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Adsorption Behaviour of Pyrazolo [3, 4-b] Pyridine on Corrosion of Stainless Steel in HCl Solutions

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ABSTRACT

The properties of stainless steel makes the alloy suitable for many application; but this tends to change at very aggressive conditions thereby making its properties to fail. The corrosion inhibition efficiency of 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester (PP) on stainless steel in HCl solution was studied by weight loss method. The adsorption mechanism was investigated using adsorption isotherms. The experimental data fit Flory-Huggins and Thermodynamic/El-Awady models. The values for free energy of adsorption, ΔG°_{ads}, of PP at different surface coverage, θ, were also calculated by applying the mathematical model of Bockris-Swinkels adsorption isotherm. The variation of free energy of adsorption ΔG°_{ads}.with surface coverage, θ, was rationalised in term of interaction between adsorbed PP molecules. A possible adsorption model of PP molecules on to the steel surface was suggested.

Key words: Corrosion inhibitor, Bockris-Swinkels adsorption isotherm, free energy, stainless steel

INTRODUCTION

Corrosion resistance properties of stainless steels make them ideal base materials for many commercial applications. They exhibit excellent resistance to attack in neutral media even at elevated temperatures (Veenstra *et al*., 2007; Baddoo, 2008; Cardoso *et al*., 2008). Stainless steels are also known to exhibit resistance to corrosion under conditions of erosion and cavitation such as occurred on the blade of water turbines and on ship propellers (Nethercot and Gardner, 2002). However, the esteemed corrosion resistance properties give way in aggressive media (Garcia-Alonso *et al*., 2007). Thus, as it is the practice with less corrosion resistance metals, in order to retard the corrosion rate, the use of inhibitor had also been employed for some stainless steels (Noor and Al-Moubaraki, 2008). The assessment and corrosion prevention study of metals in pipeline also has become imminent as a means of protecting public, financial, investment and environment from such failures (Noor *et al*., 2011).

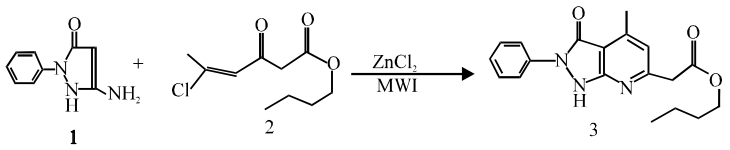
A number of heterocyclic organic compounds have been investigated for corrosion protection of stainless steel in aggressive media and it is generally agreed that the inhibitors passivate the metals by forming protective films on their surfaces (Assaf *et al*., 2007; El-Maksoud, 2008; Oluwadare and Agbaje, 2007). The readily polarisable high electron density centres of the inhibitor molecule are frequently considered as their interaction centre with the metal surface. Therefore, the development of efficient inhibitors demands an understanding, evaluation and optimization of the adsorption interactions between the inhibitor molecules and the metal surface. These adsorption interaction

are often evaluated with adsorption isotherms such Langmuir, Temkin, Frumkin, Flory-Huggins and El Awady/thermodynamic model (Ebenso, 2003; Tang *et al*., 2006; Abiola and Otaigbe, 2008).

According to Abiola and Otaigbe (2008), a review of the literature revealed scanty application of Bockris-Swinkels isotherm in investigating adsorption mechanism of hererocyclic compounds on metal surfaces despite the valuable information that can be deduced from its thermodynamic parameters Pyrazolo[3,4-b]pyridine, PP, had been indicated to inhibit the corrosion of stainless steel in HCl solution but its adsorption mechanism is yet to be examined (El-Mhammedi and Chtaini, 2007). In continuation of our efforts at exploring Bockris-Swinkels isotherm to study the adsorption of organic corrosion inhibitors on metal surfaces, this study reports adsorption thermodynamics parameters of PP on stainless steel.

MATERIALS AND METHODS

Synthesis of the pyrazolo[3,4-b]pyridine derivatives: PP (Scheme1) was synthesized under microwave irradiation according to the procedure of Xiang *et al*. (2006). The synthesis can be described by the reaction shown in scheme 1.



Scheme 1: Synthesis of 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester

A dry flask (25 mL) was charged with 3-amino-1-phenylpyrazol-5-one (1 mmoL) butyl (5-chlorohex-3-one-4-enoate)nn 2 (1 mmoL), glycol (2 mL) and catalyst $ZnCl_2$ (0.05 mmoL). The flask was then connected with refluxing equipment. After microwave irradiation for 8-12 min, the reaction mixture was cooled and washed with ethanol. The crude products obtained were purified by recrystallization from 95% ethanol to afford 3.

The experiments were performed with commercial stainless steel 316 having the chemical composition given in Table 1 and the corrosion rate was monitored by weight loss method.

Weight loss measurements: The Stainless steel was mechanically pressed-cut into coupons of dimension 3×3 cm and used as procured without further polishing but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use. All reagents are BDH grade and used as sourced without further purification. Double distilled water was used for all solution preparations. The heterocyclic compound (2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester) was added to acidic media without pre-treatment. The effect of addition of the inhibitor pyridazine compounds tested at different

Table 1: Chemical composition of commercial 316 stainless steel

	Chemical composition (%)										
Specimen	C	Si	Mn	Cr	Ni	Mo	Cu	N	P	S	Fe
316	0.02	0.50	1.71	16.20	11.00	2.18	0.35	0.07	0.03	0.02	68.06

concentrations on the corrosion of steel in 0.1 M HCl solution was studied by weight-loss at 298 K after 6 h of immersion period at concentrations of 4.57×10^{-5}, 9.13×10^{-5}, 3.65×10^{-4}, 4.57×10^{-4} and 6.85×10^{-3} M at 25°C. 0.1 M HCl solutions were employed as blank. Inhibition efficiency (I.E%) is calculated as follows:

$$I.E\% = \left(1 - \frac{W}{W_o}\right) \times 100 \quad (1)$$

where, W and W_o are the corrosion rates of steel with and without the inhibitor, respectively.

The surface coverage values θ at electrode are calculated from the corrosion rate of stainless steel in the electrolytes: surface coverage values θ was calculated by:

$$\theta = \frac{I.E\%}{100} \quad (2)$$

RESULTS AND DISCUSSION

The dependence of corrosion rate on concentration of PP in the supporting electrolyte (0.1 M HCl) at 25°C is shown in Fig. 1. The corrosion rate of the stainless steel in the electrolytes decreases with increasing concentration of PP in the electrolytes; suggesting that PP is a corrosion inhibitor for stainless steel in these electrolytes. And this result is in agreement with previous reports on pyridine derivatives as corrosion inhibitors (Abd El-Maksoud and Fouda, 2005).

The variation of the inhibition efficiency with the logarithm of bulk concentration is presented in Fig. 2. The S-shaped curve of the graph portrays the formation of a protective barrier film of inhibitor molecules on the steel surface. The electron rich centres of the heteroatoms of the inhibitor molecules are potential centres of Lewis acid-base interaction with the metal surface. Although, the N- and O-atoms in PP have lone pair of electron, Lewis acid-base of PP with metal surface is more likely through the N-atoms.

It had been suggested that metal corrosion inhibition of pyridine derivatives is often through coverage or blocking the metal surface from excessive contact with the corrosion media. Upon adsorption on the metal surface it imposes higher energy barrier to the dissolution of the metal in

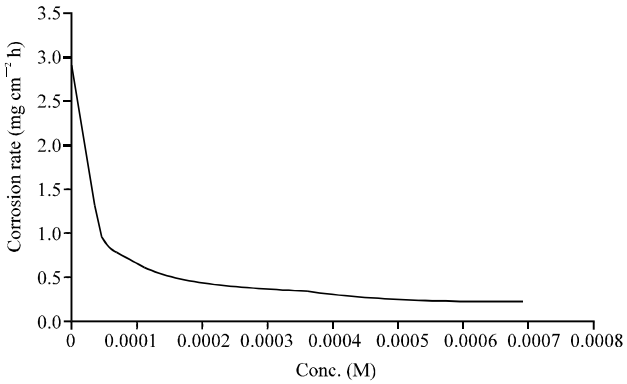


Fig. 1: Variation of corrosion rate (mg $cm^{-2}h$) with concentration of (2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester) on the stainless steel in 0.1 M HCl at 25°C

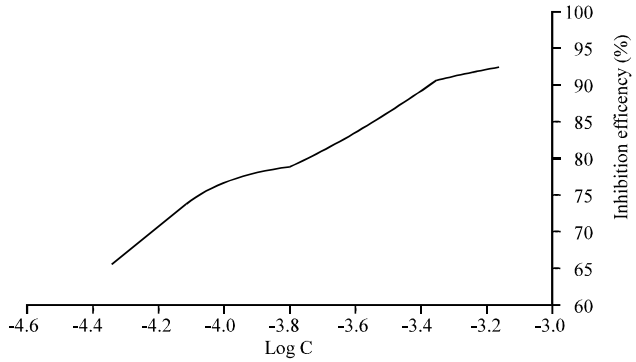


Fig. 2: Relationship between Inhibition Efficiency and concentration of 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester) (PP)

the corrosion media. It is explained that the protective action is a function of the π-electron density on the nitrogen atom and the size of the organic molecule (Kuprin *et al*., 1999). The corrosion inhibitive properties of pyrazole derivatives and some pyridine-pyrazole compounds had also been reported (Abdallah, 2003; Tebbji *et al*., 2005; Elayyachy *et al*., 2005; Chetouani *et al*., 2005) no study of the adsorption behaviour of the fusion of Pyrazolo [3, 4-b] Pyridine groups has been conducted. Table 2 depicts the linearization parameters and the free energies of adsorption of PP on stain steel surface in 0.1 M HCl.

Precise elucidation of the mechanism of adsorption of the inhibitor on metal surface is crucial for the design and evaluation of corrosion inhibitors. This makes adsorption isotherms imperative for elucidating the mechanism of surface (organo-electrochemical) reactions. Evaluation with an adsorption isotherm involves: fitting the data with the isotherm, optimisation of the adjustable parameters of the isotherm and appraisal of the physical reasonableness of the optimizing parameters in terms of the physical/chemical principle (s) on which the isotherm. The result presented in Table 2 revealed that the data are reasonably fitted by Flory-Huggins and El-Awady model. The data did not agree with a active centre 1:1 type adsorption mechanism. However, it is consistent with localized adsorption models that take into consideration for adsorbate-adsorbate interactions and adsorbent-adsorbate interaction via displacement of solvent molecules. Also, the data displayed less agreement for models with consideration for mobility of the adsorbed molecules (Volmer and Hill-De Boer isotherms).

Quasilattice models considered the surface of the electrode in aqueous solution 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:

$$nH_2O_{\text{electrode}} + \text{Organic}_{\text{solution}} \rightarrow \text{Organic}_{\text{electrode}} + nH_2O_{\text{solution}} \quad (3)$$

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 (ΔG°_{ads}) for the adsorption process can be evaluated from θ values with Bockris-Swinkels equation (Bockris and Khan, 1993).

Based on substitutional adsorption process for the space filling models of adsorption of organic molecules on electrode surface, for $5 \leq n \leq 1$ for adsorption of PP on the stainless steel surface, the

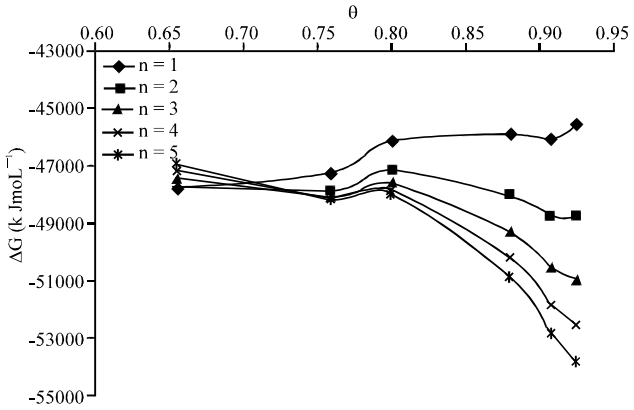


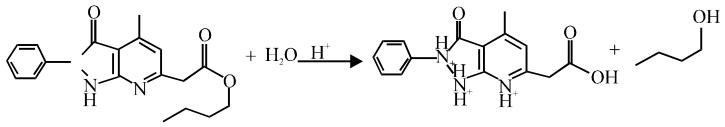
Fig. 3: ΔG°_{ads} J moL^{-1} for 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester (PP) on stainless steel as a function of surface coverage θ in 0.1 M HCl as the suporting electrolyte

Table 2: Parameters of linearization of adsorption models for 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester (PP) adsorption in acidic solutions

Isotherm	Equation	R^2	ΔG°_{ads} ($J moL^{-1}$)
Langmuir	y = 0.046x - 0.00005	0.836	
Frumkin	y = -3.074x + 12.64	0.880	-41267.40
Volmer	y = 4.392x + 45.21	0.916	
Flory-Huggins	y = -1.517x - 11.08	0.973	-37402.38
Thermodynamic/El-Awady	y = 0.686x + 3.243	0.982	-23718.11
Hill-De Boer isotherm	y = 33.22 - 10.77	0.828	16738.57

values of ΔG°_{ads} for the adsorption process were calculated at each θ values by using Bocris-Swinkels equation is presented in Fig. 3. The graph showed that the free energies of adsorption decreases with increasing surface coverage for when n value = 1, on the other hand, for n>1 ΔG°_{ads} value increases with increasing surface coverage. This suggests positive or cooperative adsorption at higher concentration and surface coverage.

It is important to put in to consideration that, the butyl ester group fragment of the in the inhibitor molecule is susceptible hydrolysis to give butanol and the remaining acid fragment. In addition the three N-atom centres are also prone to protonation in the acidic media. The resulting cation in solution is shown in scheme 2.



Scheme 2: The hydrolysis and protonation reaction of 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester) in acidic solutions

These cations can adsorb on the stainless steel metal surface even at high chloride ion concentration. It had been shown that anions (from the electrolyte) on the electrode surface provide

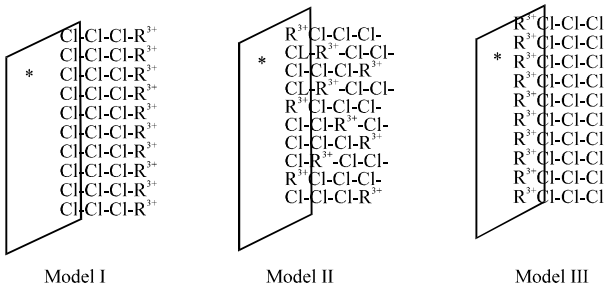


Fig. 4: Adsorption models for 2-(4-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazolo [3, 4-b] pyridin-4-yl) acetic acid butylester) (PP) on the stainless steel surface in HCl media; * the steel surface

a better electrostatic condition which promotes a direct adsorption of cations on the surface via formation of ion pair. On this basis, adsorption models for PP on the stainless steel surface in the acidic media are proposed.

At low concentrations of PP or surface coverage [$\theta = 0.7$] PP, cations (R^{3+}) from solution cluster around Cl^- and neighbourhood by strong coulombic attraction on the metal surface where, Cl^- are previously adsorbed (Fig. 4; Model I). The strong coulombic attraction restricts the mobility of the cations which may be responsible for the relatively low conformity of the data with isotherms that give provisions for mobility of adsorbed molecules. The cations which are essentially acid fragment of the hydrolysis product can interact with one another through condensation reaction. The secondary amine group of one cation fragment can undergo amide formation with the acid group of another. This reaction is accompanied with the release of a molecule of water. This accounts in part for the considerable fitting of the data with models that take into consideration for adsorbate-adsorbate interaction and the observed increasing value of ΔG°_{ads} with increasing surface coverage for n value>1. A model similar to model I had been proposed for adsorption of Vitamin B1 derivatives in HCl solution (Abiola and Oforka, 2004). For a situation of weak adsorption of chloride ions, R^{3+} at high concentration withdraw the anions on the surface into the solution, coadsorption of the cations and Cl^- ions is possible as in model II with increasing the concentration of PP. The degrees of desorption of Cl^- ions from the surface depends on the degree of adsorption of R^{3+} which is a function of the concentration of PP. At much higher concentrations of PP, the Cl^- ions on the surface provide a better electrostatic condition which promotes a direction adsorption of the cations on the surface through its pie electron system as depicted in model III (Abiola, 2005).

Although on the basis of energetics of the adsorption process: two types of adsorption process had been established; physisorption (electrostatic interaction between the electron density of the molecules and surface atoms of the metal) in which the ΔG°_{ads} is up to -20 kJ mol^{-1} and chemisorption (in which there exist a chemical bond between the molecule or ion and the metal surface) where the ΔG°_{ads} is more negative than -40 kJ mol^{-1} (Abiola, 2005; Abiola, 2006). The values of Δg°_{ads} obtained (from Bocris-Swinkels equation for n = 1, 2, .., 5) range -45.54 to-53.83 kJ mol^{-1} K^{-1} support chemisorption mechanism with strong extra coulombic bonding of the inhibitor to the stain steel surface.

CONCLUSION

From the present study, following conclusion can be made:

- The corrosion rate of the stainless steel in the supporting electrolytes decrease with the increase in adsorbability of PP (values of surface coverage, θ
- The negative values of ΔG°_{ads} suggest the spontaneous adsorption of PP on the mild steel
- The magnitude of ΔG°_{ads} indicates physisorption mechanism and PP molecules in cationic form adsorb on the stainless steel surface via formation of ion pair with chloride ion acting as bridge between them
- The adsorption data is consistent with Flory-Huggins and Thermodynamic/El-Awady

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