CORROSION INHIBITOR PERFORMANCE OF N-HEXADECANE-DIYL-1, 2-ETHANE-BIS-AMMONIUM BROMIDE FOR BRASS ALLOY IN ACIDIC ENVIRONMENT

Omar A. Algeidi and Abduelmaged B. Abduallah

Department for Chemical Engineering, College of Engineering in Sabratha,
University of a Zawia, Libya
E-mail:- algeidi@yahoo.com E-mail:- abd_mbrk@yahoo.com.

الملخص

تم في هذه الورقة البحثية دراسة إمكانية استخدام سيرفيكتانت تؤمي، تحديدا الهكساديكان ديل 1, 2 ايتان بس آمونيام بروما يد (HDEAB)، كمثبط لتآكل سبيكة معدنية من النحاس الأصفر (Brass alloy) في وسط من حمض النيتريك ($3N\ HNO_3$) بعياريه مساوية لـ (3N). تم انجاز هذه الدراسة باستخدام طريقة قياس الفقد في الوزن واستخدام جهازي الجهد الديناميكي المستقطب وجهاز الاعاقه الالكتروكيميائية الضوئي. تم حساب قيم طاقتي التنشيط والطاقة الحرة للامتزاز للمركب المدروس (HDEAB) من أجل إلقاء بعض الضوء على الآلية التي يتم من خلالها تثبيط التآكل. ومن خلال النتائج وجد أن المركب المستخدم يعتبر من المثبطات المختلطة وأن الآلية تتم بإغلاق المواقع النشطة في السبيكة المعدنية بعد امتزاز المثبط على سطحها. كما اتضح من النتائج أن عملية الامتزاز في الوسط الحمضي تتبع علاقة لنقمار للامتزاز الايزوتيرم وان كفاءة التثبيط متغيرة مع تغير تركيز مثبط التآكل (HDEAB) وأن التركيز الحرج أو المثالي هو المفتاح الأساسي لفاعلية تثبيط التآكل في هذه السبيكة.

ABSTRACT

Gemini-surfactant namely N-Hexadecane-Diyl-1, 2-Ethane-Bis-Ammonium Bromide (HDEAB) was investigated in the laboratory for its performance as a corrosion inhibitor for Brass alloy in nitric acid environment ($3N\ HNO_3$). The investigation was achieved using weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The values of activation energy and free energy of adsorption of the HDEAB compound were calculated to investigate the mechanism of corrosion inhibition. The results of potentiodynamic polarization studies revealed that the HDEAB compound was mixed type inhibitors and inhibit the corrosion of Brass by blocking the active sites of the metal. The adsorption of the HDEAB compound on Brass surface in the acid solution was found to obey the Langmuir adsorption isotherm. The inhibition efficiency of the HDEAB compound was found to vary with the HDEAB inhibitor concentration and the critical micelle concentration is found to be the key factor in determining the effectiveness of a corrosion inhibitor.

KEYWORDS: Gemini Surfactants; Electrochemical Techniques; Potentiodynamic Polarization; Impedance Technique; Corrosion inhibition mechanism

INTRODUCTION

Brass alloy is a common constructional material for many industrial units mainly because of its excellent properties. However, it suffers severe attack in service particularly in process in which nitric acid environment (HNO_3) is needed. In order to reduce the corrosion of metals, several techniques have been applied. The use of inhibitors was one of the most practical methods for protection against corrosion in acidic media. Most well-known acid inhibitors were organic compounds, such as those containing phosphorus, nitrogen, sulphur, an aromatic ring and oxygen atoms. 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 transportation of water and corrosive active species to the surface [1-2].

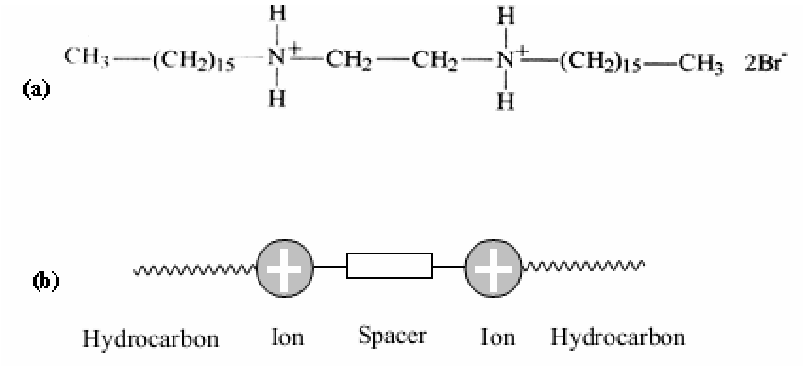
Inhibitors which reduce corrosion on metallic materials can be divided into four kinds: (i) inorganic inhibitors, (ii) organic inhibitors, (iii) surfactant inhibitors, and (iv) mixed material inhibitors. Surfactants are well known for their capabilities as corrosion inhibitors [3]. The effectiveness 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 [4-5].

Recently, a new generation of surfactants, Gemini Surfactants, has provoked 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 [6-7]. These surfactants show superior performance as compared to conventional surfactants particularly near their critical micellar concentration values. Although the majority of work done in this area was conducted using stainless steel material [5,8] these inhibitors have been shown to work very well in acidic media, and thus a study the corrosion inhibiting behaviour of a Gemini-surfactant on Brass alloy in acidic media is really necessity.

In this study N-Hexadecane-Diyl-1,2-Ethane-Bis-Ammonium Bromide (HDEAB) Gemini-surfactants was used to inhibit the corrosion of Brass in nitric acid environment (3N HNO_3). The HDEAB was evaluated as corrosion inhibitor for Brass in nitric acid environment by three different techniques; these are: weight loss technique, polarization measurements and impedance measurements. Various inhibitor concentrations were used to investigate the concentration effect and find the optimum concentration of the inhibitor. The obtained results were also compared using a piece of unprotected Brass alloy as reference.

MATERIALS AND EXERIMENTAL METHODS

Brass having composition [(wt %): 69 % Cu, 29.9 % Zn, 0.5 % Pb, 0.04 % Sn, 0.09 % others] were used for the experiments. AR grade of nitric acid and doubled distilled water were used for preparing test solutions of 20% nitric acid for all studies. This concentration is widely used in industry. The chemical and molecular structure of the investigated surfactant (N-Hexadecane-Diyl-1,2-Ethane-Bis-Ammonium Bromide (HDEAB)) is shown in Figure (1-a). The two methene groups (CH_2-CH_2) in between the nitrogen ions (N^+) are consider to be the spacer as it is shown in Figure (1-b).



$CH_3—(CH_2)_{15}—\overset{H}{\underset{H}{N^+}}—CH_2—CH_2—\overset{H}{\underset{H}{N^+}}—(CH_2)_{15}—CH_3\ 2Br^-$

Figure 1: N-Hexadecane-Diyl-1, 2-Ethane-Bis-Ammonium Bromide (HDEAB)
(a) Molecular structure of the HDEAB inhibitor
(b) Schematic representation for HDEAB inhibitor [8].

Weight loss technique

Weight loss study was carried out at 30 °C temperature and 3 hours time duration in 3N nitric acid solution. The Brass plate of size (2.0 cm X 2.5 cm X 0.25 cm) was used. All the concentrations of the inhibitor, were taken in ppm by weight. The experiments were performed as per ASTM method described [9]. Corrosion rates were calculated and recorded by the software Sequencer/ Version 5. To find the optimum concentration of the inhibitors the weight loss measurements were preformed for different concentrations of the inhibitor at temperature of 30 °C, namely 25, 50, 100, 150, 200, 250, 300 ppm. In order to find the optimum concentration of the inhibitors the weight loss measurements were preformed for different concentrations of the inhibitor. The effect of temperature on the performance of the inhibitor at the optimum concentration was investigated by performing the weight loss measurements at three different temperatures namely at 30, 40 and 50 °C. A blank sample (0 ppm inhibitor concentration sample) was used as a reference.

Tafel polarization technique

Potentiodynamic experiment was carried out using EG and G PARC potentiostat / galvanostat (model 173), universal programmer (model 175) and X-Y recorder (model RE 0089). A platinum electrode was used as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The working electrode (WE) was in the form of a rod from Brass slide. All the potentiodynamic polarization studies were carried out at room temperature (25±3°C) with scan rate of 1 mV/s at open cell potential (OCP) and equilibrium time leading to steady state is in range of 30 to 40 min. The polarization curves were obtained after immersion of the electrode in the solution until a steady state was reached. Only three inhibitor concentrations (0, 50 and 250 ppm) were tested.

Impedance technique

The impedance measurements were performed for Brass in 3N HNO_3 at room temperature in absence and presence of 50 and 250 ppm of HDEAB at E_{corr} with the A.C. voltage amplitude 5 mV in the frequency range 5 Hz to 100 Hz. The measurements were done with 10 points per decade at OCP after a stabilization period of 5 to 10 min. The potential values reported here were versus SCE. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. All the measurements were carried out with an EG&G PAR (model 5301A) lock-in-amplifier, using an IBM computer.

RESULTS AND DISCUSSION

Weight loss technique

Detailed experimental results of the Weight loss measurements at different inhibitor concentrations at 30 °C were collected in Table (1) and graphically represented in Figure (2). Table (1) shows the variation of the weight loss as the inhibitor concentration changes. The largest weight loss is shown when the concentration of the HDEAB inhibit is zero while the lowest weight loss is shown when the concentration of the HDEAB inhibit is 250 ppm. This is clear indication that the HDEAB inhibits the corrosion process of Brass in 3N HNO_3 corrosive medium.

It is obvious from Table (1) that, the weight loss decreased, and therefore the corrosion inhibition strengthened, with increase in inhibitor concentration. 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 [6].

Table 1: Dependence of the weight loss, surface coverage, inhibition efficiency and the corrosion rate of Brass, on the inhibitor concentrations.

Inhibitor concentrations (ppm)	Weight loss (mg)	Surface coverage *(θ)*	Inhibition efficiency (%)	Corrosion rate (mm/year)	Log (C)	Log [θ/(1- θ)]
0	386	-	-	678.7	-	-
25	32.5	0.960	96.0	11.1	1.39	1.38
50	28.3	0.965	96.5	9.7	1.69	1.44
100	23.5	0.970	97.0	8.0	2.00	1.52
150	21.0	0.975	97.5	7.2	2.17	1.59
200	15.3	0.980	98.0	5.3	2.30	1.69
250	13.0	0.985	98.5	4.4	2.40	1.80
300	13.4	0.984	98.4	4.5	2.47	1.79

Figure (2) shows the variation of inhibition efficiency (IE) and the corrosion rate (CR) with inhibitor concentrations (25-300 ppm) of HDEAB. The inhibition efficiency was obtained from weight loss measurements at different inhibitor concentrations at 30°C. The percentage inhibition efficiency, (IE), of the surfactant is calculated by applying the following equation [10]:

$$IE = \left[\frac{W_o - W}{W_o} \right] X100 \quad (1)$$

Below 250 ppm HDEAB inhibitor concentration the data shows that the corrosion rate decreases by increasing the concentration of HDEAB indicating that this compound acts as efficient corrosion inhibitor in 30°C. The inhibition efficiency increases with increasing HDEAB concentration, and the highest inhibition efficiencies are observed when the HDEAB concentration reaches 250 ppm. Higher than 250 ppm concentration shows inflection points at which inhibition efficiency decreases and corrosion rate increases. From these inflection points, the maximum, and hence the best concentration value, is at low dosages, where the minimum concentration is considered as the critical micellar concentration (CMC) for HDEAB inhibitor. As the concentration of surfactant molecules approaches the CMC, micelles form in solution, and similar aggregate structures such as bilayers and multilayers form on the surface [7].

Consequently, in this case, the CMC marks an effective boundary condition below which surfactant adsorption is typically below the monolayer level, and above which adsorption can consist of multiple layers of adsorbed surfactant molecules. Above the CMC, increasing surfactant concentration leads to the gradual formation of multilayers that further reduce the rate of corrosion.

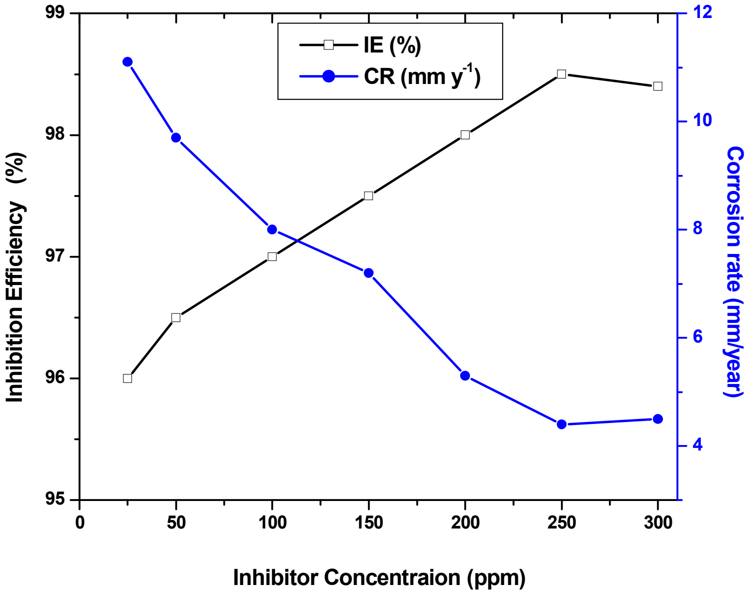


Figure 2: Variation of the inhibition efficiency (IE) and the corrosion rate (CR) of Brass with the concentration of the inhibitor.

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

$$\theta = \left[\frac{W_0 - W}{W_0}\right]. \qquad (2)$$

where W_0 and W are the weight losses per unit area in the absence and presence of the inhibitor, respectively.

The results showed the surface coverage (θ) of compound increased more clearly as the inhibitor concentration increases. The θ value for different concentrations of inhibitors was tested graphically by fitting to various isotherms. Figure (3) shows a plot of *log (θ/(1- θ))* versus *log (C)* for different concentration was linear.

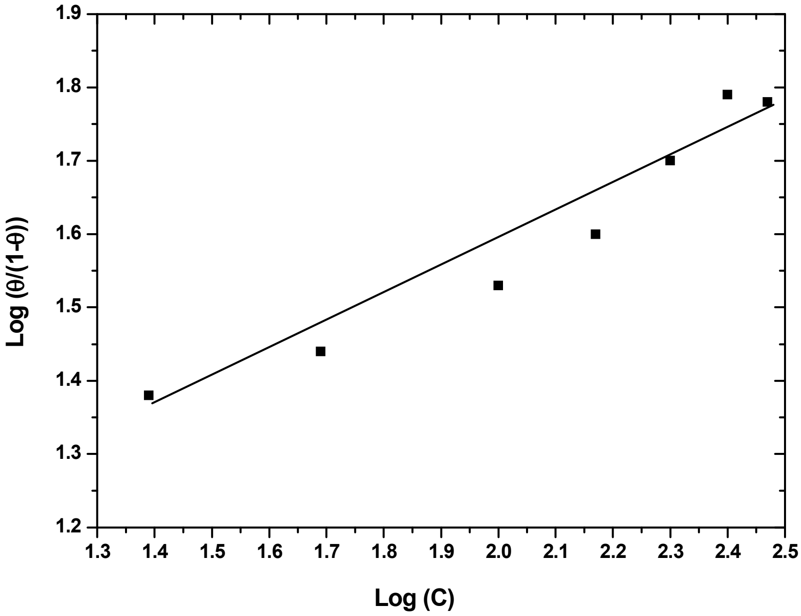


Figure 3: Langmuir adsorption isotherm plots for the adsorption of various concentrations of HDEAB inhibitor.

The linear plot suggests that the adsorption of the inhibitor on the Brass surface follows the Langmuir adsorption isotherm. Thus HDEAB inhibitor obeys the relation

$$\left[\frac{\theta}{1-\theta}\right] = k\cdot C\cdot \ell^{\frac{\Delta G_{ads}}{RT}} \qquad (3)$$

Where ΔG_{ads} is the free energy of adsorption, k is the equilibrium constant for the adsorption process, R is the ideal gas law constant; T is the absolute temperature and C is the concentration of the inhibitor.

The higher inhibitive property of HDEAB inhibitor is attributed to the presence of quaternary nitrogen atom and the alkyl chain length which takes greater coverage of the metallic surface [11]. The variation of the weight loss (mg) of Brass with different corrosion temperature (30, 40, and 50°C) in HNO_3 at the optimum inhibitor concentration are shown in Table (2)

Table 2: Dependence of the weight loss, surface coverage, inhibition efficiency, the corrosion rate of Brass and Adsorption Gibb's free energy on the temperature

Temperature (°C)	Weight loss (mg)	Surface coverage	Inhibition efficiency (%)	Corrosion rate (mm/year)	ΔG_{ads} (kJ/mol)
30	13.0	0.985	98.5	4.4	- 9.3
40	14.1	0.981	98.1	4.8	-9.2
50	18.1	0.976	97.6	6.1	-9.0

The results show that inhibition efficiency decreases with an increase in corrosion temperature, indicating that the high temperature result in desorption of the inhibitor molecules from the Brass surface. The values of activation energy (Ea) were calculated using the Arrhenius equation [12-13].

$$\ln\left(\frac{CR_2}{CR_1}\right) = -\frac{E_a \cdot \Delta T}{R \cdot T_1 \cdot T_2} \tag{4}$$

Where CR_1 and CR_2 are the corrosion rates at T_1 and T_2, respectively; Ea is the activation energy; and $\Delta T = T_2 - T_1$; R is the gas constant.

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

$$\Delta G_{ads} = -R \cdot T \cdot \ln(55.5 \bullet K) \tag{5}$$

Where ΔG_{ads} is the free energy of adsorption; R is the gas law constant; T is the absolute temperature; and K is the equilibrium constant, which calculated by:

$$K = \frac{\theta}{1-\theta} \cdot C \tag{6}$$

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

The results showed that E_a value at room temperature for inhibited system (11.8 kJ mol^{-1}) is higher than E_a value of uninhibited system (10.1 kJ mol^{-1}), which indicates that HDEAB inhibitor is very effective at room temperature. This result agrees with the reported results by Quraishi when he used HDEAB as inhibitor for mild steel in hydrochloric acid and sulphuric acid [14]. The smaller spacer and long alkyl chain, the denser will be the adsorption layer on the Brass surface, and thus higher efficiency for inhibition. On the other hand the adsorption Gibb's free energy in Table (2) showed a negative value indicating spontaneous adsorption and strong interaction of the inhibitor molecule with the Brass surface, this is in a good agreement with literature [15-16].

Tafel polarization measurements

Figure (4) shows the polarization behaviour for Brass in varying concentrations (0, 50, 250 ppm) of HDEAB inhibitor, at 25±3 °C temperatures. Both anodic and cathodic polarization curves are captured for each case. As a result of unclear linear portion of the Tafel curve the exact values of the corrosion current (I_{corr}) cannot be obtained, however, the curves clearly show that the presence of inhibitor causes a markedly decrease in the corrosion rate, i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the corroded surface. It is also clear that the presence of inhibitor causes a markedly decrease in the corrosion current and thus the inhabitation efficiency increases as it has been shown in weight loss results.

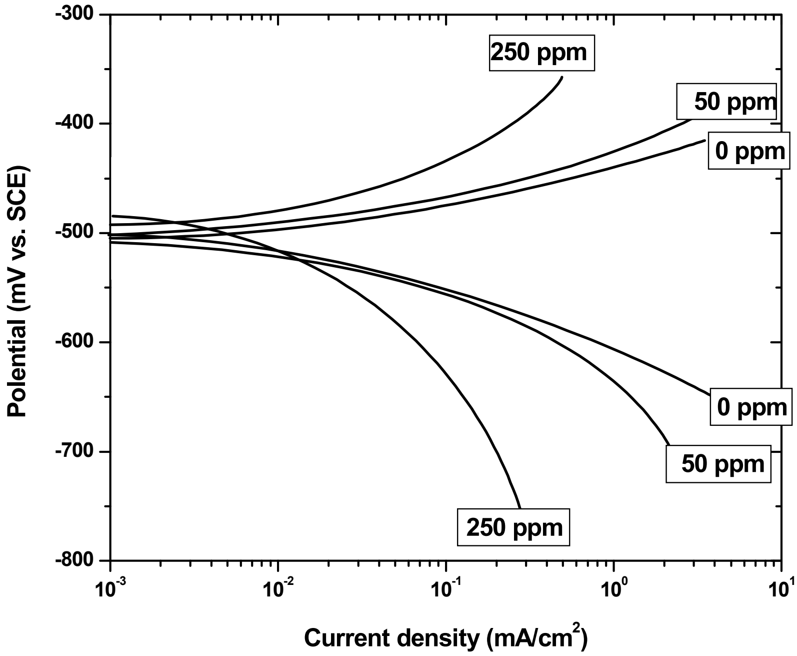


Figure 4: Tafel polarization curve for Brass in 3N HNO_3 at 25±3°C in absences and presence of various HDEAB concentrations (0, 50, 250 ppm).

The lower corrosion current density in presence of the inhibitors without causing significant changes in corrosion potential suggest that the compound are mixed type inhibitors and are adsorbed on the surface thereby blocking the corrosion reaction [17]. This way, the surface area available for hydrogen evolution is decreased, while the actual reaction mechanism may remain unaffected.

Impedance measurements

The equivalent circuit model employed for this system is shown in Figure (5), where the solution resistance (R_S) charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are shown.

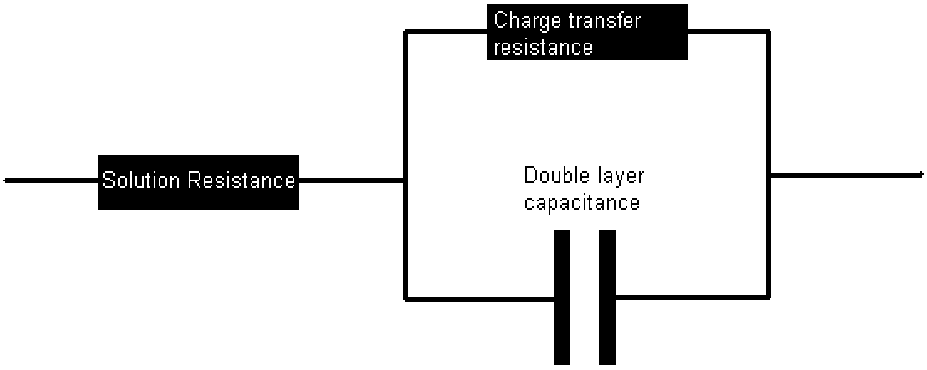


Figure 5: The equivalent circuit model used in impedance measurements.

The impedance diagrams obtained from frequency range 5 Hz to 100 kHz at E_{corr} for Brass alloy in 3N HNO_3 are shown in Figure 6 (a) and (b). Although the impedance diagrams are not perfectly semicircles, the charge transfer resistance value and the double layer capacitance value were obtained from the diameter of the semicircles of the Nyquist plots Figure (6 a). The obtained results are tabulated in Table (3).

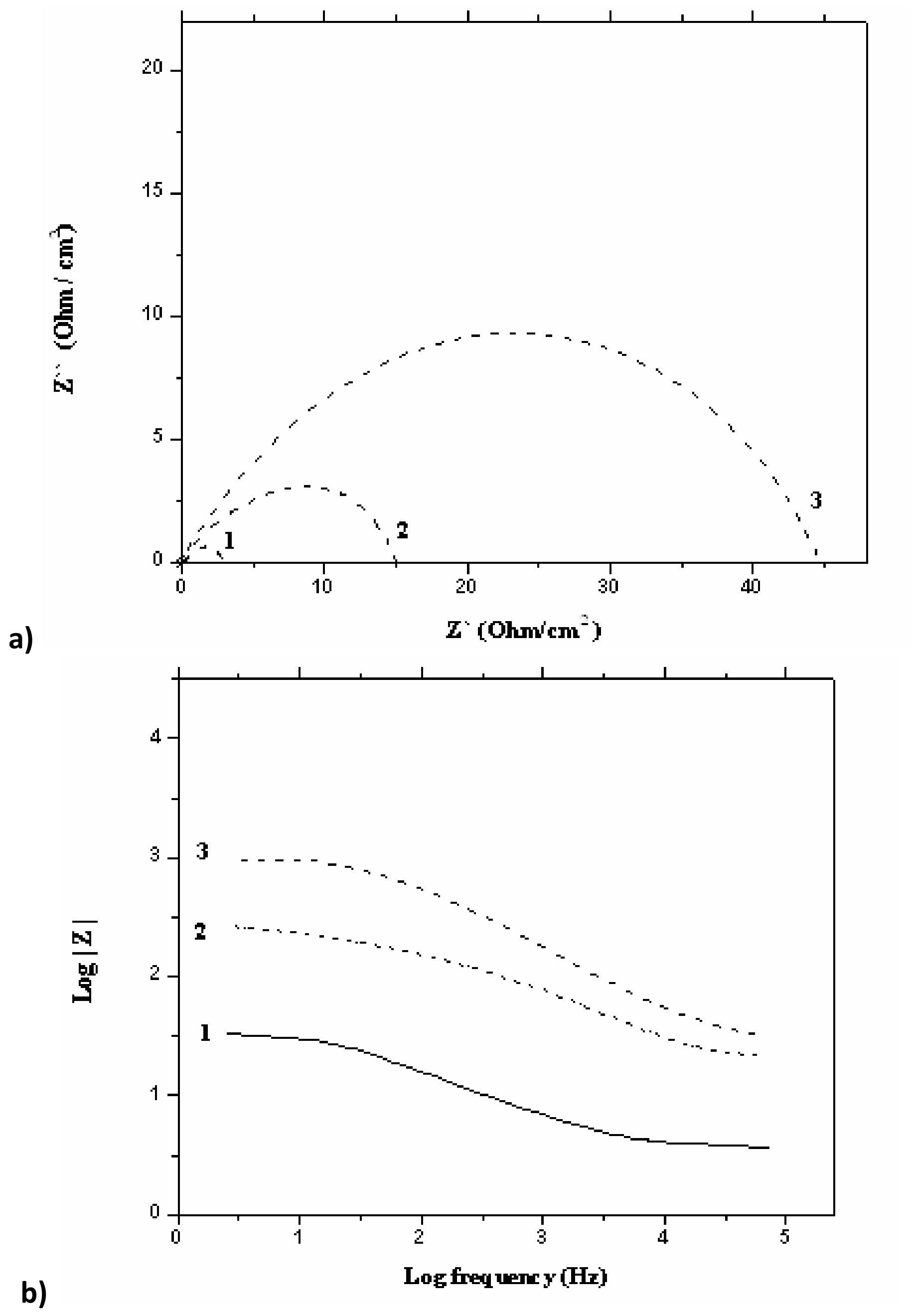


Figure 6: (a) Nyquist plot and (b) Bode plot for Brass in the equivalent circuit model used in impedance measurements (the numbers 1, 2 and 3 are stand for inhibitor concentrations 0, 50 and 250 ppm, respectively).

The imperfection in the circulation has been attributed to frequency dispersion [18]. The charge transfer resistance values that obtained from Nyquist plots (Figure 6a) were used to calculate the inhibition efficiency *(IE)* using the following equation:

$$\mathrm{IE} = \left[\frac{\frac{1}{R_{to}} - \frac{1}{R_{ti}}}{\frac{1}{R_{to}}} \right] \mathrm{x100.} \qquad (7)$$

where R_{to} and R_{ti} are the charge transfer resistance without and with inhibitor, respectively.

The value of the R_t when the inhibitor concentration is 0 ppm is 1.75 Ohm.cm^{-2}, while in 50 and 250 ppm R_t become 14.59 and 44.8 Ohm.cm^{-2}, respectively. The values of R_t is clearly increased as the concentration of the HDEAB inhibitor increased. This is in turn leads to an increase in the inhibition efficiency as shown in Table (3).

On the other hand the values of C_{dl} (shown in Table 3) decrease dramatically in the presence of inhibitors, and as the HDEAB inhibitor increase the C_{dl} value becomes smaller. The decrease in the C_{dl} value in presence of the HDEAB inhibitor, suggests that the inhibition can be attributed to surface adsorption of the inhibitor [19].

Table 3: Electrochemical impedance parameters for the corrosion of Brass alloy in nitric acid with HDEAB surfactant at various concentration and 30 °C

Inhibitor concentration	Solution resistance (Ohm.cm^2)	C_{dl} (μf.cm^{-2})	IE (%)
0	15.56	1513.6	-
50	44.25	316.2	64.2
250	93.10	158.5	82.9

Suggested mechanism of corrosion inhibition

The mechanism of the corrosion inhibition may be explained on the basis of adsorption isotherm behaviour [20]. The molecular weight of HDEAB is large thus HDEAB can easily be adsorbed on the Brass surface by Van der Waals force. In addition, the main hydrophilic part HDEAB ($^+NH_2$) may attack the Brass surface while the main hydrophobic part ($-C_{16}H_{33}$) may extend to the solution face. Furthermore HDEAB may chemically adsorbed at Brass-solution interface via chemical bond between positively charged nitrogen atoms and negatively charged Brass surface so, bromide ion acts as an adsorption mediator of an adsorption composite film in which bromide ion are sandwiched between metal and positively charged part of the inhibitor. This film acts as a barrier facing corrosion process.

According to the adsorption Gibb's free energy results the corrosion inhibition depends on the adsorption ability of the surfactant molecules on the corroding surface, which is directly related to the capacity of the surfactant to aggregate and form clusters (micelles). The critical micelle concentration, CMC, is a key factor in determining the effectiveness of a corrosion inhibitor. Below CMC as the surfactant concentration increases, the molecules tend to aggregate at the interface, and this interfacial aggregation reduces the surface tension. Above CMC the metal surface is covered with a monolayer of surfactant molecules and the additional molecules combine to form micelles or multiple layers. This, consequently, does not alter the surface tension and the corrosion rate [21].

CONCLUSIONS

The following conclusions can be drawn from this study:

- The investigated Gemini-surfactant (HDEAB) acts as an effective corrosion inhibitor for Brass alloy in 3N HNO_3 solution. The results also showed that HDEAB surfactant acts as an inhibitor of mixed type.
- The inhibition efficiency increased as the concentration of the inhibitor increased, and the inhibition efficiency reached to the maximum value (98.50 %) at 250 ppm of the inhibitor.
- The adsorption of HDEAB inhibitor on Brass alloy surface obeyed Langmuir adsorption isotherm, and is chemically adsorbed on the metal surface. The thermodynamic parameters of adsorption process was studied using Langmuir equation it was found that ΔG_0 value is negative indicating that the adsorption process is spontaneous process.
- The activation energy (Ea) decreases as HDEAB inhibitor concentration increases. This can be explained as due to the enhancement of the inhibitor adsorption onto Brass alloy surface at higher concentrations, which indicates that the critical micelle concentration is a key factor in determining the effectiveness of a corrosion inhibitor.

REFERENCES

[1] M.M. Osman, A.M.A. Omar, A.M. Al-Sabagh, Mater. Chem. Phys. 50 (1997) 271–274.

[2] M.M. Osman, R.A. El-Ghazawy, A.M. Al-Sabagh, Mater. Chem. Phys. 80 (2003) 55–62.

[3] N.A. Negm, A.M. Al Sabagh, M.A. Migahed, H.M. Abdel Bary, H.M. El Din, Corros. Sci. 52 (2010) 2122–2132.

[4] M.A. Migahed, H.M. Mohamed, A.M. Al-Sabagh, Mater. Chem. Phys. 80 (2003) 169–175.

[5] M.A. Migahed, M. Abd-El-Raouf, A.M. Al-Sabagh, H.M. Abd-El-Bary, J. Appl. Electrochem. 36 (4) (2006) 395–402.

[6] T. Zhao, G. Mu, Corros. Sci. 41(1997) 1937-1938.

[7] M. J. Rosen, in 'Surfactants and Interfacial Phenomena', (Wiley, New York, 1978), pp. 1–301.

[8] F. A. Ansari, M. A. Quraishi, Portugaliae Electrochimica Acta, 28(5) (2010) 321-335.

[9] ASTM, Standard Practice for Laboratory Immersion Corrosion Testing of Metals, Annual Book of Standards, G 31-72, 3.02, 1990.

[10] A. Singh, V. K. Singh, Quraishi M.A, Rasayan J. Chem. 3 (4) (2010) 811-824.

[11] L.G. Qiu, A.J. Xie, Y.H. Shen, Mater. Chem. Phys. 87 (2004) 237.

[12] R.T. Vashi, V.A. Champaneri, Ind. J. Chem. Tech. 4 (1997) 180.

[13] I.N. Putilova, S.A. Blazin, U.P. Baranik, Metal Corrosion Inhibitors, Pergamon Press, New York, NY, 1960, pp. 31.

[14] M.A. Quraishi, F.A. Ansari, J. Appl. Electrochem. 36 (2006) 309.

[15] Y.A. El-Awady, A.I. Ahmed, J. Ind. Chem. 24A (1985) 601.

[16] E.E. Oguzie, V.O. Njoku, C.K. Enenbebeaku, C.O. Akalezi, C. Obi, Corros. Sci. 50 (2008) 3480.

[17] M.A. Quraishi, A.S. Mideen, M.A.W. Khan, M. Ajmal, Indian J. Chem. Technol. 1 (1994) 329.

[18] S. Muralidhran, K. L. N. Plani, S. Ravichandran, and S. V. K. Iyer, Electrochem. Soc. USA, 142 (1995)1478..

[19] M.A. Quraishi, J. Rawat, M. Ajmal, Corrosion, 54 (12) (1998) 996.

[20] M.A. Quraishi, A.S. Mideen, M.A.W. Khan, M. Ajmal, Indian J. Chem. Technol. 1 (1994) 329.

[21] M. A. Migahed, M. Abd-El-Raouf A. M. Al-Sabagh, H. M. Abd-El-Bary, Electrochimica Acta. 50 (2005) 4683–4689.