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An Insight into Further Limitation of the Use of Thermometric Method for Determination of Corrosion Inhibition Efficiency of Zn in Hydrochloric Acid Solution

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The effect of some amino compounds on the dissolution of zinc in hydrochloric acid solution was determined by the thermometric and weight loss methods. The two methods gave different results. The thermometric method shows that these compounds act as corrosion inhibitors, but the weight loss method shows that these compounds are efficient accelerators. The mechanism of Donnely lends support to the results of weight loss method. So the thermometric method for determining dissolution rates in these conditions can be unreliable.

INTRODUCTION

Mylius[1] made use of the thermometric method for determining the corrosion rates of aluminium and its alloys. More recently Aziz and Shams-El-Din[2,3] applied the Mylius method as a rapid technique for investigation of certain corrosion inhibition efficiency for some compounds. According to this method, a piece of metal of specified area is dropped into a definite volume of hydrochloric acid solution and the variation of the temperature of the thermally isolated system is followed as a function of time. The temperature rises during the course of the reaction to attain a maximum value. The reaction number R.N. is defined as:

$$\text{R.N.} = \frac{T_m - T_i}{t} = \frac{\Delta T}{t}\ \text{C}^\circ/\text{min.}$$

where T_m and T_i are the maximum and initial temperatures respectively, and t is the time in minutes taken to attain T_m.

Easily corroding metals are characterized by high reaction numbers through the diminution of the value of t or/and increase in T_m. The reaction number is proportional, therefore, to the rate of corrosion of the metal. The corrosion inhibition or acceleration efficiency of a compound was calculated as the percent change in [R.N.] caused by addition of this compound to the corroding solution. El-Basiouny[4] studies the effect of some aminobenzoic acids on the rate of dissolution of mild steel in nitric acid using weight loss and thermometric methods. This study shows that the two methods gave considerably different results. The difference

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was ascribed to the reaction between iron, nitric acid and the aminobenzoic acids at the higher temperatures reached in the thermometric method, leading to the production of phenols. The results indicate that the thermometric method for determining the corrosion inhibition efficiency of this compound can be unreliable. El-Basiouny[5] studies the effect of aminosulfonic acids on the dissolution of mild steel in nitric acid solution by thermometric, weight loss, and potentiometric methods. This study shows the agreement between the weight loss and the potentiometric methods, that these compounds act as accelerators but the thermometric method shows that they act as inhibitors. This false apparent retardation of the corrosion given by the thermometric method was explained to be due to the reactions between nitric acid, iron and the aminosulfonic acids leading to the formation of diazonium compounds which decomposed by temperature to form the corresponding phenol.

Now the effect of these compounds on the dissolution of zinc in hydrochloric acid solution will be tested, where there is no side reaction like that occurred in the case of iron and nitric acid.

EXPERIMENTAL

The procedure for the determination of metal dissolution rate by the thermometric method has been described previously[2,3]. The percentage composition of zinc was as follows: Cd 0.05; Pb 0.25; Cu 0.09%, the remainder is Zn. The dimensions of the test pieces were 100 × 10 × 1 mm. Before immersion in hydrochloric acid, the zinc specimens were abraded successively with 0,00,000 emery paper and then degreased with acetone. Each experiment was carried out with 20 ml. of the acid solution and with fresh test pieces. The temperature was measured to ±0.1 °C. The initial temperature in all experiments was 25 ± 0.1°C. All chemicals used were of A.R. quality. The procedure followed in weight loss measurements was similar to that reported previously[6].

RESULTS AND DISCUSSION

The curves of Fig. 1 represent the variation of the temperature as a function of time when test pieces of zinc were made to react with 20 ml of hydrochloric acid of different concentrations. The curves show that the increase in acid concentration is accompanied by a corresponding increase in the maximum temperature T_m. The time required to reach T_m decreased with the increase of acid concentration.

The variations of temperature with time for Zn in 2.5 N HCl containing a range of concentration of the additives have been investigated. Figures 2 and 3 (as an example) show temperature/time curves for Zn in

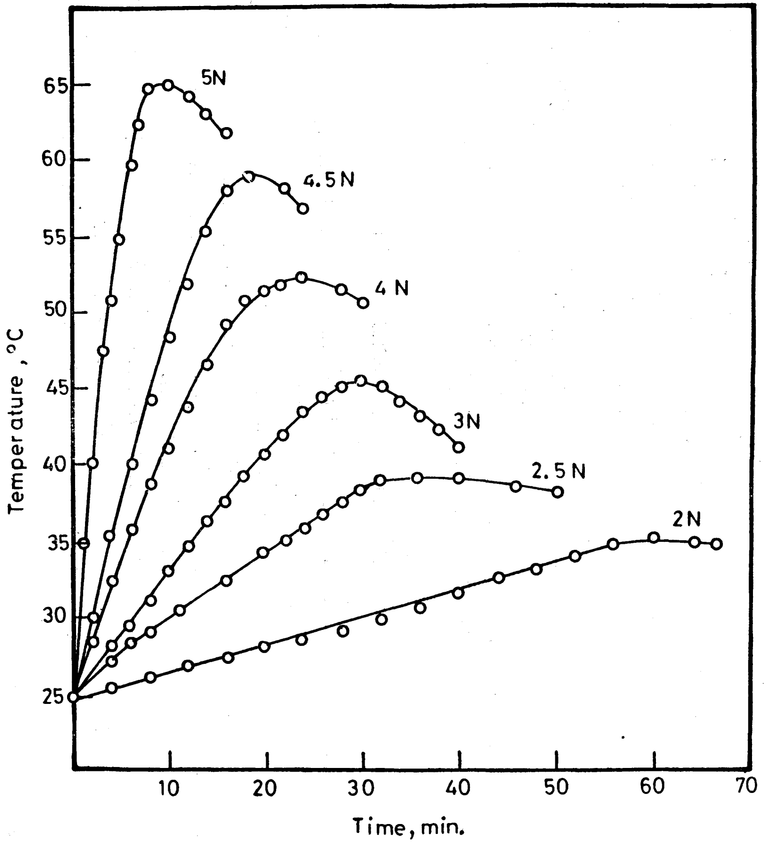

Fig. 1 Temperature-time curves for the reaction of Zn with HCl at different concentrations.

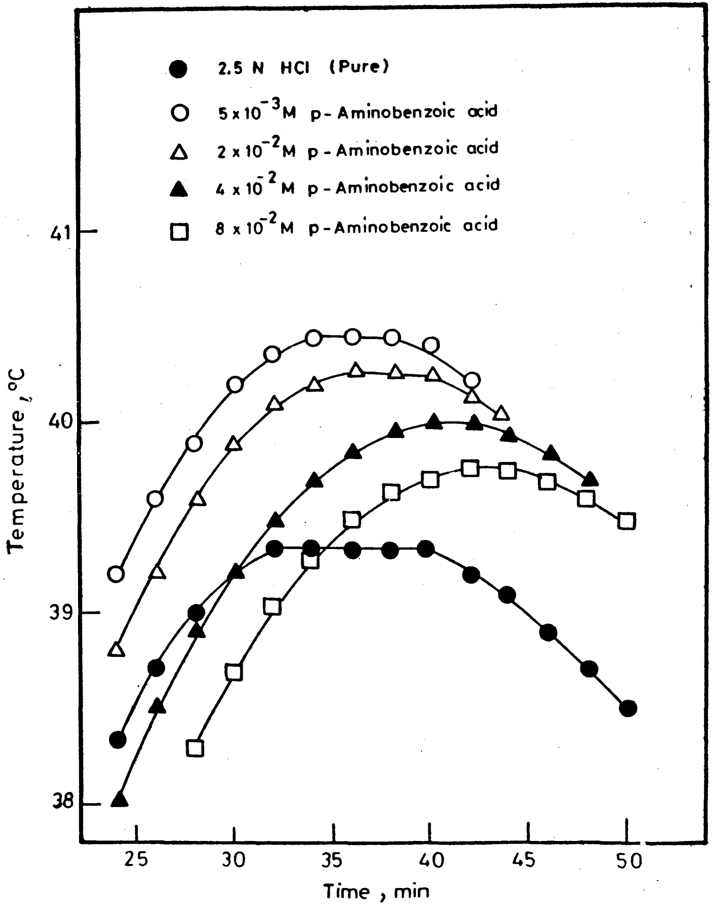

Fig. 2. Temperature-time curves for the reaction of Zn with 2.5 N HCl containing a range of concentration of *p*-aminobenzoic acid.

2.5 N HCl containing a range of *p*-aminobenzoic acid and *p*-aminobenzene sulfonic acid respectively.

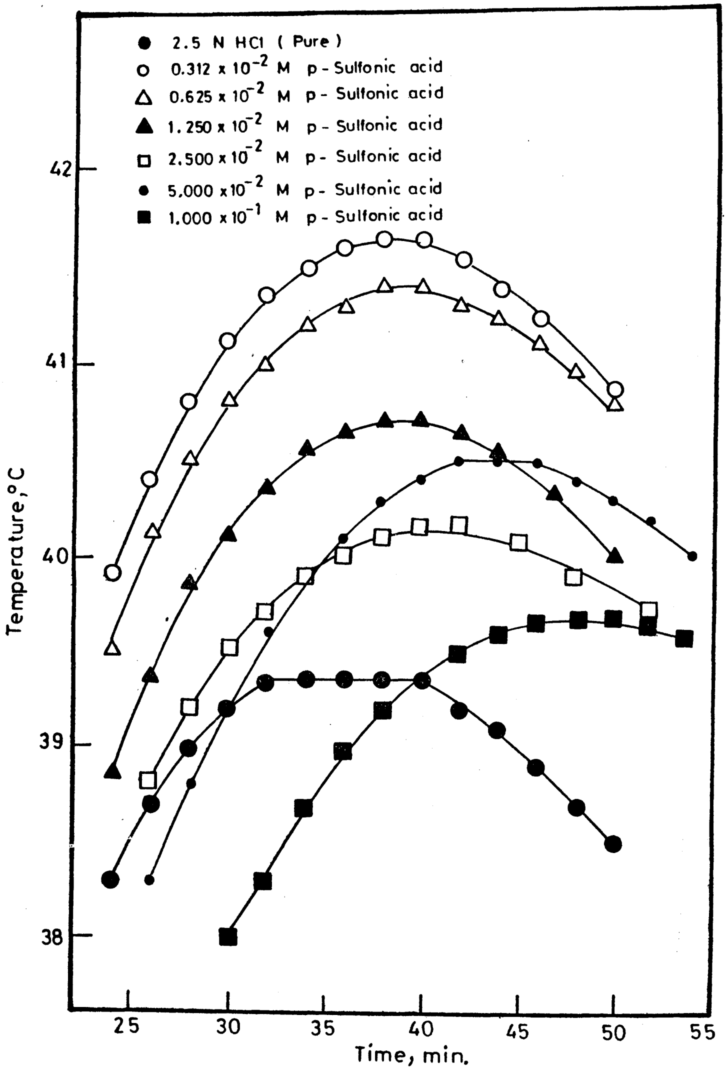

Fig. 3. Temperature-time curves for the reaction of Zn with 2.5 N HCl containing a range of concentration of *p*-aminosulfonic acid.

The relation between the concentration of the additives and the per cent change: in R.N., in weight loss and in ΔT were represented in one figure (Fig. 4A, B, C) respectively to give a clearer picture and compari-

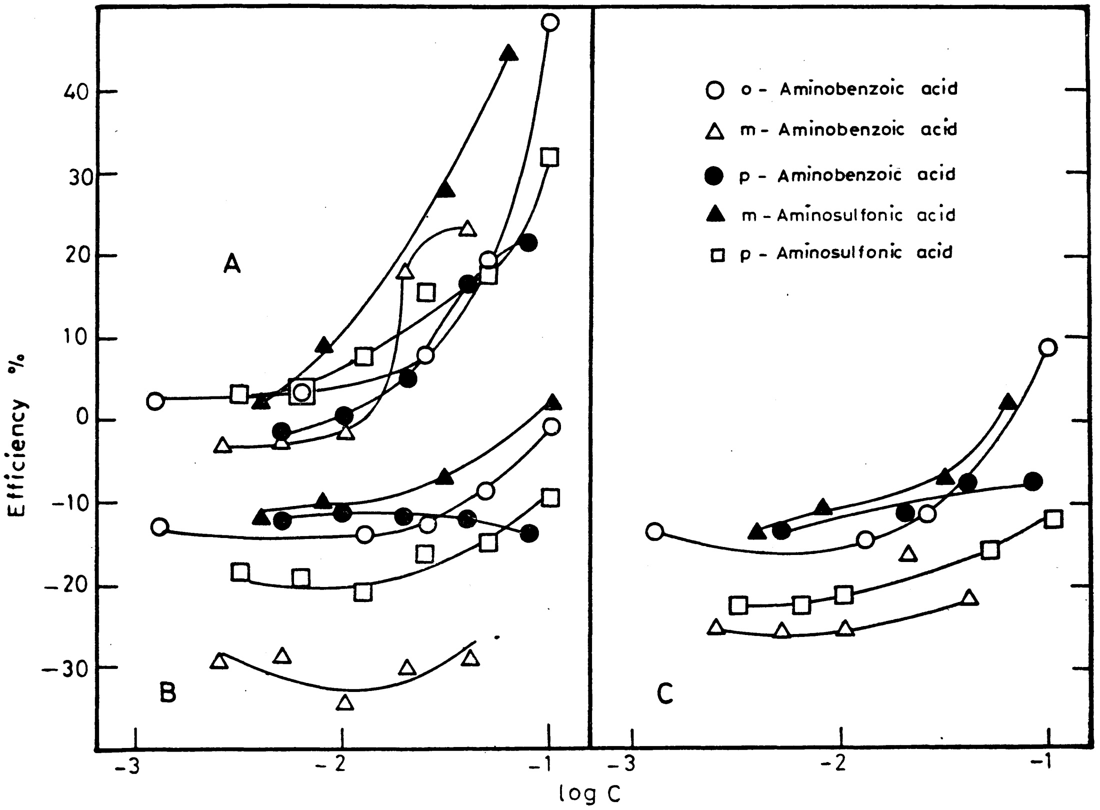

Fig. 4. Percent change: in R.N. (A), in weight loss (B) and in ΔT (C) as a function of logarithm of concentration of various additives in 2.5 N HCl
[—ve efficiencies: acceleration; +ve efficiencies: inhibition]

son for these investigations. Examination of the curves of the thermometric method Fig. 4A showed that these compounds act as inhibitors with efficiencies reaches 50% when calculated as the percent change in reaction number R.N. But the results of weight loss method (Fig. 4B) showed clearly that all the additives act as accelerators with efficiencies reaching 35%. The plot of the percent change in ΔT as a function of additives concentration (neglecting the time required to reach T_m), gave curves of Fig. 4C which were comparable to that of the weight loss method[4,5].

To explain all these behaviours we have to study the mechanism by which these additives act. In the light of the studies of Donnely[7], when a compound is adsorbed on the metal surface through its electron donor atom, it will introduce a partial negative charge at the point of interaction which develops into larger negative charge at the metal surface. According to the electroneutrality principle[8], the tendency for the atom in the metal to be as near as possible to the zero oxidation state, will give rise to distribution of the negative charge as soon as adsorption occurs. There are two main ways by which the negative charge on the metal atom can be reduced either by back donation to the adsorbed atom when it has *d*-orbitals of symmetry compatible with some of the *d*-orbitals of the metal atom, thus overlaping of the two *d*-orbitals, of the adsorbed atom and the metal atom, forming a π-bond which decreases the negative charge on the metal atom, or by redistribution of the charge into convenient places at some distance from the adsorption centre (cathodic site).

In the amino acids, adsorption occurs through oxygen or nitrogen atoms which have no *d*-orbitals, hence incapable to form such π-bonding, so these partial negative charges will go to other sites (cathodic sites) of metal and reduce H^+ ions; so it accelerates the hydrogen evolution reaction. Then the corrosion takes place at a faster rate in presence of these compounds because they make negative charge on the cathodic site more easily available than the Cl^- ions themselves, although the electronegativity of the Cl^- ion is greater than that of oxygen or equal to that of nitrogen. This is because the Cl^- ion has available *d*-orbitals to overlap with the *d*-orbitals of Zn atoms, leading to decrease in the negative charge on the cathodic site.

The previous Donnely mechanism lends support to the results of weight loss method which prove that the investigated compounds act as accelerators. So it is clear from the results and the mechanism of corrosion reaction that the misleading results obtained by applying the thermometric method are due to the false apparent elongation of time needed to reach T_m.

Figure 5 represents the relation between the time needed to reach T_m

and the concentration of the additives, increasing the concentration of the additives increases the time needed to reach T_m. We can conclude that this apparent elongation of time may be due to self-cooling (loss of some heat) resulting from H_2 evolution process which is produced from corrosion reaction. This elongation of time increases as corrosion and H_2 evolution increased. This cooling can be avoided by closing the cell because this will increase the pressure on the system causing disturbance of the reaction rate or damage of the cell.

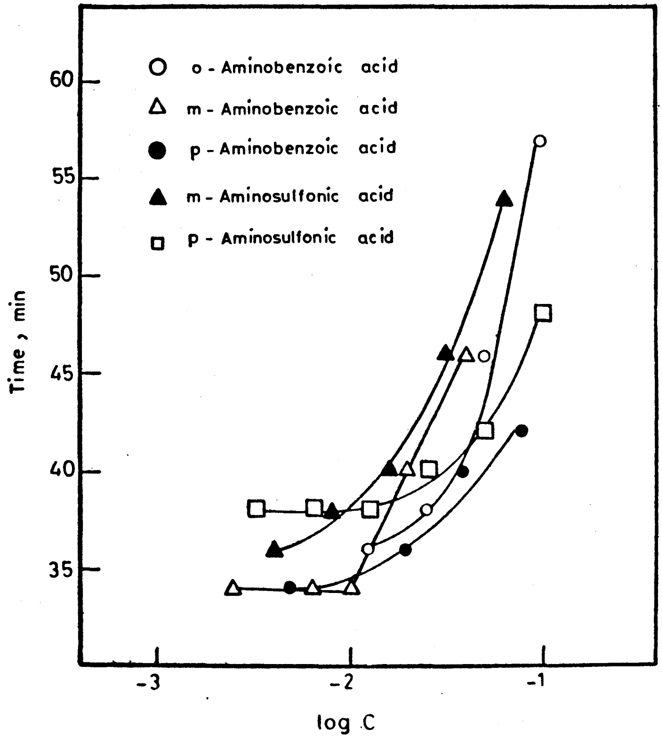

Fig. 5. The time needed to reach T_m as a function of log concentration of various addltives is 2.5 N HCl.

So for these compounds, the two methods gave different results. The results indicate that the thermometric method for determining dissolution rates in these conditions can be unreliable. It also made it clear that the thermometric method of determining inhibitor efficiency must be used with high caution and in some very limited types of reactions.

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