Use of Imidazole and Its Deriatives in Corrosion Protection of Phosphor Bronze in Synthetic Acid Mine Water

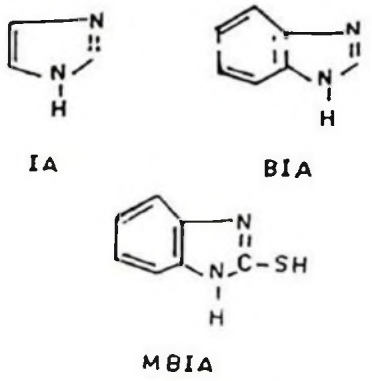
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Imidazole (IA), Benzimidazole (BIA), 2-Mercaptobenzimidazole (MBIA) have been studied as corrosion inhibitors for phosphor bronze in acid water (AW) and synthetic acid mine water (SMW) (pH 2.5). Complete protection (100%) to the alloy in AW is obtained by BIA and MBIA at a concentration of 0.04 and 0.02 mM respectively, but the maximum inhibition offered by these inhibitors (at 10.0 mM) in the mine water is 64.4 and 85.3% respectively. IA provided poor inhibition (48.4%) for corrosion of the alloy in the mine water. The influence of various parameters such as the duration of exposure to the solution, concentration of aggressive ions (Cl^- and Fe^{3+}) and temperature on the inhibitor effectiveness is evaluated and the order of protectivity have been compared. The inhibition arises due to an adsorption process and follows Langmuir adsorption isotherm.

Various organic compounds containing N and S atoms in the molecule have been found to be efficient inhibitors for protection of copper and its alloys [1-11]. In continuation of our studies [12], this paper describes the tests carried out with various imidazoles as corrosion inhibitor of the acid mine water corrosion of phosphor bronze alloy. Acid mine water corrosion problem is quite severe, in Ledo Colliery (New Mine) of North Eastern Coalfields (NEC), Margherita, Assam. The mine water selected for this study is a likely representative of this.



(IA) Imidazole (BIA) Benzimidazole (MBIA) Mercaptobenzimidazole

EXPERIMENTAL

The phosphor bronze used for the present study has the following composition: Sn = 3.48; P = 0.25; Pb = 0.01; Fe = 0.06; remainder is copper. Specimens having dimensions 40x25x1 mm were used for the weight loss studies. For polarization measurements, the apparent exposed area of the working electrode was 1 cm^2 and it was encased in araldite. Potentials between the working electrode and reference electrode (SCE) were controlled by using an AIS Floyd Bell potentiostat model V-2LR. The working electrode potentials were measured with an ECI Digital Electronic Multimeter model DM 6103.

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Metallographic studies were carried out using JEOL Model JSM-840A scanning electron microscope. The samples had been prepared using conventional metallographic techniques. All the azoles (analar or guaranteed reagent grade) were dissolved in minimum quantity of absolute alcohol before adding to the test solutions. Table 1 shows chemical composition of synthetic acid mine water (SMW) used in this study. Acid water (AW) was H_2SO_4 solution of pH 2.5. The details regarding preparation of SMW and the bronze surface, corrosion studies, potentiostatic experiments and metallographic studies are given in a previous paper [3].

Table 1

Chemical Composition of Natural Mineral Water (NMW) and Synthetic Acid Mine Water (SMW)

Component (ppm)	SMW pH = 2.5	NMW pH = 2.68
Fe^{3+}	400	303.5
Cu^{2+}	3	2.9
Zn^{2+}	2	1.4
Ca^{2+}	100	81.7
Mg^{2+}	150	182.3
Na^{+}	50	30.5
K^{+}	25	8.5
Cl	50	28.5
SO_4^{2-}	2000	2070.3

Data for SMW from Ref [2]
NMW from 14 L Sump water of Ledo Colliery (new mine) of North Eastern Coalfields, Margherita, Assam, India

RESULTS AND DISCUSSION

Weight Loss Studies

The results of weight loss studies is given in Table 2. Of all the imidazoles studied, MBIA is found to be the most effective inhibitor for the corrosion of the bronze in the solutions. BIA and MBIA give complete (100%) protection to the bronze in AW at 0.04 and 0.02 mM respectively, whereas IA offered maximum inhibition of 76.4% (at 0.045 mM) in the solution. In case of the mine water, maximum inhibition afforded by IA, BIA and MBIA is 48.4 (at 7.5 mM), 64.4 (at 10.0 mM) and 85.3% (at 10.0 mM) respectively. Analysis of the inhibition data reveals the following relative order of inhibitive power of the imidazoles:

MBIA > BIA > IA

The protective ability of the imidazoles is significantly reduced in the mine water which may mainly be ascribed to the aggressive nature of Fe^{3+} and Cl^- ions (discussed later) present in the mine water. The other ions present in the mine water - Cu^{2+}, Zn^{2+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+ and SO_4^{2-} probably favour dissolution of the alloy by increasing electrical conductivity. MBIA brings about an appreciable inhibition of corrosion of the alloy in the solutions, especially in AW which is not much affected by time within the test duration (1 to 7 days). This may be due to formation of insoluble adsorbed layer on the alloy surface. A similar trend is observed in case of the mine water, but the efficiency of the inhibitors was relatively low and further it decreased with time.

From the corrosion rates in the mine water at ambient temperature for different concentrations of the inhibitors, adsorption isotherms are obtained. It is assumed that the inhibitor molecules shield a fraction of the alloy surface at any instant, and the free fraction ($1-\theta$) reacts with the corrosive

Table 2

Variation of inhibitor efficiency (%) with Concentration of the Inhibitor in Acid water and Synthetic Acid Water

Inhib.Conc mM	IE % (Values in Parenthesis show Corrosion rate in MPY) IA	BIA	MBIA
Acid Water (AW)			
0.01	39.3 (3.40)	63.4 (2.05)	93.9 (0.90)
0.015	54.0 (2.58)	75.7 (1.36)	94.0 (0.34)
0.02	58.9 (2.30)	88.5 (0.64)	100 (0.00)
0.025	63.9 (2.02)	94.3 (0.32)	100 (0.00)
0.03	66.4 (1.88)	95.5 (0.25)	—
0.035	69.2 (1.72)	97.0 (0.17)	—
0.04	71.2 (1.61)	100 (0.00)	—
0.045	76.4 (1.32)	100 (0.00)	—
0.05	76.1 (1.34)	—	—
Synthetic Acid Water			
0.05	12.9 (23.95)	19.8 (22.50)	46.5 (14.71)
0.075	15.5 (22.25)	22.5 (21.31)	8.7 (14.10)
0.1	16.6 (22.93)	25.0 (20.62)	50.2 (13.69)
0.25	25.1 (20.59)	35.6 (17.71)	60.7 (10.80)
0.5	36.4 (17.49)	46.6 (14.68)	69.7 (8.33)
0.75	37.5 (17.18)	47.5 (14.43)	71.8 (7.75)
1.0	44.1 (15.37)	48.2 (14.25)	76.5 (6.46)
2.5	46.8 (14.63)	56.8 (11.88)	80.6 (5.33)
5.0	48.4 (14.19)	58.9 (11.30)	82.7 (4.75)
7.5	47.7 (14.19)	63.4 (10.06)	63.4 (4.56)
10.0	—	64.4 (9.79)	85.3 (4.04)
0.01	39.3 (3.40)	64.0 (9.90)	81.2 (5.17)

solution as it does in the absence of inhibitor, then the following relationship [5,6] is valid.

$$1 - \theta = k_i/k_o$$

where k_o and k_i are the corrosion rates without and with inhibitor respectively. All the inhibitors showed a linear plot of log $(\theta/1-\theta)$ *vs* log C which indicates a Langmuir adsorption isotherm. Analogous behaviour is shown by copper-BIA system in 3% NaCl solution [5]. The inhibitors may act through the process of adsorption on to the alloy surface resulting in the formation of a protective surface layer which retards the corrosion. Comparatively high order of inhibition afforded by MBIA may be due to the presence of two centres of adsorption (N and S atoms) in its molecule, while BIA and IA molecules contain a single polar atom (N) for the establishment of the adsorption process.

It is assumed that both the N and S atoms present in MBIA molecule may simultaneously be adsorbed by the alloy surface covering more effective area compared to that by the other two imidazoles. The inhibition potentiality of the compounds may also be explained on the basis of size of the molecules (spacial effect). IA provides least inhibition which may be understood in terms of its smaller size; this results in a smaller effective coverage of the corroding alloy surface. While reporting inhibition of corrosion of copper in chloride solutions by heterocylic compounds, Trabanelli *et. al.* [7] pointed out that the introduction of -SH group in a molecule appears to be beneficial for an increase in the inhibition because of direct interaction between Cu and the -SH group. Every and Riggrs [8] also reported S-containing compounds as superior to N-containing compounds and it is demonstrated that mixtures containing both N and S centres are more effective than either of the parent compounds alone. Gupta *et. al.* [9] studied the inhibition efficiency of various azoles for the corrosion of 70/30 brass in 1% H_2SO_4, and found that the S-containing compound, 2-mercapto-benzothiazole (2-MBT) is more effective than a N-containing benzotriazole or BIA.

Effect of Cl^- and Fe^{3+} Ions on Inhibitor Efficiency

The presence of Cl^- ions did not appreciably affect the inhibitive performance of MBIA in acid water. In the case of BIA, the inhibition is slightly affected by the addition of Cl^- ion, whereas this effect is a little more pronounced in case of IA. Inhibition afforded by IA, BIA and MBIA (0.015 mM) in acidic chloride solution containing 150 ppm Cl^- ion are 38.6, 56.1 and 77.4% respectively. The decrease in the inhibitive effectiveness of the compounds in the chloride solutions may be mainly due to the penetrating nature of Cl^- ions which leads to breakdown of the protective surface layer. MBIA exhibited a reasonably high inhibition (60% at 0.02 mM) in the acidic ferric solution containing 400 ppm Fe^{3+} ions, while BIA and IA at the same concentration showed an inhibition of 43.5 and 10.4% respectively. The activity of the azoles at 0.01 mM concentration level is significantly lowered in the acidic ferric solutions which may be due to rapid reduction of ferric ions, (Fe^{3+} —> Fe^{2+}), at the cathodic sites on the alloy surface causing an equivalent dissolution of the alloy at the anodic areas and may affect the rate of growth of the protective surface layer in presence of the imidazoles.

Effect of Temperature on Inhibitor Efficiency

Activation energies (E_a) are calculated from the slopes on the lines in Arrhenius plots. The E_a values are higher in presence of the inhibitors than in their absence which indicates that the dissolution of the alloy is slower in the inhibited system than that in the uninhibited one. Heats of adsorption (Q) are calculated from slopes of the lines on plots of log ($\theta/1-\theta$) *vs* 1/T. Large heat of adsorption (15 kcal.mol^{-1}) activation energy (10 kcal mol^{-1}) shown by MBIA in AW may suggest [10] that the inhibition is mostly due to chemisorption of the compound onto the alloy surface. BIA and IA exhibited significant value of Q (BIA : 7k cal mol^{-1}, IA : 4 kcal mol^{-1}) in AW which may indicate physical adsorption. All the inhibitors showed very low Q values (2-4 kcal mol^{-1}) in mine water suggesting that the inhibition process involves physical adsorption. The results show that MBIA (which function as more efficient inhibitor) has comparatively higher values of E_a and Q. The variations

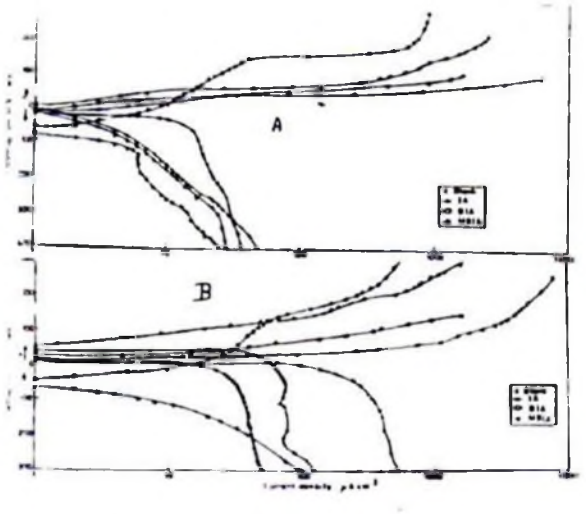


Fig. 1. Polarization graphs of phosphor bronze with different concentrations of inhibitors
A in Acid Water; B in Synthetic Mine Water

in the values of E_a and θ of the other examined imidazoles are also found to be in accordance with the inhibition data.

Polarisation Studies

The shift of both the anodic and cathodic polarisation curves (Fig.1 A & B) are most pronounced in the MBIA-inhibited solutions. IA shifted E_{corr} (Table 3) to a more noble value with a decrease in i_{corr}. The shift towards lower i_{corr} values in the anodic polarization curves in the solutions containing MBIA or BIA is well marked which is in accordance with the effectiveness of the compounds. Gupta et. al. [9] studied the polarization behaviour of 70/30 brass in 1% H_2SO_4 solution in presence of BIA & 2-MBT and reported that the inhibition is of mixed type; BIA inhibits mainly by anodic reaction, while 2-MBT is effective on the cathodic process. In the study of inhibition of copper in a neutral solution (0.1 N NaCl, Na_2SO_4 or $NaNO_3$) in presence of 2-MBT, Bonora and co-workers [11] also reported influence of the azole on both the anodic and cathodic processes, but predominantly on the cathodic process.

Table 3

Electrochemical Corrosion Parameters in Presence of the Inhibitor

Inhibitor	Conc mM	E_{corr} mV	i_{corr} μA.cm^{-2}	IE %
Acid Water Medium				
None	-	+25	13.0	-
IA	0.02	+30	3.5	73.1
BIA	0.02	+35	2.2	83.1
MBIA	0.02	-80	0.5	96.2
Synthetic acid Mine Water Medium				
None	-	+5	68.0	-
IA	5.0	+110	38.0	44.1
BIA	5.0	+40	27.0	60.3
MBIA	5.0	-75	13.0	80.9

SEM Study

The scanning electron micrographs in Fig. 2A a & b show grain structure of the phosphor bronze alloy. The inhibited surface of the alloy after exposure to synthetic mine water containing 10.0 mM MBIA for 24 h is shown in Fig. 2B a & b. The microphotographs of the inhibited surface of the alloy reveal formation of a protective surface film which was pale yellow-blue-green in appearance. Apart from the inhibitor film, red-brown and some blackish film was also noticed. The former may be attributed [12] to Cu_2O and the latter to CuO. The inhibitor film may reinforce the copper oxide film usually present on the alloy surface [13]. IR spectroscopy and X-ray diffraction studies may confirm the identity of the corrosion products and the exact nature of protectiveness of the inhibitor films.

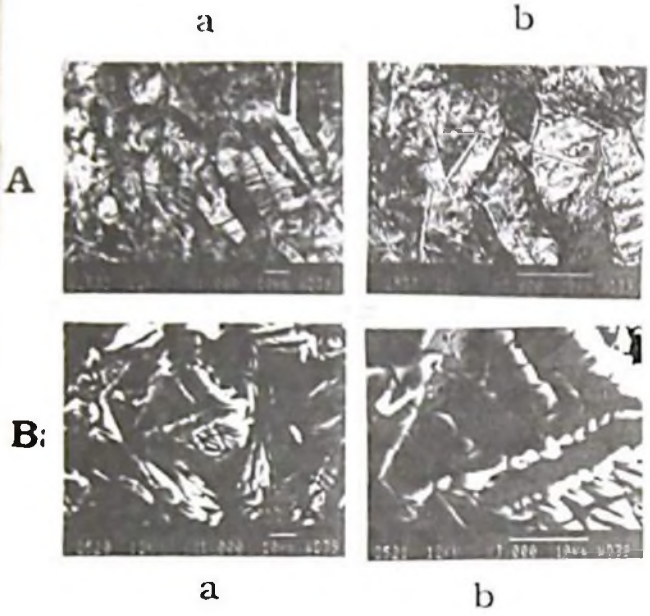


Fig.2. Microstructure of phosphor bronze
Etchant : $K_2Cr_2O_7$ + H_2SO_4 + NaCl (Sat.)
A As it is
B after corrosion tests in SMW with 10 mW MBIA (a) x1000 (b) x3000

CONCLUSION

The corrosion inhibition may involve adsorption of the imidazoles following Langmuir isotherm. Considerably high values of Q (15 kcal.mol^{-1}) and E_a (10 kcal mol^{-1}) of MBIA in AW indicates mostly chemisorption of the compound. The inhibition of BIA and IA may be due to physical adsorption. Complete (100%) protection to the bronze in AW is obtained by BIA (at 0.04 mM) and MBIA (at 0.02 mM), but the maximum inhibition obtained by IA is 76.4%. In the mine water also, IA provides least protection (48.4%) while BIA (64.4%) and MBIA (85.3%) offer appreciable inhibition. The inhibition efficiency is as per the order : MBIA > BIA > IA. The efficiency of MBIA and BIA in the solutions is not much affected by time. The protective ability of MBIA is also appreciable in acidic chloride and (lower concentrations) of ferric solution. The imidazoles act as mixed inhibitors; IA and BIA exhibited slight predominace of anodic inhibition, while MBIA showed predominant effect on cathodic process.

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