

Effect of Temperature & Inhibitors on the Corrosion of Aluminium in 2N HCl Solution: A Kinetic Study

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The influence of temperature in the absence and presence of some hydrazine derivatives on the dissolution of aluminium in 2N HCl has been investigated by hydrogen evolution technique. It is found that the efficiency of these inhibitors decreases by increasing the temperature of the dissolution reaction indicating that the inhibition of aluminium dissolution occurs through a physical adsorption. The dissolution reaction of aluminium in hydrochloric acid solution is zero order and remains so when hydrazine derivatives are present. The rate constant decreases as the inhibition efficiency increases. The activation energy of the dissolution reaction increases with increasing inhibition efficiency of the additives used. Values of the Arrhenius activation energy agree with those obtained for an activation controlled process.

In our earlier studies¹ it was found that hydrazine compounds inhibit the corrosion of aluminium in hydrochloric acid solution. The inhibition was attributed²⁻⁴ to the adsorption of these compounds on the aluminium metal surface via bonding through the carbonyl group, and the charge density on this group was found to affect the inhibition efficiency.

In the present investigation the work is extended to examine the effect of temperature on the performance of the hydrazine compounds in the retardation of aluminium dissolution in hydrochloric acid solution using hydrogen evolution technique. Kinetic studies on the dissolution reaction have been also carried out to compare the results with those of Gimbitskaya *et al.*⁵ who reported that the dissolution of aluminium in conc. acetic acid solution is a zero order reaction.

Isobutyryl (I), salicylyl (II), diformyl (III), trichloroacetyl (IV) and cyanoacetyl (V) hydrazines were prepared by refluxing the methyl or ethyl ester of the acid with hydrazine⁶. The acid (2N HCl), degreasing mixture and additive solution were prepared as previously described³. The chemical composition of the aluminium sheet used was: Al, 99.535; Si, 0.15; Fe, 0.19; Mn, 0.005; Mg, 0.1; Cu, 0.02. The dimensions of the test pieces were 1 × 10 × 0.5 cm. The test pieces were degreased and cleaned as usual.

In the hydrogen evolution method the vessel was the same as that employed before¹. A weighed aluminium sample was dropped into 100 ml of 2N HCl and the

volume of hydrogen evolved was recorded as a function of time (± 0.05 ml). The efficiency of a given inhibitor was evaluated as the percentage reduction in reaction rate (RR), viz.,

$$\% \text{ reduction in RR} = (R_{\text{free}} - R_{\text{inh}})100/R_{\text{free}}$$

where R_{free} and R_{inh} are the rates of aluminium dissolution in free acid and in the presence of the given inhibitor respectively, both measured at the same time.

In metallographic investigation, an optical microscope (model MNM-8M) was used.

The dissolution of aluminium in 2N hydrochloric acid solution has been studied by the hydrogen evolution method in the temperature range 25°-40°C. The mass-time curves obtained in the absence and presence of hydrazine compounds indicate that the rate of aluminium dissolution increases as the temperature increases. Fig.1 shows representative mass-time curves obtained for trichloroacetyl hydrazine. Thus, the inhibition efficiency of the hydrazine compounds examined, as calculated by the % reduction in reaction rate (RR), decreases with increase in temperature (Fig.2). This behaviour indicates that the inhibition of aluminium dissolution occurs through physical adsorption of the additives on

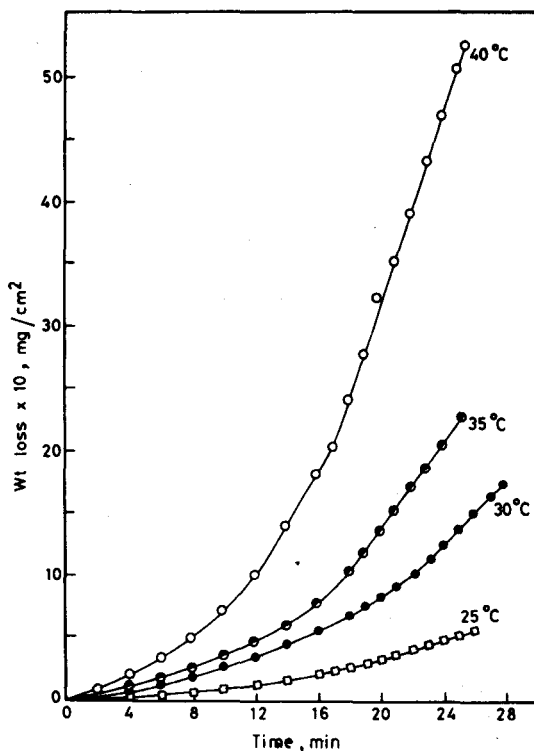


Fig.1—Mass-time curves for aluminium dissolution in the presence of trichloroacetyl hydrazine at different temperatures.

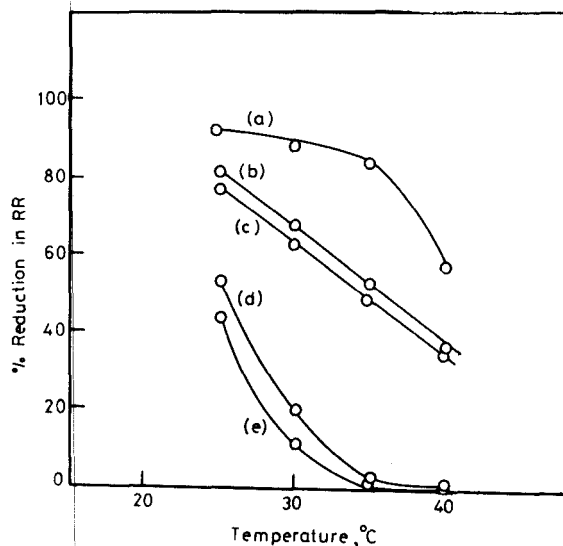


Fig. 2—Plots of % reduction in reaction rate (RR) against temperature in the presence of different inhibitors [a, cyanoacetyl hydrazine; b, trichloroacetyl hydrazine; c, diformyl hydrazine; d, salicylyl hydrazine; e, isobutyryl hydrazine].

the aluminium surface. Desorption is aided by increasing temperature.

The order of inhibition efficiencies of the additives, as described elsewhere¹, was not affected by the temperature. At all temperatures studied the inhibition efficiency of the hydrazine compounds examined decreased in the order: V > IV > III > II > I.

The mass-time curves obtained by hydrogen evolution method (Fig. 1) indicate that after a certain time interval, the mass dissolved increases linearly with time. This initial time interval can be attributed to both an induction period representing the breakdown of the oxide film on the metal surface and the start of attack.

The dissolution of aluminium oxide in acid solutions is not accompanied by hydrogen evolution, so that the rate of hydrogen evolution increases slowly till the oxide film is completely dissolved. Consequently, it can be surmised that the dissolution of aluminium itself is linearly related to the reaction time. This behaviour is characteristic of zero order reaction. The zero order equation is generally given by the relation $x = kt$, where x is the fraction of aluminium converted into reaction products at time t and k is the rate constant of the reaction. The values of k calculated from the slopes of the x - t curves are given in Table I. It is evident that the value of k increases with increase in temperature. Also, the value of k decreases with the increase in the inhibition efficiency of the hydrazine derivatives. This prompts one to suggest that the

Table I—The Specific Rate Constants of Aluminium Dissolution in 2N Hydrochloric Acid in the Absence and Presence of Inhibitors and Energies of Activation.

Substance	Sp. rate constant at the temp. (°C)				E (kcal mol ⁻¹)
	25	30	35	40	
Free acid	0.194	0.339	0.375	1.150	9.5
I	0.100	0.300	0.370	1.146	12.0
II	0.089	0.270	0.364	1.121	14.2
III	0.042	0.125	0.180	0.750	14.8
IV	0.036	0.108	0.175	0.750	16.0
V	0.014	0.040	0.047	0.478	19.8

values of the rate constant can be used to compare the inhibition efficiency of the additives.

In the case of all hydrazine derivatives the logarithm of rate constant is a linear function of $1/T$. The Arrhenius activation energy values, E , obtained from the slopes of $\log k$ vs $1/T$ plots, are presented in Table I. These values increase with increasing inhibition efficiency of hydrazine derivatives and suggest that the process is activation controlled. Thus, the increase in activation energy of aluminium dissolution with the increase in inhibition efficiency of hydrazine derivatives could be attributed to an increased adsorption of the inhibitor on the metal surface. Accordingly, increase in inhibitor concentration also increases the activation energy.

The metallographic examination of the corrosion of aluminium in 2N hydrochloric acid solution indicates that the acid attacks the metal uniformly (surface corrosion). No pits were observed. The mechanism of this attack can be explained as follows: first the acid attacks the oxide film originally present on the metal surface, then the acid attacks the surface of the metal uniformly. These results are in good agreement with the kinetic studies which emphasize that the reaction is zero order i.e. the effective factor is the surface area of the metal.

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