

The stabilities of secondary tin minerals: abhurite and its relationships to Sn(II) and Sn(IV) oxides and oxyhydroxides

R. EDWARDS, R. D. GILLARD, AND P. A. WILLIAMS*

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, U.K.

Abstract

The true formula of abhurite is $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$. A stability constant for the phase has been determined at 298.2 K. For the reaction $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6 (\text{s}) + 26\text{H}^+ (\text{aq}) \rightleftharpoons 21\text{Sn}^{2+} (\text{aq}) + 16\text{Cl}^- (\text{aq}) + 20\text{H}_2\text{O} (\text{l})$, $\log K_{\text{H}^+}$ (298.2 K) is equal to -39.9 (7). This value is used to assess the relative stability of abhurite in the natural environment and to evaluate its modes of occurrence in relation to other secondary Sn(II) and Sn(IV) species.

KEYWORDS: abhurite, tin minerals, stability constant.

Introduction

THE corrosion of tin in saline environments usually results in the formation of stannous and stannic oxides, although chloride-containing tin phases have been reported on numerous occasions. Abhurite, originally found in surface blisters on tin ingots recovered from a wreck in the Red Sea (Matzko *et al.*, 1985), is one of the latter.

Numerous preparations of tin hydroxychloride have appeared, dating back some decades (Ditte, 1882; Carson, 1919). A number of stoichiometries, including $\text{SnCl}_2 \cdot 4\text{SnO} \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot \text{SnO} \cdot 4\text{H}_2\text{O}$, $2\text{SnCl}_2 \cdot 3\text{SnO} \cdot 5\text{H}_2\text{O}$, $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$ and $2\text{SnCl}_2 \cdot 7\text{Sn}(\text{OH})_2$, were reported and Britton (1925) found a range of compositions from $\text{Sn}_{0.5}(\text{OH})_{0.76} \cdot \text{Sn}_{0.5}\text{Cl}_{1.33}$ at pH 1.9 to $\text{Sn}_{0.5}(\text{OH})_{1.86} \cdot \text{Sn}_{0.5}\text{Cl}_{0.14}$ at pH 7. More recent investigations have pointed to the fact that only one basic tin(II) chloride exists and that the phases isolated by previous workers are mixtures of basic tin chloride and hydrous tin oxide. Randall and Murkami (1930) prepared 'SnCl(OH) (s)' under conditions similar to those specified by previous investigators, although the degree of hydration of the phase was uncertain.

Donaldson *et al.* (1963) prepared a salt of composition $\text{Sn}_4\text{Cl}_2(\text{OH})_6$; the synthesis has been reported to yield other substances. Hayek (1933) formulated the compound he obtained as $\text{Sn}(\text{OH})_2 \cdot \text{SnCl}_2$, while Randall and Murkami (1930) used the formula $\text{SnOHCl} \cdot \text{H}_2\text{O}$ to derive the free energy of formation of the salt. Ichiba and Takeshita (1984) suggested that the true composition was $\text{Sn}_3\text{Cl}_2(\text{OH})_2\text{O}$ and this is the stoichiometry which has been attributed to abhurite.

However, von Schnering *et al.* (1981) have determined the single-crystal X-ray structure of the basic tin(II) chloride, and showed that the correct formula is $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$. Nevertheless, this has been overlooked by recent investigators. Attention is here drawn to the fact that abhurite and the synthetic phase $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ are identical. Through repeat synthesis and comparison of physical and analytical data and results, it was demonstrated that all preparations of the basic tin(II) chloride result in the above compound. Discrepancies in previous formulations may be the result of the presence of tin(II) oxychlorides and adsorbed water; the latter is well-known for hydrous Sn(II) oxides. If the product is for example dried at temperatures above 368 K, dehydration to $\text{Sn}_9\text{Cl}_4\text{O}_7$ occurs, with subsequent decomposition to other tin(II) oxychlorides. Hydrolysis of stannous ion in

* Present address: Department of Chemistry, University of Western Sydney Nepean, P.O. Box 10, Kingswood, NSW 2747, Australia.

aqueous, chloride-containing solutions gives abhurite as the sole oxyhydroxide at low pH. While a number of stoichiometries have been proposed for such hydrolysis products in the past, it is now clear that solids obtained were almost invariably mixtures of abhurite and an oxychloride formed as an artefact of the synthetic and isolation procedures adopted.

Abhurite was originally described as an alteration product of tin ingots recovered from a shipwreck in the Red Sea (Matzko *et al.*, 1985). Chemical analysis gave a stoichiometry of $\text{Sn}_3\text{Cl}_2(\text{OH})_2\text{O}$. The mineral was shown to be rhombohedral, space group $R\bar{3}m$, $R\bar{3}m$ or $R32$, with $a = 10.0175(3)$, $c = 44.014(2)\text{\AA}$, $Z = 21$ (for the formula given above), $D_c = 4.35$ and $D_m = 4.29\text{ g cm}^{-3}$. $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ is rhombohedral, space group $R32$, with $a = 10.018(1)$, $c = 44.030(2)\text{\AA}$, $Z = 3$, $D_c = 4.417(1)$ and $D_m = 4.42\text{ g cm}^{-3}$. These crystallographic data are virtually sufficient to establish the identities of the natural and synthetic phases. Extensive listings of powder X-ray diffraction data provided in the two papers further show that abhurite has the indicated formula.

It would be a difficult task to derive the stoichiometry of abhurite by chemical analysis alone. Nonetheless, the determination of the single-crystal X-ray structure puts the composition of abhurite beyond doubt. It is interesting to note that $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ can also be shown to be the correct composition of the basic tin chloride made by Carson (1919) through the decomposition of SnCl_2 in dilute $\text{KOH}(\text{aq})$. Comparison of the reported analytical data with that for $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$ indicates this is the correct formula, rather than $3\text{SnCl}_2 \cdot 5\text{SnO} \cdot 3\text{H}_2\text{O}$, as originally suggested.

For some time we have been interested in describing the corrosion mineralogy of archaeological metal artefacts. The aim has been to provide a chemical model for the corrosion products and to use it to develop methods for consolidation and restoration. Since tins, leads and pewters are frequently recovered from the archaeological content, these elements are of particular interest.

A number of oxides and oxyhydroxides of Sn(II) and Sn(IV) have been reported as corrosion products of archaeological tin, principally from non-saline environments. However, abhurite appears to be a common corrosion product of archaeological tin recovered from sea water. We have thus determined its stability constant at 298.2 K in order to assess its likely mode of formation in the supergene environment in relation to other Sn(II,IV) oxides and oxyhydroxides. The results of the study are reported below.

Experimental

All solutions were prepared from freshly boiled, degassed water. To prevent air oxidation of stannous solutions, all reactions were carried out under dinitrogen. N_2 (g) was purified by passing it through Fieser's solution, then conc. H_2SO_4 , conc. aqueous NaOH, saturated aqueous lead acetate and NaCl (1M), in turn.

Titration of SnCl_2 with base. Solutions of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ are prepared with difficulty in conc. aqueous HCl and thus anhydrous SnCl_2 was prepared for subsequent solution experiments, as follows. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (10.0 g) was dissolved in HCl (11.8 M, 10 cm^3) and H_2O (5 cm^3). The reaction vessel was fitted with a condenser and tin metal added to the mixture, which was boiled until a clear supernatant was obtained. The mixture was cooled to c. 80 °C and aqueous ammonia (2M) added dropwise to a pH of approximately 0.8. The resulting mixture was filtered hot and the filtrate cooled under dinitrogen. Long needles of white, anhydrous SnCl_2 were deposited and these were collected at the pump on a sintered glass frit washed with small amounts of alcohol and diethyl ether, and dried *in vacuo* over silica gel at room temperature, m.p. 246 °C (lit. 246 °C: Lide, 1990).

In a typical titration, SnCl_2 (0.207 g, 1.05 mmol) was dissolved in oxygen-free H_2O (50 cm^3). After about 5 minutes the solution became cloudy and had a pH of 2.41, but the cloudiness did not increase during one hour. Addition of conc. HCl (0.1 cm^3) to the solution caused the precipitate to dissolve. The pH of the clear solution was 1.28. Aqueous, oxygen-free NaOH (83 mmol dm^{-3}) was added slowly to the acidified tin(II) chloride solution, resulting in a gradual increase of pH. After the addition of 12.5 cm^3 of solution, the pH had increased to 1.44, but no precipitate was observed. Between pH 1.44 and 2.10 (27 cm^3 titre), a fine white precipitate formed on each addition of base and redissolved on stirring. The precipitate persisted at higher pH values. No clear endpoints were observed up to a titre of 52 cm^3 (pH 9.93) but after two weeks, brown-black SnO had formed in the more basic solutions. This transformation is still faster when the white solids are left in contact with the solution under yet more basic conditions. Titrations were also performed with varying chloride ion concentrations (0.2 to 2 M NaCl), and at different temperatures (0 to 50 °C). In all cases the titrations mirrored the above observations.

To determine the composition of the precipitates produced in aqueous solutions of SnCl_2 at various pH values, differing amounts of NaOH

(0.11 M) were added slowly to oxygen-free solutions of SnCl_2 (0.02 M, 100 cm^3). These solutions were equilibrated at 25 °C for one hour. Solution pH was measured *in situ*, and the white solids collected at the pump on Whatman GF/F fibreglass filter paper. The solids were washed with a small amount of water and acetone and dried *in vacuo* over silica gel at room temperature. Compounds isolated at various pH values and identified as mentioned immediately below are shown in Table 1.

Synthesis of abhurite. Tin(II) hydroxychloride was synthesised following two reported methods (Donaldson *et al.*, 1963; Ichiba and Takeshita, 1984). During the preparations, care was taken neither to boil the solutions nor subject them to prolonged heating. Slow precipitation results in the formation of crystalline solids, but fast precipitation gives poorly crystalline solids which are difficult to identify.

The resulting white, crystalline solids were identified as abhurite by comparison of their infrared spectra (KBr pellet) and powder X-ray diffraction patterns (Debye-Scherrer camera, $\text{Cu-K}\alpha$ radiation) with data available in the literature (von Schnering *et al.*, 1981; Matzko *et al.*, 1985). The solids produced from numerous repeat preparations were identical.

Stability constant determination for abhurite. A typical experiment is described. Tin(II) chloride dihydrate (2.4000 g) was dissolved in concentrated hydrochloric acid (3 cm^3). To the solution was added tin metal (0.0250 g); the mixture cleared upon warming. H_2O (10 cm^3) was pipetted into the cooled solution which was thermostatted in a water bath at 25 °C. The pH of the acidified stannous chloride solution was then raised by the addition of aqueous NaHCO_3 (0.091 M). Care was taken to maintain the pH below 2 during the addition. The mixture became cloudy after the addition of the aqueous NaHCO_3 (48.0 to 50.0 cm^3) and a milky-white precipitate formed with time.

The reaction vessel was sealed under dinitrogen and wrapped in aluminium foil. During the stability constant measurements, it was necessary

to protect the solutions from light. Under certain circumstances, photochemical decompositions, first noted by Tobias (1958), contaminate the product with yellow tin(IV) oxide. The sealed, protected flask was thermostatted in a water bath at 25 ± 0.3 °C, using a circulating control unit, for one week. Preliminary measurements showed that equilibration of the solid phase with the supernatant is achieved well within this time. After 7 days, the pH of the solution was measured *in situ* using a Radiometer PHM 85 precision pH meter fitted with a Radiometer GK 2401C combination electrode. The solution was suction filtered through Whatman GF/F fibreglass filter paper. The filtrate was stored under dinitrogen and the solid was washed with water and acetone and dried *in vacuo* over silica gel. No traces of yellow tin(IV) oxide were observed and abhurite was identified as the sole solid phase by IR and powder X-ray methods.

The total tin content of the filtrate was measured by AAS using a Varian 275 Series atomic absorption spectrophotometer. Total chloride ion concentrations were determined gravimetrically. Total sodium ion content was calculated from a knowledge of concentrations and titres of the starting materials. Results for these determinations and those for similar repeat experiments are listed in Table 2.

Concentrations of free ions in solution were calculated using the computer program COMICS (Perrin and Sayce, 1967). Stability constants used for hydrolysed species of Sn^{2+} at 25 °C are summarised in Table 3, together with values for other species taken into account. Calculated concentrations and other derived data also are listed in Table 2. Free stannous and chloride ion concentrations were corrected for ionic strength using the Davies modification of the Debye-Hückel limiting law.

Results and discussion

Titration of Sn(II) with base. In contrast to the case of Pb(II), titration of an oxygen-free

TABLE 1
Analytical results for the precipitates formed after the addition of oxygen-free aqueous NaOH (0.11 M) to an acidified solution of SnCl_2 (0.02 M, 100 cm^3).

pH Range	Vol. NaOH (cm^3)	Precipitate
< 2.18	< 3.0	none
2.40 - 3.20	4.0 - 15.0	abhurite
3.50 - 5.48	19.0 - 28.0	abhurite + hydroromarchite
> 5.58	> 29.0	hydroromarchite

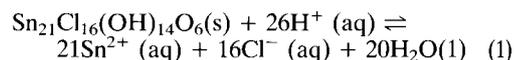
aqueous solution of tin(II) chloride with oxygen-free aqueous sodium hydroxide shows no distinct end-points. Neutralisation of an acidic solution of tin(II) chloride (for example 0.02 M) with NaOH(aq) (for example 0.11 M) results in the precipitation of abhurite between pH 2.40 and 3.20. At all temperatures and chloride concentrations studied, abhurite is the first phase to crystallise from solution. As the chloride ion concentration increases, the pH at which abhurite will form falls, as expected; it crystallises at about pH 1.3 in solutions containing about 0.8 M chloride. As the concentration of OH⁻ increases, the chloride ions of the complex species in solution are gradually replaced, and Sn₆O₄(OH)₄ precipitates above a pH of about 3.20. This phase dominates about pH 5.58.

The extent of this and related phases is uncertain, a fact reflected in the formulation of a number of compounds precipitated from tin(II) solutions, including those containing chloride. Proposed compositions for hydrous tin oxides range from Sn(OH)₂, synthesised by an anhydrous organometallic method (Honnick and Zuckerman, 1976), to 5SnO.2H₂O (Donaldson and Moser, 1961). Donaldson (1961) has prepared crystalline hydrous tin oxides, which have had the formulae 5SnO.2H₂O and, latterly, 3SnO.H₂O ascribed to them (Howie and Moser, 1973). The

discrepancy in composition (one mol H₂O per fifteen mol SnO) is attributable to the presence of chemisorbed water on the surface of the microcrystalline solid (as verified by IR measurements). The true formula of the oxide, which corresponds to the mineral hydroromarchite, is, by comparison of powder X-ray data, Sn₆O₄(OH)₄ (Howie and Moser, 1973).

Solid phases produced in the intermediate pH range are mixtures of the tin oxyhydroxide and tin hydroxychloride, with the ratio of basic tin(II) chloride to tin(II) oxyhydroxide decreasing as the pH of the solution increases. As indicated previously, an increase in chloride concentration extends the range of stability of abhurite, and in certain solutions it persists to pH 6 (Donaldson *et al.*, 1963). This may have great significance with respect to the natural occurrence of abhurite.

The stability of abhurite and its mineralogical relationships. A stability constant for abhurite (K_{H+}) has been derived in terms of equation (1), using the data of Table 2. Log K_{H+}(298.2 K)



is equal to -31.9(7) and this value in turn leads to one for ΔfG° (abhurite, s, 298.2 K), of -7602.2(7.4) kJ mol⁻¹, using corresponding values for component ions and water taken from

TABLE 2
Experimental and derived results for dissolution of abhurite at 298.2K.

[Sn ²⁺] ^a /10 ⁻¹	[Cl ⁻] ^a /10 ⁻¹	[Na ⁺] ^a /10 ⁻¹	pH	I ^b
1.517	9.088	5.437	1.184	0.39
1.462	9.043	5.437	1.199	0.39
1.335	8.945	5.461	1.281	0.39
1.264	8.896	5.461	1.281	0.39
1.264	8.829	5.484	1.305	0.39
1.011	8.705	5.484	1.330	0.40
1.036	8.690	5.484	1.350	0.40

[Sn ²⁺] ^b /10 ⁻³	[Cl ⁻] ^b /10 ⁻¹	[Na ⁺] ^b /10 ⁻¹	γ^{\pm}	γ^+	log K _{H+}
8.471	4.163	3.301	0.292	0.735	-32.19
8.037	4.198	3.290	0.292	0.735	-32.22
7.061	4.286	3.263	0.292	0.735	-31.12
6.530	4.341	3.247	0.292	0.735	-31.75
6.681	4.294	3.261	0.292	0.735	-31.02
4.812	4.533	3.190	0.291	0.735	-32.98
5.020	4.490	3.203	0.291	0.735	-32.15

^aTotal analytical concentrations at equilibrium.

^bCalculated concentrations at equilibrium using the COMICS program. All concentrations are in units of mol dm⁻³.

TABLE 3
Summary of Sn^{2+} hydrolysis at 25°C (Baes and Mesmer, 1976);
 $\log Q_{xy} = \log K_{xy} + a \frac{1}{I^2} / (1 + I^2) + bmx$.

Species	$\log K_{xy}$	a	b	σ ($\log Q_{xy}$)
SnOH_4	-3.40	-1.022	0.06	± 0.4
$\text{Sn}(\text{OH})_2$	-7.06	-1.022	0.0	
$\text{Sn}(\text{OH})_3^-$	-16.61	0	-0.11	± 0.1
$\text{Sn}_2(\text{OH})_2^{2+}$	-4.77	-1.022	0.3	± 0.4
$\text{Sn}_3(\text{OH})_4^{2+}$	-6.88	-2.044	0.45	± 0.1

Formation constants for other species taken into account in the calculations; T = 25°C, I = 0.4
M; values extrapolated from data reported by Smith and Martell (1976).

Species	$\log \beta$
NaOH	-0.20
NaCl	0.19
SnCl^+	1.06
SnCl_2	1.72
SnCl_3^-	1.46
SnCl_4^{2-}	1.50

the compilations of Robie *et al.* (1978) and Krauskopf (1982). Errors associated with value of the free energy of formation of the aqueous $\text{Sn}(\text{II})$ ion have not been included in the above calculation. The result is clearly more accurate than the former value reported (Randell and Murakami, 1930) for the basic tin(II) chloride, ' $\text{Sn}(\text{OH})\text{Cl}$ ', a formula which is incorrect (*vide supra*). These new quantities have been used to construct an equilibrium model for the formation of the basic tin(II) chloride with respect to tin oxides and oxyhydroxides in order to elucidate the mineralogical relationships of tin corrosion.

Free energies of formation at 298 K of $\text{Sn}(\text{II})$ and $\text{Sn}(\text{IV})$ salts romarchite, cassiterite and SnCl_2 are -259.94 , -519.90 and -282.00 kJ mol^{-1} , respectively (Robie *et al.*, 1978; Krauskopf, 1982; Barner and Scheuerman, 1978, respectively). All other thermodynamic data necessary for the calculations were taken from the usual source (Robie *et al.*, 1978). Stability field diagrams for the $\text{SnO-HCl-H}_2\text{O}$ system at 298.2 K are shown in Fig. 1. These illustrate the relationship between abhurite and romarchite. Under natural saline conditions, for example in seawater with chloride concentrations about 0.5 M and pH

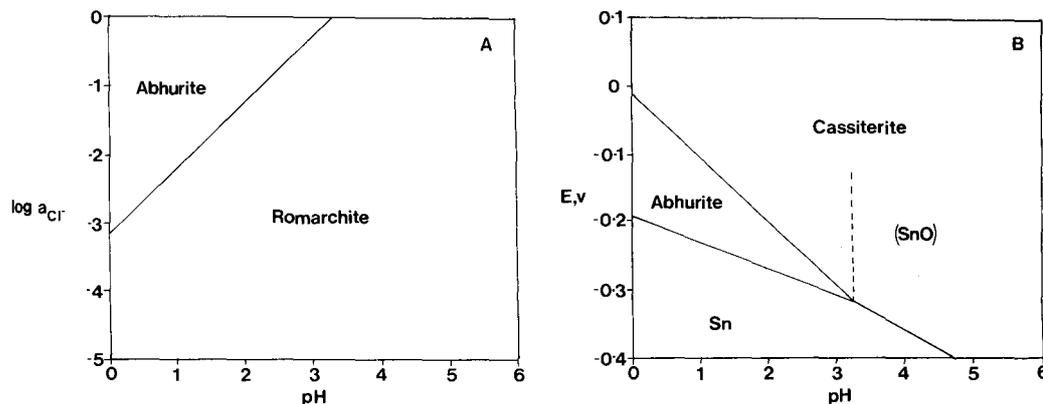


FIG. 1. (a) Stability field diagram for the $\text{SnO-HCl-H}_2\text{O}$ system at 298.2 K and 10^5 Pa; (b) Potential-pH diagram for the $\text{Sn-H}_2\text{O-HCl}$ system at $a_{\text{Cl}^-} = 1$. The limit of stability of abhurite with respect to SnO is shown by the dashed line.

about 8, romarchite (or its hydrated analogue hydroromarchite) is the stable phase. Romarchite is probably the thermodynamically stable phase with respect to hydroromarchite, but this is not completely certain. In nature, and at neutral pH, both phases are found together (Organ and Mandarino, 1971), in particular on corroding tin objects recovered from saline and similar conditions.

Increasing salinity and reduction in pH gives rise to conditions which favour the formation of abhurite. Abhurite was first observed on the surface of corroding tin ingots in surface blisters where the pH of the encapsulated solution was approximately 1. Such high acidity would not be unexpected in an undisturbed micro-environment, and results from the hydrolysis of tin ions. Basic tin(II) salts on the surface of corroding tin objects have been reported on a number of occasions. Some of these are undoubtedly abhurite and its occurrence may be more frequent than might at first be thought. It can persist, together with hydroromarchite, up to pH 6 under highly saline conditions.

The compound SnCl_2 does not appear on the stability field diagram; very high chloride concentrations and extremely acidic conditions are required for its stabilisation. Thus reports of SnCl_2 on corroded tin objects recovered from sea water are probably spurious, with the 'chloride-containing' salt described more likely being abhurite.

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