

## Role of Added Anions in Dissolution of Tin in Acid Solutions

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The effects of added  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  on the dissolution of tin in  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  media have been studied by the thermometric method. Regardless of the slight dissolution enhancement of tin observed, when small amounts of  $\text{Cl}^-$  are added to  $\text{HNO}_3$ , the various halide additives decrease the reaction number (R.N.) in  $\text{HNO}_3$  and  $\text{HCl}$  in the order:  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ . This order represents the ability of the anions to displace the attacking ions from the adsorption sites of the metal surface and runs parallel to their energies of adsorption. These additives have no effect on the dissolution of tin in  $\text{H}_2\text{SO}_4$ . The oxidizing agents, namely  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  promote dissolution of tin in  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  solutions. The augmentative effect of the oxidizing agents is attributed to the fact that reduction of the additive provides a cathodic reaction complementing the dissolution process. The effect of added halates additives is explained by assuming two counteracting effects: their reduction promoting dissolution; and adsorption of the reduction products retarding dissolution. Any one of these effects can prevail depending on the type of halate used and the concentration employed.

In previous work<sup>1</sup> the dissolution of tin in  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  was studied thermometrically. The work was also extended to include the effect of the addition of increasing amounts of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$  and the anions of these acids on the dissolution rate of tin in 4.0 M  $\text{HNO}_3$  solution. As a further extension we have presently investigated the effect of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions on the dissolution of tin in  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . An attempt has also been made to correlate the inhibiting or accelerating action of these anions with their type and concentration.

### Materials and Methods

The reaction vessel and the procedure have been described by Aziz and Shams El-Din<sup>2</sup>. The tin used (Egyptian Company for Metals Trading) contained 0.03% As. Tin strips measuring  $64 \times 10 \times 0.5 \text{ mm}^3$  were lightly abraded with 2/0 and 3/0 emery papers, then degreased by rubbing with cotton cloth moistened with methanol and washed twice with distilled water (complete wetting of the strip upon washing was a criterion of the cleanliness of its surface) and dried. Each experiment was carried out with a new tin strip and 10 ml of the air-free (deaerated) corroding solution, and repeated to ensure reproducibility of the results.

Solutions (4.0 M) of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were prepared and standardized. Due to the limited dissolution rate of the metal in 4.0 M  $\text{HCl}$ , 10.0 M solution of the acid was used instead when testing the

effect of halides. The potassium salts of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  were used. All the chemicals were of AR grade and were used as such.

The reaction number (R.N.) is defined as:  $\text{R.N.} = \Delta T/t$  (in  $^\circ\text{C}/\text{min}$ ), where  $\Delta T = T_m - T_i$  ( $T_m$  represents the maximum and  $T_i$  the initial temperatures) and  $t$  is the time (in min) taken to reach  $T_m$ . All experiments were started at  $20 \pm 0.1^\circ\text{C}$  ( $T_i$ ).

### Results and Discussion

#### Effect of halide additions

The effect of adding different concentrations of the various halide additions on the R.N. of tin in 4.0 M  $\text{HNO}_3$  is graphically shown in Fig. 1. The mode and magnitude of the effect is seen to depend upon both the nature and the concentration of the added anion. Both

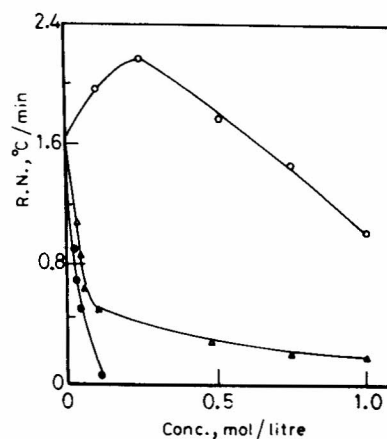


Fig. 1—Variation of R.N. with halide concentration in 4.0 M  $\text{HNO}_3$  solution

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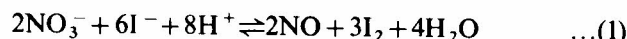
dissolution promotion and retardation was observed with increase in the  $\text{Cl}^-$  ions content in the reaction mixture, while only retarding effect was observed in the presence of  $\text{Br}^-$  ions, the addition of which in increasing amounts brought about decrease in R.N. The behaviour of  $\text{Cl}^-$  ion addition needs explanation. It is achieved that  $\text{Cl}^-$  ion at low concentration may prevent the formation of a protective precipitate of metastannic acid on the metal surface and if at all the precipitate is formed it is peptised thereby facilitating its entry into the solution. This state enhances the dissolution of metal. On the other hand  $\text{Cl}^-$  ion at higher concentrations may help in the formation of a protective precipitate of metastannic acid and/or the insoluble tin oxychloride,  $\text{Sn}(\text{OH})\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$  on the metal surface, thereby decreasing the rate of metal dissolution<sup>1,3,4</sup>.

The curves of Fig. 2 represent the effect of varying the concentration of added  $\text{I}^-$  ions on the thermometric behaviour of tin in 4.0 M  $\text{HNO}_3$  solution. These curves exhibit a number of features which deserve special mention. A small amount of the additive causes a noticeable change in the shape of the thermometric curve with respect to that obtained in iodide-free acid solution. Thus the curves manifest at first an induction period, during which the temperature rises slowly with time. The induction period progressively increases with increasing concentration of iodide in solution. After this induction period the temperature increases suddenly to attain a maximum value,  $T_m$ , and then falls sharply.

The measured  $T_m$  is independent of the additive concentration. This indicates that addition of  $\text{I}^-$  ions

retards the dissolution of tin by adsorption and displacing the attacking anion. After considerable time the surface concentration of  $\text{I}^-$  ions is brought down to zero by interaction with  $\text{HNO}_3$ , whereby the temperature rises in the above described manner.

The dissolution of tin in 4.0 M  $\text{HNO}_3$  solution in the presence of  $\text{I}^-$  ion additive can be visualised as shown in Scheme 1.



Scheme 1

The reaction (1) depicts oxidation of  $\text{I}^-$  ions. The resulting  $\text{I}_2$  in solution containing  $\text{I}^-$  ion is adsorbed on the metal surface in the form of  $\text{I}_3^-$ . The adsorbate-free metal sites are attacked by acid solution to form  $\text{Sn}^{2+}$  according to the reaction (2). Immunity of Sn attained in acid solutions, attributed to the high  $\text{H}_2$ -evolution overpotential<sup>5-8</sup> can't be reached in the prevailing conditions, since reduction of  $\text{HNO}_3$  and oxidation of  $\text{Sn}^{2+}$ , according to Eqs (3) and (4) promote the metal dissolution by reaction (2). In addition to this effect, reaction (4) facilitates the desorption of  $\text{I}_3^-$  leading to increase of the metal surface area exposed to the attacking ions. As the whole surface becomes free, the temperature increases violently. The large decrease in R.N. is, therefore, a resultant of two effects, namely anion adsorption and acidity decrease, through reaction (1).

This state of affairs differs, however, from that of  $\text{Br}^-$  ion as additive, where retardation is due to anion adsorption only. The observed decrease in the slope of the rising part of the thermometric curve indicates that the anion interferes with the anodic reaction, since this part of the curve represents the actual rate of dissolution of metal<sup>9</sup>.

Due to the limited effect of HCl on the dissolution of tin, higher acid concentration, namely 10.0 M solution was used to study the effect of added  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions on the dissolution process. Figure 3 represents the thermometric curves of the dissolution of tin in 10.0 M HCl solutions containing increasing amounts of KCl. Similar curves are obtained using KBr and KI as additives instead of KCl. The corresponding R.N. values have been calculated and plotted as a function of additive concentration in Fig. 4. These additives retard the dissolution process as indicated by decrease in the corresponding R.N. values. This decrease is caused by the decrease in  $T_m$  and simultaneous increase in the time,  $t$ , necessary to reach it. This indicates that the dissolution process in the prevailing condition is a surface reaction in which the

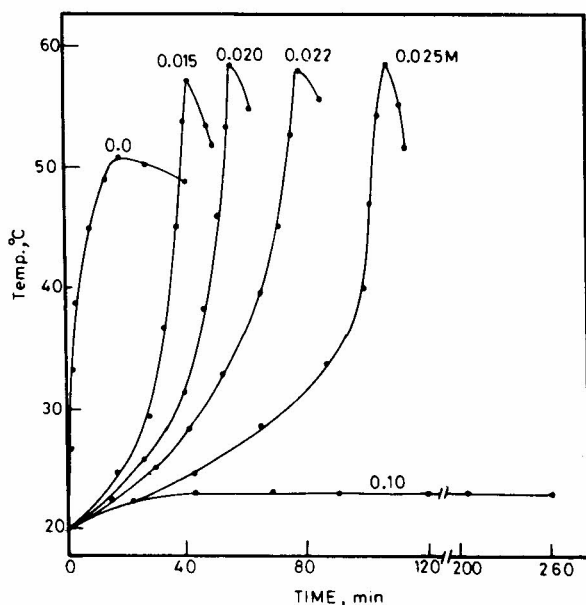


Fig. 2—Thermometric curves for the dissolution of Sn in 4.0 M  $\text{HNO}_3$  containing increasing amounts of  $\text{I}^-$

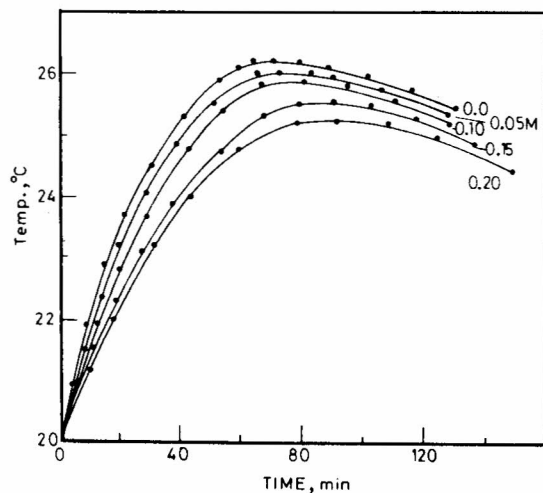


Fig. 3—Thermometric curves for the dissolution of Sn in 10.0 M HCl containing increasing amounts of  $\text{Cl}^-$

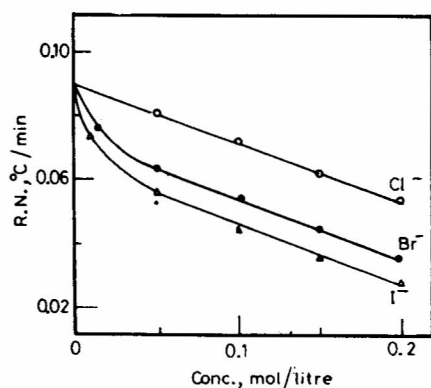


Fig. 4—Variation of R.N. with halide concentration in 10.0 M HCl solutions

participating particles are adsorbed on the metal surface<sup>10</sup>. The reaction inhibition in the presence of the additive is thus the result of displacement of one of the main reaction partners from adsorption sites. Again the slope of the rising part of the curves of Fig. 3 and other similar ones, decrease with increasing additive concentration. This indicates that the adsorbed anion displaces one of the anodic reaction partners<sup>9,10</sup>.

These results allow evaluation of the relative effect of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  on the dissolution of tin in both  $\text{HNO}_3$  and  $\text{HCl}$  acids. Regardless of the slight enhancement of tin dissolution observed when small amounts of  $\text{Cl}^-$  is added to  $\text{HNO}_3$ , the three anions retard the reaction in both the acid media. The magnitude of inhibition is affected by both the nature and concentration of the added salt. From the variation of R.N. at one and the same anion concentration, the different anions are found to retard the dissolution in the order:  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ .

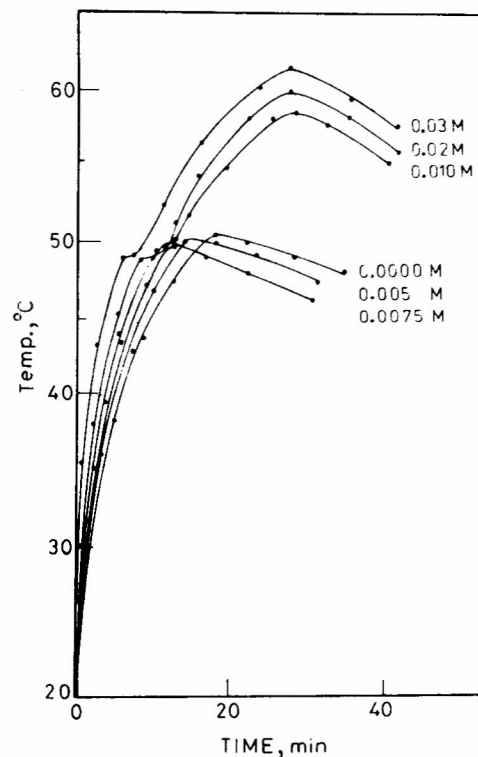


Fig. 5—Thermometric curves for the dissolution of Sn in 4.0 M  $\text{HNO}_3$  containing increasing amounts of  $\text{Cr}_2\text{O}_7^{2-}$

This order represents the ability of the anions to displace the attacking ions from the adsorption sites of the metal surface and runs parallel to their energies of adsorption<sup>11</sup>, and this order is in accordance with that observed by Shams El-Din and coworkers<sup>12</sup>, who pointed out that  $\text{I}^-$  ions retard the dissolution of Al in  $\text{HCl}$  solution to a higher extent as compared to  $\text{Br}^-$  ions under similar conditions.

Additions of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  up to 1 M have no effect on the dissolution of Sn in 4.0 M  $\text{H}_2\text{SO}_4$ .

#### Effect of added oxidizing agents

It is reported<sup>13</sup> that addition of an oxidizing agent enhances acid dissolution of tin and this is attributed to the fact that the reduction of the additive provides a cathodic path, thermodynamically more feasible than hydrogen evolution<sup>13</sup>. In this section the thermometric method for corrosion assessment has been used to correlate the effect of some oxidants on the acid dissolution rate of tin to their oxidizing power.

The effect of adding varying amounts of the potassium salts of the anions, viz.  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$  and  $\text{NO}_3^-$  on the dissolution of tin in 4.0 M  $\text{HNO}_3$  has been studied. Three types of thermometric curves are obtained. When  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{BrO}_3^-$  salts are used, the curves are characterized by two segments (Fig. 5). This behaviour is similar to that obtained using  $\text{HNO}_3$  of

concentration  $\geq 5.4 M$  (ref. 1). A similar explanation can also be given. The two sigmoid curves of Fig. 5 are the result of two exothermic processes, namely, metal dissolution and interaction between primary products and additive. This conclusion was proved experimentally as follows. In an experiment in which the acid solution contained  $0.025 M K_2Cr_2O_7$ , further addition of the additive, after the attainment of  $T_m$ , resulted in a large increase in the temperature of the system.

In the second type of curves with  $KIO_3$  as additive the thermometric curves exhibit features somewhat similar to those of  $KI$  (Fig. 2). Thus small amount of the additive decreases R.N. without any noticeable change in the shape of the curve. Higher concentrations of the additive cause, first, a slow increase of the temperature followed by a higher rate of temperature change. The elapsed time of the slow rising part of curves progressively increases with the additive concentration. This behaviour may be attributed to the adsorption of  $I_2$  resulting from the reduction of  $IO_3^-$ . However the curves of  $KIO_3$  differ from those of  $KI$  in the fact that  $T_m$  of the latter is concentration-independent.

The third type of curves obtained with  $KClO_3$  exhibit no unusual features (Fig. 6). The additive promotes the dissolution process as indicated by increase in R.N. values. This increase is brought about by an increase of  $T_m$  with a simultaneous decrease in the time  $t$ , needed to reach it.

The relative effects of these anions as revealed by the corresponding R.N. values at similar concentration

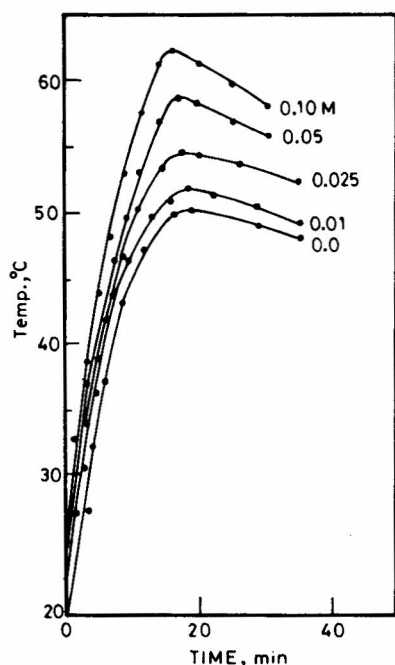


Fig. 6—Thermometric curves for the dissolution of Sn in 4.0 M  $HNO_3$  containing increasing amounts of  $ClO_3^-$

follow the order:  $Cr_2O_7^{2-} > S_2O_8^{2-} > ClO_3^- > BrO_3^- > NO_3^- > IO_3^-$ . The order of decrease of oxidizing power of these anions as judged from their  $E^\circ$  values<sup>14</sup> is:  $S_2O_8^{2-} > BrO_3^- > ClO_3^- > Cr_2O_7^{2-} > IO_3^- > NO_3^-$ . The disagreement between the two orders may be due to anomalous behaviour of  $S_2O_8^{2-}$  which preserves its oxidation properties in the presence of a suitable catalyst<sup>15</sup>, and also the decomposition of  $S_2O_8^{2-}$  leads to the formation of  $SO_4^{2-}$  which in turn retards the process of tin dissolution, and to the adsorption of the reduction products. In the given experimental conditions the oxidizing halates are reduced forming the corresponding halogens<sup>14</sup>. The manner in which the different halates influence the dissolution process may be the result of two counteracting effects: (i) oxidation effect which enhances the dissolution; and (ii) adsorption of the reduction products which retards the process. The presence of  $ClO_3^-$  and low concentration of  $BrO_3^-$  in the reacting media enhances the metal dissolution as a result of their oxidizing effect. On the other hand  $IO_3^-$  and high concentrations of  $BrO_3^-$  retard the process as a result of the strong adsorption of the reduction products.

Normal thermometric curves are obtained in the presence of Sn in  $HCl$  and  $H_2SO_4$ . It is observed that addition of an oxidizing agent to Sn in contact with  $HCl$  or  $H_2SO_4$  results in an augmentation of R.N. This increase is brought about by an increase in,  $T_m$ , and simultaneous decrease in time,  $t$ , needed to reach it. The increase in R.N. may be due to the fact that reduction of the additive provides a cathodic reaction complementing the dissolution process. It is expected therefore that higher the oxidation power of the additive the larger will be the increase in the dissolution rate. This can be checked by a comparison of the various oxidizing agent. The results obtained reveal that R.N. values decreased in the order:  $Cr_2O_7^{2-} > IO_3^- > BrO_3^- > S_2O_8^{2-} > ClO_3^- > NO_3^-$  (in 4.0 M  $HCl$ ) and  $BrO_3^- > Cr_2O_7^{2-} > S_2O_8^{2-} > ClO_3^- > IO_3^-$  (in 4.0 M  $H_2SO_4$ ).

There is no similarity in these orders and the arrangement of the anions according to their oxidizing power may be attributed to specific adsorption effects.

Using Mössbauer spectroscopy and X-ray diffraction, Shibuya<sup>16</sup> identified the formation of  $SnO_2 \cdot nH_2O$ ,  $Sn_4(OH)Cl_2$  and  $SnSO_4$  as corrosion products<sup>5</sup> in  $HNO_3$ ,  $HCl$  and  $H_2SO_4$  media respectively. The formation of a film containing chromic oxide and tin oxide, when the metal was treated with chromic acid, was reported by Shrier<sup>8</sup>.

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