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Effect of temperature on the corrosion inhibition of carbon steel in 3 % NaCl by hexa propylene glycol cyclotriphosphazene

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ABSTRACT

The corrosion rates in the presence of Hexa Propylene Glycol Cyclotriphosphazene (HPGCP) ascarbon steel corrosion inhibitor in 3 % NaCl has been investigated in temperature ranging from 298 to 328 K using weight loss measurements and electrochemical polarisation. The inhibition efficiency of HPGCP decreases with the rise of temperature. HPGCP is adsorbed on the steel surface according to Langmuir isotherm model. Both kinetic parameters (activation energy, enthalpy of activation and entropy of activation) and thermodynamics of adsorption (enthalpy of adsorption, entropy of adsorption and Gibbs free energy) were calculated and discussed. The fundamental thermodynamic functions were used to obtain important information about HPGCP inhibitory behavior.

Key words: Cyclotriphosphazene, carbon steel, 3 % NaCl, weight loss, electrochemical polarisation and Langmuir isotherm model.

INTRODUCTION

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, where they are deployed in various service environments containing, acids, alkalis and salt solutions [1–4].

Therefore, the protection of steel from corrosion is an important topic among the researchers due to its wide range of industrial applications [5]. The use of inhibitors is an important method of protecting materials against deterioration due to corrosion [6].

Most of the corrosion inhibitors are heterocyclic compounds containing heteroatoms such as oxygen, nitrogen,sulphur, phosphorous, unsaturated bonds or plane conjugated systems [7-10]. The inhibitory action of these compounds is usuallyattributed to their adsorption interaction with the metal surface [11-14]. A bond may be formed between electron pairs and/or electron cloud of the donor atoms of the inhibitors and the metal surface, thereby reducing the corrosive attack in environments containing, acids, alkalis and salt solutions.The stability of the adsorbed inhibitor film on the metal surface depends on some physico-chemical properties of the molecule related to

their functional groups, aromaticity, the possible steric effects, electronic density of donor atoms, type of corrosive environment and the nature of the interaction between the π orbital of the inhibitors and the'd' orbital of iron [15].
The objective of the present work is to study the thermodynamic and the kinetic characterisation of carbon steel corrosion in 3% NaCl in the range of temperature from 298 to 308 K at different concentrations, in the presence of hexa propylene glycol cyclotriphosphazene denoted hereafter HPGCP[16-19]. Various thermodynamic and kinetic parameters for inhibitor adsorption on carbon steel surface were estimated and discussed.

MATERIALS AND METHODS

Materials

Carbon steel strips containing C 0.11 wt.%, Si 0.24 wt.%, Mn 0.47 wt.%, Cr 0.12 wt.%, Mo 0.02 wt.%, Ni 0.1 wt.%, Al 0.03 wt.%, Cu 0.14, Co <0.0012 wt.%, V <0.003 wt.%, W 0.06 wt.% and the remainder iron were used for gravimetric studies and potentiodynamic polarization measurements. Prior to all measurements, are abraded with a series of emery paper from 400 to 1200 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol.The neutral solution of 3% NaCl as a corrosive solution. We prepared 100 ml of 3% NaCl, namely 3g of NaCl, which are dissolved in 100ml of distilled water.The chemical structure of the studied compound is presented in figure 1.

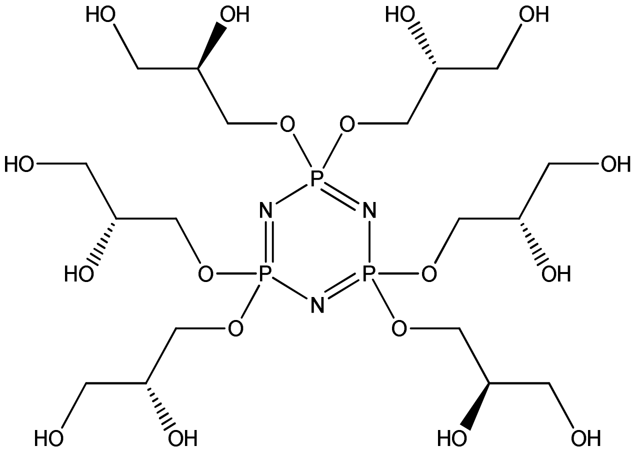

Figure 1. Structure of hexa propylene glycol cyclotriphosphazene(HPGCP)

Gravimetric measurements

The carbon steel sheets of 5 cm ×1 cm ×0.2 cm were abraded with different emery papers (grade from 400 to1500), washed with double distilled water, rinsed with ethanol and then dried at room temperature. After weighing accurately, the specimens were immersed in beakers contained 100 ml of 3% NaCl solution with different concentrations of the tested inhibitor for 48 h at various temperatures (298-328 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) [20–21] :

$$W_{corr}=\frac{W_0\text{-}W_i}{St} \quad (1)$$

$$\theta = \frac{W_0\text{-}W_i}{W_0} \quad (2)$$

$$E_w = \frac{W_0\text{-}W_i}{W_0} \times 100 \quad (3)$$

where W_o 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.

Potentiodynamic polarization measurements

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 3% NaCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -1200 to 300 mV/Ag/AgCl versus corrosion potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (i_{corr}). From the polarization curves obtained, the corrosion current (i_{corr}) was calculated by curve fitting using the equation (4) :

$$i = i_a + i_c = i_{corr} \,.\, \{exp[b_a \times (E - E_{corr})] - exp[b_c \,.\, (E - E_{corr})]\} \quad (4)$$

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:

$$\beta = \frac{\ln(10)}{b} = \frac{2.303}{b} \quad (5)$$

The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship:

$$\eta = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}^{0}} \times 100 \quad (6)$$

where$i_{corr}^{0}$and i_{corr} are the corrosion current density in absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION

Effect of temperature

Gravimetric measurements

The influence of temperature on the corrosion behaviour of steel/ 3% NaCl in the presence and absence of the HPGCP at various concentrations is investigated by weight-loss trend in the temperature rang 298-328K during 24h of immersion.

Table 1 collects the values of corrosion rate of mild steel at different concentrations of HPGCP determined by weight loss measurements at various temperatures (298-328 K) as well as the corresponding inhibition efficiencies and surface coverage.

Table 1. Influence of temperature on the corrosion rate and inhibition efficiency of carbon steel in 3% NaCl at different concentrations of HPGCP

	Concentration© (M)	**W_{corr} (mg/cm^2h^1)**	**E_w%**	**Θ**
		298 K		
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
		308 K		
Blank	00	5.51	-	-
HPGCP	10^{-6}	0.78	86	0.86
	10^{-5}	0.67	88	0.88
	10^{-4}	0.52	90	0.90
	10^{-3}	0.41	92	0.92
		318 K		
Blank	00	8.89	-	-
HPGCP	10^{-6}	1.93	78	0.78
	10^{-5}	1.76	80	0.80
	10^{-4}	1.58	82	0.82
	10^{-3}	1.31	85	0.85
		328 K		
Blank	00	11.45	-	-
HPGCP	10^{-6}	2.88	75	0.75
	10^{-5}	2.53	78	0.78
	10^{-4}	2.28	80	0.80
	10^{-3}	2.05	82	0.82

The evolution of corrosion rate and inhibition efficiency with temperature for carbon steel in 3% NaCl of HPGCP at different concentrations is shown in figure2.

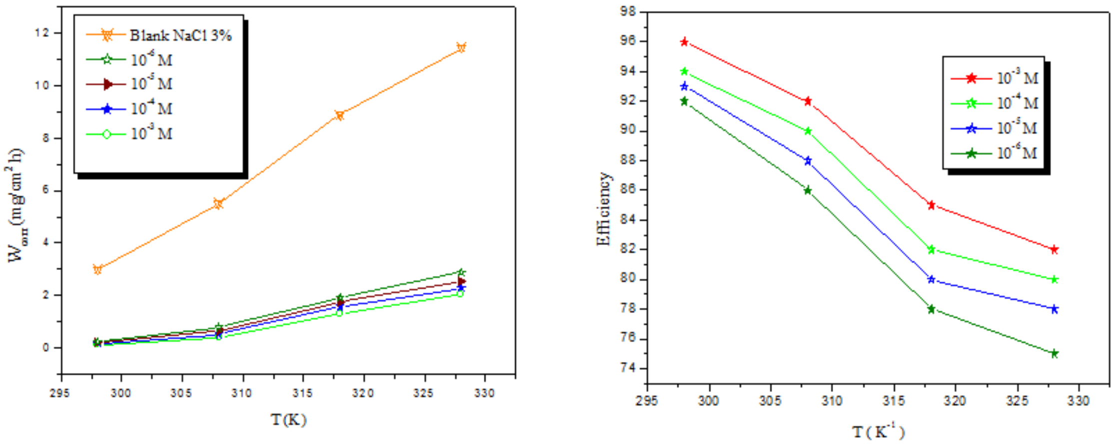

Figure 2. Variation of corrosion rate and inhibition efficiency with temperature for carbon steel in 3% NaCl at different concentrations of HPGCP.

The results indicate that for a given temperature, the corrosion rate of steel decreased with increasing inhibitor concentration. The values of inhibition efficiency obtained from the weight loss for different inhibitor concentrations and at various temperatures in 3% NaCl are given in table 1 and figure 2.

Is clear that inhibition efficiency increased with increase in inhibitor concentration. The maximum value of inhibition efficiency (E_w%) obtained for 10^{-3}M of HPGCP is 96 % at 298 K. It shows that inhibition efficiency decreased at higher temperatures. This behavior indicates desorption of inhibitor molecule [22].

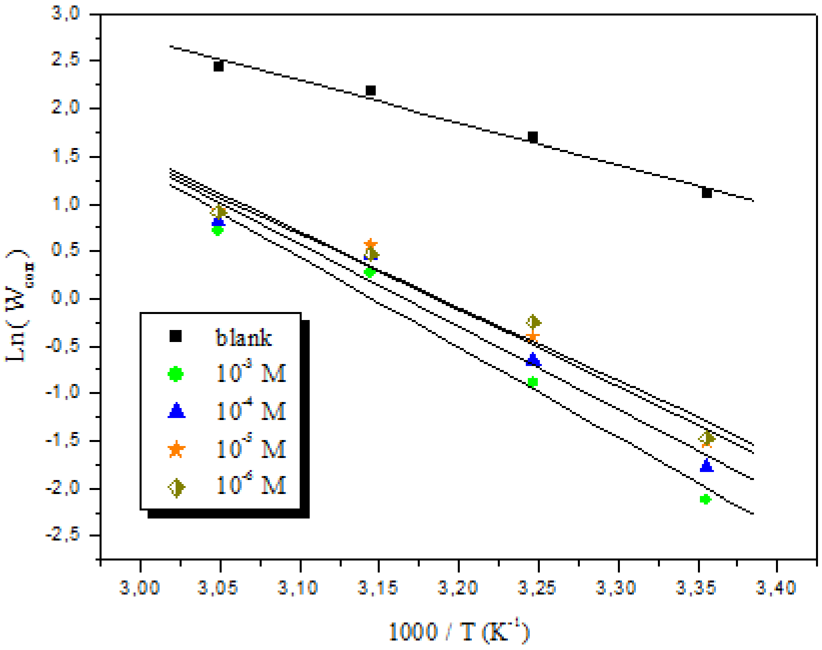

Figure 3. Arrhenius plots of carbon steel in 3% NaCl at different concentrations of HPGCP.

Kinetic parameters of activation corrosion process

The adsorption process was well elucidated by using a thermodynamic model.A kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. To calculate kinetic and thermodynamic activation parameters at different concentrations of HPGCP such as activation energy E_a, entropy ΔS* and enthalpy ΔH* of activation, Arrhenius Eq. (7) and its alternative formulation called transition state Eq. (8) are used :

$W_{\text{corr}} = \text{A} \exp\left(-\frac{E_a}{\text{RT}}\right)$ (7)

$$W_{corr} = \frac{RT}{hN} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (8)$$

where E_a represents the apparent activation energy, R is the universal gas constant, T is the absolute temperature, h is Plank's constant, N is Avogadro's number, and A is the pre-exponential factor.

The activation energy E_a is calculated from the slope of the plots of Ln (W_{corr})vs. 1/T(Figure. 3). Plots ofLn (W_{corr}/T)vs. 1/T give straight lines with slopes of ΔH*/Rand intercepts of (Ln(R/Nh)+ ΔS*/R) as shown in figure 4. From equation 8, the values of ΔH^* and ΔS^* can be calculated.

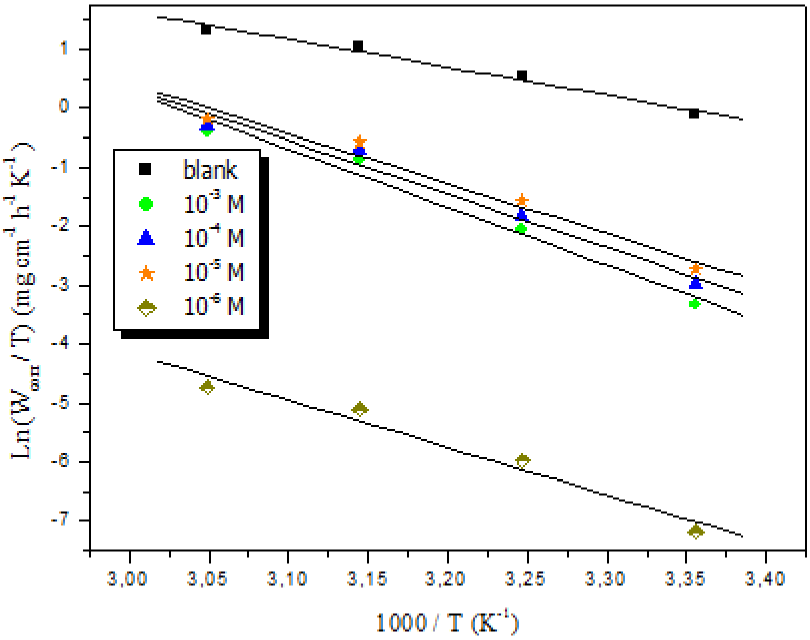

Figure 4. The relationship between Ln (W_{corr}/T) and 1/T for carboon steel at different concentrations of HPGCP.

The calculated parameters at different concentrations of the inhibitor are collected in Table 2. The activation energy E_a increase in the presence of HPGCP. Generally, the inhibitive additives cause a rise in activation energy value when compared to the blank solution. The change of the values of the apparent activation energies can be interpreted as an indication of adsorptive film formation by a physical (electrostatic) mechanism [23].

Table 2.Values of activation thermodynamic parameters for carbon steel dissolution in 3% NaCl in the absence and presence of different concentrations of HPGCP.

Concentration C(M)	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J.mol^{-1} K^{-1})
00	35.82	39.22	-66.06
10^{-6}	64.32	66.73	-31.83
10^{-5}	67.64	70.22	16.95
10^{-4}	70.63	72.21	31.16
10^{-3}	78.95	81.52	49.53

The kinetic data obtained in Table 2 show that all parameters of corrosion process increases with HPGCP concentration. The positive value of the enthalpy ΔH^* is an endothermic nature of the carbon steel dissolution process [24], while the increase of the entropy of activation ΔS^*eveals that an increase in disordering takes place on going from reactant to the activated complex [25]. This behavior can be explained as a result of the replacement process of water molecules during adsorption of HPGCP on steel surface.

Adsorption isotherm and thermodynamic parameters

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.According to this isotherm, the surface coverage (Θ) is related to inhibitor concentration (C_{inh}) by [16]:

Langmuir isotherm

$$\frac{\theta}{1-\theta} = K_{ads} C_{inh} \quad (9)$$

Rearranging Eq. 9 gives:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process, C_{inh} is the inhibitor concentration and Θ is the surface coverage. This model for Langmuir's adsorption isotherm has been used extensively in the literatures for various metal/inhibitor/alkaline chloride solution systems [26-29].

For obtaining the best description of adsorption behavior of the inhibitor, all of the above adsorption isotherms were tested. The plot of C_{inh} / θ versus C_{inh}yielded a straight line with a slope near to 1 and correlation coefficient 0.999, as shown in Figure 5.

The K_{ads} values can be calculated from the intercept lines on the C_{inh} / θ-axis. This is related to the standard free energy of adsorption (ΔG°_{ads}) with the following equation 10:

$$\Delta G^{\circ}_{ads} = -RTLn\,(55.5\,K_{ads})\ (10)$$

where the value of 55.5 is the molar concentration of water in solutionmol/dm^3, R is the universal gas constant, and T is the absolute temperature.

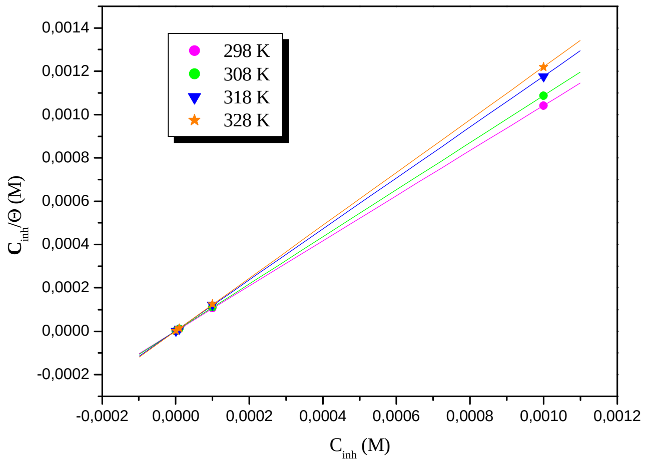

Figure 5. The relationship between C_{inh} / θ and C_{inh} of HPGCP at various temperatures.

Table 3. Thermodynamic parameters of adsorption of HPGCP on the carbon steel surface at different temperatures.

T (K)	$K_{ads}\times10^6$ (L/mol)	ΔG°_{ads} (kJ/mol)
298	1.18	-44.57
308	1.02	-45.69
318	0.86	-46.72
328	0.59	-47.17

The values of K_{ads} indicate that the inhibitor molecule possesses strong adsorption ability onto the carbon steel surface [30].Generally, values of ads ΔG°_{ads} up to -20 kJ mol^{-1} are consistent with physisorption, while those around -40 kJ mol^{-1} or higher are associated with chemisorption because of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [31].The large values of ΔG°_{ads} and its negative sign is usually characteristic of strong interaction on the carbon steel surface, suggesting electrons sharing or transferring between HPGCP molecule and carbon steel surface by co-ordinate type of bonds [32].

Potentiodynamic polarization measurements

In order to confirm the results extracted from weight loss test and to acquire more information about corrosion mechanisms,using potentiodynamic polarization curves.

The effect of temperature on the various corrosion parametersE_{corr}, I_{corr} and η (%) was studied in 3% NaCl at temperature range 298-328 K in the presence of 10^{-3} M of HPGCP (Figure 6). Variation of temperature has almost no effect on the general shape of the polarization curves. The results were listed in Table 4

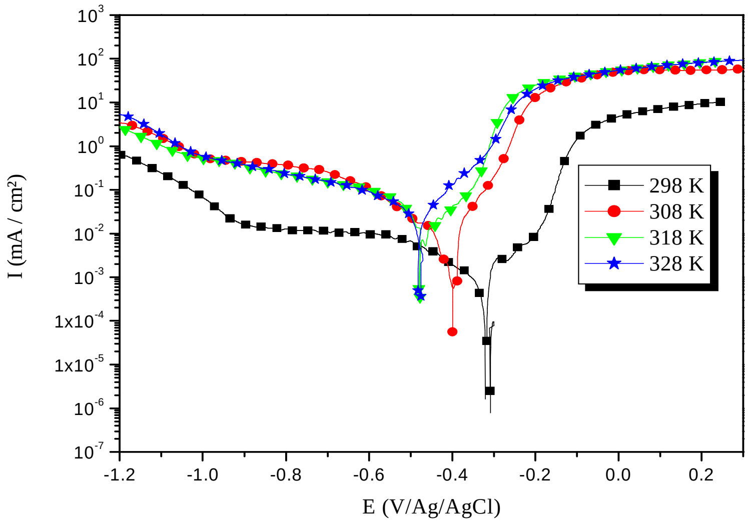

Figure 6. Potentiodynamic polarisation curves of carbon steel in 3% NaCl in the presence of 10^{-3}M of HPGCP at different temperatures.

Table 4. The influence of temperature on the electrochemical parameters for carbon steel electrode immersed in 3% NaCl and 3% NaCl + 10^{-3} M of HPGCP.

T (K)	E_{corr} mV/Ag/AgCl		$I_{corr}\times10^6$ (A/cm²)		η %
	Blank	10^{-3} M of HPGCP	Blank	10^{-3} M of HPGCP	-
298	-559	-320	280	3	99
308	-568	-415	345	23.4	93
318	-653	-486	556	85.8	85
328	-677	- 492	706	137.5	80

An inspection of Table 4 shown that, as the temperature increased, the values of E_{corr} shift in the negative direction, while the values of I_{corr} increase and η (%) decrease. This behaviour reflects physical adsorption of HPGCP on the steel surface [33].

Kinetic parameters of activation corrosion process

Effect of temperature on the corrosion parameter can be deduced by comparing the activation energy in the presence and absence of the inhibitor.In order to calculate the activation energy of the corrosion process and investigation of the mechanism of inhibition, polarization measurements was carried out at various temperatures. The dependence of the corrosion rate on temperature can be expressed by the Arrhenius equation (11)[34–37] :

$$i_{corr} = A \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

where i_{corr} is corrosion current, A is the constant, E_a is the activation energy of the metal dissolution reaction, R is the gas constant and T is the temperature. Arrhenius plots for the corrosion rate of carbon steel were given in Figure 7. Value of E_a for carbon steel in 3% NaCl and presence of the optimum concentration 10^{-3} M of the inhibitor were estimated by calculating the slope of Ln (i_{corr}) vs. 1/T. Moreover, the Arrhenius equation can be converted an alternative equation as follow [38]:

$$i_{corr} = \frac{RT}{hN} exp\ (\frac{\Delta S_a}{R}) exp\left(-\frac{\Delta H_a}{RT}\right) \quad (12)$$

where N is Avogadro's constant, h is the Plank's constant, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation (Figure 8). A plot of Ln ($^{i_{corr}}/_{T}$) against 1/T should give a straight line with a slope of ($^{\Delta H_a}/_{T}$)and intercept of[$Ln(^{R}/_{Nh}) + (^{\Delta S_a}/_{R})$], E_a, ΔH_a and ΔS_a were calculated and tabulated in Table 5.

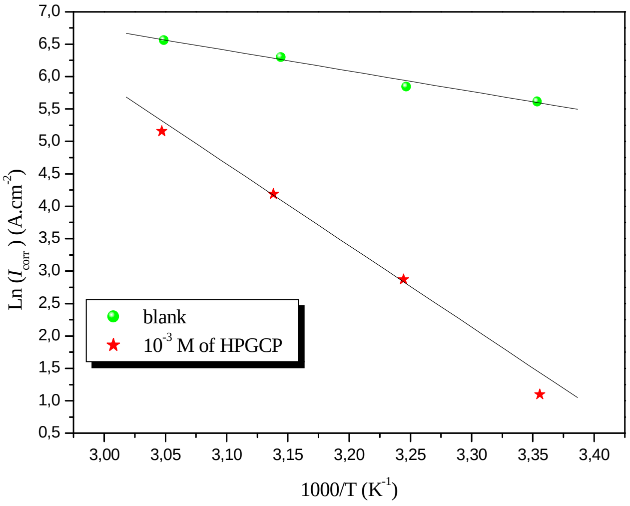

Figure 7. The relationship between Ln (i_{corr})and 1/T for carbon steel in 3% NaCl in the absence and presence of HPGCP.

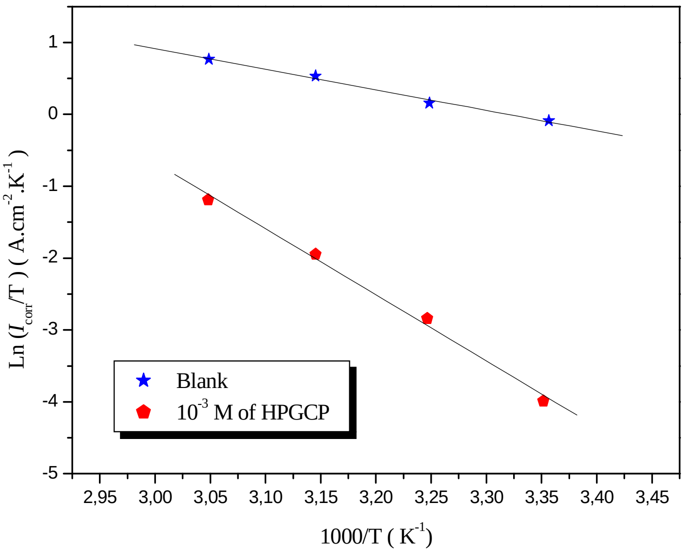

Figure 8. Transition state plots for carbon steel in 3% NaCl in the absence and presence of 10^{-3} M concentration of HPGCP.

Table 5. The influence of temperature on the electrochemical parameters for carbon steel in 3% NaCl and 10^{-3}M of HPGCP.

	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J.mol^{-1} K^{-1})
Blank	26.38	23.80	-118.42
10^{-3} M of HPGCP	79.52	76.44	26.26

Inspection of Table 5 shows that values of both E_a and ΔH_a obtained in presence of HPGCP are higher than those obtained in the inhibitor-free solutions.There are two possibilities : in the first case ($E_{a,\ inh} > E_{a,\ NaCl}$) the inhibitor is adsorbed on the most active adsorption sites (having lowest energy) and the corrosion process takes place predominantly on the active sites of higher energy. In the second case ($E_{a,\ inh} < E_{a,\ NaCl}$), i.e. a smaller number of more active sites remain uncovered which take part in the corrosion process.This observation further supports the proposed physical mechanism [39].

On the other hand, the positive value of ΔH_a reflects the endothermic nature of the carbon steel dissolution process [40], while the increase of ΔS_a reveals that an increase in disordering takes place on going from reactant to the activated complex [41]. This behavior can be explained as a result of the replacement process of water molecules during adsorption of HPGCP on steel surface.

CONCLUSION

The following conclusions may be drawn from the study :

1) Results obtained qualified that HPGCP tested is an efficient inhibitor.
2) Data obtained from gravimetric measurements are in good agreement with those of the polarization resistance method.
3) Increase of temperature leads in a decrease of efficiency and an increase of theactivation corrosion energy.
4) The adsorption of HPGCP on the carbon steel surface from 3 % NaCl obeys a Langmuir adsorption isotherm.
5) Taking into account the increase of activation energy for the kinetic process of iron dissolution and the values of Gibbs free energy and heat energy for thermodynamic process of HPGCP adsorption on carbon steel surface, the authors believe that the adsorption mechanism of HPGCP physisorption.

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