Iraqi Journal of Chemical and
Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.4 (December 2016) 1- 10
ISSN: 1997-4884

University of Baghdad
College of Engineering

Corrosion Inhibition of Carbon Steel in Hydrochloric Acid under Dynamic Conditions

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Abstract

In this work, studying the effect of ethylenediamine as a corrosion inhibitor was investigated for carbon steel in aerated HCl solution in range of 0.1-1N under dynamic conditions, i.e., rotational velocity of 400–1200 rpm in the temperature range 35 – 65 ºC. Weight loss method was employed in absence and presence of the inhibitor as an adsorption type in concentration range 1000 – 5000 ppm using rotating cylinder specimens. The experimental results showed that corrosion rate in absence and presence of inhibitor is increased with increasing temperature, rotational velocity and concentration of acid. It is decreased with increasing inhibitor concentration for the whole range of temperature, rotational velocity and concentration of acid solution. Under these conditions maximum inhibition efficiency obtained was 86% while minimum inhibition efficiency was 36%. The adsorption of this inhibitor on carbon steel surface is found to obey Langmuir adsorption isotherm.

Key words: corrosion inhibition, carbon steel, hydrochloric acid, ethylenediamine, weight loss method, rotating cylinder.

Introduction

Carbon steel is employed widely in most industries due to its low cost, availability and ease of fabrication for various applications, e.g., condenser and heat exchanger tubes, tanks [1]. The corrosion of carbon steel in such environments and its inhibition constitute a complex problem. The pipelines, etc. Corrosion characteristics of steel in aggressive mineral acid media have been widely investigated. Corrosion of iron and its alloys and inhibition by different organic inhibitors in acid solutions have been studied by several authors [2]. Hydrochloric acid is widely used for the removal of rust and scale in several industrial operations. It is the most difficult of common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys. Corrosion inhibition is the most common way of mitigating internal-walls corrosion in industrial facilities (pipelines, tanks, reactors, etc.). Most of the well-known corrosion inhibitors are organic compounds containing nitrogen, sulfur and/or oxygen atoms

[3]. The corrosion protection by these inhibitors is based mostly on the modification of metal surfaces by surface adsorption of these molecules and subsequent formation of a protective (blocking) surface layer as self-assembled-monolayers (SAMs) on the metal surface, since these types of layers have been shown to offer better protection and tailoring (functionalization) properties than non-structured (amorphous) adsorbed layers.

Experimental Work

The experimental work is divided into two parts, the first part using weight loss in order to determine the average corrosion rates without inhibitor under the following temperatures 35, 42, 50, 58 and 65 °C, velocities 400, 570, 800, 1030 and 1200 rpm, and acid concentrations0.1, 0.29, 0.55, 0.81 and 1N. These were performed to assess corrosion behavior of carbon steel. Second part was executed in order to determine average corrosion rates in the presence of the inhibitor in the concentration range of 1000, 2000, 3000, 4000 and 5000 ppm and velocities of 400, 570, 800, 1030 and 1200 rpm, and acid concentration of 0.1, 0.29, 0.55, 0.81 and 1N which was performed to assess corrosion rates of carbon steel. These were executed at three temperature 35, 50, 65 °C. Also, measurement of corrosion potential as a function of time against Saturated Calomel Electrode (SCE) was made for all weight loss experiments in parts 1 and 2. Cylindrical carbon steel specimens were prepared in triplicate using a rotatable specimen’s holder. The surface area of each specimen was 7.85 cm^2 having dimensions of 1 cm long (L) and 2.5 cm outside diameter (d_o) which were measured using electronic digital caliper. The chemical composition of carbon steel is shown in Table 1. It was analyzed by (XRF) in the Department of Engineering Inspection, Directorate of Technical Affair, Ministry of Science and Technology.

Table 1 Chemical composition of carbon steel metal

C	Mn	Cu	Mo	Fe
0.09	0.57	0.18	0.06	Balance

A rotating shaft holder made of Teflon on which three carbon steel specimens were fixed for rotation. The dimensions and shape of RCE are shown in Figure 1.

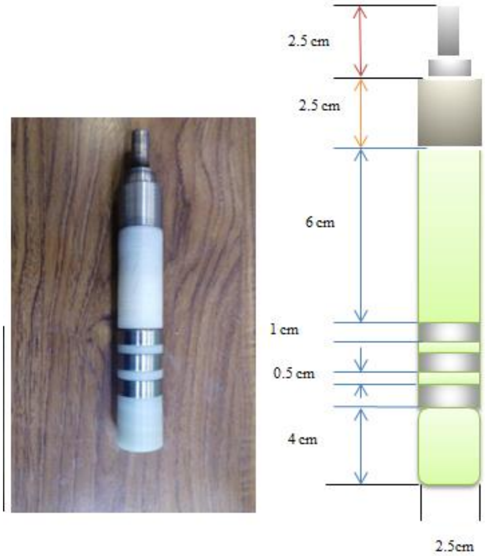


Fig. 1: rotating shaft holder, dimensions in (cm)

Five different solutions were prepared by diluting concentrated acid 11.5N using distilled water where the above concentration was prepares according to the flowing formula:

$$N_1V_1 = N2\,V_2 \qquad ...(1)$$

The inhibitor used (ethylenediamine) is a colorless viscous liquid to light yellow substance at ambient temperature with purity 99.9 and structure formula $C_2H_8N_2$.

Experimental Procedure

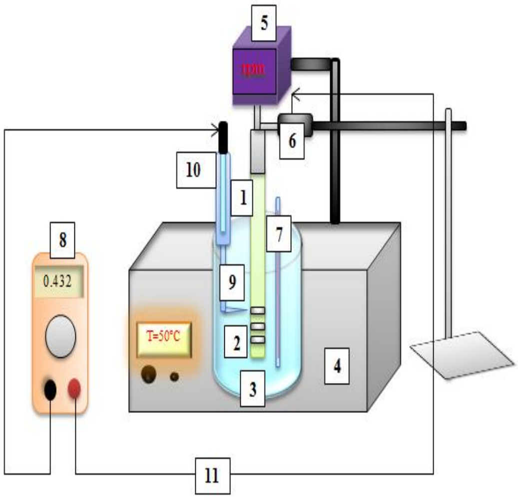
Before each experiment the carbon steel specimen (working electrode) was abraded with glass emery paper of grade numbers; 180, 220, 400 and 2000 respectively, washed continuously with brushing by plastic brush under running tap water, followed by distilled water, dried with a clean tissue, rinsed with acetone and dried with clean tissue, followed by ethanol and dried with clean tissue. After that they were exposed to corrosion environment for 2 h immersion at desired concentrations of acid, and inhibitor. After each test, the specimen was washed by running tap water with brushing to remove the weakly adherent corrosion products formed on the specimen surface, washed with tap water, followed by distilled water, dried with clean tissue, rinsed with acetone, dried with clean tissue, followed by ethanol, dried with clean tissue, then the specimen was kept in a desiccator for 24 h to dry over silica gel, and accurately weighed to the fourth decimal of gram (w2) to determine corrosion rate as follows:

$$C.R = (\Delta W)/(A \times t) \qquad \ldots(2)$$

For a rotating cylinder electrode with outer diameter, do (m), Reynolds number is given by:

$$Re = (\rho\ do\ u)/\mu \qquad \ldots(3)$$

The experimental runs were carried out in triplicate using the holder shown in Figure 1. Average corrosion was calculated and reported in present work. Corrosion potential of the working electrode was recorded as a function of time against Saturated Calomel Electrode SCE using Lugging capillary tip placed at a distance of 1- 2 mm from the working electrode. An impedance voltmeter was used to read the potential directly.



1 Rotating shaft (holder), 2 Working electrode (specimen), 3 Beaker, 4 Water bath, 5 Stirrer, 6 Brush, 7 Thermometer, 8 Voltmeter, 9 Luggin capillary tip, 10 Reference Saturated Calomel Electrode (SCE), 11 Electrical wires

Fig. 2: Half-cell set- up

Results and Discussion

The experimental work and the results analysis are employ to second-order Rotatable Design Box-Wilson Design [4], which is also known as Central Composite Rotatable Design (CCRD) was used for experimental layout. In order to minimize the number of experimental runs for determining the corrosion rate of carbon steel due to hydrochloric acid, second order rotatable design of three independent variables was adopted. Second order rotatable design was used to obtain the response within the region of the dimensional observation spaces, which allows one to design a minimal number of experimental runs. Corrosion behavior of carbon steel in hydrochloric acid solution with and without inhibitor was studied under different conditions stated above. Anodic reaction, which is the dissolution process of iron:

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \qquad \ldots(4)$$

Since the environment is acidic solution and not deaerated, so one of the cathodic reaction takes place is oxygen reduction expressed as:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad \ldots(5)$$

The other cathodic reaction takes is hydrogen evolution reaction expressed as:

$$2H^+ + 2e^- \longrightarrow H_2 \quad \ldots(6)$$

a. Uninhibited Solutions

Effect of Velocity and Temperature on the Corrosion Rate

From Figure 3 It is clear that increasing the flow velocity leads to an increase in the corrosion rate as presented for a given temperature. This can be attributed to the increase in the transport rate of oxygen close to the metal surface by eddy transport. The rate of oxygen reduction reaction is generally limited by the speed at which oxygen can reach the surface of the metal. Previous studies [5, 6] indicate that the greater turbulence due to high velocities results in more uniform oxygen concentration near the surface, and that is clear in Figure 4 where corrosion rate at 570 rpm (Re = 28827) is lower than that at 1030 rpm (Re = 52092) for a given temperature. From Figure 4 It is clear that the corrosion rate increases with increasing temperature at a given rotational velocity. Increasing temperature leads to change two variables that act in a conflicting way. Firstly, increasing temperature accelerates the reaction rates of both reactions as dictated by Arrhenius equation. Moreover, diffusion rate of dissolved oxygen is also increased due to increased molecular diffusion coefficient. Secondly, as the temperature increases the oxygen solubility decreases [7, 8]. This is clear in Figure 3 Where corrosion rate at 58 ^{o}C is higher than that at 42 ^{o}C. Therefore; increasing Re (or velocity) will increase Increasing amount of oxygen arriving to the surface and hence the corrosion rate is increased. Increasing (Re) leads to decrease the thickness of diffusion layer in the wall vicinity that represents the main resistance to oxygen transport [9]. Figure 5 illustrates that the corrosion rate increases with increasing velocity, but at high velocities the corrosion rate is nearly constant with increasing velocity. This is attributed to limited influence of agitation at high velocities. Figure 6 and Figure 7 Show the 3D surface plot of corrosion rate against temperature and velocity.

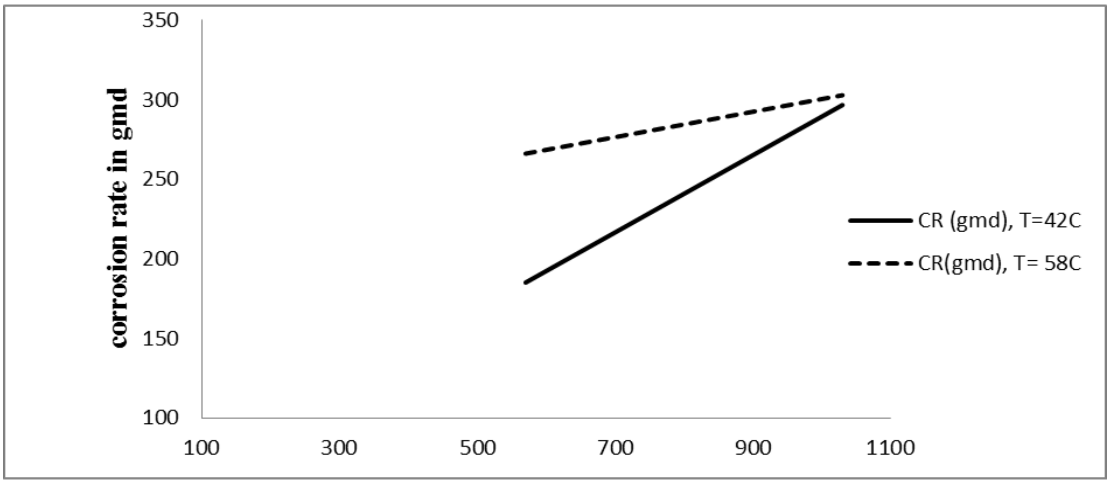


Fig. 3: Variation of corrosion rate with velocity at different temperatures in acid concentration of 0.29 N for 2 h immersion time

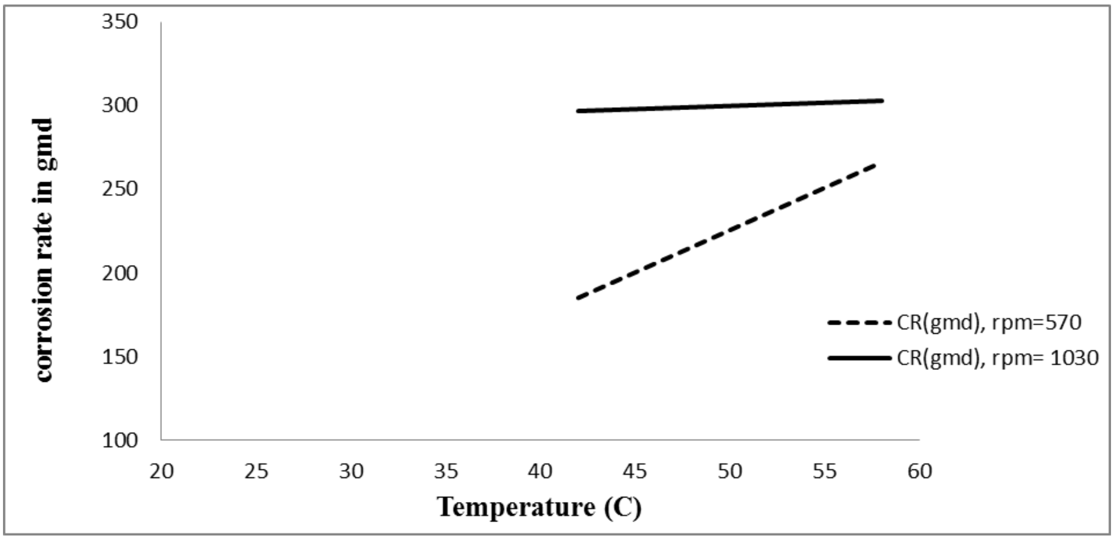


Fig. 4: Variation of corrosion rate with temperature at different rotational velocities and 0.29 N acid concentration for 2 h immersion time

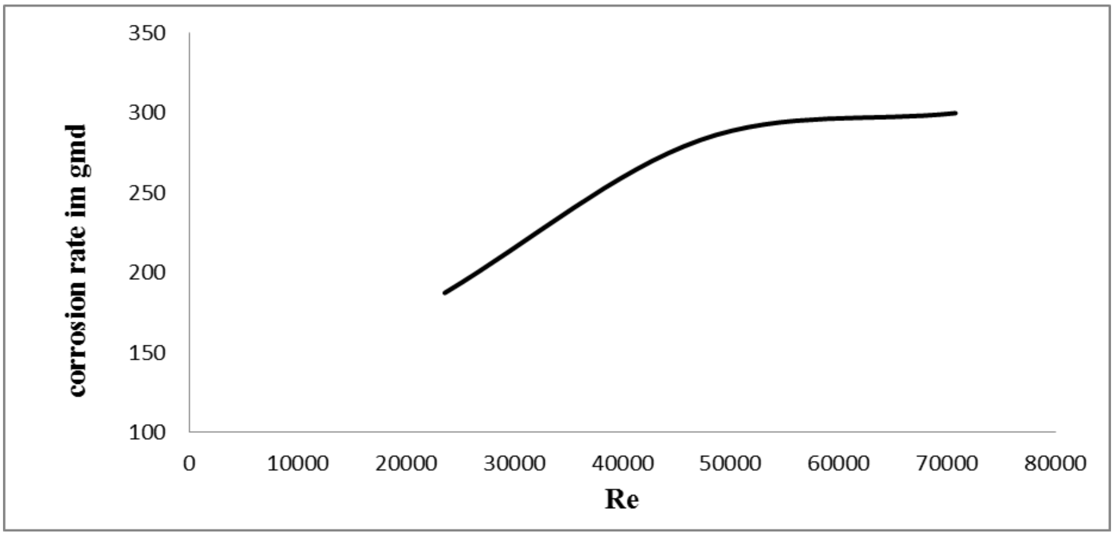


Fig. 5: Variation of corrosion rate with Re at 50 ^{o}C and 0.55 N acid concentration for 2 h immersion time

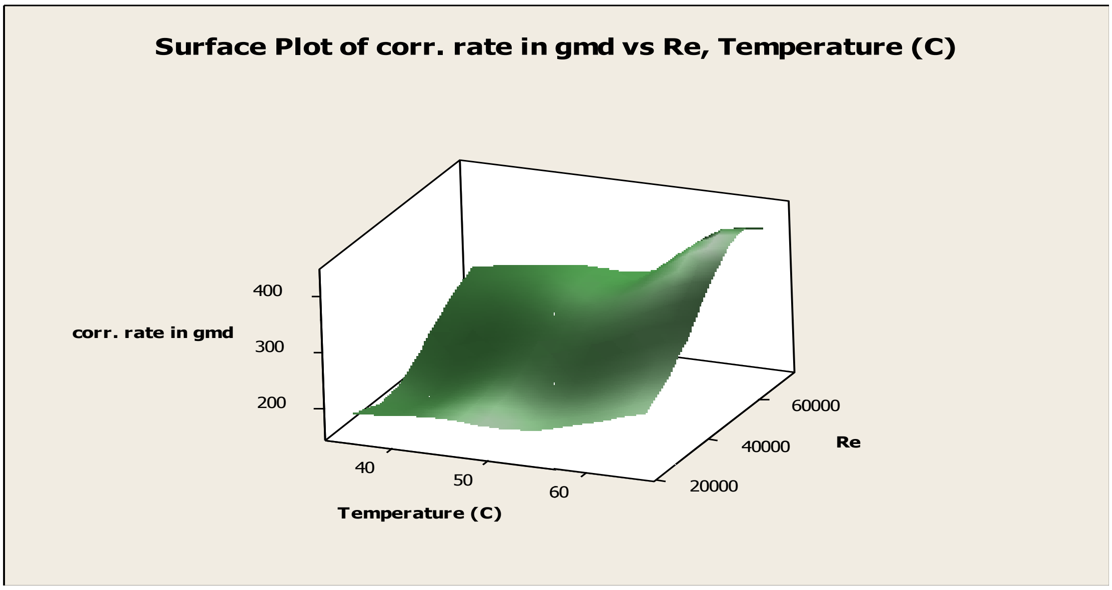


Fig. 6: 3D surface plot of corrosion rate against temperature and velocity

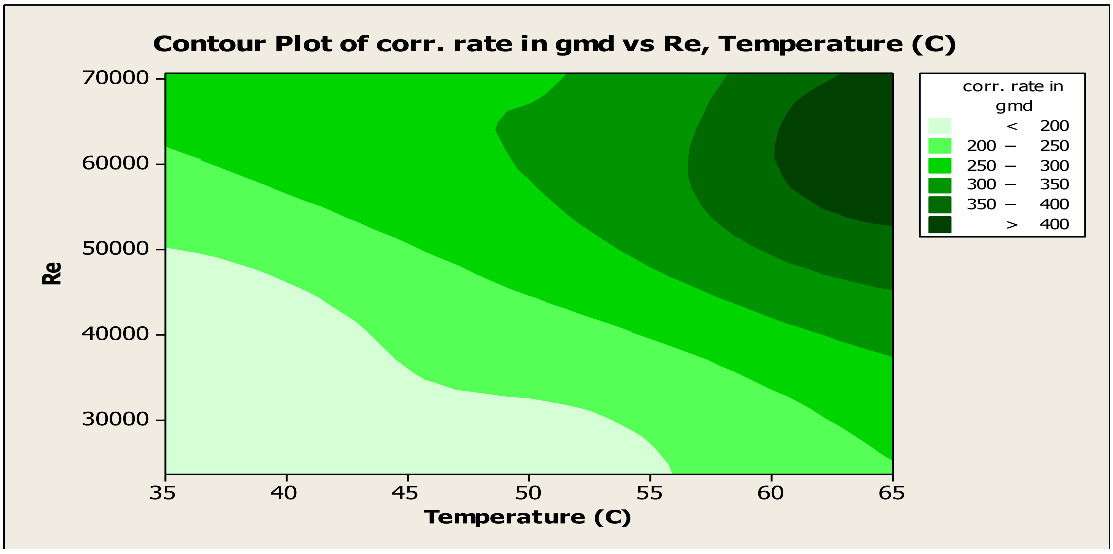


Fig. 7: Contour plot of corrosion rate against temperature and velocity

Corrosion Kinetic Parameters

In general, the rate of most chemical reactions increases with temperature following Arrhenius equation. Temperature favors the kinetics of corrosion reactions and more specifically, the anodic dissolution of the metal. The activation energy of the corrosion process can be obtained from the plots of Arrhenius according to the following equation:

$$\text{Corrosion rate} = A\,e^{-Ea/RT} \qquad \ldots(7)$$

Where Ea is the activation energy of the process (J/mol), R is the universal gas constant (8.314 J/ (mol.K)), T is the temperature (K) and A Arrhenius is a constant. Taking the logarithm of the Arrhenius equation yields:

$$\text{Log (Corrosion rate)} = \text{Log A} - \frac{Ea}{2.303\ RT} \qquad \ldots(8)$$

The value of activation energy of corrosion in 0.81 N HCl can be determined from the slope of Log (Corrosion rate) versus 1/T plots. Actual values of activation energy for each case of carbon steel corrosion with temperature variations in the range of 35 to 65 ^{o}C and rotational velocity, i.e., 570, 800, and 1030 rpm are plotted according to Equation 7 in Figure 8 and Figure 9. From the gradient of the plotted curves, the calculated Ea values are listed in Table 2.

b. Inhibited Solutions

Effect of Velocity and Temperature in Presence of Inhibitor on Corrosion Rate

Figure 10 indicates the variation of corrosion rate with flow velocity in absence and presence of 3000 ppm at 50 ^{o}C and 2 h immersion time. One can see from Figure 10 That the corrosion rate increases with velocity at 50 ^{o}C in the absence of the inhibitor. It decreases with the addition of inhibitor i.e., at constant temperature, the corrosion rate increases with increasing flow rate. These increases are much lower than that in uninhibited solutions. An increase in the rotational velocity from 400 to 1200 rpm (Re of 23579 to 70743) at 3000 ppm inhibitor concentration and 50 ^{o}C (central condition of rotatable design) gives an inhibition efficiency of 70%, 64%, 51% at 400, 800 and 1200 rpm respectively. Figure 11 shows the variation of corrosion rate with temperature in the absence and presence of 3000 ppm of the inhibitor concentration at 800 rpm and 0.55 N acid solution concentration. Figure 11 clearly shows concentration acid the corrosion rate increases with increasing temperature at 800 rpm without the inhibitor, while it decreases with its addition, i.e., at constant velocity. These increases are much lower than that in uninhibited solutions. An increasing in the temperature from 35 to 65 ^{o}C at 3000 ppm inhibitor concentration and 800 rpm in 0.55 N acid concentration (central condition of rotatable design), the inhibition efficiency is found to be 67%, 64%, and 47% at 35, 50 and 65 ^{o}C respectively. As shown in Figure 11 The corrosion rate linearly increases with the increase of temperature. In an inhibited acid at an elevated temperature the metal dissolution reaction is complex and causes the following changes [11]: a) Desorption of pre-adsorbed inhibitor molecules occur from metal surface.

b) The active area of the metal surface changes because of rapid etching.

c) Decomposition and rearrangement of some inhibitors may take place.

d) Heterogeneous reaction rate increases at uninhibited metal surface. The adsorption and desorption of inhibitor molecules continuously occur at the metal surface. At a particular temperature equilibrium is set up between these two processes.

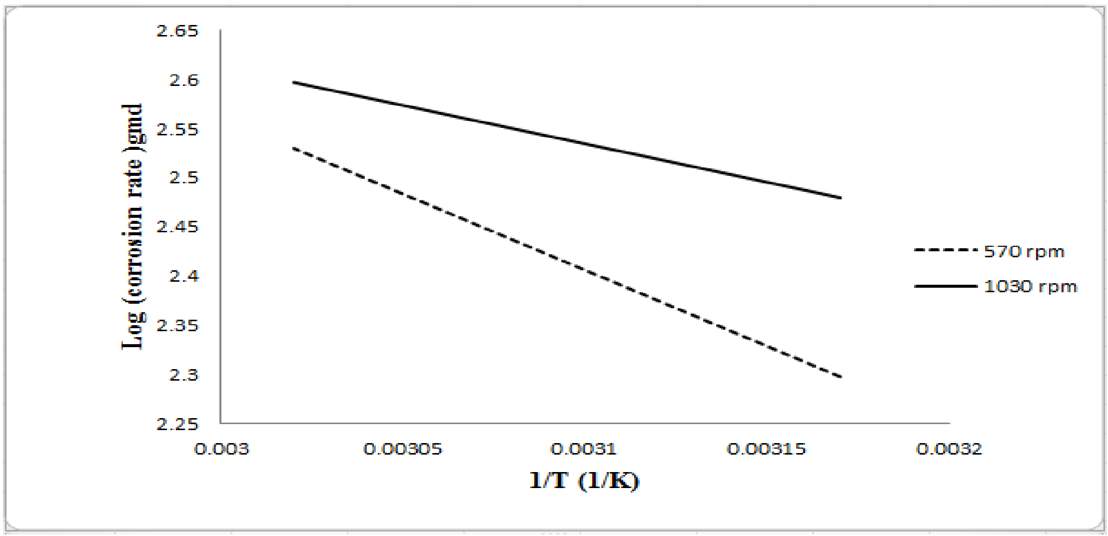


Fig. 8: Arrhenius plots in 0.81 N HCl, uninhibited solution

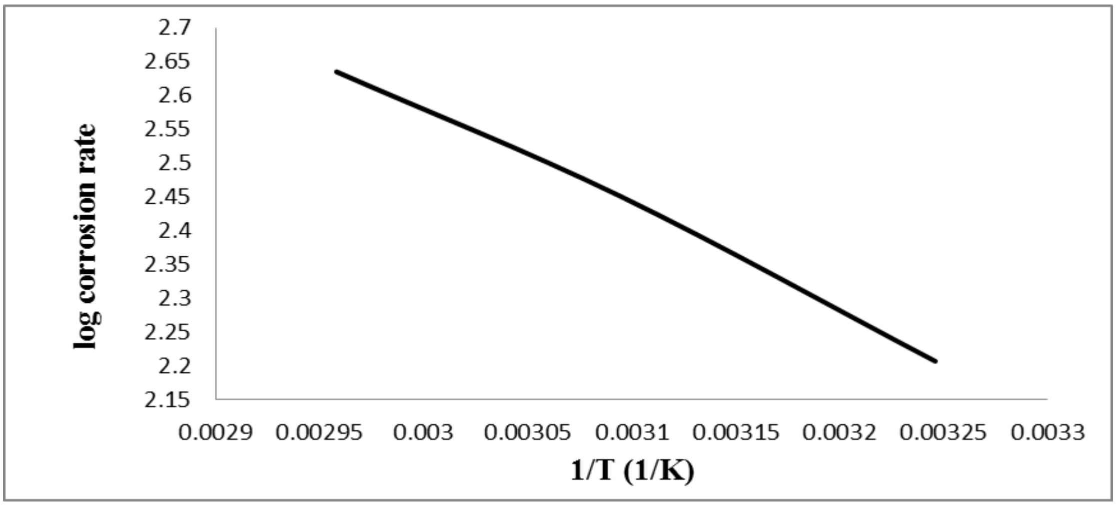


Fig. 9: Arrhenius plots in 0.0.55 N HCl, uninhibited solution and velocity 800 rpm

Table 2: Activation energy values for uninhibited solutions

Velocity (rpm)	Ea (KJ/mol)	Log A (gmd)	Conc.of solution (N)
570	14.99	2.52	0.81
800	29.6	2.82	0.55
1030	29.32	2.64	0.81

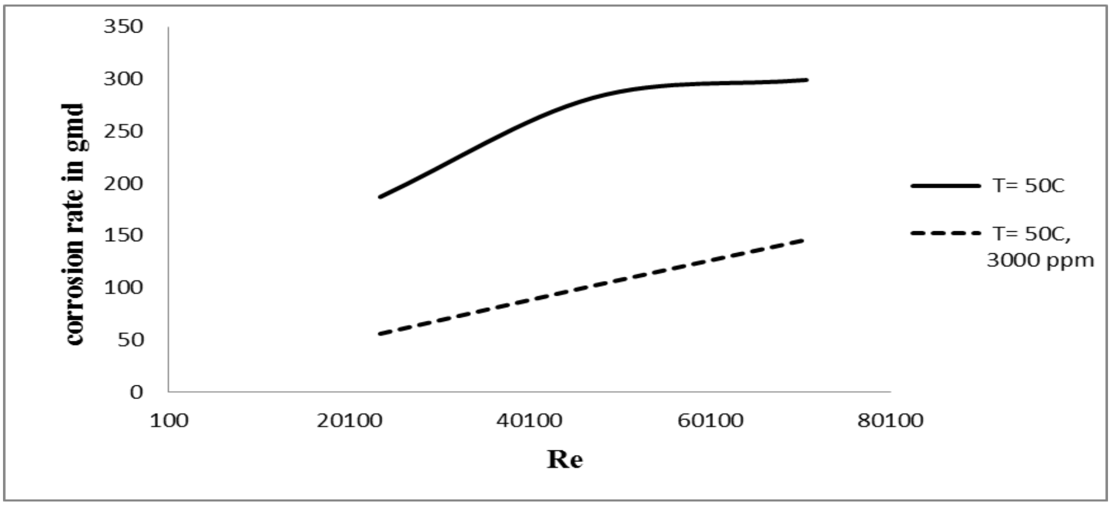


Fig. 10: Variation of corrosion rate with Re in the presence of 3000 ppm and concentration solution 0.55 N for 2 h immersion time

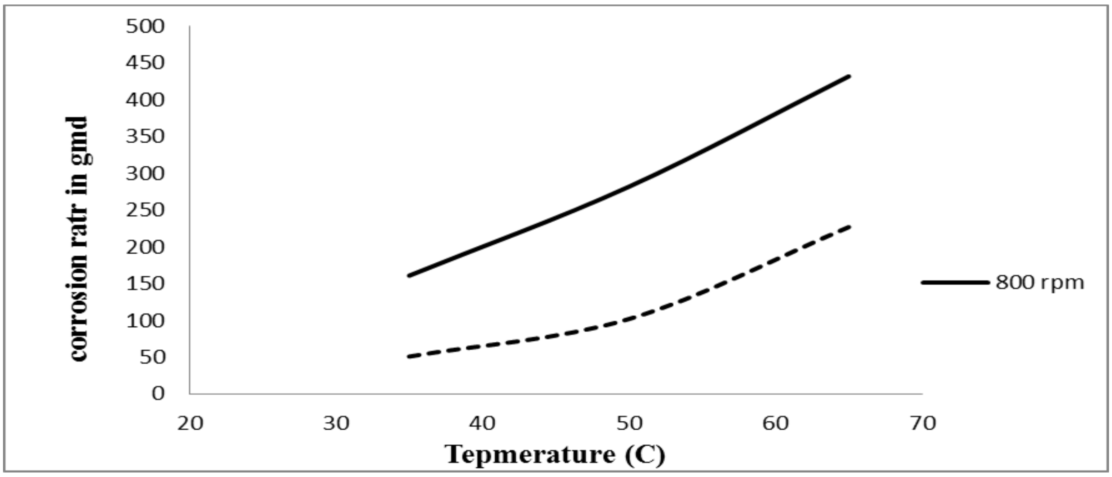


Fig. 11: Variation of corrosion rate with temperature in the absence and presence of 3000 ppm concentration inhibitor and 0.55 N solution concentration at 800 rpm and 2 h immersion time

Figure 12 illustrates the variation of IE% with inhibiting concentration at 800 rpm and 35 ^{o}C in 0.55 Nacid solution. Figure 12 shows that the inhibition efficiency for 800 rpm is 86% at 5000 ppm and 67% and 48% at 3000 ppm and 1000 ppm respectively. This reveals that the efficiency at 5000 ppm is almost high, and this means that these concentrations (Figure 12) are good enough to form a protective layer. The surface coverage (θ) data are very useful while discussing the adsorption characteristics [12]. The surface coverage of inhibitor at a given concentration is calculated using the following equation:

$$\theta = 1 - \frac{(C.R.)_{in}}{(C.R.)_{un}} \qquad \dots(9)$$

Where $C.R_{in}$ and $C.R_{un}$ are the corrosion rates with and without inhibitor respectively. The corrosion rate data can be used to analyze the adsorption mechanism. The Langmuir isotherm is expressed as:

$$\theta = \frac{KC}{1+KC} \qquad \dots(10)$$

Where K is the equilibrium constant for the adsorption isotherm representing the degree of adsorption (i.e. the higher the value of K indicates that the inhibitor is strongly adsorbed on the metal surface. C is inhibitor concentration (ppm) and θ is the surface coverage. Rearranging equation will give:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad \dots(11)$$

Figure 13 shows plots of C/θ vs. C for ethylenediamine as corrosion inhibitor in 0.55 N HCl acid at 35, 50 and 65 ºC. The data fit straight lines indicating that ethyelendiamine is adsorbed according to the Langmuir adsorption isotherm from the intercept of straight line on the C/θ axis, K values are to be calculated as given in Table 3. The rectilinear natures of Figure 13 indicate an increase in adsorption with an increase in concentration of and that adsorption occurs in accordance with Langmuir adsorption equation. It is also noted in Figure 13 that the lines accumulated and approximately looked like one line this is due to the very close range of inhibition efficiency (36 – 86%).

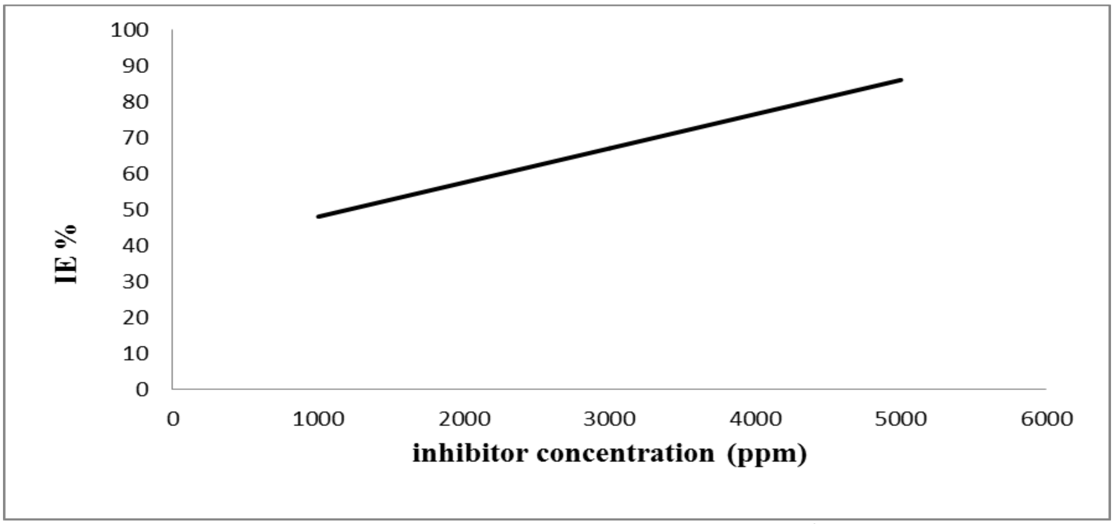


Fig. 12: Variation of IE% with inhibitor concentration at 800 rpm and 35 ^{o}C in 0.55 N acid solution

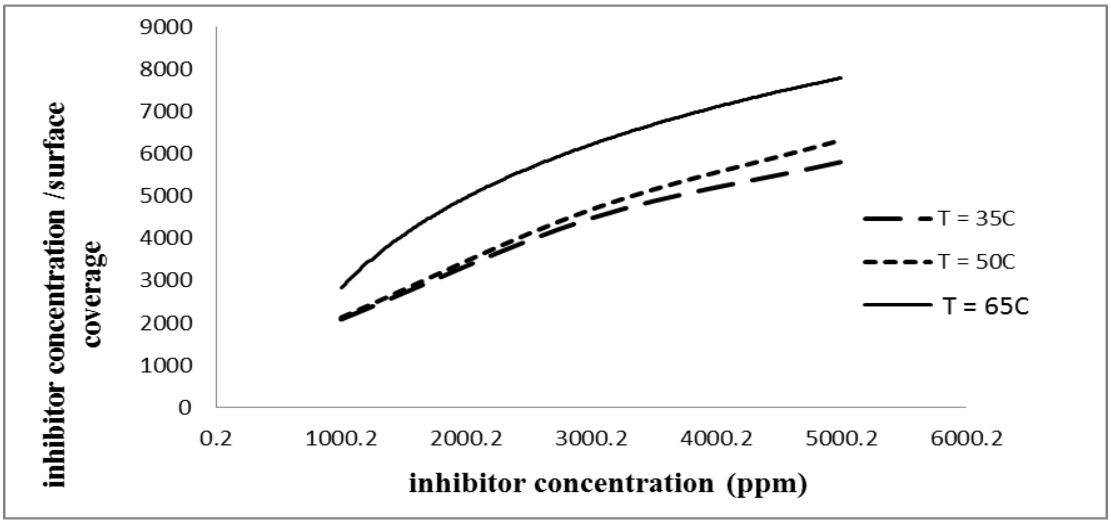


Fig. 13: Langmuir adsorption isotherm of ethylenediamin on low carbon steel in 0.55 N HCl and 800 rpm as flow velocity at different temperature

Table 3: Equilibrium Constant for Langmuir Type Adsorption of the inhibitor in 0.55 N HCl acid solution and 800 rpm as flow velocity at different temperatures

Temperature (^{o}C)	K value (g/l)	slope
35	0. 97	1.07
50	0. 5	1.12
65	0. 34	1.22

Conclusions

1. Corrosion rate in absence and presence of the inhibitor is increased with the increasing temperature of the corrosive solution and the rotational velocity.
2. Corrosion rate decreases with increasing the inhibitor concentration for the whole range of temperatures and rotational velocities.
3. The efficiency of inhibitor increases with increasing inhibitor concentration and also increases with decrease in temperature and flow velocity.
4. The maximum inhibition efficiency obtained was 86% and the minimum inhibition efficiency obtained was 36%.
5. Increased adsorption with an increase in concentration of inhibitor and that adsorption occurs in accordance with Langmuir adsorption isotherm.

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