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INFLUENCE OF SOME ALCOHOLS ON THE DISSOLUTION OF TIN IN NITRIC ACID

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The behaviour of tin metal in nitric acid solutions was investigated using thermometric (Mylius) technique. Addition of alcohols to 4 M nitric acid showed a marked decrease in the dissolution rate as methanol < ethanol < propanol < butanol < isobutanol. The inhibition action is attributed to alcohols adsorption on the metal surface through –OH group. The alcohol adsorption follows Langmuier adsorption isotherm.

INTRODUCTION

Tin is a moderately corrosion-resistant metal and finds its most important outlets as an electrodeposited coating on steel or copper, rather than as a metal or alloy in its right, but as such presents very large surface area subjected to corrosive environments. The dissolution of tin in mineral acids has been studied by various authors[1–8]. It is generally agreed that in air-free solutions and in the absence of any cathodic depolariser, tin resists attack by non-oxidising acids. This is attributed to its higher hydrogen overpotential. Addition of certain organic compounds to acid pickling solutions greatly diminished their aggressiveness. The decrease in corrosion rate is attributed to physical or chemical adsorption[9,10] but action of restrainers is contravarial[8,9]. General blockage of the whole surface has been suggested[9]. The purpose of the present contribution is to determine the influence of alcohols in the dissolution of tin in HNO_3 and the mode of their adsorption.

EXPERIMENTAL

The reaction vessel and procedure have been described by Shams El-Din[11]. Tin metal test pieces were cut into sheets with total surface area of 12 cm^2 (p.a. Merck). Surface treatment included successive light abrasions with a fine grade emery paper, 400 and 600 grades, then degreasing with acetone. Duplicate experiments were carried out with a newly-polished sample with a 15 cm^3 volume of fresh solution. The initial temperature was always the same in all experiments 20 ± 0.1°C. All chemicals used in the present investigation without further purification were of p.a. Merck chemicals. The reaction number (R.N.) is defined by Mylius as[12]:

$$\text{R.N.} = \frac{\Delta T}{t} \text{ (in °C/min)}$$

where $\Delta T = T_m - T_i$ (the maximum and initial temperature respectively), and t is the time in min. taken to reach T_m.

RESULTS AND DISCUSSION

The dissolution of tin in 4M HNO_3 was accompanied by temperature change. This temperature change was followed in the absence and presence of different concentrations of the following alcohols, methanol, ethanol, propanol, isopropanol, butanol and isobutanol. The thermometric curves obtained in the presence of methanol and ethanol are shown in Figs. 1 and 2 and similar behaviour is obtained in the case of other alcohols. The general shape of the curves as well as the values obtained from them are concordant to those manifested by Shams El-Din *et al.*[13–15] It is clear from the curves that methanol and other alcohols retard the dissolution of tin in 4M HNO_3 solutions. The smaller concentration of any of these additives brings a marked shift of the maximum temperature

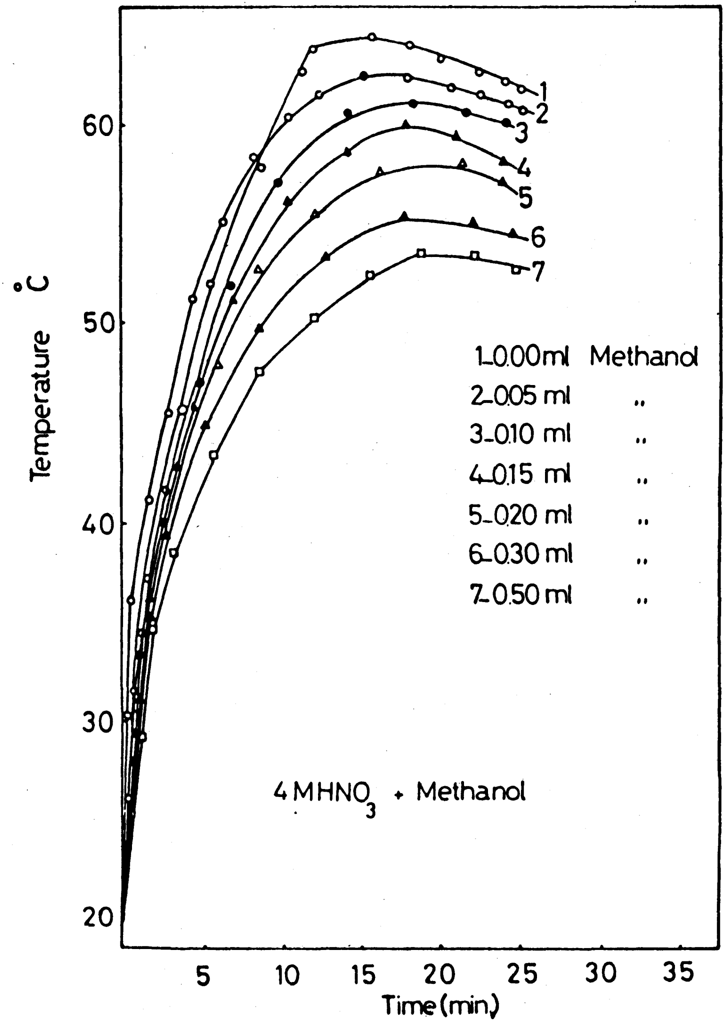

Fig. 1 Temperature-time curves in absence and in presence of varying concentration of methanol.

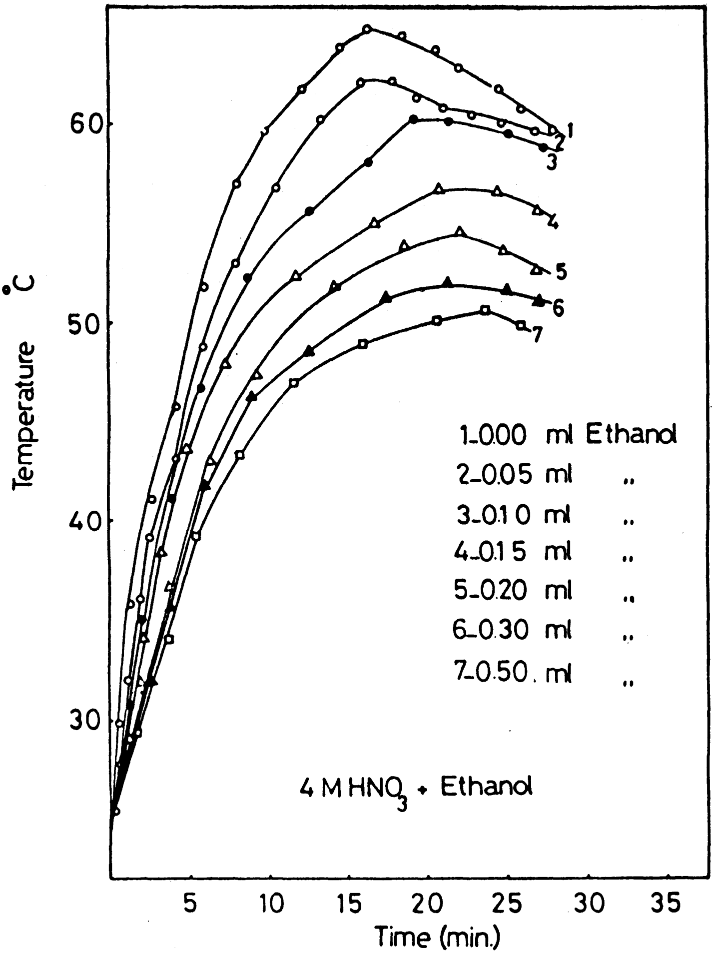

Fig. 2 Temperature-time curves in absence and in presence of varying concentration of ethanol.

(T_{max}) towards lowering T_{max} and a marked shift of T_{max} towards longer time. From these resulted curves, it can be seen that the dissolution rate of tin is inhibited by the presence of alcohols, even in small amounts. This indicates that alcohols act as restrainers.

Fig. 3 reveals the relation between the variation of reaction number percentage with logarithm of alcohol concentration. These results manifested that the dissolution of tin is inhibited by the presence of alcohols.

The inhibitory action of methanol may be explained on the basis that its adsorption on the surface of the metal forms a monolayer covering and the alcohol has a possibility of a chemical reaction between alcohol and HNO_3[16], which formed by autocatalytic mechanism, causing the destruction of the acid leading to the retardation of tin dissolution, the dual effect of the alcohol causes, at a certain concentration.

The adsorption mechanism for the action of organic inhibitors[17,18] as well as some by-products of manufacture[19] in acids has also been reported. From data on the degree of surface coverage by the inhibitor, assuming that the inhibitor

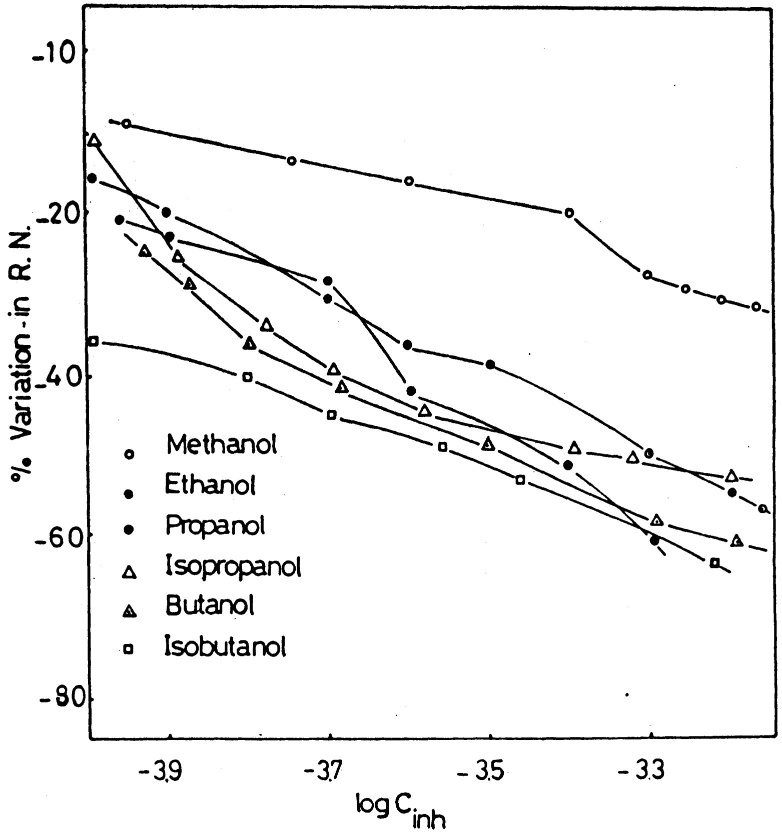

Fig. 3 Variation of reaction number percentage with logarithm of alcohols concentration.

gives a monolayer of adsorption, the surface coverage (θ) can be determined, according to Damaskin[20], from the formula

$$\theta = 1 - \frac{I}{I_0} \qquad (1)$$

where I and I_0 are the current densities of the given potentials in electrolytes with and without inhibitors respectively. The current density can be replaced by the capacitance of the double layer, dissolution rate, adsorption potential or weight loss[20,21].

Accordingly, it seems promising to use R.N. values, as a relative indication of corrosion[22], instead of any of these variables. Eq. (1) can thus be written as

$$\theta = 1 - \frac{RN}{RN_0} \qquad (2)$$

where RN and RN_0 are the values with and without the inhibitor. It is available from the results of the present investigation to calculate the surface coverage, θ.

The Langmuier adsorption isotherm may be written in the form[23]:

$$\ln \frac{\theta}{1-\theta} = \ln (BC) - \frac{\Delta G}{RT} \qquad (3)$$

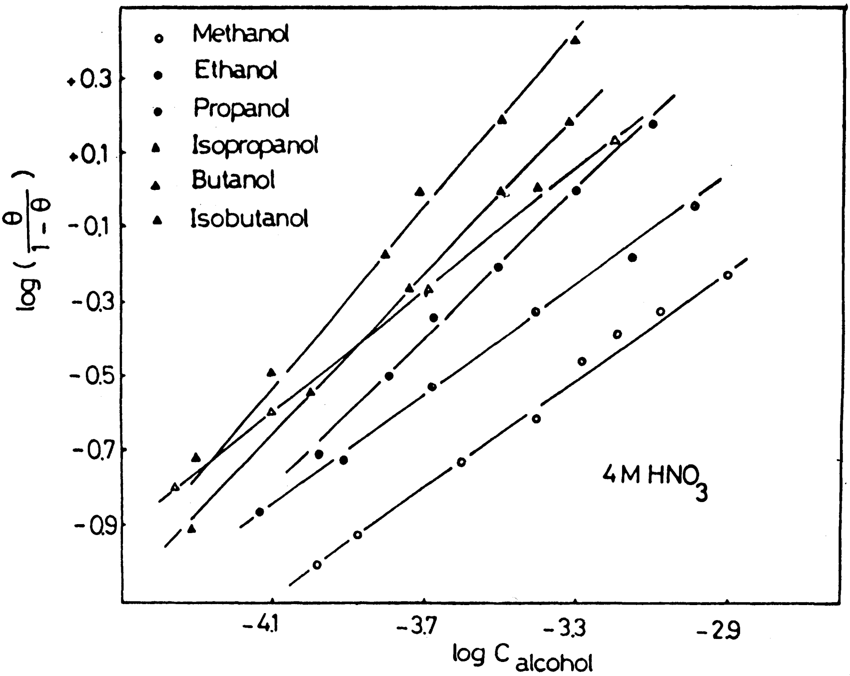

Fig. 4. Langmuier adsorption isotherm for adsorption of different alcohols on tin in 4 M HNO_3.

or

$$\log \frac{\theta}{1-\theta} = B \log C - (\Delta G/2.303\ \mathrm{RT})] \qquad (4)$$

where B^1 is the adsorption equilibrium constant and ΔG is the free energy of adsorption. Plotting log $\theta/1-\theta$ against log $C^1$of the alcohol gives straight line.

Fig. 4 indicates almost a general agreement with Langmuier adsorption isotherm, and the applicability of R.N. values as a relative measure of corrosion.

In conclusion, the adsorption of alcohols on the tin metal surface should take place through the –OH group[23] and would depend on its charge density. The adsorbability of the studied alcoholic function group indicates that isobutanol in which –OH group is thought to be more electron donor than the other alcohols, because it has three $-CH_3$ groups attached to α-carbon atom or the highest adsorption tendency. On the other hand, methanol is the least adsorbate under this condition because –OH group attached to α-carbon atom which has three hydrogen atoms is a weaker electron donor than $-CH_3$ group. This difference in behaviour is apparently associated with corresponding disparities in the strength of corresponding metal/additive adsorption bonds.

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