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Full Length Research Paper

Inhibition of mild steel corrosion in hydrochloric acid by 2-acetylpyridine and 2-acetylpyridine phosphate

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The corrosion of mild steel in hydrochloric acid solution has been significantly inhibited by 2-acetylpyridine and 2-acetylpyridine phosphate at 30°C and 40°C by the weight loss method. The inhibition efficiencies of both compounds increased with increase in inhibitor concentration but decreased with increase in temperature. Physical adsorption mode has been proposed for the adsorption of the inhibitors on mild steel surface. Both compounds obeyed the Langmuir adsorption isotherm and the thermodynamic-kinetic model. The negative values of ΔG_{ads} indicate the spontaneity of the inhibition process. The difference in the inhibitory actions of the compounds has been incorporated in the present investigation.

Keywords: inhibition, steel, hydrochloric acid, acetylpyridine

INTRODUCTION

The search for efficient inhibitors for mild steel corrosion is ongoing globally. Due to their cost effectiveness, a lot of research effort is now geared at inhibiting the corrosion of mild steel in acidic medium using organic compounds (Larabi et al., 2004; Umoren et al., 2006; Abdel-Aal and Morad, 2001; Ebenso and Oguzie, 2005; Ebenso, 2003; Ita, 2005; Ita, 2004; Ita and Offiong, 2000; Ita et al., 2007; Ita et al., 2007; Ita and Offiong, 2001; Ita and Abakedi, 2006). Organic inhibitors reduce the rate of corrosion of a metal/alloy by adsorbing on its surface, thereby blocking its active corroding sites. This work reports on the corrosion inhibition actions of 2-acetylpyridine and 2-acetylpyridine phosphate on mild steel corrosion in HCl solution using the weight loss method. The percent inhibition efficiency, I(%) was calculated using the formula (Ibok et al., 1993):

$$I\% = 100X\left(\frac{W_0 - W_1}{W_0}\right) \quad \text{---------------(1)}$$

where w_1 and w_0 are the weight losses of mild steel in HCl solutions, with and without inhibitors, respectively.

The degree of surface coverage, θ, is given by the equation:

$$\theta = \frac{W_0 - W_1}{W_0} \quad \text{---------------------(2)}$$

where w_1 and w_0 are the weight losses of mild steel in HCl solutions, with and without inhibitors, respectively. The corrosion rate, δ (mg dm^{-2} day^{-1} or mdd) of mild steel was obtained using the equation (Rajappa and Venkatesha, 2003):

$$\delta = \frac{\Delta W}{S\ X\ t} \quad \text{---------------(3)}$$

where ΔW is the weight loss of mild steel (mg), S is the total geometric surface area (dm^2) while t is the duration of exposure (day).

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Experimental

Material preparation

The mild steel sheets used for this study were 0.07cm in thickness and had the following composition: C = 0.12%, Mn = 0.90%, S = 0.066%, P = 0.05%, Si = 0.01% and Fe = 98.854%. It was mechanically press - cut into coupons (4cm X 5cm) having a small hole at one end for the insertion of hooks. Each coupon had 40.0cm^2 total geometric surface area. The coupons were degreased in absolute ethanol and mill scales removed by scrubbing with bristle brush, rinsed in absolute ethanol again, dried in acetone and stored in a desiccator.

Both compounds used as inhibitors (2- acetylpyridine and 2 - acetylpyridine phosphate) were recrystallized twice in absolute ethanol and were prepared in the concentration range of 1X10^{-4}M – 5X10^{-4}M in 0.1M HCl solution.

Weight loss measurements

The pre - cleaned and weighed mild steel coupons were suspended with glass rods and hooks in 250ml beakers containing 200ml of test solutions maintained at 30℃ and 40℃ in a thermostatic bath. The weight loss was determined by retrieving the coupons at 24 hours intervals progressively for 168 hours (7 days), washed in 20% NaOH solution containing 200gl^{-1} of zinc dust with bristle brush, rinsed in de-ionized water, cleaned, dried in acetone and reweighed (National Association of Corrosion Engineers (NACE), 1984). The weight loss was taken as the difference between the weight at a given time (W_t) and the original weight (W_o) of the coupons. The measurements were carried out for the uninhibited solution (blank) and in the presence of the inhibitors.

RESULTS AND DISCUSSION

Effect of inhibitor concentration on inhibition efficiency

There was a marked reduction in the weight loss of mild steel in HCl solution containing 2- acetylpyridine phosphate (Fig. 1) and 2- acetylpyridine (Fig. 2) at 40℃, compared to the uninhibited solution. Similar plots were obtained at 30℃, though with lower weight losses. This indicates that the mild steel coupons corrode less in the HCl solution containing the additives than in their absence.

Fig. 3 shows the effect of 2- acetylpyridine (ACP) and 2- acetylpyridine phosphate (APP) concentration on the corrosion of mild steel in HCl solutions at 30℃ and 40℃. At 30℃, the inhibition efficiencies of mild steel in the presence of both compounds increased with increase in inhibitor concentration to maximum values of 53.62% (for 1X10^{-4}M APP) and 52.80% (for 1X10^{-4}M ACP), respectively. Thus, APP was a better inhibitor for mild steel corrosion than APP, at 30℃. An increase in inhibition efficiency with increase in inhibitor concentration indicates a strong interaction between the mild steel surface and the inhibitors. Fig. 3 also reveals that at 40℃, APP conferred a better protection on mild steel than ACP of equivalent concentration. Thus, APP was a better inhibitor for mild steel corrosion in HCl than ACP.

Effect of temperature on inhibition efficiency

The inhibition efficiency of mild steel in the presence of ACP and APP, respectively, decreased with increase in temperature from 30℃ to 40℃. A decrease in the inhibition efficiency of mild steel with increase in temperature suggests a weakening of the adsorption bonds between mild steel and inhibitors.

Presented on Tables I and II are the corrosion rates, inhibition efficiencies, surface coverage and the activation energies for the corrosion of mild steel in HCl solutions containing ACP and APP, respectively.

The activation energies (E_a) for the corrosion of mild steel in HCl solutions were obtained using equation (4)[16]:

$$log\left(\frac{\delta_2}{\delta_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{-----------------(4)}$$

where δ_1 and δ_2 are the corrosion rates (mdd) at T_1(303K) and T_2 (313K) while R is the Universal gas constant (8.314 J mol^{-1}).

The average E_a values of 95.268 kJ mol^{-1} and 102.195 kJ mol^{-1} for the corrosion of mild steel in HCl containing APP and ACP, respectively, were higher than 68.133kJ mol^{-1}, the E_a value in the uninhibited HCl solution. The higher E_a value in the inhibited solution compared to the uninhibited solution (blank) coupled with a decrease in the inhibition efficiencies of the compounds with increase in temperature indicates physical adsorption of both ACP and APP on mild steel surface. The findings in this work agree with a report by other researchers that the higher activation energy value in the presence of the inhibitor compared to that in its absence is due to physical adsorption (Foroulis, 1985).

Adsorption consideration

The adsorption of ACP and APP on mild steel surface occurred via the Langmuir adsorption isotherm defined as (Larabi et al., 2004):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{------------------ (5)}$$

where C is the inhibitor concentration, Ө is the degree of surface coverage while K_{ads} is the equilibrium constant of adsorption. Hence a plot of C/Ө against C should be

Table I. Calculated values of corrosion rate, inhibition efficiency, surface coverage and activation energy for mild steel corrosion in 0.1M HCl containing ACP from weight loss measurements.

Inhibitor	Corrosion rate (mdd)		Inhibition efficiency, I %		Surface overage,ϴ		Activation energy, E_a (KJ mol^{-1})
concentration	30℃	40℃	30℃	40℃	30℃	40℃	30° – 40℃
$1X10^{-4}M$	55.89	190.57	45.00	20.97	0.56	0.21	96.736
$2X10^{-4}M$	53.07	198.36	47.79	17.75	0.53	0.18	103.979
$3X10^{-4}M$	49.04	205.54	51.77	14.76	0.49	0.15	113.012
$4X10^{-4}M$	47.96	187.14	52.80	22.40	0.48	0.22	107.372
$5X10^{-4}M$	55.43	173.25	45.45	28.16	0.55	0.28	89.874

Average E_a = 102.195kJ mol^{-1}

Table II. Calculated values of corrosion rate, inhibition efficiency, surface coverage and activation energy for mild steel corrosion in 0.1M HCl containing APP from weight loss measurements.

Inhibitor	Corrosion rate (mdd)		Inhibition efficiency, I%		Surface coverage,ϴ		Activation energy, E_a (KJ mol^{-1})
concentration	30℃	40℃	30℃	40℃	30℃	40℃	30° – 40℃
$1X10^{-4}M$	50.64	195.79	50.16	18.81	0.50	0.19	106.647
$2X10^{-4}M$	49.86	183.39	50.95	23.95	0.51	0.24	102.711
$3X10^{-4}M$	47.68	157.68	53.09	34.61	0.53	0.35	94.325
$4X10^{-4}M$	47.14	150.11	53.62	37.75	0.54	0.38	91.343
$5X10^{-4}M$	53.29	149.43	47.58	38.03	0.48	0.38	81.314

Average E_a = 95.268kJ mol^{-1}

Table III. Adsorption parameters for the adsorption of APP and ACP in 0.1M HCl on mild steel at 40℃.

Inhibitor	1/K	K	R^2	ΔG_{ads} (kJ mol^{-1})
APP	$4X10^{-4}$	$2.50X10^3$	0.9537	-30.812
ACP	$3X10^{-4}$	$3.33X10^3$	0.9911	-31.560

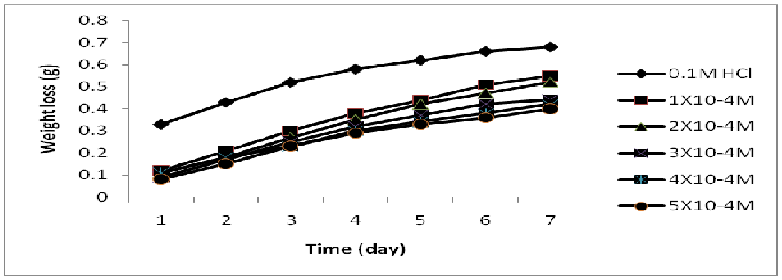

Fig. 1. Variation of weight loss of mild steel in hydrochloric acid containing various concentrationsof 2-acetylpyridine phosphate (APP) at 40℃.

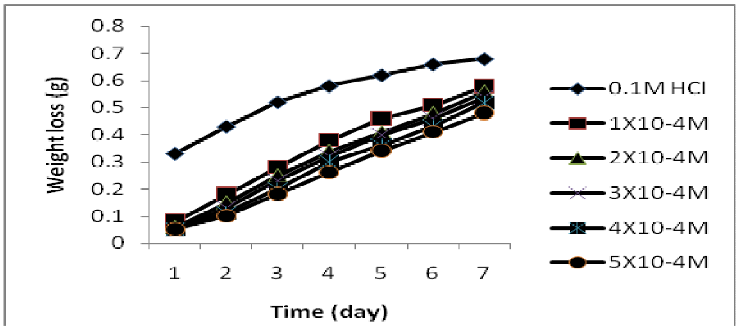

Fig. 2. Variation of weight loss of mild steel in hydrochloric acid containing various concentrations of 2-acetylpyridine (ACP) at 40℃.

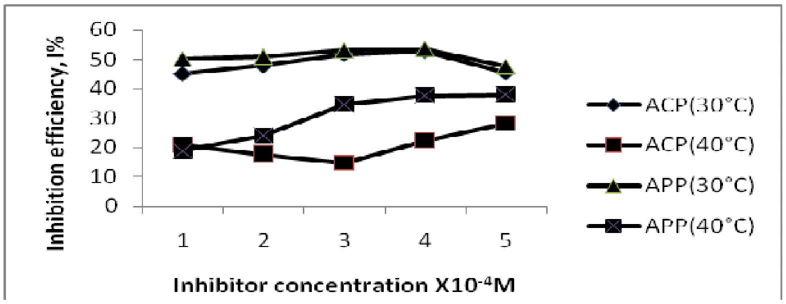

Fig.3. Variation of inhibition efficiency (I%) with inhibitor concentration (M) for mild steel corrosion in 0.1M HCl containing ACP and APP, respectively, at 30℃ and 40℃.

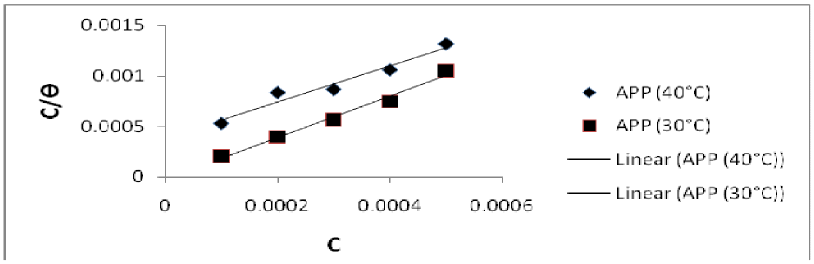

Fig. 4. Plot of C/Θ vs. C (Langmuir isotherm) for mild steel in 0.1M HCl containing 2-acetylpyridine phosphate (APP) at 30℃ and 40℃.

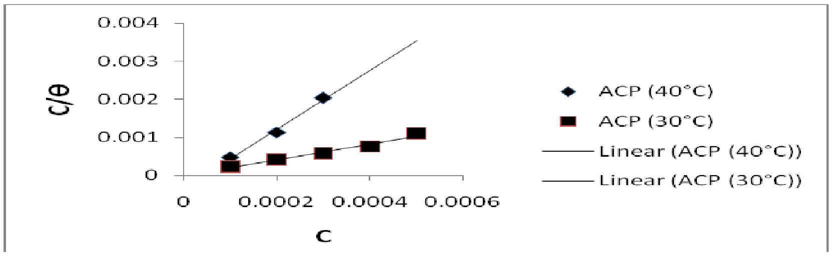

Fig. 5. Plot of C/Θ vs. C (Langmuir isotherm) for mild steel in 0.1M HCl containing 2-acetylpyridine (ACP) at 30℃ and 40℃.

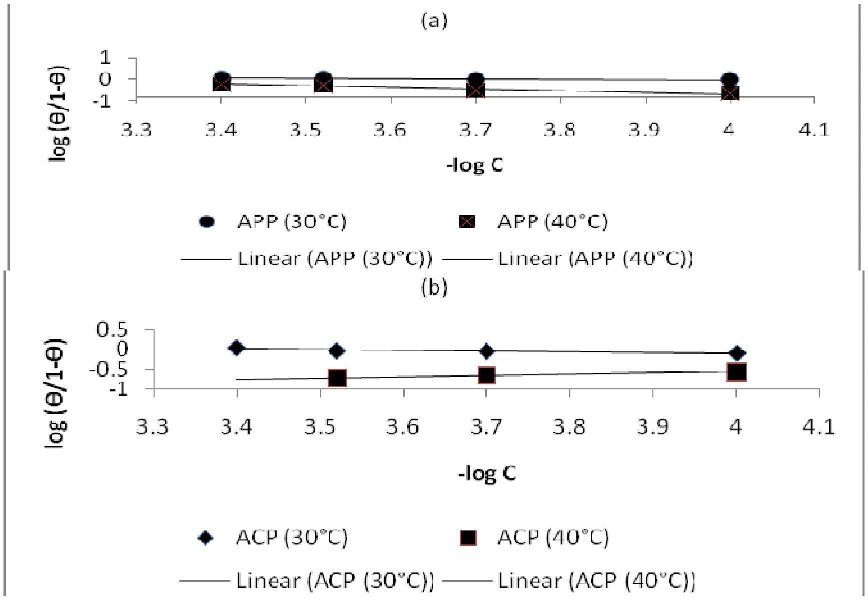

Fig. 6. Plot of log (Θ/1-Θ) vs log C (the kinetic model) for mild steel corrosion in 0.1M HCl in the presence of APP and ACP, respectively, at 30℃ and 40℃.

linear, if the Langmuir adsorption isotherm is obeyed, with an intercept of $1/K_{ads}$.

The equilibrium constant of adsorption (K_{ads}) is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula (Moussa et al., 2007; Fouda et al., 2000):

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad \text{-----------(6)}$$

where R is the Universal gas constant, T is the absolute temperature while 55.5 is the molar concentration of water in the solution.

Straight lines obtained on plotting C/θ against C confirm that the adsorption of both APP (Fig. 4) and ACP (Fig. 5) on mild steel surface obeyed the Langmuir adsorption isotherm.

Table III contains the adsorption parameters for the corrosion of mild steel in HCl. The negative values of ΔG^0_{ads} for both APP and ACP indicate the spontaneity of the adsorption process. Additionally, the values of ΔG^0_{ads} for both compounds (in this work) being less than -40kJ mol^{-1} indicate physisorption of the inhibitors on mild steel surface (Ebenso et al., 2006).

Furthermore, on plotting log (θ/1-θ) against log C straight lines (Fig. 6) were obtained showing that the results gotten from this work also fit the thermodynamic-kinetic model stated as (Abd El Rehim et al., 2004):

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y log\ C \qquad (7)$$

where θ is the degree of surface coverage, C is the inhibitor concentration while K is the equilibrium constant of adsorption.

Comparison of corrosion inhibition behavior of 2-acetylpyridine (ACP) and 2-acetylpyridine phosphate (APP)

This study shows that APP was a better inhibitor for mild steel corrosion than APP at both 30℃ and 40℃. The difference in the inhibitory effects of these compounds can be rationalized on the difference in the molecular structures of these compounds. The main structural difference between ACP and APP is that APP has $-COCH_3$ group attached to pyridine moiety while ACP has $(-COCH_3)PO_4^{3-}$ group attached to pyridine moiety . The remainder of the molecule remains the same. APP therefore has three adsorption centers (the pyridyl nitrogen, the carbonyl oxygen and the PO_4^- group) while ACP has two adsorption centres (the pyridyl nitrogen and the carbonyl oxygen). Through these adsorption centers, both ACP and APP probably form co-ordinate bonds with the vacant d-orbitals of Fe^{2+} of mild steel. Based on its higher number of co-ordinate bonds, APP is expected to be a better inhibitor than ACP. This occurred at both 30℃ and 40℃.

The better inhibitory action of ACP over APP may also be attributed to its higher surface coverage (Tables I and II) and consequently a better protection of the mild steel surface. APP seems to form stronger adsorbate layers which covers and protects mild steel better than APP's layers.

CONCLUSIONS

The corrosion of mild steel in HCl solutions has been studied by the weight loss method. The additives, 2-acetylpyridine (ACP) and 2-acetylpyridine phosphate (APP), significantly inhibited the corrosion process at 30℃ and 40℃, with 2-acetylpyridine phosphate exhibiting a better inhibitory behavior. The inhibition efficiencies of both compounds increased with increase in inhibitor concentration and decrease in temperature. Both compounds obeyed the Langmuir adsorption isotherm. The molecular structures and the strength of co-ordinate bonds formed seem to play significant roles in the corrosion inhibition process.

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