Gemini-Surfactant Effect on the Inhibition of Corrosion of Brass in Acid Environment

Dr. Abduelmaged Abduallah ***Dr. Omar Algeidi***
Department of Chemical Engineering
Faculty of Engineering - Sabratha
Zawia University

Abstract:

The influence of gemini surfactants namely: N-trimethyl butane-diyl-1,2-ethane-bis-ammonium bromide, N-hexane-diy l-1,2- ethane -bis-ammonium bromide and N - dodecane - diy l-1,2- ethane-bis-ammonium bromide has been investigated for controlling the corrosion of brass in formic acid. Weight loss and potentiodynamic polarization have been employed for the study, and the effect of the gemini surfactants concentrations were investigated. The findings have showed that the inhibition efficiency for all the gemini surfactants increases with increasing their concentrations and the *maximum inhibition efficiency of each inhibitor was achieved at 250 ppm concentration. Furthermore the results of potentiodynamic polarization studies revealed that all the compounds were mixed type inhibitors and inhibit the corrosion of brass by blocking the active sites of the metal. The adsorption of the compounds on brass surface in formic acid has been found to obey the Langmuir adsorption isotherm. The investigation also showed that the hydrocarbon chain length in the surfactant has a positive effect on the inhibition efficiency.*

Keywords: Gemini surfactants, Electrochemical techniques, Potentiodynamic polarization, Impedance technique, Corrosion inhibition mechanism.

Introduction:

Corrosion is the result of chemical reactions that occur between a metal or a metal alloy and its environment [1]. Corrosion impacts our daily life, causing in many cases grave economic consequences or life-threatening situations. Infrastructure items that can be significantly damaged and eventually destroyed by corrosion include pipelines, bridges, automobiles, storage tanks, airplanes and ships. Corrosion represents a major industrial setback, which causes the detriment of materials and considerable economic losses [2-4]. The most common environments for corrosion are in natural waters, atmospheric moisture, rain and man-made solutions [5]. The corrosion phenomenon is particularly important for the industrial processes that involve acidic environment such as formic acid, which is considered a highly corrosive acid [6,7]. Brass alloys which have found widely applications in industries like electrical, marine, fabrication, air conditioning and so on, in many organic and inorganic chemicals do not suffer from corrosion but in formic acid solutions corrosion occur [8].

In order to retard or prevent corrosion from occurring in the process, streamlines corrosion inhibitors are use, which significantly diminish the corrosion rate. A corrosion inhibitor therefore, can be defined as a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of that inhibitor is thus expressed by a measure of this improvement.

The availability of the corrosion inhibition efficiency is wide, and the development of new prototypes with enhanced efficiencies, which satisfy environmental requirements, and understanding of the corrosion/ inhibition mechanism are research goals worldwide. This paper focus on one prototype of inhibitors that is surfactants. The effectiveness of surfactant corrosion inhibitors is due to both the functional group of the molecule and the hydrocarbon chain of the molecule. Many different surfactant molecules have been evaluated for their corrosion inhibition abilities[9-13].

Recently, a new generation of surfactants, Gemini Surfactants, has produced great concerns. This kind of surfactant contains two hydrophilic groups and two hydrophobic groups in the molecule, separated by a rigid or flexible spacer, rather than one hydrophilic group and one hydrophobic group for conventional surfactants, and they are more efficient at reducing surface tension and forming micelles than conventional surfactants. Gemini surfactants show many unique properties as compared with single chain conventional surfactants, such as lower micelles, better wetting properties and more effectiveness in lowering the surface tension of water [14, 15].

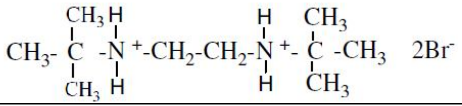
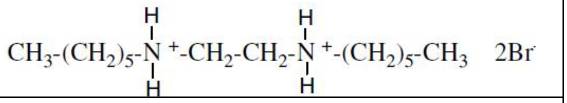
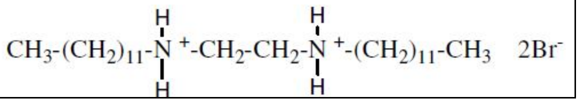
The application of surface–active agents containing nitrogen, sulphur, or both give excellent corrosion inhibition was found to have remarkable inhibition efficiency near their critical micellar concentration values [12,13]. In this study, three Gemini surfactants, N-trimethyl butane-diyl-1,2-ethane bis ammonium bromide (BEAB), N-hexane-diyl-1,2-ethane-bis ammonium bromide (HEAB) and N-dodecane-diyl-1,2-ethane-bis ammonium bromide (DDEAB), were developed as novel corrosion inhibitors for brass in 20% formic acid solution, and their inhibition effectiveness was evaluated by electrochemical studies.

Materials and Experimental Work:

Material characteristics :

Brass having composition of 69 wt % Cu, 29.9 % wt Zn, 0.5 % wt Pb, 0.04 % wt Sn, 0.09 wt% and 0.47 wt% others were used in the experiments. The experiments were carried out in Chemvitz University in Germany. Concentrated formic acid and distilled water were used in preparing test solutions of 20% formic acid for all studies. The gemini surfactants were characterized through their spectral data; their purity was confirmed by thin layer chromatography (TLC). Names and molecular structures of the investigated compounds are given in Table 1.

Table 1: Name, abbreviation and molecular structure of the Gemini surfactants.

Inhibitors name	Inhibitors abbreviation	Molecular structure
N-trimethyl butane-diyl-1,2-ethane bis ammonium bromide	BEAB	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{N}}{}^+-CH_2-CH_2-\overset{H}{\underset{H}{N}}{}^+-\overset{CH_3}{\underset{CH_3}{C}}-CH_3\quad 2Br^-$
N-hexane-diyl-1,2- ethane bis ammonium bromide	HEAB	 $CH_3-(CH_2)_5-\overset{H}{\underset{H}{N}}{}^+-CH_2-CH_2-\overset{H}{\underset{H}{N}}{}^+-(CH_2)_5-CH_3\quad 2Br^-$
N-dodecane-diyl-1,2- ethane bis ammonium bromide	DDEAB	 $CH_3-(CH_2)_{11}-\overset{H}{\underset{H}{N}}{}^+-CH_2-CH_2-\overset{H}{\underset{H}{N}}{}^+-(CH_2)_{11}-CH_3\quad 2Br^-$

Weight loss measurement :

Weight loss study was carried out at 30 °C temperature and 3 hours time duration in 20% formic acid solution. The brass plate of size (2.0 cm × 2.0 cm × 0.25 cm) was used for weight loss measurements. All the concentrations of the inhibitor taken for weight loss, were taken in ppm by weight. The experiments were performed as per ASTM method described [16]. Corrosion rates were calculated and recorded by the software Sequencer/ Version 5 and inhibition efficiencies (IEs) (%) were calculated using equation 1. To find the 250 ppm of the inhibitors weight loss measurements were preformed for different concentrations of the inhibitor at temperature of 30 °C.

Potentiodynamic polarization :

Potentiodynamic polarization studies were carried out at room temperature (25±3°C) using EG and G PARC potentiostat / galvanostat (model 173), universal programmer (model 175) and X-Y recorder (model RE 0089). A platinum foil was used as auxiliary electrode, a saturated calomel electrode was used as reference electrode and brass strip was used as the working electrode. The scan rate of 1 mV/s at O.C.P. The polarization curves were obtained after immersion of the electrode in the solution until a steady state was reached.

Results and Discussion:

Effect of inhibitor concentration on inhibition efficiency :

Figure 1 shows the variation of the weight loss (mg) of brass with the inhibitor concentrations changes from 0 ppm to 250 ppm at 30 °C for all the investigated inhibitors. It is obvious from Figure 1 that, the weight loss decreased, and therefore the corrosion inhibition strengthened, with increase in inhibitor concentrations. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration; thus the surface is efficiently separated from the medium [17].

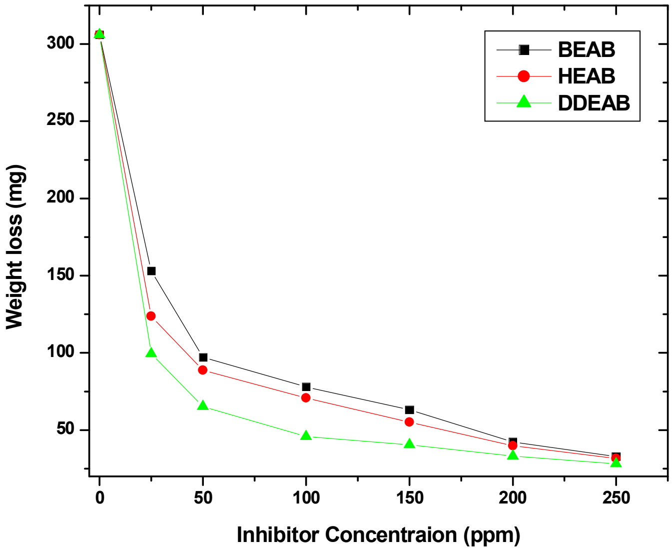


Figure 1: Inhibitors concentration effect on the measured weight loss of the brass in formic acid for 3 hours and 30 °C, where BEAB HEAB and DDEAB are stand for N-trimethyl butane-diyl-1,2-ethane bis ammonium bromide, N-hexane-diyl-1,2-ethane bis ammonium bromide and N-dodecane-diyl-1,2-ethane bis ammonium bromide, respectively.

The ability of a surfactant molecule to adsorb on a metal surface and inhibit corrosion is a function of the behaviour of surfactant molecule, which is dominated by parameters that include surfactant type, hydrocarbon chain length, and ionic strength. This might explain, the variation in the degree of inhabitation for the investigated inhibitors which can be observed from the variation in the curves gradient in Figure 1, where N-dodecane-diyl-1,2- ethane bis ammonium bromide (DDEAB) showed the lowest weight lost. This is illustrated more clearly in Figure 2 using the inhibition efficiency, (IE). The inhibition efficiency of each concentration were calculated using the following equation:

$$Inhibition\ Efficiency\ \% = \frac{(CR_{unhinhibited} - CR_{inhibited})\langle 100\rangle}{CR_{unhinhibited}} \qquad 1$$

where $CR_{uninhibited}$ = corrosion rate of the uninhibited system

$CR_{inhibited}$ = corrosion rate of the inhibited system

The variation of the inhibition efficiencies obtained from the weight loss with different inhibitor concentrations at 30 °C are shown in Figure 2.

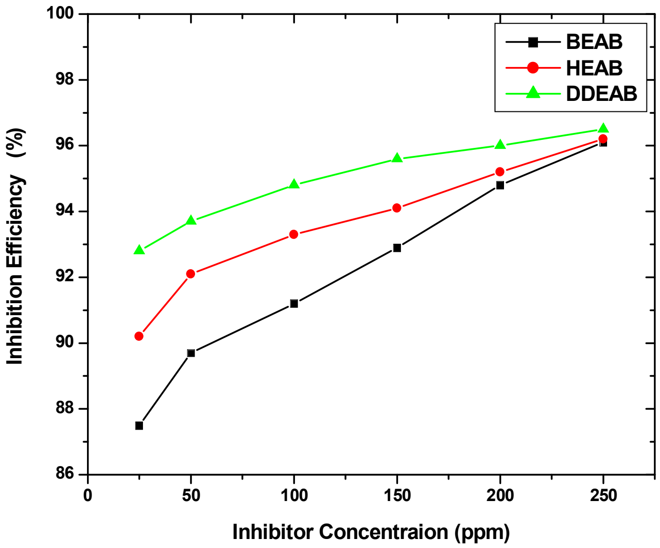


Figure 2: Inhibition efficiencies as a function in inhibitor concentration for three investigated inhibitors for the brass in formic acid for 3 hours and 30 °C.

The results show that inhibition efficiency for all the inhibitors increases as the concentration of inhibitor increases from 0 to 250 ppm. Although the maximum inhibition efficiencies for all the inhibitors were larger than 95% the inhibition efficiency for DDEAB inhibitor was found to be the largest at any concentrations of the inhibitors. This is attributed to the large length of the hydrocarbon chains in the DDEAB (11 methene group) inhibitor comparing with BEAB (only 5 methene group). The maximum inhibition efficiency of each inhibitor was achieved at 250 ppm concentration. The inhibition was estimated to be more than 88% at very low concentrations (25 ppm), and at 250 ppm its protection was more than 95%, which is considered to be 250 ppm. This trend may result from the fact that the adsorption amount and the coverage of surfactant on the brass alloy increase with the inhibitor concentration, thus the brass alloy surface is efficiently separated from the medium as has been shown in literature[18, 19].

Electrochemical polarization measurements :

Figure 3 shows polarization curves for brass alloy in formic acid without and with different Gemini surfactants at 250 ppm and 30 °C.

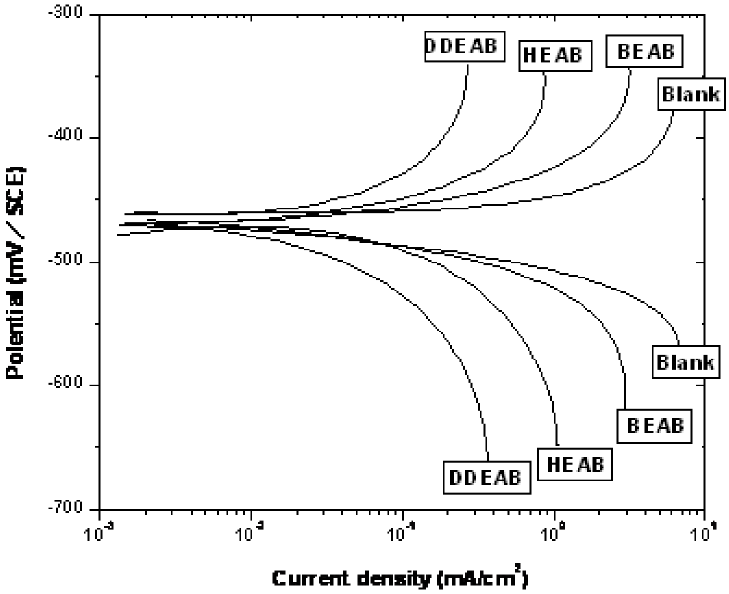


Figure 3. Potentiodynamic polarization curves for brass alloy in formic acid without and with different Gemini surfactants at 250 ppm concentration and 30 °C.

The various electrochemical corrosion parameters obtained from polarization measurements are listed in Table 2. The lower corrosion current density (I_{corr}) values in presence of the inhibitors without causing significant changes in corrosion potential (E_{corr})

indicates that the compound are mixed type inhibitors and are adsorbed on the surface thereby blocking the corrosion reaction [20].

Table 2: Electrochemical polarization parameters for the corrosion of brass alloy in formic acid without and with different Gemini surfactants at 250 ppm and 30 °C.

System	E_{corr} (mV vs. SCE)	I_{corr} (mA.cm^{-2})	IE (%)
Blank	-487	0.24	-
BEAB	-501	0.060	74.6
HEAB	-507	0.035	86.8
DDEAB	-492	0.024	89.0

This way, the surface area available for hydrogen evolution is decreased, while the actual reaction mechanism remains unaffected. Adsorption of inhibitor molecules on the metallic surface often involves the removal of the adsorbed water molecules, replacing them with anion from the acid and with the inhibitor.

Mechanism of corrosion inhibition :

The mechanism of the corrosion inhibition may be explained on the basis of adsorption isotherm behaviour [20]. The surface coverage values (θ) of different inhibitor concentration for three compounds were evaluated using corrosion rate values (CR) that obtained from weight loss method.

The surface coverage value (θ) of each concentration were calculated using the following equation:

$$\theta = \frac{(CR_{unhinhibited} - CR_{inhibited})}{CR_{unhinhibited}} \qquad 2$$

As the results showed the surface coverage (θ) of compounds increased more clearly as the inhibitors concentrations increases from 0 ppm to 250 ppm at 30 °C for all the investigated inhibitors. The θ value for different concentrations of inhibitors were tested graphically by fitting to various isotherms. Figure 4 shows a plot of *log (θ/(1- θ))* versus *log (C)* for different concentration was linear.

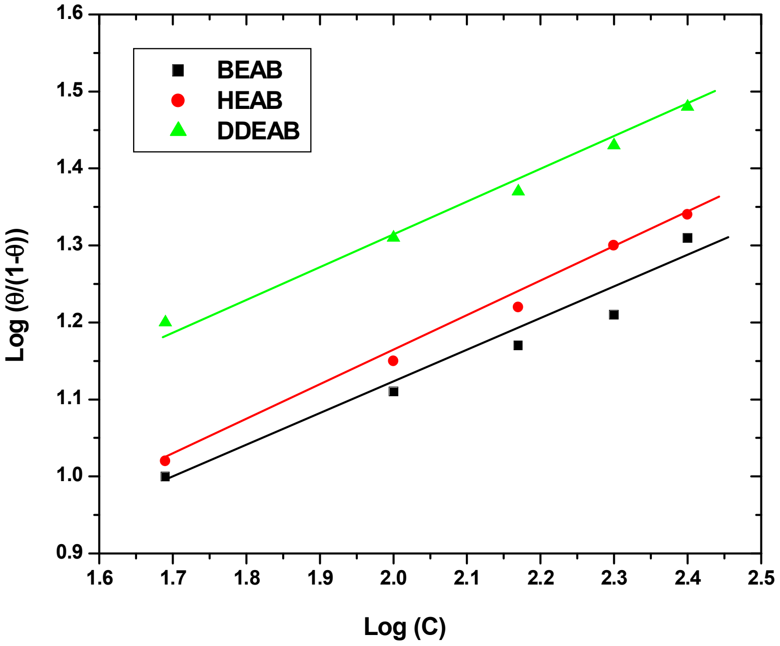


Figure 4: Langmuir adsorption isotherm plots for the adsorption of various inhibitors.

The linear plot suggests that the adsorption of the compounds on the brass surface follows the Langmuir adsorption isotherm. Thus these inhibitors obey the relation:

$$\theta/(1-\theta) = k\, C \exp(\Delta G_{ads}/RT) \qquad 3$$

where ΔG_{ads} is the Gibbs free energy of adsorption and C is the concentration of the inhibitors.

The higher inhibitive property of gemini surfactants is attributed to the presence of quaternary nitrogen atom and the alkyl chain length which covers greater coverage of the metallic surface [21].

The Gibb's free energy of adsorption (ΔG_{ads}) was calculated from the equation:

$$\Delta G_{ads} = - RT \ln(55.5K) \qquad 5$$

where ΔG_{ads} is the free energy of adsorption; T is the absolute temperature; K is the equilibrium constant, which calculated by:

$$K = \theta/(1-\theta)\, C \qquad 6$$

where θ is the degree of surface coverage on the metal surface; C is the inhibitor concentration.

The resulting values of ΔG_{ads} are given in Table 3. The smaller spacer and long alkyl chain, the denser will be the adsorption layer on the brass surface, and thus higher efficiency for inhibition. The low and negative values of Gibb's free energy of adsorption (ΔG_{ads}) indicate spontaneous adsorption and strong interaction of the inhibitor molecule with the brass surface [22, 23].

Table 3: Gibb's free energy of adsorption (ΔG_{ads}) for brass in formic acid in absence and presence of various gemini surfactants at 30 °C.

System	Log (C)	Log [θ/(1- θ)]	ΔG_{ads} (KJ mol^{-1})
BEAB	2.40	1.31	8.3
HEAB	2.40	1.34	8.4
DDEAB	2.40	1.48	8.8

The micellization of surfactant molecules and their size and shape in aqueous media are mainly influenced by the length of the hydrophobic tails and interaction charged head groups [24]. The adsorption becomes larger as the difference in the chain length of the molecules increases. Smaller spacer size [25] means shorter distance between two head groups in unit gemini molecule and thus the charge density of the head groups is enhanced, which is further more favourable for the adsorption of the surfactant.

Suggested modes of adsorption of gemini surfactant :

Figure 5 shows adsorption modes of gemini surfactant that suggested by the authors based on the obtained results.

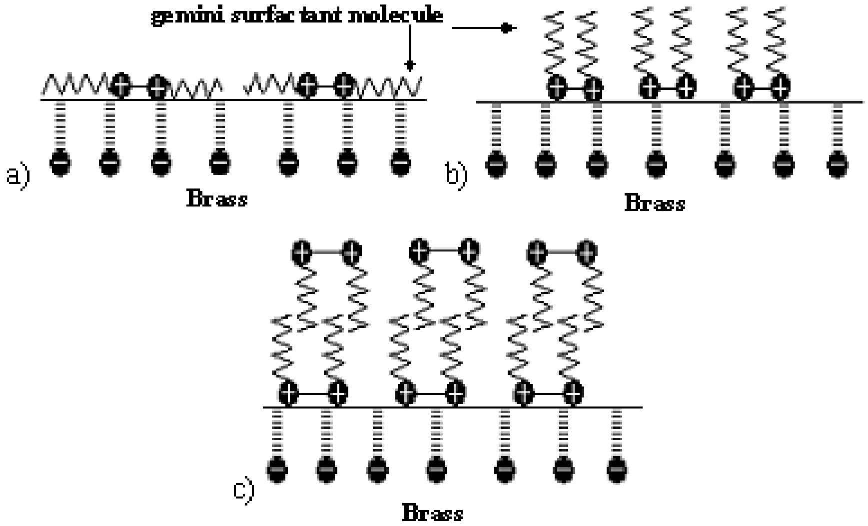


Figure 5. Schematic representation of modes of adsorption of gemini surfactant for various concentration of inhibitor, a) low b) middle c) high gemini surfactant concentrations.

Figure 5 indicates that the first step occurs at very low concentration and corresponds to a binding of individual dimeric surfactants to charged sites. With further increase in the surfactant concentration in the solution, more molecules are adsorbed around initial occupied surfactants by hydrophobic interaction and finally form the surface aggregates.

The inhibition efficiency results show that the adsorption behaviour of gemini surfactant is more complicated than that of conventional surfactant. The adsorption of surfactant may occur in three different modes or stages of adsorption:

Firstly at low concentrations, the normal adsorption takes place, which occurs by horizontal binding of the surfactant molecule (Figure 5(a)). This adsorption is favoured by an electrostatic interaction between the two ammonium groups (N+) and the cathodic sites on the one hand, and on the metallic surface on the other hand. *Secondary* when the inhibitor concentration increases, there would be no space where other molecules can lay in the horizontal direction, while the inhabitation effect still increases this indicates that the direction of a alignment is changed from horizontal to vertical which is called perpendicular adsorption. The perpendicular adsorption takes place as a result of an inter-hydrophobic chain interaction as shown in Figure 5(b). *Thirdly* when further increase of the inhibitor concentration, an efficiency plateau appears, there is one capacitive loop at high frequencies, which could be attribute to the formation of a biomolecular layer on the metal surface as shown in Figure 5(c).

Conclusions:

Corrosion test results revealed a trend of increasing in both weight loss and inhibition efficiencies as the concentration of the inhibitors increases. The inhibitors showed good performance as a corrosion inhibitors in formic acid, however, a largest inhibition efficiencies in the investigated concentration range of concentration was achieved at 250 ppm concentration. All the inhibitors acted as mixed inhibitors as shown from the electrochemical polarization measurements. Furthermore all the three inhibitors, inhibited corrosion by adsorption mechanism, which is found to occur in three different modes of adsorption following Langmuir's adsorption isotherm.

References:

1. Marek, M.I., Thermodynamics of aqueous corrosion. In: Davis, .J.R. (Ed.), ASM Handbook, Corrosion. Vol. 13. ASM International, USA, 1987, pp. 18.
2. Zanneti, R. Chem. Eng. 97(1990) 10.
3. Newman, R. C. Nature 415 (2002) 743.
4. Brown, G. E., Jr. Science 294 (2001) 67.
5. Fontana, M.G., Corrosion Engineering. McGraw-Hill, New York, 1986
6. Zumdahl, Steven S. (2009). Chemical Principles 6th Ed.. Houghton Mifflin Company. p. A22.
7. Dean, John (1992). Lange's Handbook of Chemistry (14 ed.). McGraw-Hill. pp. 2.79–2.80.
8. M. Mihit, M. Belkhaouda, L. Bazzi, R. Salghi, S. El Issami,E. Ait Addi, Portugaliae Electrochimica Acta. 25 (2007) 471-480.
9. A. Tizpar, Z. Ghasemi, Appl. Surf. Sci. 252 (2006) 8630.
10. M.A. Migahed, Mater. Chem. Phys. 93 (2005) 48.

11. M.A. Deyab, Corros. Sci. 49 (2007) 2315.
12. N.A. Negm, A.S. Mohamed, J. Surfact. Deterg. 7 (2004) 23.
13. S.T. Kerra, N.A. Negm, S.M. Ahmed, A.M. Badwai, J. Sci. Indus. Res. 61 (2002) 712.
14. M. El Achouri, M.R. Infante, F. Izquierdo, S. Kertit, H.M. Gouttaya, B. Nciri, Corros. Sci. 43 (2001) 19.
15. R. Zana, Adv. Colloid Interf. Sci. 97 (2002) 203
16. ASTM, Standard Practice for Laboratory Immersion Corrosion Testing of Metals, Annual Book of Standards, G 31-72, 3.02, 1990.
17. Zhao T, Mu G, Corros. Sci. 41 (1997) 1937.
18. T. P. Zhao, G. N. Mu, Corros. Sci. 41 (1999) 1937.
19. M. Lebrini, F. Bentiss, H. Vezin, M. Lagrenee, Corros. Sci. 48 (2006) 1279.
20. M.A. Quraishi, A.S. Mideen, M.A.W. Khan, M. Ajmal, Indian J. Chem. Technol. 1 (1994) 329.
21. L.G. Qiu, A.J. Xie, Y.H. Shen, Mater. Chem. Phys. 87 (2004) 237.
22. Y.A. El-Awady, A.I. Ahmed, J. Ind. Chem. 24A (1985) 601.
23. E.E. Oguzie, V.O. Njoku, C.K. Enenbebeaku, C.O. Akalezi, C. Obi, Corros. Sci. 50 (2008) 3480.
24. D. Asefi, M. Arami, A.A. Sarabi, N.M. Mahmoodi, Corros. Sci. 51 (2009) 1817.
25. W. Huang, J. Zhao, Colloids Surf. A: Physicochem. Eng. Aspects 278 (2006) 246.