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## RESEARCH ARTICLE

## Synthesis, Characterization and Evaluation of 1, 3-bis ((2-aminopropyl) amino) methyl)-5-methylimidazolidine-2, 4-dione (BAMMD) as corrosion inhibitor for carbon steel and Brass alloys in 0.2M NaCl.

Hadi Z. Al-Sawaad

University of Basra, College of Science, Chemistry department

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#### \*Corresponding Author

Hadi Z. Al-Sawaad

### Abstract

3-bis ((2-aminopropyl) amino) methyl)-5-methylimidazolidine-2,4-dione (BAMMD) was synthesized and characterized by FTIR and NMR techniques then studied as corrosion inhibitor for carbon steel and brass alloys at 0.2M sodium chloride. The optimal concentration of BAMMD is 50ppm, which give an efficiency about 64.64% in case of carbon steel alloy while in case of brass is 84.75% at same concentration of the mentioned inhibitor at constant temperature 25 °C. The effect of temperatures on its ability as corrosion inhibitors against NaCl was studied at ranged (25-55) °C where, the inhibitor where, in both cases of the two alloys as the temperature increased, the inhibition efficiency increased from 64.64% at 25 °C to 90.35% at 55 °C for carbon steel alloy and from 84.75% at 25 °C to 89.24% at 55 °C. The thermodynamic and kinetic studies is done where the thermodynamic study is applied for the inhibitor then the results insist that the inhibitor obeyed to Timken isotherm in case of carbon steel alloy while obeyed to Langmuir isotherm in case of brass alloy where, BAMMD depict a chemical adsorption mode for the reaction with each one of the two alloys. On the other hand, BAMMD explain an anodic inhibition behavior. Generally the data of the study of corrosion behavior reveal that brass alloy is more resistance than carbon steel alloy whether in absence or in presence of BAMMD.

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## INTRODUCTION

Corrosion is a deterioration of a metal or alloy in presence of another metal with greater reduction potential than the mentioned metal or alloy in addition to corrosive environment or in presence of corrosive environment alone [1-3]. The effect of corrosion imply the economic losses due to partial or total replacement of equipment and structure, repair plant shutdowns in addition of social safety and health of people either working in industries or living in nearby towns [4-5]. The protection of metals or alloys against corrosion can be achieved by several methods one of them is corrosion inhibitors, which can treat or prevent the metals or alloys by suppressing the aggressiveness of environment, by slow down the oxidation of the metal i.e., the corrosion of metal then the inhibitor is called anodic inhibitor or by suppressing the cathode reaction which called cathodic inhibitors. Furthermore, there are inhibitors have these dual effects then the inhibitors are called mixed inhibitors [6-9]. On the other hand, corrosion inhibitors are classified according to their chemical structures include Inorganic inhibitors and Organic inhibitors [10]. The action of organic corrosion inhibitors against corrosion implies by adsorption of the molecules of inhibitor on the metal surface either by chemical adsorption i.e., forming coordination bond between the inhibitor's molecule and metal surface by physical adsorption i.e., by electrostatic force of attraction between them. Both two types of adsorption can be occurred due to heteroatoms like S, O, N, Se, or P atoms in the inhibitors i.e., the organic inhibitors should be hetero compounds whether aliphatic or aromatic compounds due to the presence of one pair of electrons in a heteroatom [11-12]. On the other hand, one of the most corrosive environment is saline medium [13-

14]. The corrosion of both carbon steel and brass alloys were investigated in different environment i.e., acidic or saline solutions by several authors [15-18]. Organic compounds like heterocyclic compounds have been reported to inhibit carbon steel or brass alloys [19-24]. The aim of present work is evaluation of one of the heterocyclic compound as corrosion inhibitor for both carbon steel and brass alloys in saline water in order to compare its action on two different alloy at different concentrations of inhibitor against sodium chloride as corrosive environment at different temperatures to explain the inhibition behavior of the inhibitor 1,3-bis((2-aminopropyl) amino) methyl)-5-methylimidazolidine-2, 4-dione (BAMMD) on both alloys by studying the adsorption behavior of the mentioned inhibitor.

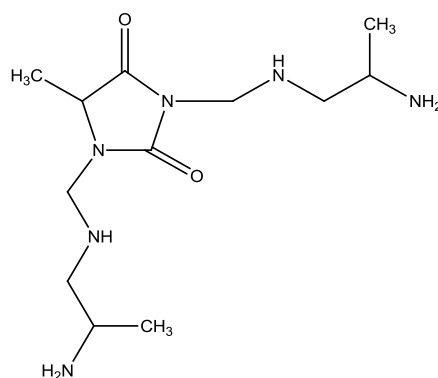
## 2. Experimental Part:

### 2.1-Chemicals:

The chemicals that used to use in this study are supplied from several sources where, 1, 2-diamnopropane, dimethyl formamide. From Fluka, Absolute ethanol, acetone from GCC, sulfuric acid (98%), Sodium chloride, from BDH.

### 2.2-Synthesis of BAMMD [25]:

The reaction was carried out in 100mL three neck flasks fitted with stirrer, dropping funnel and condenser. The reaction vessel was charged by (1.0 mole) of 1,2-dimethyl propane in ( $50\pm5^\circ\text{C}$ ), 0.1mL of sulfuric acid is added, then 1,3-bis(hydroxymethyl)-5-methylimidazolidine-2,4-dion(BHM) (0.5 mole) was added drop wise over a period of one hour. After end of addition, the temperature was raised to ( $100\pm5^\circ\text{C}$ ) maintained at this temperature for three hours, at the end of reaction the product was dissolved by (DMF) and dried at ( $70\pm5^\circ\text{C}$ ) under vacuum 0.1mmHg, the purification process repeated for three times, and the product kept away from atmosphere (hygroscopic). Its structure shown below in Figure 1below:



1,3-bis(((2-aminopropyl)amino)methyl)-5-methylimidazolidine-2,4-dione

**Figure (1): The chemical structures for BAMMD.**

### 2.3-Instruments:

1. FTIR Schimadzu 8400 S.

2. Corrosion measurement system model 350A, (EG&G PARC, US).

All the instruments were recalibrated with standard materials adopting standard procedure recommended for each system or instrument.

### 2.4-characterization of BAMMD:

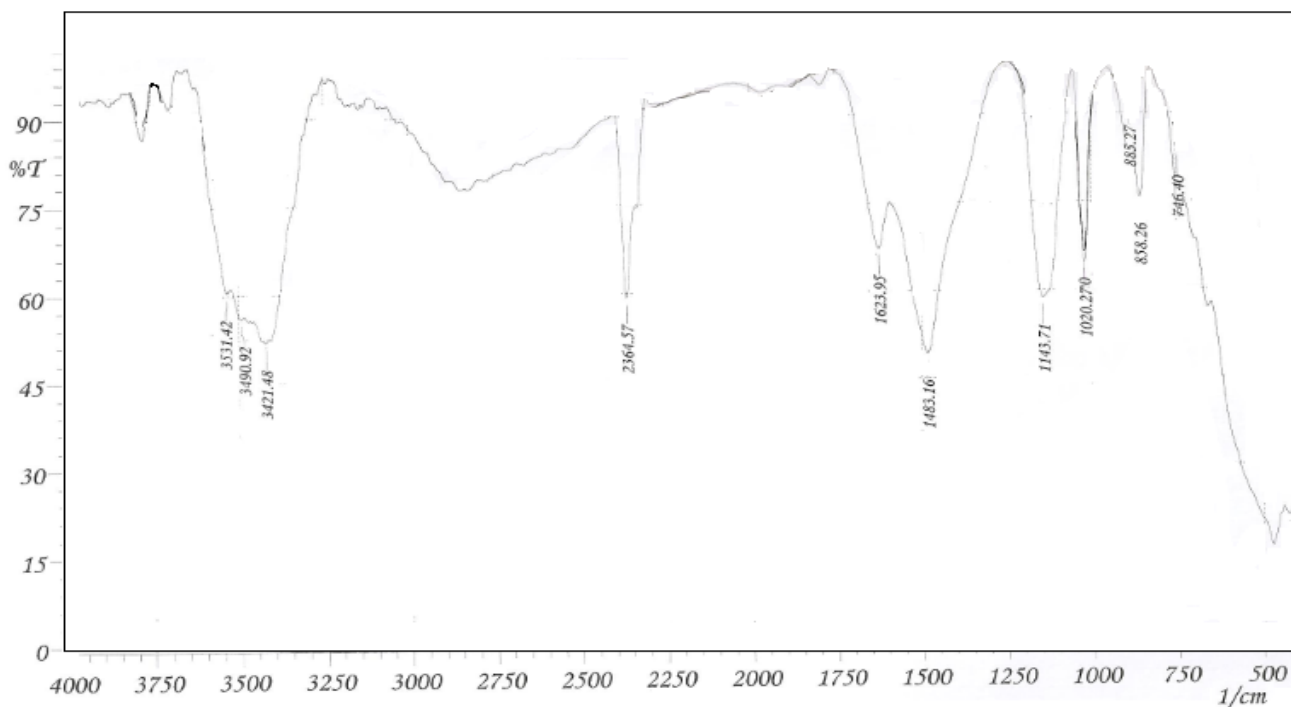
#### 2.4.1-FTIR

Figure 2 and Table 1 explain FTIR of BAMMD and data of the functional groups for BAMMD as below:

**Table 1: FTIR data for BAMMD explaining the functional group frequencies in  $\text{cm}^{-1}$ .**

Functional group	N-H Primary	N-H Secondary	C-H	C=O	N-H bend	C-H bend	C-N	C-O
Wave No. ( $\text{cm}^{-1}$ )	3490-3421	3531	3200-3150	1750	1623	1483	1141	1020

According to Figure 2 and Table 1 there are two bands ranged  $3490\text{--}3421\text{cm}^{-1}$  belong to asymmetric, symmetric bands for primary amino groups in addition to  $3531\text{ cm}^{-1}$  belong to secondary amino groups. On the other hand, the small wave number value belong to symmetric stretching vibration while the other belong to asymmetric stretching vibration values. Furthermore, the other functional groups explained in Table 1 above, N-H bending is shown at  $1623\text{ cm}^{-1}$ .



**Figure 2: FTIR of BAMMD.**

#### **2.4.2- $^1\text{H}$ NMR spectroscopy:**

Figures (3-4) explain  $^1\text{H}$ NMR spectra for BAMMD that explain the position of protons in BAMMD where, Figure 3 explain the basic  $^1\text{H}$ NMR spectrum for BAMMD while, Figure 4 explain  $^1\text{H}$ NMR for the same compound with resolution at region ranged (0-2) ppm of the chemical shift. Generally the two figures showed that the region (1-1.3)ppm belong to the protons of isopropylene structure  $\text{--CH}_2\text{--CH--CH}_3$ , while the region (3.8-4.2)ppm belong to the interaction between the proton of C-atom of the ring and the methyl group that attached it as in Figure 4. Furthermore, the region (2-2.2) ppm belong to the protons that attached to N-atoms while the region 4.3ppm belong to singlet of methylene group that lies between N-atom of the ring and N-atom of the diamine branch as in Figure 3

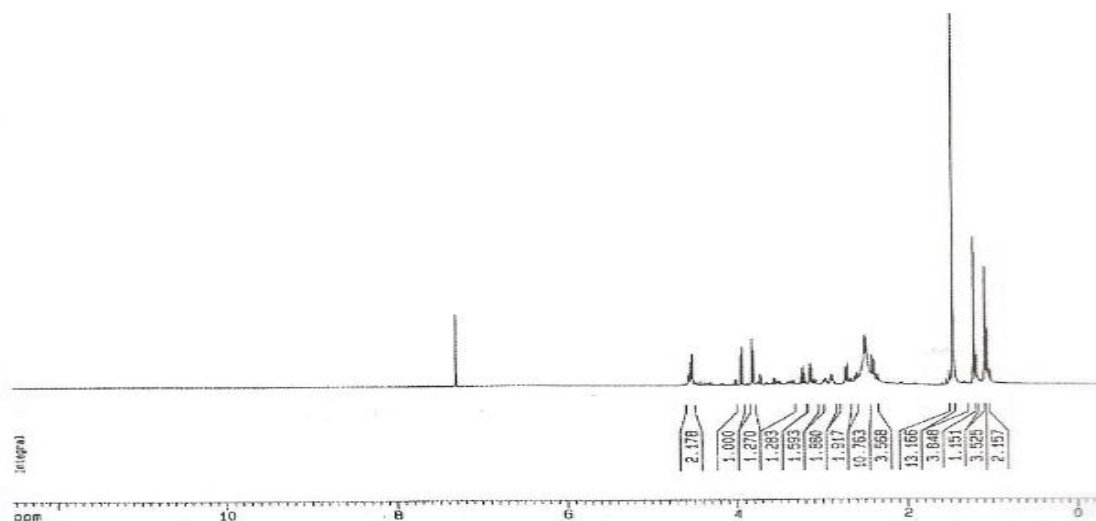


Figure 3: NMR spectroscopy for BAMMD.

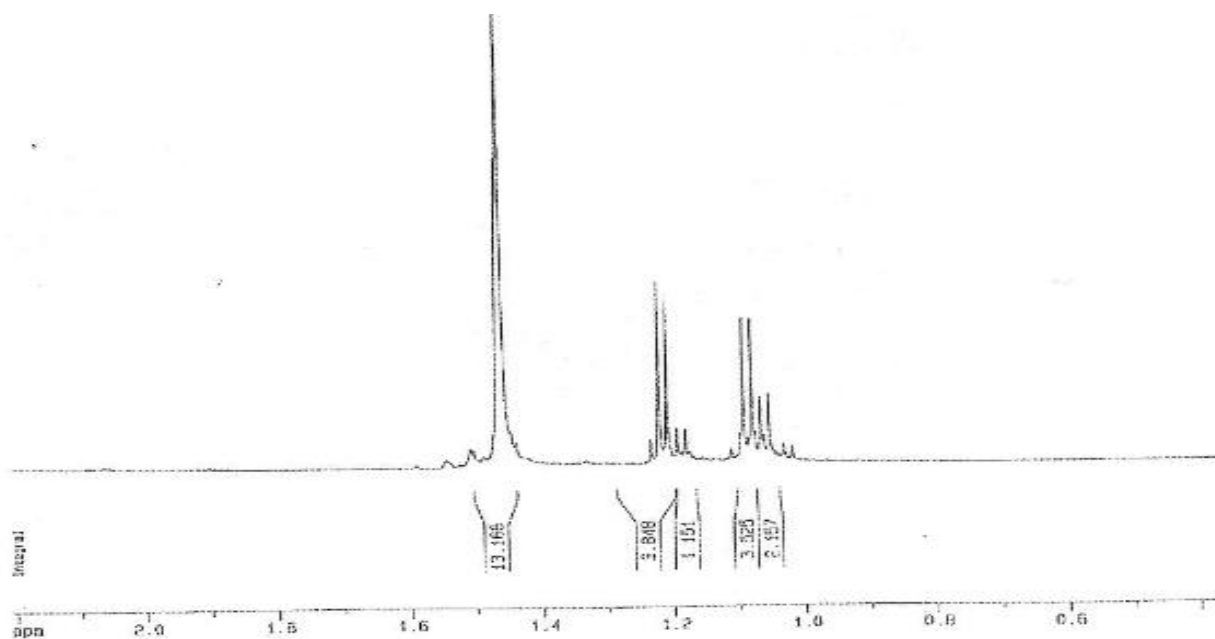


Figure 4: NMR Spectroscopy for BAMMD at (0-2) ppm region.

### Corrosion inhibitors studies of BAMMD:

#### 3.1-Experimental

##### 3.1.1Composition of alloys:

In this study, two types of alloys have been used include carbon steel and Brass, which have the composition illustrated in Table (2)

**Table (2) Chemical composition of carbon steel and Brass alloys**

Alloy	Composition
Carbon steel	0.3%C, 1.2%Mn , 0.05%P , 0.06%S , Fe for balance (%by weight)
Brass	68.75%Cu, 28%Zn, 1%Fe, 1.2%Al , 0.05%As , 1%other (%by weight)

### 3.2. Preparing the specimen:

Both of carbon steel or brass discs were prepared with (1.4-1.7 cm) diameters and 2-3 mm thickness. The opposing faces of each specimen were then grind and polished by emery cloth paper to 400 micron. Thereafter, the specimens were degreased with acetone, washed with distilled water and ethanol and dried with hot air. The specimens were stored in a desiccators containing silica gel during the interval between polishing and polarization measurements.

### 3.3-Results and discussions:

Table3 below explain an electrochemical data that obtained from Tafel plots at different concentrations of BAMMD as corrosion inhibitor for each of carbon steel and brass alloys respectively. Generally, for both alloys as shown from the above table as concentration of BAMMD increased, the inhibition efficiency increased due to reduce the corrosion current density, corrosion rate and increasing in polarization resistance of for both alloys in presence of BAMMD compared with the absence of it whereas the strong adherent of the inhibitor on the surface is increased i.e., the protective surface is provided in presence of the BAMMD on carbon steel or in brass alloys but, in case of brass the inhibition efficiency is greater than in case of carbon steel alloys where the inhibition efficiency of BAMMD on carbon steel about 64.64% at 50ppm of BAMMD while in case of brass is about 84.75% at same concentration of BAMMD this may be attributed to the lower ability for brass to corrode than carbon steel alloy in presence of sodium chloride solution as corrosive environment because the lower oxidation potential for brass compared with carbon steel alloy in addition to the ability of the inhibitor to reduce the corrosion in both alloys) i.e., the diffusion of  $\text{Cu}_2^+$  ions from the metal surface in brass has a little influence on anodic current[26-29]. On the other hand,  $E_{\text{corr}}$  values in Table 3 refers to anodic inhibition behavior for BAMMD on carbon steel and brass alloys refers to anodic inhibition behavior for BAMMD on both two alloys. Furthermore, both two cases (for brass and carbon steel alloys) BAMMD has the anodic and cathodic mechanism controlled according to  $\beta_a$  and  $\beta_c$  values as shown in Table 3 [30-31], Tafel plots for two cases above is shown below in Figures 5&6:

**Table 3:** Tafel plot data in presence and absence of BAMMD for each of carbon steel and brass alloys 25°C.

comp	Alloy	Conc. ppm	$\beta_c$ mV/decade	$\beta_a$ mV/decade	$R_p$ ( $\Omega$ )	$I_{\text{corr}}$ $\mu\text{A}/\text{cm}^2$	$E_{\text{corr}}$ Volt	CR mpy	inh.eff%
NaCl	Carbon steel	1170*	278	19	1510	32.7	-0.883	15.10	....
BAMMD	Carbon steel	10	333	100**	1250	26.9	-0.689	12.37	18.08
BAMMD	Carbon steel	20	289	90**	1820	16.4	-0.718	7.54	50.07
BAMMD	Carbon steel	30	281	73	1870	13.4	-0.710	6.16	59.21
BAMMD	Carbon steel	40	293	121**	1800	12.5	-0.725	5.75	61.92
BAMMD	Carbon steel	50	311	90**	1900	11.6	-0.694	5.34	64.64
NaCl	Brass	1170*	307	34	15200	4.65	-0.139	2.23	.....
BAMMD	Brass	10	374	87**	10210	3.00	-0.120	1.44	35.43
BAMMD	Brass	20	.....	...	9911	1.50	-0.128	0.72	67.71
BAMMD	Brass	30	410	21*	7167	1.20	-0.125	0.58	73.99
BAMMD	Brass	40	409	65	10680	1.00	-0.100	0.48	78.48
BAMMD	Brass	50	336	58	8416	0.70	-0.130	0.34	84.75

\*Refers to 0.2M sodium chloride when it convert in ppm units.

\*\*Calculated according to the following equation:

$$\beta_a = \frac{2.303 R_p I_{\text{corr}} \beta_c}{\beta_c - 2.303 R_p I_{\text{corr}}} \dots \dots \dots 1$$

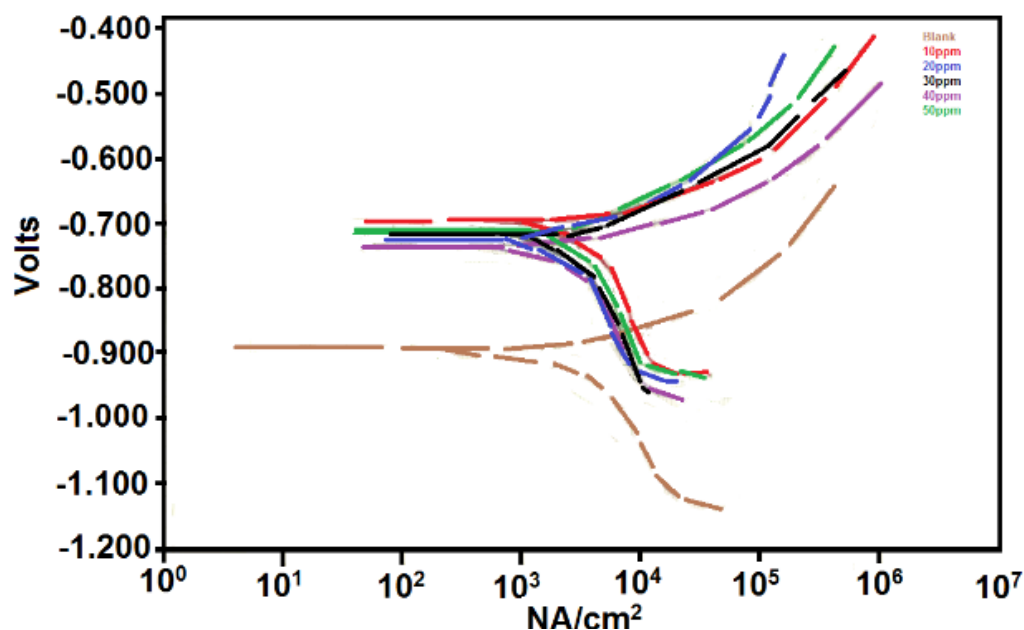


Figure 5: Tafel plots for different concentrations of BAMMD compared with corrosive environments for carbon steel alloy.

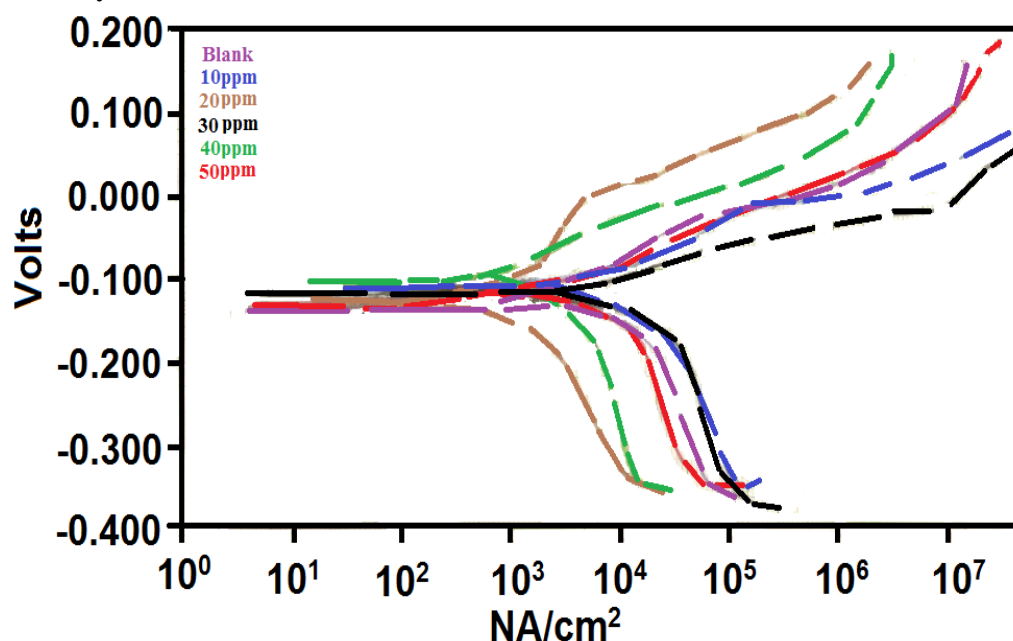


Figure 6: Tafel plots for different concentrations of BAMMD compared with corrosive environment for brass alloy.

#### Thermodynamic calculations:

In this study thermodynamic functions like enthalpy  $\Delta H$ , Entropy  $\Delta S$  and free energy  $\Delta G$  will be calculated in order to understand the best adsorption of the inhibitor BAMMD on the surfaces of the two alloys carbon steel and brass respectively. Thus, the affinity of the inhibitor toward the metal or alloy can be calculated by the surface coverage area value  $\theta$  that is calculated according to the following equation:

$$\theta = 1 - \frac{CR_{inhib}}{CR_{uninhib}} \dots \dots \dots 2$$

The result data for two alloys is shown below in Table 4:

**Table 4: Surface coverage area values for BAMMD when adsorbed on carbon steel or brass alloy.**

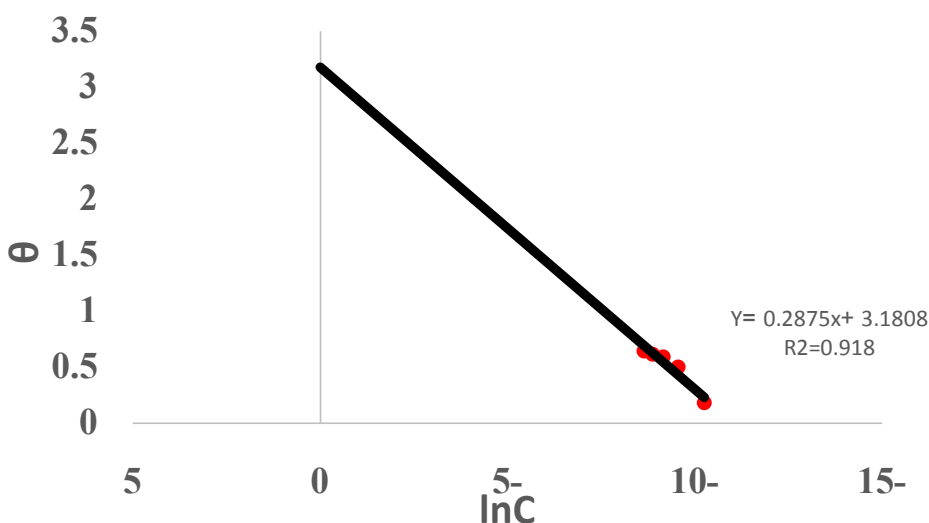
Comp.	Conc. ppm	$\theta$	Alloy	Comp.	Conc. ppm	$\theta$	Alloy
BAMMD	10	0.181	Carbon steel	BAMMD	10	0.3543	Brass
BAMMD	20	0.501	Carbon steel	BAMMD	20	0.6771	Brass
BAMMD	30	0.592	Carbon steel	BAMMD	30	0.7399	Brass
BAMMD	40	0.619	Carbon steel	BAMMD	40	0.7848	Brass
BAMMD	50	0.646	Carbon steel	BAMMD	50	0.8475	Brass

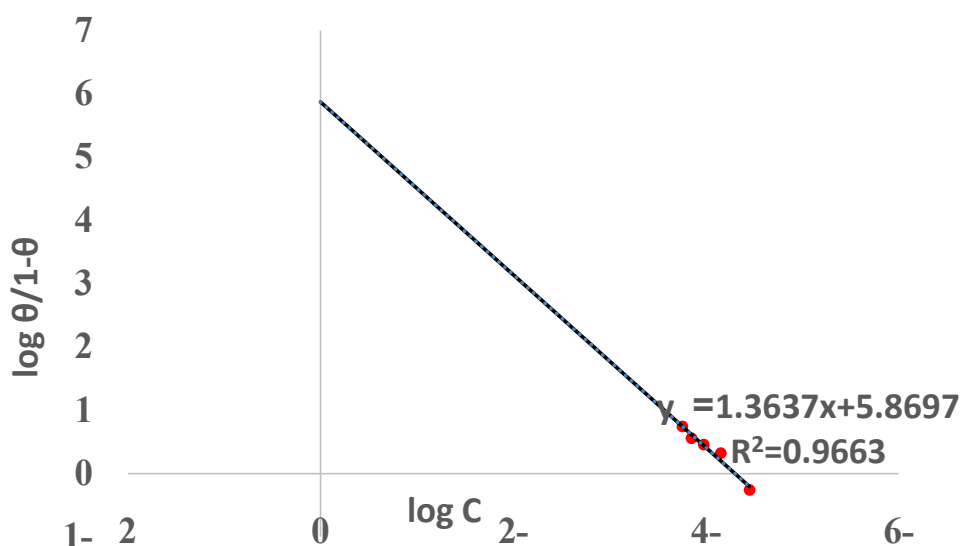
The data of surface coverage area can be employed to study the behavior of the inhibitor BAMMD when it adsorbed on the carbon steel or brass alloys by selecting a different adsorption isotherm modes like Langmuir, Timken, and Frumkin and Freundlich isotherms. The better isotherm is selected according to the higher  $R^2$  value. Hence, the convenient isotherm that described the adsorbing of BAMMD on carbon steel alloy surface is Timken isotherm where, its equation is shown below:

$$\theta = \left(-\frac{1}{f}\right) \ln K_{ads} + \left(-\frac{1}{f}\right) \ln C \dots\dots\dots 3$$

Where plotting of  $\theta$  against  $\ln(C)$  yield a slope line as shown in Figure 7 below where,  $\ln(C)$  is the natural logarithm of concentration of the inhibitor in case of carbon steel alloy while, for brass. Langmuir adsorption isotherm behavior for BAMMD on brass alloy that shown in equation 3, which explained in Figure8 respectively:

$$\log \frac{\theta}{1-\theta} = \log C + \log K \dots\dots\dots 4$$

**Figure 7: Timken adsorption isotherm for BAMMD when adsorbed on carbon steel alloy.**



**Figure 8: Langmuir adsorption isotherm for BAMMD when adsorbed on brass.**

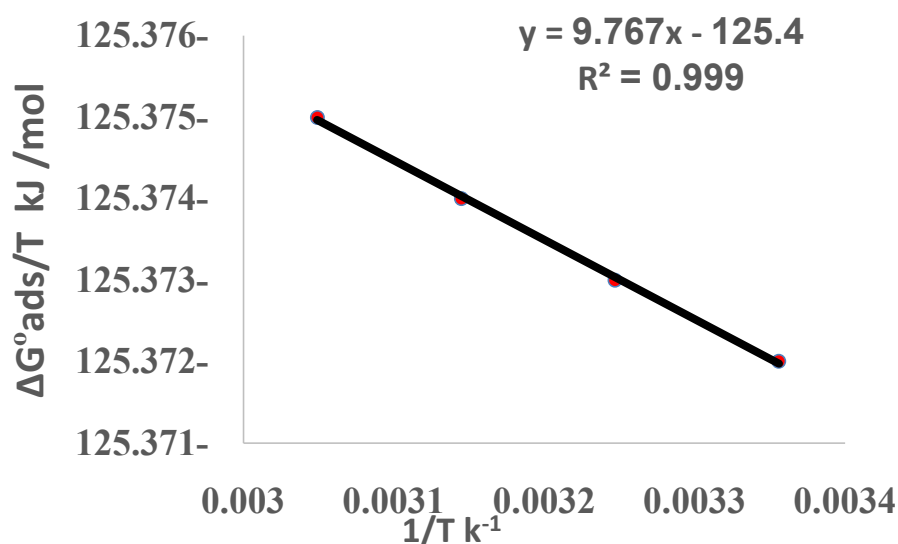
The adsorption constant is obtained from the above plotting that is used to calculate the mentioned thermodynamic functions according to the following equations:

$$\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads}) \dots\dots\dots 5$$

$$\frac{\Delta G_{ads}^{\circ}}{T} = \frac{\Delta H_{ads}^{\circ}}{T} + k \dots\dots\dots 6$$

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \dots\dots\dots 7$$

Thus, to calculate the enthalpy and entropy of adsorption according to equations 4&5 respectively, the free energy of adsorption should be calculated depending on the surface coverage area of inhibitor BAMMD that adsorbed on carbon steel and brass alloys respectively. Hence, Figures 9 and 10 below explain the enthalpy of adsorption calculation:



**Figure 9: calculation of enthalpy of adsorption of BAMMD on carbon steel alloy.**



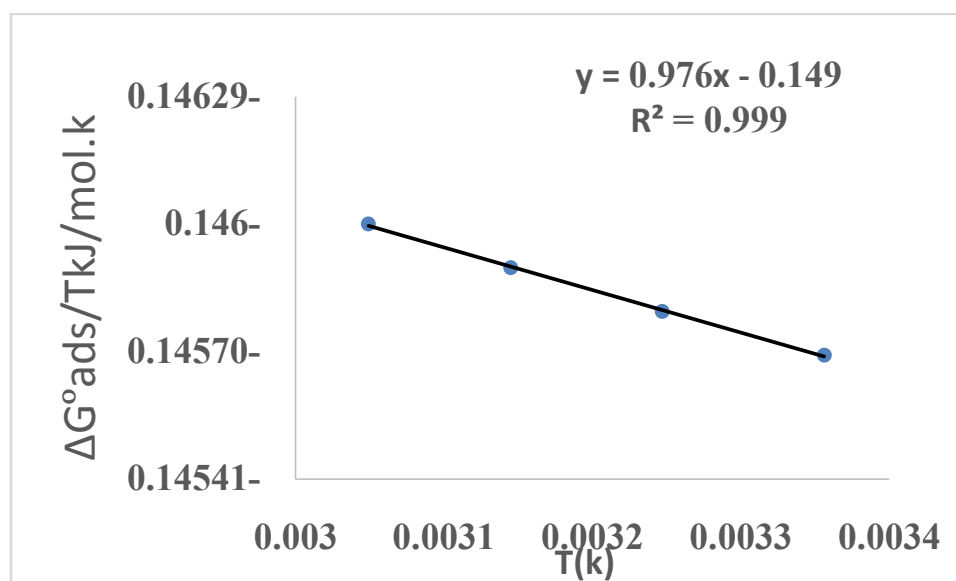


Figure 10: calculation of enthalpy of adsorption of BAMMD on brass.

Furthermore, the entropy of adsorption can be calculated according to equation 5. The thermodynamic adsorption functions for BAMMD on carbon steel alloy is summarized in Table 5 below:

Table 5: thermodynamic adsorption functions for BAMMD on carbon steel and brass alloys.

Comp.	Alloy	$K_{\text{ads}} \times 10^4$	T k°	$\Delta G^\circ_{\text{ads}} (\text{kJ.mol}^{-1})$	$\Delta H^\circ_{\text{ads}} (\text{kJ.mol}^{-1})$	$\Delta S^\circ_{\text{ads}} (\text{J.mol}^{-1}.\text{k}^{-1})$
BAMMD	Carbon steel	6.40	298	-37.362	9.767	158.151
BAMMD	Carbon steel	6.40	308	-38.616	9.767	157.087
BAMMD	Carbon steel	6.40	318	-39.869	9.767	156.088
BAMMD	Carbon steel	6.40	328	-41.123	9.767	155.152
BAMMD	Brass	74.10	298	-43.436	9.767	178.535
BAMMD	Brass	74.10	308	-44.894	9.767	177.72
BAMMD	Brass	74.10	318	-46.352	9.767	176.758
BAMMD	Brass	74.10	328	-47.809	9.767	175.538

Generally, the values of  $\Delta G^\circ_{\text{ads}}$  are negative that indicate that the adsorption process is spontaneous and the adsorbed layer of BAMMD on each one of the two alloys surfaces is stable. [32-33]. on the other hand,  $\Delta S^\circ_{\text{ads}}$  values in the presence of inhibitor are reduced as temperature increased, meaning a disordering in presence of inhibitor is reduced in order to the inhibitor is adsorbed on the metal surface. On the other hand, when the data of endothermic enthalpy of adsorption in Table 5 is compared with the inhibition efficiency in Table 3 indicate that an endothermic behavior refers to chemical adsorption mode [34]. As shown in Table 5, the adsorption constant of BAMMD in case of brass alloy is greater than in carbon steel that mean the adsorption of BAMMD on brass alloy is preferred than in carbon steel alloy which is correspond to higher negative free energy values for the adsorption of brass alloy than in case of carbon steel alloy therefore, the entropy of adsorption reaction in presence of BAMMD on brass alloy surface is greater than in case of carbon steel alloy meaning that the tendency of adsorption of BAMMD on brass surface is greater than in case of carbon steel this can be attributed to the tendency of Cu metal to chelate with N-atoms in BAMMD is greater than in Fe metal in carbon steel alloy[35]

#### Effect of temperature on the corrosion current:

The effect of temperature on corrosion reaction can be monitored by using the Arrhenius-type process, the rate of which is given by:

$$I_{\text{corr}} = A e^{\frac{-E_a}{RT}} \dots \dots \dots 87$$

Where  $I_{\text{corr}}$  is the corrosion current density, A the Arrhenius pre-exponential constant, and  $E_a$  is the activation energy for the corrosion process, which represents the energy necessary for a molecule to possess in order to react. Figures

11 and 12 indicate Tafel plots for the corrosive environment in presence of BAMMD for each of carbon steel and brass alloys at different temperatures respectively.

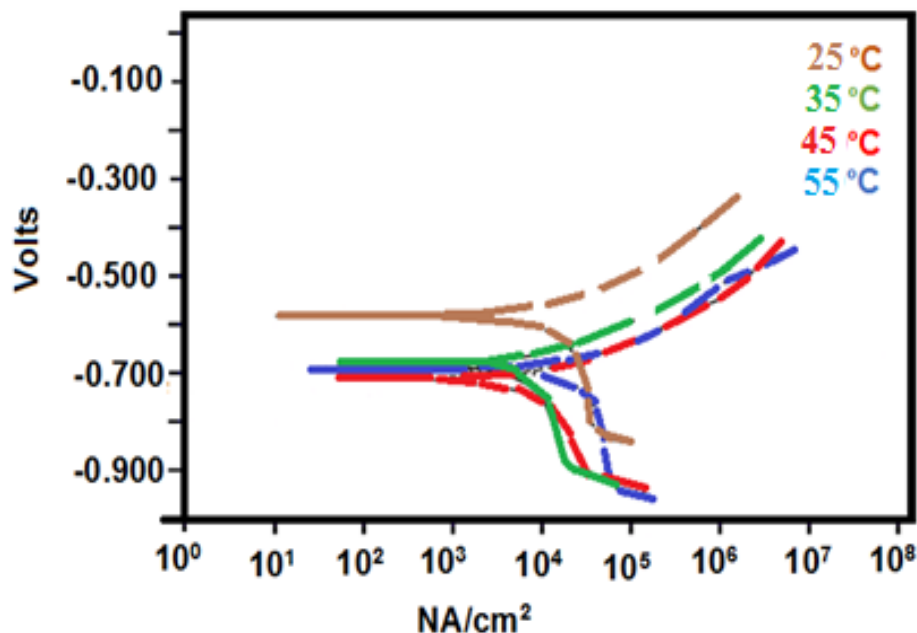


Figure 11: Tafel plots for carbon steel alloy in presence of BAMMD at different temperatures.

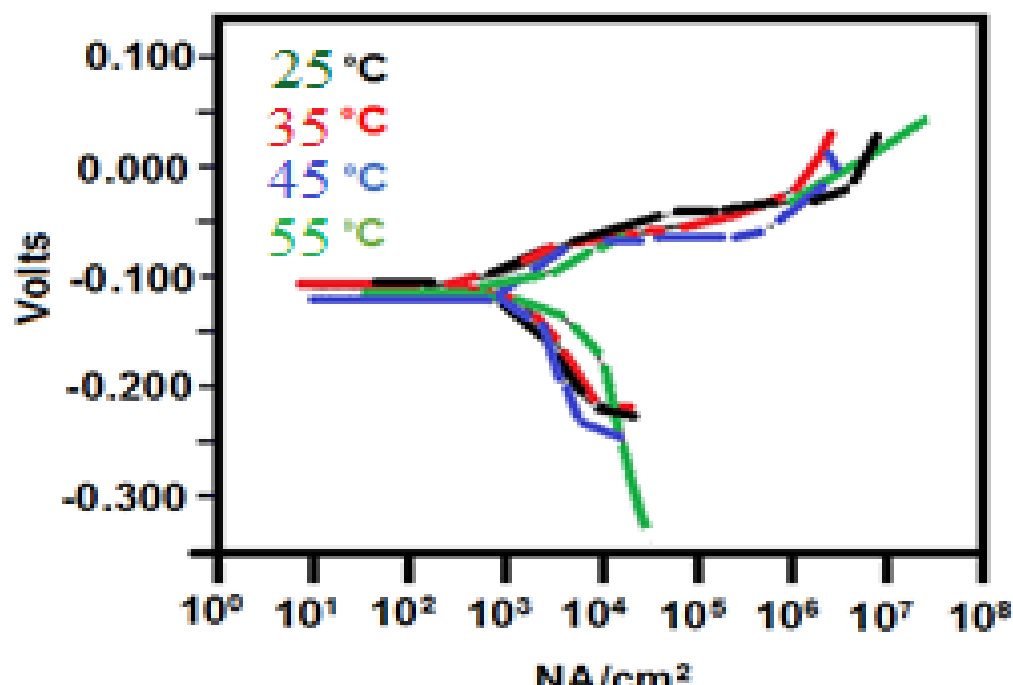


Figure 12: Tafel plots for Brass alloy in presence of BAMMD at different temperatures.

Tables 6 and 7 explain the corrosion data that acquired from Tafel plots in absence and presence of BAMMD at 50 ppm as optimum concentration at different temperatures ranged (25-55) °C respectively. As shown from Table 7 below in absence of BAMMD increasing corrosion current density, corrosion rate in addition to the polarization resistance values are reduced. On the other hand, in Table 8 below in case of carbon steel alloy, as temperature increased the presence of BAMMD make the inhibition efficiency increased from 64.64% at 25°C to 90.35% at 55°C at constant concentration (50) ppm, due to reduce the corrosion rate, corrosion current density that

corresponding to increase in resistance polarization values. On the other hand, both Tafel constants values  $\beta_a$  and  $\beta_c$  as increased then the BAMMD has the ability to control the mechanism of anodic and cathodic reactions respectively. On the other hand the same case can be shown as in Table 7 where, as increasing temperature from 25°C to 55°C at constant temperature 50 ppm, as the inhibition efficiency increased from 84.75% to 89.24% that corresponding to reduce in corrosion rate due to reduce in corrosion current density and increasing in polarization resistance[36-37]. Furthermore, reducing in both Tafel constants values  $\beta_a$  and  $\beta_c$  as temperature increased in case of brass means that the inhibition of BAMMD on brass surface as temperature increased tend to simple blocking reaction[38].

**Table 6: Tafel plot data for carbon steel and brass alloys in presence of 0.2M NaCl as corrosive environment at different temperatures.**

Comp.	Alloy	Temp °C	$\beta_c$ mV/decade	$\beta_a$ mV/decade	$R_p$ ( $\Omega$ )	$I_{corr}$ $\mu A/cm^2$	$E_{corr}$ Volt	CR mpy
NaCl	Carbon steel	25	278	191	1510	32.7	-0.883	15.10
NaCl	Carbon steel	35	392	100	2865	33.84	-0.549	15.57
NaCl	Carbon steel	45	736	35*	1470	38.87	-0.580	17.88
NaCl	Carbon steel	55	1*	141	612	41.43	-0.546	19.06
NaCl	Brass	25	307	34	15200	4.65	-0.139	2.23
NaCl	Brass	35	250	64	21710	4.73	-0.110	2.27
NaCl	Brass	45	310	*125	8031	4.81	-0.109	2.31
NaCl	Brass	55	401	*88	3593	5.22	-0.123	2.51

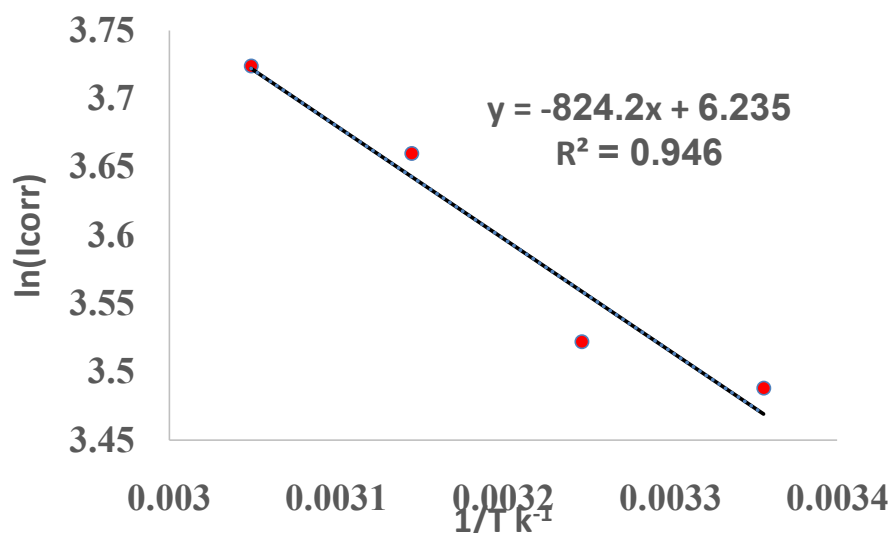
**Table 7: Tafel plot data for carbon steel and brass alloys in presence of 50 ppm of BAMMD as optimum concentration.**

comp	Alloy	Temp °C	$\beta_c$ mV/decade	$\beta_a$ mV/decade	$R_p$ ( $\Omega$ )	$I_{corr}$ $\mu A/cm^2$	$E_{corr}$ Volt	CR mpy	inh. eff %
BAMMD	Carbon steel	25	333	100*	1250	7.50	-0.689	3.45	64.64
BAMMD	Carbon steel	35	649	162	2086	6.00	-0.589	2.76	82.27
BAMMD	Carbon steel	45	384	81	3625	4.50	-0.686	2.07	88.42
BAMMD	Carbon steel	55	778	142	8440	4.00	-0.591	1.84	90.35
BAMMD	Brass	25	336	58	8416	0.70	-0.130	0.34	84.75
BAMMD	Brass	35	234	67	4790	0.62	-0.121	0.29	87.22
BAMMD	Brass	45	393	33*	8930	0.58	-0.124	0.28	87.87
BAMMD	Brass	55	358	16*	6010	0.55	-0.116	0.27	89.24

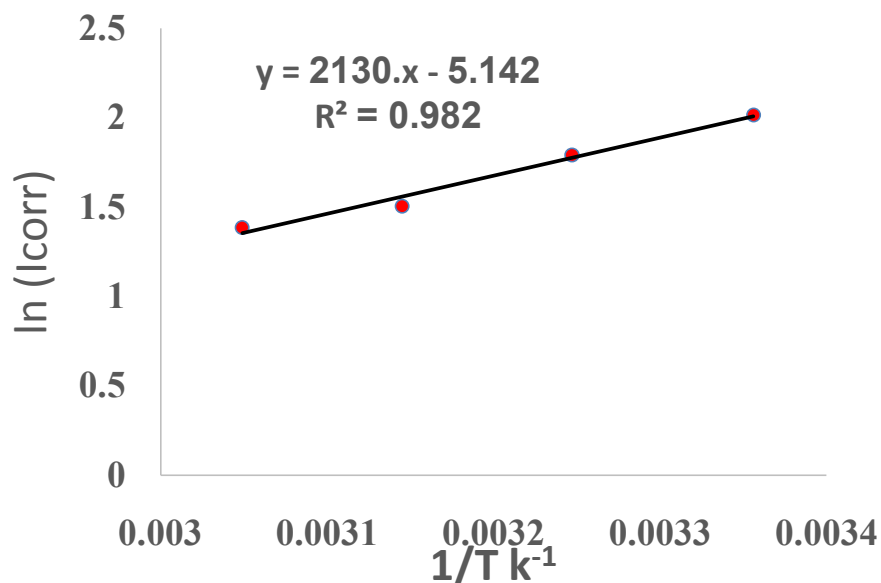
On the other hand, an energy of activation  $E^*$  can be calculated as in Figures 13-17 below, the data that calculated  $E^*$  is summarized in Table 8 below:

**Table8: show the variation of  $I_{\text{corr}}$  values with temperature in 0.2M NaCl in the absence and presence of the tested inhibitor on carbon steel alloy.**

Alloy	T(K)	$1/T \times 10^{-3} (\text{K}^{-1})$	$\ln(I_{\text{corr}})(\text{Blank})$	$\ln(I_{\text{corr}})(\text{BAMMD})$
Carbon steel	298	3.356	3.488	2.015
Carbon steel	308	3.247	3.522	1.792
Carbon steel	318	3.145	3.660	1.504
Carbon steel	328	3.049	3.724	1.386
Brass	298	3.356	1.537	-0.357
Brass	308	3.247	1.554	-0.478
Brass	318	3.145	1.570	-0.545
Brass	328	3.049	1.652	-0.598



**Figure 13: Arrhenius plot for corrosion rate for carbon steel alloy in absence of BAMMD (presence of corrosive environment alone 0.2M NaCl).**



**Figure 14: Arrhenius plot for corrosion rate for carbon steel alloy in presence of BAMMD.**

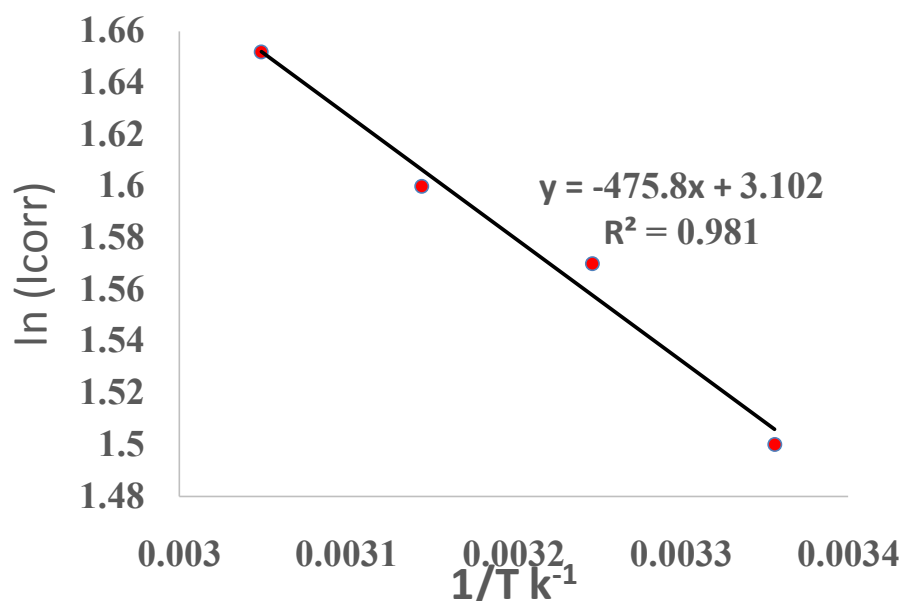


Figure 15: Arrhenius plot for the corrosion of Brass in absence of BAMMD (in presence of corrosive environment 0.2M NaCl).

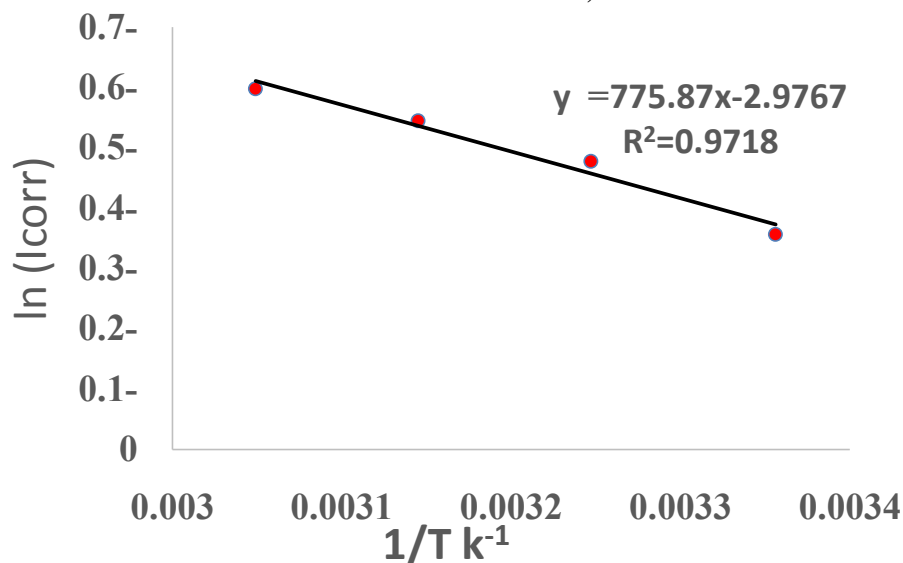


Figure 16: Arrhenius plot for the corrosion reaction for Brass alloy in presence of BAMMD.

Furthermore, other activation parameters like  $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$  can be calculated in presence and absence of BAMMD in case of carbon steel and brass alloys can be calculated as in Table 9 and as in Figures 16-19 below according the following equations below[39]:

$$\log \frac{CR}{T} = \left( \log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} \right) - \frac{\Delta H^*}{2.303RT} \quad \dots \dots \dots 9$$

Where  $R=8.314 \text{ J.k}^{-1}.\text{mol}^{-1}$ ,  $h=6.625 \times 10^{-34} \text{ J.s}$ ,  $N= 6.023 \times 10^{23} \text{ mol}^{-1}$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \dots \dots \dots 10$$

According to equation8, plotting  $\log CR/T$  against  $1/T$  is a straight line were obtained where the slope equal to  $-\Delta H^*/2.303R$  and the intercept is equal to  $\log R/Nh + \Delta S^*/2.303R$ , thus:

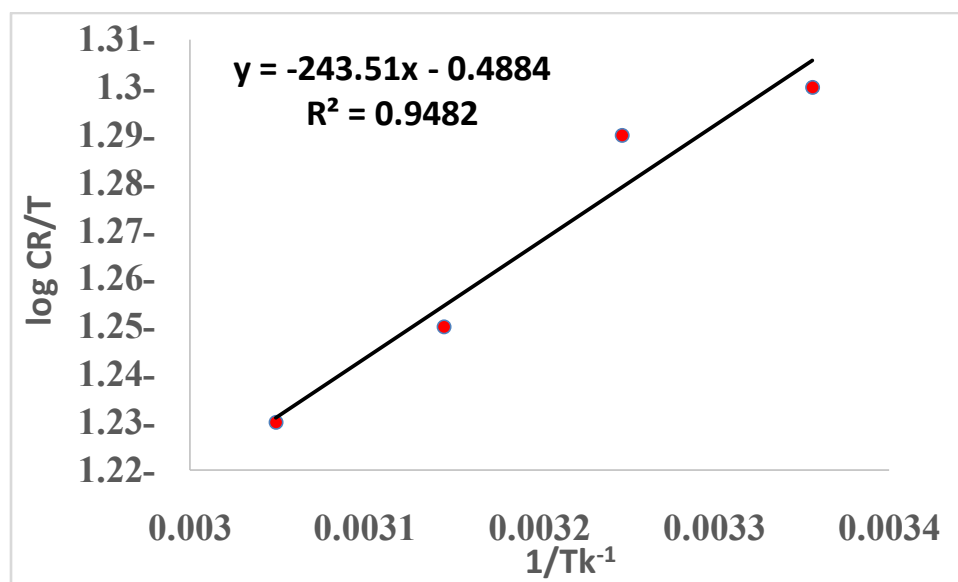
$$\log \frac{R}{Nh} = 10.319 \quad \dots \dots \dots 11$$

$$\Delta S^* = 2.303R(\text{Intecept} - 10.319) \quad \dots \dots \dots 12$$

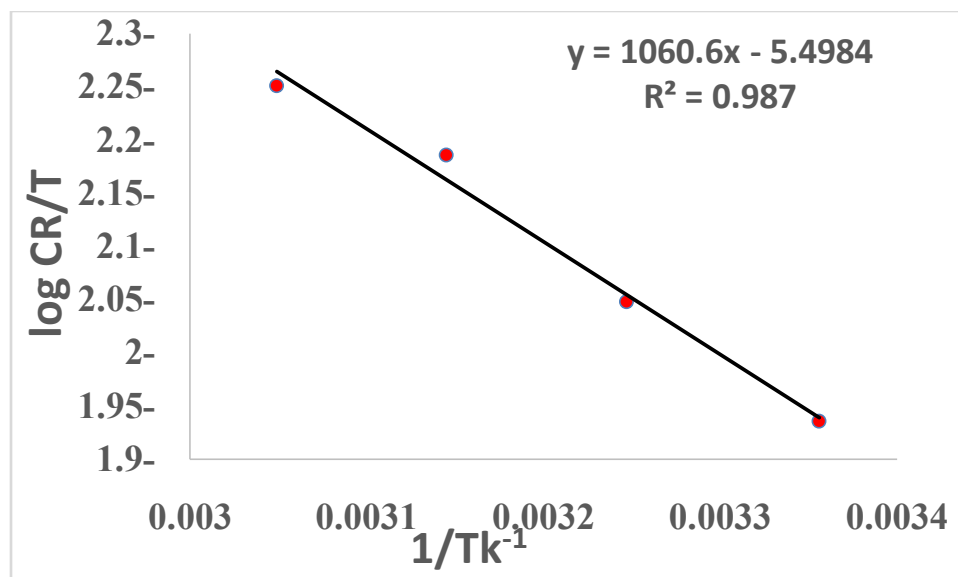
$$\Delta S^* = 19.147(\text{Intecept} - 10.319) \quad \dots \dots \dots 13$$

**Table 9: Kinetic parameters  $E^*$ ,  $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$  for carbon steel in 0.50 M HCl without and with addition of different concentrations of BAMMD Carbon steel.**

Alloy	Conc. (ppm)	$E^*$ (kJ/mol)	$\Delta H^*$ (kJ/mol)	$\Delta G^*$ (kJ/mol)	$\Delta S^*$ (J/k.mol)
Carbon steel	0	-6.853	-4.663	-1.88	-9.351
Carbon steel	50	17.72	20.31	51.68	-105.28
Brass	0	-3.96	1.02	14.16	-44.12
Brass	50	3.72	8.57	34.02	-85.39



**Figure 17: kinetic parameters calculation for corrosion reaction of Carbon steel alloy in absence of BAMMD.**



**Figure 18: kinetic parameters calculation for corrosion reaction of Carbon steel alloy in presence of BAMMD.**

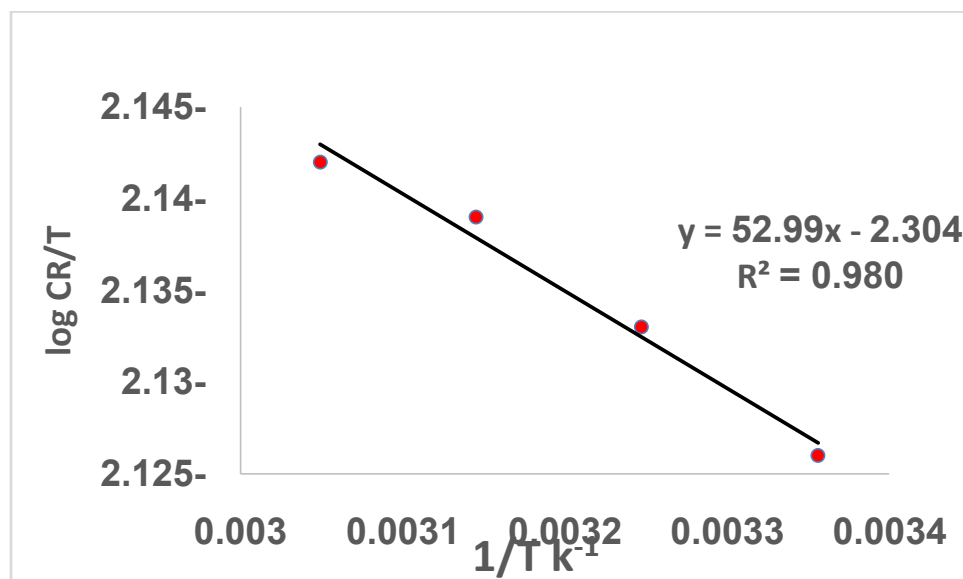


Figure 19: kinetic parameters calculation for corrosion reaction of Bassalloy in absence of BAMMD.

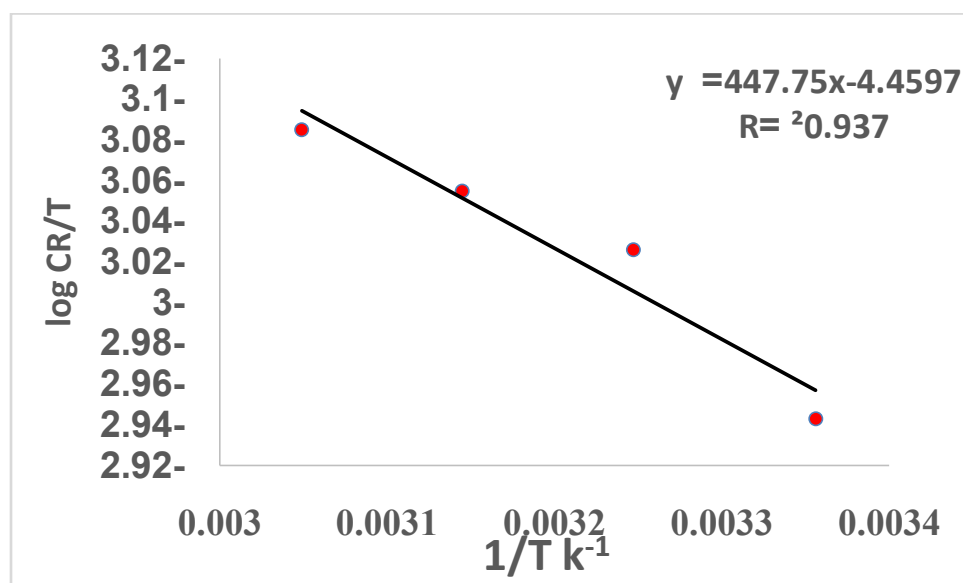


Figure 20: kinetic parameters calculation for corrosion reaction of Brassalloy in presence of BAMMD.

According to Table 9 that the kinetic parameters and of dissolution reaction for both of carbon steel and brass in presence of 0.2 M NaCl as corrosive environment (in the absence of BAMMD) is faster than in presence of the BAMMD where the energy of activation for the corrosion reaction in absence of the inhibitor very little values compared with the presence of the inhibitor where,  $E^*$  is negative values in absence of BAMMD i.e., the corrosion reaction of alloys is very fast in the absence of this inhibitor while presence of it will make the energy of activation high and positive. Furthermore, the positive sign of enthalpies except in case of the corrosion reaction of carbon steel alloy (negative i.e. exothermic reaction) refers to an endothermic nature for each of carbon steel and brass alloys dissolution process i.e. dissolution of steel or brass is difficult in presence of BAMMD compared with the absence [40]. On the other hand, according to Table 9, the entropy of activation clear that these values increased in the presence of inhibitor than in its absence in negative value i.e., reducing in entropy. Thus the negative values of entropy implies that the activation complex is the rate-determining step represents association rather than

dissociation where, the negative values of entropy of activation indicating that a decrease in disorder takes place on going from reactants to the activated complex [41-44]. The comparison between the corrosion reaction for carbon steel and brass alloys depict that in absence of BAMMD the reaction is spontaneous in carbon steel alloy (Gibbs free energy is negative) while in case of brass is nonspontaneous (Gibbs free energy is positive) as in Table 9 above because the copper in brass alloy tend to be a passive oxide layer as CuO compared with iron in carbon steel alloy that formed a porous oxide layer  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  hence, the carbon steel alloy is easily corroded than brass alloy where the reaction in carbon steel alloy is an exothermic while an endothermic in case of brass alloy [45]. On the other hand in presence of BAMMD in case of carbon steel alloy the corrosion reaction is tend to be an endothermic, non-spontaneous, less entropy (increasing the negative value of  $\Delta S^*$ ) as in Table 9, thus, in case of brass the same concentration of BAMMD increased the endothermic, non-spontaneous and reduce entropy for corrosion reaction of brass compared with the absence of it as in Table 9 meaning that BAMMD has a greater effect to reduce the corrosion reaction for carbon steel alloy where the optimum concentration of BAMMD (50 ppm) has the ability to covered the most surface of this alloy to inhibit the corrosion reaction[43].

## Conclusions

Several points can be concluded according to the results acquired that can be summarized as below:

1. For two alloys carbon steel and brass, as concentration increased, the inhibition efficiency increased at same optimum concentration (50 ppm) but in brass alloy is greater than in carbon steel this attributed to affinity of BAMMD to chelate with copper in brass alloy greater than in iron in carbon steel alloy.
2. As temperature increased, as the inhibition efficiency of BAMMD increased for both alloys which corresponding to chemical adsorption mode for BAMMD with each one of the two alloys.
3. The chemical adsorption mode in two cases corresponding with the kinetic parameters where, an endothermic, non-spontaneous properties in addition to negative values of entropy of activation.
4. According to thermodynamic study, the surface coverage area is obeyed Timken isotherm in case of carbon steel alloy while in case of brass is obeyed to Langmuir isotherm. Furthermore, the adsorption reaction between BAMMD whether with carbon steel or brass alloys is spontaneous and endothermic that corresponding with chemical adsorbing mode.
5. Anodic inhibition behavior is shown for BAMMD in two cases, where the inhibitor tend to anodic reaction mechanism controlled greater than the cathodic reaction.

## References:

1. Tayeb Chieb, Kamel Belmokre, Mohammed Benmessaoud, Sidi El Hassane Drissi, Najat Hajjaji, Abdellah Shhiri, The Inhibitive Effect of 3-Methyl 4-Amino 1,2,4 Triazole on the Corrosion of Copper-Nickel 70 - 30 in NaCl 3% Solution, Materials Sciences and Applications, 2011, 2, 1260-1267.
2. Natural Products as Corrosion Inhibitors of Some Metals in Aqueous Media, M.Sc thesis, Noha Mosa Al-Qasmi. Kingdom of Saudi Arabia, Ministry of High Education, Umm Al-Qura University Faculty of Applied Science for Girls Chemistry Department, 2010
3. Green Inhibitors for Corrosion Protection of Metals and Alloys Hindawi Publishing Corporation, International Journal of Corrosion, Volume 2012, Article ID 380217, 15 pages doi:10.1155/2012/380217, B. E. Amitha Rani and Bharathi Bai J. Basu
4. Halambek\*, Marijana Jukić, Katarina Berković, Jasna Vorkapić-Furač, Investigation of Novel Heterocyclic Compounds as Inhibitors of Al-3Mg Alloy Corrosion in Hydrochloric Acid Solutions, Int. J. Electrochem. Sci., 7 (2012) 1580 – 1601.
5. N-heterocyclic amines and derivatives K. Babic´-Samardz´ija, K.F. Khaled and N. Hackerman, Anti-Corrosion Methods and Materials Volume 52 · Number 1 · 2005 · 11–21
6. Int. J. Electrochem. Sci., 7 (2012) 3436 - 3452 International Journal of electrochemical science, Electrochemical and Quantum Chemical Study of Albendazole as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution I. Ahamad, R. Prasad, Eno E. Ebenso, M.A. Quraishi
7. R.T. Loto and C.A. Loto, Effect of P-Phenyldiamine on the Corrosion of Austenitic Stainless Steel Type 304 in Hydrochloric Acid, Int. J. Electrochem. Sci., 7 (2012) 9423 – 9440,
8. Y. H. Ahmad, A. S. Mogoda\*, A. G. Gadallh, Investigation of the Inhibiting Effect of Some Triazole Derivatives for the Corrosion of Mild Steel in 1 M H<sub>2</sub>SO<sub>4</sub> Solution, Int. J. Electrochem. Sci., 7 (2012) 4929 - 4941
9. I.B. Obot, S. A Umoren and N.O. Obi-Egbedi Corrosion inhibition and adsorption behaviour for aluminum by extract of Anigeria robusta in HCl solution: Synergistic effect of iodide ions, J. Mater. Environ. Sci. 2 (1) (2011) 60-71,



10. P. Bothi Raja and M.G. Sethuraman, Studies on the Inhibition of Mild Steel Corrosion by Rauvolfia serpentina in Acid Media,, Journal of Materials Engineering and Performance Volume 19(5) July 2010—761
11. A. Ghazoui, A. Zarrouk, N. Bencat, R. Salghi, M. Assouag, M. El Hezzat, A. Guenbour and B. Hammouti, Journal of Chemical and Pharmaceutical Research, 2014, 6(2):704-712 Research New possibility of mild steel corrosion inhibition by organic heterocyclic compound
12. Hadi.Z.AL-Sawaad, Evaluation of the Ceftriaxone as Corrosion Inhibitor for Carbon Steel Alloy in 0.5M of Hydrochloric Acid. *Int. J. Electrochem. Sci.*, 8 (2013) 3105 - 3120
13. *Materials Research*. 2014; 17(1): 255-264, The Inhibition Effect of Mad Honey on Corrosion of 2007-Type Aluminium Alloy in 3.5% NaCl Solution, Husnu Gerengia, Haydar Goksu, Pawel Slepiski
14. E.M.Sherif and Su-Moon Park. Effect of 1,5-Naphthalenediol on Aluminium corrosion as a corrosion inhibitor in 0.5M NaCl, Journal of The Electrochemical Society, 152(6)B205-B211(2005)
15. Recent Patents on Corrosion Science, 2013, 3 No1, Impact of Synthesized and Natural Compounds in Corrosion Inhibition of Carbon Steel and Aluminium in Acidic Media ,Nabel A. Negm\*, Mona A. Yousef and Salah M. Tawfik
16. International Journal of hydrogen energy 35 (2010)11387-11396, Inhibition effect of newly synthesized heterocyclic organic molecules on corrosion of steel in alkaline medium containing chloride, M.A. Ameer, A.M. Fekry
17. Leonardo Electronic Journal of Practices and Technologies ISSN 1583-1078 Issue 12, January-June 2008 p. 1-14 , The Inhibition Effect of Heterocyclic Compounds towards the Corrosion of Iron in Phosphoric Media Khadija HNINI, Salah FADEL, Molay Abderrahim EL MHAMMEDI, Abdelilah CHTAINI and El Mustapha RAKIB
18. Strojniški vestnik - Journal of Mechanical Engineering 56(2010)2, 121-130 ,Effect of Antioxidants and Corrosion Inhibitor Additives on the Quenching Performance of Soybean Oil Daniel Komatsu 1 - Elki Cristina Souza - Ester Carvalho de Souza- Luralice de Campos Franceschini Canale - George Edward Totten
19. PHYTOCHEMICALS AS GREEN CORROSION INHIBITORS IN VARIOUS CORROSIVE MEDIA: A REVIEW, J Buchweishaija, *Tanz. J. Sci. Vol 35 2009*
20. SOME TETRAZOLIC COMPOUNDS AS CORROSION INHIBITORS FOR COPPER IN NITRIC ACID MEDIUM, M. Mihit, L. Bazzi, R. Salghi, B.Hammouti ,S. El Issami, E. Ait Addi, International Scientific Journal for Alternative Energy and Ecology № 6 (62) 2008
21. Electrochimica Acta 53 (2008) 3484–3492, Molecular simulation, quantum chemical calculations and electrochemical studies for inhibition of mild steel by triazoles, K.F. Khaled
22. Environ. Sci. 2 (1) (2011) 13-17, Heterocyclic compounds as corrosion inhibitors for mild steel in hydrochloric acid medium — correlation between electronic structure and inhibition efficiency. F. Bentiss , M. Lagrenée (2013) 3105 – 3120.
23. S.S.Mahmoud, Portugaliae Electrochimica Acta, 24(2006) 441-445, Corrosion inhibition of Muntz (63% Cu, ~37%Zn) Alloy in HCl solution by some naturally occurring Extracts.
24. International Journal of Engineering Science and Technology, Vol. 2(11), 2010, 6417-6426, ADSORPTION AND CORROSION INHIBITION OF MILD STEEL IN HYDROCHLORIC ACID MEDIUM BY N-[MORPHOLIN-4-YL(PHENYL)METHYL]BENZAMIDE, A. Jamal Abdul Nasser and M. Anwar Sathiqn
25. A.M.Haddad, **Ph.D thesis**, Univ. of Basra, Iraq (2002).
26. M.Saleh, "*Mat.Chem. Phys.*", **98** (2006).
27. M.H.Wahdan, A.A.Hermas, M.R.Morad, "*Mat.Chem. Phys.*", **76** (2002).
28. E.Abelev, D.Starovetsky, "*Electr.Chem .Acta*", **52**(2007).
29. M.Hossen, S.F.L.Mertenz, M.Ghorbani, "*Mat.Chem. Phys.*", **78** (2003).
30. M.Lebrini, M.Lagrenée, H.Vezin, M.Traisnel, and F.Bentiss, "*Corrosion Science*", **49** (2007).
31. S.G.Zhang, W.lei, M.Z.Yia, "*J. of Molecular Structure*", **732**(2005).
32. E.M.Sherif, S.M.Park, "*Electr.Chem .Acta*", **51**(1)(2006).
33. J.Cruz, R.Martinez, J.Genesca, "*J of Electro. Anal.Chem*", **566**(2004).
34. F.A.Hameed, **M.Sc thesis**, Univ. of Basra, Iraq (2006).
35. F.A.Cotton and G.Wikinson, Advanced Inorganic Chemistry, A Comprehensive Text, Wiley-Interscience Publisher, New York, 6<sup>th</sup> Ed, 1999
36. Guo Gao and Chen Hao Liang, corrosion science 49(2007) 3479-3493, 1,3-Bis-diethylamino-propan-2-ol as volatile corrosion inhibitor for brass.
37. M.M. El-Naggar, corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds, corrosion science 49(2007) 2226-2236.
38. C.L.Aravindra, V.S.Muralidharan, and S.M.Mayanna, *J.Appl.Electro.Chem*", 31(2001).

39. Imran Naqvi, A. R. Saleemi, S. Naveed, *Int. J. Electrochem. Sci.*, 6 (2011) 146 - 161 Cefixime: A drug as Efficient Corrosion Inhibitor for Mild Steel in Acidic Media. Electrochemical and Thermodynamic Studies.
40. M.A.Ameer, E.Khamis, and G.Al-Senani, "*J.Appl.Electro.Chem*", **32(2)** (2002).
41. K.Tebbi, I.Bouabdellah, and A.Aouniti, "*Material Letters*", (2006).
42. E. Khamis, A. Hosney, S. El-Khodary, *Afinidad* 52 (1995) 95.
43. Hadi Z.M. Al-Sawaad, *J. Mater. Environ. Sci.* 2 (2) (2011) 128-147
44. Priyanka Singh<sup>1</sup>, M.A. Quraishi Eno. E. Ebenso<sup>2</sup> *Int. J. Electrochem. Sci.*, 7 (2012) 12270 - 12282 investigation of Gliclazide Drug as Novel Corrosion Inhibitor for Mild Steel in 1 M HCl Solution
45. Nestor Perez, *Electrochemistry and corrosion science*, Kluwer Academic Publishers, New York, 2004.