Voltammetric method for the study of corrosion kinetics

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The variation of metal corrodability, solution corrosiveness and corrosion rates for brass in acidic medium as a function of time have been studied. Although corrosion is a long process but it takes place at a faster rate in the beginning which goes on decreasing with due course of time. The methods prevalent in the field of corrosion rate determination furnish an average value for a long time interval. In the present paper the corrosion rates of brass in 2 N H_2SO_4 solution with and without inhibitor have been reported using gravimetric and some electrochemical methods.

The present investigation is focused on the corrosion behaviour of brass in 2 N H_2SO_4. The effectiveness of benzotriazole (BTA) as corrosion inhibitor for brass in acidic solution (2 N H_2SO_4) has been studied by gravimetric[1] [planned intervals test (PIT)] and electrochemical methods i.e. potentiodyanamic and galvanostatic polarization measurements[2].

It is a fact that, the rate of corrosion is very fast initially which goes on decreasing with due course of time[3]. The methods proposed in this field provide only an average value of corrosion rates for a long time interval[4]. However, looking at the minimum detection limits[5] of voltammetric techniques, we have developed polarographic and voltammetric methods i.e. differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) methods for the determination of corrosion rates at short time intervals, the results of which have been discussed in the paper.

Results and discussion

Gravimetric : BTA gives 63, 87 and 96% inhibition efficiency after 24 h for the dissolution of brass at concentrations of 80, 90 and 100 mg dm^{-3} 2 N H_2SO_4 solutions respectively. Above this concentration, inhibition efficiency does not increase. As such 100 mg concentration of BTA of test solution has been selected for the best inhibition efficiency. The results of weight loss determination by PIT method are shown as corrosion rates in the presence and absence of BTA inhibitor in Table 1.

The data obtained for the period A_1 and B suggests that solution corrosiveness increases in the base solution, while in the presence of BTA it decreases ($B < A_1$). The higher corrosivity of the solution can be attributed to the increase in concentration of Cu^{II} and Zn^{II} ions in the solution. The

Table 1. Corrosion rates of carbon steel in 2 N H_2SO_4 by gravimetric PIT measurements with and without inhibitor

Exposure	Without BTA inhibitor		With BTA inhibitor		Inhibitor efficiency
	Concn.*	CR**	Concn.*	CR**	(%)
A_1 (3 h)	21.37	23.90	6.05	6.76	71
A_t (24 h)	39.72	5.55	12.48	0.17	96
A_{t+1} (24 + 3)	42.96	5.33	14.48	0.18	97
B (3 h)	3.19	3.56	8.76	0.98	72
A_c (27–24) h	3.24	3.62	2.20	0.02	99

*Concentration in (mg dm^{-3}).

**Corrosion rate $\times$ 10^4 (mg cm^{-2} h^{-1}).

data suggests that BTA molecules reduce the stimulating effect of Cu^{II} and Zn^{II} ions[6]. A comparison of the data relating to period B and A_c it can be concluded that metal corrodibility decreases ($A_c < B$) as a function of time in presence of BTA. This indicates that the formation of an inhibitor film require some time, i.e. the inhibition process has an induction period. The increased inhibition effect of BTA may be due to its complex formation between metal ions Cu^{II} and Zn^{II} coming out in the solution and also due to the formation of complex film at the metal surface[7].

Galvanostatic polarization measurements : The anodic and cathodic polarization curves for brass in 2 N H_2SO_4 solution, without and with inhibitor are shown in Fig. 1. No passivation has been observed in the absence of inhibitor, while in presence of BTA good passivation is observed and both anodic and cathodic currents are decrease. These result reveal that BTA is mixed type of inhibitor.

Potentiodyanamic polarization measurements : It shows that the inhibitor increases the polarization resistance. To reach the same current density I, a higher polarization po-
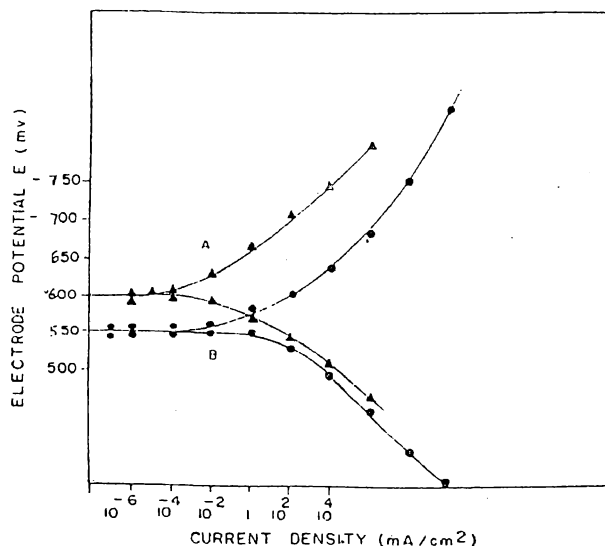
Fig. 1. Galvanostatic polarization curves of brass in 5 N H$_2$SO$_4$ with and without inhibitor : (A) Δ with inhibitor, (B) ● without inhibitor.

tential (from E_1 to E_2) is needed in the inhibited system. It could be concluded that the inhibitor influences both the anodic and cathodic partial reactions of the corrosion process.

Voltammetric measurement :

Figs. 2a and 2b are the differential pulse polarograms (DPP) and differential pulse anodic stripping voltammogram (DPASV) for corrosion solutions after 5 min in 0.1 M KCl and 0.001% gelatin at pH 5.0 ± 01. On recording polarograms/voltammograms of the corrosion solutions after increasing time intervals, similar curves were obtained with increased peak heights for Cu^{II} and Zn^{II}. The peack potential (E_p) values for Cu^{II} and Zn^{II} are –0.10 V and –1.12 V in DPP mode and in DPASV mode E_p values are –1.08 V[8], respectively. These curves show that using voltammetric method, it is possible to analyse the presence of Cu^{II} and Zn^{II} in the solution, simultaneously Cu^{II} and Zn^{II} produce two separate well defined polarographic/voltammetric peaks in each case. The peack hight (i_p) for Cu^{II} and Zn^{II} over the whole of the working concentration range in DPP and DPSAV modes are proportional to their respective concentrations. The corrosion rates at different time intervals with respect to Cu^{II} and Zn^{II} are reported in Table 2.

Fig. 2 show the DPP and DPASV curves for the corrosion solution to which BTA (100 mg dm^{-3}) has been added after 5 min of starting the experiment. Similar curves were obtained for corrosion solutions after different time intervals but with increased peak heights. A shift in the E_p value
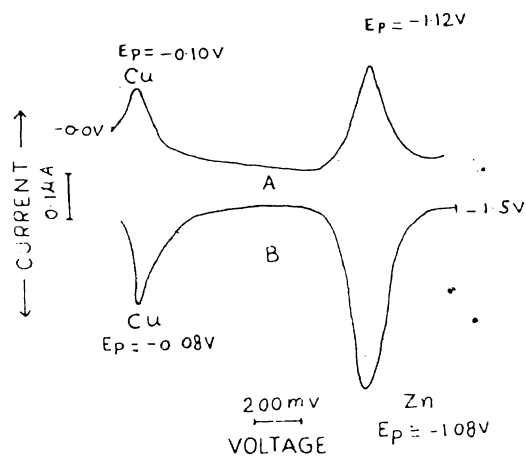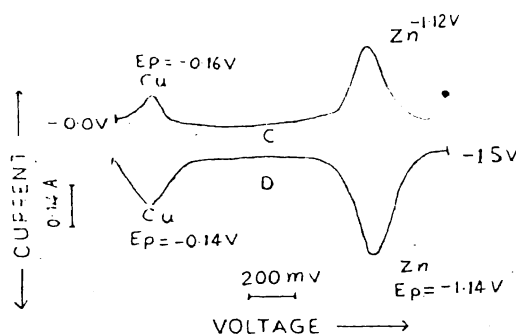

Fig. 2. (a, b) The differential pulse polarogram and differential pulse anodic stripping voltammogram of the corrosion solution (10 ml) in 0.1 M KCl + 0.001% gelatin at pH 5.0 ± 0.1 after 5 min of exposure. (c, d) The differential pulse polarogram and differential pulse anodic stripping votammogram of the corrosion solution (10 ml) containing 100 mg dm^{-3}. BTA inhibitor in 0.1 M KCl + 0.001% gelatin at pH 5.0 ± 0.1 after 5 min of exposure.

for each of the Cu^{II} and Zn^{II} indicates the M : BTA complex formation in the solution[9]. The corrosion rates in the presence of BTA are reported in Table 3.

A perusal of the data in Tables 2 and 3 clearly shows that initially the rate of corrosion of Zn is greater than that of Cu. This suggests that in the initial stages due to the establishment of the galvanic cell (Cu–Zn), there is preferential dissolution of zinc in the solution, but as a result of
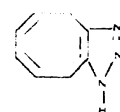
BTA

Table 2. Corrosion rates with respect to Cu^{II} and Zn^{II} for brass in 2 N H_2SO_4 solution without inhibitor using DPP and DPASV method

Time	Using DPP mode				Using DPASV mode			
	For Cu^{II}		For Zn^{II}		For Cu^{II}		For Zn^{II}	
	Concn.*	CR**	Concn.*	CR**	Concn.*	CR**	Concn.*	CR**
5 min	0.98	39.51	1.17	47.17	0.97	39.11	1.22	49.19
10 min	1.23	24.79	1.38	27.82	1.23	24.79	1.37	27.62
20 min	1.83	18.42	2.10	21.14	1.84	18.52	2.11	21.24
1 h	2.15	7.21	2.29	7.68	2.14	7.18	2.29	7.68
2 h	2.54	4.26	2.56	4.29	2.54	4.26	2.55	4.27
24 h	7.67	1.07	9.01	1.25	7.67	1.07	4.95	0.69

*Concentration in (mg dm^{-3}).

**Corrosion rate $\times$ 10^4 (mg cm^{-2} h^{-1}).

Table 3. Corrosion rates with respect to Cu^{II} and Zn^{II} for brass in 2 N H_2SO_4 with BTA inhibitor

Time	Using DPP mode					
	For Cu^{II}			For Zn^{II}		
	Concn.*	CR**	Inhibition	Concn.*	CR**	Inhibition
5 min	0.53	21.37	45	0.65	26.20	44
10 min	0.62	12.50	50	0.68	13.70	50
20 min	0.69	6.94	62	0.78	7.85	63
1 h	0.71	2.38	67	0.91	3.05	72
2 h	0.84	0.15	96	1.21	0.20	84
24 h	2.86	0.04	96	2.93	0.04	95
Using DPASV mode						
5 min	0.51	21.63	45	0.66	26.28	46
10 min	0.63	1.46	50	0.67	13.80	50
20 min	0.69	6.99	62	0.78	7.84	63
1 h	0.71	2.11	71	0.91	2.11	72
2 h	0.93	0.62	85	1.20	0.67	84
24 h	2.88	0.04	96	2.94	0.04	95

porous Cu–Cu oxide film formation on the surface of the electrode, the rate of dezincification decreases.

In the presence of BTA inhibitor, a thin black film formation was observed on the surface of specimens. This shows that the inhibition is due to the formation of some complex film with the metal ions. The organic compound used as inhibitor has the following properties :

This inhibitor acts as a proton acceptor in acidic medium. It forms an organometallic complex layer with the metal ions on the surface of the metal, thus inhibiting the corrosion. The corrosion inhibition efficiency of BTA in 2 N H_2SO_4 solution is 96% after 24 h.

A comparison of the corrosion rate data as calculated by voltammetry/DP polarography, galvanostatic and

potentiodyanamic measurements and gravimetric method clearly speaks the utility of BTA as an inhibitor for the corrosion of brass in 2 N H_2SO_4 solution.

From the figures and tables it could be concluded that voltammetric method gives dependable data for corrosion rates with respect to each species appearing in the solution i.e. Cu^{II} and Zn^{II}. Although all the other methods used in the present investigation furnish an average value for a long time period, but the proposed voltammetric method is highly useful for corrosion rate determination at short time intervals and that too with respect to each species appearing in the solution, which is otherwise not possible using methods prevalent in the field of corrosion rate determination[10,11].

Experimental

All the chemical used were of A.R./B.D.H. grade annealed 70/30 brass specimens (surface area 29.8^2) Cu, 69.3%, Zn, 30.6% and Fe, trace were used for the study of 2 N H_2SO_4 solution was used as corrosion media.

Gravimetric method :

Three polished weighed test specimens were used in the weight loss measurements. The variation of metal corrodibility, solution corrosiveness and corrosion rate as a function of time were investigated using the PIT technique. After the experiments, the specimens were cleaned with water and acetone, dried and weighed and from weight loss measurements, the corrosion rates were calculated. Similar experiment was done in the presence of 100 mg dm^{-3} BTA inhibitor.

Galvanostatic polarization measurements :

The galvanostatic polarization studies were made using 10 cm^2 cylindrical surface of the working electrode. Saturated calomel electrode (SCE) was used as reference elec-

trode. An AJCO-Electronics, India (model VT 85016) po-tentiometer, attached to a polyflex galvanometer was used for the galvanostatic polarization studies. The polariazation current was measured by using a cycle of 10 s and changing potential by 30 mV. The corrosion current density was plotted against the applied potential.

Potentiodyanamic polarization measurements :

The test specimens were sealed in a glass tube using epoxy in order to cover the sides of the rod. Only the circular cross section area of the cylinder 8 mm. Diameter was exposed to the solution. The specimen was polished and washed with distilled water before the experiment. The specimen was placed in the corrosion cell consisting of 100 ml of test solution and saturated calomel electrode (SCE) as reference electrode.

The potential rate was 50 mV/5 min. The current was recorded with the change in potential. An AJCO-Electronic, India model VT 85016 potentiometer was recorded on a polyflex galvanometer. The observed current was plotted against applied potential.

Voltammetric measurements :

An Elico (India) pulse polarograph model CL-90 was used for voltammetric studies. A cell consisting of three electrodes, viz. saturated calomel electrode as reference electrode, a coiled platinum wire as an auxiliary electrode and a dropping mercury electrode (for DPP) and glassy carbon fibre electrode (for DPASV) as working electrodes were used, respectively. The polished specimen was suspended in 250 ml 2 N H_2SO_4 solution at room temperature (25 ± 1°C). A definite aliquot of the solution was withdrawn from the test solution at short time intervals (5, 10, 20 min and 1, 2, 24 h) and polarograms and voltammograms were recorded

in deaerated 0.1 M KCl + 0.001% gelatin at pH 5.0 ± 0.1. The pH of the analyte was adjusted using HCl/NaOH solution. A similar experiment was performed using 100 mg dm^{-3} BTA in 2 N H_2SO_4 solution.

Acknowledgement

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