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Research Article

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The corrosion inhibition and adsorption behavior by compound based on cyclotriphosphazene on carbon steel in hydrochloric acid

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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. The inhibition efficiency of HPGCP decreases with the rise of temperature. The values of equilibrium constant (K_{ads}) and adsorption free energy were discussed. The adsorption of inhibitor on metal followed Langmuir's adsorption isotherm. 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 Langmuir isotherm model.

INTRODUCTION

Carbon steel, the most widely used engineering material, accounts for approximately 85% of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1, 2]. 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 [3].

Hydrochloric acid are the most commonly used acid at temperature up to 80 °C [3]. In such cases, the corrosion can be controlled by means of inhibitors in order to retard undesirable metal dissolution in acidic media [4].

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 [5–8], low price, and easy production.

Most of the corrosion inhibitors are heterocyclic compounds containing heteroatoms such as oxygen, nitrogen, sulphur, phosphorous, unsaturated bonds or plane conjugated systems [9-12]. The inhibitory action of these compounds is usually attributed to their adsorption interaction with the metal surface [13-16]. 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 an acidic medium [17]. 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 pi orbital of the inhibitors and the‘d’ orbital of iron [18-20].

The objective of the present study is to study 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 [21-26]. Various 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).

Solution

The aggressive solutions of 1 M HCl were 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 [21-26]. The concentration range of this compound was $10^{-6} – 10^{-3}$ M.

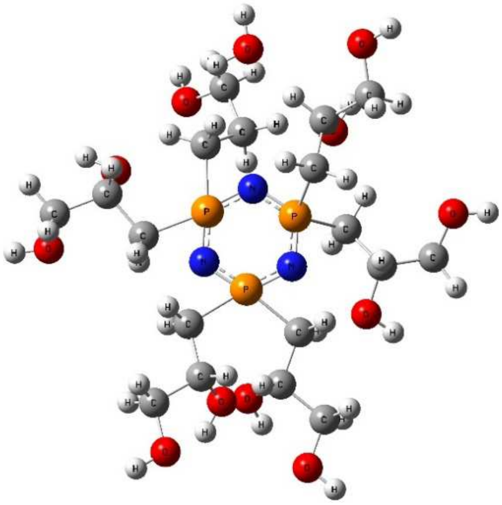


Fig 1 : Structure of Hexa propylene glycol cyclotriphosphazene (HPGCP)

Weight loss measurements

Coupons were cut to 5 cm ×1 cm ×0.2 cm dimensions for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 60 to 1500 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 weight loss was 6 h.

RESULTS AND DISCUSSION

Weight loss study

Generally, the corrosion rate of carbon steel in acidic solution increase with the rise of temperature. This is due to the decrease of hydrogen evolution overpotential. In order to understand more about the performance of HPGCP with the nature of adsorption processes, the effect of temperature is studied. For this purpose, the weight loss measurements are being employed with the range of temperature 298, 308, 318 and 328 K for 6 h of immersion. The corrosion rate (W_{corr}), surface coverage (θ) and inhibition efficiency (E_w%) were calculated from the following Eqs. (1-3)[27–28] :

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

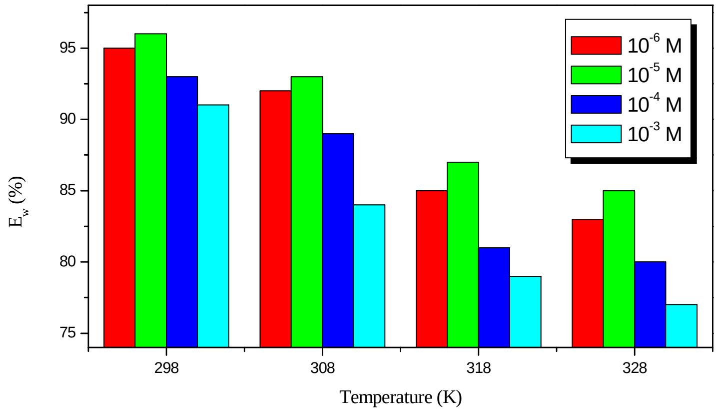
$$\theta = \frac{W_0 - W_i}{W_0} \quad (2)$$

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

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. Table 1 summarized the corresponding efficiency at various temperatures. As HPGCP has been added into the solution, the degree of surface coverage values decreases slightly with increasing temperature in which it could be caused by the desorption of inhibitor from the carbon steel surface.

Table 1 : Influence of temperature on the corrosion rate and inhibition efficiency of carbon steel in 1 M HCl at different concentrations of HPGCP

Temperature *T* (K)	Concentration *C* (M)	Weight loss 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	0.92
	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



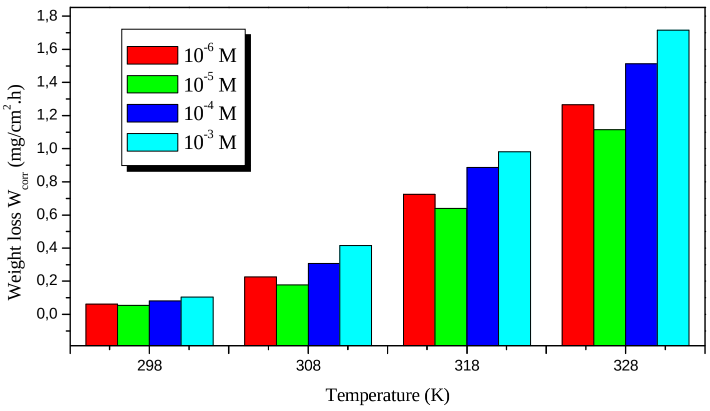


Fig 2: Variation of corrosion rate and inhibition efficiency with temperature for carbon steel in 1M HCl at different concentrations of HPGCP at various temperatures (298-328 K) during 6h of immersion

The evolution of corrosion rate and inhibition efficiency with temperature for carbon steel in 1M HCl of HPGCP at different concentrations is shown in Figure 2.

The results indicate that for a given temperature, the corrosion rate of steel increased with decreasing inhibitor concentration and attains the maximum value in concentration at 10^{-5} M. The values of inhibition efficiency obtained from the weight loss for different inhibitor concentrations and at various temperatures in 1M HCl are given in Table 1 and Figure 2.

Is clear that inhibition efficiency decreased at higher temperatures. This behavior indicates desorption of inhibitor molecule [29].

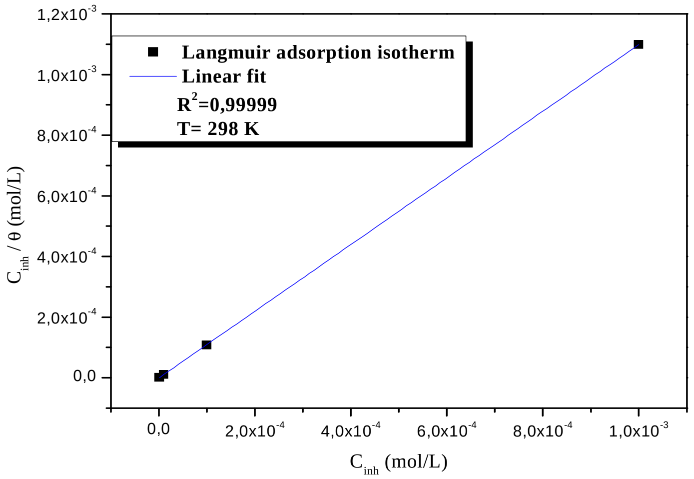
Adsorption isotherms

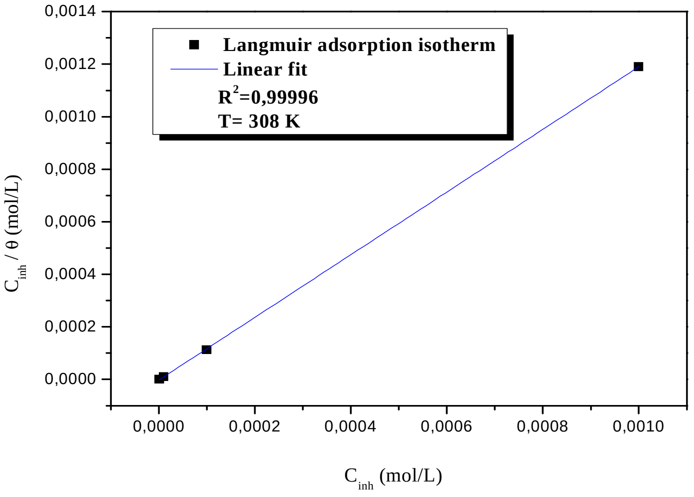
The nature of corrosion inhibition is deduced through the adsorption characteristics of the inhibitor. The metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process [30].Surface coverage degrees (θ) for various concentrations of HPGCP in 1 M HCl have been evaluated from inhibition efficiency values. These values were collected from gravimetric measurements. In order to evaluate the adsorption process of HPGCP on the carbon steel surface, many of adsorption isotherms were tested. The best fit between the experimental results and the isotherm function was found in Langmuir adsorption isotherm which is expressed as Eq. (4) [31] :

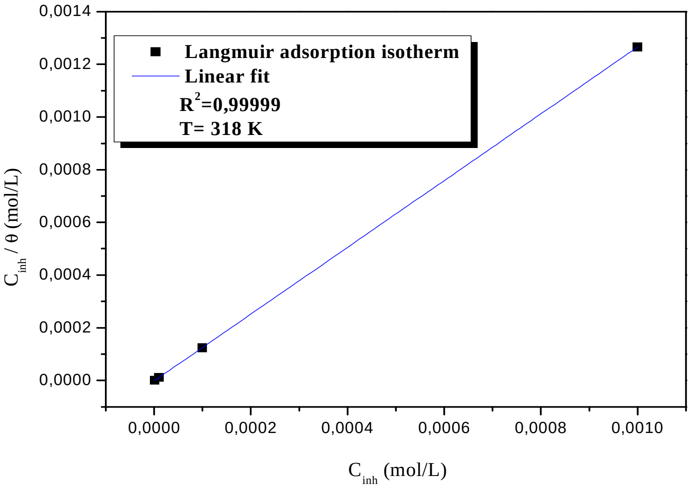
$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (4)$$

where C_{inh} is inhibitor concentration, θ is the degree of coverage on the metal surface and K_{ads} is the equilibrium constant for adsorption process. The adsorption isotherm was plotted using efficiencies that calculated from gravimetric measurements. Figure 3 shows the plots of C_{inh} / θ versus C_{inh} at 298-328 K temperature range with correlation coefficients.

The high correlation coefficients confirm the compatibility of the results with Langmuir adsorption isotherm. This isotherm assumes that the adsorbed molecules occupy only one site and it does not take into account lateral interactions between the adsorbates [32].


Langmuir adsorption isotherm
Linear fit
R^2=0,99999
T= 298 K
C_{inh} / θ (mol/L)
C_{inh} (mol/L)
1,2x10^{-3}
1,0x10^{-3}
8,0x10^{-4}
6,0x10^{-4}
4,0x10^{-4}
2,0x10^{-4}
0,0
0,0
2,0x10^{-4}
4,0x10^{-4}
6,0x10^{-4}
8,0x10^{-4}
1,0x10^{-3}


Langmuir adsorption isotherm
Linear fit
R^2=0,99996
T= 308 K
C_{inh} / θ (mol/L)
C_{inh} (mol/L)
0,0014
0,0012
0,0010
0,0008
0,0006
0,0004
0,0002
0,0000
0,0000
0,0002
0,0004
0,0006
0,0008
0,0010


Langmuir adsorption isotherm
Linear fit
R^2=0,99999
T= 318 K
C_{inh} / θ (mol/L)
C_{inh} (mol/L)
0,0014
0,0012
0,0010
0,0008
0,0006
0,0004
0,0002
0,0000
0,0000
0,0002
0,0004
0,0006
0,0008
0,0010

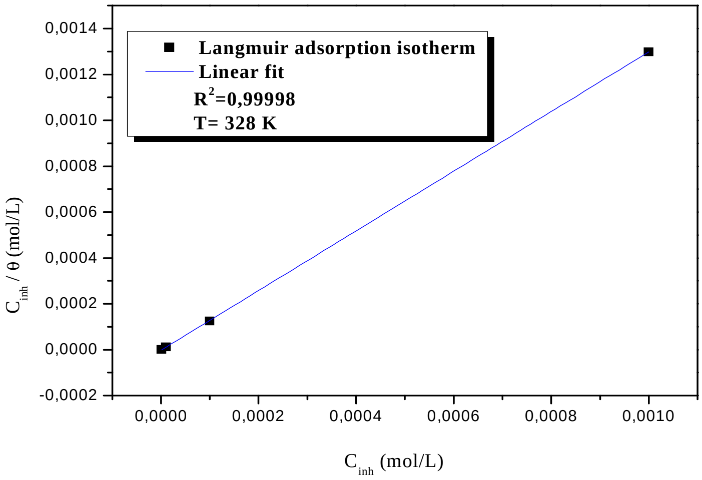


Fig 3: Langmuir adsorption plots for HPGCP on carbon steel in 1 M HCl solution at different temperatures

The standard free energy of adsorption (ΔG°_{ads}) values of HPGCP molecule was obtained using following Eq. (5) [33]:

$$\Delta G^{\circ}_{ads} = -RTLn(55,5.K_{ads}) \qquad (5)$$

where the value of 55.5 is the molar concentration of water in solution mol/dm^3, R is the universal gas constant, and T is the absolute temperature. Through the intercept of the straight lines, Kads values were obtained and related to the standard free energy of adsorption ΔG°_{ads} . The ΔG°_{ads} values were found as - 44.20, - 43.16, - 46.06 and - 46.70KJ mol.1 respectively for 298-328 K temperature range. The variation of the ΔG°_{ads} values versus temperature were presented in Table 2.

Table 2: Thermodynamic adsorption parameters for HPGCP on carbon steel in 1 M HCl solution at different temperatures

Temperature T(K)	**Adsorption constant K_{ads} (L.mol^{-1}.10^6)**	ΔG°_{ads} **(kJ/mol)**
298	1.02	- 44.20
308	0.38	- 43.16
318	0.67	- 46.06
328	0.49	- 46.70

The decreasing value of ΔG°_{ads} reflects the increasing of adsorption capability and its negative sign is usually characteristic of strong interaction on the carbon steel surface [34].

With regard to the free energies of adsorption process, it is currently accepted that values of ΔG°_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged molecules and charged metal surface (physisorption) ; those around -40 kJ mol^{-1} or higher involve charge sharing or transfer from heterocyclic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [35]. Noteworthy ΔG°_{ads} values rose with increasing temperatures, indicating that the adsorption was favorable. In accordance with this, it could be said that the interaction seems to be physical ; however a chemical contribution may act on adsorption mechanism and temperature facilitates this effect.

Adsorption mechanism

Many mechanisms have been proposed for the inhibition of metal corrosion by heterocyclic inhibitors. Generally, it has been assumed that the first stage in the action mechanism of the inhibitor in the aggressive acid media is based on its adsorption on the metal surface [36, 37].

The processes of adsorption of inhibitors is influenced by the nature of the metal surface, the chemical structure of the heterocyclic inhibitor, the distribution of charge in the molecule, the type of aggressive electrolyte, and the type of interaction between heterocyclic molecules and the metallic surface [38, 39].

In most inhibition studies, the formation of donor-acceptor surface complexes between π-electrons of an inhibitor and the vacant d-orbital of metal are postulated [40-44].

Nitrogen-based compounds are effective inhibitors for carbon steel corrosion in aqueous solutions [45].

The presence of lone pairs of electrons on the nitrogen atoms of the additional nitrogen delocalized atoms produces a delocalization of 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 [46].

It is also known that the adsorption of the inhibitor can be influenced by the nature of the anions in acidic solution. The presence of Cl^- in the solution should be mentioned. They are characterized by strong adsorbability on the metal surface, which brings about a negative charge favoring the adsorption of cation type inhibitors [47-48].
The performance of HPGCP in HCl can be explained in the following way. In aqueous acidic solutions, the HPGCP exists either as neutral molecules or in the form of cations as indicated in Figure 4.

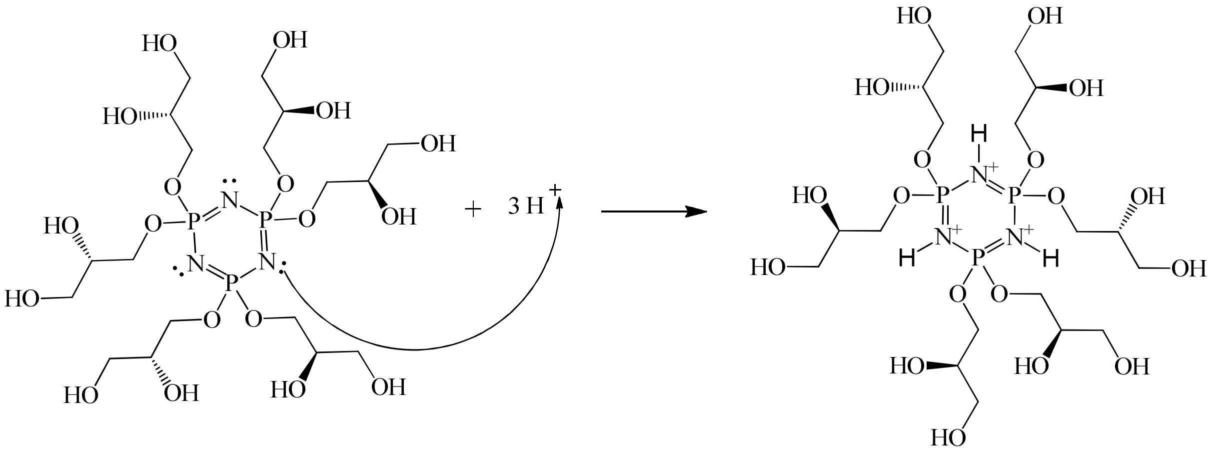


Fig 4 : Molecular form of HPGCP in an acid medium

Thus, the adsorption of the HPGCP as neutral molecules on the metal surface can occur directly involving the displacement of water molecules from the metal surface and sharing of electrons between the nitrogen atoms and the metal surface [49].

These heterocyclic nitrogen compounds may also absorb through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface [50].

A schematic representation of the adsorption behaviour of HPGCP on carbon steel in 1 M HCl solution is shown in Figure 5. When a carbon steel test piece is immersed in dilute solution of HCl containing HPGCP, three kinds of species can be adsorbed on its surface.

If the metal surface is positively charged (Figure 5) with respect to the potential of zero charge (PZC), the chloride ions will first be adsorbed on the metal surface, which in turn will attract the cationic forms of HPGCP and protonated water molecules. Thus, a closes packed triple layer will form on the metal surface and inhibit the entry of iron ions to the solution. Hence, with an increase in the positive charge on the metal surface, the adsorption of HPGCP would increase, and the HPGCP content of the solution would decrease.

If the metal surface is negatively charged (Figure 6) with respect to the PZC, the protonated water molecules and the cationic forms of HPGCP would be directly adsorbed on the metal surface. With increasing negative charge on the metal surface, adsorption of HPGCP would increase and its concentration in solution would decrease.

When the metal surface attains the potential at which the surface charge becomes zero, none of the ions (neither cations nor anions) adsorb on the surface through their ionic centre. A few HPGCP molecules may, however, become adsorbed through their planar p π - orbitals on the metal surface (which prossesses vacant d π-orbitals) (Figure 7).

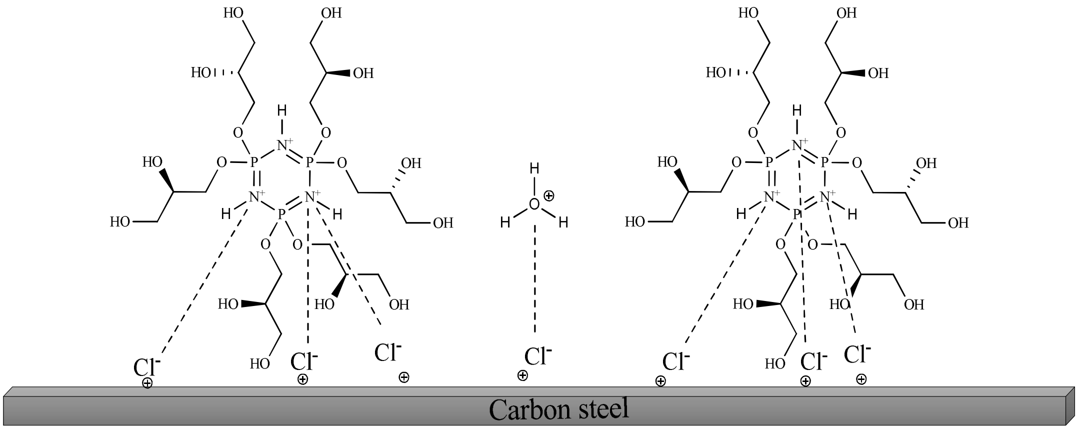


Fig 5: Schematic representation of adsorption behaviour of HPGCP on carbon steel in 1 M HCl solution: Carbon steel surface with positive charge

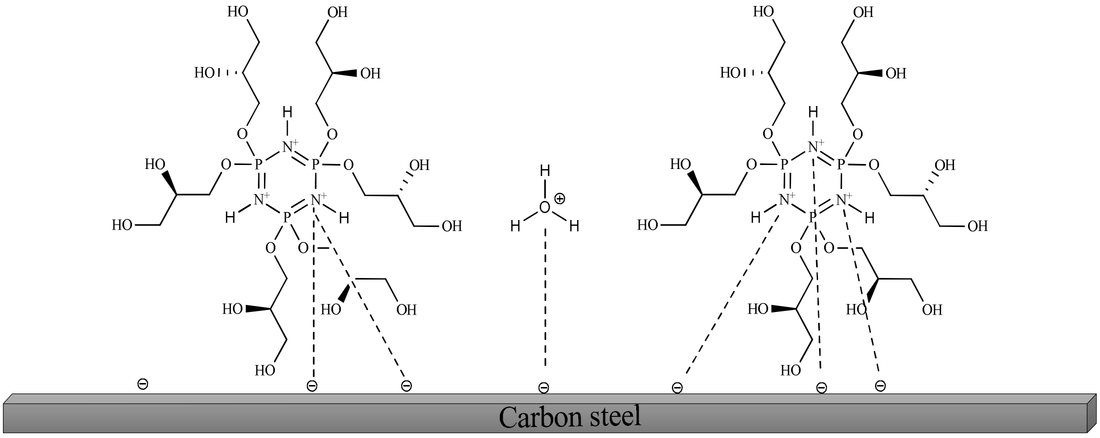


Fig 6: Schematic representation of adsorption behaviour of HPGCP on carbon steel in 1 M HCl solution: Carbon steel surface with negative charge

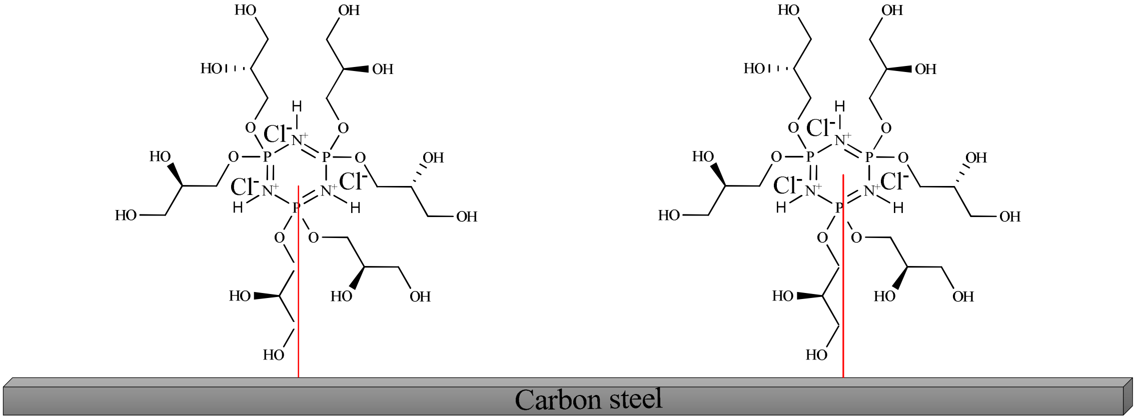


Fig 7:Schematic representation of adsorption behaviour of HPGCP on carbon steel in 1 M HCl solution: Carbon steel surface at a potential of zero charge

CONCLUSIONS

- HPGCP exhibit corrosion inhibition properties for carbon steel in 1M HCl.
- The inhibition efficiency for all weight loss measurements were in good agreement at the concentration of 10^{-5}M but decreases with the increase of temperature.

- The adsorption of HPGCP on the carbon steel surface from 1 M HCl obeys a Langmuir adsorption isotherm.
- The free energy of adsorption ΔG°_{ads} indicates that the process was chemically adsorbed (chemisorption) onto the carbon steel surface.

REFERENCES

[1] GY Elewady; AS Fouda; MN El-Haddad,*Canadian Journal on Scientific and Industrial Research.*, **2011**, 2(1) 1-18.
[2] MN Katariya; AK Jana; PA Parikh,*Journal of Industrial and Engineering Chemistry.*,**2013**, 19 (1) 286-291.
[3] NO Egbedi; KEEssine; IB Obot; EE Ebenso,*International Journal of Electro-chemical Science.*,**2011**, 6(4), 913-930.
[4] SM Shaban; A Saied; SM Tawfik; AA Elaal; I Aiad,*J. Ind. Eng. Chem.*, **2013**, (19), 2004-2009.
[5] G Avci,*Colloids Surf. A.*,**2008**, 317(1), 730–736.
[6] O Benali; L Larabi; M Traisnel; L Gengembra; Y Harek,*Appl. Surf. Sci.*, **2007**, 253(14), 6130–6139.
[7] F Xu; J Duan; Sh Zhang; B Hou,*Mater. Lett.*,**2008**, 62(25), 4072–4074.
[8] MA Khalifa; M El Batouti; F Mahgoub; A Bakr Aknish, *Mater. Corros.*, **2003**, 54(4), 251–258.
[9] MA Hegazy; AS El-Tabei; AH Bedair; MA Sadeq,*Corros. Sci*,**2012**, 54, 219-230.
[10] R Solmaz; E Altunbas; G Kardas,*Mater. Chem. Phys.*,**2011**, 125(3), 796-801.
[11] A Mohammed;KF Amin;Q Khaled;HA Mohsen;A Arida,*Corros. Sci.*,**2010**, 52(5), 1684-1695.
[12] MJ Bahrami; SM A Hosseini; P Pilvar,*Corros. Sci.*,**2010**, 52(9), 2793-2803.
[13] VVTorres; VA Rayol; M Magalh~aes; GM Viana;LCS Aguiar; SP Machado; H Orofino; E D'Elia,*Corros. Sci.*,**2014**, 79, 108-118.
[14] MA Quraishi; FA Ansari; D Jama,*Mater. Chem. Phys.*,**2002**, 77(3), 687-690.
[15] AM Fekry; RR Mohamed,*Electrochim. Acta.*,**2010**, 55(6), 1933-1939.
[16] R Agrawal; TKG Namboodhiri,*Corros. Sci*.,**1990**, 30 (1) 37-52.
[17] VV Torres; RS Amado; CF DeSa; TL Fernandez; CAS Riehl; AG Torres; E D'Elia,*Corros. Sci.*,**2011**,53(7), 2385-2392.
[18] KF Khaled,*Appl. Surf. Sci.*,**2010**, 256(22), 6753-6763.
[19] B Sanyal, Prog. *Org. Coat.*,**1981**, 9(2), 165-236.
[20] PV Dholaria; D Joshi, *International Journal of Chemtech Applications (INTJCA) An Open Access Free Online Scientific Journal*., **2015**, *4*(3).
[21] ODagdag; M El Gouri ; M Galai; R Ziraoui; M Ebn Touhami; A Essamri and A El Harfi,*Der Pharma Chemica*, **2015**, 7(1), 46-54.
[22] O Dagdag ; M El Gouri ; M Galai ; M Ebn Touhami ; A Essamri and A Elharfi.*Der Pharma Chemica.*, **2015**, 7(4), 284-293.
[23] O Dagdag; M Galai; M Ebn Touhami; A El Harfi,*International Journal of Innovation and Applied Studies.*,**2015**,10(1), 295-304.
[24] M El Gouri; A El Bachiri; S E Hegazi; M Rafik and A El Harfi,*Polym Degrad Stab.*, **2009**, 94(11), 2101.
[25] M El Gouri; A El Bachiri; SE Hegazi; R Ziraoui; M Rafik and A El Harfi,*J Mater Environ. Sci.*, **2011**, 2(4), 319-334.
[26] M El Gouri; SE Hegazi; M Rafik and A El Harfi,*Annales de Chimie Sci Mat.*, **2010**, 35, 2739.
[27] AH Espejel; MAD Crespo; RC Sierra; CR Meneses; EMA Estrada,*Corros Sci.*, **2010**, 52(7), 2258-2267.
[28] S Nesic, *Corros Sci.*, **2007**, 49(12), 4308-4338.
[29] F El-Hajjaji; RA Belkhmima; B Zerga; M Sfair; M Taleb; M Ebn Touhami; B Hammouti,*J Mater Environ Sci*.,**2014**, 5, 263.
[30] LR Chauhan; G Gunasekaran,*Corros. Sci.*,**2007**, 49(3), 1143-1161.
[31] R Solmaz; E Altunbas; G Kardas,*Protec. Met. Phys. Chem. Surf*, **2011**, 47 (2), 264-271.
[32] J O'M Bockris; AKN Reddy; MG Aldeco,*Modern Electrochemistry 2A Fundamentals of Electrodics, second ed., Kluwer Academic/Plenum, New York.*, **2000**, 942.
[33] E Bayol; K Kayakırılmaz; MErbil,*Mater. Chem. Phys.*, **2007**, 104(1), 74-82.
[34] T Gua; Z Chena; X Jianga;L Zhoua; Y Liaoa; M Duanb; H Wangb; Q Puc,*Corrosion Science.*, **2014** DOI: 10.1016/j.corsci.2014.10.004 article in press.
[35] SA Refay; F Taha; AM Abd El-Malak,*Appl Surf Sci.*, **2004**, 236(1), 175-185.
[36] Y Abboud; A Abourriche; T Saffaj; M Berrada; M Charrouf; A Bennamara; A Cherqaoui; D Takky,*Applied Surface Science.*, **2006**, 252(23), 8178–8184.
[37] RR Annand; RM Hurd; N Hackerma,*J. Electrochem. Soc.*, **1965**, 112(2), 138-144.
[38] B Sathianandhan; K Balahrishman; N Subramyar,*Br. Corros. J*,**1970**, 5(6), 270-273.
[39] F Zucchi; G Trabanelli; G Brunoro,*Corros. Sci*,**1992**, 33(7), 1135-1139.
[40] GK Gomma; MH Wahdan,*J. Mater. Chem. Phys.*,**1994**, 39(2), 142-148.

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[41] GK Gomma; MH Wahdan,*Bull. Chem. Soc. Jpn.*,**1994**, 67(10), 2621-2626.
[42] MS Abdel Aal; MH Wahdan; GK Gomma,*Mater. Chem. Phys.*,**1995**, 39(4), 290-297.
[43] GK Gomma; MH Wahdan,*Ind. J. Chem. Technol.*, **1995**, 2, 107-110.
[44] F Zucchi; G Trabanelli; C Monticelli,*Corros. Sci.*,**1996,** 38(1), 147-154.
[45] M Outirite; M Lagrenée; M Lebrini; M Traisnel; C Jama; H Vezin; F Bentiss,*Electrochimica Acta.*, **2010**, 55(5), 1670–1681.
[46] ZA Iofa; GN Tomashov,*Zh Fiz. Khim.*,**1960**, 34(5), 1036-1043.
[47] LI Antropov; EM Makushin; VF Panasenko,*Technika, Kiev.*, **1981**.
[48] IL Rozenfeld,*Khimia, Moscow.*, **1977**.
[49] N Hackerman; AC Makrides,*J. Phys. Chem.*,**1955**, 59(9), 707-710.
[50] CA Man,*Trans. Electrochem. Soc.*,**1936**, 69(1), 105-113.