# The stabilities of secondary tin minerals. Part 2*: The hydrolysis of tin(II) sulphate and the stability of $Sn_3O(OH)_2SO_4$

R. EDWARDS

School of Chemical and Physical Sciences, Liverpool John Moores University, Byrom Street, Liverpool, L3 3AF, UK

R. D. GILLARD

Department of Chemistry, University of Wales, Cardiff, P.O.Box 912, Cardiff CF1 3TB, UK

AND

P. A. WILLIAMS

School of Chemistry, University of Western Sydney, Nepean, P.O.Box 10, Kingswood, NSW 2750, Australia

## Abstract

Tritin(II)dihydroxyoxosulphate, $Sn_3O(OH)_2SO_4$, is a rare corrosion product found on the surfaces of certain tin alloys. A new synthesis based on the hydrolysis of $SnSO_4$ is described. The stability constant determination of $Sn_3O(OH)_2SO_4$,s, at 298.2K and $10^5$Pa is determined using direct measurements via electrodes, of the activities of tin(II) and sulphate ions. $\Delta fG^0$(298.2K) is equal to $-1563.1 \pm 0.9$ kJ $mol^{-1}$.

KEYWORDS: tin minerals, stability, tritin(II) dihydroxyoxosulphate.

## Introduction

VERY few tin compounds other than tin(IV) oxides and hydroxides are known to occur in nature or as a result of corrosion. Only under extreme conditions are the soluble species $Sn^{2+}$(aq), $Sn(OH)_3^-$(aq) and $Sn(OH)_6^{2-}$(aq) stable (Pourbaix, 1966).

Such conditions are encountered in the natural environment, albeit infrequently, mirrored in the occurrence of compounds such as the basic tin(II) salts $Sn_3O_2SO_4$ (MacLeod, 1982) and abhurite, $Sn_{21}Cl_{16}(OH)_{14}O_6$ (Edwards et al., 1992; Hosking, 1970; Keller, 1917; Matzko et al., 1985) and various stannates(IV) (Faust and Schaller, 1971; Marshukova et al., 1984; Marshukova et al., 1982; White and Nelen, 1973).

Basic tin(II) sulphate is a rare corrosion product found on the surfaces of tin and tin alloys. It is even less common than the basic tin(II) chloride abhurite. $Sn_3O_2SO_4$ was identified on corroding brass and bronze objects recovered from seawater (MacLeod, 1982). $Sn_3O(OH)_2SO_4$, a hydrated form of the corrosion product, has been synthesized several times (Carson, 1926; Ditte, 1882; Davies and Donaldson, 1967), and its crystal structure reported (Davies et al., 1975; Grimvall, 1975).

Basic tin(II) sulphate is known to form only at low pH, but we now find that certain aqueous solutions of tin(II) sulphate actually hydrolyse to produce it. When the concentration of tin(II) ions is sufficient, their hydrolysis will cause the pH of the solution to decrease into the specific range which facilitates the formation of tin(II) hydroxy sulphate. A simpler method of synthesis has thus been found.

$Sn_3O(OH)_2SO_4$ or its dehydrated form has not been described as a mineral, but it seemed worthwhile to compare its relationship with tin(II) oxide and assess the likelihood of its occurrence as a corrosion product. A different approach was adopted

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TABLE 1. Analytical results for precipitates formed after the equilibration of $SnSO_4$ in oxygen-free $H_2O$ (100 cm$^3$)

| $SnSO_4$(g) | pH | Nature of precipitate |
|---|---|---|
| 0.001 | 4.91 | $3SnO \cdot H_2O$ |
| 0.005–0.100 | 4.58–3.00 | $3SnO \cdot H_2O + Sn_3O(OH)_2SO_4$ |
| 0.300–4.970 | 2.60–1.70 | $Sn_3O(OH)_2SO_4$ |

to determine the free energy of formation of $Sn_3O(OH)_2SO_4$(s) from equilibrated solutions. Tin amalgam and sulphate ion-selective electrodes (ISE) were used to determine the respective activities of tin and sulphate ions.

## Experimental

All preparations were carried out in degassed water under an atmosphere of dinitrogen to ensure the exclusion of dioxygen.

*Sn$_3$O(OH)$_2$SO$_4$.* This was made following the method of Davies and Donaldson (1967). Tin(II) sulphate (5 g) was dissolved in a minimum of water containing a few drops of concentrated sulphuric acid. The pH of the clear solution was increased to approximately 1.8 by adding NaOH(aq) (0.5 M). The resulting white precipitate was collected at the pump, washed with water and acetone, and dried *in vacuo* over silica gel. The basic tin(II) sulphate was identified using IR, in KBr pellets on a Perkin-Elmer 783 spectrophotometer and by powder X-ray methods (360 mm circumference Debye-Scherrer camera, Cu-*K*α radiation), by comparison with data in the JCPDS powder file.

*Hydrolysis of SnSO$_4$.* The hydrolysis of aqueous tin(II) sulphate was followed by monitoring the pH of solutions of differing concentration using a Radiometer PHM85 pH meter fitted with a Radiometer GK2401C combination electrode. $SnSO_4$ (0.001 to 4.0 g) was dissolved in deoxygenated water (100 cm$^3$) with stirring at room temperature. After 5 min the solution became more and more cloudy because of the precipitation of solid products of hydrolysis. This was accompanied by a decrease in pH. After several hours, there was no further change in pH and the system was taken to have reached equilibrium. The white precipitates were collected on sintered glass funnels, washed with water and dried *in vacuo* over silica gel. Infra red and powder X-ray methods were used to identify them. The nature of the precipitate varied, depending on the final pH. Results are given in Table 1.

A number of repeat experiments were carried out with initial tin(II) sulphate concentrations ranging between 0.03 and 0.06 M and equilibrated in a thermostatted water bath at 25°C. Reaction vessels were wrapped in aluminium foil to exclude light, thought to promote the oxidation of tin(II) under certain conditions (Tobias, 1958).

After 28 days, the pH of the solution was measured *in situ*, the white solids collected, (*see above*) and total solution tin concentrations analysed by AAS. Total sulphate concentrations were calculated from the concentration of the starting material, final tin concentration and stoichiometry of the basic sulphate, (Eqn 1). These were used to estimate the ionic strengths of the hydrolysed solutions. The results are shown in Table 2 (Fig. 1 shows the variation of $I_{final}$ with $[SnSO_4]_{initial}$).

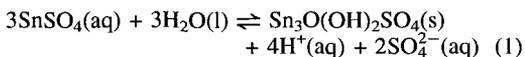$$3SnSO_4(aq) + 3H_2O(l) \rightleftharpoons Sn_3O(OH)_2SO_4(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \quad (1)$$

TABLE 2. Analytical Results for solutions used to determine the final ionic strength of hydrolysed tin(II) sulphate solutions at 298.2 K

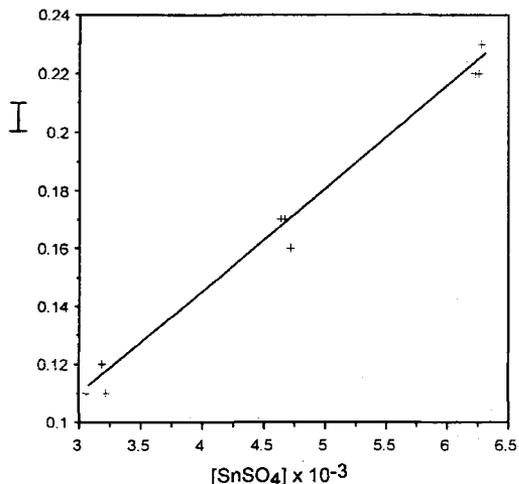| Sol. | $[SnSO_4]^a$ | $[Sn^{2+}]^b$ | $[SO_4^{2-}]$ | $pH^b$ | $I^b$ |
|---|---|---|---|---|---|
| 1 | 0.03221 | 0.02505 | 0.02989 | 2.424 | 0.11 |
| 2 | 0.03064 | 0.02404 | 0.02844 | 2.362 | 0.11 |
| 3 | 0.03193 | 0.02737 | 0.03038 | 2.472 | 0.12 |
| 4 | 0.04673 | 0.04037 | 0.04461 | 2.286 | 0.17 |
| 5 | 0.04639 | 0.03885 | 0.04388 | 2.284 | 0.17 |
| 6 | 0.04718 | 0.03806 | 0.04414 | 2.286 | 0.16 |
| 7 | 0.06277 | 0.05211 | 0.05922 | 2.203 | 0.23 |
| 8 | 0.06231 | 0.05073 | 0.05845 | 2.097 | 0.22 |
| 9 | 0.06262 | 0.05042 | 0.05855 | 2.200 | 0.22 |

$^a$ Initial,
$^b$ Final.

FIG. 1. Variation of $I_{final}$ with $[SnSO_4]_{initial}$ after hydrolysis.

*Equilibrium solubility measurements*

To determine the stability constant of $Sn_3O(OH)_2SO_4(s)$, the pH and activities of $Sn^{2+}(aq)$ and $SO_4^{2-}(aq)$ were measured in a solution at equilibrium with the solid phase. A tin amalgam electrode and an ISE were employed to measure the respective activities of the tin and sulphate ions in solution, the potentials of each electrode being recorded using a digital millivolt meter.

*$Sn_3O(OH)_2SO_4$ solutions*. To avoid complications such as liquid-junction potential errors and ionic strength corrections, all standard and test solutions were prepared at I = 1 M, by adding sodium perchlorate.

The solutions used to determine the stability constant of $Sn_3O(OH)_2SO_4$ were prepared in a similar fashion to those described above, except that the ionic strengths of the resulting solutions were corrected to 1 M using the relationship between final I and initial concentrations of tin(II) sulphate (Fig. 1). To dioxygen-free $H_2O$ (37 $cm^3$) and $NaClO_4$(aq) (1 M, 163 $cm^3$) under dinitrogen, pure $SnSO_4$(s) (2.1249 g, 9.929 mmol) was added and stirred at 25°C. After 2 h, a white precipitate settled from the cloudy solution, which was sealed and thermostatted in a water bath at 25 $\pm$ 0.3°C, excluding light. A number of repeat experiments were carried out.

The solutions were left undisturbed for 28 days. After this time the activities of the aqueous ions were measured (see below). To ensure no contamination by air, solutions were transferred to a specially designed electrochemical measuring cell made of Teflon, by means of a capillary cannula and dinitrogen pressure. Sufficient solution was transferred so that each electrode was immersed to a depth of 1 cm or more. The solutions were allowed to stand for at least 30 min, during which no solid was deposited. The pH and voltages registered, the corrections and activities deduced for the tin(II) ions and sulphate ions of each solution are given in Table 3. The solid phase remaining in the reaction vessel was collected (as above) and identified as $Sn_3O(OH)_2SO_4$ by IR and XRD analysis.

TABLE 3. Experimental and derived results for the dissolution of $Sn_3O(OH)_2SO_4$,s at 298.2 K

| $SnSO_4$ (g)[a] | $Hg/Sn$[b] | $ISE$[b,c] (Expt.) | $ISE$[b,d] (Zero) |
|---|---|---|---|
| 2.1249 | −421 | +36 | +51 |
| 2.1230 | −423 | +33 | +49 |
| 2.1428 | −422 | +30 | +50 |
| 2.1534 | −421 | +34 | +51 |
| 2.1829 | −421 | +30 | +51 |

| $ISE$[b,e] (Corr.) | pH[f] | log $aSn^{2+}$ | log $aSO_4^{2-}$ | log $K_{H^+}$ |
|---|---|---|---|---|
| −15 | 1.595 | −2.57 | −3.48 | −4.81 |
| −16 | 1.570 | −2.63 | −3.44 | −4.96 |
| −20 | 1.567 | −2.60 | −3.20 | −4.81 |
| −17 | 1.507 | −2.57 | −3.40 | −5.08 |
| −21 | 1.479 | −2.57 | −3.24 | −5.03 |

[a] Mass of tin sulphate (total volume 200 $cm^3$). [b] Electrode potentials in mV. [c] Experimental result for ISE. [d] ISE readings at a given tin(II) activity and zero sulphate activity. [e] Corrected ISE result (see Table 4). [f] Final.

*Preparation and calibration of the electrodes.* Tin activity was measured using a tin amalgam electrode and a saturated calomel reference electrode. This was calibrated with tin(II) perchlorate following the method of Tobias (1958). The ionic strengths of the solutions were brought to 1 M by adding $NaClO_4$(s). A calibration slope of 30.8 mV per decade was obtained at 25°C for [$Sn^{2+}$] ranging from 0.0931 to 0.0233 M. Results for the calibration are presented in Table 4.

A sulphate ion-selective electrode was constructed following a method similar to that described by Rechnitz *et al.*, (1972). $Na_2SO_4$ solutions at I = 1M were used to calibrate it. A response of −25.3 mV per decade at 25°C was obtained for sulphate concentrations between 0.0500 and 0.00100 M. The ion selective electrode also responded to varying tin(II) activity. Results are presented in Table 4.

## Results and discussion

Direct measurement of the activities of ions in solution removes the need to correct their concentrations measured analytically (e.g. AAS), for contributions from the complex species concerned. This is particularly valuable when little is known of the complex species involved, especially in complicated systems.

The need to employ ISEs to measure the activities of the free ions in equilibrated solutions of $Sn_3O(OH)_2SO_4$ stems from the paucity of work concerning the properties of tin(II) sulphate solutions. However, Discher (1953*a*, *b*), O'Connor (1937) and Miyamoto (1932) have studied such systems.

In dilute solutions, Discher proposed that the predominant species were $Sn^{2+}$(aq) and $SnSO_4^0$(aq). This is in agreement with O'Connor's (1937) conclusion that, in very low concentrations of tin(II) sulphate, complete dissociation occurs. Increasing the concentration of $SnSO_4$ points to the existence of $Sn[Sn(SO_4)_2]$ and its related ions, whilst

in yet more concentrated solutions, the presence of $Sn_2[Sn(SO_4)_3]$ has been suggested. Miyamoto (1932) also postulated $Sn(SO_4H)_2$ and $Sn_2(SO_4)(SO_4H)_2$ as the probable species in the $SnSO_4$–$H_2O$ system.

Many anomalies remain concerning the species distribution in such solutions. Data are not available for the equilibrium constants of the postulated species, so in equilibrated solutions of $Sn_3O(OH)_2SO_4$, the free ion activities of $Sn^{2+}$(aq) and $SO_4^{2-}$(aq) cannot be elucidated in the usual manner.

The activity of $Sn^{2+}$(aq) can readily be determined using the Sn-Hg electrode (Gobom, 1976; Wanda, 1977). Research on electrodes able to measure the activity of $SO_4^{2-}$(aq) is sparse, although a method for the preparation of an ISE responding to sulphate has appeared (Rechnitz *et al.*, 1972). By slight modification of the procedure for its preparation, a satisfactory ISE for sulphate determination was constructed.

### Stability studies and their application to the corrosion and mineralogy of tin

A stability constant has been derived in terms of eqn 2. Results for the determination of $K_{H^+}$ are given in Table 3. The average value of log $K_{H^+}$ for $Sn_3O(OH)_2SO_4$ is −4.9(1), which in turn leads to a value of $\Delta_f G^0$ ($Sn_3O(OH)_2SO_4$,s,298.2K) of −1563.1 ± 0.9 kJ $mol^{-1}$. Errors associated with the free energy of formation of aqueous Sn(II) have not been included in the above calculation.

$$Sn_3O(OH)_2SO_4(s) + 4H^+(aq) \rightleftharpoons 3Sn^{2+}(aq) + SO_4^{2-}(aq) + 3H_2O(l) \quad (2)$$
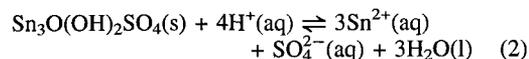
The hydrolysis of tin(II) has been utilized to synthesize the basic tin(II) sulphate, $Sn_3O(OH)_2SO_4$ and to determine its stability. The phases produced in the stability constant determinations are identical with previously synthesized compounds (Donaldson and Davies, 1967). $Sn_3O(OH)_2SO_4$ is stable only at low pH. An increase of pH above ~3 results in the

TABLE 4. Results for electrode calibration in standard solutions at 298.2K. The reference was a saturated calomel electrode

| $aSn^{2+}$ (M) | Sn—Hg (mV) | ISE (mV) | $aSO_4^{2-}$ (M) | ISE (mV) |
|---|---|---|---|---|
| 0.014 | −399 | +76 | $8.414 \times 10^{-3}$ | −52 |
| $7.109 \times 10^{-3}$ | −409 | +65 | $2.190 \times 10^{-3}$ | −32 |
| $2.923 \times 10^{-3}$ | −420 | +52 | $2.373 \times 10^{-4}$ | −12 |

Note: In $SnSO_4$ solutions the ISE is used to determine the activity of sulphate by correcting the experimental result for interference from tin activity.
Experimental (mV) = Sn activity (mV) + $SO_4$ activity (mV).

formation of hydrous tin(II) oxide, $3SnO \cdot H_2O$: the solids precipitated from such solutions are admixtures, to varying degrees, of $Sn_3O(OH)_2SO_4(s)$ and $3SnO \cdot H_2O(s)$.

To evaluate the relationship of $Sn_3O(OH)_2SO_4$ to other tin(II) minerals and compounds, an equilibrium model has been developed for the formation of the various phases. Thermodynamic data for romarchite, SnO, and other values necessary were taken from the compilations of Robie et al. (1978) and Krauskopf (1982).

Figure 2 is a stability field diagram for the SnO–$H_2O$–$H_2SO_4$ system, which illustrates the relationship between $Sn_3O(OH)_2SO_4$ and romarchite, SnO. $SnSO_4$ does not appear on the diagram as its stability lies outside the limits chosen. In natural environments, e.g. seawater, the $SO_4^{2-}$ concentration is approximately $3 \times 10^{-2}$ M and the buffered pH about 8 (Krauskopf, 1982). Romarchite, SnO, or the hydrated form hydroromarchite, $3SnO \cdot H_2O$, are the phases which should crystallize under these conditions. Observations of their occurrence (Bannister, 1926; Howie and Moser, 1973; Smythe, 1940) bear this out. No distinction is made here between the two. The presence of tin(II) hydroxysulphate as a corrosion product or mineral species is very unlikely; conditions required for its formation (low pH and high sulphate concentration) are rarely encountered. Nevertheless, $Sn_3O_2SO_4$ has been reported along with cassiterite, $SnO_2$, as a minor component of corrosion on bronze objects from a wreck approximately 1 km south of Point Cloates, Australia (MacLeod, 1982). It has also been found on the surface of 'brass' from the same wreckage.

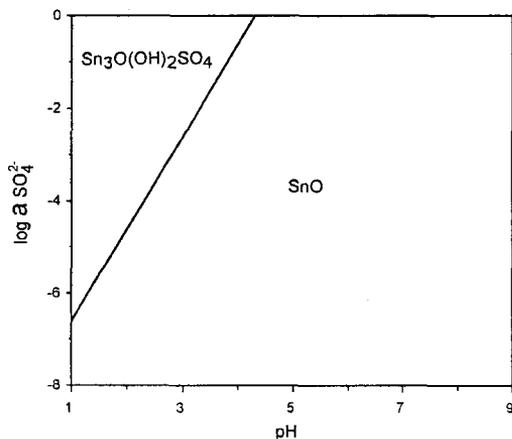Extreme pH values are not unknown in isolated circumstances of tin corrosion (due to its hydrolysis).

A pH of 1 has been recorded for fluid inclusions in surface blisters, relating to the occurrence of abhurite, $Sn_{21}Cl_{16}(OH)_{14}O_6$ (Matzko et al., 1985). Furthermore, the formation of $Sn_3O_2SO_4$ is favoured on Cu-containing Sn alloys, when sulphate is available.

Of the various basic tin(II) salts prepared from aqueous sulphate solutions, only one gave a clearly defined crystalline phase, tritin(II)dihydroxy(oxy)-sulphate. The pure material is prepared from solutions of pH 1.5 to 2.4; precipitates obtained at higher pH are not true basic salts. $Sn_3O(OH)_2SO_4$ crystallizes in the orthorhombic system with space group $Pbc2_1$ and unit cell dimensions $a = 4.983$, $b = 13.128$, $c = 12.212$ Å (Davies et al., 1975; Grimvall, 1975). The structure confirms the work of Tobias (1958), who showed that the predominant polynuclear ion in aqueous solution was $Sn_3(OH)_4^{2+}$ or $Sn_3O(OH)_2^{2+}$, he was unsure to what degree the complex was hydrated. Crystalline $Sn_3O(OH)_2SO_4(s)$ contains discrete $[Sn_3O(OH)_2]^{2+}$ rings.

Attempts at syntheses of the basic tin(II) sulphate where no precautions were taken to exclude air, resulted in the crystalline compound, $Sn_7(OH)_{12}(SO_4)_2$, which contains a mixture of $Sn^{2+}$ and $Sn^{4+}$ ions in the ratio 6:1 (Grimvall, 1982). $(Sn_7(OH)_{12}(SO_4)_2$ crystallizes in the orthorhombic system with space group $Pbca$. The unit cell parameters, $a = 12.472$, $b = 12.649$, $c = 12.676$ Å are similar to those of $Sn_3O(OH)_2SO_4$. Bearing in mind the solution chemistry of tin and the conditions prevailing in natural aerobic environments where the basic tin(II) sulphate might be encountered, the mixed oxidation state tin hydroxysulphate would actually be thermodynamically stable (although no data exist to substantiate this statement), rather than pure tristannous dihydroxy oxide sulphate prepared under ideal conditions.

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FIG. 2. Stability field diagram for the $SnO-H_2O-H_2SO_4$ system at 298.2K and $10^5$ Pa.

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