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## Application of hexa propylene glycol cyclotriphosphazene as corrosion inhibitor for copper in 3% NaCl solution

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### ABSTRACT

The product namely Hexa Propylene Glycol Cyclotriphosphazene (HPGCP) was synthesized and its inhibitive performance as corrosion inhibitor towards the corrosion of copper in neutral solution of 3% NaCl has been investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). Polarization curves indicate that HPGCP is a mixed inhibitor, affecting both cathodic and anodic corrosion currents. The inhibition efficiency of HPGCP, which reached 96 %, was observed in  $10^{-3}$  M concentration. The adsorption of the inhibitor on the copper surface in the 3% NaCl solution was found to obey Langmuir's adsorption isotherm. The inhibition mechanism was determined by potential of zero charge measurements and some electronic parameters.

**Keywords:** Electrochemical impedance spectroscopy, cyclotriphosphazene, corrosion of copper, potentiodynamic polarization.

### INTRODUCTION

Copper has been one of the most important metals in industry owing to its high electrical and thermal conductivities, mechanical workability and its relatively noble properties. It is widely used in many applications in electronic industries and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers, etc. For this reason, corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted the attention of many investigators [1–8]. Various strategies have been developed to address the growing need for the inhibition of copper corrosion. One of the most important methods in the protection of copper against corrosion is the use of heterocyclic inhibitors. Heterocyclic compounds containing polar groups including nitrogen, phosphorus, sulfur and oxygen [9–15] and heterocyclic compounds with polar functional groups and conjugated double bonds [16–20] have been reported to inhibit copper corrosion.

So far, different types of heterocyclic compounds have been explored to act as copper inhibitors. Cyclotriphosphazene is one of the most effective heterocyclic inhibitor in neutral-chloride aqueous solutions. In addition, amines,azole derivatives and Mercapto-imidazole compounds are also potentially effective copper's corrosion inhibitors [21].

The inhibiting action of these heterocyclic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups regarded as the reaction centre that stabilizes the adsorption process [22].

In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of the electrolyte solution [23].

In this study, we have investigated the ability of hexa propylene glycol cyclotriphosphazene, HPGCP (Fig. 1) to inhibit copper corrosion in 3% NaCl solution.

This study was also conducted by using potentiodynamic polarization curves and electrochemical impedance spectroscopy diagrams and scanning electron microscopy (SEM) technique to examine the changes of the copper surfaces corroded in test solutions with and without the inhibitor.

### EXPERIMENTAL MATERIAL AND PROCEDURES

The chemical structure of the studied compound is presented in figure 1. HPGCP is relatively cheap and easy to be produced in purity greater than 95%. The non-toxic of HPGCP makes the investigation of its inhibiting properties significant in the context of the current priority to produce “environmentally friendly” inhibitors. HPGCP was obtained according to the procedure literature [24-27].

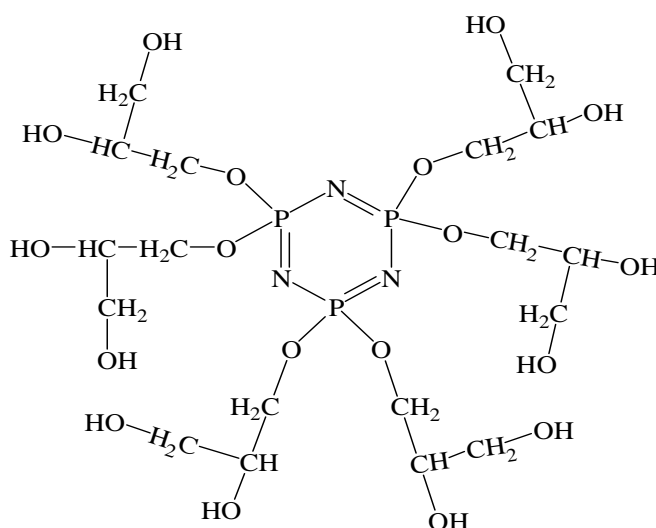


Figure1. Structure of Hexa propylene glycol cyclotriphosphazene (HPGCP)

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the copper specimen as working electrode (WE), platinum mesh as counter electrode (CE), and (Ag/AgCl) is used as the reference electrode with a 3M concentration of Cl<sup>-</sup> as the reference electrode. The counter electrode was separated from the working electrode compartment by fritted glass. Prior to each experiment, the copper electrode was first polished successively with metallographic emery paper treatments from 60 up to 1500 grades to a smooth and planar surface which was obtained, washed several times with bi-distilled water then with ethanol and then dried using a stream of air. The electrode potential was allowed to be stabilized 40 min before starting the measurements. The aggressive environment used to be 3% NaCl solution with different concentrations of HPGCP. All experiments were conducted at 298K and the temperature was kept constant using thermostat.

Potentiodynamic polarization curves were obtained by changing the electrode potential automatically from (-1200 to +600 mV/Ag/AgCl) versus open circuit potential with a scan rate of 1mVs<sup>-1</sup>. To evaluate corrosion kinetic parameters, a fitting by Stern–Geary equation was used. So, the overall current density values,  $i$ , were considered as the sum of two contributions, anodic and cathodic current  $i_a$  and  $i_c$ , respectively. For the potential domain not too far from the open circuit, it may be considering that both processes follow the Tafel law [28]. Thus, it can be derived from Eq. (1):

$$i = i_{\text{corr}} \times \left\{ \exp[b_a \times (E - E_{\text{corr}})] - \exp[b_c \times (E - E_{\text{corr}})] \right\} \quad (1)$$

$$i = i_a + i_c$$

where  $i_{corr}$  is the corrosion current density ( $A\ cm^{-2}$ ), and  $b_a$  and  $b_c$  are respectively the Tafel constant of anodic and cathodic reactions ( $V^{-1}$ ). These constants are related to the Tafel slope  $\beta$  ( $V\ dec^{-1}$ ) in usual logarithmic scale by:

$$\beta = \frac{\text{Log } 10}{b} = \frac{2.303}{b} \quad (2)$$

EIS measurements were carried out in a frequency range of 100 kHz to 10 MHz with amplitude of 10 mV peak-to-peak using ac signals at respective corrosion potential.

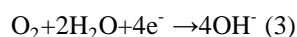
Electrochemical experiments were carried out by using a transfer function analyzer (Voltalab PGZ100, Radiometer Analytical).

The surface analysis of the copper electrode, without and with  $10^{-3}M$  of HPGCP after a hold time immersion of 2 days, was carried out by using scanning electron microscopy (SEM, JOEL JSM-5500).

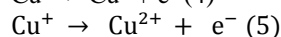
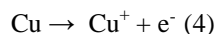
## RESULTS AND DISCUSSION

### Potentiodynamic polarization measurements

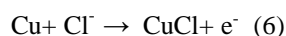
Figure 2 shows the manifestation of cathodic and anodic polarization curves recorded for copper in 3% NaCl at different concentrations of HPGCP. In figure 2, it is obvious that HPGCP causes a significant decrease in current density ( $i_{corr}$ ) as a consequence of the blocking effect of inhibitor on the metal surface. The three distinct regions that appeared were the active dissolution region (apparent Tafel region), the active-to passive transition region, and the limiting current region [29]. The cathodic corrosion reaction in NaCl solution should be the reduction of oxygen [30, 31]:



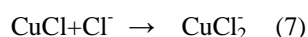
In general, the dissolution process of Cu (anodic corrosion reactions) is [32, 33]:



But the dissolution process of Cu in the presence of complexing ions such as  $Cl^-$  proceeds via a two step reaction mechanism. In the first step, copper is ionized under the influence of a  $Cl^-$  ion, yielding CuCl adsorbed on the electrode by the following reaction [34, 35]:



This adsorbed compound dissolves by combination with another  $Cl^-$  ion and the diffusion of the resulting  $CuCl_2$  through the solution is the rate determining step of the dissolution process [36]:



Compared with the blank solution, the corrosion potential ( $E_{corr}$ ) shifted more positive direction and both the anodic and cathodic currents were decreased. This indicates that HPGCP acts as a mixed-type corrosion inhibitor [37].

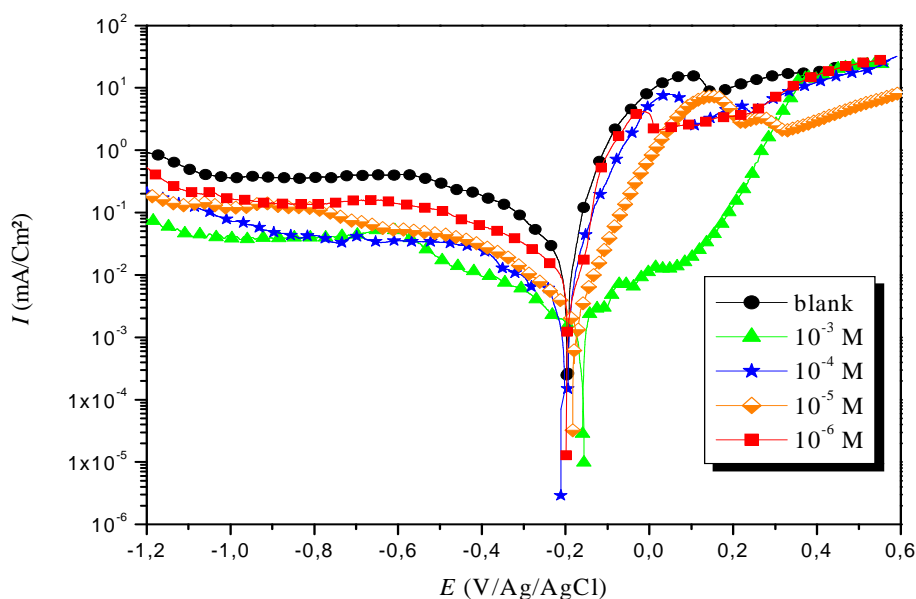


Figure2. Potentiodynamic polarization curves for copper in 3% NaCl solutions without and with different concentrations of HPGCP after immersion for 40 min

Table 1 illustrates some kinetic parameters such as corrosion potential,  $E_{corr}$ , corrosion current density,  $i_{corr}$ , anodic and cathodic Tafel slopes,  $b_a$ ,  $b_c$ , and inhibiting efficiency,  $\eta(\%)$ . The corrosion inhibition efficiency is determined by the following equation :

$$\eta \% = \left( 1 - \frac{i_{corr}}{i_{corr}^0} \right) \times 100 \quad (8)$$

where  $i_{corr}^0$  and  $i_{corr}$  are the corrosion current density values without and with the inhibitor respectively.

Table 1. Electrochemical parameters for the copper electrode in 3% NaCl containing different concentrations of HPGCP

	C (M)	$E_{corr}$ (mV/Ag/AgCl)	$i_{corr} \times 10^6$ (A/cm²)	$-\beta_c$ (mVdec <sup>-1</sup> )	$\beta_a$ (mVdec <sup>-1</sup> )	$\eta$ %
Blank	00	-190	24	391	325	-
HPGCP	$10^{-6}$	-155	14	415	62	42
	$10^{-5}$	-172	4.5	409	94	81
	$10^{-4}$	-206	3.5	319	210	85
	$10^{-3}$	-100	1.1	229	212	95

### Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a convenient technique in studying corrosion mechanisms and adsorption phenomena [38]. Figure 3 shows Nyquist for copper electrodes in 3 % NaCl. In the presence of HPGCP the impedance spectra for the Nyquist plots clearly show a depressed semicircle in the high frequency region followed by a straight line portion at low frequency values. The high frequency semicircle is attributed to the charge transfer and double-layer capacitance [39,40]. The diameter of this semicircle grows with increasing concentration of the inhibitor. The large semicircle observed from high to low frequencies in the presence of inhibitor indicates that the charge-transfer resistance became dominant in the corrosion process due to the adsorption of HPGCP.

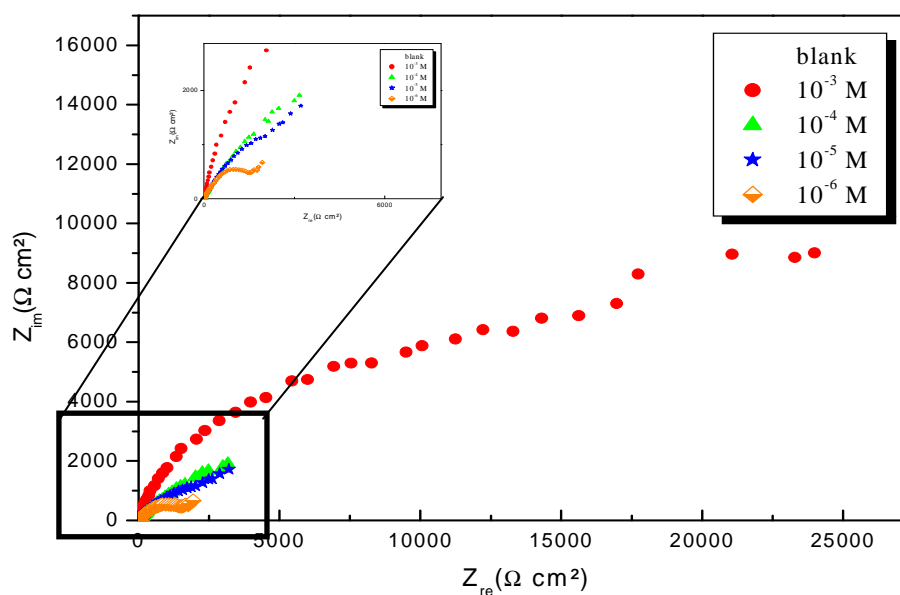


Figure 3. Nyquist plots for copper in 3 % NaCl without and with different concentrations of HPGCP.

The equivalent circuit model used to analyse impedance characteristics is shown in figure 4. This circuit model was also reported in many studies for copper/chloride solution interface. The parameters obtained by fitting the equivalent circuit and the calculated inhibition efficiencies are tabulated in table 2. Here, ( $R_s$ ) represents the solution resistance, charge transfer resistance ( $R_{ct}$ ) and resistance associated with the layer of products formed ( $R_f$ ). In addition, the ( $n_f$ ) and ( $n_{ct}$ ) are the depressed features in Nyquist plot, can characterize different physical phenomena such as inhomogeneities of the surface resulting from the surface of impurities, the adsorption of the molecules inhibitors forming a porous layer [41,42]. In this case, the impedance can be written according to the following equation [43]:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (9)$$

where  $Y_0$  is CPE constant,  $\omega$  is angular frequency ( $\text{rad s}^{-1}$ ),  $j^2 = -1$ , imaginary number, and  $n$  is CPE exponent. Depending on  $n$ , CPE can represent resistance ( $Z_{CPE} = R$ ,  $n = 0$ ), an ideal double-layer capacitance ( $Z_{CPE} = C_{dl}$ ,  $n = 1$ ), inductance ( $Z_{CPE} = L$ ,  $n = -1$ ) or Warburg impedance ( $n = 0.5$ ) [44]. The following equation is used to convert  $Y_0$  into  $C_{dl}$ .

$$C_{dl} = Y_0 (w_m'')^{n-1} \quad (10)$$

where  $w_m''$  is the frequency at which the imaginary part of the impedance has a maximum.

The fitted data from the equivalent circuit are summarized in table 2.

The HPGCP may act by adsorption at the metal/ solution interface, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [45]. The values of  $R_p$  increased with further increase of HPGCP concentration. The inhibition efficiency ( $\eta$  %) of the HPGCP on the copper surface is described in Eq. (11) [46] :

$$\eta \% = \frac{R_p - R_p^0}{R_p} \times 100 \quad (11)$$

where  $R_p^0$  and  $R_p$  are the resistance polarization values in the absence and in the presence of inhibitor, respectively.

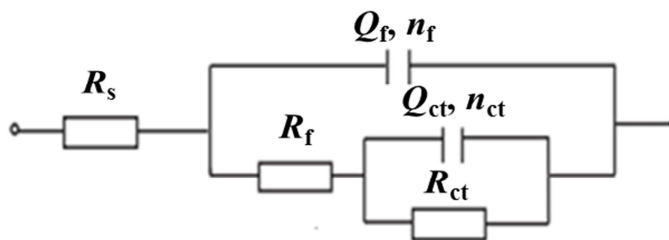


Figure 4. The equivalent circuit used to simulate the impedance data

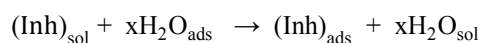
Table 2. Parameters obtained by fitting the Nyquist plots with the equivalent circuit for the copper electrode

	$R_s$ ( $\Omega \cdot \text{cm}^2$ )	$R_f$ ( $\text{K}\Omega \cdot \text{cm}^2$ )	$Q_f$ ( $\mu\text{F}/\text{cm}^2$ )	$n_f$	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	$n_{ct}$	$R_{ct}$ ( $\text{K}\Omega \cdot \text{cm}^2$ )	$R_p$ ( $\text{K}\Omega \cdot \text{cm}^2$ )	$\eta\%$
Blank	20	-	-	-	-	0.75	0.95	1.2	-
$10^{-3}\text{M}$	5	12.2	31	0.78	106	0.71	21.3	33.5	96
$10^{-4}\text{M}$	3	0.065	35.9	0.19	227	0.53	8	8.1	85
$10^{-5}\text{M}$	12	0.076	51	0.52	301	0.88	6.6	6.7	82
$10^{-6}\text{M}$	18	0.067	16	1	674	0.57	2.1	2.15	44

The inhibition efficiencies calculated from  $R_p$  also increase with increasing concentration of the inhibitor, and the maximum value is 96 % at  $10^{-3}$  M HPGCP concentration. Thus, due to the adsorption of HPGCP on the copper surface, the corrosion reactions have been inhibited to a great extent. In conclusion, EIS results are consistent with the data obtained by polarisation and provide further confirmation of the ability of HPGCP as a good inhibitor for copper corrosion in 3% NaCl solution.

#### Adsorption isotherm and thermodynamic consideration

The adsorption of heterocyclic inhibitors on metal surface can markedly change the corrosion resisting properties of the metals. So, the investigation of relation between the adsorption and corrosion inhibition is important [47]. The efficiency of inhibitor molecules as a successful corrosion inhibitor mainly depends on their adsorption ability at the metal/solution interface which takes place through the replacement of water molecules by inhibitor molecules according to following process [48].



where  $\text{Inh}_{(\text{sol})}$  and  $\text{Inh}_{(\text{ads})}$  are inhibitor molecules in the solution and adsorbed on the metal surface, respectively.  $x$  is the number of water molecules replaced by the inhibitor molecules. The adsorption isotherms can give valuable information on the interaction of inhibitor and metal surface. So, it is essential to know the mode of adsorption and the adsorption isotherm. Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor, which obeys the following Eqs. (12) and (13) [49]:

$$\frac{\theta}{1-\theta} = K_{\text{ads}} C_{\text{inh}} \quad (12)$$

$$K_{\text{ads}} = \frac{1}{55.55} \exp\left(-\frac{\Delta G_{\text{ads}}^{\circ}}{RT}\right) \quad (13)$$

$C_{\text{inh}}$  is the inhibitor concentration,  $\theta$  is the fraction of the surface coverage,  $K_{\text{ads}}$  is the adsorption equilibrium constant and  $\Delta G_{\text{ads}}^{\circ}$  is the standard free energy of adsorption.

Figure 5 shows the dependence of the fraction of the surface coverage  $C_{\text{inh}}/\theta$  as a function of the concentration ( $C_{\text{inh}}$ ) of HPGCP.

The degree of surface coverage  $\theta$  for different concentrations of the inhibitor in 3% NaCl has been evaluated from weight loss measurements. The obtained plot of the inhibitor is linear. The regression coefficient is  $R^2 = 0.999$ . The intercept permits the calculation of the adsorption equilibrium constant  $K_{\text{ads}}$  which is equal  $239762.2 \text{ M}^{-1}$  and leads to evaluate  $\Delta G_{\text{ads}}^{\circ} = -40.646 \text{ kJmol}^{-1}$ . The value of  $\Delta G_{\text{ads}}^{\circ}$  indicates the strong interaction between inhibitor molecules and the copper surface [50,51].

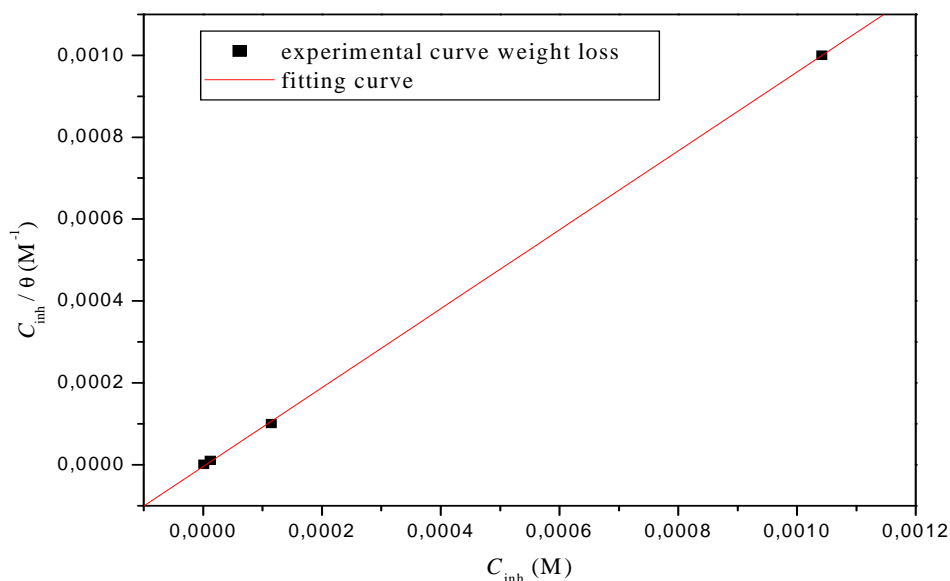


Figure 5. Langmuir adsorption plot of copper in 3% NaCl solution containing various concentrations of HPGCP

#### Mode of adsorption of HPGCP on the copper surface

The surface charge of metal can be defined by the position of corrosion potential in respect to the respective potential of zero charge (PZC), which plays a very important role in the electrostatic adsorption process. The EIS offers a good method in order to determine the PZC of metals. For this purpose, EIS study was applied at different potentials and a plot of C<sub>dl</sub> vs. applied potential was obtained (Fig. 6) [52].

In the work, we showed that the potential of zero charge (PZC) is -224 mV/Ag/AgCl which is more negative than the corrosion potential is -174 mV/Ag/AgCl (Fig. 6). This result suggests that the carbon steel surface is positively charged [53].

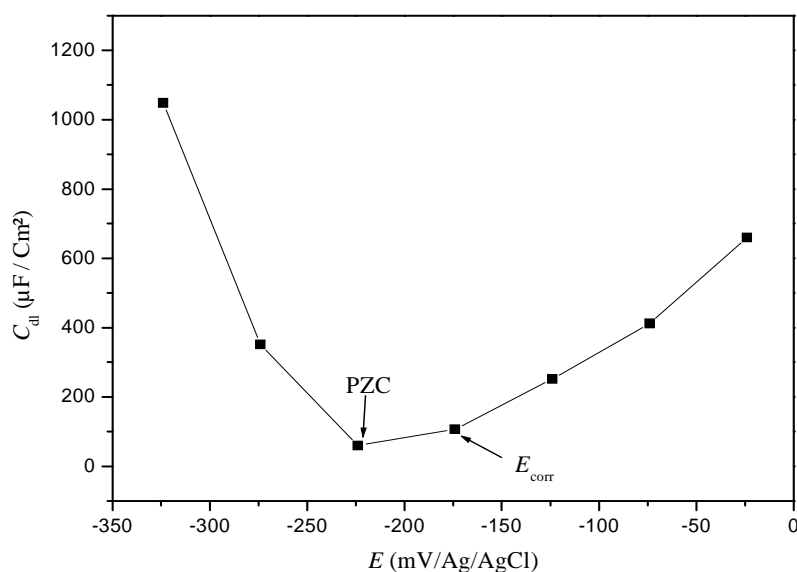
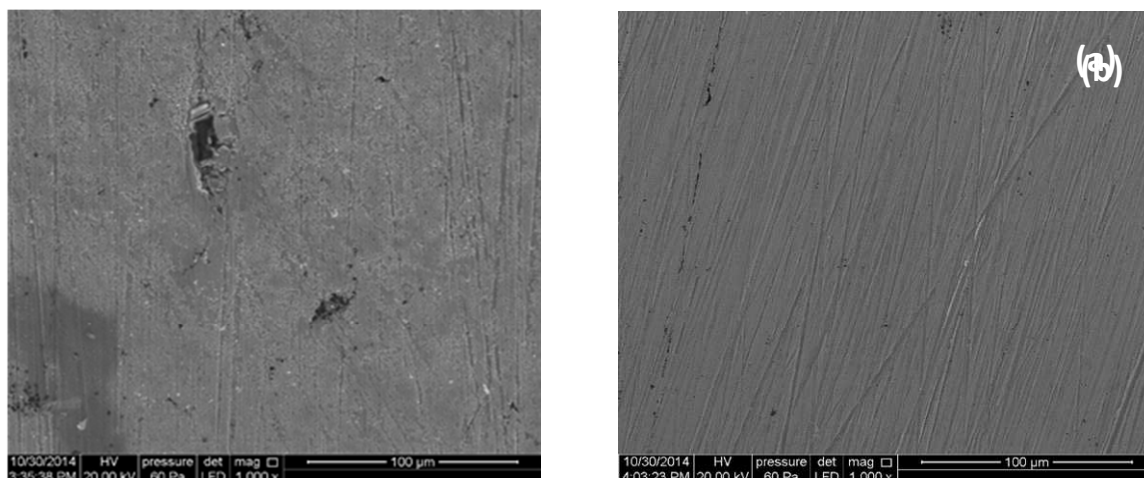


Figure 6. Relationship between C<sub>dl</sub> values and the applied potential for carbon copper electrode in 3% NaCl solution at 298 K



**Scanning electron microscopy**

The surface morphology of copper that exposed to 3% NaCl solution with and without  $10^{-3}$  M of HPGCP for 2 days were examined by scanning electron microscopy (SEM) technique.



**Figure 7. SEM micrographs of copper after 2 days of immersion in 3 % NaCl: (a) without inhibitor and (b) with  $10^{-3}$  M of HPGCP**

In Figure 7(a), large areas of the copper surface are obviously covered with loose corrosion products in the absence of HPGCP. This finding may be an indication that corrosion products easily leave the metal surface and then develop stronger corrosion activity.

Figure 7(b) presents the SEM micrograph obtained in the presence of HPGCP, which shows a relatively flat surface. The micrograph reveals that, inhibitor molecules adsorbed on active sites of copper and a smoother surface was observed when compared to the surface treated with uninhibited 3% NaCl solution.

**CONCLUSION**

On the basis of the obtained results, we can conclude that:

- (1) HPGCP exhibited good inhibiting properties for copper corrosion in 3% NaCl solution. The inhibition efficiency increased with increasing the concentration of HPGCP.
- (2) Potentiodynamic polarization results revealed that HPGCP in 3% NaCl solution acted as a mixed-type inhibitor.
- (3) EIS measurement results indicate that the resistance of the copper electrode increases greatly and its capacitance decreases by increasing the inhibitor concentration.
- (4) Data obtained from EIS measurements are in good agreement with those of the polarization resistance method.
- (5) The adsorption of inhibitor molecules on the copper surface obeys a Langmuir adsorption isotherm.
- (6) The adsorption of inhibitor molecules on the copper surface obeys Langmuir adsorption isotherm. The value of  $\Delta G_{ads}^{\circ}$  indicates the strong interaction between inhibitor molecules and the copper surface.
- (7) The copper surface carry positive charge in the test solution.
- (8) The SEM indicate that copper corrosion can be inhibited evidently due to the adsorption of HPGCP on the copper surface.

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