



## Synthesis, Characterization and evaluation of new Polymer Surfactant as inhibitor for carbon steel

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### ABSTRACT

A new polymer surfactant derived from cis-1,4-cyclohexane bis(methylamine) and ethylenediaminetetraacetic acid [2,2'-(1,12-bis(4-(aminomethyl)cyclohexyl)-3,10-dioxo-2,5,8,11-tetraazadodecane-5,8-diyl) diacetic acid ] was synthesized and characterized by FTIR and <sup>1</sup>HNMR. A series of electrochemical measurements, including corrosion potential and corrosion current has been made on the surfactant for carbon steel samples in corrosive environment. Results showed that the surfactant can offer some degrees of protection in the corrosive environments. The corrosion study of this polymer outline that it have a good resistant to the corrosion of carbon steel in 0.1 M solution of HCl, which can be indicate to uses as anti-corrosion materials.

**Keywords:** Synthesis; polymer; Surfactant; corrosion.



# Council for Innovative Research

Peer Review Research Publishing System

**Journal:** Journal of Advances in Chemistry

Vol. 12, No. 2

[editor@cirjac.com](mailto:editor@cirjac.com)

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## INTRDICTION

surfactants show interesting interfacial and bulk properties<sup>1</sup>, and have a wide variety of uses<sup>2</sup>, which are mostly met by conventional representatives. Changes in the molecular structure and type to improve upon their properties have attracted the attention of chemists<sup>[3-6]</sup>. This has led to the preparation of new generation surfactants such as geminis. Conventional surfactant has a single hydrophobic tail connected to an ionic or polar head group, whereas a gemini has in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. To provide greater surface activity, chemists have been in search of newer surfactants and the preparation started with bis-surfactants, which were later renamed as 'gemini' surfactants. Geminis are considerably more surface-active than conventional surfactants. Gemini surfactants are amphiphiles composed of two identical hydrophobic chains linked to two head groups with a spacer moiety. Several reviews<sup>[7-9]</sup> have reported their unique surface properties. Microemulsions with gemini surfactants were first presented by Dreja et al.<sup>[10,12]</sup>, who focused on the use of cationic gemini surfactants for polymerization of styrene microemulsions.

In recent years, preparation of polymer materials either soluble or insoluble in water with various functional groups has been developed, which can adsorb metal ions in aqueous and non-aqueous media. In general, functionalized polymers for metal ion complexation can be prepared either by derivation of a basic polymer (precursor) with the desired ligand or by polymerization of the corresponding ligand derivative<sup>[13-16]</sup>. Corrosion is one of the most serious problems in the industrial world. In the last few years the use of conducting polymers for protection of metals against corrosion has been investigated<sup>[17,18]</sup>.

In this study we report the synthesis and characterization of novel polyamide surfactant based on cis-1,4-cyclohexane bis(methylamine) and A-EDTA, and using it as corrosion inhibitor for Carbon steel in 0.1M solution of HCl.

## 2. Experimental

### 2.1. Materials and Instruments

EDTA, cis-1,4-cyclohexane bis(methylamine), acetic anhydride were purchased from Merck and used without any further purification. Pyridine and dimethyl formamide were distilled before use. The infrared spectra were recorded in the 4000-400  $\text{cm}^{-1}$  range from a Fourier transform Shimadzu spectrometer and <sup>1</sup>HNMR spectra was recorded by <sup>1</sup>HNMR BRUKER 300 MHz. The materials which used in the present study were carbon steel coupons of rectangular shape in (53.5 × 1.8 × 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 (0.1M HCl) were prepared by dilution of analytical grade 37% HCl with doubly distilled water. To apply constant potential or current, a Bank Eielktronik Type MLab 200 was used.

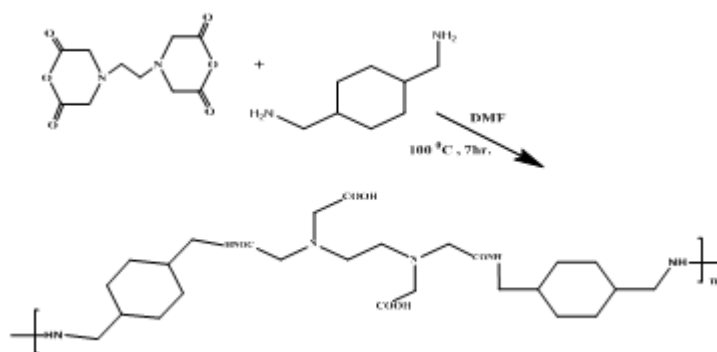
### 2.2. Synthesis of EDTA Dianhydride (EDTA- DA)

EDTA (10.0 g, 34 mmol), pyridine (16 mL) and acetic anhydride (14 mL) were placed in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The acetic anhydride reaction was carried out at 65°C for 16 h. 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<sup>19</sup>.

### 2.3. Polymer Inhibitor Preparation

The new surfactant [2,2'-(1,12-bis(4-(aminomethyl)cyclohexyl)-3,10-dioxo-2,5,8,11-tetraazadodecane-5,8-diyl)diacetic acid] polyamide was prepared by mixed of (0.51 gm, 0.001 mole) of (A-EDTA) that dissolved in 10 ml of DMF with (0.4 gm, 0.002 mole) of cis-1,4-cyclohexane bis(methylamine) in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 100°C for 7hr. After that the product was drying under rotary evaporator then, purified by recrystallization with acetone. The formation reactions of poly amide was given in Scheme1 :

Scheme 1: Probable structure of the polymer



## 2.4.Spectroscopic Characterization

Infra-Red spectra of the synthesized polymer 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 spectra of polyamide exhibited the prominent amide band at  $1679\text{cm}^{-1}$ . Simultaneously, the bands of the dianhydride group, i.e. bands at  $1758$  and  $1809\text{cm}^{-1}$ , disappeared, and the absorption regions of polymer observed a stretch and very broad band appears at  $3411\text{cm}^{-1}$  belong 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  $1735\text{cm}^{-1}$  attributed to carboxylic carbonyl group and very strong band at  $1679\text{cm}^{-1}$  refers to amidic carbonyl group, while a weak band at  $1560\text{cm}^{-1}$  belong to N-H bending vibration. Also  $\text{CH}_2$  and  $\text{CH}_3$  stretching occurs at  $2921\text{cm}^{-1}$  and  $2854\text{cm}^{-1}$  symmetric and symmetric aliphatic C-H respectively. C-H and C-O stretching bands occur at  $1217\text{cm}^{-1}$ .

$^1\text{H}$ NMR spectra of synthesized resin sample had been obtained using  $\text{D}_2\text{O}$  as solvents on a (BRUKER 300 MHz). The  $^1\text{H}$ NMR spectra with assignment of chemical shifts are shown in figure ( 3 ). The  $^1\text{H}$ NMR spectra of polyamide testified the signal protons of ethylenediamin  $\text{NCH}_2\text{CH}_2\text{N}$  which constitute the basic skeleton of EDTA at 3.15 ppm.

And signal appears at (3.1-3.3) ppm belong to protons of methylene  $-\text{CH}_2-$  that related with amide group also observe a multiple signal at range (3.5-3.7) ppm attributed to protons of methylene  $-\text{CH}_2-$  that located at the following part:

And a chemical shift at 1.6 ppm contributed to cyclic  $-\text{CH}_2-$ .

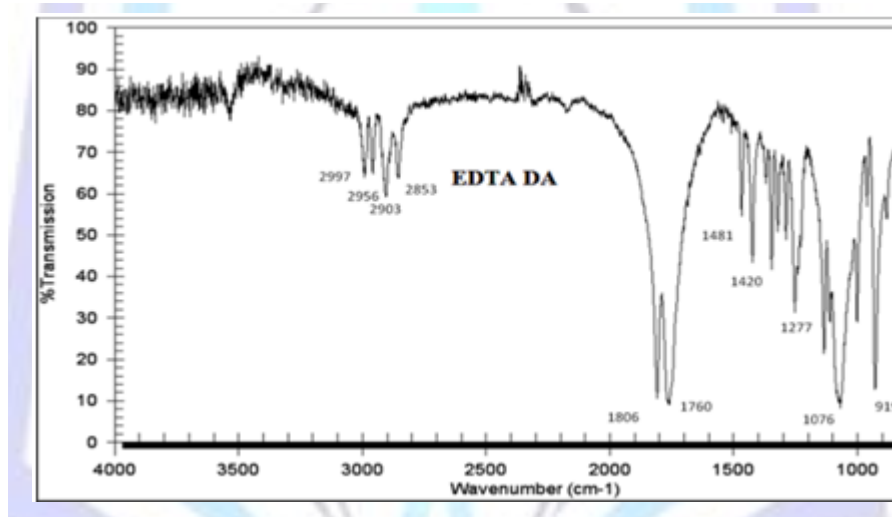


Figure 1: Spectrum of EDTA-DA.

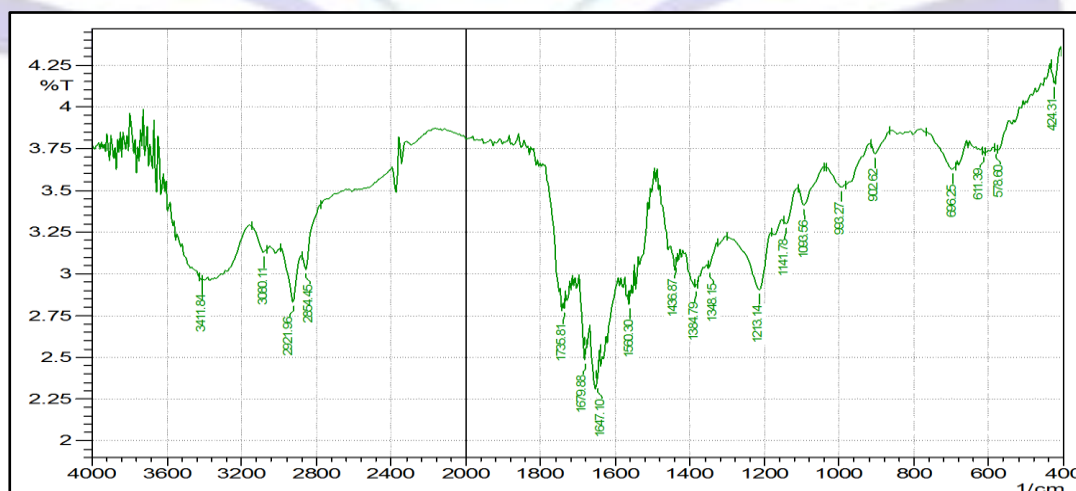


Figure 2: FTIR spectrum of polymer.

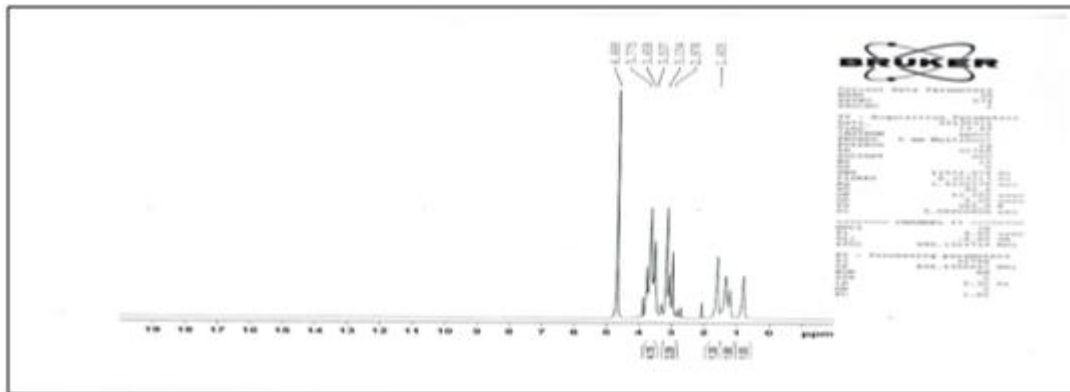


Figure 3: <sup>1</sup>HNMR spectrum of polymer.

## 2. 5. Weight Loss Measurements

The carbon steel coupons were ground and polished with emery paper up to 1200 grade, rinsed with distilled water, dried on a clean tissue paper, degreased by acetone for (5 sec) and dried by air at room temperature. After weighing accurately, the coupons were suspended vertically in a 100 ml beaker which contained (0.1M HCl) with and without the additives of different concentrations of an inhibitor. After (2 hours) immersion duration, the coupons were taken out, rinsed with doubly distilled water, washed with ethanol, dried and weighed according to ASTM (G1 – 71). Then the tests were repeated at different temperatures by using magnetic stirrer hot plates. In order to get good repeatability, experiments were carried out twice, and the average weight loss of two reading was reported.

## 3. Results and Discussion

### 3. 1. Critical Micelles Concentration (CMC)

Micelles consist of hydrophobic interior regions where hydrophobic tails interact with one another. These hydrophobic regions are surrounded by the hydrophilic regions where the heads of the surfactant molecules interact with water. At very low concentration in water, surfactant molecules are un-associated. At higher concentration of surfactant in water, micelles form. The concentration at which micelles form is called the Critical Micelles Concentration (CMC).

In this paper, we obtain different dilute solution of the prepared surfactant (0.1-10<sup>-4</sup>) and record perusal the revulsion in the electrical conductivity (G) for the prepared product at 25<sup>0</sup>C and convert it to specific conductivity (L) and draw it with revulsion of concentration and extract the CMC from the diagrammatic that which illustrated in Figure 4.

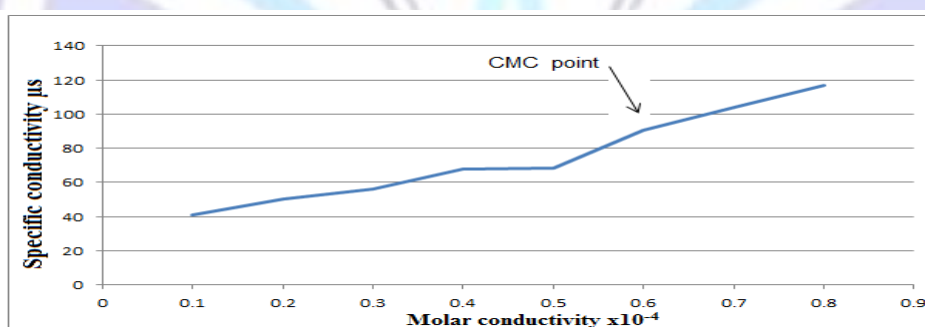


Figure 4: Critical Micelles Concentration (CMC) of surfactant.

#### . 1.HLB System

HLB, the so-called Hydrophile - Lipophile Balance, is the ratio of oil soluble and water-soluble portions of a molecule . ranging from 0 to 20. It was calculated according to this relation (1):

$$HLB=20 \frac{Mh}{M} \text{ -----(1)}$$

, where *Mh* is the molecular mass of the hydrophilic portion of the molecule, and *M* is the molecular mass of the whole molecule. The *HLB* value of this surfactant is ( 3.3 ) which concedered as water/oil (w/o)Emulsifier.



### 3.2. Weight loss measurement

The study included using the prepared polymer as corrosion inhibitor for carbon steel in 0.1M solution of HCl. This method was used to determine the corrosion rate ( $R_{corr}$ ) and efficiency percentage (IE) of the prepared polymer as a corrosion inhibitor using the following relation:

$$\% IE = \left[ 1 - \frac{W_{add}}{W_{free}} \right] \times 100 \quad \text{-----(2)}$$

,Where  $W_{add}$  is the weight loss with present of inhibitor (gm), and  $W_{free}$  is the weight loss in absence of inhibitor (gm) .

$$R_{corr} = \frac{W}{st} \quad \text{-----(3)}$$

,Where  $W$  is the weight loss of the carbon steel sheet,  $S$  is the surface area of the specimen, and  $t$  is the immersion time. First we determined the weight loss without used surfactant (without inhibition) that which illustrated in Figure 5 and then determined the weight loss with used of surfactant Figure 6. The values of percentage inhibition efficiency (%IE) and corrosion rate ( $R_{corr}$ ) obtained from weight loss method at different concentrations and temperatures are showed in Figure 7 and summarized in Table (1). It were observed that the inhibition efficiencies of the surfactant increase with increasing the inhibitor concentration.

**Table 1: Corrosion parameters obtained from weight loss of carbon steel in 0.1M HCl solution containing various concentrations of surfactant at different temperatures.**

Temp. (°C)	30			40			50			60		
	Wt-loss gm	Rcorr gm.cm <sup>-2</sup> .hr. <sup>-1</sup>	% IE	Wt-loss gm	Rcorr gm.cm <sup>-2</sup> .hr. <sup>-1</sup>	% IE	Wt-loss gm	Rcorr gm.cm <sup>-2</sup> .hr. <sup>-1</sup>	% IE	Wt-loss gm	Rcorr gm.cm <sup>-2</sup> .hr. <sup>-1</sup>	% IE
0.00	0.006	14.42X10 <sup>-4</sup>	-	0.0106	25.48X10 <sup>-4</sup>	-	0.021	50.48X10 <sup>-4</sup>	-	0.031	74.51X10 <sup>-4</sup>	-
0.1	0.0055	1.32X10 <sup>-3</sup>	8.33	0.008	1.92X10 <sup>-3</sup>	24.52	0.0103	2.47X10 <sup>-3</sup>	50.95	0.0184	4.42X10 <sup>-3</sup>	40.64
0.2	0.0047	1.12X10 <sup>-3</sup>	21.66	0.0048	1.15X10 <sup>-3</sup>	54.71	0.0052	1.25X10 <sup>-3</sup>	75.23	0.0154	3.70X10 <sup>-3</sup>	50.32
0.5	0.0042	1.009X10 <sup>-3</sup>	30	0.0045	1.08X10 <sup>-3</sup>	57.54	0.005	1.20X10 <sup>-3</sup>	76.19	0.0116	2.78X10 <sup>-3</sup>	62.58
1	0.0037	8.89X10 <sup>-4</sup>	38.33	0.0041	9.85X10 <sup>-4</sup>	61.32	0.0049	1.17X10 <sup>-3</sup>	76.66	0.0114	2.74X10 <sup>-3</sup>	63.22

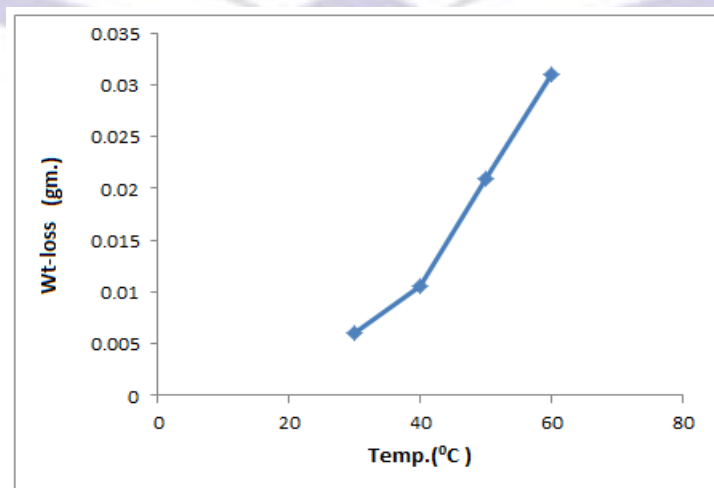


Figure 5: Wight loss of the carbon steel sheet in 0.1 M HCl solution without inhibitor.

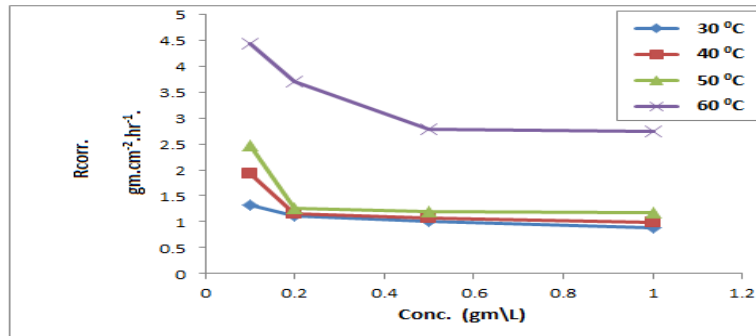


Figure 6: Rate corrosion with inhibitor at deferent concentrations and temperatures.

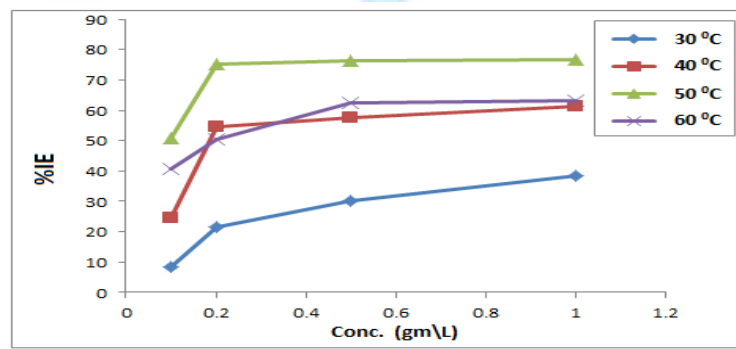


Figure 7: Inhibition efficiency of surfactant at deferent concentrations and temperatures.

By all that result we notice the effect of temperature variation on the percentage of inhibition efficiency for the prepared compound was studied using weight loss method at four temperature degrees 30 ,40 ,50 ,and 60 °C time of 240 min and (0.1, 0.2, 0.5 , 1.0)gm.The percentage of inhibition efficiency increased by increasing the temperature and the average of corrosion rate in the presence of inhibition was less than in absence of inhibitors.

### Electrochemical polarization measurements

The electrochemical corrosion parameters current density ( $i_{corr}$ ), corrosion potential ( $E_{corr}$ ), efficiency percentage (IE), anodic and cathodic tafel slopes ( $\beta_a$  and  $\beta_c$ ) obtained from polarization measurements are listed in Table 2 and Figures (8 , 9 ) were show polarization curves for carbon steel in 0.1M Hydrochloric acid without and with surfactant (polyamide ) respectively. The corrosion potential of polyamide-inhibitor samples was shifted toward anodic direction ( -216.3mv) compared to the uncoated samples(-323.9 mv). The anodic tafel slope was 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 was 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 apassive layer on iron due to the redox properties of polyamide.

Table 2: Some parameters of corrosion for carbon steel alloy in acidic media

Sym.	Conc (M)	$i_{corr}$ $\mu A/cm^2$	$E_{corr}$ mV	$\beta_c$ mV.dec <sup>-1</sup>	$\beta_a$ mV.dec <sup>-1</sup>	IE %
Blank	0.00	301.39	-323.9	-120.4	530.0	-
Polymer	1	43.23	-216.3	-135.7	93.9	85.68

inhibitor						
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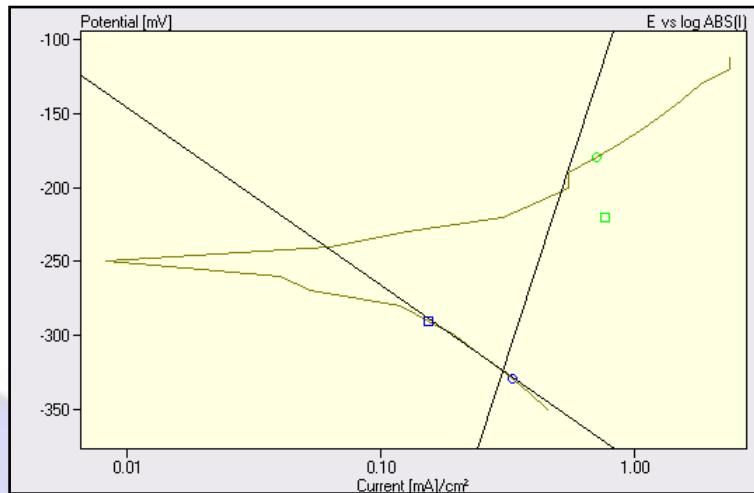


Figure 8: Polarization curve to the carbon steel in acid solution (0.M 1 HCl) without inhibition.

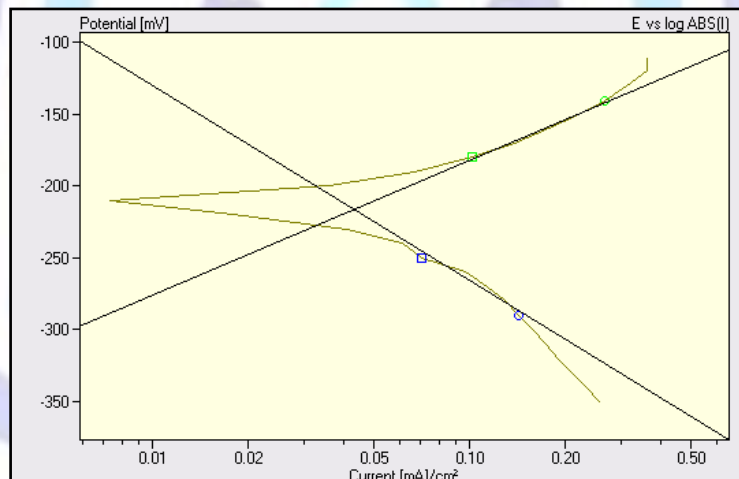


Figure 9: Polarization curve to the carbon steel in acid solution (0.M 1 HCl) with inhibition.

### Conclusions

A new surfactant was synthesized and characterized. The synthesized surfactant showed good performance as corrosion inhibitors for carbon steel in 0.1M solution of HCl. Their inhibition efficiency is concordant to their order of CMC. Results obtained showed that the percentage inhibition increases with the increasing of inhibitors concentration and decreases with the increasing of temperature. 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.

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