Effect of Inorganic Salts on the Dissolution of Tin in Nitric Acid Solution

G.A.Noubi, H.Mansour and M.M. Kamal

Faculty of Science, Chemistry Dept., Assiut Uni., Qena, Egypt.

The dissolution of tin in nitric acid solutions of varying concentrations has been studied by the thermometric method, and the dependence of the rise in temperature (ΔT) and the reaction number (R.N) on solution concentration has been established. The effect of concentration of some inorganic additives KCl, KBr, KI, K_2SO_4, KNO_3, $K_2Cr_2O_7$ and Na_3PO_4 on the dissolution rate of tin in 6.0 N HNO_3 has been examined. It was found that; KCl, KBr, KI and K_2SO_4 have an inhibitive effect while KNO_3, $K_2Cr_2O_7$ and Na_3PO_4 accelerate.

It is well-established fact(1) that certain anions promote corrosion while others act as inhibitors. The difference is attributed to the solubility of the reaction product, adsorption, ion size and charge, ion deformability and the electrostatic field set up by the negative charge of the anion on adsorption sites(2-6).

In the present work, it was found that the dissolution of tin in nitric acid solutions is exothermic, so we have made use of this property and applied the Mylius thermometric technique(7). The effect of some additives KCl, KBr, KI, K_2SO_4, KNO_3, $K_2Cr_2O_7$ and Na_3PO_4 on the dissolution rate of tin in 6.0 N HNO_3 was investigated.

EXPERIMENTAL

The reaction vessel and the procedure for determining metal dissolution by the thermometric method have been described previously(8). Tin wire of 5.0 Cm^2 surface area was degreased for 30 seconds at 80°C in an alkaline bath of 15 g./l. Na_2CO_3 + 15 g./l. Na_3PO_4. This was followed by rinsing with running distilled water and drying between filter papers. Each experiment was carried out with 15 ml. of the corroding solution and with fresh test piece. The temperature was measured to ± 0.1°C. All chemicals used were of A.R. quality and employed with further purification. The initial temperature (T_i) in all experiments was 30 ± 0.1°C.

RESULTS AND DISCUSSION

(i) DISSOLUTION OF TIN IN HNO_3 SOLUTIONS:

The dissolution of tin in nitric acid solutions using Mylius method has been studied. Fig.1 represents the variation of temperature as a function of time when test pieces of tin metal were made to react with HNO_3 solutions of different normalities. As can be seen from these curves, an increase in the concentration of the acid is accompanied by a corresponding increase in the maximum temperature measured during the course of reaction. On the other hand, the time required to reach T_m (the maximum temperature) decreases with the increase of the acid strenght.

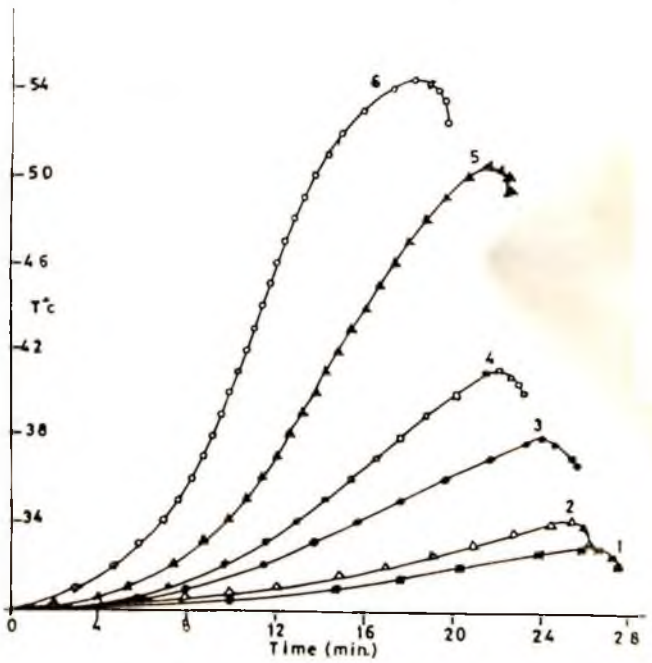


Fig. 1 Effect of HNO_3 concentration on the dissolution rate of tin.

1) 2.0 M 2) 3.0 M 3) 4.0 M
4) 5.0 M 5) 6.0 M 6) 8.0 M

Within the concentration range studied Δt i.e (T_m-T_i), increases linearly with the normality of the acid solution. A plot of the reaction number (R.N.) or corrosion rate as a function of the normality (N) of the solutions on logarithmic coordinates shows that the two variables are related by a power function of the form:

R.N. = AN^n ---------- (1)

Where A and n are constants. For HNO_3 log A equal to -1.2 and n is equal to 2.04.

(ii) EFFECT OF INHIBITORS:

The effect of potassium bromide on the dissolution rate of tin in 6.0 N HNO_3 is shown in fig.2 indicates that the increasing the concentration of the additive, the time necessary to reach T_m increases, while the maximum temperature (T_m) decreases. The other studied additives (KCl, KI and K_2SO_4) exhibit the same behaviour.

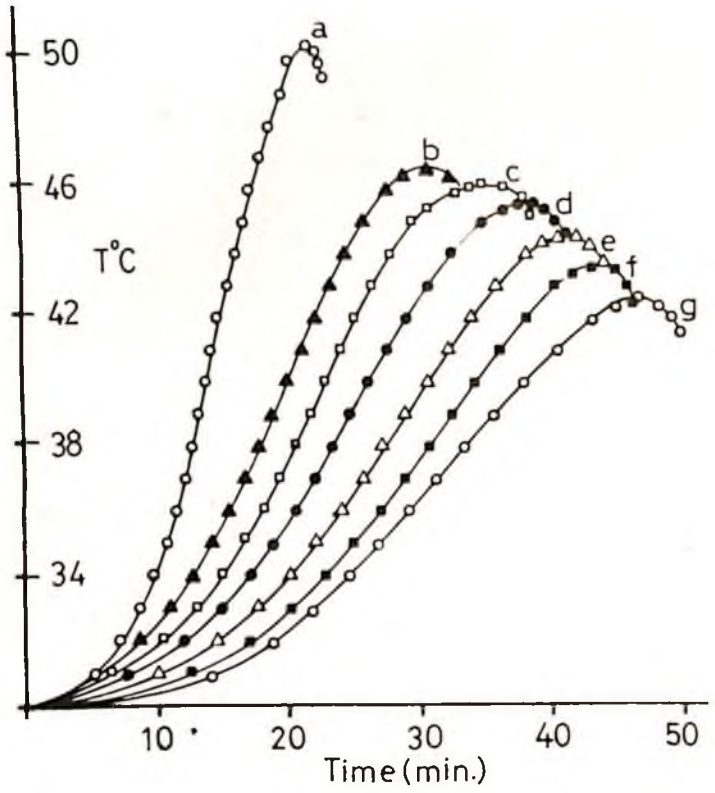


Fig. 2 Effect of KBr on the dissolution rate of tin in 6.0 N HNO_3.

a - 0.0
b - a + 50 mM. KBr
c - a + 100 mM. KBr
d - a + 150 mM. KBr
e - a + 200 mM. KBr
f - a + 250 mM. KBr
g - a + 300 mM. KBr

The values of reaction number (R.N. x 100) in presence of KCl, KBr, KI and K_2SO_4 are plotted as a function of log C as shown in fig. 3 which shows that the corrosion rate (expressed in R.N.) decreases upon increasing the additive concentration. This indicates the inhibition effect of the studied additives. Above a certain additive concentration viz. 148 mM, the corrosion

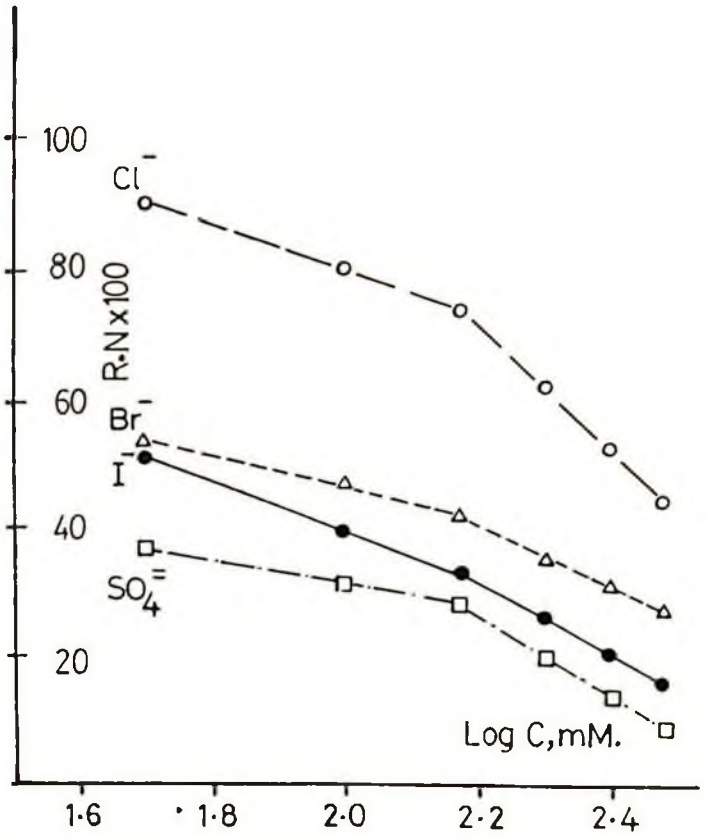


Fig. 3 R.N - Log C plot.

rate decreases more rapidly than at lower additive concentrations.

Fig.3 shows that the inhibition action of the halides can be arranged in the order: $I^- > Br^- > Cl^-$. This is in the order of their ionic radius or ionic volume. The inhibition action of the halides is considered to be due to their adsorption on the metal surface. The high inhibition effect of $SO_4^=$ can be due to the formation of a hard adsorbed sulfate layer and to the higher ionic volume of $SO_4^=$ as compared to that of halides.

(iii) EFFECT OF ACCELERATORS:

The effect of KNO_3, $K_2Cr_2O_7$ and Na_3PO_4 on the dissolution rate of tin in 6.0 N HNO_3 has been studied using the thermometric technique(7). These three compounds behave alike. Representative temperature-time curves for the effect of varying concentrations of KNO_3 on the dissolution rate of tin in 6.0 N HNO_3 are given in fig.4. It is observed that increasing KNO_3 concentration is accompanied by an increase in the maximum temperature (T_m) and decrease in time required to reach it.

The values of reaction number (R.N. x 100) in

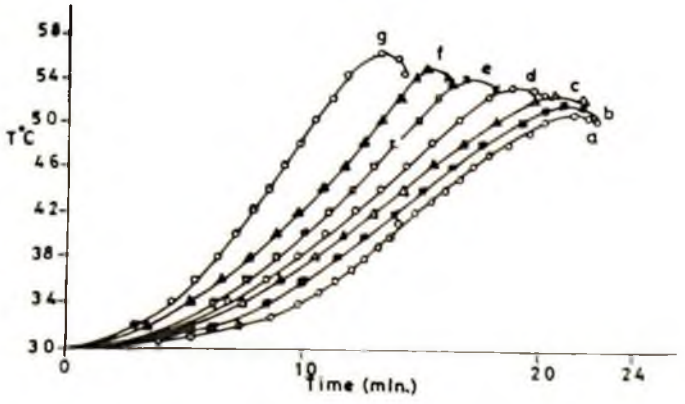


Fig. 4 Effect of KNO_3 on the dissolution rate of tin in 6.0 N HNO_3.

a : 0.0
b : a + 50 mM
c : a + 100 mM
d : a + 150 mM
e : a + 200 mM
f : a + 250 mM
g : a + 300 mM

presence of these three additives are plotted as a function of log C (Fig. 5). It is seen here that increasing the additive concentration is accompanied by a parallel increase of the reaction number values. This indicates the accelerating action of NO_3^-, $Cr_2O_7^=$ and PO_4^{3-} on the dissolution rate of tin in nitric acid solutions.

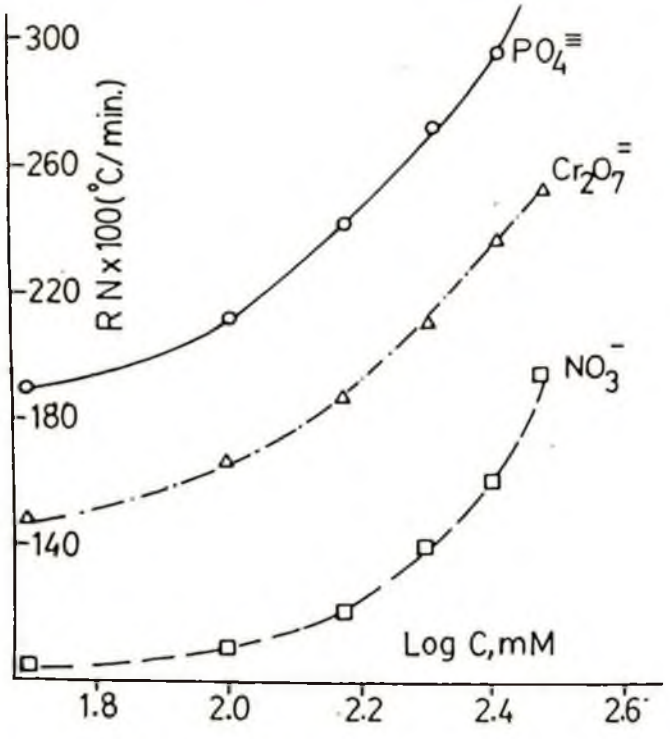


Fig. 5 R.N - Log C plot.

The accelerating action of NO_3^- and $Cr_2O_7^{2-}$ on the dissolution rate of tin in nitric acid solution may be attributed to the contribution of these anions in the cathodic process due to their reduction. On the other hand, the acceleration effect of PO_4^{3-} may be due to its autocatalytic effect on the dissolution process.

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