An inexpensive inhibitor for Corrosion on Mild Steel in 1M Hydrochloric Acid Solution – A kinetic study

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Abstract

This current research focuses on the protective mechanism of mild steel when exposed to 1M hydrochloric acid solution in the presence of synthesized 1,1,4,4-tetramethyl-1,4-diocty lethylenediammonium bromide (TDEDB) as an inexpensive inhibitor using weight loss studies. The following parameters namely effect of inhibitor, the effect of temperature and the effect of pH were evaluated at different concentrations and conditions. It was revealed that the coverage of the inhibitor and the interaction over the mild steel is by the process called adsorption. A remarkable improvement was observed by the addition of inhibitor when compared to blank solution. More over increasing the concentrations of synthesized inhibitor played a vital role and the same was proven by the weight loss methodology. It evidences that at 250 ppm the maximum adsorption occurs on the mild steel which results in curtailment of the corrosion reaction.

Key words: Mild Steel, Inhibitor, Weigh loss, Corrosion, Quaternary ammonium salt

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Mild steel is a material, which is used for a variety of applications because of its durability, but due to its nature, it readily undergoes corrosion reactions. Many methodologies are available for preventing mild steel from corrosion reaction. But one of the wisest, simple, and most common methodologies is using an inhibitor (Edoziuno *et al.*, 2020), (Eugene *et al.*, 2016; Raja *et al.*, 2016). Inhibition efficiencies of quaternary ammonium salts in presence of benzyl ring (Bereket and Yurt, 2002) were tested on low carbon steel and found to increase with the increase in the chain length. The quaternary ammonium salts act as phase transfer catalysts (Meena, Umapathy and Yoganand, 2021), (Yoganand *et al.*, 2009; Meena and Umapathy, 2016; Meena, Nanjundan and Umapathy, 2016) in the polymerization reaction, other organic synthesis and also as corrosion inhibitors (Yoganand, Meena and Umapathy, 2022). In the concentration range of 0.0001 to 0.001 molL^{-1}, the cationic surfactants exhibited the best inhibiting efficiency in $2MH_2SO_4$ on carbon steel surface (Fuchs-Godec, 2006). The adsorption behaviour of streptomycin (Rezaierod, Rahimi and Chaghazardi, 2014), a drug that is used in the treatment of tuberculosis was tested on sample steel in presence of 1M HCl at various temperatures and exhibited corrosion inhibition characteristics. Alcoholic plant extracts (Al-Otaibi *et al.*, 2014) of a few plants showed promising corrosion inhibiting efficiency on mild steel in 0.5 M HCl media. The corrosion rate of aluminum was minimized in presence of the Delonix regia(Abiola *et al.*, 2007) plant extract. An increased anti-corrosion protection efficiency was reported on aluminum metal in 0.5 M HCl in presence of dry areca nut seed (Raghavendra and Bhat, 2016). 95% the anticorrosive property was reported in presence of alkyl ammonium

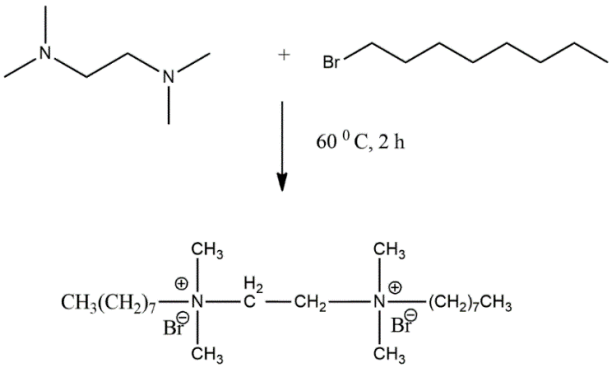
bromides(Chen *et al.*, 2019) on X70 mild steel specimens.

In our current research, we elucidated the performance of 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide (TDEDB) as a corrosion preventer for mild steel in 1M HCl using weight loss analysis.

Materials and Methods

Synthesis of Inhibitor

The inhibitor 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide was synthesized (Meena, M, Umapathy, 2020) as reported by refluxing 1:2 molar ratios of M N,N,N',N'- tetramethylethylenediamine and 1-bromooctane at 60 °C for 2 h. The precipitate obtained was filtered, purified, and dried. The synthesized inhibitor was characterized by FT-IR, ^{1}HMNR, ^{13}CNMR spectroscopies as well as elemental analysis were carried out.



Scheme1: Synthesis of 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide

Preparation of the corrosive solution

One molar hydrochloric acid solution was prepared using distilled water. This solution acted as a corrosive solution for the mild steel coupons.

Preparation of mild steel sample

Mild steel coupons of size 4 cm^2 and with the composition of C=0.7%, P =0.03%, Mn =0.3-0.6%, S =0.035%, Si=0.5-0.75%, and the rest iron was used for testing corrosion by weight loss method. Prior to subjecting the coupons for corrosion test, they were cleaned mechanically with emery sheets and acetone to remove rust and oil before the analysis. Corrosion inhibition experiments were conducted by immersing the coupons in the prepared test solution taken in the glass beakers.

Weight loss measurements

The performance of synthesized corrosion inhibitor was evaluated by varying the concentrations from 50,100…to 250 ppm. To evaluate the efficiency of inhibitor, a constant temperature bath, glass beakers along with test coupons containing acid solution and inhibitors of known concentration were taken. Corrosion measurements of the immersed coupons were carried out by varying the pH as well as temperature. Based on the weight loss, corrosion rate (CR) (Xavier Stango and Vijayalakshmi, 2018) was calculated as follows.

Corrosion Rate = 0.1 mm/y (4 mpy)

$$mils\ per\ year = \frac{534.W}{DAt} \quad 1$$

Where, 1 mil = 10^{-3}in, W = mass lost (mg), D = specimen density (g/cm^3), A = specimen area (in^2), t = exposure time (hr).

To improve the precision, triplicate tests were conducted by changing the parameters like concentration of inhibitor, pH, and temperature, and an average was taken.

Corrosion inhibitor efficiency

Inhibitor efficiency (Chen *et al.*, 2019) was determined as mentioned below.

$$\text{Inhibitor Efficiency (\%)} = 100 - \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{unhibited}} \quad 2$$

Results and Discussion

Impact of TDEDB concentration and corrosion rate

Weight loss studies were performed in the absence and presence of synthesized TDEDB at various concentrations and temperatures. Corrosion inhibition tendency of TDEDB on mild steel in 1 M HCl was tested by varying the concentration from 0 to 250 ppm at three different temperatures. From the observations of weight loss methodology, it was evidenced that the addition of inhibitors minimized weight loss (Gadow and Fakeeh, 2022). Though the temperature was increased from 25^{0}C to 45^{0}C, weight loss started decreasing in presence of the inhibitor. The corrosion rate was calculated as per equation 1 and the same is depicted in Figure 1.

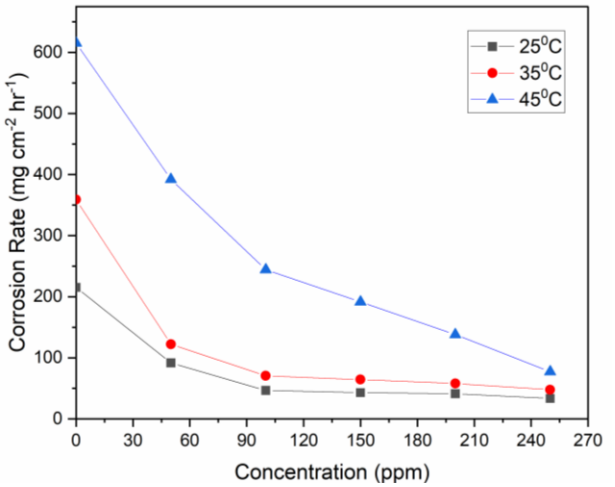


Figure 1 Concentration Vs Corrosion Rate

The decrease in rate of corrosion explains the inhibiting nature of the synthesized quaternary ammonium salt.

Corrosion Inhibition Efficiency

The concentration of TDEDB was varied from 50 ppm to 250 ppm and the efficiency of TDEDB was determined as per equation 2. Among the various concentrations, the inhibitor showed an exemplified behavior at 250 ppm even at 45⁰C. Increasing the inhibitor concentration, favours the adsorption (Scaria *et al.*, 2022) over mild steel and also slowed down the rate of corrosion.

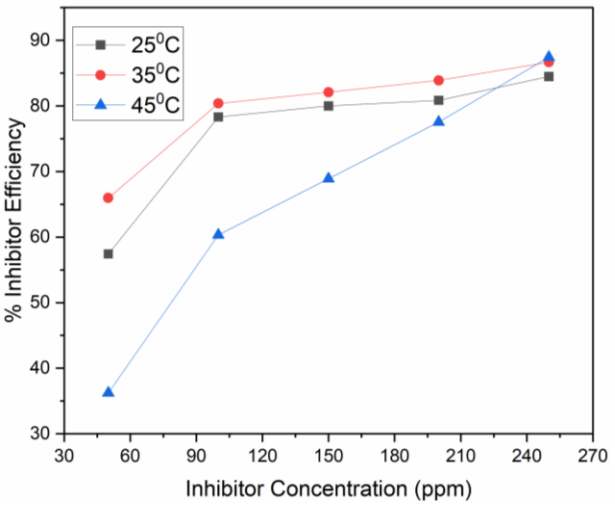


Figure 2 Inhibitor concentration Vs % Inhibition efficiency

Figure 2, ensures the protection of the mild steel after the addition of TDEDB. This may be attributed to the affirmation of bonding of organic groups present in the quaternary ammonium salts over the metallic surface which in turn favours a better efficacy of the inhibitor.

Effect of temperature

The inhibition efficiency was ascertained by varying concentrations from 25ppm to 125ppm and also at three different temperatures that are 25⁰C to 45⁰C. In general, corrosion of mild steel is expected to accelerate as the temperature increases because the conductance of the medium increases with temperature rise. But in this case, the added inhibitor minimizes the effect of corrosion with temperature. The trend observed was depicted in Figure 3. Though the inhibitor was not satisfactory at lower concentration and around room temperature, it exhibited its protective nature at its highest operative temperature of the present system

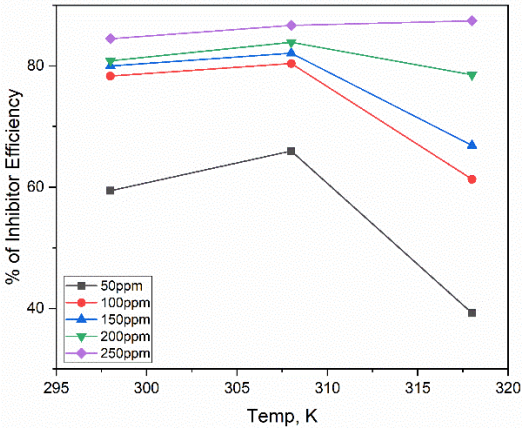


Figure 3 Temperature Vs Inhibitor efficiency

The inhibitor provides a layer on the surface of the mild steel and acts as a barrier thus preventing the mild steel from further corrosion. The activation energy, Ea was evaluated from the plot of 1/T versus log CR (Figure 4) and tabulated in Table 1.

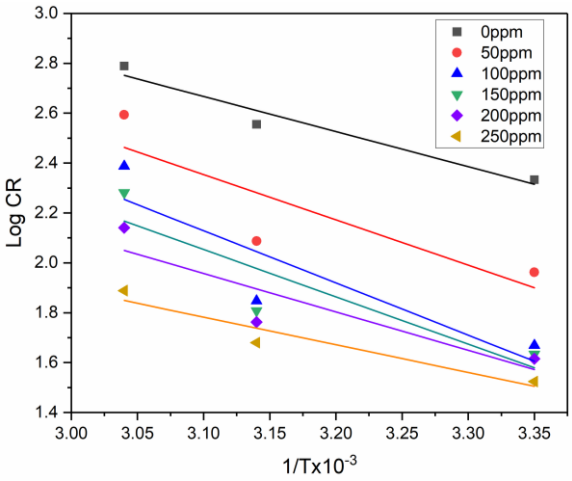


Figure 4 – Arrhenius plot of TDEDB

Table 1

Activation energy of corrosion of mild steel in 1M HCl in the presence and absence TDEDB

Concentration, ppm	0	50	100	150	200	250
Activation Energy, kJ mol^{-1}	26.94	34.74	40.05	36.29	29.50	21.23

Based on Table1, it is observed that there occurs a decrease in activation energy from 0 ppm to 250ppm. It is also evident that with increase in concentration of the inhibitor, there observed a decrease in activation energy (Qiu *et al.*, 2022).

Adsorption isotherm of TDEDB

The best fitting adsorption isotherm model was computed for the TDEDB inhibitor - on mild steel in 1M hydrochloric acid solution system and the straight-lines were obtained with a regression coefficient almost equal to one, which indicates that the system fits into Langmuir's adsorption isotherm.

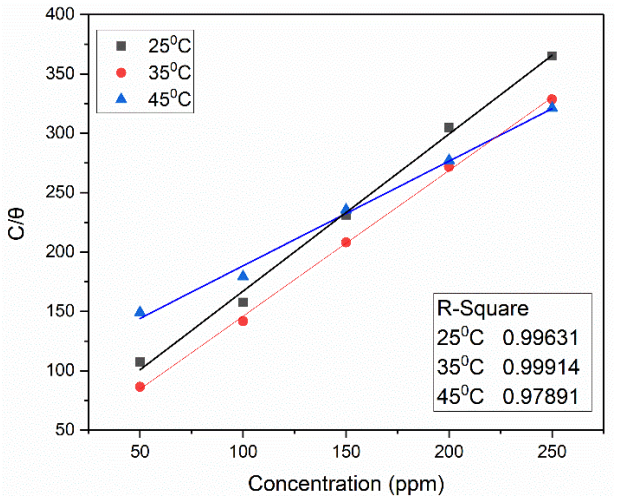


Figure 5 TDEDB on Surface coverage

According to mild steel and its prevention aspects, chemical adsorption tends to form a bond between inhibitor that is the bromide ions present in the salt and the mild steel surface, which in turn may form a primary layer on the mild steel and thus prevented it from further deterioration.

Influence pH over TDEDB

In order to determine the effect of pH on the mild steel in presence of TDEDB, corrosion rates have been investigated from the range of more acidic to neutral. According to the Pourbaix diagram, basic pH does not affect the mild steel by corrosion reaction. Figure 6 evidences that the action of inhibitor was given good results over moderate acidic medium (Yang *et al.*, 2022) to neutral medium.

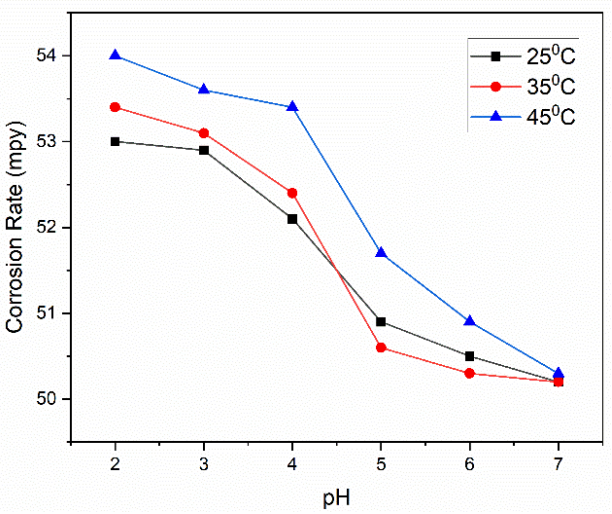


Figure 6 Change of Corrosion rate with pH

Conclusion

The quaternary ammonium salts are proved to be excellent corrosion inhibitors. In line with this, the synthesized 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide also exhibited its characteristic as a corrosion inhibitor. The corrosion was minimal in the concentration range of 250 ppm and slightly above room temperature. It has exhibited an efficiency of 87% at 45⁰C. The ascertained energy of activation was also less at the maximum concentration of 250 ppm and the highest operating temperature of the system that is 45⁰C. The system also exhibited Langmuir's adsorption model.

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6/TABLES/7.

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