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Inhibition effect of N, N'-Dimethylaminoethanol on the Corrosion of Austenitic Stainless steel type 304

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Abstract

The effect of N,N'-dimethylaminoethanol on the corrosion of austenitic stainless steel type 304 in 3M H₂SO₄ has been studied by weight-loss method and linear polarization measurement in different concentrations of the compound. The inhibition efficiencies of the inhibitor compound on the corrosion of the stainless steel were evaluated through assessment of the anodic and cathodic polarization curves of the alloy, the spontaneity of the electrochemical process, inhibition mechanism and adsorption isotherm. The inhibitor efficiency increased with increase in the inhibitor concentration. Results obtained reveal that the inhibitor performed effectively on the stainless steel providing good protection against pitting and uniform corrosion in the chloride containing acidic solutions. The compound act through physiochemical mechanism on the stainless steel surface and obeyed Langmuir adsorption isotherm. The values of the inhibition efficiency calculated from the two techniques are in reasonably good agreement. Polarization studies showed that the compounds behave as mixed type inhibitor in the aggressive media.

Key words: N, N'-dimethylaminoethanol, corrosion, stainless steel, tetraoxosulphate(vi) acid, inhibitor

1.0 INTRODUCTION

Corrosion of metals is a major industrial problem that has attracted numerous investigations and researchers (Tarab and Al.Turkustani, 2006, Eddy and Ebenso, 2010). Millions of dollars are lost each year because of corrosion (Kadry, 2008). Much of this loss is due to the corrosion of iron and steel. The problem with steel as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing "pitting". Extensive pitting eventually causes structural weakness and disintegration of the metal (Kadry, 2008). Stainless steel derives their corrosion resistance from a thin durable layer of chromium oxide that forms at the metal's surface and gives stainless steel its characteristic 'stainless quality'. The passive film on stainless steel surface consists of a mix of iron oxide and chromium oxide (Tuthill and Avery, 1992). The formation of this film is instantaneous in an oxidizing atmosphere such as air, water, or other fluids that contain oxygen. Once the layer has formed, the metal becomes "passivated" and the oxidation or "rusting" rate will slow down significantly. Breakdown of the protective films leads to localized corrosion failures. The corrosion of stainless steel in acidic solutions has received considerable amount of attention (Abdallah, 2003). The highly corrosive

nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety conditions. Acidic solutions are aggressive to this film layer and results in severe pitting formation (Galal et al., 2005, Fouda et al., 2010). Several mineral acid solutions such as sulphuric acid are widely used for various treatments of materials in industry. Sulphuric acid is used for pickling, descaling, acid cleaning; oil-well acidizing, etc (Ahamad et al., 2010) Sulphuric acid is generally the choice in steel surface treatment basically due to its lower cost, minimal fumes and non-corrosive nature of the SO₄²⁻ ion. Since steel could be attacked by the acidic media during its various application processes, the presence of corrosion inhibitors in the solutions is of utmost importance to keep the surface of steel intact (Hosseini et al., 2009). The use of inhibitors is one of the most practical methods of metallic protection against corrosion (Umoren ey al., 2009). Most of the efficient inhibitors used in industry are organic compounds, which mainly contain nitrogen, oxygen, sulphur atoms, and heterocyclic compounds containing functional groups and conjugated double bonds, and multiple bonds in the molecule through which they are adsorbed on metal surface by the formation of an adherent



film (Abd El-Maksoud and Fouda, 2005, Aljourani et al., 2010, Hasanov et al., 2010, Abd El-Maksoud, 2003, Xu et al., 2008, Abboud et al., 2007, Awad and Gawad, 2005, Chetouani, 2003). The compounds containing both nitrogen and sulphur can provide excellent inhibition, compared with compounds containing only nitrogen or sulphur (Aljourani et al., 2010, Abboud et al., 2007). Generally, inhibitor molecules may physically or chemically adsorb on a corroding metal surface. In any case, adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from corrosion (Elayyachy et al., 2005, Bouklah et al., 2006). It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption (Ajmal et al., 1994). In this way, the metal acts as an electrophile; and the nucleophile centers of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond (Fang et al., 2002). The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, containing functional electronegative groups and π -electron in triple or conjugated double bonds, are usually good inhibitors. Heteroatoms, such as sulphur, phosphorus, nitrogen, and oxygen, together with aromatic rings in their structure are the major adsorption centers. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of molecules on the metallic surface (Quraishi and Sharma, 2002).

The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions.

Different classes from organic compounds are used as corrosion inhibitors for iron alloys in various acid media (Growcock et al., 1998, Hettiarachchi et al., 1989, Gad Alla and Tamous, 1990, Agrawal, and Namboodhiri, 1990, Moretti, 1996, Agrawal and Namboodhiri, 1997, Abdel-Aal and Morad, 2001, Mthar et al., 2002, Selvi et al., 2003, Bentiss et al., 2004, Noor, 2005, Yurt et al., 2005). Unfortunately, most of the organic inhibitors used are very expensive

and health hazards. Their toxic properties limit the field of their application. Thus, it remains an important objective to find low-cost inhibitors of the non-hazardous type for the protection of metals against corrosion.

N,N-dimethylethanolamine belongs to the group of alkanolamines, chemical compounds that carry hydroxy (-OH) and amino (-NH₂, -NHR, and -NR₂) functional groups on an alkane backbone. Alkanolamines have the combined physical and chemical characteristics of both alcohols and amines in one molecule, which makes them useful intermediates in the synthesis of various target molecules for use in many diverse areas such as pharmaceutical, urethane catalysts, coatings, personal care, products, Water treatments and gas treating industries, Dimethylaminoethanol used specifically for the synthesis of dyestuffs, textile auxiliaries and pharmaceuticals [such as procaine] contributing to its extensive industrial utilization and low cost (N,N DIMETHYLETHANOLAMINE). A major problem with evaluating these inhibitors is that they are commonly used as part of complex formulations, marketed under trade names, whose compositions are uncertain.

This study aims to investigate the corrosion inhibition effect of N, N dimethylethanolamine an amino alcohol compound and its ability to provide protection against pitting and uniform corrosion at different concentrations in 3M H₂SO₄ solution using linear polarization and weight loss techniques.

2.0 EXPERIMENTAL PROCEDURE

2.1 Material

Commercially available Type 304 austenitic stainless steel was used for all experiments of average nominal composition; 18.11%Cr, 8.32%Ni and 68.32%Fe. The material is cylindrical with a diameter of 1.80cm (18mm).

2.2 Inhibitor

N, N-Dimethylaminoethanol (DMAE) a colorless, transparent liquid is the inhibitor used. The structural formula of DMAE is shown in Fig. 2. The molecular formula is C₄H₁₁NO, while the molar mass is 89.14 g mol⁻¹.

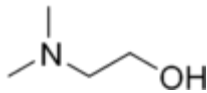


Fig. 1 Chemical structure of N, N Dimethylaminoethanol (DMAE)

DMAE was prepared in various concentrations of 0%, 2.5%, 5%, 7.5%, 10%, 12.5% and 15% was used as the inhibiting medium

2.3 Test Media

3M tetraoxosulphate (VI) acid with 3.5% recrystallised sodium chloride of Analar grade were used as the corrosive medium

2.4 Preparation of Test Specimens

The cylindrical stainless steel (1.80cm dia.) was mechanically cut into a number of test specimens of different dimensions in length ranging from 1.78 and 1.88cm coupons. The two surface ends of each of the specimen were ground with Silicon carbide abrasive papers of 80, 120, 220,800 and1000 grits. They were then polished with 6.0µm to 1.0µm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator for further weight-loss test and linear polarization.

2.5 Weight-loss Experiments

Weighted test species were fully and separately immersed in 200ml of the test media at varying concentrations of the inhibitor for 18days at ambient temperatures. Each of the test specimens was taken out every three days (72 hours), washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) and corrosion rate (mmpy) versus exposure time (hours) (Figs. 2 & 3) and those of percentage inhibition efficiency (%IE) (calculated) versus exposure time (hours) and percentage inhibitor concentration (Fig. 4 & 5) were made from Table 1.

The corrosion rate (R) calculation is from this formula:

$$R = \left[\frac{87.6W}{DAT} \right] \text{ eqn. 1}$$

Where W is the weight loss in milligrams, D is the density in g/cm², A is the area in

cm², and T is the time of exposure in hours. The % inhibitor efficiency, (I.E), was calculated from the relationship.

$$\left[\frac{W_1 - W_2}{W_1} \right] \times 100 \text{eqn. 2}$$

Where W₁ and W₂ are the corrosion rates in the absence and the presence respectively of a predetermined concentration of inhibitor. The %IE was calculated for all the inhibitors on the 18th day of the experiment [Table 1], while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W_2}{W_1} \right] \text{eqn. 3}$$

Where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent, the unit of m is mol.g⁻¹. W₁ and W₂ are the weight loss of austenitic stainless steel coupon in free and inhibited acid solutions, respectively.

2.6 Linear polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 2.54 cm². The electrode was polished with different grades of silicon carbide paper, polished to 6µm, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 mL of electrolyte, with and without inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5V versus OCP to +1.5 mV versus OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density (j corr) and corrosion potential (E corr) were determined from the Tafel plots of potential versus log I. The corrosion rate (r), the degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated as follows

$$r \text{ (mmpy)} = \frac{0.00327 \times i_{corr} \times eq.wt}{D} \text{ eqn.4}$$



Where i_{corr} is the current density in $\mu A/cm^2$, D is the density in g/cm^3 , $eq.$ is the specimen equivalent weight in grams;
 The percentage inhibition efficiency (% IE) was calculated from corrosion current density values using the equation.

$$\%I.E = 1 - \left[\frac{c_2}{c_1} \right] 100 \quad \text{eqn.5}$$

where C_1 and C_2 are the corrosion current densities in absence and presence of inhibitors, respectively.

3. Results and Discussion

3.1 Weight-loss measurements

Weight-loss of austenitic stainless steel at various time intervals, in the absence and presence of different concentrations of (DMEA)

in 3M sulphuric acid at 25°C was studied. The values of weight-loss (wt), corrosion rate (CR) (mmpy) and the percentage inhibition efficiency (IE %) are presented in Table 1. It is clear that the decreasing corrosion rate is associated with increase in the inhibitor concentration which indicates that more inhibitor molecules are adsorbed on the metal surface, thereby providing wider surface coverage (Emregul, 2003). Fig. (2, 3 & 4) shows the variation of weight-loss, corrosion rate and percentage inhibition efficiency with exposure time at different inhibitor concentration while fig. 5 shows the variation of %IE with inhibitor concentration. The curves obtained indicate progressive increase in %IE with increase in inhibitor concentration accompanied by a reduction in corrosion rate.

Table 1. Data obtained from weight loss measurements for austenitic stainless steel in 3M H2SO4 in presence of different concentrations of the DMEA at 312hrs

| Sample | Inhibitor Concentration (%) | Weight Loss (mg) | Corrosion Rate (mmpy) | Inhibition Efficiency (%) |
|--------|-----------------------------|------------------|-----------------------|---------------------------|
| A | 0% | 5345 | 49.1071 | 0 |
| B | 2.5% | 2006 | 11.8126 | 62.45 |
| C | 5% | 1774 | 11.7695 | 66.81 |
| D | 7.5% | 1082 | 7.4023 | 79.76 |
| E | 10% | 725 | 4.1509 | 86.44 |
| F | 12.5% | 518 | 3.4562 | 90.31 |
| G | 15.0% | 542 | 3.2186 | 89.86 |

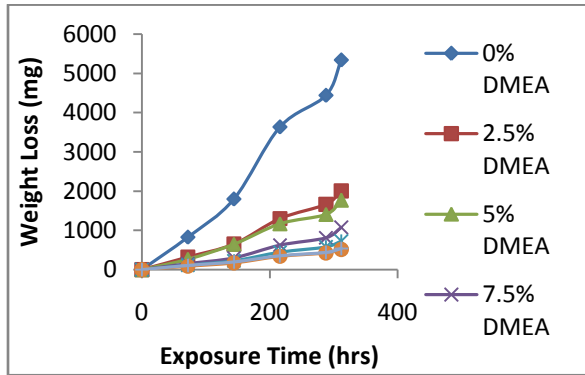


Fig. 2 Variation of weight-loss with exposure time for samples (A – G) in (0% -15%) DMEA concentrations.

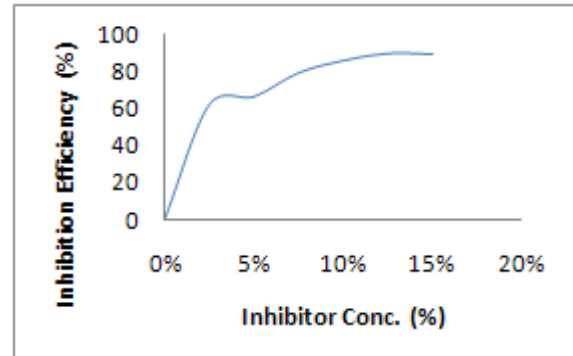


Fig. 5 Percentage inhibition efficiency of DMEA at varying concentrations from weight loss.

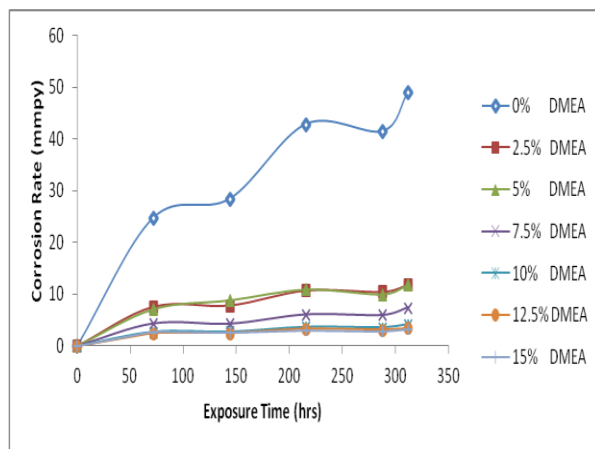


Fig. 3 Effect of percentage concentration of DMEA on the corrosion rate of austenitic stainless steel.

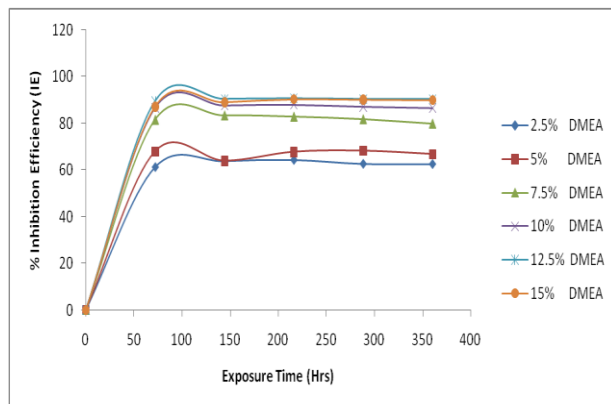


Fig. 4. Plot of inhibition efficiencies of sample (A-G) during the exposure period

3.2 Polarization studies

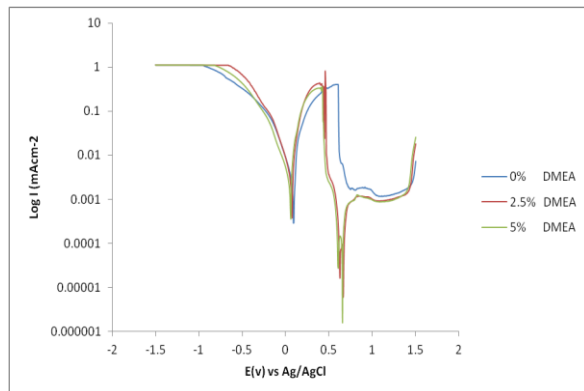
The potential was scanned from -1.50 to 1.50 V vs. SCE at a rate of 0.0166 mV s^{-1} , which allows the quasi-stationary state measurements. The effect of the addition of DMEA on the anodic and cathodic polarization curves of austenitic stainless steel type 304 in 3 M H_2SO_4 solutions at 25°C was studied. Fig. 6 (a & b) shows the polarization curves of austenitic stainless steel in absence and presence of DMEA at different concentrations. Anodic and cathodic currents were inhibited effectively with increasing concentrations of inhibitor. The inhibitor appeared to act as mixed type inhibitor since anodic [metal dissolution] and hydrogen evolution reactions were significantly influenced by the presence of compounds in the corrosive medium. Generally, all scans exhibit slightly similar behavior over the potential domain examined, indicating similar electrochemical reactions took place on the metal. The electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion current density (I_{corr}), cathodic Tafel constant (bc), anodic Tafel slope (ba), surface coverage θ and percentage inhibition efficiency (%IE) were calculated and given in Table 2. These results show that the %IE increased while the corrosion current density generally decreased with the addition of DMEA until 10% and 12.5% concentration where there was a sharp increase before decreasing at 15% concentration. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolating anodic and cathodic Tafel lines, % IE was calculated from Eq. 6



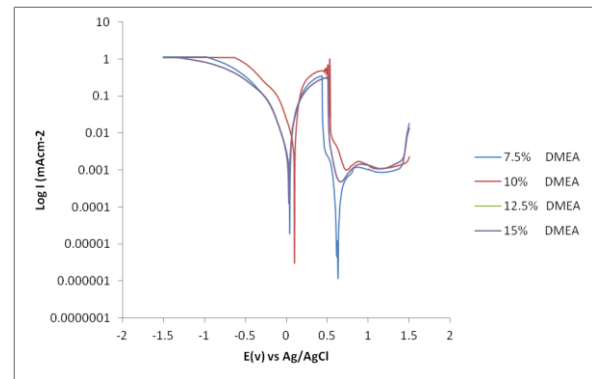
$$\% I.E = \frac{CR1 - CR2}{CR1} \% \text{ eqn. 6}$$

Table 2 Data obtained from polarization resistance measurements for austenitic stainless steel in 3M H2SO4 in presence of different concentrations of the DMEA

| Inhibitor Conc. (%) | Inhibitor Conc. [Molarity] | Corrosion Rate (mppy) | Inhibition Efficiency (%) | Rp | Ecorr | i (A) | I(A/cm2) | bc | ba |
|---------------------|----------------------------|-----------------------|---------------------------|-------|-------|------------------------|------------------------|-------|-------|
| 0% | 0 | 7.995 | 0 | 2.269 | -328 | 1.979x10 ⁻² | 7.782x10 ⁻³ | 0.456 | 0.227 |
| 2.5% | 0.00028 | 2.765 | 65.42 | 3.499 | -243 | 6.843x10 ⁻⁴ | 2.691x10 ⁻⁴ | 0.210 | 0.026 |
| 5% | 0.00056 | 2.074 | 74.06 | 9.107 | -263 | 5.133x10 ⁻⁴ | 2.018x10 ⁻⁴ | 0.185 | 0.058 |
| 7.5% | 0.00084 | 1.556 | 80.54 | 8.448 | -317 | 3.851x10 ⁻⁴ | 1.514x10 ⁻⁴ | 0.207 | 0.036 |
| 10% | 0.00112 | 1.241 | 84.48 | 5.146 | -348 | 3.072x10 ⁻² | 1.208x10 ⁻² | 0.434 | 0.084 |
| 12.5% | 0.00140 | 1.051 | 86.85 | 1.513 | -364 | 2.601x10 ⁻² | 1.023x10 ⁻² | 0.572 | 0.158 |
| 15% | 0.00168 | 1.003 | 87.46 | 3.888 | -364 | 2.483x10 ⁻³ | 9.762x10 ⁻⁴ | 0.249 | 0.089 |



(a)



(b)

Fig. 6 Comparison plot of cathodic and anodic polarization scans for austenitic stainless steel in 3M H₂SO₄ + 3.5% NaCl solution in the absence and presence of different concentrations of DMEA at 25°C. (a) 0% - 5% DMEA (b) 7.5% - 15% DMEA

Anodic and cathodic currents were inhibited effectively with increasing concentrations of DMEA. This compound appeared to act as a mixed type inhibitor since both cathodic (hydrogen evolution) and anodic (metal dissolution) reactions were influenced by the presence of DMEA in the corrosive medium, with the anodic effect being more significant suppressed than the cathodic reactions.

As shown in Table 2, the values of cathodic Tafel slope constants (bc) varied differentially in the presence of DMEA concentrations, indicating changes in the mechanism of its inhibition. This suggests that inhibitor affects the mechanism of cathodic reaction (hydrogen evolution and oxygen reduction reaction) which is the main cathodic process under activation control and the addition of DMEA modifies and suppresses the reaction. Results suggests that the inhibition

mode of the tested DMEA is by simple blockage of the surface via adsorption, accompanied by an increase in the number of adsorbed organic molecules on the steel with increase in inhibitor concentration, which impede more the diffusion of ions to or from the electrode surface as the degree of surface coverage (θ) increases (Mohamed et al., 2009).

The anodic Tafel lines (ba) are observed to change with addition of inhibitors suggesting that the inhibitor were first adsorbed onto the metal surface and impedes the passage of metal ions from the oxide-free metal surface into the solution, by merely blocking the reaction sites of the metal surface thus affecting the anodic reaction mechanism. Increasing the concentration of the inhibitor gives rise to a consistent decrease in anodic and cathodic current densities indicating that DMEA acts as a mixed type inhibitor (Muralidharan et al., 1995).



Corrosion potentials slightly shifted in the positive direction. A compound can be classified as an anodic- or a cathodic-type inhibitor when the change in the E_{corr} value is larger than 85mV (Musa et al., 2010, Li et al., 2010). If displacement in E_{corr} is <85, the inhibitor can be seen as mixed type. In this study the maximum displacement in E_{corr} value was 54mV.. Small changes in potentials can be a result of the competition of the anodic and the cathodic inhibiting reactions (Fouda et al., 2010). However, in the anodic range from the corrosion potential, the current density starts to increase very steeply due to active metal dissolution reaction, and then stabilizes over a passivation zone extending to ~1000 mV indicating strong resistance to pitting corrosion before it starts again to increase faster due to breakdown of the passive film and pit initiation.

The values of the anodic Tafel slope can be attributed to surface kinetic process rather than a diffusion-controlled one (Amin et al., 2010), where the inhibitor molecules are adsorbed via their polycentric adsorption sites on to the steel surface forming a protective layer. Furthermore, the results in Table 2 demonstrate clearly demonstrate the inhibitory effect of DMEA on the stainless steel corrosion whereby both i_{corr} and CR decreases, accompanied by a decrease in polarization resistance (R_p). The inhibition mechanism of these DMEA compounds is a combination of surface blockage and electrostatic repulsion between adsorbed species and chloride ions. The adsorption of DMEA depends on the inhibitors concentrations. DMEA act on both anodic and cathodic sites and reducing the corrosion rate without a significant change in the corrosion potential, generally by surface adsorption over the surface of the steel in contact with the inhibitor and consequently forming a thin protective layer. It is clear that the cathodic reaction [hydrogen evolution] is inhibited and the inhibition increases along with the inhibitor concentration (Soeda and Ichimura, 2003). This controls corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion (Gaidis, 2004). The variable constancy of this cathodic slope can indicate that the mechanism of proton discharge reaction changes by addition of the DMEA to the acidic media.

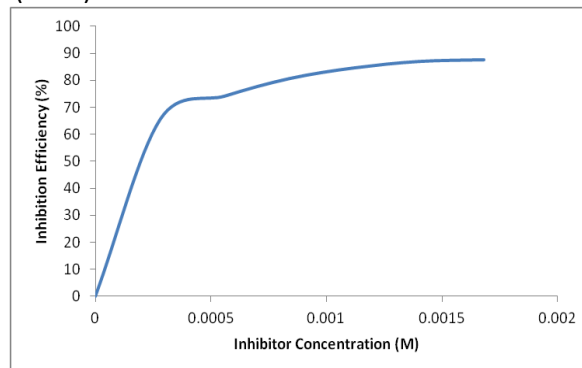


Fig. 7. The relationship between % IE and inhibitor concentration for polarization test

3.3 Mechanism of inhibition

As far as the inhibition process is concerned, the adsorption of the inhibitors at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Inhibition of austenitic stainless steel in H_2SO_4 solution by the DMEA can be explained on the basis of adsorption. Adsorption depends on the nature and the state of the metal surface on the type of corrosive medium and on the chemical structure of the inhibitor. Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film (Cruz et al, 2004).

Four types of adsorption may take place involving organic molecules at the metal solution interface (i) electrostatic attraction between charged molecules and the charged metal, (ii) interaction of n electrons with the metal, (iii) interaction of uncharged electron pairs in the molecule with the metal and (iv) a combination of the above (Ajmal et al., 1994). It is apparent that the adsorption of DMEA on the steel surface could occur directly on the basis of donor acceptor between the lone pairs of the heteroatoms, the extensively delocalized π electrons of the DMEA molecule and the vacant d-orbitals of iron surface atoms (Abdel-Aal and Morad, 2001). The functional group responsible



for DMEA adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface act as a Lewis acid because they accept electrons from a donor group. Amines adsorption is influenced by the electronic properties of the functional groups, R, bound to the nitrogen atom (Ormellesse et al., 2009).

In acidic solution, these compounds can exist as protonated species; these protonated species may adsorb on the cathodic sites of the stainless steel and decrease the evolution of hydrogen. These compounds are able to adsorb on anodic sites through N atoms, which is an electron donating groups. The adsorption of these compounds on anodic sites decreases anodic dissolution of stainless steel by the electron-rich heteroatoms in DMEA which adsorbs on the anodic site through their lone pairs of electrons of nitrogen thus reduces the anodic dissolution of metal. The performance of DMEA is also attributed to the presence of OH

Inhibition of the stainless steel corrosion DMEA was also found to depend on its stability in acidic solutions. Transfer of lone pairs of electrons on the nitrogen to the surface to form coordinate type linkage is favored by the presence of vacant orbital in iron atom of low energy. Polar character of substituent in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule. The presence of one active adsorption centers [one N-atoms] do not necessarily impact on the electron charge density on the molecule but increase in the inhibition efficiency as this occurs with increasing concentration of the compound. The presence of chloride ion in some way increases this migration; the passive barrier becomes less effective at holding iron ions inside. Finally, at some point, the film ceases to exist and is replaced by an anodic site. The mechanism by which chloride ion accelerates corrosion of steel is complex, but one or more of the following descriptions (Abd El-Maksoud and Fouda, 2005) may be appropriate:

- (1) Penetration of oxide film by chloride ion.
- (2) Adsorption of chloride ion rather than a passivating species.
- (3) Field effect of chloride ion pulling ferrous ions out of the metal.
- (4) Catalysis of corrosion reaction by a bridging structure.

(5) Complex formation between chloride ion and some form of iron (Trautenberg and Foley, 1971)

Some of the inhibition mechanisms identified by a previous study in aqueous solutions suggested that DMEA was able to displace chloride ions from the steel surface and to protect the surface passive film. This differed from the finding from the study in aqueous solutions (Welle et al., 1997), where the DMEA-to-chloride concentration ratio was much higher and a durable passivating film was formed by DMEA on the steel surface. DMEA effectively delayed the onset of steel corrosion and inhibited the steel corrosion even when the passive film was compromised. According to (Hansson et al 1998) the strong absorption of DMEA onto the steel surface inhibited the cathodic reaction of steel corrosion by limiting the access of oxygen to the steel.

Generally, the adsorption of organic compounds can be described by two main modes of interaction: physisorption and chemisorption. The former requires the presence of electrically charged metal surface and charged species in the bulk of solution, while the latter involves charge-sharing or charge-transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of a bond (Donahue and Nobe, 1965, Moretti et al., 2004, Zhao and Mu, 1944)

3.4 Adsorption isotherm

The mechanism of corrosion protection may be explained on the basis of adsorption behavior (Allam, 2007). Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The adsorptive behavior of a corrosion inhibitor is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction (Emregul et al., 2003). Interaction information between the inhibitor molecule and metal surface can be provided by adsorption isotherm (Emregul et al., 2006). For an inhibitor to have a high surface coverage on the surface, a chemical bond between the inhibitor and the metal atom stronger than the one for water molecules should be formed. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms. Langmuir adsorption isotherm



was applied to describe the adsorption mechanism for DMEA compounds as it fits the experimental results at 25 °C.

The conventional form of the Langmuir isotherm is,

$$\left[\frac{\theta}{1-\theta} \right] = K_{ads}C \quad \text{eqn.7}$$

where θ is the degree of coverage on the metal surface, C is the inhibitor concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process. The plots of $\frac{C}{\theta}$ versus the inhibitor concentration were linear (Fig. 8) indicating Langmuir adsorption.

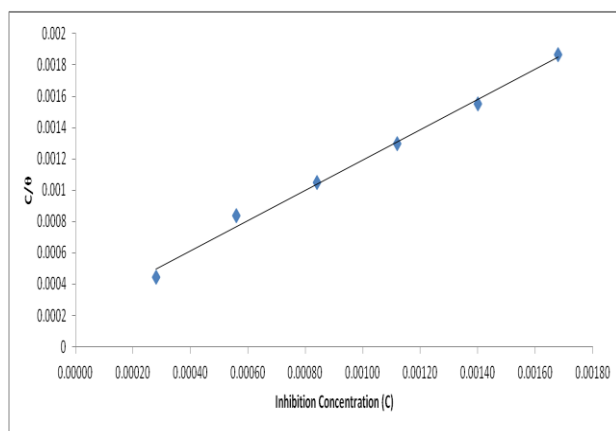


Fig. 8 Relationship between $\frac{C}{\theta}$ and inhibitor concentration (C)

Table 3 Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of DMEA

| Inhibitor Concentration (M) | Free energy of Adsorption (ΔG_{ads}) | Surface Coverage (θ) | Equilibrium Constant of Adsorption (K_{ads}) |
|-----------------------------|--|-------------------------------|--|
| 0 | 0 | 0 | 0 |
| 0.00028 | 31.52 | 0.625 | 6009.62 |
| 0.00056 | 30.24 | 0.668 | 3591.40 |
| 0.00084 | 30.91 | 0.798 | 4694.12 |
| 0.00112 | 31.38 | 0.864 | 5684.21 |
| 0.00140 | 31.76 | 0.903 | 6639.71 |
| 0.00168 | 31.20 | 0.899 | 5288.24 |

The free energies of adsorption, ΔG_{ads} , were calculated from the equilibrium constant of

The deviation of the slopes from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. Langmuir isotherm assumes that:

- (i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.
- (ii) ΔG_{ads} is the same for all sites and it is independent of θ .
- (iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG_{ads} (Villamil et al, 1999).

adsorption using the following equation as shown in table 3

$$\Delta G_{ads} = -2.303RT \log [55.5K]$$



Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature. Generally, values of ΔG_{ads} around -20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal [physisorption]; those around -40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (Obot et al., 2009). The value of ΔG_{ads} reflects the

strong adsorption capability. The negative values of ΔG_{ads}

showed that the adsorption of inhibitor molecules on the metal surface is spontaneous (Hosseini et al., 2003). The values of ΔG_{ads} calculated ranges between -30.24 and -31.76 kJ mol⁻¹ for DMEA. Accordingly, the values of ΔG_{ads} obtained in the present study indicate that the adsorption mechanism of DMEA on austenitic stainless steel involves two types of interaction, chemisorption and physisorption. Indeed, due to the strong adsorption of water molecules on the surface of stainless steel, one may assume that adsorption occurs first due to the physical forces. The removal of water molecules from the surface is accompanied by chemical interaction between the metal surface and the adsorbate, and that turns to chemisorptions (Vračar, L.M and Dražić, 2002). It is assumed from observation that the adsorbed layer was of one-molecule thickness at all sites, resulting in equal energies and enthalpies of adsorption. The intermolecular bonding to the adsorption sites can be either chemical or physical, but is sufficiently strong to prevent displacement of adsorbed molecules along the surface (Da, browski, 2001).

The nitrogen and oxygen atoms of the inhibitor molecules are readily adsorbed onto the metal surface, forming insoluble stable films on the metal surface, thus decreasing metal dissolution Saliyan (V.R and Adhikari, 2008).

4. Conclusions

- (i) N,N'-dimethylaminoethanol is a inhibitor for austenitic stainless steel in acidic chloride environment
- (ii) The inhibition efficiency increases with inhibitor concentration.

(iii) The investigated compound inhibits corrosion by adsorption of the inhibitor on the steel surface blocking the active sites and inhibition of the hydrogen evolution reactions.

(iv) The adsorption of the compounds on the stainless steel surface was found to obey Langmuir adsorption isotherm.

(iv) The order of the inhibition efficiency of inhibitor at varying concentration as given by linear polarization measurements is in good agreement with that obtained from weight loss measurements.

(v) N,N'-dimethylaminoethanol provide protection against pitting corrosion of austenitic stainless steel in presence of chloride ions.

(vi) The free energy of adsorption indicates that the process was spontaneous and inhibition was due to physiochemical reactions on the steel surface.

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