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Theoretical studies of cyclophosphazene derivative as corrosion inhibitor for carbon steel in sodium chloride

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ABSTRACT

The aim of the work is to assess the inhibition performance of hexa propylene glycol cyclotiphosphazene (HPGCP) on the corrosion of carbon steel in 3% NaCl solution and examine its inhibition mechanism, furthermore, to elucidate the possible adsorption model on the corroding carbon steel surface and advance the understanding of interactions between the inhibitor molecules and the carbon steel surfaces. The effect of this inhibitor on the carbon steel was studied by weight loss and quantum chemical calculations. The adsorption of HPGCP on the carbon steel surface was well described by the Langmuir adsorption model. The inhibition mechanism was determined by potential of zero charge measurements and some electronic parameters.

Key words: Quantum chemical calculations, potential of zero charge, HPGCP, carbon steel, 3% NaCl.

INTRODUCTION

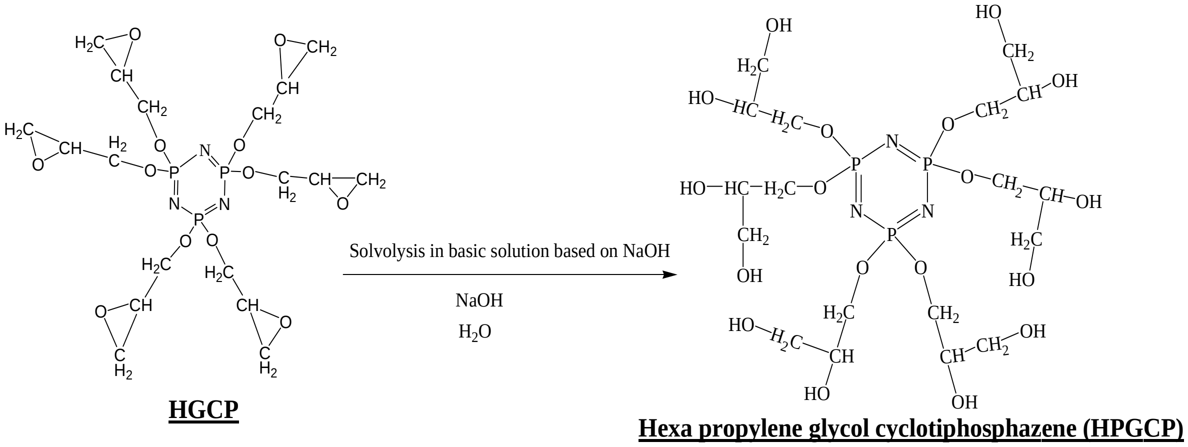
The chemistry of heterocyclic molecules containing functional groups and heteroatoms such as nitrogen, oxygen, phosphorus and sulphur is attracting current interest in life sciences, due to their specificity for biological targets, due to their specificity for biological targets. These compounds are also of importance for building polynuclear complexes as models for bioorganic systems [1-4]. A number of these compounds were found to be excellent inhibitors of steel corrosion [5-6]. The presence of the heteroatoms in these molecules has a major effect on the inhibition efficiency and consequently on the phenomenon of absorption of these compounds can form either a strong coordination bond with metal atom or a passive film on the surface [7-10].

In this work, Hexa propylene glycol cyclotiphosphazene (HPGCP) has been prepared by the solvolysis of HGCP epoxy resin [11-13] in basic solution of NaOH to investigate its inhibition effect on the corrosion of carbon steel in3% NaCl solution.The effect of this inhibitor on the carbon steel was studied by weight loss and quantum chemical calculations. The adsorption of HPGCP on the carbon steel surface was well described by the Langmuir adsorption model. The inhibition mechanism was determined by potential of zero charge by electrochemical impedance spectroscopy (EIS) measurements.

MATERIALS AND METHODS

2.1 Materials

Hexaglycidyl cyclotriphosphazene (HGCP) was synthesized in one-step according to the procedure literature [11]. 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 The Hexa propylene glycol cyclotiphosphazene (HPGCP). This latewas obtained by solvolysis of HGCP with basic solution of NaOH (Fig. 1).



HGCP

Hexa propylene glycol cyclotiphosphazene (HPGCP)

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

2.2 General procedure to product 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 (0.10mol) 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 yieldsabout 95%.

2.3. Quantum chemical calculations

The quantum chemical calculations were performed on an Intel (R) core $(TM)_2$ Quad CPU (2.4 GHz and 5 GB RAM) workstation.

For the theoretical study, complete geometry optimizations of HGCP and HPGCP were performed using the Density Functional Theory (DFT) with the Beck’s three parameter exchange functional and the Lee Yang–Parr non-local correlation functional (B3LYP) [14–16] with 6-31++G(d,p)basis set of atomic orbitals. It was drawn using Gauss View, 5.0implemented in Gaussian 03 package [17]. This approach was shown to yield geometries in agreement with experiment for a wide variety of systems. Furthermore, DFT was considered a very useful technique to probe the inhibitor/surface interaction.

The corresponding geometries were optimized without any geometry constraints for geometry optimization. Frequency calculations were executed simultaneously and no imaginary frequency was found indicating a minimal energy structure. According to Koopman’s theorem [18], E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential, I, and the electron affinity A, respectively, by the following relations:

$$I = - E_{HOMO} \quad (1)$$

$$A = - E_{LUMO} \quad (2)$$

The number of transferred electrons (ΔN) was also calculated according to Eq. (3) [19].

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} - \eta_{inh})} \quad (3)$$

Whereχ_{Fe}andχ_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively, η_{Fe} andη_{inh}denote the absolute hardness of iron and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential (I) [20].

$$\chi = \frac{I + A}{2} \quad (4)$$

$$\eta = \frac{I - A}{2} \quad (5)$$

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 [21],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).

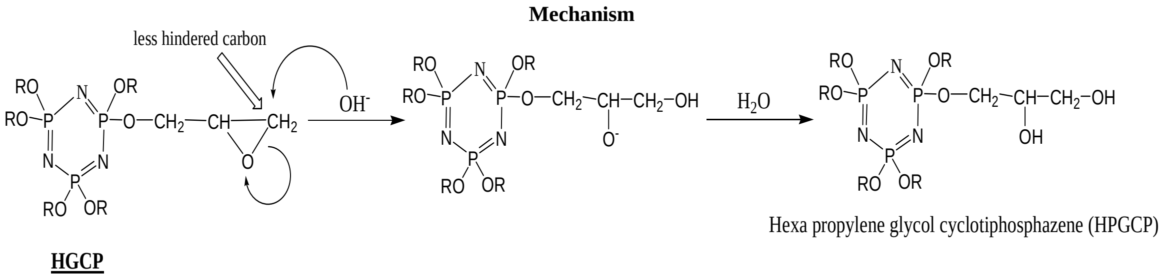


Figure 2. Mechanism of ring opening reaction of epoxides duringsolvolysis of HGCP in basic solution based on NaOH

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. 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. Global molecular reactivity

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible of the interaction metallic surface/molecule [22–24]. The terms involving the frontier molecular orbitals (FMO) could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference ($\Delta E = E_{LUMO} - E_{HOMO}$).

The HOMO energy (E_{HOMO}) is often associated to the electron donating ability of the molecule; therefore, inhibitors with high values of E_{HOMO} have a tendency to donate electrons to appropriate acceptor with low empty molecular orbital energy. Conversely, the LUMO energy (E_{LUMO}) indicates the electron accepting ability of the molecule, the lowest its value the higher the capability of accepting electrons. The gap energy between the frontier orbitals (ΔE) is another important factor in describing the molecular activity, so when the gap energy decreased, the inhibitor efficiency is improved [25].That is tosay, a large HOMO–LUMO gap implies high stability for the molecule in chemical reactions.

In this study, quantum chemical calculations were performed to investigate the relationship between two molecular structures of cyclophosphazene derivatives and their inhibition effects. The two optimized molecular structures and the frontier molecule orbital density distribution of the studied molecules are shown in figure 4, and the calculated quantum chemical parameters E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO} - E_{HOMO}), the electronegativity (χ), the dipole moment (μ), the global hardness (η) and number of transferred electrons (ΔN) were calculated are given in Table 1.

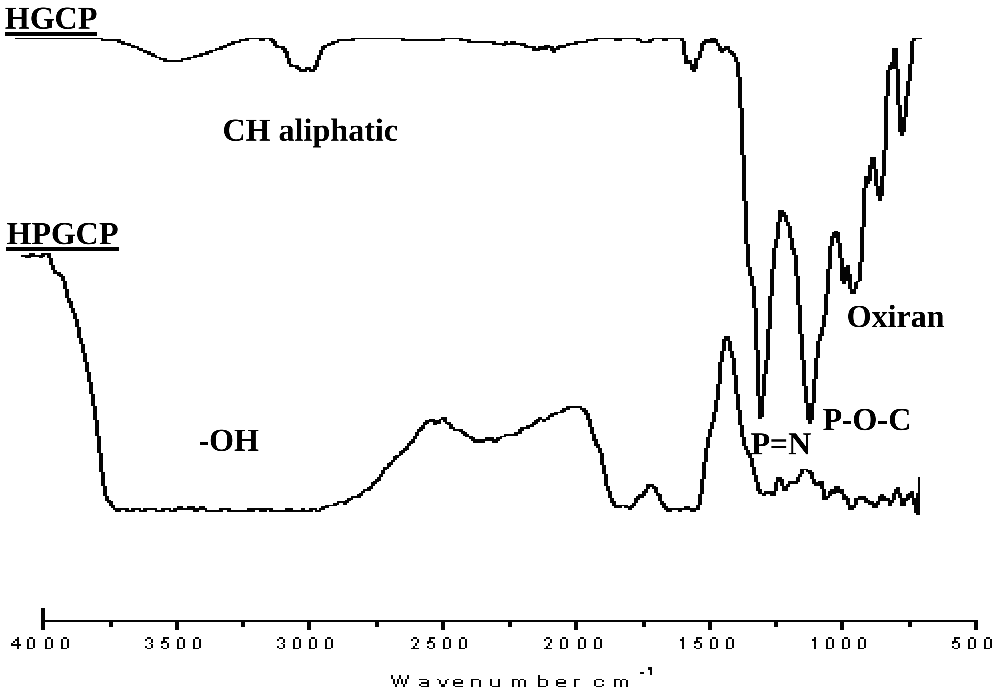


Figure 3.FTIR spectra of HGCP and HPGCP

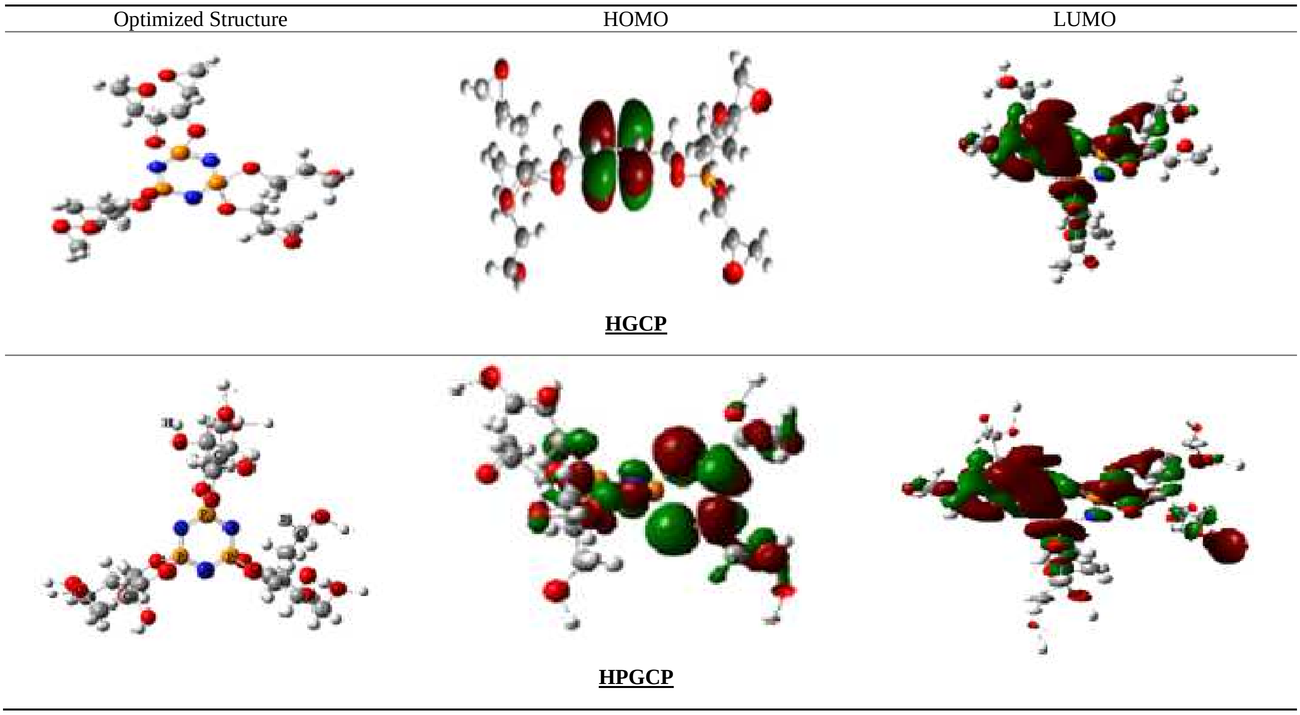


Figure 4. Optimized molecular structures, HOMO and LUMO distribution for HGCP and HPGCP

Table 1. Geometrical parameters of the studied inhibitors calculated at B3LYP/6-31++G (2d, 2p)

Product	Method	E_{Homo}(eV)	E_{Lumo} (eV)	ΔE (eV)	μ (D)	A (eV)	I (eV)	χ (eV)	η (eV)	ΔN
HGCP	DFT	-5,243	- 0,679	5,841	9,112	0,679	5,243	2,961	2,282	0,885
HPGCP	DFT	-8,91	-4,01	4,9	11,21	4,01	8,91	6,46	2,45	0,110

It is seen that the highest E_{HOMO} is obtained for HPGCP, this result is not sufficient to conclude that HPGCP is more efficient than HGCP. Therefore, the high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low empty molecular orbitals. Indeed, the excellent corrosion inhibitors are usually the heterocyclic compounds which not only give electrons to the unoccupied orbital of metal, but also to accept free electrons from it [26].

The dipole moment (μ) provides information on the polarity of the whole molecule. High dipole moment values are reported to facilitate adsorption by influencing the transport process through the adsorbed layer [27]. Several study have stated that the inhibition efficiency increases with dipole moments values [28,29]. The dipole moments of HGCP and HPGCP are 9,112 D and 11,21 D, respectively, which are higher than that of H_2O ($\mu = 1.88$ D). The high dipole moment value of these compounds probably indicates strong dipole–dipole interactions between them and metallic surface [30].

The theoretical values of $\chi_{Fe}$and η_{Fe} are 7 and 0 eV/mol, respectively [31]. The fraction of electrons transferred from inhibitor to the iron molecule (ΔN) was calculated. According to other reports [31, 32], if the value of the fraction of electrons transferred (ΔN) is below 3.6, which indicates the tendency of a molecule to donate electrons to the carbon steel surface, then the higher its value the better the corrosion inhibitive efficiency. The obtained values of ΔN reported in Table 1, show that the HPGCP have the highest value of ΔN (0.110) and HGCP have the lowest value (0.845), which implies good disposition of HPGCP to donate its electrons to the carbon steel surface when compared to HGCP because of the opening of epoxy rings create more hydroxide groups responsible to the good adsorption in surface carbon steel.

The optimized geometries of the studied compounds in the neutral form including their HOMO and LUMO distributions density are shown in figure. 4.

It can be seen that HGCP and HPGCP have a similar LUMO distribution. In addition, the HOMO electronic density in HPGCP was distributed on its entire, while in HGCP, HOMO electronic density was restricted to the core of cyclophosphazene.

3.3. Adsorption isotherm

From the above finding, we can say that HPGCP is adsorbed on carbon steel. As far as the inhibition processif is concerned, it is generally assumed that the adsorption of the inhibitor at the metal–solution interface is the first step in the action mechanism of inhibitors in aggressive media. Four types of adsorption may take place involving organic molecules at the metal solution interface: (1) electrostatic attraction between charged molecules and the charged metal, (2) interaction of unshared electron pairs in the molecules with the metal, (3) interaction of π-electrons with the metal, and (4) a combination of the above [33].

Chemisorption involves charge sharing or charge transfer from the inhibitor molecules to the surface to form a coordinate-type bond. In fact, electron transfer is typical for transition metals having vacant, low-energy electron orbitals. Electron transfer can be expected with compound having relatively loosely bound electrons [34].

A correlation between θ and inhibitor concentration (C) in the electrolyte can be represented by the Langmuir adsorption isotherm, which expressed as [35, 36]:

$$\frac{\theta}{1-\theta} = K_{ads} C_{inh} \qquad (6)$$

Or

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (7)$$

where K is the equilibrium constant of the adsorption process and C the inhibitor concentration.

The best fitted straight line was obtained from the plot of C/θ against C (Fig. 5). The correlation coefficient (R^2) was used to choose the isotherm that best fit with the experimental data (Table 2).

Figure 5. Plot of the Langmuir adsorption isotherm of HPGCP on the carbon steel surface at 298K

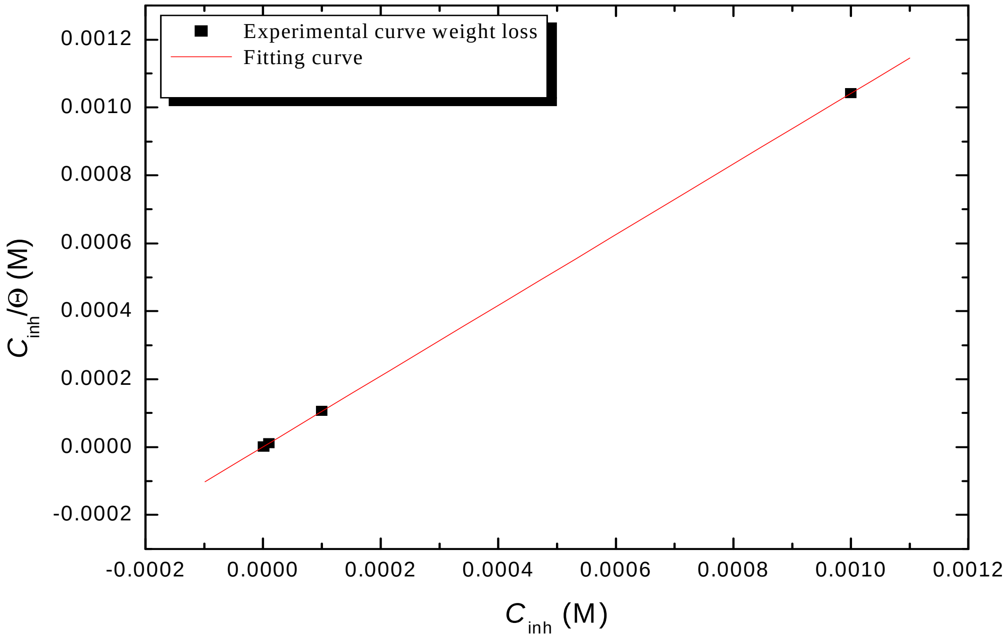


Table 2. Corrosion rate of carbon steel and inhibition efficiency at different concentrations of HPGCP in 3% NaCl obtained from weight loss

	Concentration (M)	**Gravimetric measurements**
Blank	00	-
HPGCP	10^{-6}	92 %
	10^{-5}	93 %
	10^{-4}	94 %
	10^{-3}	96 %

It is known that K_{ads} denotes to the strength between adsorbate and adsorbent. Large values of K_{ads} imply better inhibition efficiency [37].

The results showed high value of K_{ads} indicating a strong interaction and a strong adsorption.

The relation between equilibrium constant of adsorption K_{ads} and the standard free energy ΔG^0_{ads} was given by the following equation [38] (Table 3) :

$$K=\frac{1}{55.55}\exp\left(-\frac{\Delta G^0_{ads}}{RT}\right) \qquad (8)$$

where R is the universal gas constant, value 55.55 is the water concentration in the solution (M).

Table 3. Langmuir adsorption parameters.

HPGCP	**K_{ads} ($M^{-1}\times10^6$)**	**ΔG°_{ads} (kJ mol^{-1})**	**R^2**
Gravimetric measurements	1,18	-44.62	0.9999

It is well known that values 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 inorganic heterocyclic molecules to the metal surface to form a co-ordinate.

The calculated value for hexa propylene glycol cyclotiphosphazene is slightly superior to - 40 kJ/mol, indicating strong interaction of HPGCP onto the carbon steel surface [39, 40].

3.4. Adsorption mechanism

The inhibitors usually act at the metallic surface by forming an adsorption film or by inducting the formation a layer of corrosion products. This adsorption depends on the charge of the metallic surface, the charge or the dipole moment of the inhibitor molecule and the adsorption of other ionic species present on solution [41].

The surface charge of a metal can be determined by comparison of its corrosion potential (E_{corr}) with respective the potential of zero charge (PZC), which plays an important role in the adsorption electrostatic process [42].

To know if the charge of the electrode is positive or negative the difference between the corrosion potential and PZC of the corroding metal was determined. Thus, a set of impedance spectra for carbon steel in 3% NaCl in a potential gamme between -709 mV/Ag/AgCl and -409 mV/Ag/AgCl was obtained.

The results deduced from the measured impedance spectra at selected electrode potentials were depicted in figure 6. The potential of zero charge (PZC) is - 659 mV/Ag/AgCl which is more negative than the corrosion potential is - 559 mV/Ag/AgCl. This result suggests that the carbon steel surface is positively charged [43].

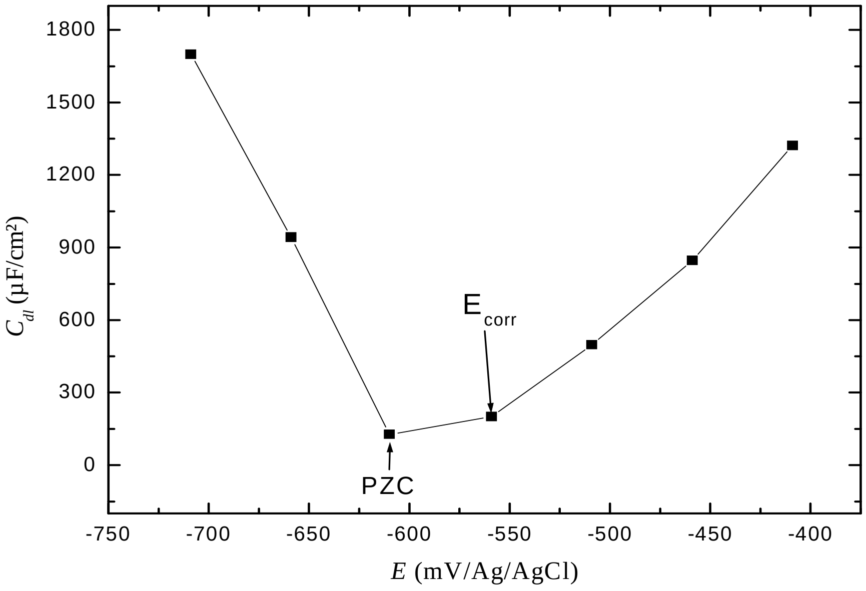


Figure 6. Plot of C_{dl} vs. applied electrode potential (E/ Ag/AgCl) in blank solution

The adsorption of HPGCPon the metal surface can occur either directly on the basis of donor–acceptor interactions between the oxygen and the vacant d-orbitals of steel surface atoms or an interaction of organic nitrogen compounds with already adsorbed groups. Immediately afterward, as the corrosion reaction starts, ferrous ion is surrounded by two oxygen atoms as explained in figure 7.

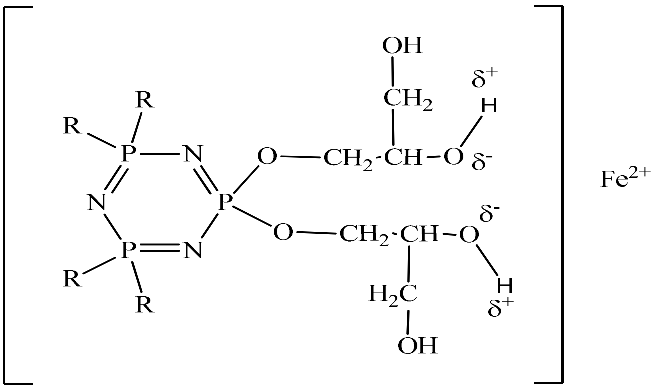


Fig.7. Polarization form suggested to be formed on the carbon steel surface

The following explanations are postulated: HPGCP interferes in the dissolution reaction by adsorption at the metal surface. The inhibitor competes with the molecules of water and Cl^- ions for sites on the water covered anodic surface as shown in figure 8.

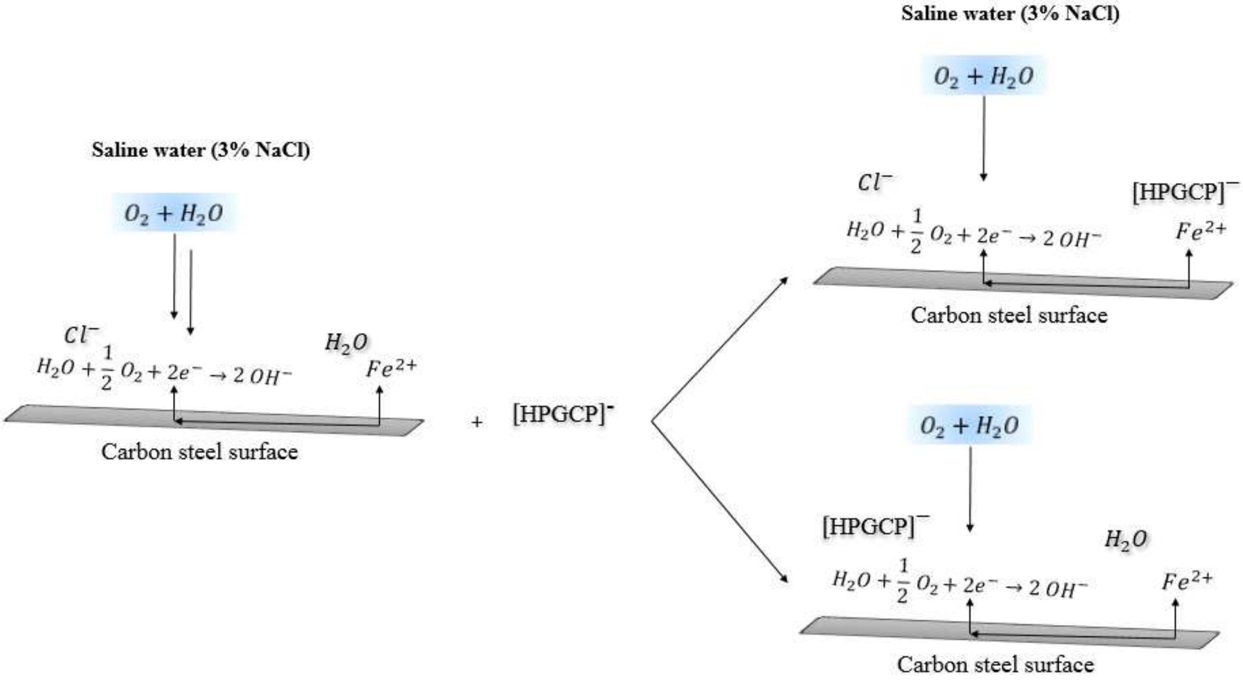


Figure 8. Schematic representation of competitive adsorption of HPGCP in sodium chloride

CONCLUSION

It can be concluded on the basis of the result obtained that:
1) The selection of parameters is in important step in theoretical study. The relationship between the parameter(s) and activity should be strong, and therefore efficiency predictions will be more promising.
2) The HOMO energy calculations show that HPGCP molecule has the higher energy therefore he could be better corrosion inhibitor in this study.
3) The density distributions of the frontier molecular orbitals (HOMO and LUMO) show that HGCP and HGCP-S adsorb through the actives centres nitrogen, oxygen and π electrons of the cyclophosphazene.
4) The adsorption of inhibitor molecules on the carbon steel surface obeys a Langmuir adsorption isotherm.
5) The carbon steel surface carry positive charge in the test solution.

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