Di-n-Butylamine as an Inhibitor for the Corrosion of Pure Aluminium in Hydrochloric Acid Solutions

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ABSTRACT

Di-n-butylamine has been found to be a satisfactory inhibitor for the corrosion of pure aluminium in hydrochloric acid solutions. Polarization studies indicate that the anode polarization is negligible, whereas the cathode polarization is considerable. The Tafel plot holds good in this case. The dissolution of the metal is electrochemical in character, and it is possible to obtain cathodic protection by impressed current. The corrosion process with this amine appears to be under cathodic control.

INTRODUCTION

The corrosion of aluminium in hydrochloric acid solutions has been studied by Muller and Low[1], and Straumanis and Wang[2] with high purity, and by de Angelis and Carunchio[3] as well as Pavelka[4] with pure metal. Several substances have been mentioned as inhibitors, but detailed information of an academic character is not available in most cases. The inhibition of the corrosion of pure aluminium in hydrochloric acid solutions has been studied in detail in this laboratory with the following substances: acridine, thiourea, nicotinic acid, dextrin, ond tannic acid[5-8]. The present work formed part of the investigations on corrosion inhibition by amines. This paper presents the results of studies with di-n-butylamine. The reports covering n - and tri-n-butylamine have been communicated separately[9, 10].

EXPERIMENTAL AND RESULTS

The aluminium sheet (S.W.G. 22) was of the composition corresponding to the specification SIB HH-aluminium 99.5 (min.), copper 0.05, manganese 0.05, silicon 0.3 and iron 0.4 per cent (max.). The metal coupon was punched in one piece with a steel die. It was of a circular design to minimise the edge effects, diameter 2 cm. with a handle 3 cm. long and 0.3 cm. wide, the total weight being approximately 800 mg. The corrosion rates were determined under the following conditions. (*a*) concentration of hydrochloric acid 1.0, 1.25, 1.5 and 2N, (*b*) temperature 32±0.1°C and (*c*) immersion period 1, 2, 3, 4, 5 and 6 hours. Inhibitor efficiencies were determined by the weight loss method, the concentration of amine ranging from 0.1—1.0 g/l of nitrogen (1 g. of inhibitor contains 0.108 g. of nitrogen). Polarization studies were made with aluminium electrodes. The anode polarization was quite small throughout, less than 5 mv. The weight loss of the anode was also taken. The experimental details have been described in previous papers. Table I presents some typical results on inhibitor efficiencies, and Table II shows the effect of current density on cathode polarziation and anode weight loss at the optimum inhibitor concentration. The current density is calculated on the basis of apparent surface area.

SUMMARY OF RESULTS AND DISCUSSION

Di-n-butylamine is a satisfactory inhibitor for the corrosion of pure aluminium in hydrochloric acid solutions. The efficiency is somewhat low during the one hour period and is thereafter practically independent of time. It increases with increase in the inhibitor concentration up to a certain value beyond which it is constant. The efficiency increases with acid concentration from 1 to 1.25N, remains practically constant at 1.5N and then decreases to some extent. An acid concentration of 1.25N and an inhibitor concentration of 0.5 g/l of nitrogen can be regarded as the optimum from the view point of the efficiency, the values being in the range 80-87 per cent. Under similar conditions n-butylamine is less efficient, but the tri-n-butylamine is more efficient as an inhibitor[9, 10].

TABLE I

Inhibitor Efficiencies

Temperature 32°C, apparent surface area 6.3 sq. cm., 1.25N acid.

Immersion period, hrs.	*Inhibitor efficiency%, for inhibitor conc. g/l of N_2*			
	0.1	*0.25*	*0.5*	*1.0*
1	37	42	63	63
2	67	77	80	81
3	80	83	86	87
4	81	82	87	88
5	82	83	87	89
6	78	82	85	90

TABLE II

Anode weight loss and cathode polarization

Apparent surface area 3.14 sq. cm., immersion period 2 hrs. for anode weight loss, temp. 32°C, inhibitor conc. 0.5 g/l of N_2.

*Open circuit potential (—ve sign) in volts on hydrogen scale.

	[Anode weight loss, mgm.]		Cathode polarization, mv	
c.d. amp/dm²	*Without inhibitor*	*With inhibitor*	*Without inhibitor*	*With inhibitor*
0.0	29	6	*0.566	*0.577
0.32	44	18	3	22
0.64	65	30	4	55
0.96	73	40	6	76
1.28	81	50	11	88
1.60	90	61	19	96
1.92	105	72	27	103
2.56	125	89	42	115
3.20	146	105	56	125

Di-n-butylamine has been found to be an inhibitor for steel in sulphuric acid, the efficiency being about 85 per cent[11].

The steady state corrosion potential is shifted to a more negative value by the addition of the inhibitor. Straumanis and Wang[2] have reported a value of –0.58 v for the potential. Increase in the anode current density increases the corrosion rate and decreases the inhibitor efficiency. Without the inhibitor the cathode polarization is appreciable and is increased by the inhibitor. Cathode polarization and weight loss measurements show that cathodic protection of aluminium is possible. A current density of 1.6 amp/dm² is necessary to protect the metal in 1.25N acid, and with optimum concentration of inhibitor this is reduced to 0.48 amp/dm². Cathode polarization for the other two amines is consistent with their efficiency values.

The corrosion of the metal is electrochemical in character as shown by the existence of the negative difference effect during anodic polarization. In this case the weight loss due to local cell action with impressed current is greater than the normal weight loss without current. Straumanis and Wang[2] have also observed the negative difference effect and attributed the same to the presence of a protective film on the metal surface and self-corrosion by external current. Anodic protection due to protective film formation has not been observed at high current densities. This is to be expected since the anodic polarization is negligible.

The Tafel equation is obeyed for the plot of

cathode polarization against the logarithm of current density. The Tafel plot gave following values for slope b, exchange current density i_0, and energy transfer coefficient, without and with inhibitor under optimum conditions: 0.13, 0.10; 11.2 x 10^{-5}, 1.8 x 10^{-8} amp/cm^2; 0.48, 0.61. The values of these parameters, are in fair agreement with the literature values for the cathodic hydrogen evolution reaction, and indicate that the rate determining step is the discharge of the hydrogen ion[12]. A rough calculation of the inhibibitor efficiency from the exchange current gives a value of the order of 84 per cent, which is quite close to the observed efficiency.

Cathode and anode polarization values indicate that the effect of the inhibitor is essentially on the cathodic reaction. The decrease in the exchange current density by the amine shows that the inhibitor functions by adsorption on cathodic regions [13, 14]. The effect of the inhibitor on the corrosion potential also suggests the polarization of local cathodes due to its adsorption on the metal surface. The mechanism is similar for inhibition by n- and tri-n-butylamines, thiourea, dextrin and nicotinic acid for aluminium, and also di-n-butylamine for steel in acid[11]. The experimental results indicate that the corrosion process is under cathodic control.

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