

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Study the Efficiency of Some Amine Derivatives as Corrosion and Scale Inhibitors for Cooling Water Systems

M. A. Migahed¹, A. A. Attia², R. E. Habib²

¹ *Egyptian Petroleum Research Institute, Nasr City, Cairo (11727), Egypt*

² *Chemistry Department, Faculty of Science, Zagazig University, Egypt*

Abstract

Corrosion and scaling are the main problems in cooling water systems. For this purpose, this paper is aimed to study the inhibition efficiency of some amine derivatives for C-Steel in sea water by using electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The selected compounds with different structure and size were found to be adsorbed on carbon steel surface and had good performance as corrosion and scale inhibitors. Potentiodynamic polarization studies indicate that amine derivatives act as mixed type corrosion inhibitors, while the data obtained from EIS data revealed that, the value of the charge transfer resistance (R_t) increased by increasing the inhibitor concentration leading to increasing the inhibition efficiency. Also, the obtained results from this study showed that the selected amines can decrease scale build-up growth under experimental conditions. The surface morphology of carbon steel was investigated in the absence and presence of the selected inhibitors through scanning electron microscopic (SEM) and energy dispersive analysis of X-rays.

Keywords: Cooling water system, Corrosion and scale inhibitors, Amine derivatives, Carbon steel, Potentiodynamic polarization, EIS, SEM, EDX.

Corresponding author e-mail: mohamedatiyya707@hotmail.com

1. Introduction

Two of the main problems of cooling water systems are corrosion and scale phenomena. These problems have a great economic impact, since the first involves deterioration of metallic surface, whereas the second causes loss of capacity for thermal exchange. These phenomena occur simultaneously in many industrial applications like cooling systems, and hence a study of their development and inhibition under real conditions becomes an issue of great interest. Significant scientific and technological efforts have been made to control these phenomena, yet they are still controlled through addition of chemicals that inhibit their development. Many inhibitors have been used in cooling water systems in order to solve these problems [1–4]. Corrosion and scale occur because of the electrochemical oxidation reduction reaction and the metal salt sediments on the metal surface [5].

Water is the most commonly used cooling fluid in industrial systems, such as in heat exchangers, cooling towers, and related equipment. Depending on the quality and availability of fresh water supply, the recirculating cooling water systems contain varying amounts of solids suspended or dissolved, most likely both [6]. Dissolved solids usually consist of mineral complexes in the form of crystals, which in a process described as nucleation continue to grow; they are characterized by the extent of their solubility and especially of their potential insolubility at particular temperatures.

Carbon steel has many industrial applications because of its easy availability, low cost, uncomplicated fabrication and extensive usage, such as in water pipe lines [7, 8], cooling water systems [9], boilers, process industries, oil and gas, refining and extraction, etc.

Corrosion occurs when an electric current flows from one part of the metal (anode) through the water (electrolyte) to another part of the metal (cathode). Corrosion takes place at the anode only. This process degrades the metal, reduces its strength, thickness, and in some extreme cases, creates pits and then holes in the material. Corrosion, in general, and pitting corrosion, in particular, must be guarded against in order to ensure the long term integrity of the cooling system [10].

Corrosion inhibitors are substances which, when added in small concentrations to a corrosive media, decrease or prevent the reaction of the metal with the media [11]. Most of the effective inhibitors contain heteroatoms such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface [12–21]. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule [22–47]. Amines are well known as corrosion inhibitors for iron and its alloys. The relatively high water solubility of low molecular weight amines is an advantage for their use as corrosion inhibitors [48–53]. The efficiency of an organic compound as an inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of a replacement of water molecules at a corroding interface.

Scale is formed from minerals, formerly dissolved in water, that were deposited from the water onto heat transfer surfaces or in-flow water lines. As water is evaporated in a cooling tower, the concentration of dissolved solids becomes greater until the solubility of a particular scale-causing mineral salt is exceeded. The most common scaling minerals are calcium

carbonate (CaCO_3), calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$, calcium sulfate (CaSO_4), and silica. Formation of magnesium silicate scale is also possible under certain conditions. Silica will form in areas having the lowest water temperature, such as in the cooling tower fill [54]. The critical parameters for cooling water are: conductivity, total dissolved solids (TDS), hardness, pH, alkalinity and saturation index [55]. A number of techniques such as the controlled acidification of sea water [56], the use of anti-scale agents [57, 58] and the utilization of sponge – ball cleaning are employed to control scaling.

Some of amine derivatives have been evaluated as corrosion inhibitors against several industrial media [59] which showed an inhibition efficiency in the range of 50 – 80%. Since scale formation and metal corrosion problems appear in cooling water systems, this work aims to examine the inhibition efficiency of some amine derivatives as corrosion and scale inhibitors for cooling water systems. The added value of this work arises from the point that the prepared compounds act as both corrosion and scale inhibitors which provide a double acting protection properties. On other hand using a double acting chemical replace injecting two different chemicals into cooling water systems which provides an economic advantage. Moreover eliminates potential interference in case of using two difference chemical injections for corrosion and scale inhibition in the system. This work is an onset of a series of works currently under investigation in our labs.

2. Experimental

2.1. Materials

2.1.1. Specimens preparation.

The principal material used in the experiments is cylindrical carbon steel of grade X-65 with 1 cm² surface area. The electrodes were degreased with acetone in an ultrasonic water bath for about 10 min, air-dried, embedded in two-component epoxy resin, and mounted in a PVC holder. A copper wire was soldered to the rear side of the coupons as an electrical connection. The exposed surface of the electrode (of area 1 cm²) was wet polished with silicon carbide abrasive paper up to 800 grits, rinsed with ethanol, placed in an ultrasonic acetone bath for about 5 min to remove possible residue of polishing, and air-dried. This was used as the working electrode during the electrochemical tests.

2.1.1.1. Chemical composition of the tested carbon steels

The average range of chemical composition of the tested carbon steel are shown in [Table 1](#).

2.1.2. Chemical composition of the studied cooling water

Most of the elements that can be found on earth are present in seawater, at least in trace amounts. However, 11 of the constituents account for 99.95 percent of the total solutes, as indicated in [Table 2](#), with chloride ions being by far the largest constituent. The concentration of dissolved materials in the

sea varies greatly with location and time because rivers dilute seawater, rain, or melting ice and seawater can be concentrated by evaporation.

The most important properties of seawater are:

- i) Remarkably constant ratios of the concentrations of the major constituents worldwide.
- ii) High salt concentration, mainly sodium chloride.
- iii) High electrical conductivity.
- iv) Relatively high and constant pH.
- v) Buffering capacity.
- vi) Solubility for gases, of which oxygen and carbon dioxide in particular are of importance in the context of corrosion.
- vii) The presence of a myriad of organic compounds.
- viii) The existence of biological life, to be further distinguished as microfouling (e.g., bacteria, slime) and macrofouling (e.g., seaweed, mussels, barnacles, and many kinds of animals or fish).

Some of these factors are interrelated and depend on physical, chemical, and biological variables, such as depth, temperature, intensity of light, and the availability of nutrients. The main numerical specification of seawater is its salinity.

2.2. Inhibitors

Amines and its derivatives are good selected compounds in this work which inhibit the corrosion and scale deposition for carbon steel in cooling water

systems. The chemical structure, 3D structure, nomenclature and molecular weight of the inhibitors used in this work are listed in [Table 3](#).

2.3. Techniques

2.3.1. Potentiodynamic polarization measurements

Electrochemical measurements were carried out using Volta lab80 (Tacussel-radiometer PGZ402) controlled by Tacussel corrosion analysis software model (Volta master 4). Platinum electrode was used as auxiliary electrode. All potentials were measured against saturated calomel electrode (SCE) as a reference electrode. All measurements were carried out in air saturated solutions and at ambient temperature (298 K). Tafel extrapolation method by taking the extrapolation interval of 250 mV with respect to E_{corr} .

2.3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance (EIS) measurements were carried out using Volta lab 80 potentiostat (Tacussel-radiometerPGZ402) controlled by Tacussel corrosion analysis software model (Volta master 4). Impedance spectra were obtained in the frequency range between 100 kHz and 50 mHz using 20steps per frequency decade at open circuit potential after 1 hour immersion time. AC signal with 20 mV amplitude peak to peak was used to perturb the system. EIS diagrams are given in both Nyquist and Bode representations.

2.3.3. Evaluation of the selected amine derivatives as a scale inhibitor for calcium sulfate deposition

Experimental procedure involves dissolving 9.11 g of CaCl_2 per L of double distilled water (brine A). On the other hand the sulfate solution (brine B) can be prepared by dissolving 7.3 g of Na_2SO_4 per L of double distilled water. Test protocol consists of mixing 50 mL of calcium solution to 50 mL of sulfate solution. The solutions are then incubated in water thermostat at 90 °C for 24 hours. At the end of test duration, the solution is filtered through a 0.22micron filter paper and the calcium concentration is analyzed by titration using 0.01 M EDTA and Murexide as indicator. Experiments were repeated for different doses (25 – 125 ppm) of the selected amine derivatives at the same test duration [60].

2.3.4. Scanning electron microscopy (SEM)

Immersion corrosion analysis of carbon steel samples in Sea water with and without the optimal concentration of the inhibitor (III) was performed using SEM. In order to study the surface morphology, the samples were subjected to SEM immediately after the corrosion tests using JSM-6510LA Analytical Scanning Electron Microscope.

2.3.5. Energy dispersive analysis of X-rays (EDX)

EDX system attached with a JSM-6510LA Analytical Scanning Electron Microscope was used for elemental analysis or chemical characterization of

the film formed on carbon steel surface before and after applying the compound (III).

3. Results and discussion

3.1. Potentiodynamic polarization measurements

The dynamic potential polarization is the common method that evaluates inhibition efficiency of corrosion inhibitor [61].

The electrochemical measurements were carried out in a cell with three electrodes mode; platinum electrode and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The 1 cm² area of carbon steel sample as working electrode (WE) was abraded, washed, finally immersed in the cooling water. The working electrode was first immersed into the test solution for 1 h to establish a steady state open circuit potential. After determination the open circuit potential, Potentiodynamic polarization curves were obtained with a scan rate of 1mVs⁻¹ in both cathodic and anodic potentials to investigate the polarization behavior . Figure (1) shows the cathodic and anodic polarization curves of carbon steel immersed in sea water in the absence and presence of different concentrations of compound (III) as a representative sample.

Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) were calculated [62] and listed in Table 4. The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship. the inhibition efficiency IE% were calculated from the flowing equation:

$$\text{I.E. \%} = [(I_{\text{corr}} - I_{\text{corr}}(\text{inh})/I_{\text{corr}})] \times 100 \quad (1)$$

Where I_{corr} and $I_{\text{corr}}(\text{inh})$ are the corrosion current values without and with the addition of various concentration of inhibitor.

From Fig. 1, it is clear that both anodic metal dissolution and cathodic reduction reactions were inhibited when the compound III was added to the sea water and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the inhibitor. The results show that the increase of the inhibitor concentration leads to decrease the corrosion current density (I_{corr}), but the (β_{c} and β_{a}) are approximately variable indicating that the retardation of the two reactions (cathodic oxygen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism. The obtained results indicate that the percentage inhibition efficiency (IE%) of compound III is greater than that of compounds II and I respectively.

3.2. Electrochemical impedance spectroscopy (EIS)

In order to understand the corrosion behavior of carbon steel in sea water in the absence and presence of various concentrations of compounds I, II and III as a representative sample, electrochemical impedance spectroscopy (EIS) measurements were carried out. Nyquist plots for compound III is shown in Fig. 2 and Bode plot also is shown in Fig. 3.

The previous plots show that the impedance response of carbon steel in sea water was significantly changed after the addition of the inhibitor molecules. Various parameters such as the charge transfer resistance (R_t), double layer capacitance (C_{dl}) and percentage inhibition efficiency IE% were calculated according to the following equations and listed in Table 5.

The percentage inhibition efficiency IE% was calculated from the values of R_t using the following equation [63]:

$$IE\% = [1 - (R_t/R_{t(inh)})] \times 100 \quad (2)$$

Where R_t and $R_{t(inh)}$ are the charge transfer resistance values in the absence and presence of inhibitor, respectively. Increasing the value of charge transfer resistance (R_t) and decreasing the value of double layer capacitance (C_{dl}) by increasing the inhibitor concentration indicate that the inhibitor molecules inhibit corrosion rate of carbon steel in sea water by adsorption mechanism [64]. For analysis of the obtained impedance spectra, the equivalent circuit (EC) was obtained using Boukamp program as shown in Fig. 4, where R_s is the solution resistance, R_t is the charge transfer resistance, C_{dl} is the electrochemical double layer capacitance, R_f is the film resistance and C_f is the film capacitance. From EIS data it was found that the percentage inhibition efficiency of inhibitor (III) is greater than that of inhibitors (I and II) thereby, agreeing with aforementioned results of potentiodynamic polarization measurements.

3.3. Evaluation of the selected amine derivatives as scale inhibitors

The present work was extended to establish the effectiveness of the selected amine derivatives as a scale inhibitor for calcium sulfate deposition in sea water. The laboratory procedures were carried out as described in the experimental part. The percentage inhibition efficiency was calculated as follow:

$$\text{Scale inhibition efficiency \%} = [Ca_i - Ca_b / Ca_c - Ca_b] \times 100 \quad (3)$$

Where,

Ca_i = Calcium ion concentration for the sample treated with the inhibitor after precipitation.

Ca_b = Calcium ion concentration in the blank solution after precipitation.

Ca_c = Calcium ion concentration in the blank solution before precipitation.

The obtained results are listed in [Table 6](#) and graphically shown in [Fig. 5](#). It is clear that the percentage inhibition efficiency increase by increasing the inhibitor concentration, reaching 86.7 % at 125 ppm.

3.4. Scanning electron microscopy (SEM)

[Fig. 6a](#) shows SEM image of polished carbon steel surface. The micrograph shows a characteristic inclusion, which was probably an oxide inclusion [65]. [Fig. 6b](#) shows SEM of the surface of carbon steel specimen after immersion in sea water for 90 days in absence of inhibitor, while [Fig. 6c](#) shows SEM of the surface of another carbon steel specimen after immersion in sea water for the same time interval in the presence of 300 ppm of the compound III. The resulting scanning electron micrographs reveal that, the surface was strongly damaged in the absence of the inhibitor, but in the presence of 300 ppm of the compound III, there is less damage in the surface. This confirms the observed high inhibition efficiency of compound III at this concentration.

3.5. Energy dispersive analysis of X-rays (EDX)

The EDX spectrum in [Fig. 7a](#) shows the characteristic peaks of some elements constituting the polished carbon steel surface. The spectrum of the polished carbon steel surface after immersion in the sea water in the absence and presence of compound III for 90 days is shown in [Figs. 7b](#) and [7c](#),

respectively. The spectrum of Fig. 7c shows that the Fe peak is considerably decreased relative to the samples in Figs. 7a and 7b. This decreasing of the Fe band is indicated that strongly adherent protective film of compound III formed on the polished carbon steel surface, which leads to a high degree of inhibition efficiency [66]. EDX and SEM examinations of carbon steel surface support the results obtained from chemical and electrochemical methods that the compounds are a good inhibitors for carbon steel in sea water.

The results of both SEM and EDX techniques confirm the formation of a good protective layer on the surface of carbon steel in the presence of 300 ppm of the inhibitor (III).

3.6 Inhibition mechanism of the selected amine derivatives

3.6.1 Corrosion inhibition mechanism

The adsorption of amine derivative molecules on carbon steel surface can take place by chemisorption. The adsorption process arises from the donor-acceptor interactions between p-electrons of nitrogen atoms and vacant d-orbitals of iron [67, 68]. The orientation of molecules may depend on the pH and/or electrode potential [69]. In this case, the molecules can be adsorbed on the surface of carbon steel through the chemisorption mechanism that occurred by the displacement of the adsorbed water molecules from the metal surface then sharing electrons between the hetero atom and iron. The schematic illustration of different modes of adsorption on metal/solution interface is shown in Fig. (8) [70].

The corrosion inhibition efficiency for inhibitors (I-III) was tested by using Potentiodynamic polarization and EIS technique and follows the sequence:

$$\text{III} > \text{II} > \text{I}$$

From the obtained results, one can conclude that, as the number of nitrogen atoms in the amine derivatives increase, their inhibition efficiency as corrosion inhibitor were increased.

3.6.2 Scale inhibition mechanism

Scale inhibition is a technique in which a certain type of chemical additive has been used to inhibit the growth rate of scale crystal formed in aqueous media. This process leads to delay, reduce or prevent scale formation upon adding a small amounts to normally scaling water. The use of chelating agent such as amine derivative can break up acid resistant scale by isolating and locking up the scale metallic ions within closed ring, like structure as shown in [Fig.\(9\)](#) [71].

4. Conclusions

The results showed that all compounds used in this work act as effective corrosion and scale inhibitors for carbon steel in sea water. The percentage inhibition efficiency (IE%) of the inhibitors increases by introducing number of Ethylene amine units into inhibitor molecule. EIS data indicated that the value of charge transfer resistance (R_t) increased by increasing the inhibitor concentration while, the value of electrochemical capacitance (C_{dl}) decreased. The potentiodynamic polarization curves indicated that the inhibitor molecules inhibit both anodic metal dissolution and also cathodic oxygen reduction. So that the inhibitors used in this work are classified as mixed type. The inhibition mechanism is attributed to the strong adsorption ability of the selected amine derivatives on carbon steel surface, forming a

good protective layer, which isolates the surface from the aggressive environment as confirmed by SEM and EDX techniques.

References

- [1] L.L. Sheir, R.A. Jarman, Corrosion, third ed. Butterworth-Heinmann Ltd., Great Britain, (1994).
- [2] S.N. Banerjee, An introduction to Science of Corrosion and its Inhibition, Oxonian Press PVT Ltd., India, (1985).
- [3] I.L. Rozenfeld, Corrosion Inhibition, McGraw-Hill Inc., USA, (1981).
- [4] D.A. Jones, Principles and Prevention of Corrosion, Macmillan Publishing Company, USA, (1991).
- [5] S. H. You, D. H. Tseng, G. L. Guo and J. J. Yang, “The Potential for the Recovery and Reuse of Cooling Water in Taiwan,” Resources, Conservation and Recycling, Vol. 26, No. 1, (1999) 53-70
- [6] D.-J. Choi, S.-J. You, J.-G. Kim, Development of an environmentally safe corrosion, scale, and microorganism inhibitor for open recirculating cooling systems, Mater. Sci. Eng. A 335 (2002) 228–236
- [7] R.E. Melchers, R. Jeffery, Corros. Rev. 1, (2005) 84

- [8] R.E. Melchers, R. Jeffery, *Corros. Rev.* 6, (2005) 297
- [9] G. Saha, N. Kurmaih, N. Hakerman, *J. Phys. Chem.* 59, (1955) 707
- [10] P.R. Roberge, *Handbook of Corrosion Engineering*, McGraw- Hill, (1999)
- [11] A. Singh, Eno E. Ebenso, and M. A. Quraishi¹, *Int. J. Corros.*, (2012) 2012
- [12] A.G. Christy, A. Lowe, V. Otieno-Alego, M. Stoll, R.D. Webster, *J. Appl. Electrochem.* 34,(2004) 25
- [13] H. Otmacic, J. Telegdi, K. Papp, E. Stupnisek-Lisac, *J. Appl. Electrochem.* 34, (2004) 545
- [14] H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, *J. Appl. Electrochem.* 32, (2002) 65
- [15] F. Zucchi, G. Trabanelli, M. Fonsati, *Corros. Sci.* 38, (1996) 2019
- [16] F. Zucchi, G. Trabanelli, N. Alagia, *ACH-Models Chem.* 132, (1995) 579
- [17] C. Wang, S. Chen, S. Zhao, *J. Electrochem. Soc.* 151, B11 (2004)
- [18] M. Kendig, S. Jeanjaquet, *J. Electrochem. Soc.* 149, B47 (2002)
- [19] H.Y. Ma, C. Yang, B.S. Yin, G.Y. Li, S.H. Chen, J.L. Luo, *J. Appl. Surf. Sci.* 218,(2003) 143

- [20] G.K. Gomma, M.H. Wahdan, Mater. Chem. Phys. 39, (1994) 142
- [21] K.F. Khaled, N. Hackerman, Electrochem. Acta 49, (2004) 485
- [22] E. Khamis, F. Bellucci, R. Latanision, M. El Ashry, Corrosion 47, (1991) 677
- [23] E. Khamis, E.S.H. El Ashry, A.K. Ibrahim, Brit. Corros. J. 35, (2000) 150
- [24] E.S.H. El Ashry, A. El Nemr, S.A. Esawy, S. Ragab, Electrochim. Acta 51, (2006) 3957
- [25] E.S.H. El Ashry, A. El Nemr, S.A. Esawy, S. Ragab, S. Chem. Physics: Indian J., 1(2006) 41(<http://pcaij.tsijournals.com>)
- [26] D.P. Schweinsberg, V. Ashworth, Corros. Sci. 28, (1988) 539
- [27] S.N. Raicheva, B.V. Aleksiev, E.I. Sokolova, Corros. Sci. 34, (1993) 343
- [28] M.A. Quraishi, M.A. Khan, D. Jamal, M. Ajmal, S. Muralidharan, S. Iyer, J. Appl. Electrochem. 26, (1996) 1253
- [29] M.A. Quraishi, M. Khan, D. Jamal, M. S. Muralidharan, S.V.K. KIyer, Brit. Corros. J., 32(1997) 72
- [30] B. Mernari, H. Attari, M. Traisnel, F. Bentiss, M. Lagrene'e, Corros. Sci. 40, (1998) 391

- [31] V. Hluchan, B.L. Wheeler, N. Hackerman, *Mater. Corros.* 39, (1988) 512
- [32] X.L. Cheng, H.Y. Ma, S.H. Chen, R. Yu, X. Chen, Z.M. Yao, *Corros. Sci.* 41, (1999) 321
- [33] M. Bouayed, H. Rabaa, A. Schiri, J. Saillard, A. Ben Bachir, A. Le Beuze, *Corros. Sci.* 41,(1999) 501
- [34] M. El Azhar, B. Mernari, M. Traisnel, L. Gengembre, F. Bentiss, M. Lagrene´e, *Corros. Sci.*43, (2001) 2229
- [35] F. Bentiss, M. Traisnel, M. Lagrene´e, *J. Appl. Electrochem.* 31, (2001) 41
- [36] L. Wang, G. Yin, *Corros. Sci.* 43, (2001) 1197
- [37] M.A. Quraishi, M. Khan, M. Ajmal, S. Muralidharan, *Electrochim.Acta* 13, (1995) 63
- [38] M.A. Quraishi, M.A.W. Khan, M. Ajmal, S. Muralidharan, S.V.K. Iyer, *Corrosion* 53,(1997) 475
- [39] M.A. Quraishi, M.A.W. Khan, M. Ajmal, *Meth. Mater.* 43, (1996) 5
- [40] A.G. Gad Alla, H.M. Tamous, *J. Appl. Electrochem.* 20, (1990) 488
- [41] R. Agrawal, T.K.G. Namboodhiri, *Corros. Sci.* 30, (1990) 37
- [42] M. Elayyachy, B. Hammouti, A. El Idrissi, *Appl. Surf. Sci.* 249, (2005)

176

- [43] M. Bouklah, B. Hammouti, M. Lagrene'e, F. Bentiss, *Corr. Sci.* 48, (2006) 2831
- [44] M. Ajmal, A.S. Mideen, M.A. Quraishi, *Corros. Sci.* 36, (1994) 79
- [45] J. Fang, J. Li, *J MolStruct. (Theochem)* 593, (2002) 179
- [46] M.A. Quraishi, H.K. Sharma, *Mater. Chem. Phys.* 78, (2002) 18
- [47] F.B. Growcock, N.R. Lopp, R. Jasinski, *J. Electrochem. Soc.* 135, (1988) 823.
- [48] R. D. Braun, E. L. Lopez and D. P. Vollmer, *Corros.Sci.* 34, (1993) 1251.
- [49] T. Szauer and A. Brandt, *Electrochim. Acta* , 26, (1981) 1209-1219.
- [50] E. S. Lisac, A. Brnada, A.D. Mance, *Corrosion Science*, 42, (2000) 243- 257.
- [51] J. de Damborenea, J. M. Bastidas and A. J. Vhunquez, , *Electrochim. Acta* , 42, (1997) 45459.
- [52] D. Martínez , R. Gonzalez , K. Montemayor , A. J. Hernandez , G. Fajardo ,M. A. L. H. Rodriguez, *Wear* ,267 (2009) 255–258.
- [53] D. Q. Zhang, L. Gao, G. D. Zhou, *Surf. Coat. Technology*, 204 (2010)

1646–1650.

- [54] M. Machado , "Cooling tower Technologies and Management – Water Minimization", Australian industry group, 2010
- [55] J. kubis, "power station zero discharge ,cooling tower", NACE international, No. 08396, 2010.
- [56] K .Spiegler, A. Laird. Principles of Desalination. New York, NY: Academic Press; (1980) 667-730.
- [57] M. Elliot, Scale control by threshold treatment. Desalination 8(1970)221-36.
- [58] K. Cooper, L. Hanlon, G. Smart, R. Talbot. The threshold inhibition phenomenon Desalination 31 (1979)257-66.
- [59] Khaled M. Ismail, Evaluation of cysteine as environmentally friendly corrosion inhibitor for copper in neutral and acidic chloride solutions, Electrochimica Acta 52 (2007) 7811–7819.
- [60] NACE standard TM 0374-2001.
- [61] J. Zhang, Z. P. Li, W. M. Zhao, W. Y. Guo and Y. Wang, "Acta Petrolei Sinica," Journal of Petroleum Processing Section, Vol. 21, No. 24, (2008) 995-998.
- [62] Q.B. Zhang, Y.X. Hua , Electrochim. Acta , 54 ,(2009) 1881.
- [63] A.P. Yadav, A. Nishikata, T. Tsuru, Corros. Sci. 46 (2004) 169.

- [64] K.F. Khaled, *Appl. Surf. Sci.* 252 (2006) 4120.
- [65] ASTM E 45-87, vol. 11,(1980) ASTM, Philadelphia, PA, 125.
- [66] M.A. Amin, *J. Appl. Electrochem.* ,36 (2006)215.
- [67] M. Behpour, S.M. Ghoreishi, M. Salavati-Niasari, B. Ebrahimi;
Materials Chemistry and Physics, 107 (2008) 153–157.
- [68] A. Yurt, A. Balaban, S. UstunKandemir, G. Bereket, B. Erk;
Materials Chemistry and Physics, 85 (2004) 420–426.
- [69] L. Vracar, D.M. Drazic; *Corrosion Science*, 44 (2002) 1669–1680.
- [70] I. Ahamad, R. Prasad, M.A. Quraishi; *Corrosion Science*, 52 (2010)
1472–1481.
- [71] A. E. Martel and M. Calvin, "Chemistry of Metal Chelate
Compounds", New York, USA, Prentic-hall Inc (1952).

List of tables

Table (1) Chemical composition of carbon steel .

Element	C	Si	Mn	P	S	Ni	Cr	Mo	V	Cu	Al	Fe
Content (Wt %)	0.09	0.22	1.52	0.01	0.05	0.04	0.02	0.004	0.002	0.02	0.04	Rest

Table (2) Average concentration of the 11 most abundant ions and molecules in clean sea water (35.0% Salinity, Density of 1.023gcm⁻³ at 25°C)

Species	Concentration	
	mmol ⁻¹ .kg ⁻¹	g.kg ⁻¹
Na ⁺	468.5	10.77
K ⁺	10.21	0.399
Mg ²⁺	53.08	1.290
Ca ²⁺	10.28	0.4121
Sr ²⁺	0.090	0.0079
Cl ⁻	545.9	19.354
Br ⁻	0.842	0.0673
F ⁻	0.068	0.0013
HCO ₃ ⁻	2.30	0.140
SO ₄ ²⁻	28.23	2.712
B(OH) ₃	0.416	0.0257

Table (3) The chemical structure, 3D, nomenclature and molecular weight of the inhibitors used.

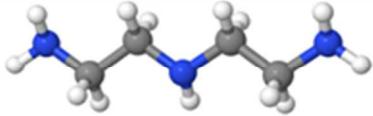
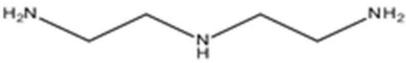
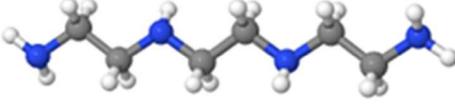
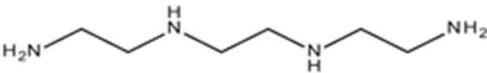
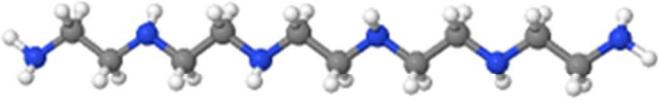
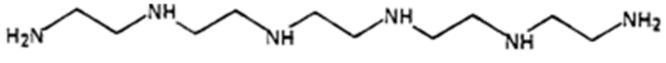
No	Inhibitor name	Chemical and 3D structure	M.wt
I	Diethylene-Triamine	  <chem>NCCNCCN</chem>	103
II	Triethylene-Tetramine	  <chem>NCCNCCNCCN</chem>	146
III	Pentaethylene-Hexamine	  <chem>NCCNCCNCCNCCNCCN</chem>	232

Table (4) Data obtained from potentiodynamic polarization measurements of carbon steel in sea water solution in the absence and presence of various concentrations of compounds I, II, and III at 298 K.

Inhibitor	Conc., ppm	$-E_{\text{corr}}$, mV vs. SCE	I_{corr} , $\mu\text{A}/\text{cm}^2$	β_a , mV dec $^{-1}$	β_c , mV dec $^{-1}$	IE%
Blank	0	760	25.62 (\pm 1.39)	119.1	301.4	-
(I)	50	776.1	14.14 (\pm 0.65)	115.1	229.6	44.78 (\pm 1.99)
	100	738	12.28 (\pm 0.65)	112.3	149.7	51.89 (\pm 4.92)
	150	807.6	10.97 (\pm 0.65)	133.2	206.8	57.18 (\pm 0.34)
	200	737.1	10.51 (\pm 0.86)	129.6	162.8	59.01 (\pm 1.69)
	250	734.4	9.15 (\pm 0.74)	125.2	138.4	64.31 (\pm 1.54)
	300	699.8	6.44 (\pm 0.83)	127.7	157.2	74.93 (\pm 2.00)
(II)	50	788.6	13.02 (\pm 1.16)	125.2	211.7	49.23 (\pm 2.68)
	100	735.7	11.96 (\pm 0.60)	120.9	190.8	53.30 (\pm 1.13)
	150	796.4	10.76 (\pm 0.95)	135.4	216.7	57.98 (\pm 3.44)
	200	714.1	9.20 (\pm 0.60)	135.2	195.3	64.09 (\pm 1.43)
	250	695.5	7.99 (\pm 0.63)	130.7	188.1	68.80 (\pm 2.03)
	300	651.7	5.68 (\pm 0.85)	131.6	144.5	77.83 (\pm 2.76)
(III)	50	689.1	9.01 (\pm 0.72)	247.8	168.7	64.86 (\pm 1.76)
	100	682.9	7.59 (\pm 0.48)	206.5	173.2	70.30 (\pm 2.67)
	150	682.1	6.70 (\pm 0.53)	199.4	171.3	73.87 (\pm 0.88)
	200	679.9	5.04 (\pm 0.66)	187.5	171.2	80.34 (\pm 2.21)
	250	672.6	3.85 (\pm 0.58)	195.1	160.7	84.99 (\pm 1.89)
	300	610.8	2.02 (\pm 0.19)	192.6	166.1	92.13 (\pm 0.34)

Table (5) Data obtained from electrochemical impedance spectroscopy (EIS) measurements of carbon steel in sea water solution in the absence and presence of various concentrations of compounds I, II and III.

Inhibitor	Conc., ppm	Coefficient	R_s ($\Omega.cm^2$)	C_s ($\mu F.cm^2$)	R_t ($\Omega.cm^2$)	C_{dl} ($\mu F.cm^2$)	IE%
Blank	0	0.99	-	-	358.13 (\pm 3.5)	1302	-
(I)	50	0.99	230	48.1	642.00 (\pm 8.0)	1217	44.21 (\pm 0.63)
	100	0.99	270	43.4	746.33 (\pm 10.0)	1104	52.01 (\pm 1.06)
	150	0.99	320	37.2	798.00 (\pm 8.0)	989.3	55.12 (\pm 0.78)
	200	0.99	350	32.5	870.33 (\pm 5.0)	930.1	58.85 (\pm 0.58)
	250	0.99	380	29.3	1001.00 (\pm 10.0)	902.5	64.22 (\pm 0.61)
	300	0.99	390	28.7	1401.00 (\pm 17.7)	887.4	74.43 (\pm 0.51)
(II)	50	0.99	250	46.2	703.00 (\pm 11.8)	1159	49.05 (\pm 0.86)
	100	0.99	290	42.4	761.45 (\pm 11.7)	1090	52.96 (\pm 0.72)
	150	0.99	350	36.7	838.33 (\pm 8.4)	970.6	57.28 (\pm 0.03)
	200	0.99	370	31.1	996.00 (\pm 3.0)	911.8	64.04 (\pm 0.42)
	250	0.99	410	28.8	1135.33 (\pm 7.1)	873.1	68.46 (\pm 0.12)
	300	0.99	420	27.6	1592.00 (\pm 20.4)	855.7	77.50 (\pm 0.20)
(III)	50	0.99	280	43.2	1015.33 (\pm 10.2)	1004	64.73 (\pm 0.37)
	100	0.99	330	40.5	1203.00 (\pm 12.0)	978.1	70.23 (\pm 0.52)
	150	0.99	390	35.2	1356.15 (\pm 12.2)	914.4	73.59 (\pm 0.50)
	200	0.99	420	29.1	1799.33 (\pm 6.7)	877.5	80.10 (\pm 0.27)
	250	0.99	430	27.9	2364.33 (\pm 8.3)	822.3	84.85 (\pm 0.15)
	300	0.99	440	26.4	3987.33 (\pm 9.0)	786.9	91.02 (\pm 0.08)

Table (6) Efficiency of the selected amine derivatives (I, II and III) as calcium sulfate scale inhibitors at various concentrations as calculated from ASTM G 3-89 Re-approved 1994

Conc., ppm	Percentage Inhibition Efficiency (IE%) of Inhibitor I	Percentage Inhibition Efficiency (IE%) of Inhibitor II	Percentage Inhibition Efficiency (IE%) of Inhibitor III
0	-	-	-
25	30.71 (\pm 0.55)	38.43 (\pm 0.31)	52.03 (\pm 0.51)
50	45.32 (\pm 0.79)	51.50 (\pm 0.52)	63.40 (\pm 1.10)
75	56.30 (\pm 0.78)	62.60 (\pm 1.08)	74.80 (\pm 1.30)
100	63.91 (\pm 1.12)	69.33 (\pm 0.67)	79.30 (\pm 0.46)
125	65.10 (\pm 1.13)	75.20 (\pm 0.46)	86.70 (\pm 0.96)

List of figures

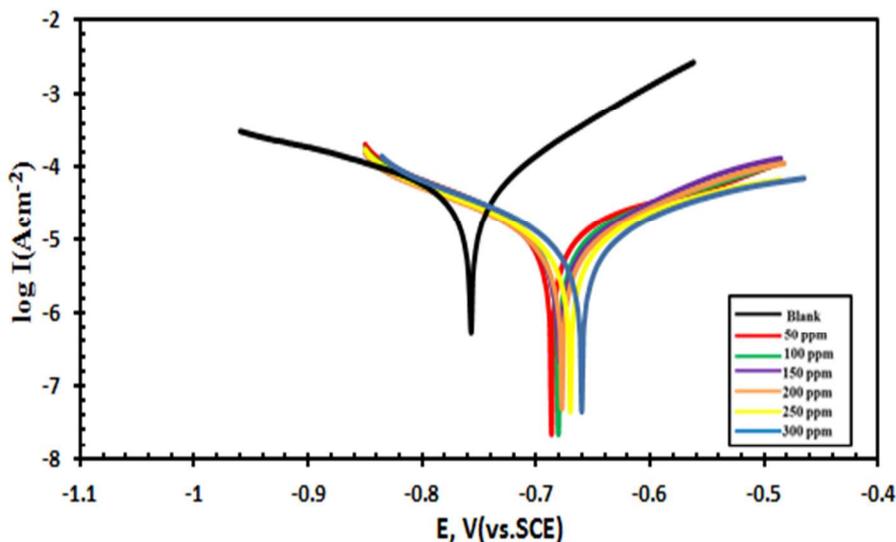


Figure (1). Potentiodynamic polarization curves ($E - \log I$ relationship) of carbon steel in sea water in the absence and presence of different concentrations of compound (III).

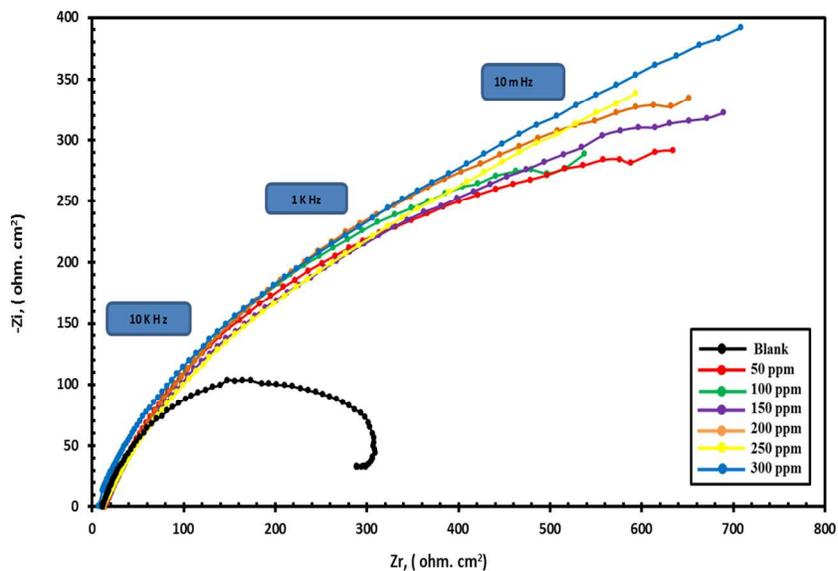
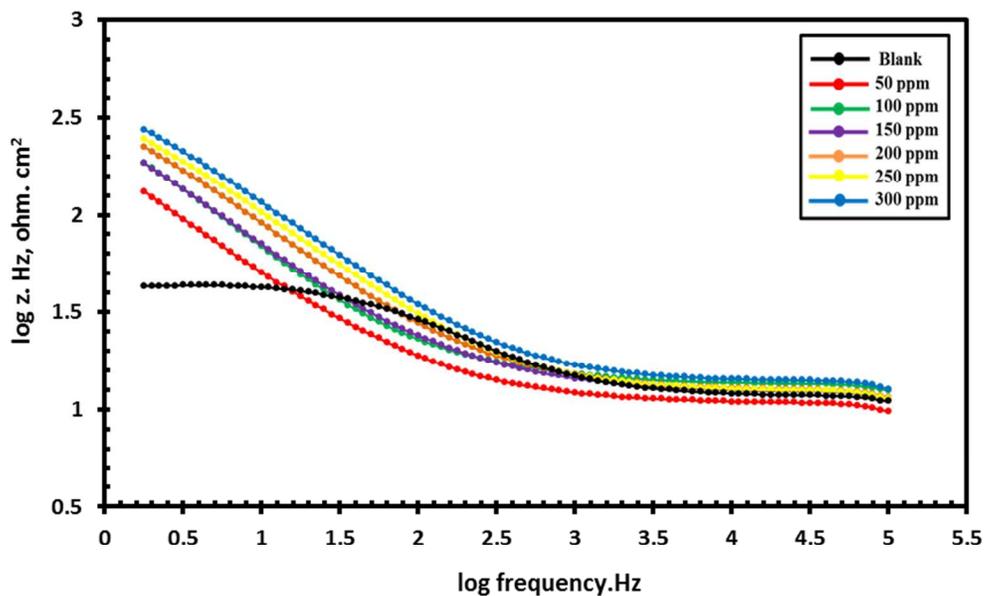
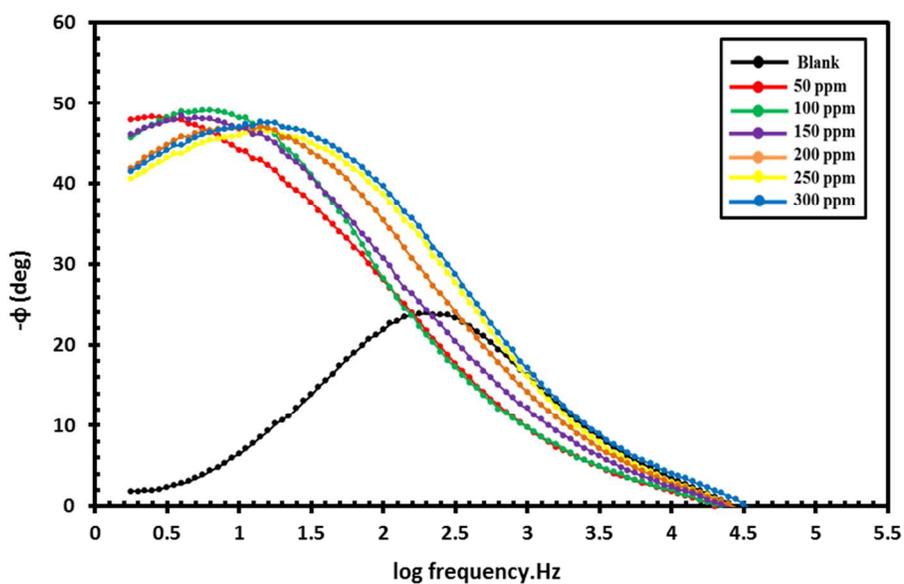


Figure (2). Nyquist plots for carbon steel in sea water in the absence and presence of different concentrations of compound III.



(a)



(b)

Figure 3. (a) Log frequency vs log Z (b) Log frequency vs Phase angle Bode plots for carbon steel in sea water in the absence and presence of different concentrations of compound III.

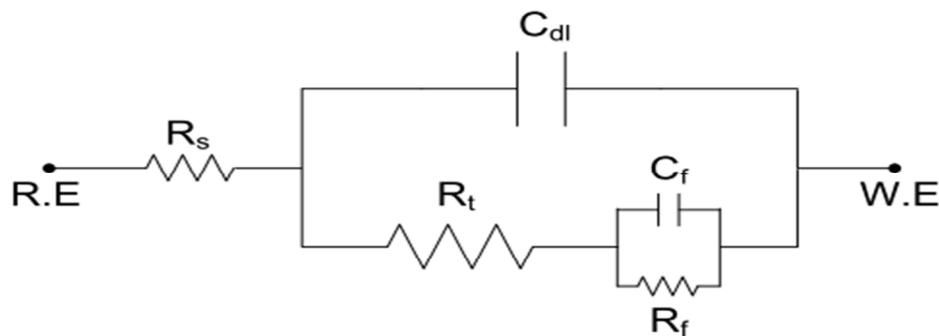


Figure (4). Equivalent circuit used to model impedance data of carbon steel in sea water.

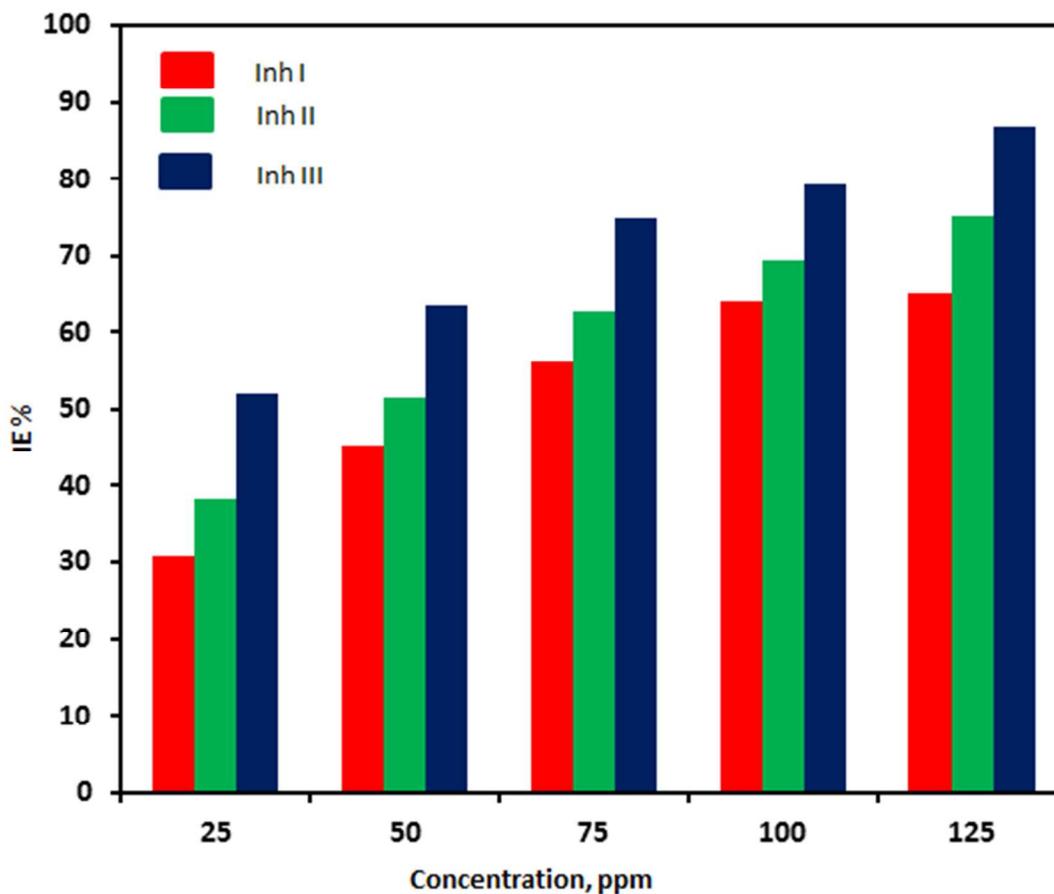


Figure (5): Variation of the efficiency of compounds (I,II and III) as calcium sulfate scale inhibitor with concentration as determined from ASTM G3-89-Re-approved 1994.

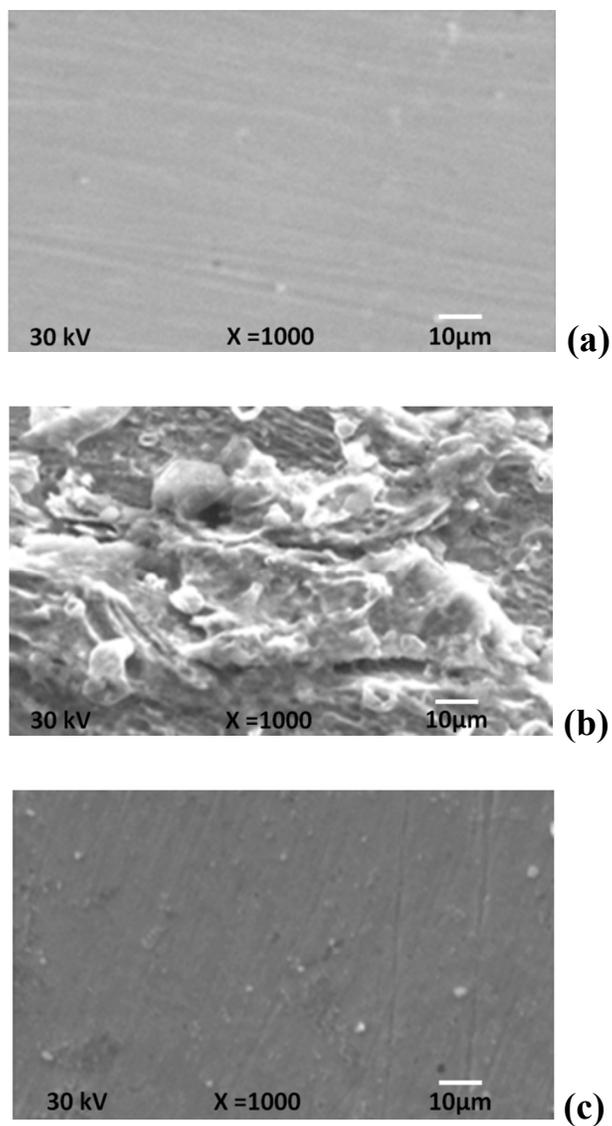


Figure (6). SEM of the carbon steel surface: (a) polished sample, (b) after immersion in the sea water and (c) after immersion in the sea water in the presence of 300 ppm of compound III.

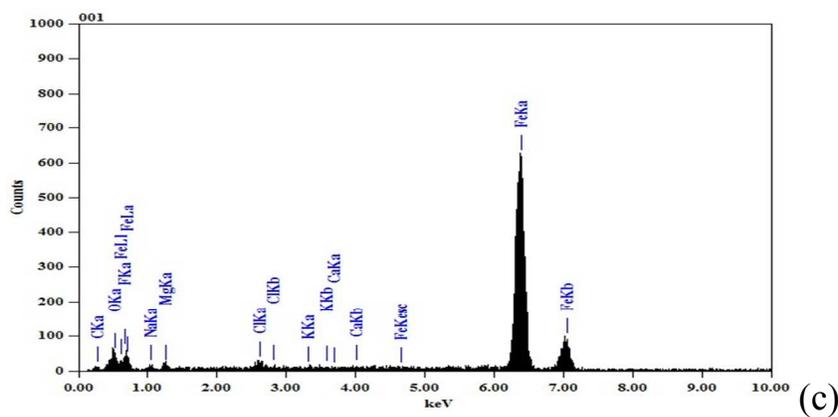
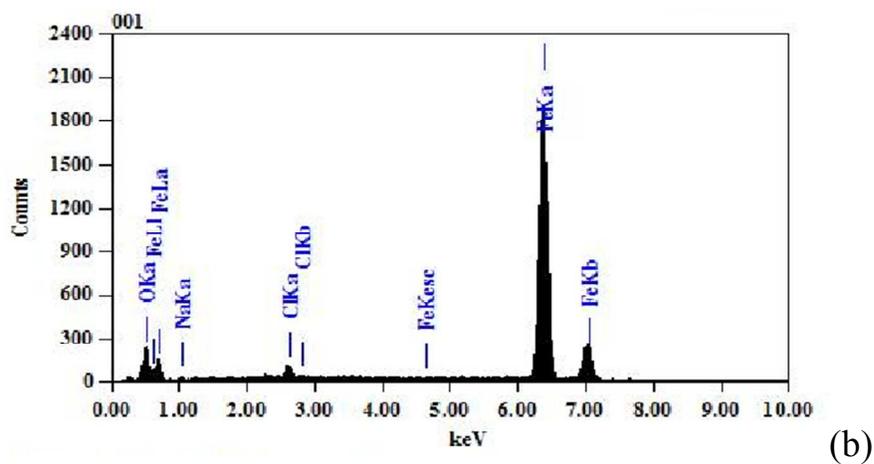
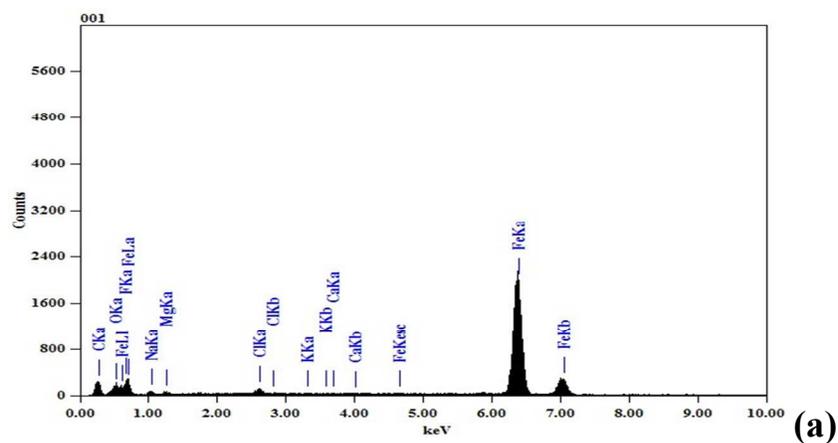


Figure (7). EDX of the carbon steel surface: (a) polished sample, (b) after immersion in the sea water and (c) after immersion in the sea water in the presence of 300 ppm of compound III.

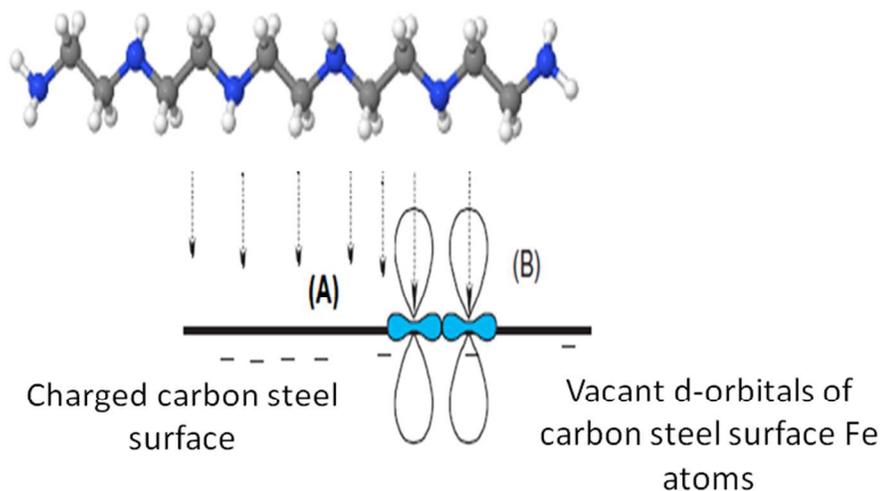


Figure (8): Interaction between pentaethylenhexamine and carbon steel surface through chemical adsorption process.

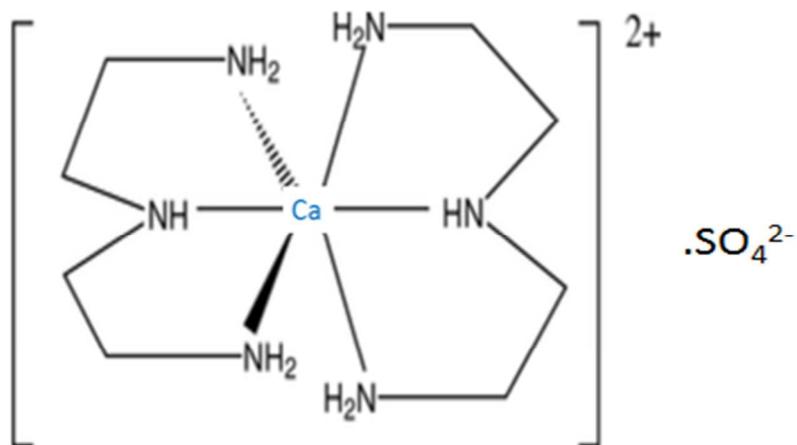


Figure (9): Chelation of diethylene triamine with calcium ion to prevent the formation of calcium sulphate scale.