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INHIBITION OF MILD STEEL CORROSION IN HYDROCHLORIC ACID BY 2-AMINOPYRIDINE AND 2-(AMINOMETHYL) PYRIDINE

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ABSTRACT

Weight loss measurements have shown that 2-aminopyridine (2AP) and 2-(aminomethyl)pyridine (2AMP) have very important effects on the corrosion of mild steel in hydrochloric acid. Both substances tend to inhibit the corrosion of mild steel in hydrochloric acid to a remarkable extent with 2AMP exhibiting higher maximum inhibition efficiency of 94% than that of 2AP (90%).Generally,inhibition was found to increase with increase in inhibitor concentration and half-life but with decrease in temperature and the first order rate constants at 30 and 40°C. Physisorption mechanism of adsorption has been proposed for the inhibitors and the difference in the inhibition behaviour of the compounds has been explained in terms of difference in their molecular weights.

Key words: Corrosion Inhibition, Pyridine, Mild Steel, Physisorption.

1. INTRODUCTION

The continued manifestation of corrosion and corrosion products on steel structures is still causing a lot of concern to corrosion scientists and engineers. Investigation into the mechanism of corrosion inhibition by certain N- and S-containing organic compounds have continued to reveal interesting results (Monticelli *et al*, 1993; Gomma and Wahdan, 1995; Jayaperumal *et al*, 1995; Singh *et al*, 1995). In our laboratory,the action of various organic substances as inhibitors of mild steel corrosion has been studied (Ita *et al*, 1994; Ekpe *et al*, 1995; Ita and Offiong, 1997). Particular attention has been paid to the influence of molecular structure on corrosion inhibition. The present investigation assesses the inhibiting effect of 2-aminopyridine and 2-(aminomethyl)pyridine on mild steel-HCl-water systems via the weight loss method and this enables the authors to illustrate the importance of environment in the process of rusting.

The inhibition efficiency, I.E(%), has been assessed using a known relation (Ekpe *et al*, 1994)

$$I.E(\%) = [(W_o - W_i)/W_o] \times 100 \quad .... (1)$$

where W_o and W_i are the weight loss in the absence and the presence of the inhibitors,respectively.

2. EXPERIMENTAL

Weight loss corrosion test method already reported elsewhere (Ita and Offiong,1997) was used for this study.

2.1 MATERIAL PREPARATION

The mild steel sheets used for this study and purity 98%Fe were mechanically press-cut into 5 x 4 cm coupons of thickness 0.07 cm. The coupons were examined carefully to check for lack of edge roughness which could influence the corrosion monitoring process. These coupons were used as supplied and without further polishing, but surface treatment of the coupons was by degreasing in absolute ethanol and drying in acetone. The treated coupons were then stored in a moisture-free desiccator before their use for corrosion studies. The inhibitors (2-aminopyridine(2AP) and 2-(aminomethyl)pyridine (2AMP)) were recrystallized twice from absolute ethanol and dried in air. Inhibitor concentrations of 1×10^{-4},2×10^{-4},3×10^{-4},4×10^{-4} and 5×10^{-4} M were prepared in 0.1 M HCl solution. All reagents were of analar grade and doubly distilled water was used for the preparation of all solutions. The prepared additive solutions were used for all measurements.

2.2 WEIGHT LOSS CORROSION TEST METHOD WITHOUT INHIBITOR

Previously weighed mild steel coupons were suspended in 0.1, 0.2, 0.3,0.4,and 0.5 M HCl solutions contained in five 250ml beakers kept at room temperature (30°C) and another series in a thermostat-controlled bath maintained at 40°C. The coupons were retrieved from their corrodent solutions at 24h intervals progressively for 168h (7 days), carefully washed separately several times in 20% sodium hydroxide solution containing $200gl^{-1}$ zinc dust until clean, dried in acetone and reweighed (Ita and Offiong,1997). The difference in weight defined as

$$W = (W_i - W_t)g \quad ...... (2)$$

was taken as the weight loss evaluated . Wt is the final weight of mild steel at time t and Wi is the initial weight of mild steel at time t = 0. Each reading reported in this paper is an average of two readings on Mettler H35 AR analytical balance to the nearest 0.0001g. The corrosion rate (C.R) for mild steel in HCl solutions was calculated in $mgdm^{-2}day^{-1}$ (mdd) using eq.(3) (NACE,1984):

$$C.R = mg/(dm^2)x(days) .... (3)$$

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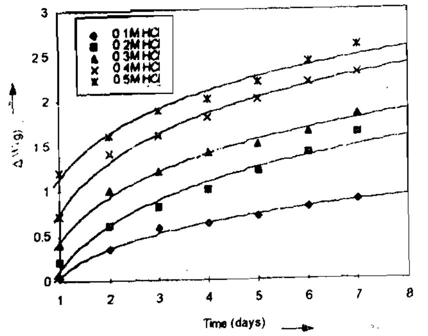

Fig. 1: Variation of weight loss with time for mild steel coupons in HCl solutions at 30 °C without inhibitor.

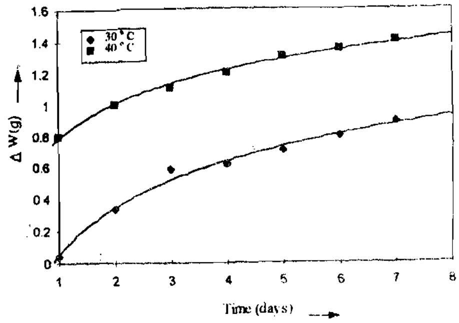

Fig. 2: Variation of weight loss with time for mild steel coupons in 0.1M HCl solution at 30 ° and 40° C without inhibitor

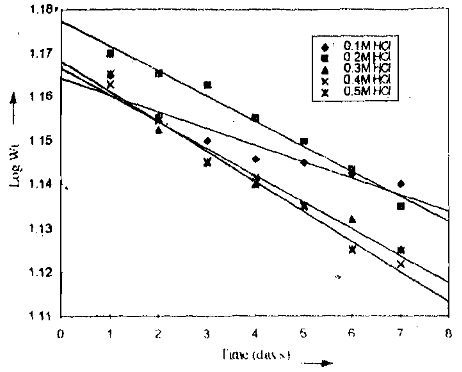

Fig. 3: Variation of log W_t with time for mild steel coupons in HCl solutions at 30 °C without inhibitor.

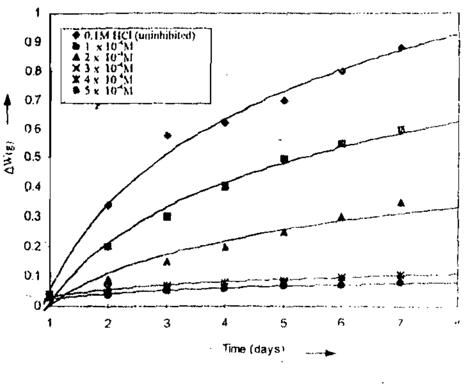

Fig. 4: Variation of weight loss with time for mild steel coupons in 0.1M HCl solution containing 2-aminopyridine at 30 °C

2.3 WEIGHT LOSS CORROSION TEST METHOD WITH INHIBITOR

The inhibitors investigated were 2-aminopyridine and 2-(aminomethyl)pyridine. Each of the previously weighed mild steel coupons was introduced into five of ten beakers containing 2-aminopyridine and the other five beakers containing 2-(aminomethyl) pyridine. Each experiment in the presence of the inhibitors was performed at 30 and 40°C. As before,each mild steel was retrieved from the corrodent-inhibitor solution at 24h intervals for 168h,washed and weighed. The difference in weights of the coupons was again taken as the weight loss.

3. RESULTS AND DISCUSSION

3.1 CORROSION BY HCl SOLUTIONS

The results obtained showed that the weight loss of mild steel in HCl solutions increased with increasing acid concentration at 30°C. For instance in Fig.1, the weight loss in 0.5M HCl was about three times more than those obtained in 0.1 M HCl solution. This observation is attributed to the fact that the rate of a chemical reaction increases with increasing acid concentration.

Fig.2 reveals that at constant HCl concentration the weight loss increases with increasing temperature. Similar plots were obtained for 0.2,0.3,0.4 and 0.5 M HCl solutions. An increased temperature favours the formation of activated molecules which may be doubled in number, with a 10°C rise in temperature, thereby increasing the reaction rate (Gross and Wiseall,1972).

3.2 KINETIC TREATMENT OF WEIGHT LOSS RESULTS WITHOUT INHIBITOR

Fig.1 reveals that mild steel corrosion by HCl solutions occurs not by simple homogeneous process but by a heterogeneous one involving several steps. This assertion is made from the non-uniformity of the plots. For this reason, the results were tested for the order of the reaction. A plot of $\log W_t$(g) against time(days) indicated a first-order kinetics with respect to mild steel in HCl solution (Fig.3). The half-lives, $t_{1/2}$ (days) obtained for mild steel in 0.1M HCl without inhibitor were 62.2 and 32.2 days at 30 and 40°C, respectively. Results obtained from eq.(3) reveal 642.6 mdd and 999.6 mdd at 30 and 40°C, respectively, as the corrosion rates. The results also showed that corrosion rate is higher at 40°C than at 30°C and is in good agreement with the observed higher weight loss at 40°C than at 30°C without inhibitor (Fig.2).

3.3 EFFECT OF INHIBITOR CONCENTRATION

Figs.4 - 7 reveal that 2-aminopyridine and 2-(aminomethyl)pyridine actually inhibit the acid corrosion of mild steel to an appreciable extent. Compared with Figs.1 and 2 lower weight loss data were recorded. Fig.8 shows that 2-(aminomethyl)pyridine (2AMP) inhibits the corrosion of mild steel in HCl solution more

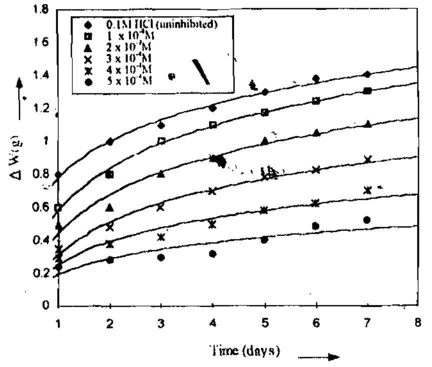

Fig. 5: Variation of weight loss with time for mild steel coupons in 0.1M HCl solution containing *2-aminopyridine at* 40 °C

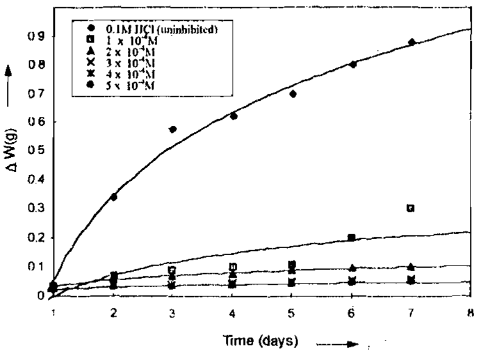

Fig. 6 Variation of weight loss with time for mild steel coupons in 0.1M HCl solution containing 2-(aminomethyl) pyridine at 30 °C

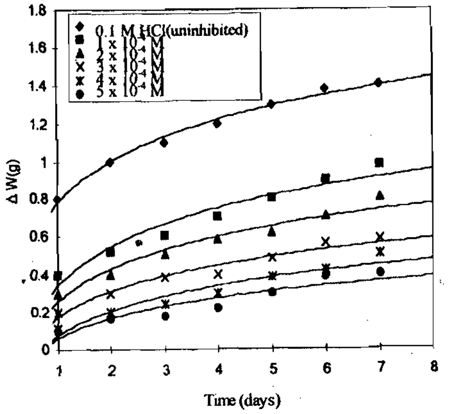

Fig. 7: Variation of weight loss with time for mild steel coupons in 0.1M HCl solution containing 2-(aminomethyl) pyridine at 40 °C.

effectively than 2-aminopyridine (2AP). Fig.8 also shows that inhibition efficiency increases with increasing inhibitor concentration but with decreasing temperature. The increase in inhibition efficiency with decreasing temperature suggests weak adsorption interaction between the mild steel surface and the inhibitors which is physical in nature (Talati and Modi,1986).

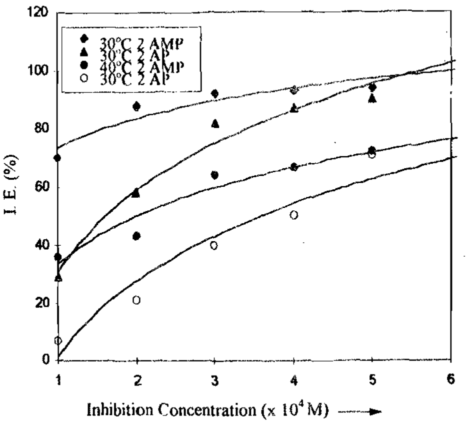

Fig. 8: Variation of inhibition efficiency (%) with inhibition concentration for mild steel in 0.1M HCl *solution containing* 2-aminopyridine *and* 2-(aminomethyl) pyridine at 30 °C and 40 °C.

3.4 KINETIC STUDY OF WEIGHT LOSS RESULT

Tables 1 and 2 give indication that 2-(aminomethyl)pyridine (2AMP) exhibits comparatively lower corrosion rates than 2-aminopyridine (2AP) at all inhibitor concentrations and temperatures studied. 2AMP also exhibits higher half-life, $t_{1/2}$(days) than 2AP, signifying that the mild steel remains protected in the HCl-2AMP system for longer times than in the HCl-2AP system. Average activation energies of 59.6 and 79.1 KJmol^{-1} are also recorded for 2AP and 2AMP, respectively.

3.5 COMPARISON OF CORROSION INHIBITION BEHAVIOUR OF 2AMP AND 2AP

From the weight loss measurement,the inhibitory actions of 2AMP and 2AP reveal that 2AMP exhibits a better corrosion inhibition tendency than 2AP. The inhibitors' action is suggestive of adsorption onto the metal surface. For a given inhibitor, an increase of its concentration generally increases inhibition efficiency. On the basis of increasing inhibition efficiency with decreasing temperature,2AMP and 2AP are both physically adsorbed on all the mild steel coupons used. Since physical adsorption is proposed, we expect to have the formation of a multi-layer protective coverage on the surface of the mild steel by the inhibitors for the inhibition to be effective. The difference in the inhibitory properties of the two compounds is closely related to the difference in their molecular weights. 2AMP with a higher molecular weight than 2AP, is therefore, expected to form a more functional blanket-like layer on the mild steel surface than 2AP.

It may be necessary to note that although a physical adsorption mechanism for the inhibitors has been proposed, this may not rule out completely the contributory effect of the structure (cyclic structure,electron donating or withdrawing groups), which in the present study plays very less significant role and is not considered sufficiently important for the purpose of the discussion (Ita and Offiong, 1997).

Table 1: Kinetic Data For 2-Aminopyridine From Weight Loss Measurements

Inhibitor Concentration (M)	Inhibitor Efficiency (%)		K_{30}	K_{40}	Half-life, $t_{½}$ (days)		Corrosion Rate (mdd)		Activation Energy ($KJmol^{-1}$)	Average Activation Energy ($KJmol^{-1}$)
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	30°C and 40°C	
1×10^{-4}	24	7	0.00733	0.01505	94.5	46.0	428.4	928.2	4.8	59.6
2×10^{-4}	58	21	0.00423	0.01263	163.8	54.9	249.9	785.4	34.3	
3×10^{-4}	82	40	0.00180	0.01025	385.0	67.6	107.1	642.6	85.2	
4×10^{-4}	87	50	0.00114	0.00675	607.9	82.7	67.8	499.8	88.3	
5×10^{-4}	90	71	0.00102	0.00583	678.4	118.9	59.3	35.7	85.5	

K is the first order rate constant in day^{-1}

Table 2: Kinetic Data For 2-(Aminomethyl) Pyridine From Weight Loss Measurements

Inhibitor Concentration (M)	Inhibitor Efficiency (%)		K_{30}	K_{40}	Half-life, $t_{½}$ (days)		Corrosion Rate (mdd)		Activation Energy ($KJmol^{-1}$)	Average Activation Energy ($KJmol^{-1}$)
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C	30°C & 40°C	
1×10^{-4}	70	36	0.00301	0.00827	230.2	83.8	178.8	678.3	27.8	79.1
2×10^{-4}	88	43	0.001196	0.00733	579.4	94.5	71.4	571.2	91.0	
3×10^{-4}	92	64	0.000716	0.00450	967.9	154.0	42.8	414.1	93.1	
4×10^{-4}	93	66	0.000597	0.00361	1160.8	192.0	40.7	385.6	89.0	
5×10^{-4}	94	72	0.0005726	0.00362	1210.3	191.4	34.3	285.6	93.5	

K is the first order rate constant in day^{-1}

However, the influence of structure would have been of importance if chemical adsorption mechanism (where there is usually a dative link between the inhibitor and the metal) had been proposed (Hackerman and Makrides, 1954).

CONCLUSIONS

The compounds (2AMP and 2AP) used as corrosion hibitors have very significant effects on the corrosion f mild steel in hydrochloric acid. The inhibition by nese compounds, increased with increased inhibitor oncentration and decreased temperature. 2AMP and AP inhibited the corrosion reaction, probably, by hysically being adsorbed onto the mild steel surface. AMP exhibited a better corrosion inhibition tendency nan 2AP.

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