Corrosion inhibitive properties and adsorption behaviour of Bismuth oxy chloride on Mild steel & Aluminium in NaCl medium

S.Chitra[1], B.Anand[2], R.Vaidiyanathan[1*],V.Balasubramanian[2*]
[1, 2] Center for Research, Department of Chemistry, Mahendra Engineering College, Namakkal, Tamilnadu, India
[1*] Department of Chemistry, Mahendra College of Engineering, Salem, Tamilnadu, India
[1]chitrachem@gmail.com
[2]chemanand27@gmail.com

Abstract

The corrosion inhibition of Aluminium & Mild steel in sodium chloride solution by Bismuth oxy chloride has been studied using weight loss & adsorption parameters techniques. The obtained result revealed that Bismuth oxy chloride performed well as corrosion inhibitor in both the materials. The inhibition efficiency increased with increasing inhibitor concentration .The maximum inhibition occurs through adsorption of the Inhibitor molecule on metal surface without modifying the mechanism of corrosion process. The adsorptions parameters were used to evaluate the inhibitive property of bismuth oxy chloride.

***Keywords*— Mild Steel; Corrosion; Adsorption; Bismuth oxy chloride; Antimicrobial agent**

Introduction

Aluminium (Al), Mild steel (MS) and its alloys are widely used in technology because of their low density, agreeable appearance, and corrosion resistance. This relevance usually induces serious corrosion effects on equipments made up of iron, aluminium and its alloys. The use of the inhibitor is most possible approaches for protecting engineered materials against corrosion, especially in basic media. For these reasons, the corrosion inhibition of Al, MS in aqueous solution has attracted the attention of many investigators [1].Corrosion can be defined as the degradation or destruction of a metal or metal alloy due to electrochemical reactions with the environment [2]. Basically, corrosion involves three components: an anode, a cathode and an electrolyte. Oxidation reactions and metal dissolution occur at the anodic site while cathodic reactions are reductive [3]. Equation 1 displays the anodic dissolution of a metal.

$$\mathbf{Me \rightarrow Me^{n+} + n^{e-}} \qquad \text{----} \quad (1)$$

Due to the interplay between anode, cathode and electrolyte, it can result in a variety of corrosion forms including uniform or general corrosion, pitting corrosion, galvanic corrosion, and crevice corrosion, cracking and dealloying (jones 1996). Corrosion is of enormous economic concern, and it has been estimated that corrosion-related issues cost approximately 3-4 percent of GNP of industrialized nations [4-5]. These costs include replacement of materials, monitoring costs, maintenance and repairs, insurance to guard against failures, redundant equipment and costs associated with remediation of spills caused by corrosion failures (javaherdashti 2008). Most of the commercial inhibitors are toxic in nature; therefore, replacement by environmentally benign inhibitors is necessary. Many studies have been carried out to find suitable non-toxic compounds to be used as corrosion inhibitors for these metals in different aqueous solutions [6,7].Among them very few are eco friendly natural products , pharmaceutically active compounds i.e. antibiotics, antibacterial etc [8]. The use of pharmaceutical compounds offers interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen, sulphur and oxygen in their structure, and they are of particular interest because of their safe use, high solubility in water and high molecular size. Some of the azosulpha, piperazine derivative and antimalarial drugs have been reported as good corrosion inhibitors [9, 10 &11].In the present work mainly focussed to find the environmentally safe, non-toxic inhibitor that would be used for inhibiting the corrosion of Mild Steel and Aluminium. The use of such substances will establish, simultaneously, the economic and environmental goals. Bismuth has an atomic number 83 and a molecular weight 208.9 Daltons. It has a white crystalline nature and occurred in two valencies (+3 and +5) [12-16]. Bismuth oxy chloride had O-atoms in its structure, regarded as important factors for good inhibitor.Therefore; Bismuth Oxy Chloride is tested as an inhibitor for the corrosion of Mild Steel & Aluminium in basic media. Adsorption mechanisms were deduced through adsorption isotherms using data obtained there from.

II. EXPERIMENTAL

A. *Material preparation*

According to ASTM method as reported already [12-15], mild steel strips were cut into pieces of 5 cm x 1 cm having the following composition (in percentage) % C=0.017; Si=0.007; Mn=0.196; S=0.014; P=0.009; Ni=0.013; Mo=0.015; Cr=0.043 and Fe=99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

B. *Preparation of Solutions*

All the solutions were prepared using NICE brand analar grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes.

C. Preparation of Inhibitor

Various concentration of inhibitor was prepared on the basis Le Chatlier's principle.

D. Weight loss measurement

Mild steel specimens were immersed 1M NaCl and 2 M NaCl for 2 h at room temperature (28 ± 2 ºC) for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen was determined. From this, the inhibiton efficiency (IE %) was calculated using the formula

$$IE\ \% = \frac{W_o - W_i}{W_o}\ x\ 100 \quad \text{-----------------} \ (1)$$

Where, W_O and Wi (in g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor respectively.

RESULTS AND DISCUSSION

Weight loss method

The comparison graph of corrosion behaviour and inhibitor efficiency of Aluminium & Mild Steel in 1M NaCl & 2M NaCl with bismuth oxy chloride which was studied by weight loss method at 2 h at room temperatures was given in Figure 1 (a) & 2 (a). From the graph, it was observed that the weight loss of Aluminium & Mild steel in the aqueous solution decreases with increasing concentration of inhibitor and the values were tabulated in Table 1 & 2 from which it was clear that the corrosion rate has decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency (BiOCl) for Aluminium and Mild Steel in 2M NaCl was 84% and 89.8% respectively at 47.86 % of the inhibitor solution for 2 hours at room temperature.

Table 1

Corrosion parameters in absence and presence of BiOCl of with 1M and 2M NaCl in Aluminium.

MEDIUM	CONCENTRATION OF INHIBITOR (mM)	CORRSOION RATE	INHIBITON EFFICIENCY (%)
1M NaCl	Blank	37.41	-
	9.573	23.36	37.57
	19.14	19.03	49.13
	28.72	15.57	58.38
	38.29	13.23	64.62
	47.86	6.83	81.73
2M NaCl	Blank	44.12	-
	9.573	22.68	48.5
	19.14	20.33	53.9
	28.72	16.43	62.7
	38.29	11.68	73.5
	47.86	6.70	84.8

It was also fulfilled that the inhibitor was very effective for Aluminium corrosion when comparing with various molality like 1M NaCl and 2M NaCl; the inhibitor efficiency was maximum in 2M NaCl than 1M NaCl. Figure 1(a) revealed the comparison of Inhibitions efficiency of Bismuth oxy chloride (BiOCl) (in %) in 1M NaCl and 2M NaCl solution at two hour at room temperature.

Table 2

Corrosion parameters in absence and presence of BiOCl of with 1M NaCl & 2 M NaCl in Mild steel

MEDIUM	CONCENTRATION OF INHIBITOR (mM)	CORRSOION RATE	INHIBITON EFFICIENCY (%)
1M NaCl	Blank	21.4	--
	9.57	14.16	33.8
	19.14	11.37	46.8
	28.72	8.94	58.2
	38.29	7.56	64.6
	47.86	2.41	86.7
2M NaCl	Blank	21.8	--
	9.57	13.3	38.6
	19.14	9.67	55.6
	28.72	7.60	65.1
	38.29	2.86	79.6
	47.86	2.20	89.8

It can be seen from Table 2 that, the addition of inhibitors to the aggressive solution reduces the corrosion rate of mild steel. The corrosion rate decreased and inhibition efficiency increased with increasing inhibitor concentration suggests that the inhibitor molecules act by adsorption on the metal surface. From the values of Table 2, it is clear that the BiOCl effectively inhibits the corrosion rate of MS in both 1M NaCl and 2M NaCl with higher inhibition efficiency in 2M NaCl medium.

Figure 1(a) - Comparison of inhibition efficiency of BiOCl in (in %) in 1M NaCl solution on Mild steel and Aluminium at two hour.

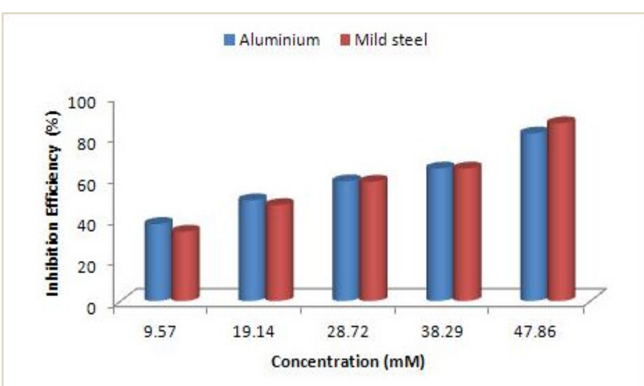
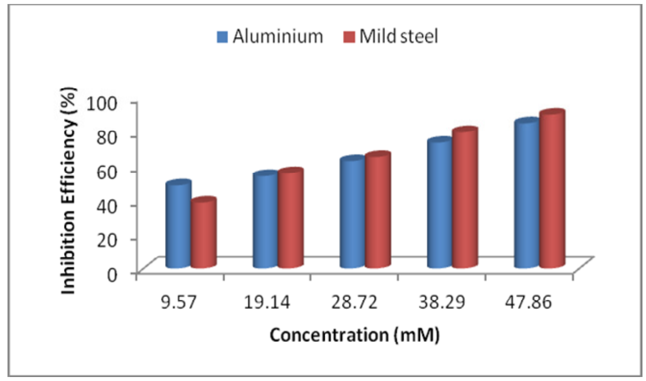


Figure 2(a) - Comparison of inhibition efficiency of BiOCl in 2 M NaCl solution on Mild steel and Aluminium at two hour



The obtained results indicated that BiOCl performs a good inhibition for the corrosion of Aluminium and Mild Steel in basic media .From the figure 1(a) and 2(a) the Inhibition efficiency of inhibitor in both the Mild steel and Aluminium metal increases as the concentration of inhibitor increases. For Mild Steel, the highest inhibition efficiency is obtained.

B. Adsorption Isotherm

In aqueous solution, the metal surface is always covered with absorbed molecule. Therefore, the adsorption of inhibitor molecule from an aqueous solution is a quasi substituted process and the inhibitor that have the ability to adsorb strongly on the metal surface will hinder the dissolution reaction of such metal in the corrosive medium.[17] Here ,the degree of surface coverage is considered as the determining factor that plays the main role in inhibition efficiency[18-20].The extend of adsorption depends on many factors, such as the nature of metal, condition of metal surface ,the chemical structure of inhibitor molecule , the nature of its functional groups, pH and type of corrosion medium [21].Basic information on the interaction between the inhibitor and the Mild steel & Aluminium metal surface can be proved by the adsorption isotherm and in general, inhibitor can function either by physical (electrostatic) adsorption or chemisorption with the metal surface . Actually, the adsorbed molecule may cause some difficulty for the surface to adsorb further molecule from neighbouring sites. To acquire more information about the interaction between the inhibitor molecules and the metal surface, a number of mathematical adsorption expressions have been developed to fit the degree of surface coverage through different adsorption isotherms in order to provide some knowledge on the nature of interaction of the adsorbed molecule [22]. The fractional surface coverage θ at different concentrations of inhibitors 1M NaCl and 2M NaCl solutions were determined from the weight loss measurements data [19] using the formula,

$$(\theta) = \frac{Wo - Wi}{Wo} \quad \text{-------------} \ (3)$$

Where, Wo and Wi are the values of weight loss of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta} \quad \text{---------} \quad (4)$$

Where, c is the concentration of the inhibitor, θ is the fractional surface coverage. The Langmuir isotherm, Eq. (4), which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant K is related to the free energy of adsorption ΔG_{ads} as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad \text{---------} \ (5)$$

Where, $C_{solvent}$ represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (5), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \quad \text{------------} \ (6)$$

so that a linear-relationship can be obtained on plotting c/θ as a function of c, with a slope of unity. The thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on Aluminium and Mild steel is obtained by Langmuir's adsorption isotherm are plotted in **Figure 3 & 4** and the obtained values are given in **Table 3 & 4.** It was found that the linear correlation coefficients clearly prove that the adsorption of (BiOCl) from 1M NaCl and 2M NaCl solutions on the Mild steel & Aluminium corrosion obeys the Langmuir adsorption isotherm. The negative values of ΔG^0_{ads} for the addition of inhibitors indicate that the process of adsorption of studied inhibitors is spontaneous in nature [23-26]. The free energy of adsorption of (ΔG_{ads}) for aluminium, in 1M NaCl was found to be -4.117 $kJmol^{-1}$ while for 2M NaCl it was found to be -4.672 $kJmol^{-1}$ respectively. On the other hand the free energy of adsorption of (ΔG_{ads}) for Mild steel, in 1M NaCl was found to be -4.913 $kJmol^{-1}$ while for 2M NaCl it was found to be -5.602 $kJmol^{-1}$ respectively.

It is well known that the values of ΔG_{ads} in the order of −20 kJ mol^{-1} or lower indicate a physisorption while those about −40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond[27].

The calculated adsorption values for the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of BiOCl at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

Table 3
Thermodynamic parameters for the adsorption of BiOCl in (1M NaCl and 2 M NaCl.) on the Aluminium.

Medium	Concentration (mM)	Surface coverage (θ)	ΔGads KJ / mol^{-1}	K x (10^{-2} M^{-1})
1M NaCl	47.86	0.817	-4.117	1.81
2M NaCl	47.86	0.848	-4.672	1.80

Figure 3 - Langmuir isotherm for adsorption of BiOCl on Aluminium surface studied at (1M NaCl and 2M NaCl).

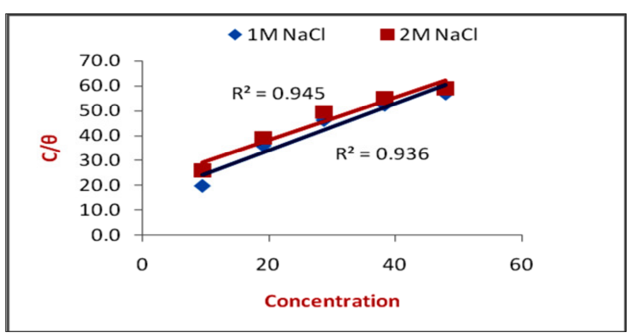
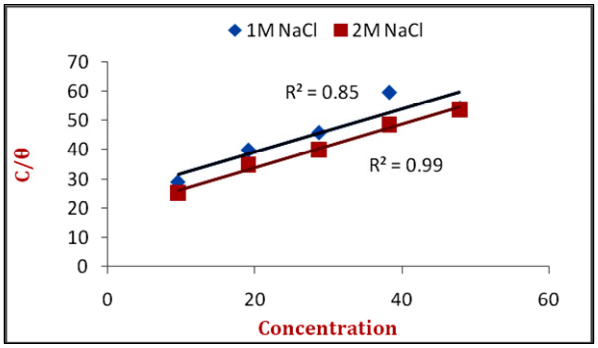


Table 4

Thermodynamic parameters for the adsorption of BiOCl in (1M NaCl and 2 M NaCl) on the Mild steel.

Medium	Concentration (mM)	Surface coverage (θ)	ΔGads KJ / mol^{-1}	K x (10^{-2} M^{-1})
1M NaCl	47.86	0.86	-4.913	1.82
2M NaCl	47.86	0.89	-5.602	1.81

Figure 4- Langmuir isotherm for adsorption of BiOCl on Mild steel surface studied at (1M NaCl and 2M NaCl).



Conclusions

Based on the above evaluation, it has shown that Bismuth oxy chloride inhibited the Mild steel more effectively when compared to the Aluminium. Nevertheless the inhibition efficiency of Bismuth Oxy chloride is more in 2M NaCl than 1M NaCl. The corrosion rate decreased with increased inhibitor concentration. The inhibition efficiency increased with increased inhibitor concentration. The adsorption of the bismuth oxy chloride on Mild & Aluminium is exothermic spontaneous as suggested by the negative values of ΔG_{ads} & obeys Langmuir's adsorption isotherm. The adherence of the data to Langmuir's adsorption isotherm support physical adsorption process.

Acknowledgement:

The author is sincerely grateful to Mahendra Engineering College for providing lab facilities to carry out this work.

Reference

[1] Sudhish K.Shukla,Eno E.Ebenso,*Int .J .Electrochem.Sci*.,6(2011) 3277-3291.

[2] Obot, I.B. Obi-Egbedi, N.O. & Umoren, S.A. (2009).Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl.Corros. Sci. 51, 1868-1875. DOI:10.1016/j.corsci.2009.05.017.

[3] Shukla, S. K., Singh, A. K., Ahamad, I. and Quraishi, M. A. (2009). Streptomycin: A commercially available drug as corrosion inhibitor for mild steel in hydrochloric acid solution. *Materials Letters* 63:819–822.

[4] Shukla, S. K and Quraishi, M. A. (2009a). Ceftriaxone:a novel corrosion inhibitor for mild steel in hydrochloric acid. Journal of Applied Electrochemistry 39:1517–1523.

[5] Eddy, N. O. and Ebenso, E. E. (2010a). Adsorption and quantum chemical studies on cloxacillin and halides for the corrosion of mild steel in acidic medium. *International Journal of Electrochemical Science* 5 (6): 731–750.H

[6] Ebenso, E. E., Eddy, N. O. and Odiongenyi, A. O. (2009). Inhibition of the corrosion of mild steel by Methocarbamol. *Portugaliae Electrochimica Acta* 27(1): 13–22.

[7] El-Naggar, M. M. (2007). Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds. Corrosion Science 49: 2226–2236.

[8] Ekop, A. S. and Eddy, N. O. (2009). Inhibition of the corrosion of mild steel by orphnadrine. *Australian Journal of Basic & Applied Science* 2(4): 1258–1263.

[9] M.Mansfeld, S.Martinez*, J Appl Electrochem* 33 (2003) 1137.

[10] M.Elayyachy, A.El Idrissi, B. Hammouti, *Corros. Sci.* 48 (2006) 2470.

[11] S. Acharya, S.N. Upadhyay, The inhibition of corrosion of mild steel by some fluoroquinolones in sodium chloride solution, Trans. Indian Inst. Met. 57 (2004) 297–306.H

[12] S. A.M. Refaey, F. Taha, and A. M. Abd El-Malak, "Corrosion and inhibition of 316 L stainless steel in neutral medium by 2-mercaptobenzimidazole," *International Journal of Electrochemical Science*, vol. 1, pp. 80–91, 2006.Gh

[13] Zaafarany, "Phenyl phthalimide as corrosion inhibitor for corrosion of C-Steel in sulphuric acid solution," *Portugaliae Electrochimica Acta*, vol. 27, no. 5, pp. 631–643, 2009.

[14] I. Ahamad and M. A. Quraishi, “Bis (benzimidazol-2-yl) disulphide:an efficient water soluble inhibitor for corrosion of mild steel in acid media,” *Corrosion Science*, vol. 51, no. 9, pp. 2006–2013, 2009.
[15] A.S. Fouda, H.A. Mostafa, H.M. El-Abbasy, Antibacterial drugs as inhibitors for the corrosion of stainless steel type 304 in HCl solution. J. Appl. Electrochem. 40, 163 (2010)
[16] F. Bentiss, M. Traisnel, M. Lagrenee, The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. Corros. Sci. 42, 127 (2000)
[17] I. Ahamad, M.A. Quraishi, Mebendazole: new and efficient corrosion inhibitor for mild steel in acid medium. Corros. Sci. 52, 651 (2010).
[18] Yurt, A., Bereket, G., Rivrak, A., Balaban, A. and Erk, B. (2005). Effect of Schiff bases containing pyridyl group as corrosion inhibitors for low carbon steel in 0.1M HCl. *Journal of Applied Electrochemistry* 35: 1025-1032.
[19] Ekop, A. S. and Eddy, N. O. (2009). Inhibition ofthe corrosion of mild steel by orphnadrine. *Australian Journal of Basic & Applied Science* 2(4): 1258 –1263.
[20] Eddy, N. O., Odoemelam, S. A. and Mbaba, A. J. (2008a). Inhibition of the corrosion of mild steel in HCl by sparfloxacin. *African Journal of Pure andApplied Chemistry* 2 (12): 132–138.
[21] Gopi, D., Govindaraju, K. M., Collins, V., Prakash, A., Manivannan, V., and Kavitha, L. (2009). Inhibition of mild steel corrosion in groundwater by pyrrole and thienylcarbonyl benzotriazoles. *Journal of Applied Eletrochemistry* (39)(2): 269–276
[22] H. Wang, X. Wang, H. Wang, L. Wang, A. Liu, *J. Mol. Mod.*, *2007*, *13*, 147.
[23] E. E. Ebenso, *Mater Chem Phys.,* **2003**, *79*, 58 .
[24] A.K. Singh, M.A. Quraishi, Adsorption properties and inhibition of mild steel corrosion in hydrochloric acid solution by ceftobiprole, J. Appl. Electrochem.41 (2011) 7–18.
[25] R.S. Dubey, Y. Potdar, Corrosion inhibition of 304 stainless steel in sodium chloride by ciprofloxacin and norfloxacin, Indian J. Chem. Tech. 16 (2009).334–338.
[26] X.H. Pang, W.J. Guo, W.H. Li, J.D. Xie, B.R. Hou, Electrochemical, quantum chemical and SEM investigation of the inhibiting effect and mechanism of ciprofloxacin, norfloxacin and ofloxacin on the corrosion for mild steel in hydrochloric acid, Sci. China Ser. B-Chem. 51 (2008) 928–936.
[27] M.M. El-Naggar, Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds, Corros. Sci. 49 (2007) 2226–2236.