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Influence of a derivative of cyclotriphosphazene as a corrosion inhibitor for carbon steel in 3% NaCl medium

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ABSTRACT

Hexa propylene glycol cyclotriphosphazene(HPGCP)was used as corrosion inhibitor and its inhibiting action on the corrosion of carbon steel in 3% NaCl solution was investigated using weight loss test potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques method has been employed in this study. Results indicated that the HPGCP compound acted as an anodic inhibitor. The inhibition efficiency of carbon steel increased with increasing concentrations of the inhibitor.

Key words: Carbon steel, corrosion test, weight loss, electrochemical measurements and anodic inhibitor.

INTRODUCTION

Iron and its alloys are widely used in many industrial and engineering applications, including construction, where they are deployed in various service environments containing acids, alkalis and salt solutions. These service environments may easily lead to an inevitable corrosion of metal exposed surfaces because of their aggressiveness [1].

Several techniques were applied to reduce the corrosion rate for metals. The use of inhibitors is one of the most convenient methods for the protection against corrosion in 3% NaCl [2-8].

Most inhibitors are heterocyclic compounds containing in their structure heteroatoms such as nitrogen, oxygen, sulfur and phosphorus [9-12].

These compounds can certainly form either a stronger coordination bond with a metal atom or a passive film on the surface [13].

The inhibition of metal corrosion can involve either physisorption or chemisorption of the inhibitor on the metallic surface. The electrostatic attraction between the hydrophilic groups, which are responsible and active centers for the metal surface, leads to physisorption. Several authors have shown that most of the inhibitors have been adsorbed on the metal surface by displacement of water molecules from the surface and forming a protective film forming a very compact barrier [14].

In this work, the Hexa propylene glycolcyclotriphosphazene (HPGCP) (Fig. 1) was prepared by solvolysis of the epoxy resin HGCP [15-18] in basic solution of NaOH. The evaluation of the inhibitory efficacy of HPGCP vis-a-vis carbon steel in 3% NaCl solution was confirmed by weight loss, electrochemical techniques using the potentiodynamic polarization curves tests and the electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL SECTION

Materials

The chemical structure of the studied compound is presented in Figure 1. HPGCP is relatively cheap and easy to produce 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 wasobtained according to the procedure literature [15-18].

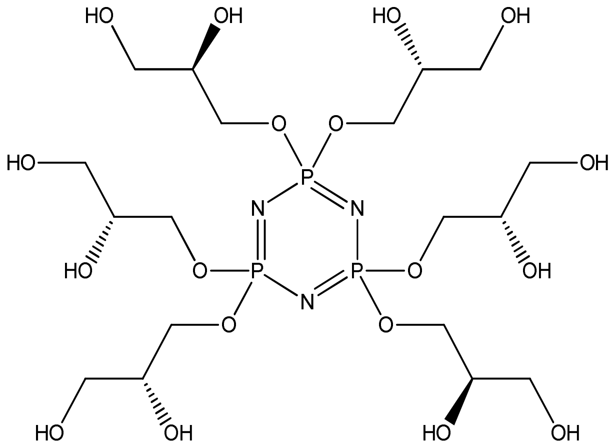

Fig 1 : Structure of Hexa propylene glycolcyclotriphosphazene (HPGCP)

Gravimetric measurements

The carbon steel sheets of $5\ cm \times 1\ cm \times 0,2\ cm$ were abraded with different emery papers (grade from 400 to 1500), washed with double distilled water, rinsed with ethanol and then dried at room temperature. After weighing accuracy, the specimens were immersed in beakers containing 100 ml of 3 % NaCl solution with different concentrations of the tested inhibitor for 24 h at 298 K.

After the specimens were taken out, washed, dried, and weighed accurately. In order to obtain good reproducibility, experiments were carried out in triplicate. The corrosion rate (W_{corr}), surface coverage (θ) and inhibition efficiency (E_{w}%) were calculated from the following Eqs. (1)–(3) :

$$W_{corr} = \frac{W_0 - W_i}{St} \tag{1}$$

$$\theta = \frac{W_0 - W_i}{W_0} \tag{2}$$

$$E_w = \frac{W_0 - W_i}{W_0} \times 100 \tag{3}$$

where W_0 and W_i are the weight loss values in absence and presence of inhibitor, respectively, S is the total area per cm^2 and $t$is the immersion time in h .

Electrochemical measurements

Electrochemical cell

The electrolysis cell is Pyrex cylinder closed by a cap with three apertures. The working electrode is a previously used carbon steel and has the following composition of (wt): C 0.11%, Si 0.24 %, Mn 0.47%, Cr 0.12 %, Mo 0.02%, Ni 0.1%, Al 0.03%, Cu 0.14, Co <0.0012 %, V <0.003%, W 0.06 % and Fe balance.

The investigated area of the surface is $1\ cm^2$. Pt plate is used as the counter electrode while $(Ag\ /\ AgCl)$ is used as the reference electrode with $3M$ concentration of Cl^-. All potentials are referred to with respect to this electrode. For long exposure experiments, between two measurements, the reference electrode was removed from the test solution to minimize its contamination by chloride ions and the working electrode was set in immersion for 30 mn before each test. Before each experiment, the working electrode was abraded by successive emery paper treatments from 60 up to 1500 grade until a smooth and a planar surface was obtained. This was followed by washing thoroughly with distilled water, degreasing by ethanol, and finally drying with compressed air.

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 $(E_{corr}\ \pm\ 20mV\ /\ Ag\ /\ AgCl)$, 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 $PZC\ \ 100$ monitored by a personal computer. For each concentration, three independent experiments are performed. The main 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 [19], so we can conclude:

$$i = i_c + i_a$$
$$i = i_{corr} \times \left\{ \exp\left[b_a \times (E - E_{corr}) - \exp\left[b_c \times (E - E_{corr}) \right]\right]\right\} \qquad (4)$$

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

$$\beta = \frac{Log10}{b} = \frac{2.303}{b} \qquad (5)$$

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 $\pm 100mV\ /\ Ag\ /\ AgCl$ around the E_{corr} else, and a significant systematic divergence is sometimes observed for both anodic and cathodic branches.

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

$$\eta\% = \left(1 - \frac{i_{corr}}{i^0_{corr}}\right) \times 100 \qquad (6)$$

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

EIS measurements

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 terms of equivalent electrical circuit using Bouckamp's program [20]. The inhibition efficiency is evaluated from R_p (which is obtained from the diameter of the semicircle in the Nyquist representation) with the following relationship:

$$\eta\% = \left(1 - \frac{R_p^0}{R_P}\right) \times 100 \qquad (7)$$

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

RESULTS AND DISCUSSION

Gravimetric measurements

Table 1 summarizes the values of corrosion rate (W_{corr}), the area covered (θ) and the percentage of the inhibiting efficiency of corrosion obtained from the steps of weight loss to carbon steel in the absence and presence of HPGCP at different concentrations at 298 K in 3% NaCl.

Table 1: Inhibition efficiency for different concentrations of carbon steel in 3% NaCl obtained from weight loss measurements at 298 K after 24 h of immersion

	Concentration *(C)* (M)	Weight loss (W_{corr}/ mg cm^{-2} h^{-1})	E_w %	θ
Blank	00	3	-	-
HPGCP	10^{-6}	0.23	92	0.92
	10^{-5}	0.22	93	0.93
	10^{-4}	0.17	94	0.94
	10^{-3}	0.12	96	0.96

From the results above, it is observed that the inhibitory efficacy increases with increased concentration of the inhibitor, and reaches a maximum value of 96 % at 10^{-3} M of HPGCP. This behavior can be attributed to the increase of the surface covered by the molecules HPGCP adsorbed on the metal surface with an increase in their concentration by the formation of a protective layer which can be explained by:

1) Electrostatic attractions between the charged sites of the metal (usually steel) and sites responsible for HPGCP.
2) The interactions between the lone pairs of the heteroatoms (O, N and P) and with HPGCP the vacant orbital of the metal.
3) The interactions between the π electron HPGCP and metal.

Potentiodynamic polarization measurements

Figure 2 shows the polarization curves of carbon steel which is obtained in 3% NaCl medium at 298 strokes after an immersion in the absence and presence of HPGCP at different concentrations.To study some phenomena which characterize metal or corrosive environment,we plotted the cathodic polarization curves of steel in a 3% NaCl solution at different concentrations. The analysis of the cathodic curves show the existence of three areas of potential which are:

The first area between the potential of corrosion (E_{corr}) and the potential corresponding at the beginning of the landing which according to the following reaction (8):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (8)$$

The second area is the pseudo-level corresponding to oxygen diffusion.

The third area which is located after the level towards the most negative potentials corresponds to the reduction of water according to the reaction (9):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (9)$$

The analysis of the anodic polarization curves of steel in 3% NaCl at different concentrations shows the existence of a speed in an exponential form which shows that the process of dissolving the metal is reacted with a pure activation kinetics. The metal oxidation reaction is as follows (10):

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (10)$$

In the presence of activate chloride ions, the anodic dissolution of the metal occurs the following reactions [21].

$$Fe + Cl^- \longleftrightarrow (FeCl^-)_{ads} \qquad (11)$$

$$(FeCl^-)_{ads} \longleftrightarrow (FeCl)_{ads} + 1e^- \qquad (12)$$

$$(FeCl)_{ads} \longleftrightarrow FeCl^+ + 1e^- \qquad (13)$$

$$FeCl^+ \longleftrightarrow Fe^{2+} + Cl^- \qquad (14)$$

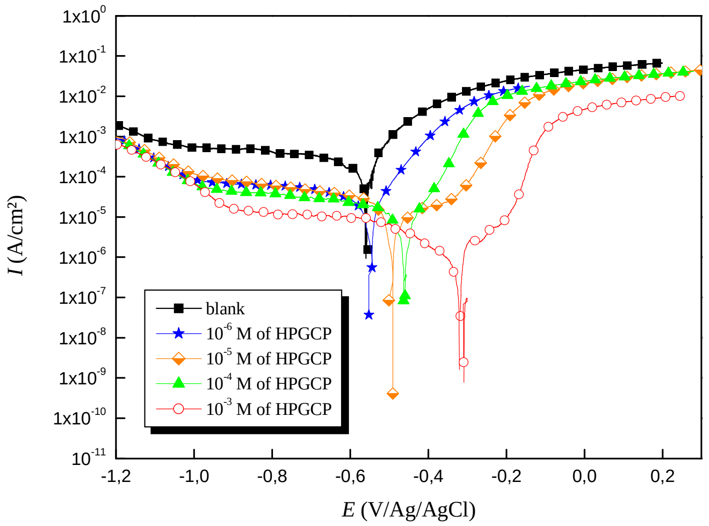

Fig 2: Polarization curves of carbon steel in 3% NaCl in the presence of different concentrations of HPGCP

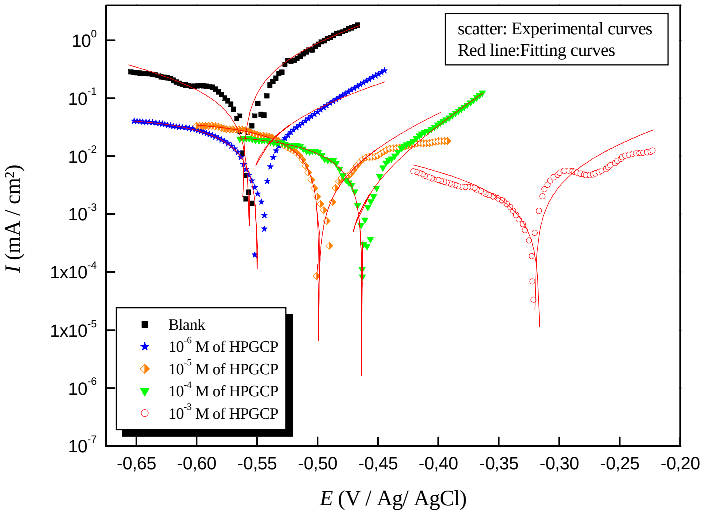

Fig 3:Comparison of experimental data and by mounting a non-linear fitting with Stern-Geary equation (for different concentrations HPGCP)

From the results obtained, we note on the one hand, an increase of current densities on the two cathodic and anodic branches after the addition of different concentrations of HPGCP with increasing inhibitory efficiency and an achieved concentration of a maximum value of 99 % at 10^{-3}M.

On the other hand, after the addition of the inhibitor, the anodic branches showed a significant change in the potential which is shifted to more anodic potential (more positive) for HPGCP in higher concentrations, which indicates that the compound is classified as an anodic inhibitor with a wider area over the passive region.These results suggest that HPGCP inhibitor reduces the anodic dissolution of iron and retards the reduction of oxygen. In addition, in the anodic area and especially for the two concentrations 10^{-3} and 10^{-4} M in HPGCP, both anodic branches recount a pseudo current level in the anodic area of potentials close to -0.3 and $-0,2V / Ag / AgCl$ respectively to 10^{-4} M and 10^{-3} M, which can be attributed to the coverage of inhibitory molecules adsorbed by forming a protective film on the surface of the carbon steel.

Also other authors noticed that the inhibitory molecules adsorbed onto the carbon steel surface can effectively screen for potential sites for the adsorption of chloride ions and then act as a barrier to block the adsorption of chloride ions on the metal surfaces [22-31].

Table 2: summarizes the different electrochemical parameters associated with carbon steel polarization curves in 3% NaCl at different concentrations HPGCP

	C (M)	***E***$_{corr}$ (mV/Ag/AgCl)	***I***$_{corr}$×10^6 (A/cm²)	***b***$_a$ (V^{-1})	***b***$_c$ (V^{-1})	***η*** %
Blank	00	-559	280	19	-19	-
HPGCP	10^{-6}	-552	40	8.9	-12.1	85
	10^{-5}	-498	27	10.5	-12.5	90
	10^{-4}	-463	14	7.9	-14.7	94
	10^{-3}	-320	3	8.9	-10.9	99

Electrochemical impedance spectroscopy

To confirm the results obtained by the polarization curves and to extract more information about the corrosion mechanisms, we used some techniques of electrochemical impedance.The Nyquist diagrams and of Bode obtained in 3% NaCl medium in the absence and presence of different concentrations for HPGCP after one hour of immersion at 298 K are shown respectively in Figures 4 and 5.

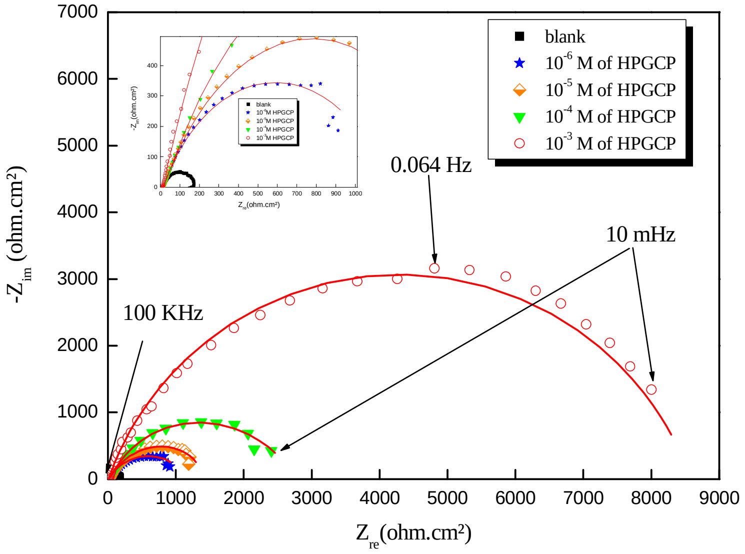

Fig 4: Comparison between the impedance measurements (Scatter) data and circuit simulation (red line) of carbon steel in 3% NaCl at different concentrations of HPGCP

The Nyquist diagram (Figure 4) drawn after an hour of prior maintaining the free corrosion potential, has a capacitive loop which can be divided into two separate loops are males and they are confirmed by the Bode diagrams. The first high frequency (HF) related to charge transfer reactions which occur in the pores and defects of the protective film that determines the process ox / red iron. The second low frequency (BF) is typically assigned to a slow process of transporting the material as the diffusion which can be attributed to the formation of a film on the surface of the carbon steel by the molecules of the inhibitor, oxides and iron hydroxides [30, 31].

We notice that the diameter of the half-circles, relative to the witness, increases with increasing concentrations of inhibitor, which means that increasing concentrations lead to an increase of the inhibiting effect, hence a delay of iron dissolution speed due to the formation of a protective film on the surface of the electrode [26].

To have the electrochemical impedance spectroscopy results, we relied on the established equivalent circuit in figure 6 which we chose to reasonably adapt to the experimental results. This circuit is composed of: R_s is the resistance of the electrolyte (Ω.cm^2), R_{ct} is the charge transfer resistance (Ω.cm^2), R_f represents the film strength (Ω.cm^2) and here R_p (Ω.cm^2) is equal to the sum of R_{ct}, R_s and R_f ($R_p = R_{ct} + R_f - R_s$), the constant CPE_{dl} and CPE_f phase elements are used to replace the double layer capacitance (C_{dl}) and film capacitance (C_f), respectively [26].

A comparison between the measured data and simulation for the impedance for the control and in the presence of different concentrations of HPGCP are shown in Figure 4.

Bode diagrams obtained in 3% NaCl medium in the absence and presence of HPGCP at different concentrations are shown in figures (5a) and (5b). In Figure (5b), we notice that the phase angle increases with increasing concentrations of the inhibitor, the values of the phase angles are respectively 52 °, 55 °, 57 ° and 70 °. These developments indicate the protecting layer by inhibitory molecules that replace the hydrated layer on the steel surface [17, 18]. According to the literature, the impedance spectra of carbon steel in NaCl solution are composed of two time constants [27-29].

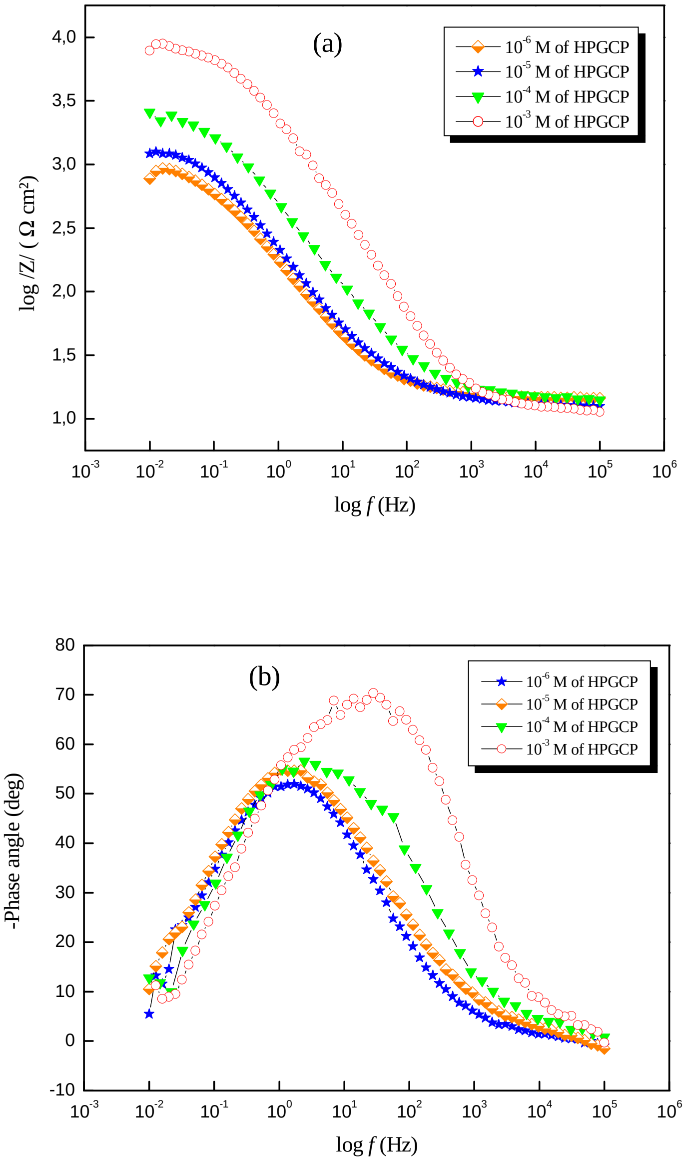

Fig 5: (a) and (b) the Bode plots for carbon steel in 3% NaCl at different concentrations of HPGCP

Table 3: Electrochemical impedance parameters for corrosion of carbon steel in 3% NaCl at various contents of HPGCP.

	C **(M)**	***R_s*** **(Ω.cm²)**	***R_f*** **(kΩ.cm²)**	***C_f*** **(µF/cm²)**	***C_{dl}*** **(µF/cm²)**	***R_{ct}*** **(kΩ.cm²)**	***Rp*** **(kΩ.cm²)**	***η%***
Blank	00	10	0.175	201	-	-	0, 165	-
HPGCP	10^{-6}	15	0.04	170	165	1.1	1,1	85
	10^{-5}	12	0.1	110	141	1.5	1,6	90
	10^{-4}	12	0.3	43	68	2.4	2,7	94
	10^{-3}	8	2.1	11	52	6.9	9	98

Electrochemical adjusted parameters are shown in Table 3 as well as the inhibitory efficiency (η%) was calculated by the previous equation (7).

The examination of Table 3 show that C_{dl} and C_f values decrease while the values of R_f and R_{ct} increase when the concentration of HPGCP increases. The significant decrease in capacitance values can be attributed to a decrease in the dielectric constant or increasing the thickness of the electrical double layer due to the adsorption of the inhibitor forming a protective layer on the carbon steel surface [32].

Similarly, when the concentration of inhibitor increases, the values of charge transfer resistance R_{ct} increase. These respective evolutions of R_{ct} suggests that the amount of inhibiting molecules formed on carbon steel increases, and consequently the decrease of active sites becomes necessary for the reactions of iron dissolution.

The remarkable increase in film strength R_f could be attributed to the formation of a protective film on the surface of the steel constituted of adsorbed inhibitory molecules and/or formed corrosion products [33, 34].

The equivalent circuit model employed for these systems is presented in Figure 6.

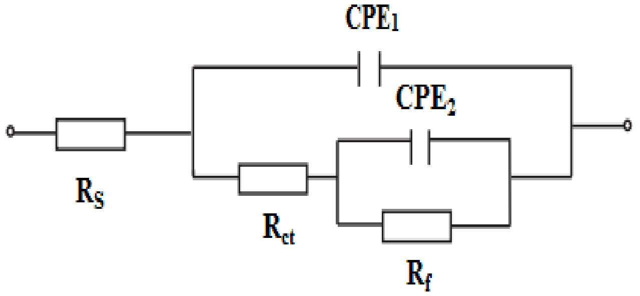

Fig 6:The electrochemical equivalent circuit used to fit the impedance spectra

CONCLUSION

The inhibition efficiency of carbon steel corrosion in 3% NaCl by Hexa propylene glycol cyclotriphosphazene(HPGCP)has been investigated weight loss test and using electrochemical measurement. The following conclusions were drawn from this study:

1) Reasonably good agreement was observed between potentiodynamic polarization and electrochemical impedance spectroscopy techniques.
2) The examined HPGCP shows excellent inhibition properties for the corrosion of carbon steel in 3% NaCl at 298 K, the efficiency values of inhibition increases substantially with increase of the concentration of the inhibitor. The maximum inhibition efficiency of 98% was observed at 10^{-3} M concentration.
3) The concentration dependence of the inhibition efficiency calculated from weight loss measurements and electrochemical studies were in good agreement. Based on the polarization results, the investigated HPGCP acts predominantly as anodic-type inhibitor.

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