Int. J. Electrochem. Sci., 3 (**2008**) 191 - 198

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Adsorption Behaviour of 1-phenyl-3-methylpyrazol-5-one on Mild Steel from HCI Solution

Olusegun K. Abiola[1,*], *J.O.E. Otaigbe*[2]

[1] Department of Chemistry, University of Lagos, Akoka, Lagos, Nigeria
[2] Department of Pure and Industrial Chemistry, University of Port Harcourt, P. M. B. 5323, Port Harcourt, Nigeria.
*E-mail: abiolaolusegun@yahoo.com

Received: 4 June 2007 / *Accepted:* 29 November 2007 / *Online published:* 20 December 2007

The adsorption of 1 – phenyl–3- methylpyrazol – 5-one (HPMP) on mild steel surface from 0.5 M HCl solution was studied by using gravimetric technique. The values for free energy of adsorption, $\Delta G^{o}_{ads.}$, were calculated at each surface coverage, θ, of the studied compound by applying the mathematical model of Bockris – Swinkels adsorption isotherm. The variation of free energy of adsorption $\Delta G^{o}_{ads.}$ with surface coverage, θ, was interpreted in terms of heterogeneous nature of the electrode. A possible adsorption model of HPMP molecules on to the metal surface was suggested and discussed. The adsorption of HPMP molecules on the surface occurs without influencing the kinetic of corrosion process.

Keywords: Mild steel; Adsorption; Bockris – Swinkels isotherm; Corrosion; 1-phenyl-3-methyl pyrazol-5- one

1. INTRODUCTION

Adsorption played a very crucial role in the understanding of electrochemical processes such as corrosion and its inhibition, electro-organic synthesis on metal surface, double layer, electrokinetics, etc. [1-5]. A detailed mechanism for inhibition of metallic corrosion, designing and development of new corrosion inhibitors is not possible without understanding of the adsorption process on metal surface [5].

The adsorption of organic molecules on metal surface in electrolytes has been modeled with different adsorption isotherms, e.g. Langmuir [6-11], Temkin [9-11], Frumkin [12], Flory-Huggins and El Awady *et al*. thermodynamic – kinetic model [11-12], to elucidate the mechanism of corrosion inhibition on metal surface. However, a cursory look at recent literature reveals that there is scarcity of information on the application of Bocris – Swinkels isotherm to study adsorption of organic compounds on metals.

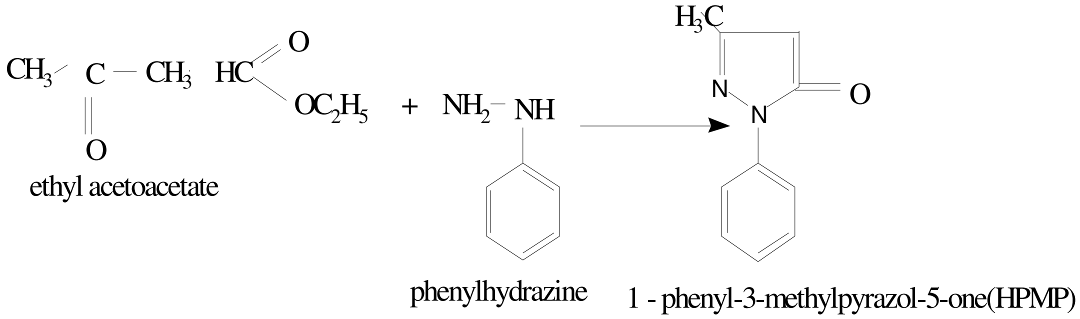
This paper is the continuation of our previous work [13-15] on the corrosion behaviour of metals in acid solutions containing 1 –phenyl-3-methylpyrazol-5-one (HPMP). In [13] the inhibition of the acid corrosion of mild steel by 1 – pheny 1-3 methylphyrazol – 5 – one (HPMP) was studied. It was found that HPMP inhibits the acid corrosion of mild steel and the adsorption data fit well into El Awady *et. al* thermodynamic – kinetic model. The aim of the present work is to investigate the adsorption of HPMP on mild steel surface according to Bockris – Swinkels adsorption isotherm by using gravimetric method.

2. EXPERIMENTAL PART

2.1. Material preparation

Synthesis of 1-phenyl-3-methyl-pyrazol – 5 – one (HPMP)

HPMP (Scheme1) was synthesized according to literature reports [16-18] and the synthesis can be described by the reaction of scheme 1.



Scheme 1.

Mild steel sheet of 0.04 cm in thickness supplied by World-Bank Engineering workshop of University of Port Harcourt, Port Harcourt, Nigeria was used for this study. The chemical composition and preparation of mild steel coupons are described in detail in previous study [19].

The compound (HPMP) was added to 0.5M HCl without pretreatment with concentrations of 0.0002, 0.0005, 0.001, 0.002 0.003, 0.004 and 0.005 M at 30^{0}C ± I.

2.2. Procedure

The procedure for gravimetric measurements was as described previously [19-20]. The immersion time for the weight – loss is 7 days at 30^{o}C. The variation of weight loss was monitored at 1 day interval progressively for 7 days.

3. RESULTS AND DISCUSSION

The study of adsorption of HPMP on mild steel from 0.5M HCl solution was studied at concentrations of 0.0002, 0.0005, 0.001, 0.002, 0.004 and 0.005M HPMP. The percentage protection (p%) is calculated using the relationship :

$$\%P = \frac{Wo - W}{Wo} \times 100 \qquad (1)$$

where Wo and W are the uninhibited and inhibited weight loses.

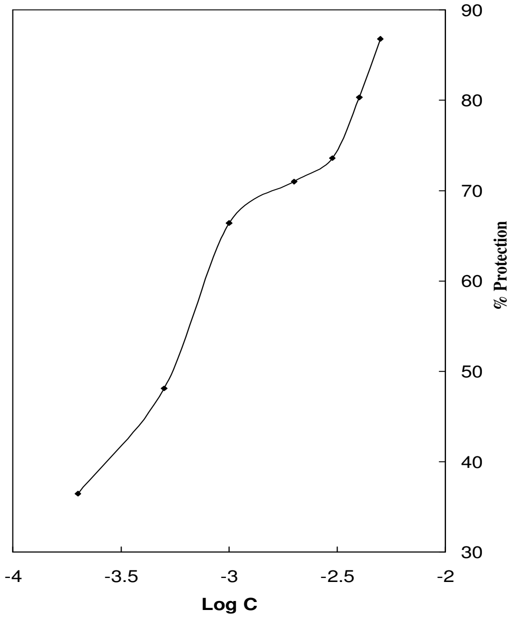


Figure 1. Relationship between protection efficiency and concentration of 1-phenl-3-methylpyrazol-5-one (HPMP)

The variation of the percentage protection with the logarithm of bulk concentration is presented in Fig.1 for 0.5 M HCl – HPMP systems at 30^0C. Figure 1 showed vividly that HPMP exhibits a clear adsorption pattern as depicted by the S – shaped curve, indicating the formation of a protective barrier film of inhibitor molecules on mild steel surface. Similar result was obtained in recent work [13]. The inhibition action of HPMP on mild steel surface immerse in HCI solution may be ascribed to the adsorption of HPMP molecules on the metal surface due to the presence of adsorption centers of the two N atoms in position 1 and 2 or the CO group in position 5(Scheme1).

HPMP acts as an inhibitor via adsorption mode as shown in Fig. 1, the percentage protection increases with increase in the concentration of HPMP. Consequently, surface coverage, θ was evaluated on the basis of a relative decrease in weight loss of mild steel sample in the HCl solution [5].

$$\theta = 1 - \frac{Wi}{Wu} \qquad (2)$$

Where θ is the surface coverage, Wi and Wu have the same meaning as in Eq. [1]

The amount of material loss depends on the degree of surface coverage, of the metal with the adsorbate.

The surface of the electrode in aqueous solution is considered to be covered with water dipoles and for adsorption of organic molecules to occur, these water dipoles must be replaced by organic molecules in a reaction as follows [5,21]

$$nH_2O_{\text{electrode}} + \text{Organic}_{\text{solution}} \rightleftharpoons \text{Organic}_{\text{electrode}} + nH_2O_{\text{solution}} \qquad (3)$$

The thermodynamics of the substitution process depends on the numbers of water molecules (n) removed by the organic molecules. The values of the apparent free energy change ($\Delta G^o_{ads.}$) for the adsorption process can be evaluated from θ values with the help of Bockris – Swinkels equation which is written as described in our previous report[5]:

$$\Delta G^0_{ads} = -\,2.303RT \log \left[\frac{55.5\theta}{C_o(1-\theta)^n} \, \frac{[\theta + (1-\theta)n]^{n-1}}{n^n} \right] \qquad (4)$$

where θ is the surface coverage, n is the number of water molecules being replaced and C_o is the concentration of the organic compound in the bulk solution.

Based on substitutional adsorption process for the space filling models [20-22] of adsorption of organic molecules on electrode surface, assuming that n=1 and 3 for adsorption of HPMP on mild steel surface, the values of $\Delta G^o_{ads.}$ for the adsorption process were calculated at each θ values by using Bocris-Swinkels equation as presented previously [5].

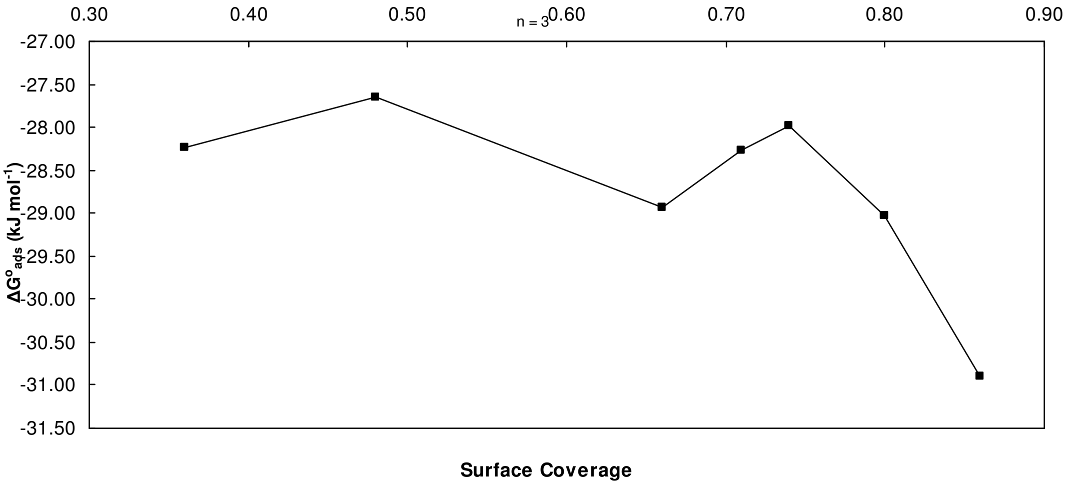


Figure 2. ΔG^o_{ads} (n=1) for 1- phenyl-3-methylpyrazol-5-one(HPMP) on mild steel as a function of surface coverage in 0.5 M HCI solution at 30° C

Figure 2 and 3 gives the variation of $\Delta G^o_{ads.}$ of HPMP with θ in 0.5 M HCI solution at n=1 and 3, respectively. As observed, Figs. (2 and 3) have the same shape with irregular variation for $\Delta G^o_{ads.}$

with θ values. In general, the more negative $\Delta G^{o}_{ads.}$ values were associated with the higher level of θ values.

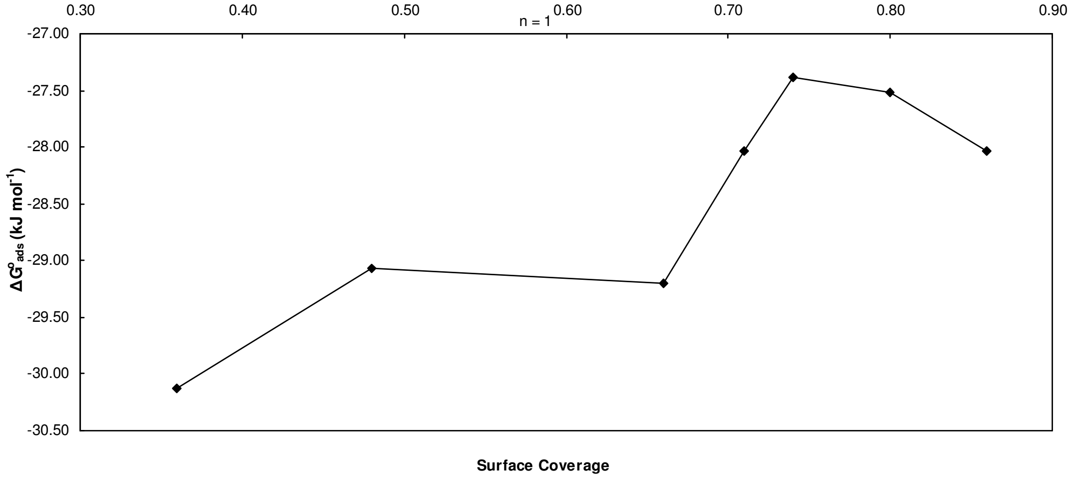


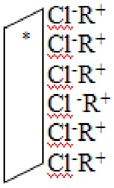
Figure 3. ΔG^{o}_{ads} (n=3) for 1- phenyl-3-methylpyrazol-5-one(HPMP) on mild steel as a function of surface coverage in 0.5 M HCI solution at 30°C

The dependence of free energy of adsorption $\Delta G^{o}_{ads.}$ of HPMP on coverage (Figs. 2 and 3) is ascribed to be due to the heterogeneous nature of the adsorbent. For solid electrode, such as mild steel, aluminium, platinium and gold, not all sites are equivalent on the surface due to heterogeneity [5, 23, 24]. There will be hierarchy of adsorption energies as observed experimental in Figs.2 and 3; since free surface energy depends on the orientation of metal crystals, and concentration of flaws (such as dislocations, vacancies, microdistortions of crystal lattice, etc) at the interface.

The negative values of $\Delta G^{o}_{ads.}$ indicate spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Literature search reveals that with regard to energetics of the adsorption process: two types of adsorption process had been established [5, 20, 25]; physisorption (electrostatic interaction between the charged molecules and charged metal) in which the $\Delta G^{o}_{ads.}$ is up to – 20 kJ mol^{-1} and chemisorption (charge sharing or transfer from the inhibitor (adsorbate)molecules to the metal surface to form co-ordinate bond) where the $\Delta G^{o}_{ads.}$ is more negative than – 40 kJ mol $^{-1}$.

The mean ΔG^{o}ads values of – 28. 7 I k J mol^{-1} (n = 3) and – 28. 48 k J mol^{-} (n = 1) support the mechanism of physisorption for the adsorbate on the mild steel surface

On this basis, adsorption model for HPMP on mild surface in HCl solutions may be proposed as in model I. In acid solution, HPMP dissolves to form cations, R^{+} by being protonated at the hetero atom [16, 18]. The protonated HPMP can be adsorbed on the mild steel surface on previously adsorbed chloride ions .Organic compounds containing O and N are able to adsorb on the metal surface even at high concentration of chloride ions [5, 10, 11, 20, 26]. The chloride ions (from the electrolyte) on the electrode surface provide a better electrostatic condition , which promotes a direct adsorption of cations on the surface through its polar group as depicted in model I. Previously [5, 20], we had proposed a similar model for the adsorption of some organic compounds on mild steel in acid electrolyte. The highest ΔG^o_{ads} value of 30.4 kJ mol^{-1} for HPMP (Fig.2) are in total agreement with ΔG^o_{ads} value for electrostatic interaction between HPMP cations and the charge metal surface as proposed for HPMP in model I.



Model I

* Mild Steel surface

4. KINETICS OF MILD STEEL CORROSION IN HCL SOLUTION WITH AND WITHOUT INHIBITOR

Figure 4 shows the dependence of log W_t (weight of mild steel at time t) as a function of time. As seen in Fig.4, the corrosion data fit the rate law for first- order reaction as expressed in equation (5):

$$\log (W_i - \Delta W_t) = -\frac{k}{2.303} t + \log W_i \qquad (5)$$

where k is the first – order rate constant, W_i is the initial weight of mild steel sample, ΔW_t is the weight loss of mild steel sample at time t and the term $(W_i - \Delta W_t)$ is the residual weight of mild steel sample at time t and can designated as W_t as shown in Fig. (4).

The obtained plots are linear; confirm a first – order kinetics for the corrosion of mild steel in HCl solution in the absence and presence of inhibitor. The anodic reaction of iron in HCI solution is

$$Fe \longrightarrow Fe^{2+} + 2e$$

And the cathodic reaction, the rate determining steps in strong acids [5, 27, 28]

$$H^+ + e \longrightarrow H_{ads}$$

Followed by

$$H_{ads} + H_{ads} \longrightarrow H_2$$

Figure 4 reflects the reaction order with respect to iron. This result (Fig 4), suggests that the adsorption of HPMP molecules do not influence the anodic reaction order. As seen in Fig.4, similar plot was obtained when $\log W_t$ was plotted against time for mild steel in HCl solution with (control) and without HPMP. Similar results were reported on the adsorption of some organic compounds [5, 20, 26] on mild steel in acid solution. HPMP by being adsorbed probably hinders the adsorption of H^+ on the surface of the electrode thereby slowing down the cathodic reaction, i.e. the rate determining steps in strong acids[5] , and consequently slowing down the removal of Fe ions from the reaction sites on the surface; the anodic reaction.

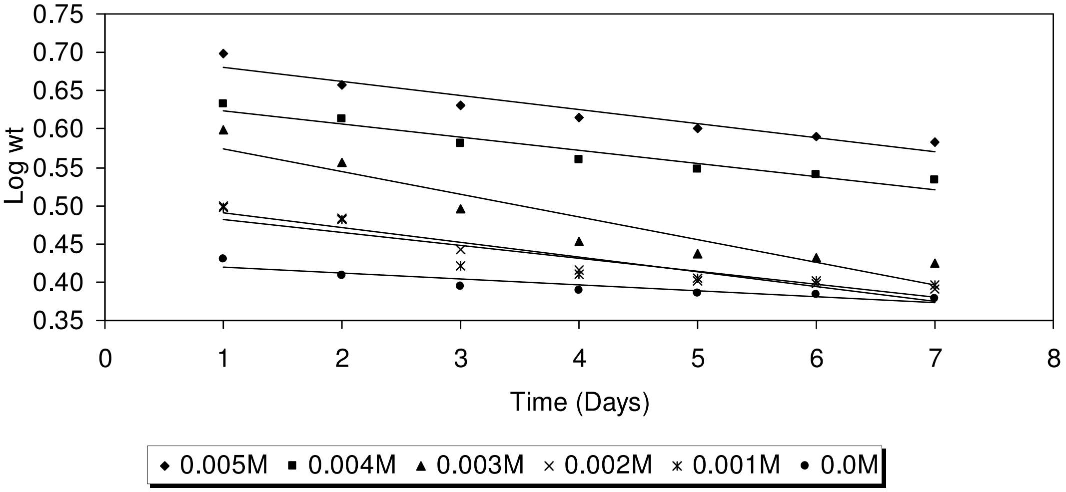


Figure 4. Variation of log W_t for mild steel coupons with time in 0.5 M HCI solution with and without 1-phenyl-3-methylpyrazol -5-one (HPMP) at 30°C

5. CONCLUSIONS

- The negative values of $\Delta G^o_{ads.}$ suggest the spontaneous adsorption of HPMP on the mild steel.
- The dependence of $\Delta G^o_{ads.}$ on surface covered, θ is due to heterogeneous nature of the mild steel surface.
- HPMP molecules in cationic form adsorb on the mild steel surface through electrostatic interaction with the mild steel surface.
- HPMP adsorbed on mild steel surface in HCl solution without modifying the kinetics of the corrosion process.

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