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Palm Oil-Based Imidazolines as Corrosion Inhibitor for Copper in 1.0 M H_2SO_4

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ABSTRACT

The inhibition effect of a palm-oil modified hydroxyethyl imidazoline on the corrosion of copper in 1.0 M sulphuric acid (H_2SO_4) has been studied by using potentiodynamic polarization curves, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements. Modified imidazoline resulted a good corrosion inhibitor for Cu in acid environment, with its inhibition efficiency increasing with its concentration, reaching its highest value when 10 ppm are added, but it decreased with a further increase in its concentration. Additionally, inhibitor efficiency increased with an increase in the immersion time. Polarization curves showed that modified imidazoline suppresses in a greater extent the cathodic oxygen reduction reaction than the anodic dissolution, acting, therefore, as a mixed type of inhibitor. EIS data indicated the decrease in the double layer capacitance and an increase in the charge transfer resistance due to the adsorption of the modified imidazoline on to the copper surface, with the formation of protective corrosion products.

1. Introduction

Copper and its alloys are widely used in industrial and atmospheric applications, electric wires, electronic building construction, etc., due to their excellent properties like thermal and electric conductivity, low cost and abundancy [1-5]. However, it is not immune to corrosion attack. Acid solutions are used in industry in order to remove corrosion products from materials surface. Sulfuric, nitric and hydrochloric acids are widely used for this purpose. Organic inhibitors are one of the most used methods in order to prevent and control corrosion. The main action of these inhibitors is a specific interaction between some functional groups and metal surface through heteroatoms such as nitrogen, oxygen and sulfur, which play a crucial role due to their free and alone electron pairs [5-8]. For instance, Tavakoli et al. [9] inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole (2-MBO) on corrosion of copper in sulphuric acid solution have been studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. They found that for 2-MBO, corrosion efficiency increased with increasing its concentration, but for SDBS, inhibition efficiency increased with its concentration up to a certain value, but it decreased with a further increase in its concentration. This was explained due to the formation of hemi-micellar aggregates that provoke inhibitor desorption from the metal/solution interface at higher concentrations. In a similar study [10] they evaluated the inhibition effect of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzimidazole (2-MBI) on corrosion of copper in sulphuric acid finding similar results for 2-SMBI than those for 2-SMBO. The inhibiting action of 5-mercapto-1-phenyl-tetrazole (5-MPhTT) in 0.001 M H_2SO_4 solution was investigated [11]. The results reveal that the anodic current density and mass loss are two times twice less lower in the presence of 5-MPhTT.The influence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) on the corrosion inhibition of Cu in 0.1M HNO_3 was also studied [12]. The action effect of PMT is compared with the influence action of other organic compounds of this type of the same family. They behave as mixed type inhibitors. The mechanism of action was chemisorption on the copper surface that follows Langmuir isotherm. On another hand, organic inhibitors such as the benzotriazole (BTA) and derivatives had demonstrated being excellent corrosion inhibitors; however their disadvantage is that they are toxic [13]. As they are most used in industrial processes they should be replaced with new ecological inhibitors in order to agree with environmental protection requirements [14, 15]. Some plants had been studied as corrosion inhibitors such as *Salvia officinalis* [16], *Musa paradisica* [17], *Capsicum annuum* [18], *Adhotada vasica* [19], among others. It was found that all the plant extracts act as good corrosion inhibitor for metal corrosion in acidic media. The corrosion inhibition of these plants extracts have been attributed to the presence of active principles present in them. These active principles form protective films on metal surfaces by coordinating with metal ions through O, N or S heteroatoms of the functional groups present in the active principles [20]. To reduce the CO_2 corrosion of carbon steel, imidazolines, which is a nitrogen-based organic inhibitor and with a chemical structure as given in Fig. 1, have been used successfully [21-22]. Yoo et al. [21] evaluated 2 imidazolines, one based on bio-diesel, and a second one based on oil, namely 2-(2-alkyl-4,5-dihydro-1H-imidazol-1-yl)ethanol, as corrosion inhibitors for mild steel in 1.0 M hydrochloric acid. It was found that for concentrations higher than 100 ppm of the bio-diesel-based imidazoline had a higher efficiency than the oil-based imidazoline. Thus, the goal of this manuscript is to evaluate the use of a palm oil-modified imidazoline as corrosion inhibitor for Cu in sulfuric acid solution.

2. Experimental Methods

2.1 Testing Material

Material used in this work consisted of commercial Cu bar, measuring 5.0 mm in diameter, embed in commercial polymeric resin, polished down to 600 grade emery paper, washed with distilled water and degreased with acetone.

2.2 Testing Solution

Molecular structure of used palm-oil modified hydroxyethyl imidazoline as inhibitor, Fig. 1, is composed of a five member ring containing nitrogen elements, where R is a C-14 saturated hydrophobic head group and OH a pendant hydrophilic group attached to one of the nitrogen atoms. Procedure to modify this imidazoline with the oil-palm has been described elsewhere [23]. Inhibitor was dissolved in pure 2-

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propanol. The concentrations of the inhibitor used in this work were 5, 10, 25, 50 and 100 ppm at room temperature, around 25 °C. Testing solution consisted of 1.0 M sulfuric acid (H_2SO_4) prepared with analytical grade reagents.

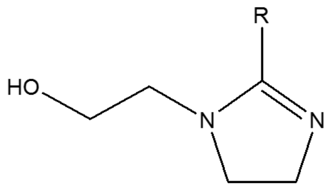

Fig. 1 General structure of a hydroxyethyl imidazoline, where R is an alkyl chain derivative

2.3 Electrochemical Techniques

Used electrochemical techniques in this research work were potentio dynamic polarization curves, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements. Polarization curves were recorded at a constant sweep rate of 1 mV/s and the scanning range was from -300 to +1500 mV respect to the open circuit potential, E_{corr}. Before starting the curves, the E_{corr} value was left to reach a steady state value, around 30 minutes, and then the specimen was polarized, starting the scanning in the cathodic branch. Corrosion current density values, I_{corr}, were calculated by using Tafel extrapolation. Measurements were obtained by using a conventional three electrodes glass cell with a graphite rod and a platinum wire as auxiliary and reference electrodes respectively. LPR measurements were carried out by polarizing the specimen from +10 to -10 mV respect to E_{corr}, at a scanning rate of 1 mV/s evry hour during 24 hours. Polarization resistance values, R_p, were calculated from here. Impedance measurements were carried out using AC signals of amplitude 10 mV peak to peak at the open-circuit potential in the frequency range 100 kHz to 1.0 mHz. LPR and EIS experiments were carried out using Interface 1000 Gamry Potentiostat/Galvanostat/ZRA analyzer. After the end of the LPR tests, these were observed in a Scanning Electronic Microscope (SEM).

3. Results and Discussion

3.1 Polarization Curves

The effect of the palm-oil modified hydroxyethyl imidazoline concentration on the polarization curves for Cu in 1.0 M H_2SO_4 is shown in Fig. 2. It can be seen that in the uninhibited solution, Cu displays an active-passive behaviour, with an E_{corr} value of -700 mV and a corrosion current density value of .004 mA/cm^2. At small anodic overpotentials, there is an increase in the anodic current density due to the dissolution of Cu in to Cu^{2+} ions. After this dissolution process, there is a small passive region between -640 and -680 mV, probably due to the formation of a porous copper oxide film [24, 25] due to the presence of oxygen, which enhances the cathodic reaction of oxygen reduction; after this unstable passive region, there is an increase in the anodic current density due to the dissolution of the passive film, but at a potential close to -480 mV an anodic limit current density as reported in previous works [26, 27]. Dissolution of copper in this environment can be described as:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e \quad (1)$$

$$Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e \quad (2)$$

Supported by oxygen reduction, which is the cathodic reaction in an aerated solution for low cathodic over potentials:

$$O_2 + 4H^+ + 4e \rightarrow H_2O \quad (3)$$

Thus, the cathodic curves close to E_{corr} in the uninhibited solution is due to the reduction of oxygen present in the solution. When the palm-oil modified hydroxyethyl imidazoline is added to the solution, the E_{corr} value shifts towards nobler values and the I_{corr} value decreases, reaching its lowest value, .0005 mA/cm^2, at an inhibitor concentration of 10 ppm. Both anodic and cathodic current density values are decreased also when the inhibitor concentration reaches 10 ppm. After this concentration, the anodic and cathodic current density values as well as the I_{corr} value increase once again, probably due to the dissolution of the corrosion products back into the solution as explained elsewhere [9, 10]. Electrochemical parameters such as E_{corr}, I_{corr}, anodic and cathodic Tafel slopes are given in Table 1. This table shows that both cathodic Tafel slopes are decreased whereas the anodic one was increased by the inhibitor, indicating that both anodic dissolution and oxygen reduction reactions are affected by the palm-oil modified hydroxyethyl imidazoline, which, therefore, acts as a mixed type of inhibitor for Cu in sulfuric acid solution. Anodic Tafel values between 20 and 30 mV/Dec have been to be dependent upon the diffusion of cupric ions [28]. In this work, anodic Tafel slopes close to this region were obtained only in the blank, uninhibited solution as well with the addition of 100 ppm, but it was 35 mV/Dec, so, the diffusion of cupric ions cannot be considered as the dominant corrosion reaction step. By using the I_{corr} values, inhibitor efficiency were calculated by using the following equation:

$$I.E\,(\%) = \left(\frac{I_{corr} - I'_{corr}}{I_{corr}} \right) x\,100 \quad (4)$$

where I'_{corr} and I_{corr} are the corrosion current density values with and without inhibitor respectively. It can be seen in Table 1 that inhibitor efficiency increases with an increase in the inhibitor concentration, reaching its highest value at 10 ppm, and after this value, inhibitor efficiency value decreases with a further increase in the inhibitor concentration. The metal surface area covered by the inhibitor, θ, increased also with increasing the inhibitor concentration reaching its highest value when 10 ppm of inhibitor are added, decreasing with a further increase in the inhibitor concentration.

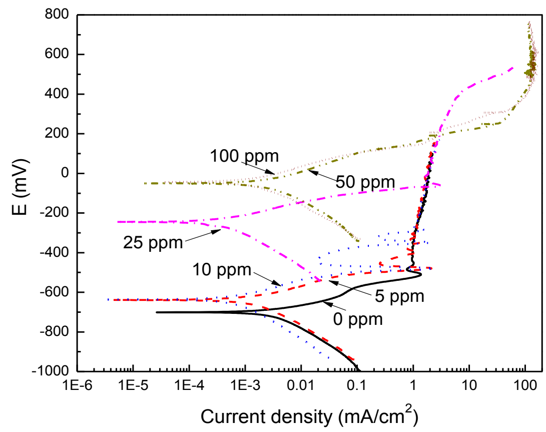

Fig. 2 Effect of palm-oil modified hydroxyethyl imidazoline concentration in the polarization curves for Cu in 1.0 M H_2SO_4

Table 1 Electrochemical parameters for Cu tested in 1.0 M H_2SO_4 at 25 °C with different concentrations of palm-oil modified hydroxyethyl imidazoline

C_{inh} (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	β_a (mV/Dec)	β_c (mV/Dec)	I.E. (%)	θ
0	-700	0.004	35	183	---	--
5	-638	0.0015	60	125	63	0.63
10	-636	0.0005	65	120	88	0.88
25	-244	0.0006	60	130	84	0.84
50	-50	0.0023	52	140	40	0.40
100	-45	0.0011	25	160	76	0.76

3.2 Linear Polarization Resistance

The effect of the palm-oil modified hydroxyethyl imidazoline concentration in the R_p value is shown in Fig. 3 It can be seen that the lowest R_p value is for the uninhibited solution, showing a value which remained more or less constant through the test, around 1000 Ωcm^2, indicating that the formed corrosion products are not protective. As soon as the inhibitor is added, the R_p value starts to increase, indicating the protective nature of the formed corrosion products. With 5 ppm of inhibitor, the R_p increases up to 10,000 Ωcm^2, one order of magnitude higher than that obtained for the uninhibited solution, but after 2-3 hours of testing, the R_p drops down to 5, 000 Ωcm^2 and remains there during the rest of the experiment. With the addition of either 10 or 25 ppm of inhibitor, the R_p value increases during the first 5 hours up to a value around 12, 500 Ωcm^2, but after this time it drops slightly and it increases once again, reaching a higher value the solution containing 10 ppm of inhibitor. This monotonic increase in the R_p value with time, indicates the protective nature of the corrosion products formed on top of the metal surface, whereas the observed drop can be due to the dissolution of the corrosion products [29].

By using the R_p values, it was possible to calculate the I.E. values by suing equation:

$$I.E. (\%) = 100 (R_{p1} - R_{p2})/ R_{p1} \quad (5)$$

where R_{p1} is the polarization resistance with inhibitor and R_{p2} the polarization resistance without inhibitor and the change in the I.E. value with time at the different inhibitor concentrations in Fig. 4. It can be seen that efficiency values rapidly increases, reaching a steady state value in less than 5 hours of exposure to the electrolyte. For the solution containing 5 ppm of inhibitor, where the lowest efficiency values were obtained, efficiency value increase up to a value close to 85%, but after 7 hours, it drops slightly down to a value of 80% remaining there during the rest of the experiment. The highest efficiency value, 92%, was obtained by adding 10 ppm of inhibitor. Efficiency values increased with an increase in the inhibitor concentration, indicating that the decrease in the corrosion rate is due to its adsorption. The increase in the inhibitor efficiency with increasing the inhibitor concentration can be interpreted on the basis that the adsorption amount and the coverage of inhibitor molecules, increases with increasing concentration [30]. According to Table 1, the metal surface area covered by the inhibitor, θ, increased with an increase in the inhibitor concentration up to 10 ppm, decreasing when the inhibitor was further increased.

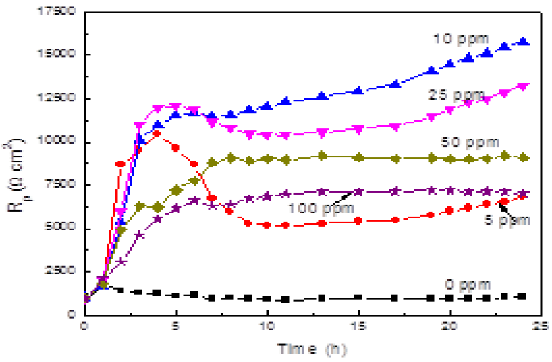

Fig. 3 Effect of palm-oil modified hydroxyethyl imidazoline concentration in the change of the R_p value with time for Cu in 1.0 M H_2SO_4

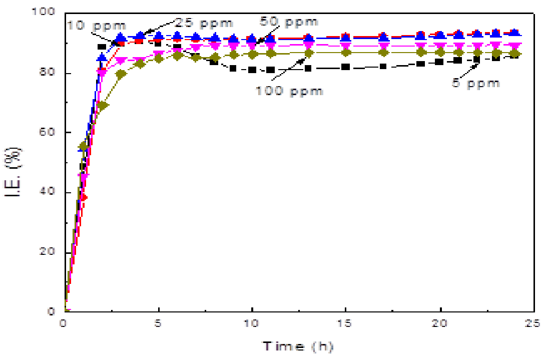

Fig. 4 Effect of palm-oil modified hydroxyethyl imidazoline concentration in the change of the inhibitor efficiency value with time for Cu in 1.0 M H_2SO_4

3.3 Electrochemical Impedance Spectroscopy

EIS data in both Nyquist and Bode plots for Cu in 1.0 M H_2SO_4 solution containing different concentrations of palm-oil modified hydroxyethyl imidazoline is shown in Fig. 5. It can be seen that for the uninhibited solution, Nyquist data, Fig. 5a, describe one capacitive-like, depressed semicircle at high and intermediate frequency values due to the oxidation of copper, followed by what looks like a second semicircle at lower frequency values, with some data dispersion, as reported elsewhere [9, 10], associated to the formation of a corrosion products film [31, 32]. When the palm-oil modified hydroxyethyl imidazoline is added, data describe only a single depressed, capacitive-like semicircle, indicating a charge transfer corrosion process control, except at an inhibitor concentration of 10 ppm, where the presence of a tale is at lower frequency values evident, which has been attributed to the accumulation of all kind of species at the metal/solution interface such as the [33, 34]. The total resistance is the sum of the charge transfer resistance, the film resistance and other accumulations at metal/solution resistance. The diameter of the low frequency semicircle increases with increasing the inhibitor concentration up to 10 ppm, but it decreases with a further increase in the inhibitor concentration. The increase in the impedance with increasing the inhibitor concentration is due to the adsorption of the inhibitor on the surface metal and an increase in the surface area covered by the inhibitor molecules. The decrease in the impedance after reaching a critical inhibitor concentration, in this case 10 ppm, is due to the dissolution of the inhibitor-formed film by the solution, leaving the metal surface unprotected [9, 10, 28]. On the other hand, Bode diagrams, Fig. 5 b, show a more or less constant phase angle value in a wide frequency interval, between 1000-10 Hz, for the uninhibited solution, whereas the presence of two peaks, and thus two time constants, is evident when the inhibitor is added, which correspond to the charge transfer resistance and the resistance of the protective corrosion products by the modified imidazoline and copper ions. The first time constant in the high frequency region has been proposed to be a result of the surface relaxation of Cu_2O [35] whereas the second time constant in the low frequency region accounts for the diffusion of dissolved O_2.

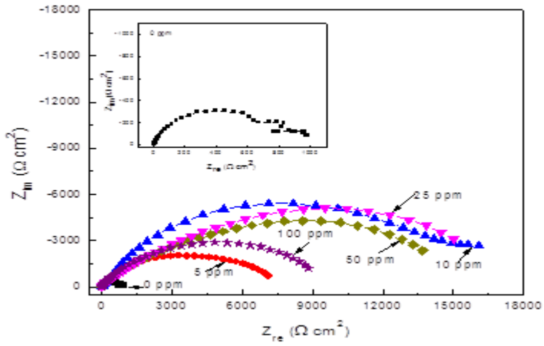

Fig. 5a Effect of palm-oil modified hydroxyethyl imidazoline concentration in the EIS data in the Nyquist

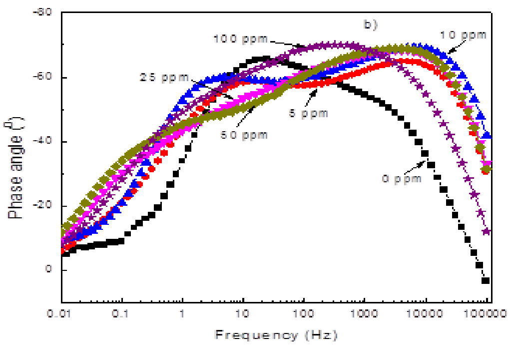

Fig. 5b Effect of palm-oil modified hydroxyethyl imidazoline concentration in the EIS data in the Bode formats for Cu in 1.0 M H_2SO_4

EIS data can be analysed with the help of equivalent electric circuits, and electrochemical parameters such as solution resistance, R_s, charge transfer resistance, R_{ct}, and the double layer capacitance, C_{dl}, can be calculated. To take into account the inhomogeneity and surface roughness, a constant phase element, CPE, is introduced. The equivalent circuit is composed of a constant phase element, in parallel with a charge transfer resistance, which at the same time is in series with solution resistance, Fig. 6. Electrochemical parameters obtained from Nyquist data are given in Table 2, whereas the change in the double electrochemical layer capacitance, C_{dl}, value with the inhibitor concentration is shown in Fig. 7. Inhibitor efficiency was calculated with following equation:

$$I.E. (\%) = 100 (R_{ct1} - R_{ct2})/ R_{ct1} \quad (6)$$

where R_{ct1} is the charge transfer resistance with inhibitor and R_{ct2} the charge transfer resistance without inhibitor. It can be seen that the R_{ct} value increases with the inhibitor concentration (decreasing the corrosion rate), reaching a highest value when 10 ppm of inhibitor are added, but it decreases with a further increase in the inhibitor concentration. On the other hand, the C_{dl} value decreases with an increase in the inhibitor concentration, reaching its lowest value with the addition of 10 ppm, and then it increases once again with a further increase in the inhibitor concentration. An increase in R_{ct} refers to more impediment of the active area at the metal surface as a result of the increase in inhibitor concentration [36, 37]. In addition, the values of the double-layer capacitance (C_{dl}) decrease by adding inhibitor in to corrosive solution. Additionally, double-layer capacitance can be calculated with equation:

$$C_{dl} = \varepsilon\varepsilon_0 A/\delta \qquad (7)$$

where ε is the double layer dielectric constant, ε^0 the vacuum electrical permittivity, δ the double layer thickness, and A the surface area. Thus, the decrease in C_{dl} value is attributed to the replacement of the adsorbed water molecules at the metal surface by the inhibitor molecules having lower dielectric constant [38] and decreasing the thickness of the double layer.

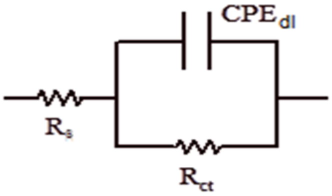

Fig. 6 Electric circuit used to simulate the EIS data for Cu in 1.0 M H_2SO_4

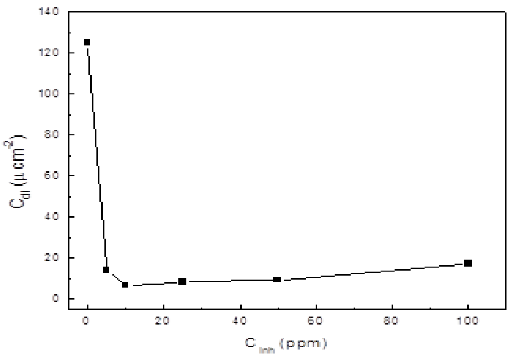

Fig. 7 Variation in the double layer capacitance value, C_{dl}, with the palm-oil modified hydroxyethyl imidazoline concentration for Cu in 1.0 M H_2SO_4

Table 2 Electrochemical impedance parameters for Cu in 1.0 M H_2SO_4 with different concentrations of palm-oil modified hydroxyethyl imidazoline

C_{inh} (ppm)	R_s (ohm cm^2)	R_{ct} (kohm cm^2)	C_{dl} (μF cm^{-2})	n	I.E. (%)
0	3.1	0.64	125	0.81	---
5	3.9	7.18	14	0.84	91
10	4.9	16.17	6.5	0.90	96
25	5.2	14.9	8.2	0.87	93
50	4.5	13.7	9.8	0.84	90
100	2.9	8.8	17.1	0.81	89

3.4 SEM Micrographs

Some SEM micrographs of corroded specimens in 1.0 M H_2SO_4 without and with modified imidazoline are shown in Figs. 8(a-f).

It is generally accepted that the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules absorbed on the metal surface:

$$Inh_{sol} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O_{sol} \qquad (9)$$

The inhibitor may then combine with freshly generated Cu^{2+} ions on copper surface, forming metal-inhibitor complexes [39, 40]:

$$Cu \rightarrow Cu^{2+} + 2e \qquad (10)$$
$$Cu^{2+} + Inh_{ads} \rightarrow [Cu\text{-}Inh]_{ads}^{2+} \qquad (11)$$

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution or increase its corrosion rate. At low concentrations the amount of inhibitor is insufficient to form a compact complex with the metal ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. Additionally, for low inhibitor concentrations, low inhibitor efficiencies are due not only by the low coverage of the copper surface, but also by the diffusion of species in the solution [35]. But at relatively higher concentrations more inhibitor molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion. Adsorption of the inhibitor on to copper surface can occur through the free electrons of the nitrogen atoms , since nitrogen accept electrons from the electrolyte to form cations which are electrostatically attracted to the adsorbed fulphate anions on copper surface [39, 40].

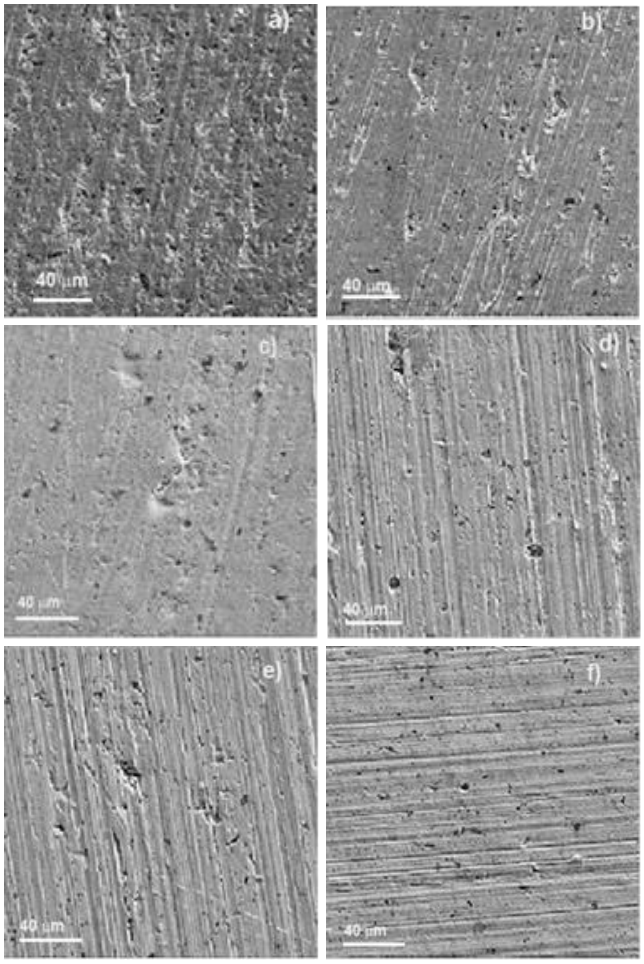

Fig. 8 SEM micrographs of Cu exposed to 1.0 M H_2SO_4 solution containing a) 0, b) 5, c) 10, d) 25, e) 50 and f) 100 ppm of palm-oil modified imidazoline

In order to see the evolution in time of the inhibitor–formed film, Fig. 9 shows Nyquist and Bode diagrams for Cu in H_2SO_4 solution containing 10 ppm of the palm-oil modified hydroxyethyl imidazoline after different immersion times. Nyquist diagrams, Fig. 9a, show that, immediately after immersing the specimen into the solution, data describe a single, capacitive-like semicircle at high and intermediate frequency values, followed for what looks like a second semicircle, which is not very clear due to the data dispersion. However, after 6 hours of exposure to the electrolyte, data describe a single, capacitive-like depressed semicircle at high frequency values, and a tale or elongation at low frequency values, which, as explained above, is due to the accumulation of inhibitor formed film and some other species. The increase in the semicircle diameters as time elapses indicates that the adsorption amount and the coverage of inhibitor molecules increases with increasing time [30], increasing the film thickness. The corrosion resistance of copper can be determined by the polarization resistance, R_p, which is given by the value of the real impedance at the lowest frequency value [41]. It can be seen that the R_p value increases with increasing the immersion time, decreasing, thus, the corrosion rate. Bode diagrams, on the other hand, Fig. 9b, show two time constants at all testing times, which correspond to the charge transfer resistance and the resistance of the protective corrosion products by the modified imidazoline and copper ions as explained above. Thus, inhibition efficiency for the palm-oil modified hydroxyethyl imidazoline not only increases with increasing its concentration reaching a highest value with the addition of 10 ppm, but also it increases with increasing the immersion time.

Thus, so far, it has been shown that modified imidazoline inhibits the corrosion of copper in sulfuric acid due to its adsorption on to the copper surface. For the adsorption, it is required the presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatom with lone pair electrons. In the sulphuric acid medium, modified imidazoline may be protonated predominantly affecting the nitrogen atoms [42].The protonated imidazoline, however, could be attached to the copper surface by means of electrostatic interaction between SO_4^{2-} and protonated imidazoline since the copper surface has positive charges in the acid medium [43]. This could further be explained based on the assumption that in the presence of SO_4^{2-}, the negatively charged SO_4^{2-} would attach to positively charged surface. When imidazoline adsorbs on the copper surface, electrostatic interaction takes place by partial transference of electrons from the polar atom (N and O atoms and the delocalized π electrons around the heterocyclic rings) of imidazoline to the metal surface. In addition to electrostatic interaction (physisorption) of modified imidazoline molecules on the copper surface, molecular adsorption may also play a role in the adsorption process. Thus we can say that the adsorption of modified imidazoline on the copper surface in sulphuric acid may be achieved by the interaction between iron atoms and cyclic molecular π orbital.

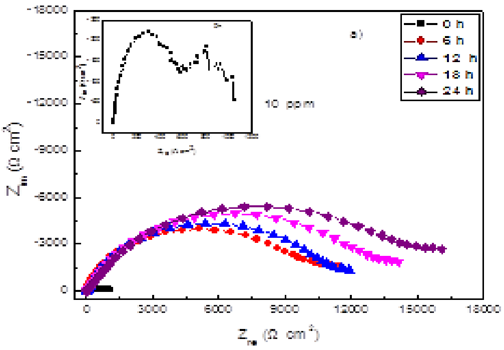

Fig. 9a Effect of palm-oil modified hydroxyethyl imidazoline concentration in the change of the Nyquist

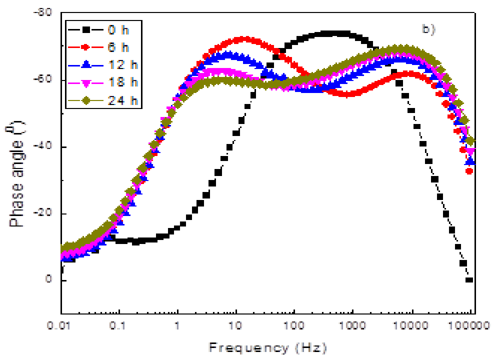

Fig. 9b Effect of palm-oil modified hydroxyethyl imidazoline concentration in the change of the Bode diagrams with time for Cu in 1.0 M H_2SO_4

4. Conclusion

Palm-oil modified hydroxyethyl imidazoline is a god corrosion inhibitor for Cu in 1.0 M H_2SO_4 with an inhibitor efficiency value increasing with increasing its concentration and reaching its highest value at 10 ppm. A decrease in the inhibitor inhibition is observed with a further increase in the inhibitor concentration. Additionally, inhibit efficiency increased with an increase in the immersion time. Inhibitor decreased the cathodic oxygen reduction reaction in a higher extent than the anodic dissolution reaction, acting, therefore, as a mixed type of inhibitor. Palm-oil modified hydroxyethyl imidazoline can be easily adsorbed on to the copper surface to form a protective complex film with copper ions. EIS results have shown that the capacitance value decrease whereas the charge transfer resistance and inhibition increase by the addition of the Palm-oil modified hydroxyethyl imidazoline.

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