

Ethoxylated fatty amines as corrosion inhibitors for carbon steel in hydrochloric acid solutions

I. A. Zaafarany^{1*} and Hamza A. Ghulman²

¹*Chemistry Department, Faculty of Applied Science, Umm Al-Qura University,
P.O.Box 118, Makkah Al Mukaramha, Saudi Arabia*

**E-mail: ishaq_zaafarany@yahoo.com*

²*Mechanical engineering department, College of Engineering, Umm Al-Qura University,
P.O.Box 5555, Makkah, 21955 Saudi Arabia*

E-mail: hghulman@gmail.com

Abstract

The effect of three compounds of non ionic surfactants, namely, ethoxylated fatty amines with different number of ethylene oxide unit on the corrosion of carbon steel (Type L52) in 1 M HCl has been studied using weight loss and galvanostatic polarization measurements. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor, number of ethylene oxide units and with decreasing temperature. The inhibitive effect of these compounds was interpreted in view of their adsorption on the steel surface, through their ethoxy groups. The adsorption of these compounds was found to obey the Langmuir isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also studied. Some activated thermodynamic parameters were calculated.

Key words: *ethoxylated fatty amines, carbon steel, polarization, adsorption.*

Received: February 25, 2013.

doi: [10.17675/2305-6894-2013-2-2-082-091](https://doi.org/10.17675/2305-6894-2013-2-2-082-091)

1. Introduction

The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [1]. Acid solutions are generally used for the removal of rust and scale in several industrial processes. Inhibitors are generally used in these processes to control the metal dissolution. Most well-known acid inhibitors for steel corrosion are organic compounds containing hetero atoms [2–12]. To be effective, an inhibitor must also displace water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevent transport ion of water and corrosion active species on the surface [13]. Organic compounds containing multiple bonds, particularly triple bonds, and higher molecular weight compounds *e.g.*, protein, polymeric and surfactants compounds have also been widely used, the effectiveness of such compounds increases with increasing chain length [14, 15].

The aim of the present work is to study the inhibitive effect of three compounds of ethoxylated fatty amines as corrosion inhibitors on the corrosion of carbon steel type L-52

in 1 M HCl using weight loss and galvanostatic polarization measurements. The effect of temperature on the dissolution of carbon steel in 1 M HCl containing 1000 ppm of the inhibitors used was also studied and some thermodynamic parameters were computed.

2. Experimental Method

The carbon steel (Type L52) had the chemical composition (wt%) C 0.25, Mn 1.35, P 0.05, Si 0.003, Nb 0.03, V 0.02 and the remainder is iron. Weight loss measurements were performed using compounds of the dimensions $1 \times 3 \times 0.2 \text{ cm}^3$. For galvanostatic polarization, a cylindrical rod embedded in araldite with exposed surface area of 0.46 cm^2 was used. The electrodes were polished with different emery papers, degreased with acetone and rinsed by distilled water, before inserted in the test solution. Weight loss measurements were carried out as described elsewhere [16]. The specimens are immersed in 100 ml of test solution for period of 24 h.

Galvanostatic polarization studies were carried out using a (PS remote) potentiostat with Zm PS6 software for calculation of corrosion parameters. Three compartment cell with a saturated calomel reference electrode was used. The inhibition efficiency IE was calculated using the following equation:

$$IE = \left[1 - \frac{I_{\text{corr.add}}}{I_{\text{corr.free}}} \right] \cdot 100 \quad (1)$$

where, $I_{\text{corr.add}}$ and $I_{\text{corr.free}}$ are the corrosion rates in free and inhibited acid, respectively.

The ethoxylated fatty amines used as inhibitors were prepared as described previously [17, 18]. They have the general formula:



where, n is the number of ethylene oxide (EO) units and equals 6, 8 and 10 for compounds **I**, **II** and **III**, respectively.

3. Results and Discussion

3.1. Weight loss measurements

Figure 1 shows the effect of increasing concentrations of compound **III** on the weight loss of carbon steel coupons vs. time curves at 25°C . Similar curves (not shown) were obtained for the other two compounds. It is obvious that the weight loss of carbon steel in presence of inhibitor varies linearly with time, and is much lower than that obtained in the blank solution. The linearity obtained indicates the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and thereafter, impede the corrosion process [19].

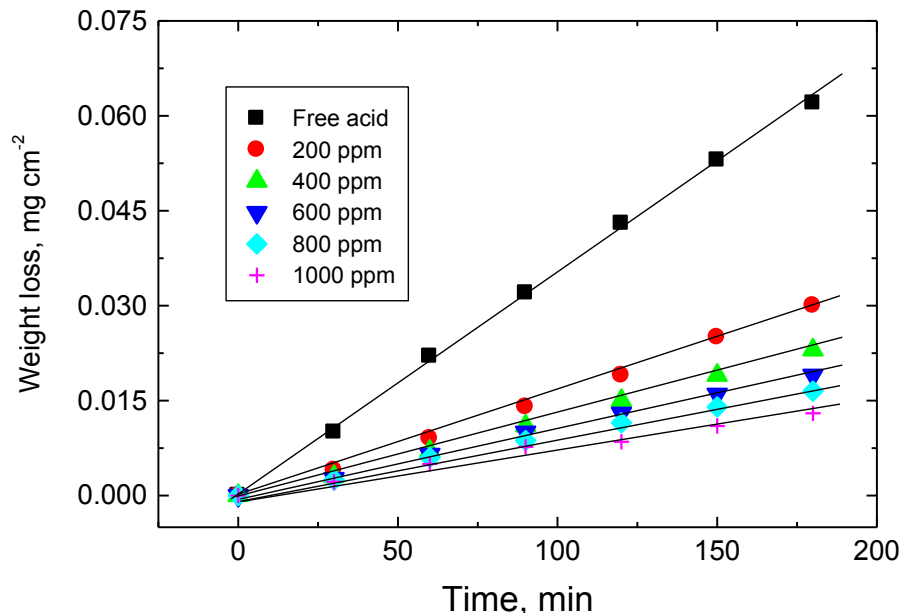


Fig. 1. Weight loss vs. time for the corrosion of carbon steel in 1.0 M HCl solution without and with compound **III**.

The percentage inhibition efficiency ($\%IE$) and a parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules were calculated using the following equations.

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

$$\theta = \left[1 - \frac{R_{\text{add}}}{R_{\text{free}}} \right] \quad (3)$$

where, R_{add} and R_{free} are the corrosion rates of C-steel in free and inhibited acid solutions, respectively. The corrosion rate R_{corr} ($\text{mg cm}^{-2} \text{min}^{-1}$) was calculated from the slopes of the straight line obtained.

Values of R_{corr} , IE and θ obtained at different inhibitor concentrations are listed in Table 1. Inspection of Table 1 reveals that as the inhibitor concentration is increased, the weight loss decreases while IE and θ increase. This behavior could be attributed to the increased surface coverage θ due to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration, the percentage of inhibition efficiency decreases in the following sequence.

compound **III** > compound **II** > compound **I**

Table 1. Effect of ethoxylated fatty amines compounds on corrosion rate (R_{corr}), inhibition efficiency (% IE) and surface coverage (θ) obtained from weight loss measurements for dissolution of carbon steel in 1.0 M HCl solution

	$R_{\text{corr}} \times 10^{-4}$ $\text{mg cm}^{-1} \text{min}^{-1}$	% IE	θ
1 M HCl + compound I			
0 ppm compound I	9.24	–	–
200 ppm compound I	4.54	50.86	0.509
400 ppm compound I	3.78	59.09	0.591
600 ppm compound I	3.12	66.23	0.662
800 ppm compound I	2.56	72.29	0.723
1000 ppm compound I	2.16	76.62	0.766
1 M HCl + compound II			
200 ppm compound II	4.13	55.30	0.553
400 ppm compound II	3.14	66.02	0.660
600 ppm compound II	2.65	71.32	0.713
800 ppm compound II	2.06	77.70	0.777
1000 ppm compound II	1.64	82.25	0.822
1 M HCl + compound III			
200 ppm compound III	3.64	60.61	0.606
400 ppm compound III	2.76	70.13	0.701
600 ppm compound III	2.14	76.83	0.768
800 ppm compound III	1.62	82.47	0.825
1000 ppm compound III	1.08	88.31	0.883

3.2. Adsorption behavior

Adsorption of the organic molecules on the metal surface occurs as the interaction energy between molecule and the metal surface is higher than that between the water molecules and surface [20]. Basic information dealing with the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm [21].

To study the adsorption behavior of ethoxylated fatty amines on carbon steel in 1 M HCl, the adsorption isotherm must be defined. Attempts were made to fit θ values to

various isotherms including Frumkin, Langmuir, Temkin and Freundlich isotherms. By far the results were best fitted by Langmuir adsorption isotherm. Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

where K is the adsorption constant. Plotting C/θ against C gave a straight line with unit slope value (Fig. 2) indicating the adsorption of ethoxylated fatty amines on the steel surface follows Langmuir adsorption isotherm. From these results one can postulate that there is no interaction between the adsorbed species.

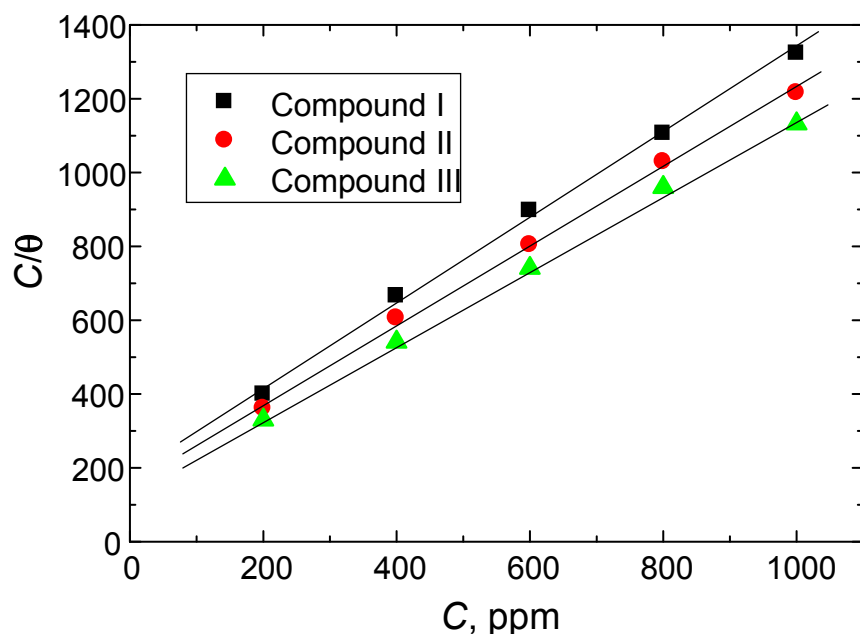


Fig. 2 Langmuir adsorption isotherm plotted as (C/θ) versus C for compounds (I–III) for the corrosion of carbon steel in 1.0 M HCl solution.

3.3. Effect of temperature

The effect of temperature on the corrosion rate of carbon steel in 1 M HCl solution containing 1000 ppm of three compounds was studied at different temperatures (30–60°C) using weight loss measurements. Curves similar to Fig. 1 were obtained (not shown).

As the temperature increases, the rate of corrosion increases and hence the inhibition efficiency of the additive decreases due to the desorption of inhibitor molecules from the steel surface, and hence low surface coverage was obtained. This is due to the desorption is aided by increasing the temperature. This behavior proves that the adsorption of inhibitors on C-steel surface occurs through physical adsorption.

The activation energy (E_a) of the corrosion process was calculated using Arrhenius equation [22]

$$\log R_{\text{corr}} = \log A + \frac{E_a}{2.303 RT} \quad (5)$$

where R_{corr} is the rate of corrosion from weight loss, A is Arrhenius constant, R is the gas constant and T is the absolute temperature.

Figure 3 represents Arrhenius plot ($\log R_{\text{corr}}$ vs. $1/T$) for uninhibited and inhibited 1 M HCl containing 1000 ppm of the studied compounds. The values of E_a can be obtained from the slope of the straight lines were found to be 22.64 KJ mol⁻¹ in 1M HCl and 26.84, 28.66 and 30.64 kJ mol⁻¹, respectively.

The increase of the activation energy in the presence of inhibitors is attributed to an appreciable decrease in the adsorption process of the inhibitors on the metal surface with increase of temperature and a corresponding increase in the reaction rate because of the greater area of the metal that is exposed to the acid [23].

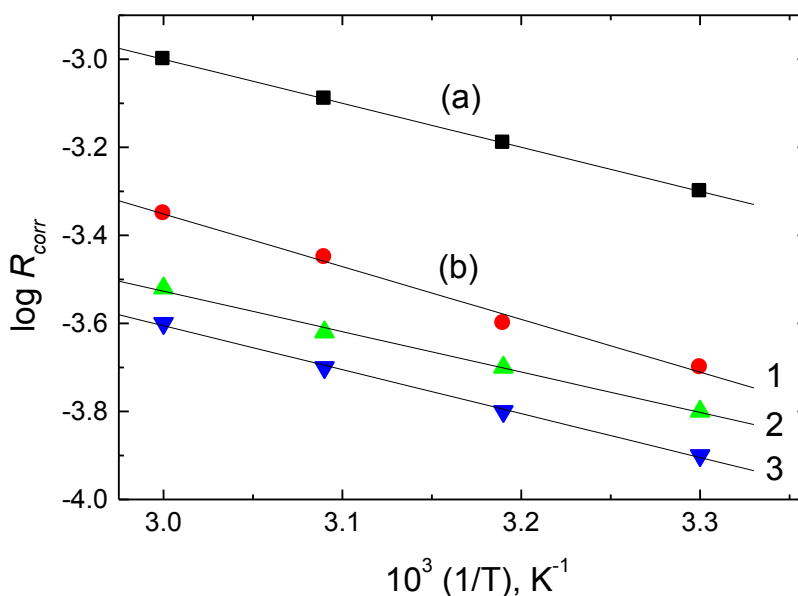


Fig. 3. $\log R_{\text{corr}}$ vs. $1/T$ plot for the corrosion of carbon steel in (a) inhibitor-free 1.0 M HCl solution and (b) 1.0 M HCl solution + 1000 ppm of: 1 – compound I; 2 – compound II; 3 – compound III.

The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for dissolution of carbon steel in 1 M HCl in presence of 1000 ppm of each used compound were obtained by applying the transition state equation [22].

$$R_{\text{corr}} = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (6)$$

where N is Avogadro number and h is Planck constant. A plot of $\log(R_{\text{corr}}/T)$ vs. $(1/T)$ (Fig. 4) should give a straight line with a slope of $(-\Delta H^*/2.303R)$ and an intercept of $[\log(R/Nh - \Delta S^*/2.303R)]$. The values of ΔH^* obtained from the slope of the straight line equal to $12.664 \text{ kJ mol}^{-1}$ in 1 M HCl and equal to 15.326, 18.684 and $20.765 \text{ kJ mol}^{-1}$ in the presence of compound **I**, **II** and **III**, respectively.

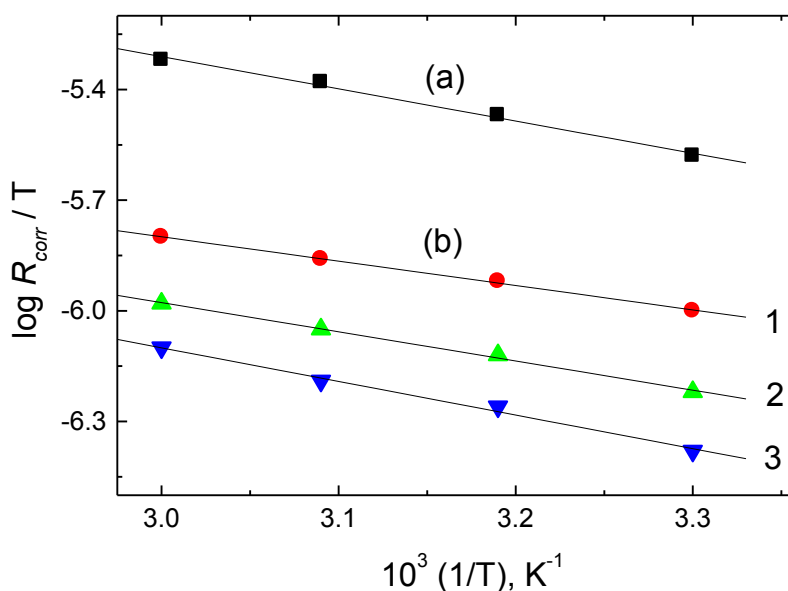


Fig. 4. Transition state plot for the corrosion of carbon steel in: (a) 1.0 M HCl solution (inhibitor-free) and (b) 1.0 M HCl solution + 1000 ppm of: 1 – compound **I**; 2 – compound **II**; 3 – compound **III**.

The values of ΔH^* are different for studied compounds which mean that their structure affects the strength of its adsorption on the metal surface. The values of ΔS^* calculated from the intercept of the straight line were found to be $-384.76 \text{ J mol}^{-1} \text{ K}^{-1}$ in 1 M HCl and -422.78 , -467.86 and $-485.67 \text{ J mol}^{-1} \text{ K}^{-1}$ for compound **I**, **II** and **III**, respectively.

The negative values of ΔS^* in the absence and presence of the inhibitors implies that the activated complex is the rate determining step and represents association rather than dissociation. It also reveals that an increase in the order takes place in going from reactants to the activated complex.

3.4. Galvanostatic polarization studies

The effect of addition of ethoxylated fatty amines on the anodic and cathodic galvanostatic polarization curves of carbon steel in 1 M HCl solution was studied. The effect of increased concentration of compound **III** is represented in Fig. 5 as an example. However, similar curves were obtained for the other compounds (not shown). The corrosion parameters such as, corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), and inhibition efficiency (IE) were calculated and

given in Table 2. Inspection of the data given in this table reveals that, as the concentration of the inhibitor increases, the values of b_a and b_c increase slightly or are approximately constant suggesting the inhibiting action of these compounds by adsorption at the metal surface according to blocking adsorption mechanism. The values of E_{corr} is shifted to more negative potentials, the values of I_{corr} decreases and the values of IE increases indicating the inhibiting effect of these compounds. The inhibition efficiency of these compounds decreases in the following order:

compound **III** > compound **II** > compound **I**

which is consistent with that obtained from weight loss measurements.

It is obvious that, the values of IE increased with an increase in the number of ethylene oxide unit. These finding could be explained on the bases of the fact that, an increase in concentration of the inhibitor would result in a lowering of the interfacial tension at the metal surface. This lowering in the interfacial tension is thought to be due to a decrease in the bulk concentration of the inhibitor and an increase in its concentration at the metal surface.

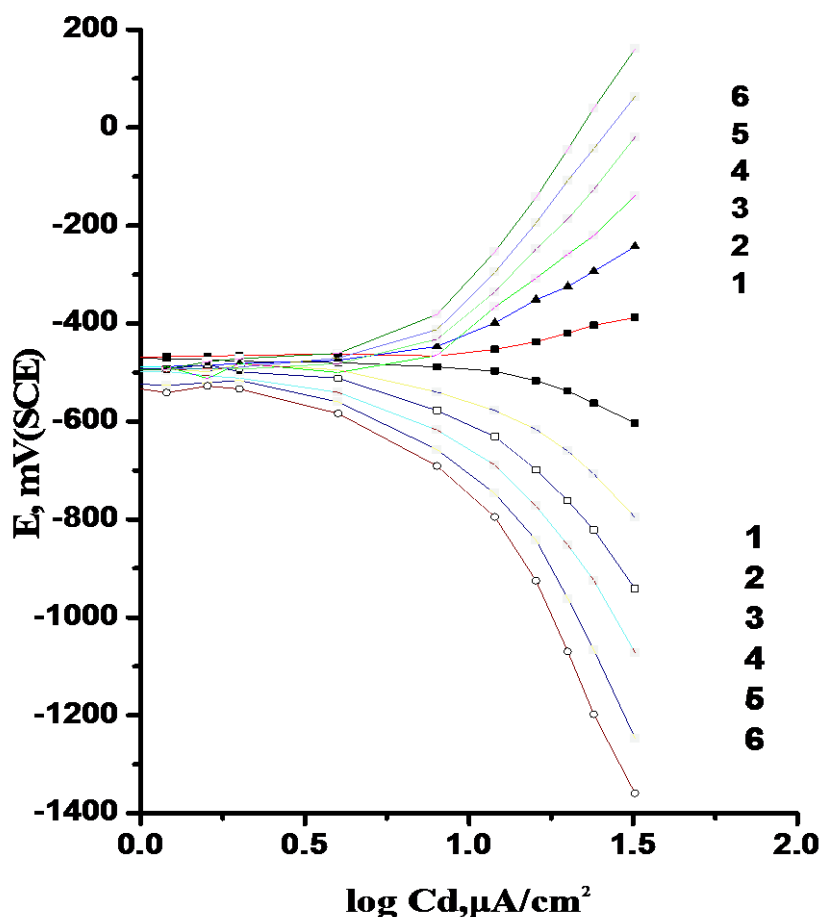


Fig. 5. Galvanostatic polarization curves of carbon steel in 1.0 M HCl containing different concentrations of compound **III**: 1 – 0.00; 2 – 200; 3 – 400; 4 – 600; 5 – 800; 6 – 1000 ppm.

Table 2. Corrosion parameters obtained from galvanostatic polarization of carbon steel in 1 M HCl containing different concentrations ethoxylated fatty amines compounds.

Inhibitor concentration	β_a , mV dec ⁻¹	$-\beta_c$, mV dec ⁻¹	E_{corr} , V (SCE)	I_{corr} , $\mu\text{A cm}^{-2}$	IE
0.00 ppm	95	108	-456	0.872	—
200 ppm compound I	150	120	-508	0.412	52.75
400 ppm compound I	154	140	-516	0.376	56.88
600 ppm compound I	160	155	-532	0.312	64.22
800 ppm compound I	168	163	-536	0.264	69.72
1000 ppm compound I	163	165	-540	0.188	78.44
200 ppm compound II	154	118	-510	0.384	55.96
400 ppm compound II	158	122	-522	0.302	65.36
600 ppm compound II	166	138	-538	0.194	77.75
800 ppm compound II	172	146	-543	0.156	82.11
1000 ppm compound II	174	152	-550	0.132	84.86
200 ppm compound III	160	122	-518	0.362	58.48
400 ppm compound III	163	132	-538	0.270	69.03
600 ppm compound III	166	153	-542	0.162	81.42
800 ppm compound III	175	160	-546	0.122	86.01
100 ppm compound III	180	164	-555	0.085	90.25

Conclusions

1. Ethoxylated fatty amines act as an inhibitors for corrosion of carbon steel in 1 M HCl solution.
2. The inhibition efficiency increases with increase of inhibitor concentrations and number of ethylene oxide unit but decreases as the temperature increases.
3. The inhibitive action of ethoxylated fatty amines due to the adsorption of their compounds on the steel surface.
4. The adsorption process follows Langmuir adsorption isotherm.
5. The inhibition efficiency obtained from weight loss measurements showed good agreement with those obtained from comparative polarization measurements.

References

1. J. M. Sykes, *Br. Corros. J.*, 1990, **25**, 175.
2. S. A. Abd El-Maksoud, *Appl. Surface Sci.*, 2003, **206**, 129.
3. K. C. Emergöl, E. Düzgün and O. Atakol, *Corros. Sci.*, 2006, **48**, 3243.
4. M. Abdallah, Basim H. Asghara, I. Zaafarany and A. S. Fouda, *Int. J. Electrochem. Sci.*, 2012, **7**, no. 1, 282.
5. M. Abdallah, Sh. T. Atwa, N. M. Abdallah, I. M. El-Naggar and A. S. Fouda, *Anti-Corrosion Methods and Materials*, 2011, **58**, no. 1, 31.
6. S. M. A. Hosseini, M. Salari, E. Jamalizadeh, S. Khezripor and M. Seifi, *Mater. Chem. and Phys.*, 2010, **119**, 100.
7. M. Abdallah, H. E. Megahed and M. S. Motae, *Mater. Chem. and Phys.*, 2009, **118**, 111.
8. M. Abdallah, E. A. Helal and A. S. Fouda, *Corros. Sci.*, 2006, **48**, 1639.
9. X. Li, S. Deng and H. Fu, *Corros. Sci.*, 2011, **53**, 3241.
10. K. S. Jacob and G. Parameswaran, *Corros. Sci.*, 2010, **52**, 224.
11. M. Abdallah, I. Zaafarany, K. S. Khairou and M. Sobhi, *Int. J. Electrochem. Soc.*, 2012, **7**, no. 2, 1564.
12. M. Abdallah and M. M. El-Naggar, *Mater. Chem. and Phys.*, 2001, **71**, 291.
13. M. Abdallah, E.A. Helal and A. S. Fouda, *Corros. Sci.*, 2006, **48**, 1639.
14. M. Abdallah, *Corros. Sci.*, 2003, **45**, 2705.
15. M. Abdallah, H. E. Megahed, M. A. Radwan and E. Abdfattah, *J. Amer. Sci.*, 2012, **8**, no. 11, 49.
16. P. B. Mathur and T. Vasudevam, *Corrosion*, 1982, **38**, 17.
17. E. Stipnisck-Lisac, A. Gazivoda and M. Madzarac, *Electrochim. Acta*, 2002, **47**, 4189.
18. F. Hanna, G. M. Sherbiniand and Y. Barakat, *Br. Corros. J.*, 1989, **24**, 296.
19. M. Abdallah, I. Zaafarany, A. S. Fouda and D. AbdEl-Kader, *J. Mater. Eng. Perform.*, 2012, **21**, 995.
20. E. McCafferty, in: *Corrosion Control by Organic Coatings*, Ed. H. Leidheiser, Jr., 1979, 279.
21. F. Bentis, M. Traisnel, N. Chaibi, B. Memari, H. Vezin and M. Lagrenee, *Corros. Sci.*, 2002, **44**, 2271.
22. I. Putilova, S. Balezin, I. N. Barannik and V. P. Bishop, *Metall. Corros. Inhibit.*, Pergamon, Oxford, 1960, 196p.
23. M. Abdallah, *Corros. Sci.*, 2004, **46**, 1981.

