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Research Article

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The effect of temperature on the inhibition of acid hydrochloric corrosion of carbon steel by hexa propylene glycol cyclotriphosphazene

Mouhsine Galai[a], Mustapha El Gouri[b,c], Omar Dagdag[c], Younes El Kacimi[a],
Ahmed El Harfi[c] and Mohamed Ebn Touhami[a]

[a]Laboratoire de Matériaux, d'Electrochimie et d'Environnement (LMEE), Département de Chimie, Faculté des Sciences, Université Ibn Tofail, Kénitra, Maroc
[b]Laboratory of Polymers, Radiation and Environment- Team of Macromolecular & Organic Chemistry, Departmentof Chemistry, Faculty of Science, University Ibn Tofail, Kenitra, Morocco
[c]Laboratory of Process, Renewable Energy and Environment, Department of Process Engineering, Height School of Technology, Sidi Mohammed Ben Abdallah University, Fez, Morocco

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ABSTRACT

Inhibition effect of Hexa propylene glycol cyclotriphosphazene (HPGCP) was studied on carbon steel corrosion in 1 M HCl has been investigated in a 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. The values of adsorption enthalpy ΔH_a *and adsorption entropy* ΔS_a *were discussed. The thermodynamic parameters of adsorption reveal that there is a strong interaction between inhibitor and carbon steel. The highest inhibition efficiency was observed* 10^{-5} *M of HPGCP concentration at different temperature.*

Key words: Hexa propylene glycol cyclotriphosphazene, carbon steel, *1 M HCl*, weight loss and electrochemical polarisation.

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. Hydrochloric and sulphuric acids are the most commonly used acids in the pickling bath between 5 and15% at temperature up to 80°C [1–5].

Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. The wide use of HCl has led to the concentration on the corrosive effects of this acid on carbon steel. However, most equipment in industries is usually corroded owing to the general aggression of acid solutions [6].

In order to reduce the corrosion rate of metals, the use of inhibitors heterocyclic is one of the most practical method for protection against corrosion in acidic media have many advantages such as high inhibition efficiency [7–10], low price, and easy production.

The objective of the present work is to study the thermodynamic and the kinetic characterisation of carbon steel corrosion in 1 M HCl in the range of temperature from 298 to 328 K at different concentrations, in the presence of Hexa propylene glycol cyclotriphosphazene denoted hereafter HPGCP. Various thermodynamic and kinetic parameters for inhibitor adsorption on carbon steel surface were estimated and discussed.

EXPERIMENTAL SECTION

Materials

The steel used in this study is a carbon steel with a chemical composition (in wt%) of 0.11 % C, 0.24% Si, 0.47 % Mn, 0.02 % Mo, 0.12 % Cr, 0.03% Al, 0.1 % Ni, <0.0012% Co,<0.003 %V, 0.06 % W, 0.14 % Cu and the remainder iron (Fe).

Solutions

The aggressive solutions of 1 M HClwere prepared by dilution of analytical grade 37% HCl with distilled water. The chemical structure of the studied compound is presented in Figure 1. This compound (HPGCP) was obtained according to the procedure literature [11-13]. The concentration range of this compound was $10^{-6} – 10^{-3}$ M.

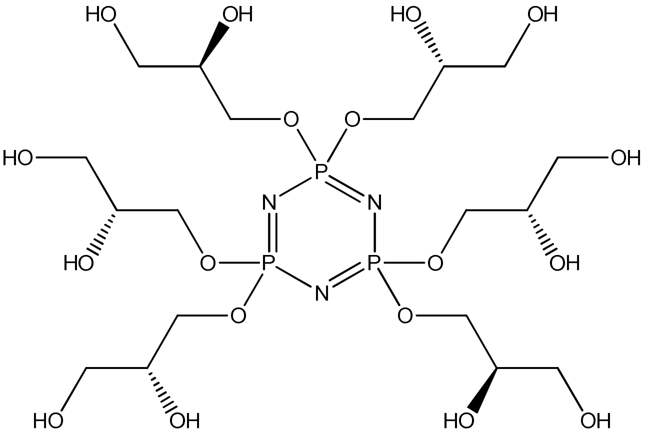

Fig 1 : Structure of Hexa propylene glycol cyclotriphosphazene (HPGCP)

Weightloss measurements

Coupons were cut to 5 cm ×1 cm ×0.2 cm dimensions for weightloss measurements. Prior to all measurements, the exposed area was mechanically abraded with 60 to 1200 grades of emery papers. The specimens were washed thoroughly with bi-distilled water, degreased and drive with ethanol. The solution volume was 50 ml. The immersion time for the weightlosswas 6 h at various temperatures (298-328 K).

Potentiodynamic polarization measurements

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recordinganodic and cathodic potentiodynamic polarization curves. Measurements wereperformed in the 1M HCl solution containingdifferent concentrations of the tested inhibitor by changing the electrodepotentialautomatically from -900 to -100 mV/Ag/AgCl versus corrosion potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curveswereextrapolated to corrosion potential to obtain corrosion currentdensities (i_{corr}).

RESULTS AND DISCUSSION

Effect of temperature

Gravimetric measurements

The influence of temperature on the corrosion behaviour of steel / 1 M HCl in the presence and absence of the HPGCP at various concentrations is investigated by weight-loss trend in the temperature rang 298-328K.

Kinetic parameters of activation corrosion process

The adsorption process waswellelucidated by using a thermodynamic model. A kinetic model wasanotherusefultool 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, entropyΔS^* and enthalpyΔH^* of activation, Arrhenius Eq. (1) and its alternative formulation called transition state Eq. (2) are used :

$$W_{corr} = A.\exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

$$W_{corr} = \frac{RT}{hN}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (2)$$

Where E_a represents the apparent activation energy, R is the universalgas constant, *T* is the absolute temperature, *h* is Plank's constant, *N* is Avogadro'snumber, and *A* is the pre-exponential factor.

Table 1 : Gravimetric results of carbon steel corrosion in 1M HCl without and with addition at different concentrations of HPGCP at various temperatures (298-328 K) during 6h of immersion

Temperature *T* (K)	Concentration *C* (M)	Weightloss W_{corr} (mg/cm^2.h)	E_w %	Surface coverage (θ)
298	00	1.2	-	-
	10^{-6}	0.061	95	0.95
	10^{-5}	0.054	96	0.96
	10^{-4}	0.082	93	0.93
	10^{-3}	0.105	91	0.91
308	00	2.522	-	-
	10^{-6}	0.227	92	0.91
	10^{-5}	0.178	93	0.93
	10^{-4}	0.307	89	0.89
	10^{-3}	0.415	84	0.84
318	00	4.831	-	-
	10^{-6}	0.725	85	0.85
	10^{-5}	0.639	87	0.87
	10^{-4}	0.887	81	0.81
	10^{-3}	0.982	79	0.79
328	00	7.441	-	-
	10^{-6}	1.265	83	0.83
	10^{-5}	1.114	85	0.85
	10^{-4}	1.512	80	0.80
	10^{-3}	1.716	77	0.77

The activation energy E_a is calculated from the slope of the plots of $Ln\left(W_{corr}\right)$ vs. $\frac{1}{T}$ (Figure. 2). Plots of $Ln\left(\frac{W_{corr}}{T}\right)$ vs. $\frac{1}{T}$ give straight lines with slopes of $\frac{\Delta H^*}{R}$ and intercepts of $\left(Ln\left(\frac{R}{Nh}\right)+\frac{\Delta S^*}{R}\right)$ as shown in figure 3. From equation 2, the values of ΔH^* and ΔS^* can be calculated.

Table 2 :Activation parameters of the dissolution reaction of carbon steel in 1 M HCl in the absence and presence different concentrations of HPGCP

Concentration C(M)	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J.mol^{-1} K^{-1})
00	49.86	47.20	-84.2
10^{-6}	83.59	72.80	-19.1
10^{-5}	84.35	81.77	6.14
10^{-4}	82.02	82.51	49.7
10^{-3}	79.94	81.60	7.39

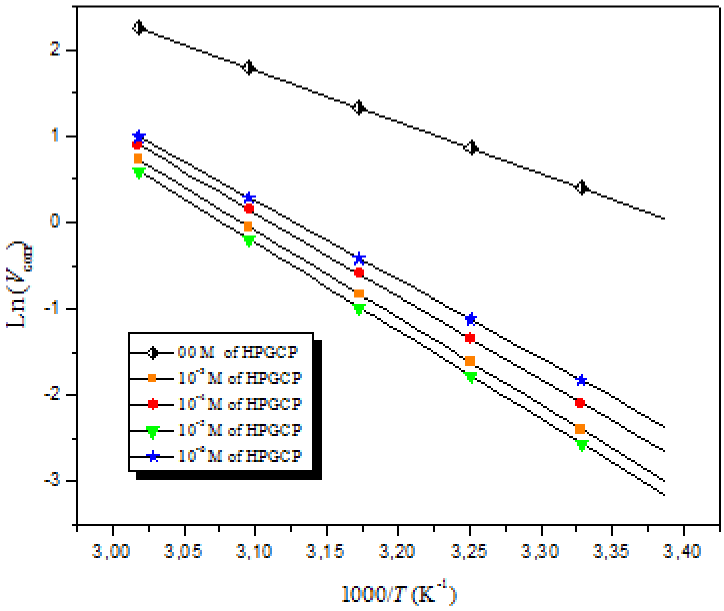

Fig 2 :Arrhenius plots of carbon steel in 1 M HCl at different concentrations of HPGCP

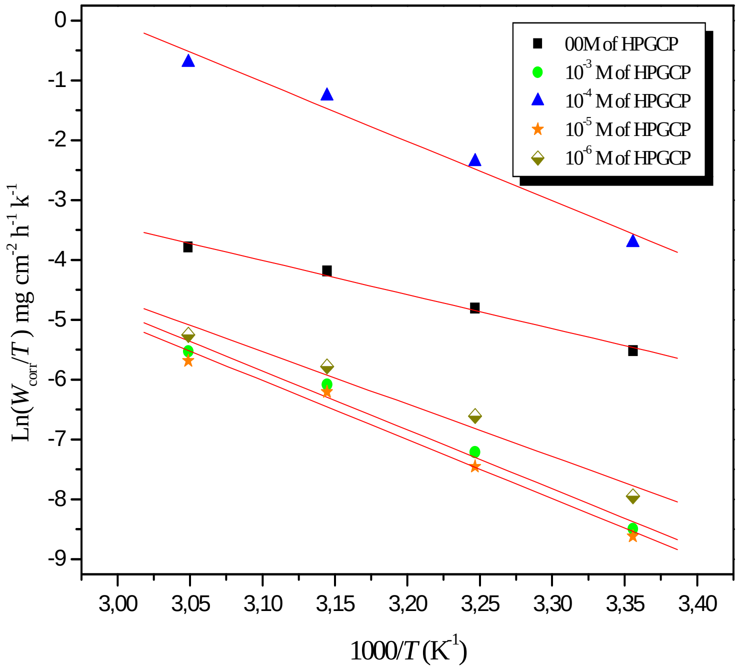

Fig 3 :The relationship between Ln (W_{corr}/T) and 1/T for carbon steel at different concentrations of HPGCP

The positive value of the enthalpyΔH^* is an endothermic nature of the carbon steel dissolution process, while the increase of the entropy of activation ΔS^*eveals that an increase in disorderingtakes place on going from reactant to the activatedcomplex[14]. This behaviorcanbeexplained as a result of the replacement process of water moleculesduring adsorption of HPGCP on steel surface.

Potentiodynamic polarization measurements

Polarization curves for carbon steel electrode in the absence and the presence of HPGCP molecule with different concentrations at temperatures between 298 and 328 K are given in Figs. 4 and 5. The related electrochemical parameters, i.e. corrosion potential (E_{corr}), corrosion current density (i_{corr}) and the inhibition efficiency (E_{ct}) values are also listed in Table 3.

The corrosion current density values were determined by Tafel extrapolation of the cathodic and anodic Tafel lines. The inhibition efficiencies (E_{ct}) of HPGCP molecule have been calculated from current density (i_{corr}) values through the following equation (3)[15]:

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

where i^{0}_{corr} and i_{corr} are uninhibited and inhibited corrosion current densities, respectively. The obtained data are given in Table 3.

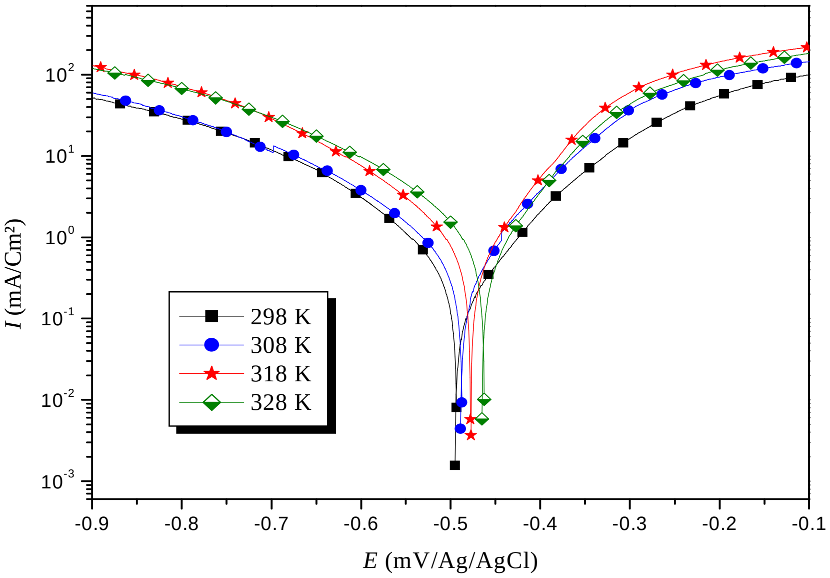

Fig 4 :Potentiodynamic polarisation curves of carbon steel in 1 M HCl at different temperatures

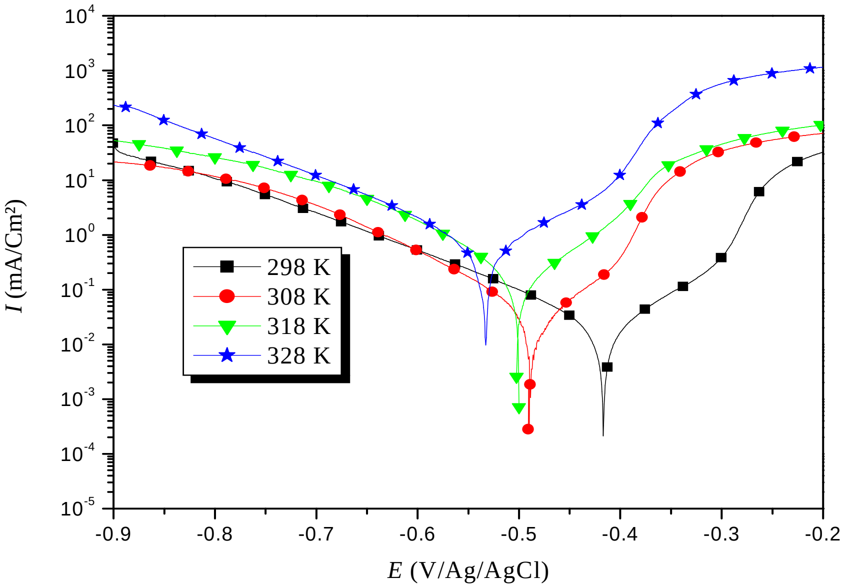

Fig 5:Potentiodynamic polarisation curves of carbon steel in 1 M HCl in the presence of 10^{-5} M of HPGCP at different temperatures

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Table 3 :The influence of temperature on the electrochemical parameters for carbon steel in 1M HCl and 10^{-5} M of HPGCP

T (K)	E_{corr} mV/Ag/AgCl		i_{corr} µA/Cm^2		E_{ct} %
	Blank	**10^{-5} M of HPGCP**	**Blank**	**10^{-5} M of HPGCP**	-
298	- 498	-414	470	23	95
308	- 491	-489	800	55	93
318	- 475	-500	1600	200	87
328	- 465	-533	2000	370	82

An inspection of Table 3 shown that, as the temperature increased, the values of Ecorr shift in the negative direction, while the values of Icorr increase and E_{ct}(%) decrease. This behaviour reflectsphysical adsorption of HPGCP on the steel surface [16].

Kinetic parameters of activation corrosion process

To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, potentiodynamic polarization measurements weretaken at various temperatures in the absence and the presence of different concentrations of HPGCP (Figs. 6 and 7). Corresponding data are given in Table 4. In the studied temperature range (298–328 K) the i_{corr} values increase with increasing temperature both in uninhibited and inhibited solutions and the values of the inhibition efficiency of HPGCP decrease with temperatures.

The activation parameters for the corrosion process werecalculated from Arrhenius type plot according to the following equation (4) [17–20] :

$$i_{corr} = A.\exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

wherei_{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 weregivenin Figure 6. Value of E_a for carbon steel in 1 M HCl and presence of the optimum concentration 10^{-5} M of the inhibitor were estimated by calculating the slope of Ln (i_{corr}) vs. 1/T. Moreover, the Arrhenius equation canbeconverted an alternative equation as follow[21] :

$$i_{corr} = \frac{RT}{hN}\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(-\frac{\Delta H_a}{RT}\right) \quad (5)$$

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 7). A plot of $Ln\left(\frac{i_{corr}}{T}\right)$ against $\frac{1}{T}$ should give a straight line with a slope of $\left(\frac{\Delta H_a}{T}\right)$ and intercept of $\left[Ln\left(\frac{R}{N.h}\right)+\left(\frac{\Delta S_a}{R}\right)\right]$, E_a, ΔH_a and ΔS_a were calculated and tabulated in Table 4.

Table 4 : Activation parameters, E_a, ΔH_a and ΔS_a, of the dissolution of carbon steel in 1 M HCl in the absence and the presence of 10^{-5} M of HPGCP

	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J.mol^{-1} K^{-1})
Blank	41.55	46.5	- 110.42
10^{-5} M of HPGCP	78.20	81.7	24.30

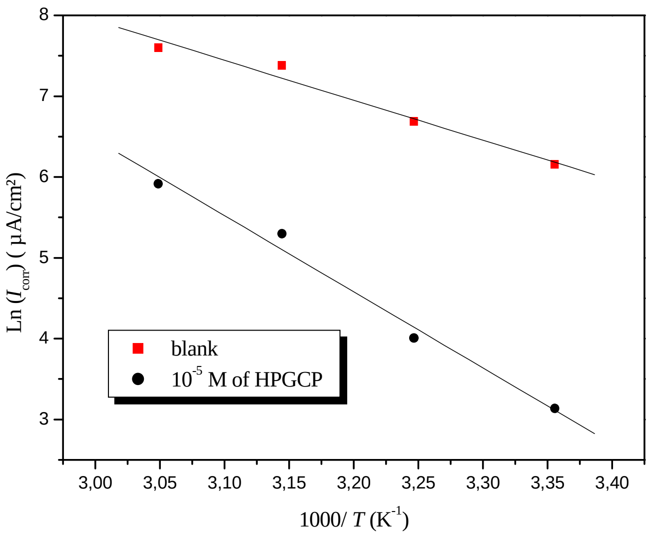

Fig 6 :Arrhenius plots for carbon steel in 1 M HCl in the absence and presence of 10^{-5} M concentration of HPGCP

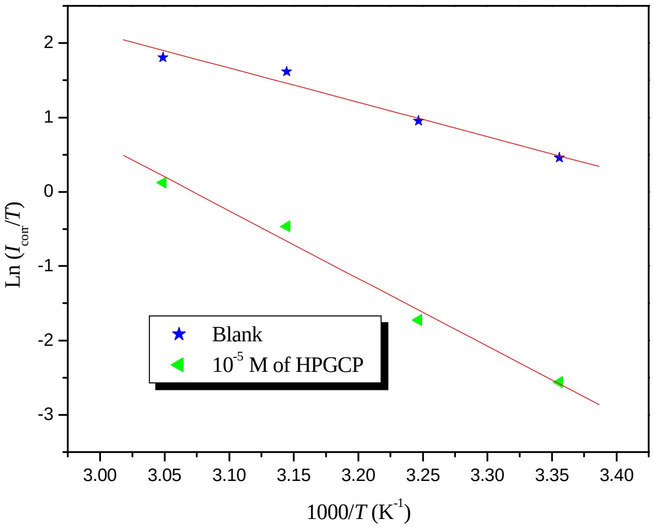

Fig 7 : Transition state plots for carbon steel in 1 M HCl in the absence and presence of 10^{-5} M concentration of HPGCP.

Inspection of Table 4 shows that values of both E_a and ΔH_a obtained in presence of HPGCP are higherthan those obtained in the inhibitor-free solutions. There are twopossibilities : in the first case ($E_{a,\ inh} > E_{a,\ HCl}$) the inhibitor is adsorbed on the most active adsorption sites (havinglowest energy) and the corrosion process takes place predominantly on the active sites of higher energy. In the second case ($E_{a,\ inh} < E_{a,\ HCl}$), i.e. asmallernumber of more active sites remainuncovered which take part in the corrosion process. This observation further supports the proposedphysical mechanism [22].

CONCLUSION

The following conclusions maybe drawn from the study :

- Results obtained qualified that HPGCP tested is an efficient inhibitor.
- Data obtained from gravimetric measurements are in good agreement with those of the polarization resistance method.

- Increase of temperature leads in a decrease of efficiency and an increase of the activation corrosion energy.
- 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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