of mild steel samples with and without 1000 ppm concentrations of Dodecylamine corrosion inhibitors in 1.0 M HCl solution at 298, 308 and 318 K for 24 hours, using SEM (Scanning electron microscopy) technique and are shown in Figure 7 (a, b).

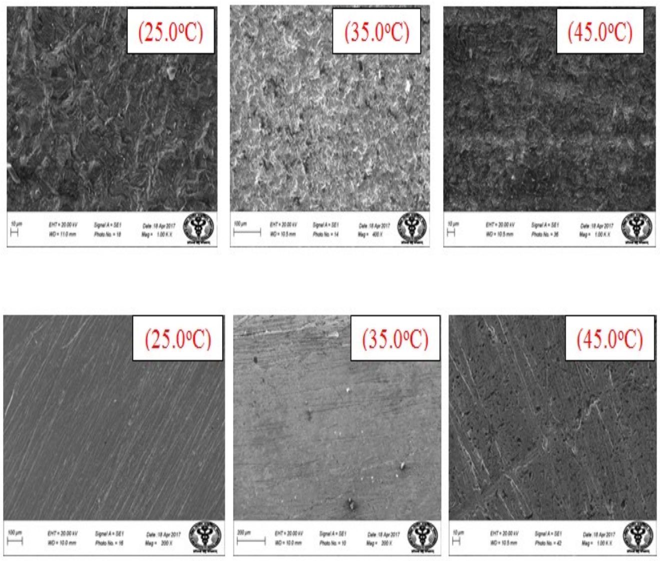

Figure 7 (a, b). SEM images of mild steel after 24 hrs immersion in (a) Blank HCl solution (b) with 1000 ppm concentration of dodecylamine.

The mild steel samples in 1.0 M HCl solution was found to be corroded and sample damages were observed in formation of large pits on to the mild steel surface (Fig. 7a).

It can be clearly seen from the SEM images of inhibitor that when mild steel samples immersed in the inhibited solution were found to be much better condition with a smooth surface with respect to blank solution (Fig. 7b). This shows that the inhibitor molecules reduce the dissolution process of MS by forming surface adsorbed layer that prevents the attack of acid on surface and thereby reducing the corrosion rate. It also confirms that the inhibitors effectively control the corrosion phenomenon by blocking the active corrosion.

IV. CONCLUSION

The following conclusions are drawn by the obtained result from different corrosion techniques used in the investigation,

1. It is found that dodecylamine act as a good corrosion inhibitor for the corrosion of mild steel in 1.0 M HCl solution at different temperature for different exposure time.
2. Weight loss measurement result shows that percentage corrosion inhibition efficiency increases with increase in concentrations of inhibitor but decreases with increase in temperature. The inhibition efficiency reaches at maximum value i.e. 88.67% respectively, at 1000 ppm concentration for 24 hrs at 298K.
3. The Langmuir adsorption isotherm was followed by dodecylamine.
4. Potentiodynamic polarization measurement indicates that dodecylamine performed as a mixed type corrosion inhibitor by decreasing both the anodic metal dissolution and cathodic hydrogen reduction reactions.
5. Electrochemical Impedance Spectroscopy data depicted that on increase in concentration of corrosion inhibitors in 1.0 M HCl solution there was increase in charge transfer resistance and decrease in double layer capacitance. Hence, percentage corrosion inhibition efficiency increases.
6. SEM (Scanning Electron Microscopy) images indicates that at maximum concentration of the inhibitor, there is formation of protective layer of corrosion inhibitor on mild steel surface with

respect to 1.0 M HCl solution in presence of corrosion inhibitors.

V. REFERENCES

[1]. G. Trabanelli, Corros, 1991, 47, 410.

[2]. Singh DDN, Singh TB, Gaur B, Corros. Sci, 1995, 37, 1005.

[3]. Shaban SM, Aiad I, El-Sukkary MM, Soliman EA, El-Awady MY, J. Mol. Liq, 2015, 203, 2.

[4]. Farag AA, Ali TA, J. Ind. Eng. Chem, 2015,21, 627.

[5]. Yousefi A, Javadian S, Dalir N, Kakemam J, Akbari J, RSC Adv, 2015, 5, 11697.

[6]. Ishwara Bhat J, Vijaya D, Alva P, Arch. Appl. Sci. Res, 2011, 3, 343.

[7]. Ostovari SM, Hoseinieh M, Pei Kari SR, Shadizadeh SJ, Hashemi, Corros. Sci., 2009, 51, 1935.

[8]. Oguzie EE, Mater. Lett, 2005, 59, 1076.

[9]. Larabi L., Harek Y, Traisnel M, Mansria A, J. Appl. Electrochem, 2004, 34, 833.

[10]. Samide A, Bibicu I, Rogalski MS, Preda M, Corros. Sci, 2005,47, 1119.

[11]. Abdallah M, Corros. Sci, 2004, 46, 1981.

[12]. Ashassi-Sorkhabi H, Ghasemi Z, Seifzadeh D, Appl. Surf. Sci, 2005,249, 408.

[13]. Samide A, Bibicu I, Surf. Interf. Anal, 2008, 40, 944.

[14]. Bentiss F, Lagrene´e M, J. Mater. Environ. Sci, 2011, 2, 13.

[15]. Obi-Egbedi NO and Obot IB, Corros. Sci., 2011, 53, 263.

[16]. Daoud D, Douadi T, Issaadi S and Chafaa S, Corros. Sci, 2014, 79, 50.

[17]. Markhali BP, Naderi R and Mahdavian M, J. Electroanal.Chem, 2014,56, 714.

[18]. Hegazy M A, Badawi AM, Abd El Rehim SS and Kamel WM, Corros. Sci, 2013, 69, 110.

[19]. Ongun Yuce A, Do˘gru Mert B, Kardas G¸ and Yazıcı B, Corros. Sci, 2014, 83, 310.

[20]. Hosseini SMA, Salari M, Jamalizadeh S, Khezripoor S, Seifi M, Mater. Chem. Phys, 2010, 119, 100.

[21]. Abdallah M, Helal EA, Fouda AS, Corros. Sci, 2006, 48, 1639.

[22]. Khaled KF, Appl. Surf. Sci, 2010, 256, 6753.

[23]. Ozcan M, Dehri I, Prog. Org. Coat, 2004,51, 181.

[24]. Larabi L, Benali O, Harek Y, Mater. Lett, 2007, 61, 3287.

[25]. Abd El-Maksoud SA, Hassan HH, Mater. Corros, 2007, 58, 369.

[26]. Mernari B, Attari HEl, Traisnel M, Bentiss F, Lagrenee M, Corros. Sci, 1998, 40, 391.

[27]. Umoren SA, Eduok UM, Oguzies EF, Port. Electrochem. Acta, 2008, 26, 533.

[28]. Rastoyi RB, Singh MM, Singh K, Yadav M, Port. Electrochem.Acta, 2005, 22, 315.

[29]. ASTM G, Standard practice for Laboratory Immersion Corrosion Testing of Metals, ASTM, West Conshohocken, PA, 1990, 31.

[30]. Divakara Shetty S, Shetty P, Sudhaker Nayak HV, Indian J. Chem. Technol, 2005, 12, 462.

[31]. Muralidharan S, Chandrasekar R, Iyer SVK, Proc. Indian Acad. Sci. (Chem. Sci.), 2000, 12, 127.

[32]. Horvath T, Kalman E, Kutsan G and Rauscher A, Br. Corr. J., 1994, 29, 245.

[33]. Gunasekaran G, Natarajan R, Muralidharan VS, Palaniswamy N and Apparao BV, Ind. J. Chem. Technol, 1998, 5, 91.

[34]. Gunasekaran G, Natarajan R, Muralidharan VS, Palaniswamy N, and Apparao BV, Proc. Ind. Acad. Sci. (Chem.Sci.), 1996, 108, 399.

[35]. Wang L, JianYin G and Guo Yin J, Corr. Sci., 2001, 43, 1197

[36]. Naqvi I, Saleemi AR, Naveed S, Int. J. Electrochem. Sci, 2011, 6, 146.

[37]. Oguzie EE, Unaegbu C, Ogukwea CN, Okolue BN, Onuchuku A I, Mater. Chem. Phys., 2004, 84, 363.

[38]. Li XH , Deng SD, Fu H, Corros. Sci, 2012, 62,163.

[39]. Bobina M, Kellenberger A, Millet JP, Muntean C, Vaszilcsim N, Corros. Sci., 2013, 69, 389.

[40]. Morad M S, J. Appl. Electrochem, 2008, 38, 1509.

[41]. Musa AY, Kadhum AAH, Mohamad AB, Rahoma AAB, Mesmari H, J. Mol. Struct.-Theochem, 2010, 969, 233.

[42]. Flis J, Zakroczymski T, J. Electrochem. Soc, 1996, 143, 2458.

[43]. Khamis E, Bellucci F, Latanision RM, El-Ashry ESH, Corros, 1991, 47, 677.

[44]. Obot IB, Obi-Egbedi N O, Umoren SA, Corros. Sci, 2009, 51, 1869.

[45]. Cano E, Polo JL, La Iglesia A, Bastidas JM, Adsorption, 2004, 10, 219.

[46]. Li W, He Q, Zhang S, Pei C, Hou B, J. Appl. Electrochem., 2008, 38, 289.

[47]. Bentiss F, Lebrini M, Lagrenee M, Corros. Sci, 2005, 47, 2915.

[48]. Khamis A, Saleh MM, Awad MI, El-Anadouti BE, Corros. Sci, 2013, 74, 83.

[49]. Negm NA, Elkholy YM, Zahran MK, Tawfik SM, Corros. Sci, 2010, 52, 3523.

[50]. Obi-Egbedi NO, Obot IB, Corros. Sci, 2011, 53, 263.

[51]. €Ozcan M, Karadag F, Dehri I, Acta Phys. Chim. Sin, 2008, 24 , 1387.

[52]. Wang X, Yang H, Wang F, Corros. Sci, 2011, 53, 113.

[53]. Cao CN, Zhang JQ, Science Press, Beijing, 2002, 172 (in Chinese).

[54]. Behpour M, Ghoreishi SM, Mohammadi N, Soltani N, Salavati-Niasari M, Corros. Sci, 2010, 52, 4046.

[55]. Lebrini M, Lagrene'e M, Vezin H, Traisnel M, Bentiss F, Corros. Sci, 2007, 49, 2254.

[56]. Wang X, Yang H, Wang F, Corros. Sci, 2011, 53, 113.

[57]. Behpour M, Ghoreishi SM, Soltani N, Salavati-Niasari M, Hamadanian M, Gandomi A, Corros. Sci, 2008, 50, 2172.

[58]. Amin MA, Khaled KF, Mohsen Q, Arida HA, Corros. Sci, 2010, 52, 1684.

[59]. Qu Q, Jiang SA, Bai W, Li L, Electrochim. Acta, 2007, 52, 6811.

[60]. Samardzija KB, Lupu C, Hackerman N, Barron AR, Luttge A, Langmuir, 2005, 21, 12187.

[61]. Roy P, Karfa P, Adhikari U, Sukul D, Corros. Sci, 2014, 88, 246.

[62]. Solmaza R, Kardas G¸ Ulha MC, Yazıcı B, Erbil M, Electrochim. Acta, 2008, 53, 5941.

[63]. Daoud D, Douadi T, Issaadi S, Chafaa S, Corros. Sci, 2014, 79, 50.

[64]. Elayyachy Hammouti B, El Idrissi A, Appl.Surf. Sci, 2005, 249, 176.

[65]. Khaled KF, Hackerman N, Electrochim. Acta, 2003, 48, 2715.

[66]. Olivares O, Likhanova NV, Gomez B, Navarrete J, Llanos-Serrano ME, Arce E, Hallen JM, Appl. Surf. Sci, 2006, 252, 2894.

[67]. Zhao J, Duan H, Jiang R, Corros. Sci, 2015, 91, 108.

[68]. Quraishi MA, Rafiquee MZA, Khan S and Saxena N, J. Appl. Electrochem, 2007, 37, 1153.

[69]. Ahamad I, Prasad R and Quraishi MA, J. Solid State Electrochem, 2010, 14, 2095.

[70]. Ferreira ES, Giancomelli C, Giacomelli FC, Spinelli A, Mater. Chem. Phys, 2004, 83, 129.

[71]. Li WH, He Q, Pei CL, Hou B R, J. Appl. Electrochem, 2008, 38, 289.

[72]. Hegazy MA, Hasan AM, Emara MM, Bakr MF, Youssef AH, Corros. Sci, 2012, 65, 67.

[73]. Wang X, Yang H, Wang F, Corros. Sci, 2011, 53, 113.