

Inhibition of dissolution of aluminium in hydrochloric acid solutions by 1,3,4-thiodiazole derivatives

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The dissolution of aluminium in 2*N* hydrochloric acid solution is retarded by the addition of some 1,3,4-thiodiazole derivatives to the medium. Three different techniques, viz., weight loss, gasometric and thermometric are applied. Temperature effect has been investigated in the range 25-40°C and the activation energies have been calculated. The inhibition efficiency decreases with the rise in temperature while the activation energy increases in the presence of the additives. The inhibitive character of the additives depends on the concentration as well as the composition of the inhibitor.

Hydrochloric acid solutions are used for pickling of aluminium or for chemical or electrochemical etching of aluminium foils¹ and lithographic plates used as substitute for zinc². The dissolution rate of the metal in such solutions is very high and, therefore, it is desirable to inhibit these solutions by adding various additives. Various triazoles were used for inhibition of copper corrosion³ and commercial aluminium in acid solutions⁴. The inhibition of the corrosion of aluminium-copper alloy in HCl acid solution by some *N*-heterocyclic compounds has been studied in relation to the concentrations of the acid and inhibitor as well as the temperature⁵. Hydrazine derivatives have been employed for the inhibition of aluminium dissolution in hydrochloric acid solution⁶. Investigations have been made for the dissolution of aluminium in acid solutions by different series of inhibitors, i.e., thiosemicarbazides⁷, acetophenone benzoylhydrazones^{8,9} and some azo compounds¹⁰. The present work is intended to explore the possible use of some 1,3,4-thiodiazole derivatives in retarding aluminium dissolution in 2*N* hydrochloric acid solution.

Experimental Procedure

In the present study, hydrochloric acid of AR grade was used for dissolution process. Doubly distilled water was used to prepare stock solutions and for dilution. The required concentrations of the inhibitors were prepared by dissolving the necessary quantities of inhibitors in 2*N* HCl acid solution. The test pieces of aluminium (99.555% Al) were cleaned and degreased as usual¹¹.

The inhibition efficiency was calculated as follows: From weight loss measurements

$$\% \text{ Inhibition} = \frac{W_{\text{free}} - W_{\text{inh}}}{W_{\text{free}}} \times 100 \quad \dots (1)$$

where w_{free} and w_{inh} are the losses in weight of the piece of aluminium in absence and presence of the inhibitor, respectively.

From thermometric measurements

$$\% \text{ Inhibition} = \frac{RN_{\text{free}} - RN_{\text{inh}}}{RN_{\text{free}}} \times 100 \quad \dots (2)$$

where

$$RN = \frac{T_m - T_i}{t}, \text{ } ^\circ\text{C min}^{-1}$$

T_i = initial temperature, T_m = maximum temperature and t = the time from start of the experiment upto maximum temperature.

From gasometric method

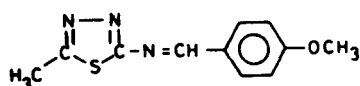
$$\% \text{ Inhibition} = \frac{R_{\text{free}} - R_{\text{inh}}}{R_{\text{free}}} \times 100 \quad \dots (3)$$

where R_{free} and R_{inh} are the rates of dissolution of aluminium (rate of hydrogen evolution) in mL min⁻¹ cm⁻¹ in free and in presence of the given inhibitor, respectively.

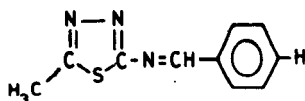
The inhibitors used in the present study are

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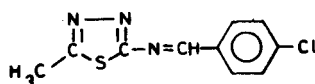
(i) *N*-(*p*-methoxybenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole



(ii) *N*-(benzylidene)-2-amino-5-methyl-1,3,4-thiadiazole



(iii) *N*-(*p*-chlorobenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole



Results and Discussion

To evaluate the influence of the investigated inhibitors on the dissolution of aluminium in 2*N* hydrochloric acid solution, weight loss was employed as a chemical testing method. Weight losses in mg cm^{-2} were determined in an open system at various time intervals in absence and presence of the studied additives. The typical weight loss-time curves for *N*-(*p*-methoxybenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole are presented in Fig. 1. It is observed that, on increasing the concentration of additive the weight loss of the aluminium sample under otherwise identical conditions decreases. Similar behaviour was observed with the other two additives also. It means that the presence of additives in the medium retards the dissolution of aluminium in 2*N* hydrochloric acid solution. Weight loss-time curves for the three additives at $5 \times 10^{-5} \text{ mol L}^{-1}$ are presented in Fig. 2. From these plots, it is seen that the weight loss of the sample depends on both the type and concentration of the additives.

The fractional surface coverage (θ) was calculated from the relation

$$\theta = \frac{W_{\text{free}} - W_{\text{inh}}}{W_{\text{free}}} \quad \dots (4)$$

The plots of the fractional surface coverage versus logarithm of molar concentration of inhibitors are given in Fig. 3. In each case, there is a steep increase in the fractional coverage in the initial stages and then it tends to become constant indicating monolayer coverage of the metal surface.

The dissolution of aluminium metal takes place according to the overall reaction:

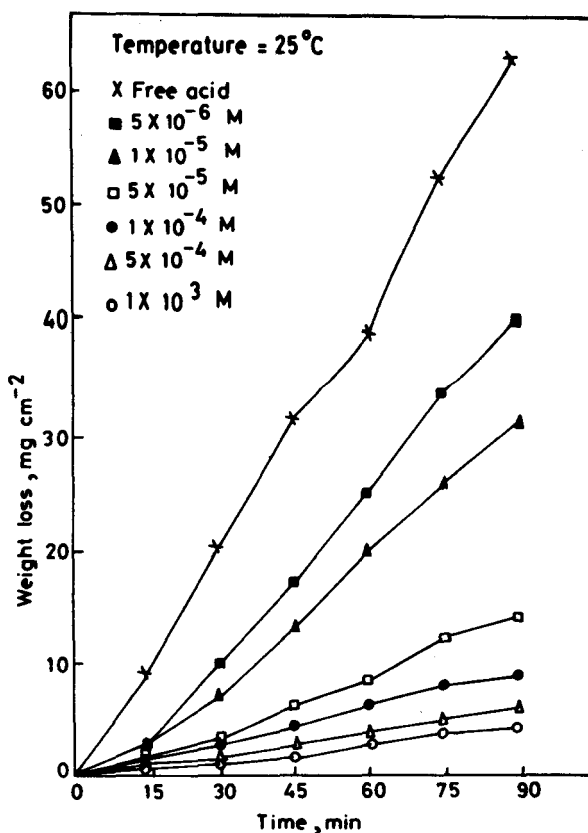
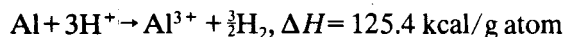


Fig. 1—Effect of inhibitor concentration on the dissolution of aluminium in 2*N* HCl solution (Inhibitor: *N*-(*p*-methoxybenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole)

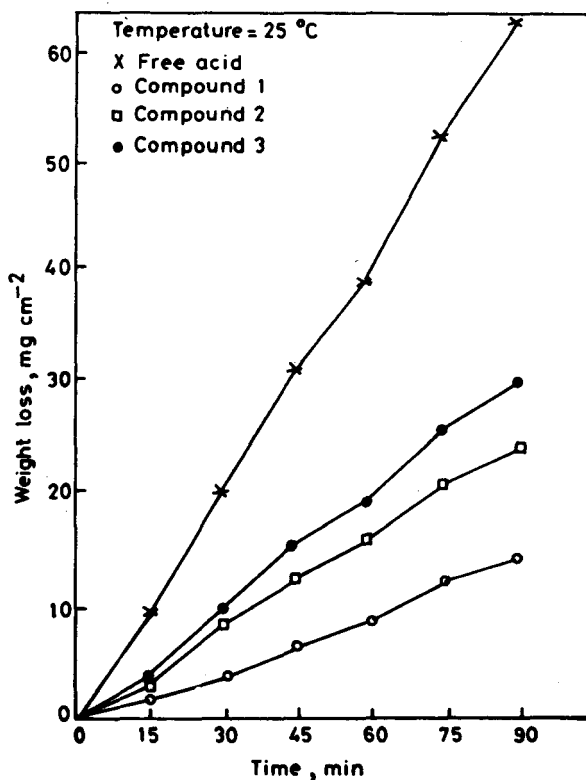


Fig. 2—Weight loss-time curves for the three additives at $5 \times 10^{-5} \text{ M}$ concentration

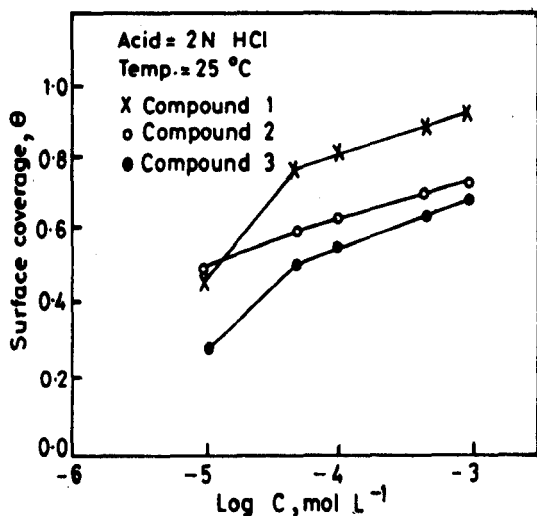


Fig. 3—Effect of inhibitor concentration on the degree of surface coverage of aluminium

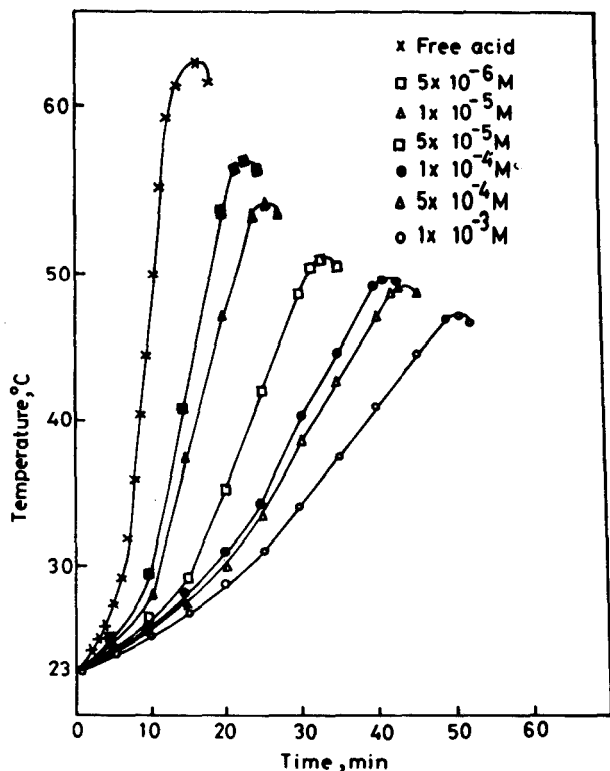


Fig. 4—Effect of inhibitor concentration on the evolution of hydrogen at 25°C (Inhibitor: *N*-(*p*-methoxybenzyl-lidene)-2-amino-5-methyl-1,3,4-thiodiazole)

The dissolution of aluminium in hydrochloric acid solutions is characterised by an initial slow rise of temperature followed by a sharp rise and finally a decrease after attaining a maximum value. The results obtained in the presence of different concentrations of compound (i) are presented in Fig. 4 as a typical example. Similar behaviour was observed for the other two inhibitors also. It is seen that as the concentration of the additives increases, the time required to reach the maximum

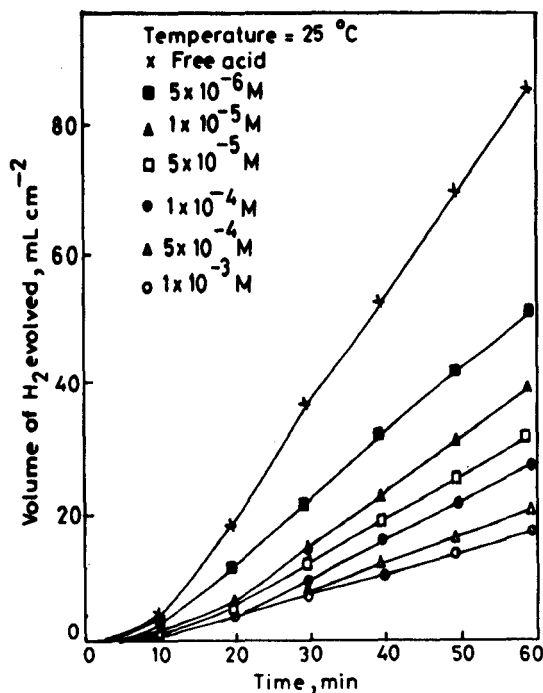


Fig. 5—Effect of inhibitor concentration on temperature-time plots (Inhibitor: *N*-(*p*-methoxybenzyl-lidene)-2-amino-5-methyl-1,3,4-thiodiazole)

temperature (t_m) increases and the rate of temperature rise decreases. Therefore, these compounds cause retardation of the dissolution of aluminium in 2N HCl solution. The present thermometric curves allow distinction between weak and strong adsorption¹². It is interesting to note that the slope of the rising part of the curve, which is a measure of the actual dissolution process¹³ depends on the concentration of the inhibitor. The slopes decrease in the presence of the additives indicating that these compounds act as general inhibitor and are adsorbed on both cathodic and anodic sites.

The retarding effect of the inhibitors has also been studied by gasometric method at different temperatures in the range 25-40°C. The volumes of the hydrogen gas evolved at different times in presence of *N*-(*p*-methoxybenzylidene)-2-amino-5-methyl-1,3,4-thiodiazole are shown in Fig. 5 as a typical example. For other compounds similar behaviour was observed. It is clear that on increasing the inhibitor concentration the percentage reduction in the reaction rate (R R) increases and it also depends upon the type of the additive. Plots of the relation between the rate of dissolution and the concentration of different inhibitors indicate that the acid corrosion of aluminium is retarded by adsorption of these additives in the molecular form at the electrode-solution interface¹⁴.

The effect of temperature on the retardation efficiency has also been studied. It is observed that the inhibition efficiency decreases with rise in

temperature, confirming the idea that the inhibition occurs through physical adsorption of the additives on metal surface. The activation energies (E_a) calculated according to Arrhenius equation are listed in Table 1. These values indicate that the presence of additives increase the activation energy of the reaction. The percentage increase in activation energy by an inhibitor is calculated according to the following equation.

$$\% \text{ Increase in } E_a = \frac{E_{\text{inh}} - E_{\text{free}}}{E_{\text{inh}}} \times 100 \quad \dots (6)$$

The percentage inhibition by the additives at different inhibitor concentrations as calculated from the three methods is listed in Table 2. It is observed that there is an agreement between the results obtained from the three different techniques. This confirms the validity of our measurement and supports the explanation given for the effect of the chemical constitution on the order of the efficiency of the additives. As shown from Table 2, the order of inhibition efficiency at all concentrations is:

N-(*p*-methoxybenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole > *N*-(benzylidene)-2-amino-5-methyl-1,3,4-thiadiazole > *N*-(*p*-chlorobenzylidene)-2-amino-5-methyl-1,3,4-thiadiazole.

The activation energy also increases as the inhibition efficiency of the additives increases (Table 1). This order can be accounted for in terms of the polar effect of the *p*-substituents.

Table 1—Activation energy and % increase in it for the additives in 2*N*.HCl acid solution

Substance	E_a , J mol ⁻¹	% Increase in E_a
Free acid	26612	—
Compound 1	58743	54.70
Compound 2	53801	50.54
Compound 3	45322	41.28

Evidence is gathered from the application of Hammett equation:

$$\log k = \log k_0 + \rho \sigma \quad \dots (7)$$

where k and k_0 are corrosion rate constants of substituted and unsubstituted inhibitor at 25°C, σ is the polar substituent constant and ρ is a proportionality constant. A plot of $\log k$ vs σ gives a straight line as shown in Fig. 6; thus demonstrating the dependence of corrosion rate on the polar character of substituents in the inhibitor molecules.

Inhibition efficiency depends on many factors¹⁵ which include the number of active centers in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes. Variation in molecular structure of the studied compounds originates from *p*-substituents in the benzylidene moiety. Vertical adsorption of the additive molecules on the aluminium oxide surface is suggested as evident from the presence of a substituent effect on inhibition action. Skeletal

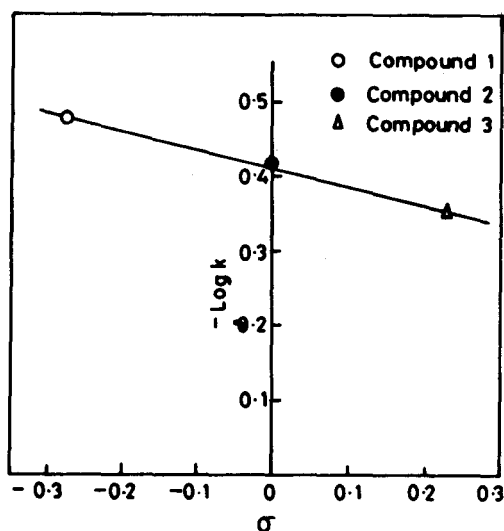
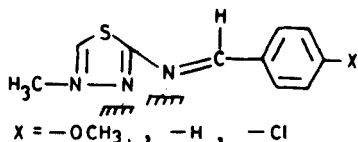


Fig. 6—Hammett equation plot for the three additives

Table 2—The percentage inhibition by the additives at different inhibitor concentrations at 25°C

Concentration mol L ⁻¹	% Inhibitor								
	Weight loss			Thermometric			Gasometric		
	1	2	3	1	2	3	1	2	3
5×10^{-6}	34.4	33.3	28.9	40.7	41.8	37.0	40.5	39.8	30.7
1×10^{-5}	47.9	46.1	30.5	49.5	51.9	35.3	54.5	46.8	41.9
5×10^{-5}	77.2	61.8	53.3	65.7	59.1	53.2	62.9	60.8	47.5
1×10^{-4}	83.2	66.6	58.5	73.8	64.4	63.3	67.8	65.9	62.9
5×10^{-4}	89.3	70.8	66.1	75.7	72.1	66.1	75.0	71.3	69.9
1×10^{-3}	92.1	74.3	71.6	80.5	81.6	75.0	80.4	76.9	75.5

representation of the mode of adsorption is shown as follows:



$x = -\text{OCH}_3, -\text{H}, -\text{Cl}$

Adsorption most probably takes place through the heterocyclic and hydrogen azomethine groups. Transfer of lone pair of electrons on the nitrogen atom to the aluminium surface to form a co-ordinate type of linkage is favoured by the presence of vacant orbital of low energy in aluminium. Strong adsorption has already been shown by the thermometric curves and the high values of inhibition efficiencies recorded for the results of the three independent techniques employed.

Conclusions

The compounds act as general inhibitor. The inhibition efficiency depends on both type and concentration of the inhibitor. The inhibition efficiency decreases with the rise in temperature. The in-

hibition process occurs through physical adsorption of the additives in the molecular form.

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