



Available online at: [www.basra-science-journal.org](http://www.basra-science-journal.org)

ISSN -1817 -2695



## **Anticorrosive properties of polyamide on the carbon steel**

Mahmoud Sh. Hussain\* and Ula J.khalaf

*Chemistry department, College of Education for pure sciences, University of Basrah, Iraq.*

Received 2-3-2014 , Accepted 10-6-2014

### **Abstract**

A new geminisurfactant polyamide derived from Hexamethylenediamine (HMDA) and ethylenediaminetetraacetic acid (EDTA) 2,2'-(1,2-diamino-8,15-dioxo-7,10,13,16-tetraazadocosane-10,13-diyl) diacetic acid was synthesized and characterized by FTIR and NMR. A series of electrochemical measurements, including corrosion potential and corrosion current has been made on polyamide-coated carbon steel samples in corrosive environment. Results showed that polyamide can offer some degrees of protection in the corrosive environments. The corrosion study of this polymer outline that a new surfactant has a good resistance to the corrosion of carbon steel in 0.1 M solution of HCl, which can indicate to use as anti-corrosion materials.

**Keywords:** Synthesis ; Surfactant ; Polyamide ; Corrosion.

\* Corresponding author. E-mail address: [mhu\\_n99@hotmail.com](mailto:mhu_n99@hotmail.com).

## Introduction

Corrosion of materials has continued to receive interest in the technological world. In the field of corrosion inhibition, scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. Addition of corrosion inhibitors to the corrosion environment with respect to the other methods of corrosion inhibition has been employed [1]. Corrosion inhibition of materials has been the focus of research for centuries and in many cases has been well analyzed and understood [2-4]. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic

media. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevent transportation of water and corrosion-active species on the metal surface.

Surfactant inhibitors can be divided into four types: (a) inorganic inhibitors, (b) organic inhibitors, (c) surfactant inhibitors and (d) mixed material inhibitors. Surfactants also called surface active agent are molecules composed of a polar hydrophilic group, the "head", attached to a non-polar hydrophobic group, the "tail". In aqueous solution the inhibitory action of surfactant molecules may be due to the physical (electrostatic) adsorption or chemisorptions onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface.

Corrosion of materials usually takes place in the presence of oxygen and moisture and involves two electrochemical reactions, oxidation occurs at anodic site and reduction occurs at cathodic site [5]. Various scientific studies deal with the subject of corrosion inhibitors. Inhibitors are normally used to protect materials against deterioration from corrosion. The inhibitors, which reduce corrosion on metallic materials, are inorganic

inhibitors, organic inhibitors, surfactant inhibitors and mixed material inhibitors. Organic compounds are well known acid inhibitors used in industry. These organic compounds have multiple bonds in their molecules that mainly contain nitrogen, sulphur, oxygen atoms through which they get adsorbed on the metal surface [6-13]. The use of ethoxylated fatty acid [14], ethoxylated fatty amines, [15] and propenethoxylated diol [16] had been used as corrosion inhibitors for steel and aluminum in acidic solutions. Effect of temperature on the inhibiting process is of enormous significance in industry [17]. Effective inhibitors are expected to perform under a wide range of conditions. The inhibition efficiency depends on the parameters of the system (temperature, pH, duration, and metal composition) and on the structure of the inhibitor molecule.

Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production [2,5,18]. Moreover, the investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency [18]. The effective type of corrosion inhibitors for these applications is film-forming inhibitors. Nowadays, surfactants are widely used and find a very large number of applications in the petroleum industry. This is attributed to their significant capability to influence the properties of surfaces and interfaces.

An important corrosion inhibition tool is the use of surfactant inhibitors, because of very little consideration towards this study. The most important action of inhibition is the adsorption of the surfactant functional group onto the metal surface [19], adsorption is critical to corrosion inhibition. The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. Most acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms [20,21].

The aim of this work was to indicate the effect of surfactants' hydrophilic groups and to clarify the role of these compounds as

corrosion inhibitor for carbon steel in 0.1 M solution of HCl.

## **2.Experimentalals**

### **2-1.Materials and Instruments**

EDTA, HMDA, acetic anhydride were purchased from Merck and used without any further purification. Pyridine and dimethylformamide were distilled before use. The infrared spectra were recorded in the 4000-400  $\text{cm}^{-1}$  range from a Fourier transform Shimadzu spectrometer. Carbon steel coupons of rectangular shape in (53.5

$\times 1.8 \times 0.3$ ) cm size having composition 0.3% C, 1.5% Mn, 0.05% p, 0.06% S, 98.39 Fe. The aggressive solutions of ( 0.1 M HCl ) were prepared by the dilution of analytical grade 37% HCl with doubly distilled water. To apply constant potential or current, a Bank Eielktronik Type MLab 200 was used.

### **2-2.Sample preparation**

The Carbon Steel N-80 samples with 1 x 1 cm dimension and 0.5 mm thickness. The samples were polished by emery cloth no. 150 and 400, respectively. Prior to coating, all samples were pretreated in acetone and ethyl alcohol solution to remove impurities.

Finally, the samples were rinsed with distilled water and dried by acetone. Prior to any experiment, the samples were treated as described and freshly used with no further storage.

### **2-3.Synthesis of EDTA Dianhydride (EDTA-DA):**

EDTA (10.0 g, 34 mmol), pyridine (16 mL) and acetic anhydride (14 mL) were placed in a 100 mL-rondflask equipped with a condenser and a magnetic stirrer. The acetic anhydride reaction was carried out at 65°C for 16 hrs. The resulting

anhydride was filtered off and washed thoroughly with acetic anhydride and dry diethyl ether. The white-cream powder was then dried under vacuum at 50°C [22].

### **2-4. Inhibitor Preparation**

EDTA-hexamethylenediamine ( polyamide) was prepared by mixing of ( 0.51 g , 0.001 mole ) of (EDTA-DA) that dissolved in 10 mL of toluene with ( 0.33 g , 0.002 mole ) of HMDA in a 100 mL-rondflask equipped with a condenser and a magnetic stirrer. The

reaction was carried out at 45°C for 7hr. After that the product was dried under rotary evaporator then, purified by recrystallization with acetone. The formation reactions of poly amide was given in Scheme 1 :

**Scheme 1: Probable structure of the synthesized polyamide**

**2-5. Spectroscopic Characterization**

Infra-Red spectrum of the synthesized polyamide sample had been obtained using KBr pallets on a FTIR spectrophotometer (Shimadzu, model-8201PC). The FTIR spectra with assignment of peaks are shown in Figures (1,2). The FTIR spectrum of polyamide exhibited the prominent amide band at  $1657\text{ cm}^{-1}$ . Simultaneously, the bands of the dianhydride group, i.e. bands at  $1765$  and  $1819\text{ cm}^{-1}$ , disappeared, and the absorption regions of polymer observed a stretch and very broad band appears at  $3419\text{ cm}^{-1}$  and belongs asymmetric aliphatic C-H respectively. C-H and C-O stretching bands occur at  $1217\text{ cm}^{-1}$  to N-H group and O-H group due to overlaps between N-H and O-H absorptions, also present of a medium band at  $1679\text{ cm}^{-1}$  attributed to carboxylic carbonyl group and very strong band at  $1652\text{ cm}^{-1}$  refers to amidic carbonyl group,

while a weak band at  $1655\text{ cm}^{-1}$  belongs to N-H bending vibration. Also  $\text{CH}_2$  and  $\text{CH}_3$  stretching occurs at  $2937\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  symmetric. The Nuclear magnetic resonance spectrum for proton ( $^1\text{H NMR}$ ) was carried out on a Bruker AC 500 MHz spectrometer apparatus in  $\text{D}_2\text{O}$ . The chemical shift values are expressed in ppm using tetramethylsilane as an internal reference. The  $^1\text{H NMR}$  spectrum of polyamide was shown in Figure 3 which includes the signal assignments in the corresponding formula. The signal at ( $\delta = 2.73\text{--}2.76\text{ ppm}$ ) for  $\text{NCH}_2\text{CH}_2\text{N}$  (4H), ( $\delta = 3.1\text{--}3.3\text{ ppm}$ ) for  $-\text{CH}_2$  (2H) which connects with the end amide group, ( $\delta = 3.5\text{--}3.7\text{ ppm}$ ) for  $\text{CH}_2\text{-COON}$  (2H) which connects with the end carboxylic acid group, ( $\delta = 1.2\text{--}1.4\text{ ppm}$ ) for aliphatic  $(\text{CH}_2)_2$  (4H), and ( $\delta = 5\text{ ppm}$ ) for  $\text{D}_2\text{O}$ .

**3. Results and discussion**

**3. 1. Electrochemical polarization measurements**

The electrochemical corrosion parameters current density ( $I_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), efficiency percentage (IE), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) obtained from polarization measurements are listed in Table 1. Figs. (4,5) show polarization curves for carbon steel in 0.1 M Hydrochloric acid without and with gemini surfactant (polyamide )

respectively. The corrosion potential of polyamide-coated samples was shifted toward anodic direction (  $-244.1\text{ mV}$ ) compared to the uncoated samples ( $-323.9\text{ mV}$ ). The anodic tafel slope is also increased for the polyamide-coated samples indicating a significant reduction of corrosion current. Also internal current shows decrease in the corrosion rate of coated samples with respect to uncoated

samples. The corrosion potential is also higher indicating proper protection of polyamide layers. In order to reveal a better understanding of the interesting, but very complex corrosion protection by

polyamide, further investigations were carried out. It is assumed that the carbon samples may be protected by formation of a passive layer on iron due to the redox properties of polyamide.

**Table 1: Electrochemical polarization parameters for carbon steel in 0.1M HCl solution in absence and presence of polyamide at 50C<sup>o</sup> temperature.**

Sym.	Conc (M)	I <sub>corr</sub> $\mu\text{A}/\text{cm}^2$	E <sub>corr</sub> mV	$\beta_c$ $\text{mV}\cdot\text{dec}^{-1}$	$\beta_a$ $\text{mV}\cdot\text{dec}^{-1}$	IE %
Blank	0.00	301.39	-323.9	-120.4	530.0	–
A	1	70.93	-244.1	-138.6	89.0	76.46

### Conclusions

A new gemini surfactant was synthesized and characterized. The synthesized surfactant showed good performance as corrosion inhibitors for carbon steel in 0.1 M solution of HCl. A series of electrochemical measurements, including corrosion potential and corrosion current has been made on polyamide-coated carbon

steel samples in corrosive environment 0.1 HCl solution. It was found that corrosion potential of the polyamide coated samples was shifted toward noble potentials indicating better performance of polyamide coating. A significant decrease in corrosion current was also observed.

### References

- 1- K. Orubite-Okorosaye, I.R Jack, M. Ochei, O. Akaranta, J. Appl. Sci. Environ. Manage., 11,27 (2007).
- 2- M.M. Caroline, P. Christian, C.S. Hannes, K. Boris, A.A. Ilhan, Langmuir., 24,1469 (2008).
- 3- S.A.A. El-Maksoud, Int. J. Electrochem. Sci.,3,528 (2008).
- 4- M.M. Antonijevic, M.B. Petrovi, Int. J. Electrochem. Sci., 3,1 (2008).
- 5- A.Kumar, E-Journal of Chemistry., 5,275 (2008) 275.
- 6- D.A. Raval, V.M. Mannari, Res Ind., 39,32 (1994).
- 7- S.T. Keera, Br Corros J., 36,150 (2001).
- 8- S.T. Keera, A.M.A. Omar, Mans Sci. Bull., 23,11 (1996).
- 9- G.K. Gomma, Material Chem. Phys., 55,235 (1998).
- 10- A.M. Al-Mayout, A.K. Al-Amury, Al-Suhybani, Corros Sci., 57,614 (2001).
- 11- A.E. Stoyanova, E.I. Sokolova, S.N. Raicheva, Corros. Sci.,39,1595 (1997).
- 12- M. Abdallah, M. Al- Agez, A.S. Fouda, Int. J. Electrochem. Sci.,4,336 (2009).
- 13- X. Joseph Raj, N. Rajendran, Int. J. Electrochem. Sci.,6,348 (2011).
- 14- B. Mernari, H. El Attari, M. Traisnel, F. Bentiss, M. Lagrenée, Corrosion Science., 40, 391 (1998).
- 15- F. Bentiss, M. Lagrenée, M. Traisnel, J.C. Hornez, Corrosion Science., 41, 789 (1999).
- 16- F. Bentiss, M. Lagrenée, M. Traisnel, J.C. Hornez, Corrosion., 55, 968(1999).
- 17- A. Zarrouk, I. Warad, B. Hammouti, A. Dafali, S.S. Al-Deyab, N. Benchat, Int.

J. Electrochem.Sci., 5,1516 (2010).

18- M. El Azhar, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenee, *Corros. Sci.*, 43 (2001) 2227.

19- I.L. Rozenfeld, *Corrosion Inhibitors*, McGraw-Hill, New York ,97(1981).

20- V. Branzoi, F. Branzoi, M. Baibarac, *Mater. Chem. Phys.*, 65,288 (2000).

21.- R. Atkin, V. S. J. Craig, E. J. Walness, S. Biggs, *J. Colloid Interface Sci.*, 266, 236(2003).

22- R.A. Beauvais, S.D. Alexandratos, Polymer-supported reagents for the selective complexation of metal ions: An overview, *React. Func.Polym.*, 36,113 (1998).

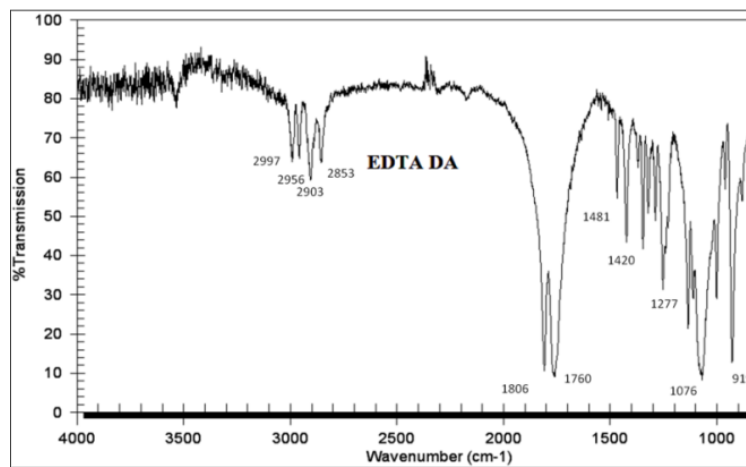


Fig.1.FTIR spectrum of EDTA-DA.

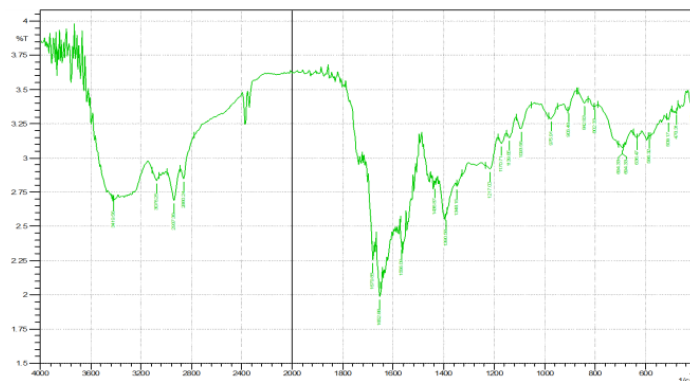


Fig. 2.FTIR spectrum of polyamide.

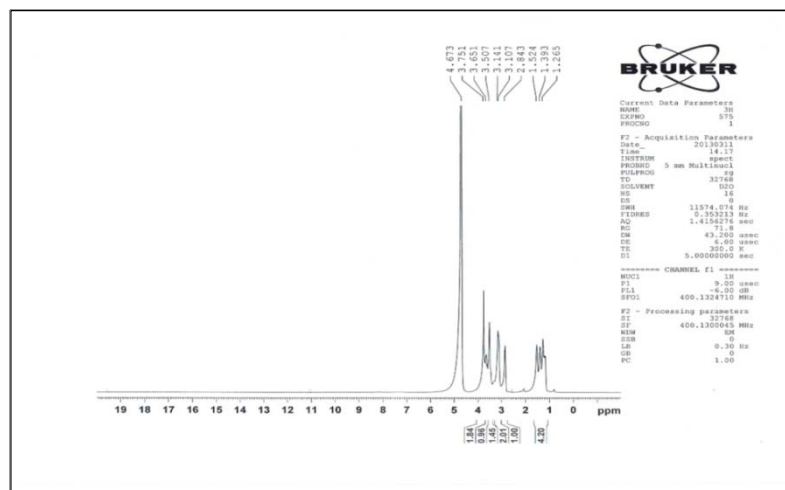


Fig. 3.NMR spectrum of polyamide.

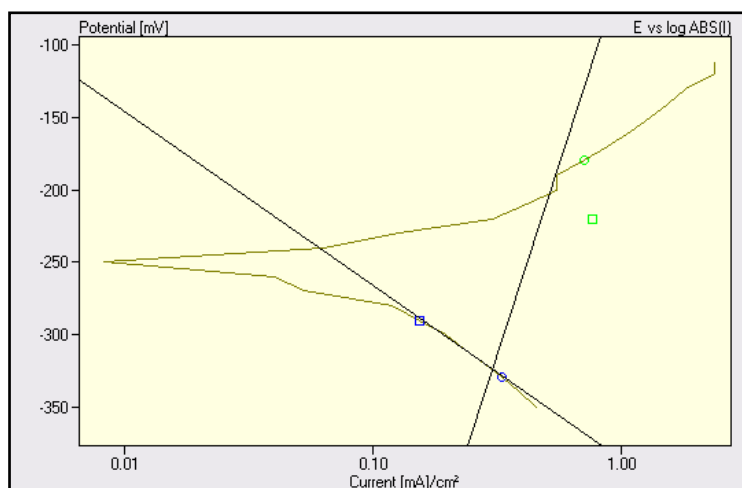


Fig. 4. Tafel plot of carbon steel in absence of polyamide in 0.1 M HCl solution.

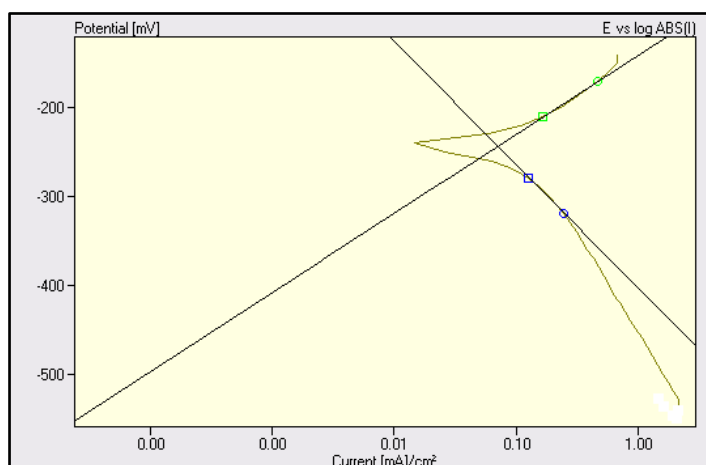


Fig. 5. Tafel plot of carbon steel in presence of polyamide in 0.1 M HCl solution.

## خصائص مضادة للتآكل لمادة البولي أميد على الكربون الصلب

محمود شاكر حسين و علا جميل خلف

جامعة البصرة- كلية التربية للعلوم الصرفة - قسم الكيمياء

### الملخص

حضر بولي أميد منشط للسطوح جديد مشتق من مفاعلة سداسي مثيلين ثنائي الامين وثنائي الاثلين رباعي حامض الخليك وتم تشخيصه بوساطة مطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي. تم إجراء سلسلة من القياسات الكهروكيميائية، بما في ذلك احتمال التآكل والصدأ الانية على عينات الكربون الصلب المغلفة بمادة البولي أميد في بيئة تآكل مكونة من حامض الهيدروكلوريك بتركيز 1 و 0 مولي. وأظهرت النتائج أن مادة البولي أميد يمكن أن تقدم بعض درجات الحماية في بيئات التآكل لمادة الكربون الصلب من حمض الهيدروكلوريك، والتي يمكن أن تشير إلى الاستخدامات كمواد مضادة للتآكل.