Performance Of some Corrosion Inhibitors For Carbon Steel In Hydrochloric Acid

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Abstract:

Corrosion tests on commercial carbon steel pipe in aerated 0.1N HCl solution under static and flow conditions with ranges of rotation velocity of 400–1400 rpm and temperature of 35 – 60ºC, were carried out by weight loss method, in absence and presence of several inhibitors which were thiourea, ethylenediamine, diethanolamine and formaldehyde as an adsorption type inhibitors in concentration range 400 – 2000 ppm using rotating cylinder arrangement. The experimental results showed that the corrosion rate in absence and presence of inhibitors is increased with the increasing temperature of the corrosive solution and the rotational velocity and is decreased with increasing the inhibitors concentration for the whole range of temperatures and rotational velocities. Highest inhibition efficiency was attained by thiourea with considerable efficiencies for other inhibitors. The order of corrosion inhibitors efficiencies was as follows: thiourea > ethylenediamine > diethanolamine > formaldehyde. Under static conditions maximum inhibition efficiency obtained was 77.59% for thiourea and the minimum inhibition efficiency was 37.12% for formaldehyde depending on inhibitor concentration and temperature. Also the results revealed that the inhibitors efficiency increases with increasing its concentration and decreases with increasing agitation speed and temperature. The thiouurea was found to be good inhibitor even at high agitation velocity while the formaldehyde failed to inhibit corrosion at high velocity.

Key words: corrosion inhibitors, carbon steel, hydrochloric acid, agitation velocity, inhibition efficiency.

Introduction :

The corrosion of metals remains a world-wide scientific problem as it affects the metallurgical, chemical and oil-industries. The increasing interest in the manufacture of hydrochloric acid has created the need for obtaining information on the corrosion resistance of mild steel to hydrochloric acid attack. Of particular importance also is the need to introduce certain organic compounds as inhibitors into the mild steel/corrodent system to prevent corrosion of the mild steel. Mild steel corrosion in acid solution has been effectively controlled by the use of organic substances containing nitrogen, oxygen, or sulphur in the conjugated system as inhibitors [1, 2]. The corrosion of mild steel in HCl solution is Aheterogeneous one, comprising of anodic and cathodic reactions [3]. Corrosion inhibitor is a substance which, when added to an Environment decreases the rate of attack by the environment of a metal. Corrosion inhibitors are usually added in small amounts to acids, cooling waters, steam, and other environments, either continuously or intermittently to prevent serious corrosion. The efficiency of an inhibitor is thus expressed by the following equation:

Inhibitor efficiency (%) =

$$100(CR_{uninhibited} - CR_{inhibited)}/CR_{uninhibited})$$

where $CR_{uninhibited}$ is the corrosion rate of the uninhibited system and $CR_{inhibited}$ is the corrosion rate of the inhibited system [4, 5]. The range of inhibitors is wide and the way to classify them is by considering their mechanism action and their composition: adsorption type inhibitors, hydrogen-evolution poisons, scavengers, oxidizers, vapor-phase inhibitors etc.

Currently, researches are focused on producing and testing environmentally friendly corrosion inhibitors. A feasible solution to this problem is the use of corrosion inhibitors derived from amino compounds; these compounds constitute an important potential class of corrosion inhibitors. Amino acids have been successfully used as corrosion inhibitors in many practical applications, because they are friendly to the environment and have very low toxic [6]. This work aims to investigate the performance of some selected organic substances as corrosion inhibitors which are thiourea, ethylenediamine, diethanolamine, and formaldehyde to inhibit corrosion of carbon steel in aerated 0.1N HCL under static and flow conditions in order to assess the influence of temperature, hydrodynamic, and concentration on the performance of these inhibitors.

Experimental work:

The Fig (1) shows the experimental arrangement that was used to investigate the inhibitive action of formaldehyde (HCHO), thiourea (CSN2H4), ethylenediamine ($(H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2)$ and diethanolamine ($HN(CH_2CH_2OH)_2$) as adsorption type inhibitors on the corrosion behavior of carbon steel in 0.1 N HCl aerated solution, for temperatures of 35 ^oC, 45 ^oC and 60 °C at rotational speeds for specimen of 0, 400, 700, 1000 and 1400 rpm. The electrolyte was hydrochloric acid of concentration 37% which has a molecular weight of 36.64 g/gmol and a density of 1180 gm/cm^3.The concentrated acid was diluted using distilled water to obtain the required normality of 0.1 N. Acetone and ethanol of concentrations ≅ 99% were used for sample degreasing and cleaning. The experimental apparatus was composed of the followings: thermometers to measure the temperature, digital pH-meter to measure and monitor the pH of the working solution during the test run (the pH-meter was calibrated using buffer solutions of pH 4, 7, and 9), water bath with temperature controller to heat and control the solution temperature, high accuracy digital balance with 4 decimal points for weight loss determination, vibrationless motor to rotate the specimen with various velocities. Carbon steel (CS) pipe was used as a working electrode in a cylindrical shape for weight loss measurements with a length of 30 mm, outside diameter of 25 mm and inside diameter of 20 mm. The carbon steel specimen composition is shown in Table 1.

Table(1) Composition of the studied carbon steel specimen.

Element	C	Mn	P	S	Fe
Weight (%)	0.1649	0.5027	0.0020	0.0068	Rest

Cylindrical specimen of area $\pi * 0.025 * 0.03\ m^2$ and wall thickness of 0.005 m was immersed in a solution of HCl of a strength 0.1N in order to assess the corrosion rates by weight loss method. Before each experimental run, the metal specimen was washed by tap water followed by distilled water, dried with clean tissue, immersed in annular ethanol for 5 minutes, rinsed with clean acetone and dried with clean tissue. The specimen was then stored in a desiccator over highly active silica gel for 2 h before use, then they was weighed and directly exposed to the corrosion environment [7-10]. For these measurements the metal sample was installed on the motor shaft and completely immersed in 2.5 liters corrosive solution contained in 3 liters volume beaker. It was exposed for period of 2 h at specified temperature, concentration of inhibitor, and rotational velocity. After the exposure to the corrosion environment, the specimen was washed by tap water then brushed by smooth brush under running tap water to remove the corrosion products. After that the specimen was washed by tap water, distilled water, and dried with clean tissue, and kept in desiccator for 2 h, and then weighed [9, 10]. Each run was repeated twice with a third run when reproducibility was in doubt. The above procedure was repeated for specimens in absence and presence of inhibitors for the whole investigated range of rotational velocity and temperature.

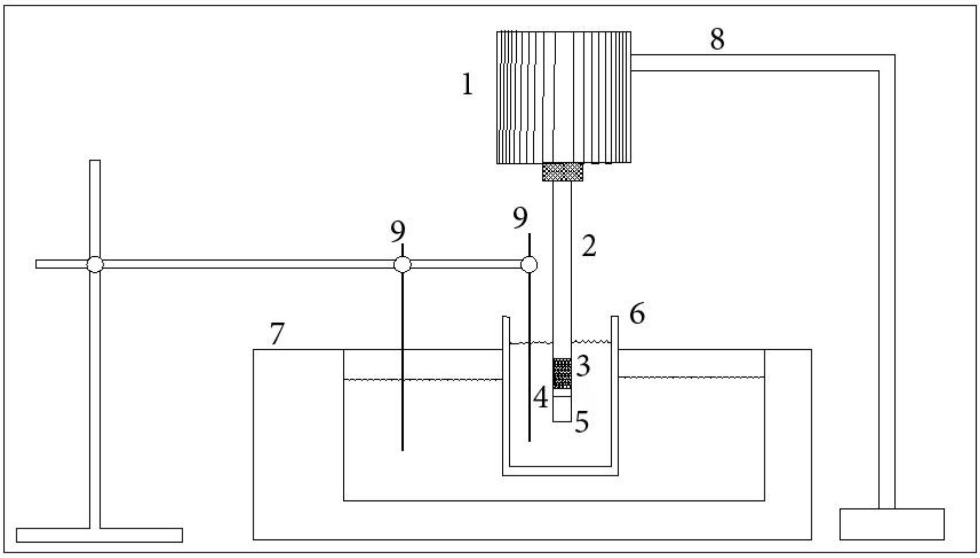


Fig. (1): Sketch showing the details of the rotating holder. 1-motor for rotating the specimens 2- Teflon rod 3- cylindrical specimen 4- Teflon washer 5- Teflon cap 6- beaker 7- water bath 8- stand to hold the motor 9- thermometer.

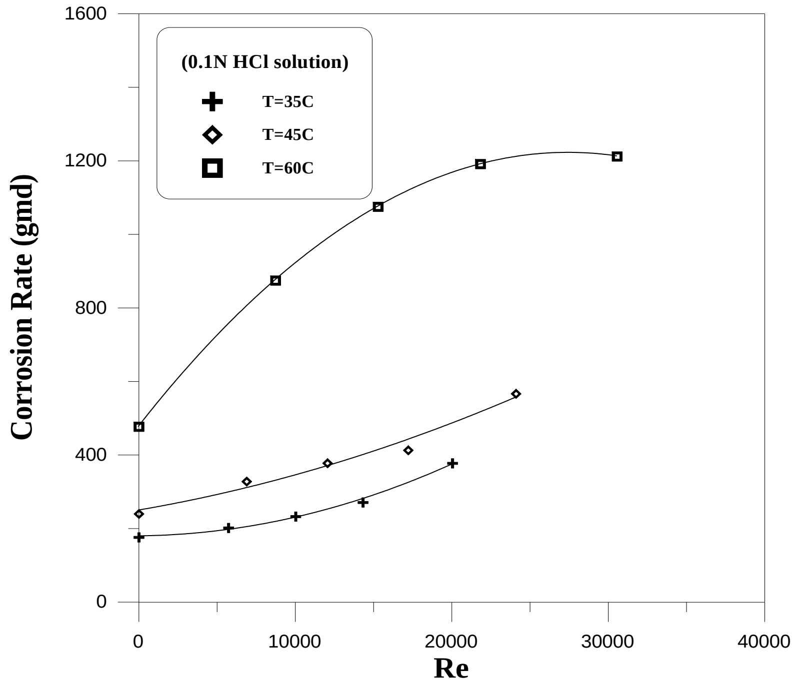
Results and discussion:

Effect of temperature and velocity in the absence of inhibitors

The effect of velocity is expressed by Reynolds number (Re) to include the change in physical properties (solution density and viscosity) with temperature change, where :

$$\mathrm{Re} = \frac{\rho \times d^2 \times N}{\mu} \qquad (1)$$

Where ρ (kg/m^3) is the solution density, μ (kg/m.s) is the solution viscosity, u is the agitation velocity (m/s), d is the pipe (specimen) diameter (m), and N is the rotational velocity (revolution/s). fig (2)shows the variation of corrosion rate of carbon steel with Reynolds number ($Re=\rho\ d\ u/\mu$) at three temperatures in 0.1N HCl before addition of inhibitors. It is evident that at a particular temperature, the corrosion rate increases with Re. For aerated systems the increase in the corrosion rate with Re (or rotational velocity) is due to the increase of oxygen transport from solution bulk to the metal surface by thinning the diffusion boundary layer thickness in the wall vicinity which represents the main resistance to mass transport and hence results in higher corrosion rate [11- 14]. Also Fig(2) indicates that under static conditions the corrosion rate increases with temperature. It is showing the values of 175.8 gmd, 239.5 gmd, and 476.7 gmd at 35 ^{o}C, 45 ^{o}C, and 60 ^{o}C respectively. Similarly at a particular Re the CR increased with increasing the temperature of the acid solution. This behavior can be interpreted as follows: increasing temperature leads to change three variables. Firstly, increasing temperature accelerates the reaction rate as dictated by Arrhenius equation [13,15]. Secondly, when the temperature increases, the molecular diffusion coefficient of dissolved oxygen increases leading to increase the corrosion rate [11, 16]. Thirdly, as the temperature increases the oxygen solubility decreases [11, 13, 17, 18] the factor that leads to decrease the corrosion rate. Hence, the influence of first two factors is more predominant than the last one (dissolved oxygen). This shows the corrosion process is not totally similar or identical under static and hydrodynamic conditions.



Fig(2) Corrosion Rate versus Reynolds Number.

Effect of inhibitors and the role of velocity and temperature:

The fig (3) to (6) show the corrosion rate versus Re in the presence of formaldehyde, diethanolamine, ethylenediamine, and thiourea at various concentrations for 35ºC respectively. These figures show the influence of concentration of each inhibitor on the corrosion rate of carbon steel. It is evident that the corrosion rate increases with Re in presence of all inhibitors and generally the higher the inhibitor concentration, is the lower the corrosion rate will be. In case of stationary conditions (Re=0), the minimum corrosion rates are obtained at highest concentrations of inhibitors. So, the thiourea exhibits the best corrosion inhibition value. The same trend is valid in the case of flow conditions (Re> 0). Organic compounds inhibitors decrease the corrosion rate by one of two ways: either adsorbed on the metal surface, forming a thin two-dimensional (2-D) film. This type can be further subdivided into non-selective and selective physisorption and chemisorptions or by forming three-dimensional (3-D) layer emerges on the metal surface resulting from, for example, the chemical reaction of an inhibitor with corrosion products to form organometallic complexes [19, 20, 21].

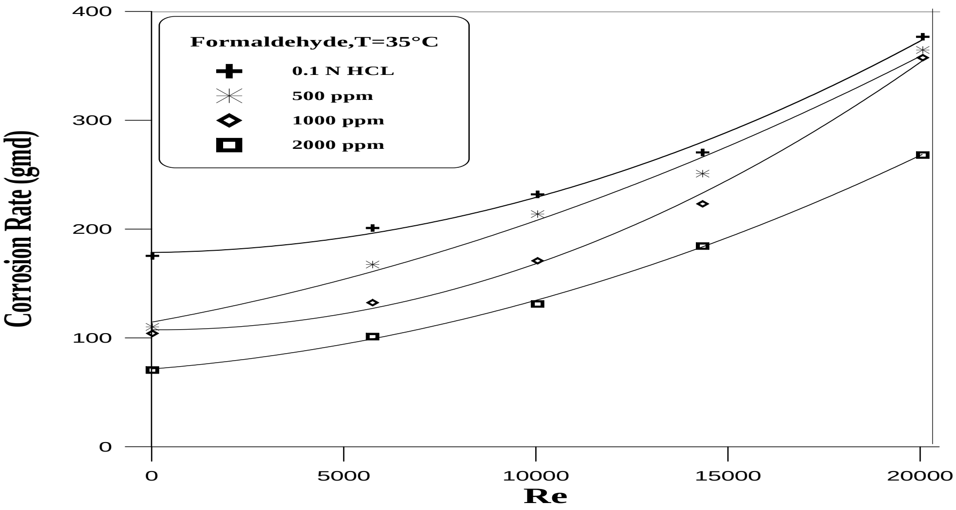


Fig (3) variation of corrosion rate with Reynolds number in the presence of formaldehyde inhibitor at T= 35°C.

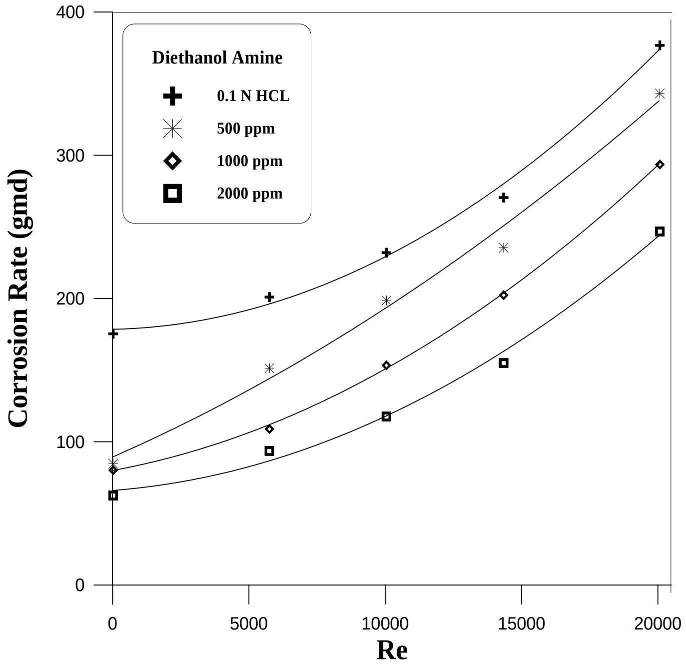


Fig (4) variation of corrosion rate with Reynolds number in presence of diethanolamine inhibitor at T= 35°C.

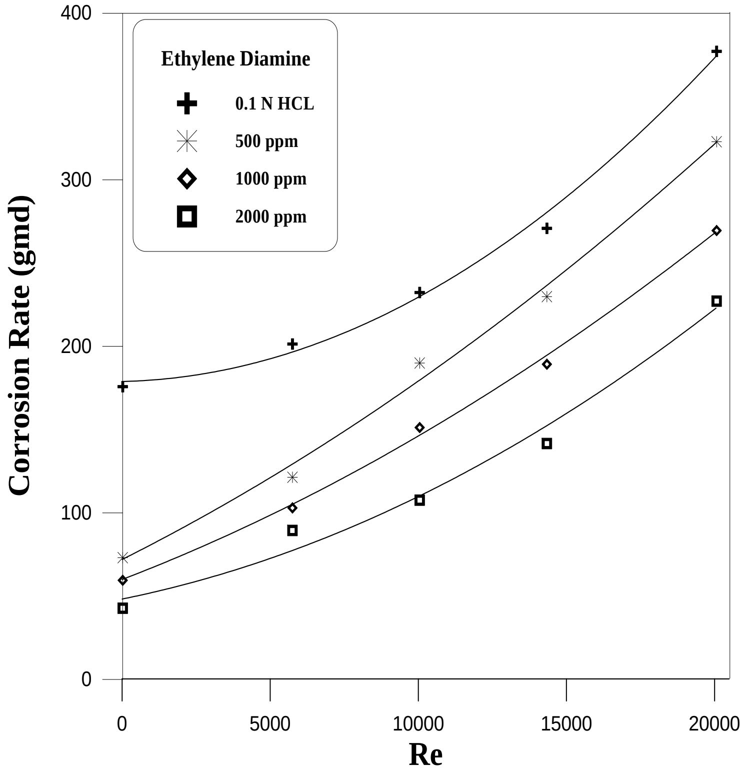


Fig (5) variation of corrosion rate with Reynolds number in presence of ethylenediamine Inhibitor at T= 35°C.

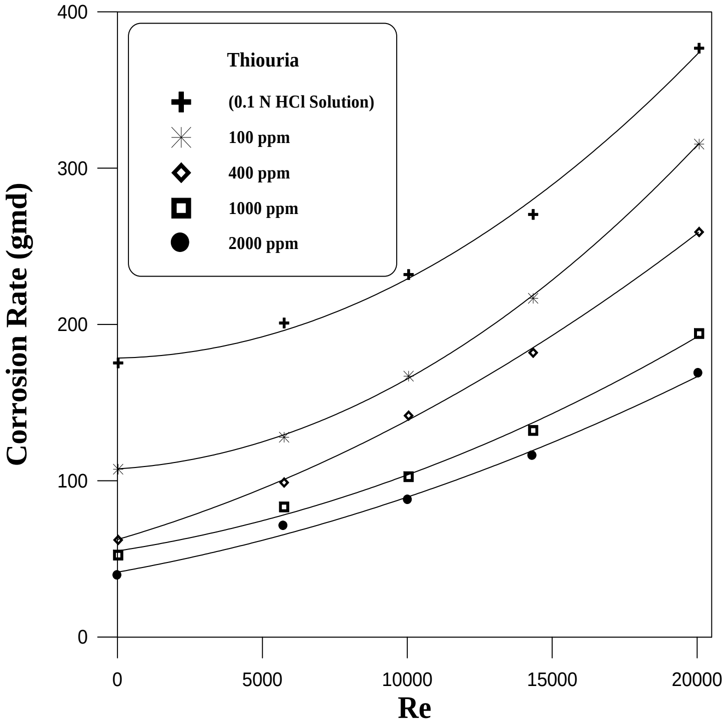
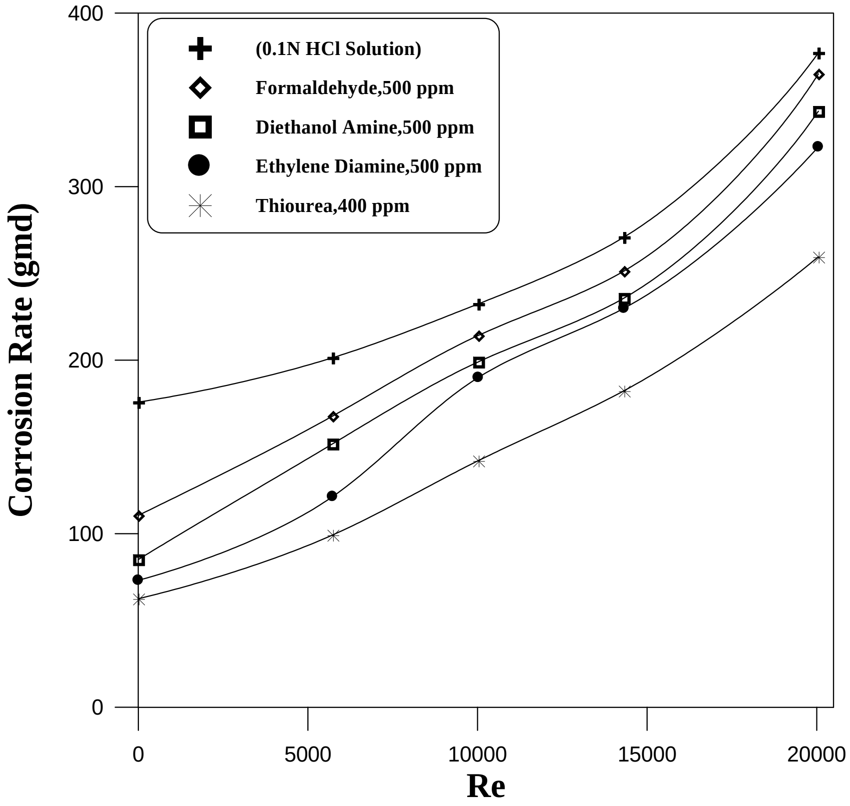


Fig (6) variation of corrosion rate with Reynolds number in presence of thiourea inhibitor at T = 35°C.

figs (7) to (9) show comparison among corrosion rates in the presence of formaldehyde, diethanolamine, ethylenediamine and thiourea at various concentrations for T=35 °C. The fig reveal that increasing inhibitor concentration decreases the corrosion rate of carbon steel It is clear that the four inhibitors give different corrosion rates. From Fig. (7), at stationary conditions (Re=0), 400 ppm of thiourea reduced the CR from 175.8 gmd to 62.5 gmd, i.e. 64.4%, and at maximum Re of 20000 it reduced the CR from 377.2 gmd to 259.5 gmd, i.e. 31%. At the same conditions the, 500 ppm of diethanolamine reduced the CR from 175.8 to 85 gmd, i.e 51.5% at stationary conditions and from 377.2 gmd to 343.5 gmd, i.e. 8.9% at Re=20000, 500 ppm of ethylenediamine reduced the CR from 175.8 gmd to 73.1 gmd,i.e. 58% at stationary conditions and from 377.2 gmd to 322.9 gmd, i.e. 14.4 % at Re=20000, 500 ppm of Formaldehyde reduced the CR from 175.8 gmd to 110.5 gmd, i.e. 37% under stationary conditions and from 377.2 gmd to 365.0 gmd, i.e. 3.2% at Re=20000. Fig. 9 shows that 2000 ppm of each inhibitor reduced the CR rate as follows, under stationary conditions : thiourea 77% , diethnolamine 64%, ethylenediamine 75.6% , Formaldehyde 59.7%, while under flow conditions at Re= 20000, the inhibition efficiencies are 55.3%, 34.5%, 39.8%, and 28.8% respectively. Hence it is evident that the thiourea gives the highest inhibition efficiency in stationary and flow conditions, followed by ethylenediamine, diaethanolamine, and formaldehyde. [22] found that ethylenediamine inhibit the corrosion of mild steel in deaerated HCl under stationary conditions by 65% when its concentration was 4.2 $\times 10^{-3}$ M and 94-98% when its concentration was 3.39×10^{-2} [23] stated that amines are cationic type inhibitors. They are often added to HCl-rich environments. When the system involved is ferrous metal, neutralizing amines work by the mechanism that modifies the pH of the electrolyte and thus inhibiting rust formation. [24] demonstrated that the behavior of ethylenediamine and thiourea on the corrosion of mild steel in 1M hydrochloric acid solution are mixed-type inhibitors, i.e. it control both anodic reaction (carbon steel dissolution) and cathodic reaction (hydrogen reduction and oxygen reduction on the carbon steel surface). [25] stated that thiourea and its derivatives decrease the corrosion rate of mild steel in aqueous solutions of HCl as well H_2SO_4, by forming adsorption layer on the metal surface to decrease the anodic reaction, i.e. it works as anodic inhibitor. [26] stated that thiourea simultaneously acts in both anodic and cathodic areas by decreasing the corrosion rate of mild steel (dissolution process of iron) in dilute HCl solution and decreasing the oxygen reduction and hydrogen evolution.



Fig(7) comparison among corrosion rates in presence of various inhibitors at T=35°C.

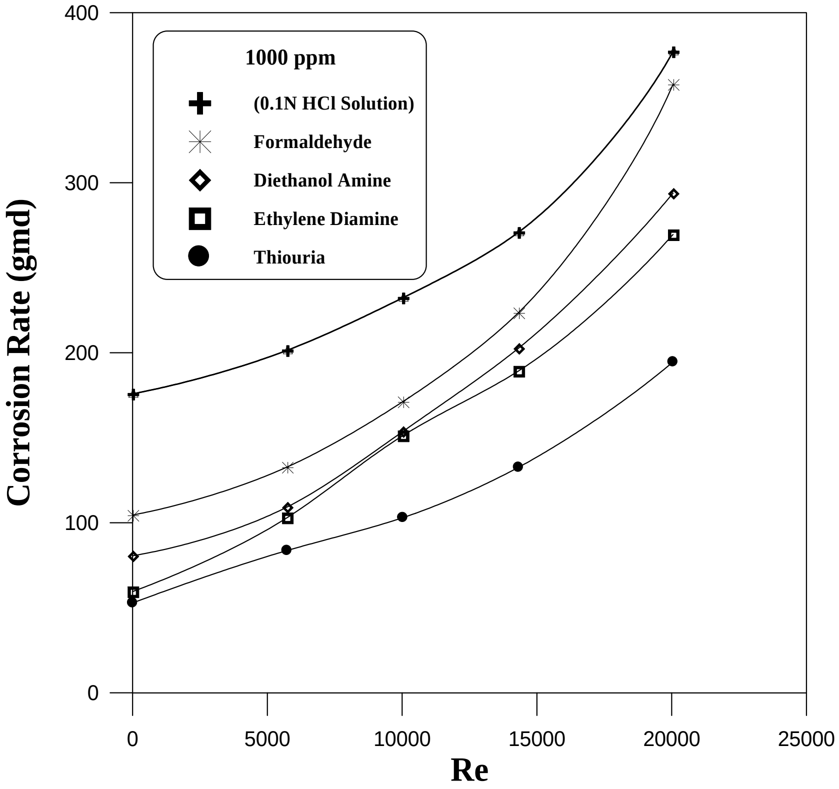


Fig (8) Comparison among Corrosion Rates in Presence of Various Inhibitors at T=35°C.

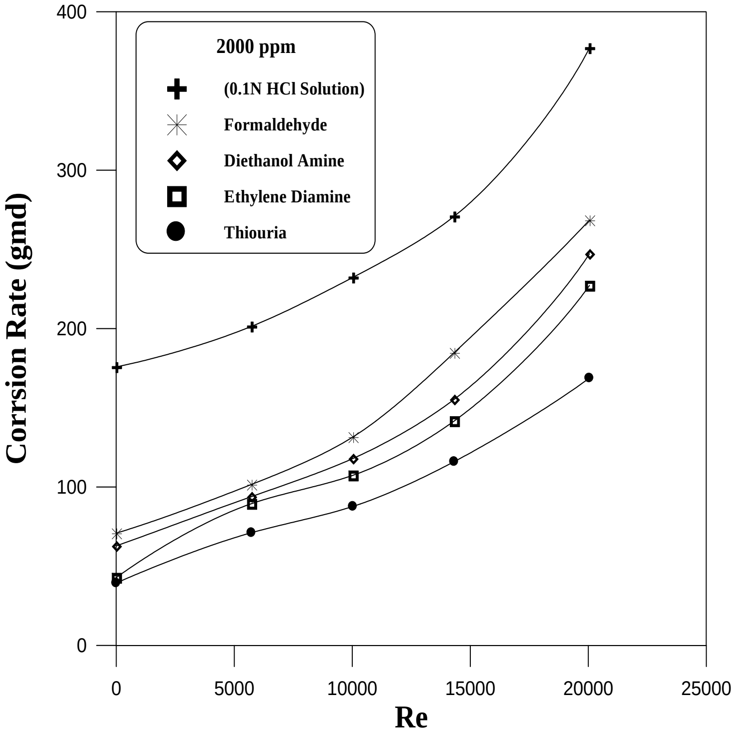


Fig (9) Comparison among corrosion rates of inhibitors at T=35°C.

fig (10) shows the comparison of inhibitors efficiencies at temperature of 35ºC. It can be seen that the efficiency of thiourea is the highest followed by ethylene diamine, diethanol amine, and formaldehyde inhibitor. The figure indicates that the efficiency of inhibitors decreases as the Re increases. This can be attributed to the fact that as Re (or velocity) increases, the shear forces exerted on the metal surface remove the adsorbed layer (protective layer) of the inhibitor from the metal surface or decrease its thickness leading to decrease the inhibitive action [27]. Also the Fig. reveals that the lowest effect of Re on the inhibitor efficiency is in the case of thiourea. This is another advantage of thiourea that it gives good inhibition even at high Re. Other types of inhibitors are shown to be poor inhibitors at high Re, where, when Re becomes larger than 10000, these inhibitors give inhibitor efficiency lower than 20% for the specified concentration.

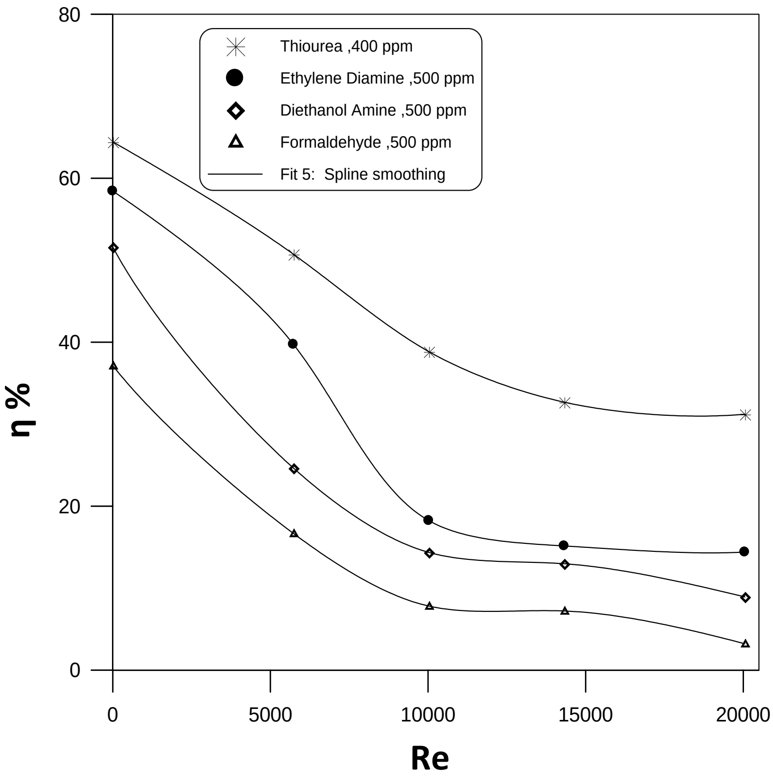


Fig (10) comparison among inhibitors efficiencies at T= 35°C.

Figs. 11 to 14 show the variation of inhibition efficiency with Re at different inhibitor concentrations for all inhibitors used. It is clear that the inhibition efficiency increases considerably with increasing inhibitors concentrations up to 2000 ppm. This is in accordance with previous studies that considered the inhibition of steel corrosion in acids and neutral solutions [2, 6, 21, 27].

Observing Figs. 11 to 14 indicates that the efficiency of thiourea exhibits the lowest decrease with increasing Re. The efficiency of ethelynediamine and diethanolamine decreases considerably at high Re in a particular at low concentrations. The Efficiency of Formaldehyde decreases greatly with increasing Re. In other words formaldehyde cannot be used at high Re.

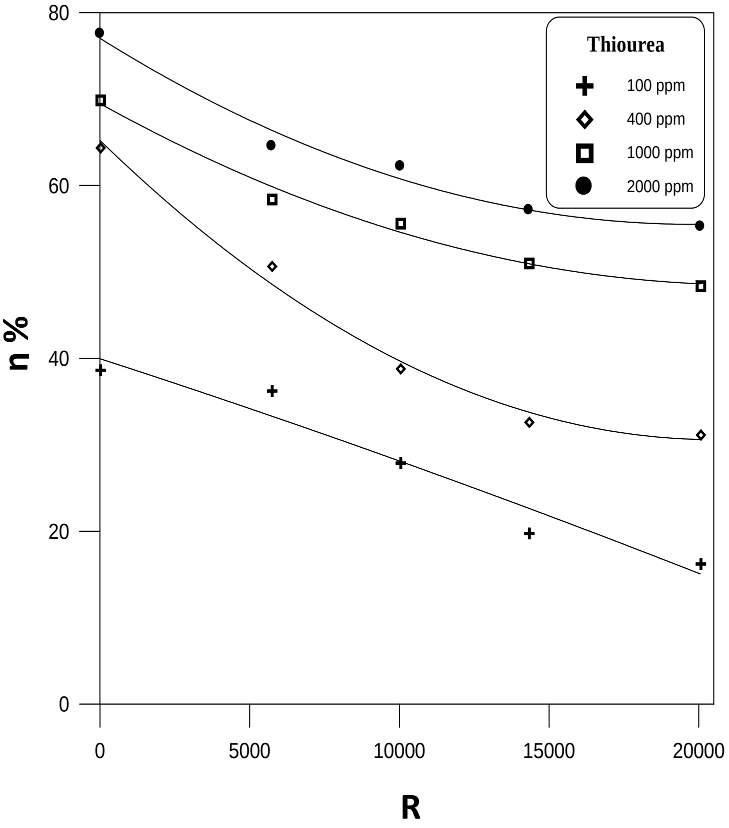


Fig (11) variation of inhibition efficiency with Reynolds number in presence of thiourea at T= 35°C.

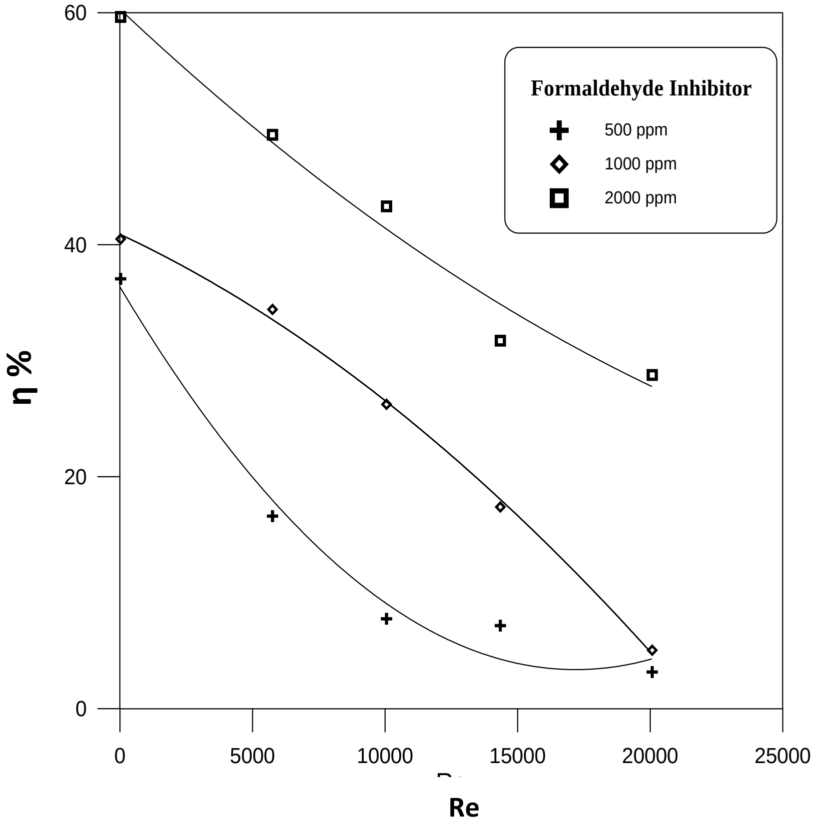


Fig (12) Variation of Inhibition Efficiency with Reynolds Number in Presence of Formaldehyde Inhibitor at T= 35°C.

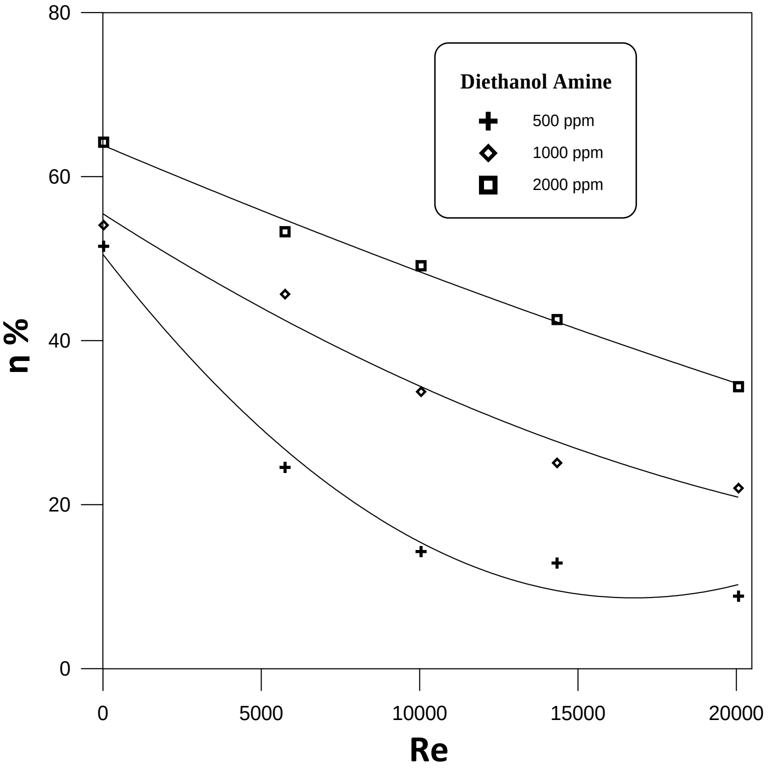


Fig (13): variation of inhibition efficiency with Reynolds number in presence of diethanolamine at T= 35°C.

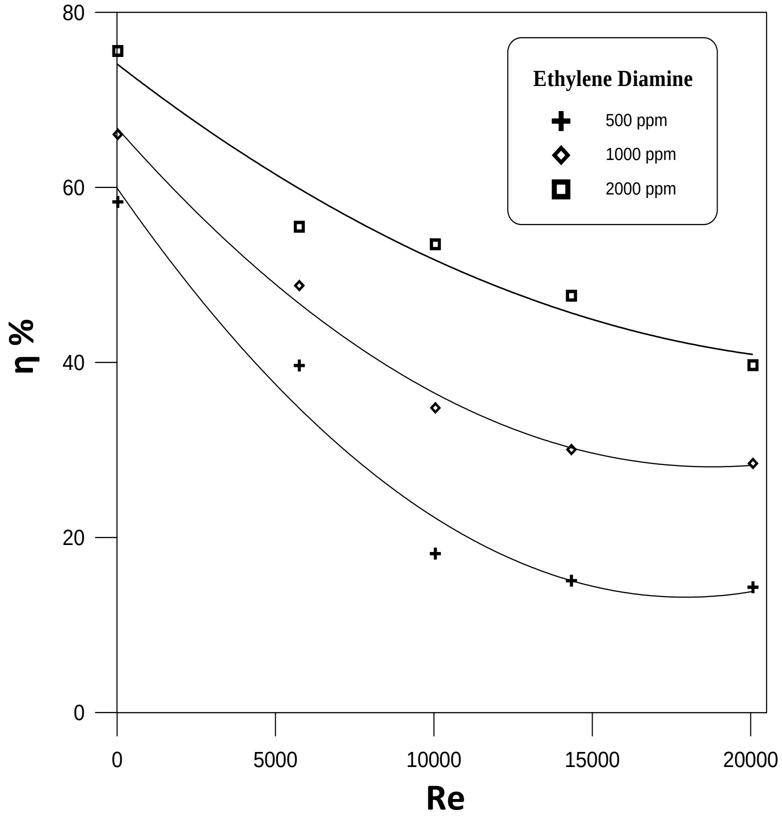


Fig (14) variation of inhibition efficiency with Reynolds number in presence of ethylenediamine at T= 35°C.

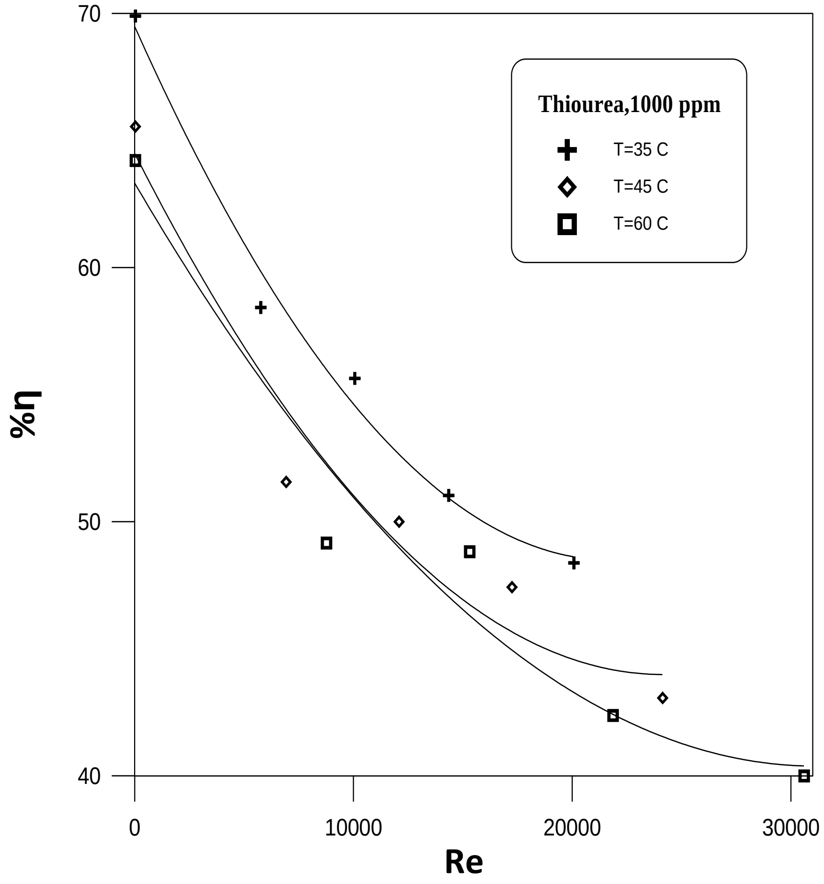


Fig (15) Inhibition Efficiency for Thiourea Inhibitor at Concentration of 1000 ppm versus Reynolds Number.

Fig 15 shows the effect of temperature on the inhibition efficiency of thiourea. It is clear that the inhibition efficiency decreases with temperature rise for the investigated range (35 ^{o}C to 60 ^{o}C) and Re. The decrease in efficiency with temperature may be attributed to the stability of adsorbed film of inhibitor molecules on the metal surface, which are more easily desorbed at higher temperature. As temperature increases Gibbs free energy rises to a higher value, so that some of the chemical bonds joining the molecules onto the metallic surface are impaired and film stability reduced. However, enthalpy has a roughly constant value in the temperature range tested depending on the tested compound [2, 21].

Conclusions:

The corrosion rate of carbon steel in aerated 0.1N hydrochloric acid increases considerably with increasing Re by increased eddy transport from the bulk of the solution to metal surface. Increasing temperature leads to increase the corrosion rate by decreasing the activation energy for hydrogen reduction reaction and increasing oxygen diffusivity. The addition of organic compounds inhibitors, thiourea, ethylenediamine, diethanolamine and formaldehyde leading to inhibit the corrosion with different efficiencies depending on temperature, Re, and inhibitor concentration. The highest inhibition efficiency is obtained by using thiourea in stationary and flow conditions. Ethelynediamine and diethanolamine show good inhibition efficiency at stationary conditions but its efficiency decreases considerably with increasing Re. Formaldehyde gives reasonable inhibition efficiency in stationary conditions when used in high concentration (2000 ppm) but it gives poor inhibition efficiency under flow conditions. Generally the inhibition efficiency for all inhibitors used, increases with increasing inhibitor concentration. The thiourea inhibition efficiency decreases with increasing solution temperature due to the desorption of the adsorbed inhibitor film from the surface.

Nomenclature:

Re	Reynolds number
d	pipe diameter (specimen), m
T	temperature, ^{o}C
ρ	solution density, kg/m^3
μ	solution viscosity, kg/m.s
u	agitation velocity, m/s
N	rotational velocity, revolution/s

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