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New Hexa Propylene Glycol Cyclotiphosphazene As Efficient Organic Inhibitor of Carbon Steel Corrosion in Hydrochloric Acid Medium

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Abstract

New cyclotriphosphazene, namely Hexa propylene glycol cyclotiphosphazene (HPGCP) was synthesis and their inhibitive action against the corrosion of carbon steel in 1 M HCl solution were investigated at room temperature by various corrosion monitoring techniques, such as weight loss, potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS) methods. The Hexa glycol cyclotriphosphazene (HPGCP) outcome of solvolysis of Hexa glycidyl cyclotriphosphazene (HGCP) in basic solution. The compounds were characterized using spectroscopic techniques (FTIR).The results showed that the investigated Hexa propylene glycol cyclotiphosphazene (HPGCP) are good corrosion inhibitors for carbon steel in 1 M HCl medium, their inhibition efficiency increased with inhibitor concentration. Polarization studies showed that both studied inhibitors were of anodic type inhibitor in 1 M HCl.The adsorption of inhibitors on the carbon steel surface obeys Langmuir adsorption isotherm. Scanning electron microscopy (SEM) was performed and discussed for surface study of uninhibited and inhibited carbon steel samples.

Keywords: Cyclophosphazene, corrosion inhibitor, HPGCP, electrochemical impedance.

1. Introduction

Acid solutions are commonly used for the removal of undesirable scale and rust in the metal working, cleaning of boilers and heat exchangers. Hydrochloric acids are most widely used for all these purposes. However, over-pickling of metal leads to a rough, blistered coating. Formation of protective film on the steel surface and characterization of metal surface is the major subject of interest. Carbon steel is among the most widely used engineering materials such as metal-processing equipment, marine applications, nuclear and fossil fuel power plants, transportation, chemical processing, pipelines, mining and construction. Iron and its alloys as construction materials in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays [1].

In order to reduce the corrosion rate of metals, several techniques have been applied. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. Inhibitors, which reduce corrosion on metalic materials, can be divided into three kinds: surfactant inhibitors [2], organic inhibitors [3] and inorganic inhibitors [4]. Heterocyclic inhibitors have many advantages such as high inhibition efficiency [5–8], low price, and easy production.

The choice of effective inhibitors is based on their mechanism of action and their electron- donating capability. Moreover, inhibitory ability is reinforced by the presence of the molecular structure of adsorption active sites with the lone pair and or π orbitals, such as heterocyclic rings containing sulphur, oxygen, phosphorus and/or nitrogen atoms [9–11]. These compounds can form either a strong coordination bond with metal atom or a passive film on the surface [12]. The corrosion inhibition of a metal may involve either physisorption or chemisorption of the inhibitor on the metal surface. Electrostatic attraction between the charged hydrophilic groups and the charged active centers on the metal surface leads to physicosorption. Several authors showed that most inhibitors were adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film [13].

The choice of an optimal inhibitor should be based on three considerations: (i) it should have a convenient synthesis from inexpensive raw materials, (ii) the presence of phosphorus, nitrogen, oxygen, sulfur and multiple bonds in the inhibitor molecule are required for its efficiency and (iii) its toxicity toward the environment must be negligible [14].

Cyclophosphazenes are an important group of inorganic heterocyclic compounds containing the [N = PX_2] repeating unit. They have active phosphorus-halogen bonds that can be replaced with nucleophiles, leading to the formation of different types of product which could be region or stereo isomers. The most common members of this family of compounds are hexachlorocyclotriphosphazene, hexaglycidyl ether Cyclotriphosphazene (HGCP) and octachlorocyclotetraphosphazene, and these compounds serve as the starting materials for the synthesis of new compounds and materials [15]. Amino derivatives of cyclophosphazenes have been especially used in a variety of applications in science and technology, such as anticancer reagents, tumor growth inhibitors, biologically active molecules, flame retardants and antimicrobial reagents [15-24].

The present work is aimed to produce the Hexa propylene glycol cyclotriphosphazene (HPGCP) that was obtained by solvolysis of (HGCP) in basic solution of NaOH and we characterize the Hexa propylene glycol cyclotiphosphazene (HPGCP) by FTIR spectroscopy as well as to evaluate its inhibition effect for carbon steel in HCl 1 M using electrochemical techniques.

The purpose of this paper is aimed to produce the Hexa propylene glycol cyclotriphosphazene (HPGCP). The organic compound had been studies on the corrosion inhibition of carbon steel in 1 M HCl at 25°C solution using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The Scanning electron microscopy (SEM) was performed and discussed for surface study of uninhibited and inhibited carbon steel samples.

2. Experimental study

2.1 Materials

Hexaglycidyl cyclotriphosphazene (HGCP) was synthesized in one step according to the procedure literature [15-17]. The reaction was a nucleophilic substitution of cyclophosphazene chlorine by the epoxy function of 2,3-epoxy-1-propanol in presence of triethylamine. HGCP is an insoluble product in water but in order to lad it soluble and test it as corrosion inhibitor, we transform HGCP to Hexa propylene glycol cyclotiphosphazene (HPGCP). This late was obtained by the solvolysis of HGCP in basic solution of NaOH (Fig. 1).

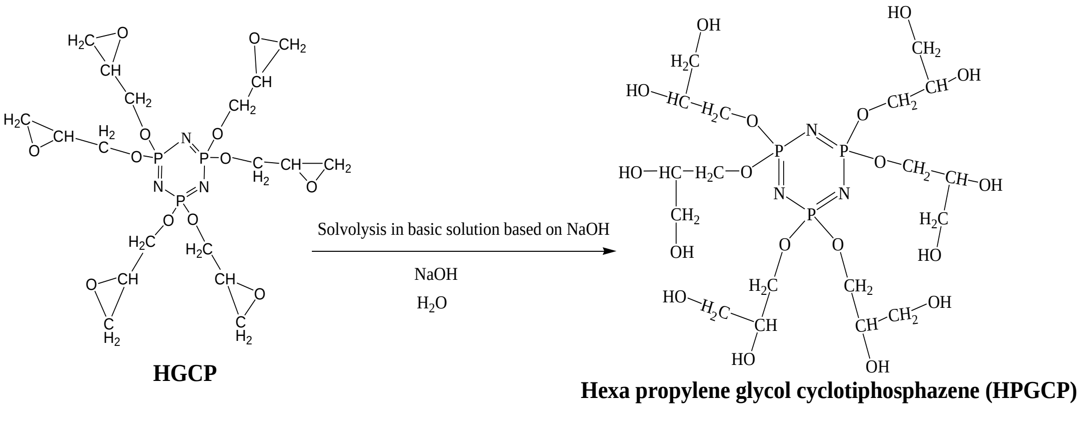


Fig.1. Solvolysis of HGCP in basic solution based on NaOHto product (HPGCP)

2.2. General procedure to produce Hexa propylene glycol cyclotiphosphazene (HPGCP)

In the dry-box, a solution of 10 g of hexaglycidyl cyclotriphosphazene (HGCP) (0.017 mol) in 20 ml of aqueous solution containing 4.18 g of NaOH (0.10 mol) was prepared at room temperature. The mixture was neutralized and filtered to remove salt and water. The obtained product was then dried over Na_2SO_4. A brown solid product, very soluble in water, was finally obtained in good yields about 95%.

2.3. Electrochemical cell

The electrolysis cell (Fig. 2) is a borrosilicate glass (Pyrex®) cylinder closed by a cap with three apertures. The working electrode is a low carbon steel previously used and its composition is summarized in Table1. The investigated area of the surface is 1 cm^2. Prior to the immersion test, the electrode is abraded using emery paper up to 1500 grade, cleaned with ethanol, washed with distilled water, and finally dried finally. Pt plate as the counter electrode while (Ag/AgCl) is used as the reference electrode. All potentials are referred with respect to this electrode. For long exposure experiments, between two measurements, the reference electrode is removed from the test solution to minimize its contamination by chloride ions and the working electrode is immersed for 30 mn before each test. Before each experiment, the carbon steel is polished using emery paper until 1500 grade. After this, it is degreased with ethanol, rinsed with distilled water and finally dried at room temperature.

The aggressive solution (1M HCl) is prepared by dilution of HCl for quality analysis to 37% with distilled water. Corrosion inhibitor solution is prepared by dissolving the desired heterocyclic weight of inhibitor in 1M HCl. Four different concentrations namely, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} mol / L by weight are used for the evaluation of corrosion inhibition.

Table 1. Chemical composition of low carbon steel used in wt%

C	Si	Mn	Cr	Mo	Ni	Al	Cu	Co	V	W	Fe
0.11	0.24	0.47	0.12	0.02	0.1	0.03	0.14	<0.0012	<0.003	0.06	Balance

2.4. Polarization measurements

The working electrode is immersed in test solution during 30 mn until the steady state corrosion potential (E_{corr}) is reached. The cathodic polarization curve is then recorded by polarization from E_{corr} towards more negative direction with a sweep rate of 1 mV/s. After this scan, the same electrode is kept in solution until the obtaining of the steady state corrosion potential ($E_{corr} \pm 0.02$ V), and then the anodic polarization curve is recorded from E_{corr} to positive direction with the same sweep rate. These measurements are carried out using Potentiostat PGZ 100 monitored by a personal computer. For each concentration three independent experiments are performed. The mean values and the standard deviations are reported as well. However, the overall current density, i, is 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, we can consider that both processes obey the Tafel law [25], so we can conclude:

$$i = i_a + i_c = i_{corr} \times \{exp[b_a \times (E - E_{corr})] - exp[b_c \times (E - E_{corr})]\} \quad (1)$$

Where i_{corr} is the corrosion current density (A cm^{-2}), 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 β (V dec^{-1}) in usual logarithmic scale by:

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

The corrosion parameters were then evaluated by means of nonlinear least square method by applying this equation using Origin 6.0 software. However, for this calculation, the potential range applied is limited to ±0.100 V around the E_{corr} else a significant systematic divergence is sometimes observed for both anodic and cathodic branches.

The inhibition efficiency (η) is calculated using the following equation:

$$\eta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (3)$$

Where i^0_{corr} and i_{corr} are the corrosion current density values without and with the inhibitor respectively.

2.5. Electrochemical impedance spectroscopy measurements (EIS)

The electrochemical impedance spectroscopy measurements are carried out using a transfer function analyzer (Voltalab PGZ100, Radiometer Analytical), over the frequency range from 100 kHz to 0.1 Hz with 10 points per decade. The applied amplitude of AC signal is 10 mV_{rms}. All experiments are performed at the open circuit potential. The obtained impedance data are analyzed in termof equivalent electrical circuit using Bouckamp's program [26]. The inhibition efficiency is evaluated from R_p (which is obtained from the diameter of the semicircle in the Nyquist representation) with the relationship:

$$\eta = \frac{R_p - R^0_p}{R_p} \times 100 \quad (4)$$

Where R^0_p and R_p are the resistance polarization values in the absence and in the presence of inhibitor respectively.

2.6. Corrosion weight loss tests

The inhibition efficiency is obtained from the weight loss measurements and the surface coverage of carbon steel at different concentrations of HPGCP in 1M HCl at 25°C after 1 h of immersion in the aggressive solution. All experiments are repeated two times. The carbon specimens are squarer in the form (5 cm×1 cm).After the corrosion test, the specimens are carefully washed in double distilled water, dried and then weighed.

Duplicate experiments are performed in each case, and the mean value of the weight loss is reported. Weight loss allows us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}.h^{-1}$.The resulting quantity, corrosion rate (W_{corr}) is thereby the fundamental measurement in corrosion. W_{corr} can be determined either by chemical analysis of dissolved metal in solution or by gravimetric method measuring weight of specimen before and after exposure in the aggressive solution applying the following equation 5:

$$W_{corr} = \frac{m_i - m_f}{St} \quad (5)$$

Where m_i, m_f, S and t denote initial weight, final weight, surface of specimen and immersion time, respectively. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4} g for determining corrosion rate [27, 28]. The inhibition efficiency E_{WL}% derived from this method was estimated by the following relation 6:

$$E_{WL}\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \quad (6)$$

Where W_{corr} and $W_{corr/inh}$ are the corrosion rate of steel without and with each inhibitor, respectively.

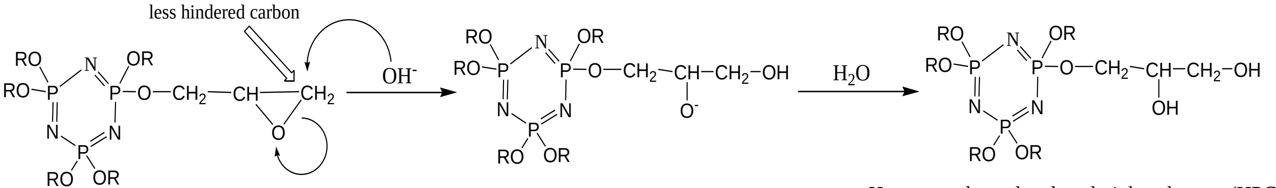
3. Results and discussion

3.1. Characterization of Hexa propylene glycol cyclotiphosphazene (HPGCP)

In this paper, we describe the synthesis Hexa propylene glycol cyclotiphosphazene (HPGCP). The method involves the solvolysis of HGCP in aqueous basic solution containing NaOH. This route leads to the exclusive formation of Hexa propylene glycol cyclotiphosphazene (HPGCP).

The reaction was a nucleophilic attack of epoxies of HGCP by hydroxyl anion of basic solution. This reaction causes the ring opening of epoxy group.

Ring-opening reactions can proceed by either SN2 or SN1 mechanisms [29], depending on the nature of the epoxide and on the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism dominates. When an asymmetric epoxide undergoes solvolysis in basic solution, ring-opening occurs by an SN2 mechanism, and the less substituted carbon is the site of nucleophilic attack, leading to what we will refer to as product Hexa propylene glycol cyclotiphosphazene (HPGCP) (Fig. 2).



Hexa propylene glycol cyclotiphosphazene (HPGCP)

HGCP

Fig. 2. Mechanism of ring opening reaction of epoxides during solvolysis of HGCP in basic solution based on NaOH

The leaving group is an alkoxide anion, because there is no acid available to protonate the oxygen prior to ring opening. An alkoxide is a poor leaving group, and thus the ring is unlikely to open without a 'push' from the nucleophile. The FTIR spectra of HGCP and HPGCP were displayed in figure 3.

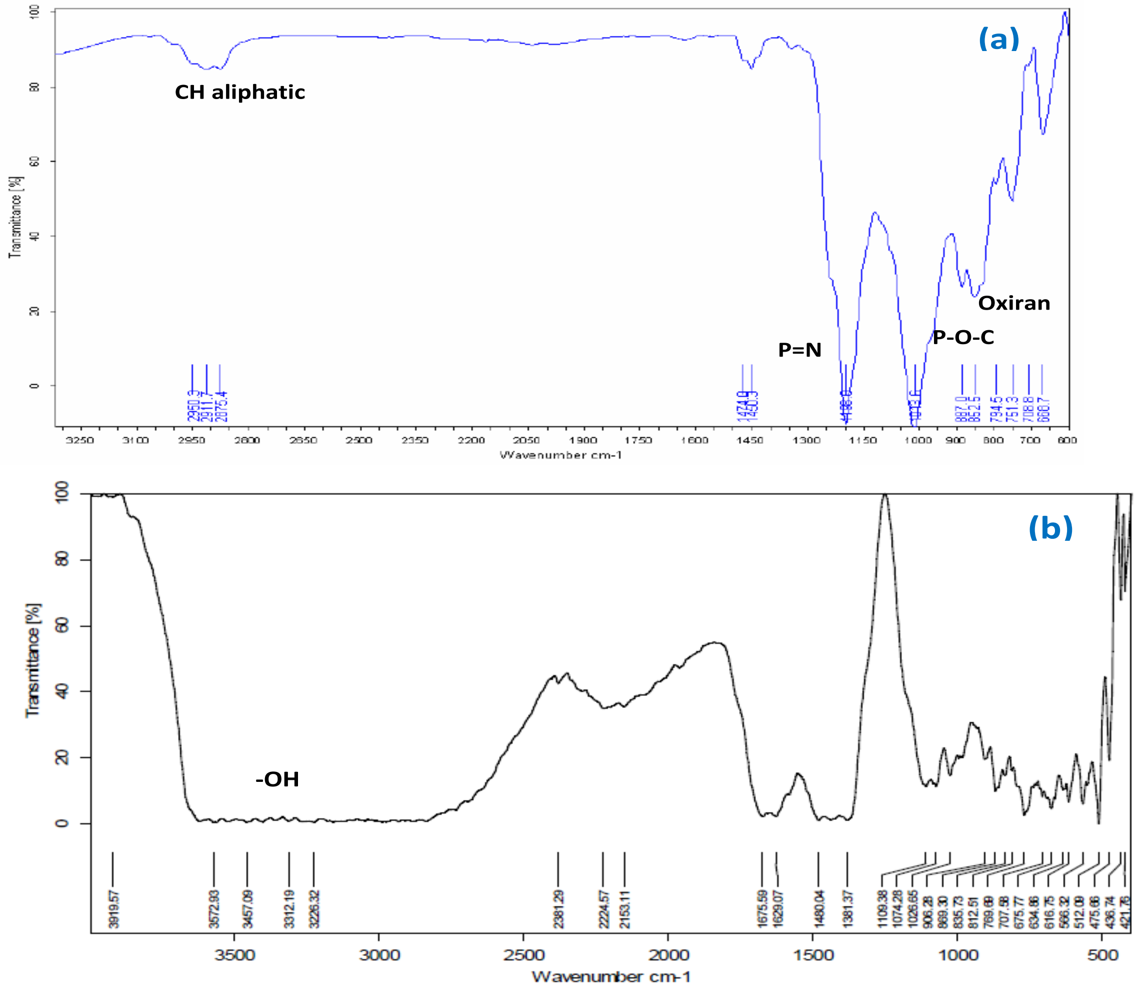


Fig. 3. FTIR spectra of HGCP (a) and HPGCP (b)

It is observed that the absorption peak between 1266 and 1200 cm^{-1} corresponds to the P=N stretching, and bands around1013 cm^{-1} for P-O-C units are observable, while the absorption peaks at 852 cm^{-1} corresponding to oxiran ring bond in the spectrum of HGCP disappear in the spectra of

HPGCP. Instead, the absorption peak at 2927, 2965 cm^{-1}indicates only the (asymmetric and symmetric γ of C–H units) in the spectrum of HGCP, a strong and large absorption peak between 2800 cm^{-1} and 3600 takes place in the spectrum of HPGCP corresponding to the hydroxyl stretching (–OH) and asymmetric and symmetric of C–H units. This proves the ring opening of epoxy groups.

3.2 Gravimetric measurements

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of carbon steel for different concentrations of HPGCP in 1M HCl at 25°C after 1 h of immersion are given in table 2.

Table 2. Corrosion rate of carbon steel and inhibition efficiency at different concentrations of HPGCP in HCl 1 M obtained from weight loss and surface coverage (θ) measurements at 298 K after 1 h of immersion

Inhibitor	**Concentration (C) M**	**Weight loss W_{corr} / mg.cm^{-2}.h^{-1}**	**E_W %**	**θ**
Blank	00	1.2	-	-
HPGCP	10^{-3}	0.105	91	0.91
	10^{-4}	0.082	93	0.93
	10^{-5}	0.054	96	0.96
	10^{-6}	0.061	95	0.95

It can be seen from table 2 that results indicate that the compound HPGCP in question inhibit carbon steel corrosion in chloride acid environments, the efficiency values of inhibition decreases substantially with the increase of the concentration of the inhibitor, but the optimum valueis10^{-5} M indicating that the upper cover of the inhibitor on the surface are obtained in a solution with a lower concentration of inhibitor.

The results obtained from weight loss measurements are in agreement with the ones obtained from impedance and polarization data.

3.3. Potentiodynamic polarization measurements

Figure 4 presents potentiodynamic polarization curves for carbon steel in 1M HCl containing different concentrations of HPGCP.

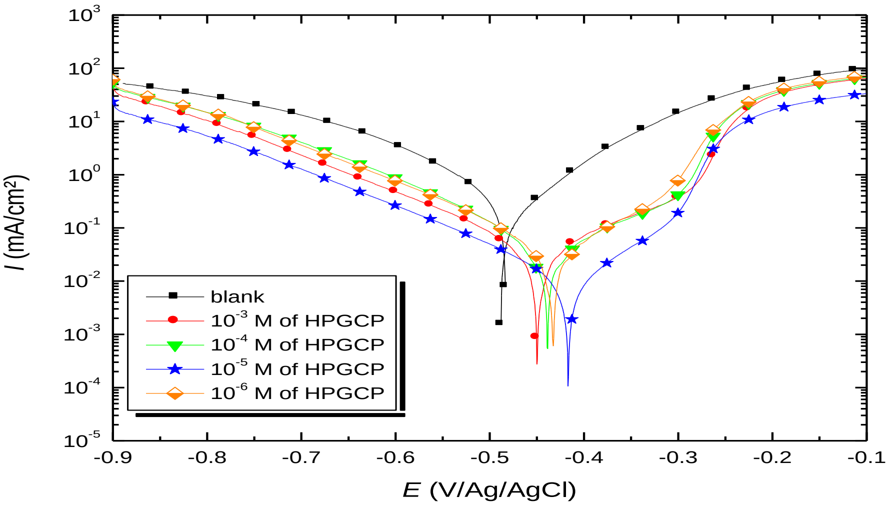


Fig.4. Polarization curves for ordinary steel in 1M HCl in the absence and presence of various concentrations of HPGCP after 30 mn of immersion at 25°C, |dE/dt | =1 mVs^{-1}

It can be remarked that the anodic branches do not exhibit well-defined Tafel regions. It is seen also that the inhibitors addition hinders the acid attack on carbon steel. Indeed, the results indicate that the compound HPGCP in question inhibit carbon steel corrosion in chloride acid environments. The efficiency values of inhibition increases substantially with the decrease of the concentration of the inhibitor and attains the maximum value of 97% at 10^{-5} M indicating that the upper cover of the inhibitor on the surface is obtained in a solution with a lower concentration of inhibitors. This inhibitor acts on the electrode dissolution reaction such as anodic type inhibitor.

However, i_{corr}, E_{corr}, β_a and β_c are evaluated from the experimental results using a user defined function of ''Non-linear least squares curve fit'' (Eq. (1)) of graphic software (Origin, OriginLab). In all cases, the correlation factor R^2 is greater than 0.99 indicating a reliable result. Figure 6 shows us for example the results of regressive calculations for the cathodic and anodic scan in the presence of different concentrations of HPGCP. In this calculation, the potential domain is limited to E_{corr} ± 100 mV.

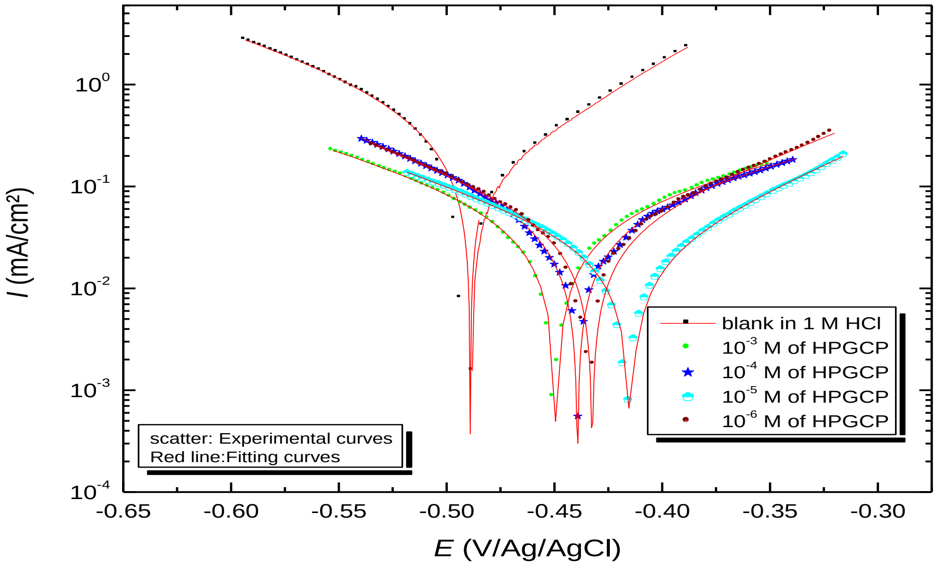


Fig.5. Comparison of experimental data by mounting a non-linear fitting with Stern-Geary equation (for different concentrations HPGCP)

It can be seen in figure 4 a good agreement between the experimental and fitting data (Fig 5).

Table 3 summarizes the obtained corrosion kinetic parameters. E_{corr} and the kinetic parameters calculated by a non-linear regression calculation from the anodic polarization scans near the open circuit potential are similar to those determined from the cathodic polarization scans, though i_{corr} is slightly higher. It can be seen that the i_{corr} values decreased with concentrations of HPGCP and the least value is obtained at 10^{-5} M, due to the increase in the blocked fraction of the electrode surface by adsorption. This may be due to the adsorption of inhibitors at carbon steel surface through non-bonding electron pairs present on nitrogen, oxygen and phosphorus atoms as well as π-electrons [9–11]. The high inhibitive performance of HPGCP suggests a higher bonding ability on carbon steel surface, which possesses higher numbers of lone pairs on heteroatoms and π-orbitals. The electron lone pair on the nitrogen will coordinate with the metal atoms of active sites [30]. The presence of lone pairs of electrons on the nitrogen atoms of the additional nitrogen atoms delocalized produces a delocalization energy that stabilizes the compound. Also, it is known that heterocyclic nitrogen compounds may also adsorb through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface [31].

Table 3. Electrochemical parameters for ordinary steel in 1M HClcontaining different concentrations (*C*) of HPGCP

HPGCP *C* (M)	E_{corr} (mV/Ag/AgCl)	I_{corr} (μA/cm²)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	η (%)
Blank	-490	774	104	164	-
10^{-3}	-449	52	184	164	93
10^{-4}	-439	49	169	125	94
10^{-5}	-414	23	105	135	97
10^{-6}	-432	39	121	121	95

3.4. Electrochemical impedance spectroscopy

The corrosion behavior of carbon steel in 1M HCl in the absence and the presence of HPGCP are investigated by EIS at 298 K after immersion for 30 mn. Nyquist plots for carbon steel in uninhibited and inhibited 1M HCl are shown in figure 6 (Impedance spectra). The impedance spectra show that a single semi circle and the diameter of the semi-cercal. The results indicate that the compound HPGCP in question inhibit carbon steel corrosion in chloride acid environments, the efficiency valuesof inhibition increases substantially with the decrease of the concentration of the inhibitor, but the optimum valueis10^{-5} M indicating that the upper cover of the inhibitor on the surface is obtained in a solution with a lower concentration of inhibitors. These diagrams show that the impedance spectra consist of one capacitive loop at high frequency, the high frequency, capacitive loop is attributed to charge transfer of the corrosion process [32].

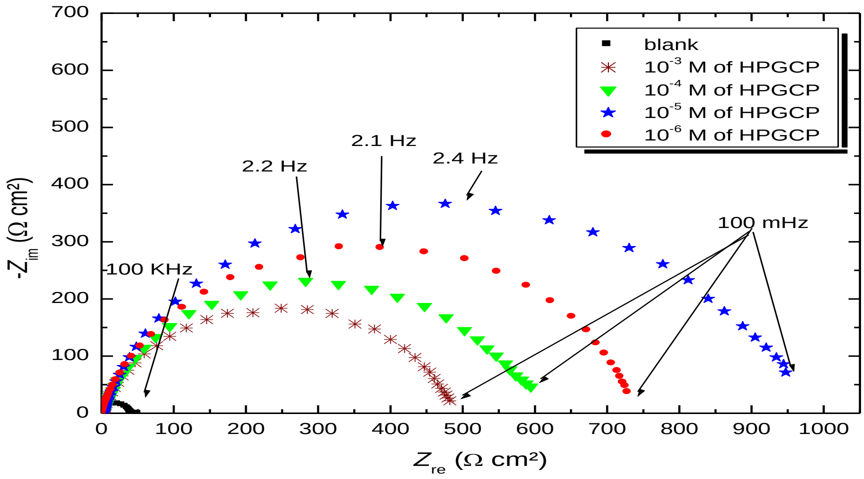


Fig.6. Nyquist diagrams for carbon steel electrode with and without HPGCP at different concentrations after 30 mn of immersion.

Figure 7 and 8 shows Nyquist plots and the representative Bode diagrams for carbon steel in 1 M HCl in the presence of various concentrations of HPGCP to the aggressive solution leads to a change of the impedance diagrams in both shape and size, in which a depressed semicircle at the high frequency part of the spectrum was observed. The increase in size of the semicircle with inhibitor concentration means that the inhibitor effect increases as well.

Values of the charge transfer resistance R_{ct} were obtained from these plots by determining the difference in the values of impedance at low and high frequencies [33]. The effective capacity C_{dl} can be estimated using the following mathematical formulas from the CPE:

$$C = Q^{1/act} * R^{(1-act)/act} \qquad (7)$$

The equivalent circuit model employed for these systems is presented in figure 9.

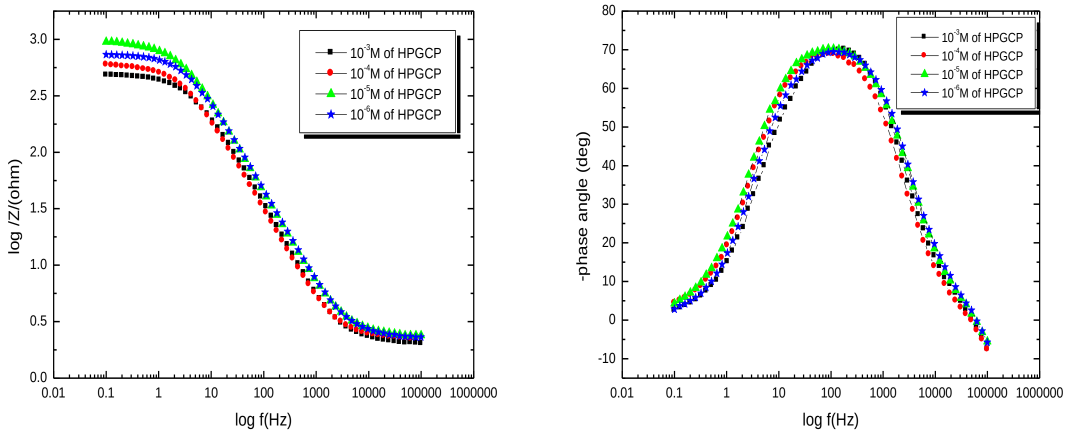


Fig .7. Nyquist and Bode diagrams for carbon steel in 1 M HCl at different concentrations of HPGCP

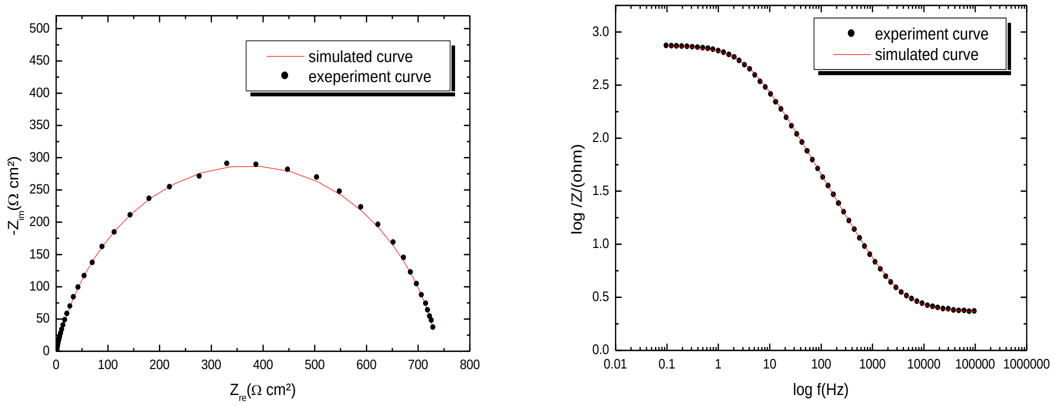


Fig.8. EIS Nyquist and Bode diagrams for carbon steel/1 M HCl + 10^{-6} M of HPGCP interface: (···) experimental; (—) fitted data using structural model in Fig. 9.

The results described below can be interpreted in terms of the equivalent circuit of the electrical double layer shown in fig. 7, which has been used previously to model the iron-acid interface [34].In this equivalent circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE is a constant phase element. Excellent fit with this model was obtained for all experimental data. As an example, the Nyquist and Bode plots for 1 M HCl solution at 10^{-6} M are presented in Fig. 8.

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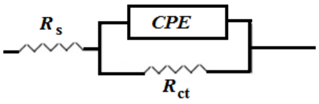

Fig.9. The electrochemical equivalent circuit used to fit the impedance spectra

Table 4 gives the values of the charge transfer resistance R_{ct}, double-layer capacity C_{dl}, and inhibition efficiency obtained from the above plots. It can be seen that the presence of HPGCP enhances the values of R_{ct} and reduces the C_{dl} values. The decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electric double layer [35], suggests that HPGCP molecules function by adsorption at the metal/ solution interface. Thus, the decrease in C_{dl} values and the increase in R_{ct} values and consequently the inhibition efficiency may be due to the gradual replacement of water by the adsorption of the HPGCP molecules on the metal surface, decreasing the extent of dissolution reaction [36].

Table 4. Electrochemical impedance parameters for corrosion of carbon steel in acid medium at various contents of HPGCP

HPGCP ***C (M)***	C_{dl} $(\mu F/cm^2)$	a_{ct}	R_{ct} $(\Omega.cm^2)$	η (%)	$f(-Z_{imax})$ Hz
Blank	295	0.62	40	-	13.35
10^{-3} M	135	0.82	488	92	2.4
10^{-4} M	120	0.82	600	93	2.2
10^{-5} M	70	0.82	963	96	2.4
10^{-6} M	98	0.84	744	95	2.1

with a_{ct} is the degree of heterogeneity

3.5. Effect of immersion time

Figures 10 shows the impedance spectra at different immersion times in 1M HCl containing 10^{-5} M of HPGCP.

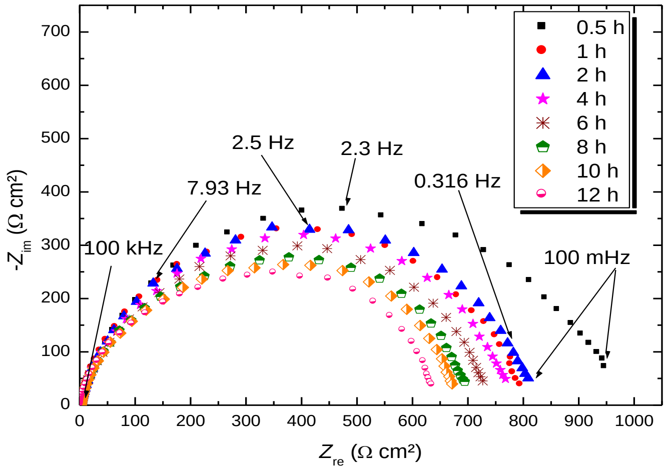

Fig.10. Electrochemical impedance spectra obtained after different immersion time in 1M HCl with 10^{-5} M of HPGCP

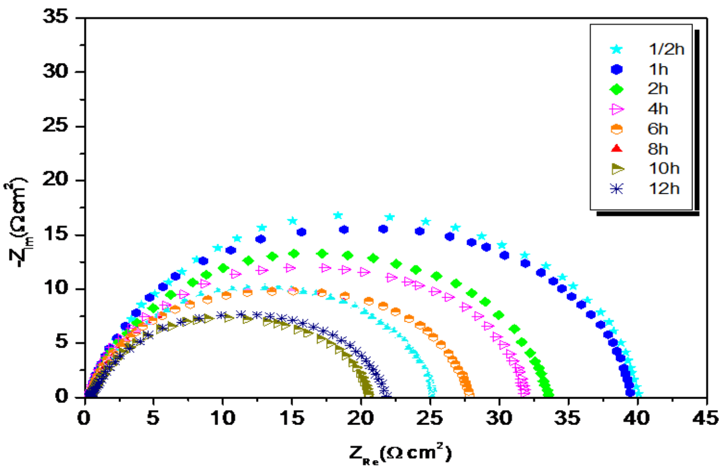

Fig.11. Electrochemical impedance spectra obtained after different immersion time in 1M HCl without HPGCP

The parameters evolution with time is summarized in Table 5. The diameter of the capacitive loop slightly decreases in size with increasing immersion time. On the other hand, at 10^{-5} M of HPGCP, the film capacitance decreases with immersion time.

To pursue the electrochemical study at different concentrations and to relate the results obtained with the demonstrated effectiveness of the HPGCP corrosion inhibiting properties has been achievedon a point basis. However, it would be a more central interest to evaluate the inhibitor's temporal behavior through the kinetics associated to relatively long immersion times. Figure 10 and 11 shows the impedance results with values reaching C_a (657 Ωcm^2) after 12 h immersion, the impedance spectra clearly depicts two well resolved time constants, one related to the substrate while the other refers to the organic molecules' charge transfer resistance as the HPGCP used suggests. Table 5 shows the variation of the R_{ct} data derived as a function of the immersion time. From this Table it is possible to note that during the 12 h the IE increases the maximum value attaint 97%.

Table 5. Electrochemical impedance parameters for carbon steel in 1M HCl with and without 10^{-5} M at different immersion times.

Time (h)	**HPGCP *C* (M)**	***C_{dl}* (µF/cm²)**	***a_{ct}***	***R_{ct}* (Ω.cm²)**	***η* (%)**
½	Blank	295	-	40	-
1		296	-	39	-
2		297	-	34	-
4		305	-	33	-
6		320	-	27.5	-
8		335	-	25	-
10		355	-	21	-
12		370	-	20	-
½	10^{-5}	70	0.82	963	96
1		100	0.87	800	95
2		105	0.86	819	95.8
4		110	0.86	781	95.7
6		113	0.85	743	96.3
8		119	0.84	711	96.5
10		125	0.83	692	97
12		133	0.82	657	97

3.6. Adsorption isotherm

It is generally assumed that the inhibitor adsorption onto the metal/solution interface is the first step in the mechanism of inhibition in aggressive media. Four types of adsorption may take place by heterocyclic molecules at the metal/solution interface: (1) electrostatic attraction between the charged metal and the charged molecules, (2) interaction of uncharged electrons pair in the molecule with the metal, (3) interaction of π electrons with the metal and (4) combination of (1) and (3) [36]. Chemical adsorption involves the share or charge transfer from the molecules onto the surface to form a coordinate type bond. Electron transfer is typical for transition metals having vacant low energy electron orbital. As for inhibitors, the electron transfer can be expected with compounds having relatively loosely bound electrons. A correlation between θ and inhibitor concentration C in the aqueous solution can be represented by the Langmuir adsorption isotherm [37, 38]:

$$\theta = \frac{KC}{1 + KC} \quad (8)$$

Rearranging this equation, it becomes:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (9)$$

Where *K* represents the constant of adsorption reaction.

Figure 11 exemplifies the relation between *C/θ* and *C* at 25°C. It yields a straight line with slope close to unity. The strong correlation ($r^2 = 0.999$) for the Langmuir adsorption isotherm plot confirms the validity of this approach. The constant *K* may be determined from the intercept in figure 10 according to the following assumptions:

(1) The inhibitor forms a mono (molecules) layer on the iron surface at the maximum corrosion inhibition using weight loss measurements.
(2) There is no interaction between the adsorbed species on the electrode surface [37].
(3) HPGCP is adsorbed via P on the iron surface.

Thus, we obtained the value of *K* for the inhibitor used: $K = 3, 46.\ 10^6$ L.mol^{-1}. The adsorptive equilibrium constant *K* is in relation with the standard free energy of adsorption [37, 39].

$$K = \frac{1}{55.55}\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (10)$$

Where *R* is the universal gas constant, *T* is the thermodynamic temperature and value of 55.55 is the water concentration in the solution (mol.L^{-1}).

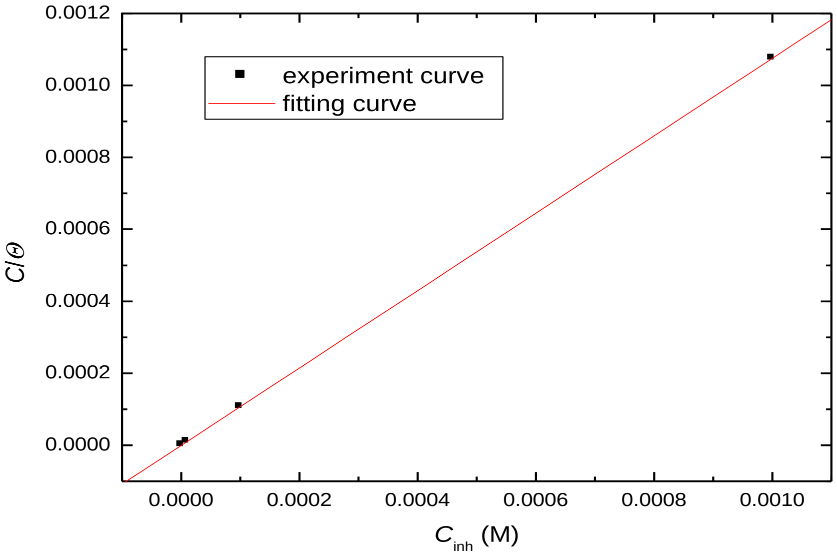

Fig.12. Plot of the Langmuir adsorption isotherm of HPGCP on the carbon steel surface at 298 K

ΔG_{ads}

The value of standard free energy of adsorption ΔG_{ads} is calculated from the adsorption isotherm. It is - 47, 23 kJ mol^{-1} at 25°C.

It is well known that values of ΔG_{ads} of the order of 20 kJ/mol or lower indicate a physisorption, those of order of 40 kJ/mol or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a co-ordinate [32, 37, 39].

The calculated ΔG_{ads} value for HPGCP is slightly superior to -40 kJ/mol, indicating strongly interaction of HPGCP onto the carbon steel surface [40, 41].

3.7. Adsorption mechanism

Adsorption of heterocyclic inhibitors on a corroding metal depends mainly on the charge of the metal surface, the charge or the dipole moment of heterocyclic inhibitors, and the adsorption of other ionic species if it is electrostatic in nature. The potential of zero charge (PZC) plays a very important role in the electrostatic adsorption process.

In the work, we showed that the potential of zero charge (PZC) is -540 mV/Ag/AgCl which is more negative than the corrosion potential is - 490 mV/Ag/AgCl **(**Fig.12). This result suggests that the carbon steel surface is positively charged [42].

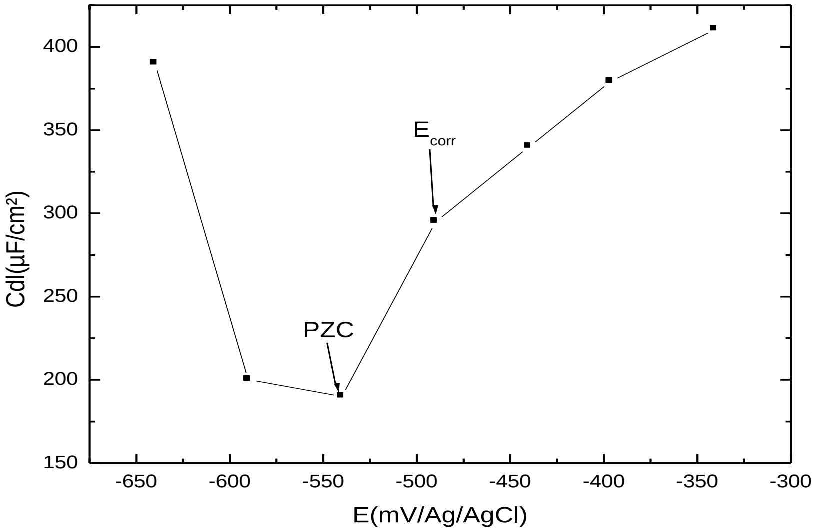

Fig.13. Relationship between C_{dl} values and the applied potential for carbon steel electrode in 1 M HCl solution at 25 °C.

Conclusion

The studied HPGCP shows excellent inhibition properties for the corrosion of carbon steel in 1M HCl at 298 K, and the results indicate that the compound HPGCP in question inhibit carbon steel corrosion in acid chloride environments, the efficiency values of inhibition increases substantially with the decrease of the concentration of the inhibitor, but the optimum valueis10^{-5} M, indicating that the upper cover of the inhibitor on the surface is obtained in a solution with a lower concentration of inhibitors. The concentration dependence of the inhibition efficiency calculated from weight loss measurements and electrochemical studies are in good agreement. Based on the polarization results, the investigated HPGCP acts predominantly as an anodic-type inhibitor. Adsorption of HPGCP on the carbon steel surface in 1M HCl obeys the Langmuir adsorption isotherm model and leads to strongly interaction adsorption of inhibition corrosion.

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