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## A critical review of thermodynamic data for inorganic tin species

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**Abstract**—The accuracy of published inorganic tin thermodynamic data was evaluated to obtain a reliable basis for modeling Sn migration in a deep repository of radioactive waste. Hydrolysis, complexation with halide ions or other inorganic compounds, and precipitation reactions of Sn(II) and Sn(IV) were studied. The Guggenheim-Scatchard Specific Interaction Theory was used to correct equilibrium constant to zero ionic strength.

Tin(II) can be hydrolysed into  $\text{SnOH}^+$ ,  $\text{Sn(OH)}_2^0$  and  $\text{Sn(OH)}_3^-$  at low concentration. For higher tin levels, the  $\text{Sn}_2(\text{OH})_2^{2+}$  and  $\text{Sn(OH)}_4^{2+}$  polynuclear species are predominant. Stability constants of these equilibria at the standard state were evaluated from data available in the literature and recommended values are proposed. Complexation reactions between tin(II) and halide ions are well known, but the complex species formed are only present in solution when halide concentration is  $> 10^{-3} \text{ mol L}^{-1}$  and at pH values  $< 4$ . In the presence of sulphides, selenides, or tellurides, the stannous ions form very stable solid phases. Because of the very low solubility of  $\text{SnO}_2(\text{s})$ , little information is available in the literature about Sn(IV) hydrolysis, complexation, or precipitation reactions. *Copyright © 2001 Elsevier Science Ltd*

### 1. INTRODUCTION

Understanding and modeling the chemical behaviour of the radionuclides in a deep repository for nuclear waste is of paramount importance for the protection of the environment. Multiple barriers will protect humans and the natural environment from radioactive and chemically toxic contaminants in the radioactive waste (De Marsily, 1997). These barriers are the container, the waste form, the buffer, and the geosphere (rock, sediments overlying the rock) (De Marsily, 1997; Allègre, 1997; Bérest, 1991). The only possible transport medium is flowing groundwater, and to estimate the quantities of waste that can be transported via the aqueous phase, it is necessary to be capable of predicting the reactions that are likely to occur in the complex repository environment (De Marsily, 1997; Chopin and Wong, 1996; Gascoyne, 1996). An accurate understanding of the relative stability of the compounds and complexes that may form under the relevant conditions is essential (Guillaumont, 1997). This information is generally provided by speciation calculations using chemical thermodynamic data.

Among the different radionuclides, tin is of interest because of the presence in radioactive waste of one of its isotopes,  $^{126}\text{Sn}$ , coming from fission; its half-life value is close to  $10^5$  years (Schapira, 1997). Inorganic tin has four oxidation states:  $-II$ ,  $0$ ,  $+II$ , and  $+IV$ . Tin can also exist as organic compounds (e.g., tributyltin, triphenyltin) that are commonly used in various industrial sectors because of their biocide properties (Blunden and Chapman, 1986; Evans and Karpel, 1985). While the chemistry of organotin compounds has been studied extensively because of their high toxicity toward numerous living organisms, less work has been achieved on the inorganic forms that are generally considered to be nonhazardous (Evans and

Karpel, 1985; Alzieu, 1989). However, the presence of  $^{126}\text{Sn}$  in the radioactive waste requires a better knowledge of the chemistry of inorganic tin to understand and model its behaviour after disposal in a deep repository. The chemical forms of dissolved inorganic tin are still not well known. Depending on the conditions prevailing in the medium, they may correspond to Sn(II) or Sn(IV) (Alzieu, 1989). Both Sn(IV) and Sn(II) tend to hydrolyse in solution to form different aqueous species. In natural waters, the following complexes have been reported:  $\text{SnO(OH)}_3^-$  at  $\text{pH} \geq 8$  and  $\text{SnO(OH)}_2^0$  at  $\text{pH} < 7$  for Sn(IV) (Benabdallah 1987) and  $\text{Sn(OH)}_2^0$  for Sn(II) in natural waters pH range (Pettine et al. 1981). Sn(II) seems to be a reactive form toward different organic and inorganic compounds and can be found under the form of complex species (e.g., associated with chlorides, sulphates, phosphates, and carbonates) (Edwards, 1995) or solid phases (e.g., tin(II) oxide, tin(II) sulphide, or tin incorporated with a number of other metals in more complex sulphides such as  $\text{Cu}_2\text{FeSnS}_4(\text{s})$  (Millman, 1957; Edwards et al., 1992, 1996). Divalent tin species also can be adsorbed onto different solid phases, namely, clays (Ticknor et al., 1996; Petridis and Bakas, 1997), manganese dioxides (Rapsomanikis and Craig, 1985), and iron oxides (Ticknor et al., 1996). However, the sorption mechanism is not well understood because of the easy oxidation of Sn(II) into Sn(IV) and the complexity of the tin(II) hydrolysis reactions (Ticknor et al., 1996; Petridis and Bakas, 1997). The mobility of Sn(IV) is considered to be very low because of the high stability of tin(IV) oxide ( $\text{SnO}_2(\text{s})$ ) (Benabdallah, 1987; Edwards, 1995; Hamaguchi et al., 1964). Methylating agents can have also an important role in the behaviour of Sn(II) and Sn(IV) in the environment with the formation of methylated complexes by abiotic or biotic activities (Rapsomanikis and Craig, 1985; Ashby and Craig, 1988; Cooney, 1988). According to the tin oxidation state, mono-, di-, tri-, and tetramethyltin can be formed (Alzieu, 1989; Errecalde, 1994).

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There is a lack of information on the geochemistry of inorganic tin, and the published studies are not always in agreement about the hydrolysed species formed, the stabilities of tin(II) and tin(IV) oxides, the redox reactions that occur between the different tin oxidation states, the complex species, and the solid phases formed with anionic compounds. A critical and comprehensive review of the available literature is thus necessary to establish a reliable thermochemical database that fulfils the requirements of a proper modeling of the behaviour of tin in the environment. Although extensive databases are available for most major elements, less work has been performed for trace elements.

The objective of this paper is, therefore, to acquire a better knowledge of inorganic tin chemistry and simultaneously to evaluate the accuracy of the inorganic tin thermodynamic constants of the literature and to propose data at the standard state.

## 2. METHODS

Only standard state constant values (25°C, 1 bar pressure, and zero ionic strength) can be used when modeling tin migration, because the temperature, pressure, and ionic strength conditions depend on the real system considered. In most published studies, equilibrium constants were determined using the standard temperature of 25°C, but some are only available for temperatures of 20 or 22°C. A correction to the standard temperature of 25°C needs to have enthalpies of reactions that are not available in the literature for these equilibria. This correction also can be performed with constant values at different temperature values. However, in most cases sets of reliable data are not available at different temperature values, making impossible such a calculation. As the variation in values over this temperature range is minor, it was assumed that the difference between constants determined in this temperature range is negligible in regard to the calculations done in this study. However, in all the tables listing tin equilibrium constants, values determined at a temperature different from 25°C are indicated with an asterisk, and the temperature assigned is given in table footnotes. If no asterisk is indicated, equilibrium constants correspond to a temperature of 25°C.

The major source of uncertainty is the method used for correcting the experimental data to an idealised standard state of infinite dilution. Indeed, most experimental measurements of formation constants have been done at high ionic strength, whereas in most environmental situations, the ionic strength of the system would be rather low. Being able to verify the method used for this kind of correction is of utmost importance for obtaining an accurate prediction of the chemical behaviour of tin by means of thermodynamic models. Equilibrium constants can be corrected to zero ionic strength by using the Davies (Davies, 1962) or the Debye-Hückel (Debye and Hückel, 1923) expressions. However, these are limited to low ionic strength, below ~0.02 and 0.05 mol kg<sub>H<sub>2</sub>O</sub><sup>-1</sup>, respectively. At high ionic strength, specific ion interaction models are needed such as the Pitzer theory (Pitzer, 1973, 1991) and the Guggenheim-Scatchard Specific Interaction Theory (SIT) (Scatchard, 1936; Guggenheim, 1966; Ciavatta, 1980). The Pitzer theory is the most accurate method but extensive individual parametrisation is required to calculate activity coefficients. SIT is based on the same principle and uses only one ion interaction parameter in addition to the Debye-Hückel term; thus it involves fewer calculations. A good description of interactions was obtained for ionic strengths up to 3.5 mol kg<sub>H<sub>2</sub>O</sub><sup>-1</sup> for some pure electrolytes (Ciavatta, 1980).

In this study, therefore, when consistent data are available directly from the literature at zero ionic strength, the value we recommend is associated with an uncertainty ( $\sigma$ ) representing the 95% level of confidence as recommended by Grenthe et al. (1992). If several different constants are available for series of ionic strengths in one ionic medium, the recommended values are calculated by applying SIT to the original data sets. The SIT methodology is summarised as follows (Grenthe et al., 1992): At the molal scale, the equation for the activity coefficient ( $\gamma_M$ ) of an ion M in the 1:1 NX electrolyte solution of ionic strength  $I_m$  is

$$\log \gamma_M = -z_M^2 D + \sum_X \varepsilon_{(M,X)} m_X \quad \text{where } D = \frac{A \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (1)$$

where

$z_M$  is the charge of the ion M, and A has a constant value of 0.5050 and 0.5091 at 20 and 25°C, respectively.  $I_m$  is the ionic strength (mol kg<sub>H<sub>2</sub>O</sub><sup>-1</sup>),  $m_X$  is the molality of the ion X, and  $\varepsilon_{(M,X)}$  is the interaction parameter between the ions M and X. This last parameter only allows a description of specific short-range interactions. Consequently, the SIT methodology supposes that the interaction parameter is small for ions of the same charge, since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species.

## 3. RESULTS AND DISCUSSION

### 3.1. Tin Hydrolysis Reactions and Formation of Solid Tin Oxides

Stability constants reported in the literature for these reactions, along with the method of determination, the corresponding ionic media, and ionic strengths, are given in Table 1.

Potentiometric titrations have been commonly used to determine the Sn(II) hydrolysis constants. These titrations are always performed under nitrogen atmosphere to avoid the oxidation of Sn(II) into Sn(IV) (Gorman, 1939; Vanderzee and Rhodes, 1952; Vanderzee, 1952; Tobias, 1958; Salvatore et al., 1997; Djurdjevic et al., 1995; Gobom, 1976; Dokic et al., 1991). Usually two measurement cells are used where the equilibrium  $H^+$  and  $Sn^{2+}$  concentrations are determined with a glass electrode and a tin amalgam electrode in each compartment (Tobias, 1958; Salvatore et al., 1997; Gobom, 1976). The analytic results are modeled by using statistical calculations to identify the complex species formed. Usually several stoichiometries are taken into account and those resulting in an adequate fit with experimental values are retained. To understand the behaviour of inorganic tin in natural waters, Pettine et al. (1981) and Macchi and Pettine (1980) have studied the Sn(II) hydrolysis reactions by using differential pulse anodic stripping voltammetry (DPASV). Because of the high sensitivity of the DPASV method, it is possible to work with very low levels of tin.

#### 3.1.1. Sn(II) hydrolysis reactions

As shown in Table 1, there is a discrepancy among authors about the different Sn(II) hydrolytic complexes formed. The  $SnOH^+$  species were identified in numerous studies (Pettine et al., 1981; Gorman, 1939; Vanderzee and Rhodes, 1952; Vanderzee, 1952; Tobias, 1958; Salvatore et al., 1997; Djurdjevic et al., 1995; Gobom, 1976; Garret and Heiks, 1941), but a lot of the studies using potentiometric measurements pointed out that the principal hydrolysis product formed is  $Sn_3(OH)_4^{2+}$  (Tobias, 1958; Salvatore, et al., 1997; Djurdjevic et al., 1995; Gobom, 1976; Dokic et al., 1991). While  $Sn_2(OH)_2^{2+}$  was also identified by Tobias (1958) and Dokic et al. (1991), other studies rejected the formation of this binuclear complex (Salvatore et al., 1997; Djurdjevic et al., 1995; Gobom, 1976). With a more sophisticated mathematical treatment of Tobias (1958) data, Chia-ch'ang and Yu-ming (1964) confirmed the presence of the trimer and dimer, showed the existence of the additional species  $Sn_2(OH)_3^+$  but rejected the formation of  $SnOH^+$ . All the polynuclear complexes were identified by using high tin(II)

Table 1. Inorganic tin hydrolysis equilibrium constants and solubility products of solid tin(II) and tin(IV) oxides

Chemical equilibrium	Method <sup>a</sup>	Medium	I (mol L <sup>-1</sup> )	-log K	Source
<i>Tin Hydrolysis</i>					
<i>Sn(II)</i>					
$\text{Sn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{SnOH}^+ + \text{H}^+$	pot(gl)	NaClO <sub>4</sub> dil	0 <sub>corr</sub>	1.70	(Gorman, 1939)
	sol	var	0 <sub>corr</sub>	2.07	(Garret and Heiks, 1941)
	pot	NaClO <sub>4</sub>	3	1.70 ± 0.08	(Vanderzee and Rhodes, 1952)
	pot(gl)	NaNO <sub>3</sub>	2	3.2	(Sillén, 1964)
	pot(gl,Sn)	NaClO <sub>4</sub>	3	3.92 ± 0.15	(Tobias, 1958)
	pot(gl,Sn)	NaClO <sub>4</sub>	3	3.77 ± 0.05	(Salvatore et al., 1997)
	pot(gl)	NaCl	3	2.18	(Djurdjevic et al., 1995)
	pot(gl,Sn)	NaClO <sub>4</sub>	3	3.70 ± 0.02	(Gobom, 1976)
	DPASV	NaNO <sub>3</sub>	0.1	4.1 ± 0.2*	(Pettine et al., 1981)
	DPASV	NaNO <sub>3</sub>	0.5	3.8 ± 0.2*	(Pettine et al., 1981)
	DPASV	NaNO <sub>3</sub>	1	4.1 ± 0.2*	(Pettine et al., 1981)
	DPASV	NaCl	0.5	3.1 ± 0.2*	(Pettine et al., 1981)
	<i>Recommended value</i>			$-\log^{\text{m}}K^{\circ} = 3.8 \pm 0.2^*$	( <i>this work</i> )
	$\text{Sn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn(OH)}_2^0 + 2\text{H}^+$	Sol	var	0 <sub>corr</sub>	7.06
DPASV		NaNO <sub>3</sub>	0.1	7.9 ± 0.2*	(Pettine et al., 1981)
DPASV		NaNO <sub>3</sub>	0.5	7.9 ± 0.2*	(Pettine et al., 1981)
DPASV		NaNO <sub>3</sub>	1	7.8 ± 0.2*	(Pettine et al., 1981)
DPASV		NaCl	0.5	8.2 ± 0.2*	(Pettine et al., 1981)
<i>Recommended value</i>				$-\log^{\text{m}}K^{\circ} = 7.8 \pm 0.2^*$	( <i>this work</i> )
$\text{Sn}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Sn(OH)}_3^- + 3\text{H}^+$	DPASV	NaNO <sub>3</sub>	0.1	17.5 ± 0.2*	(Pettine et al. 1981)
	DPASV	NaNO <sub>3</sub>	0.5	17.7 ± 0.2*	(Pettine et al., 1981)
	DPASV	NaNO <sub>3</sub>	1	17.6 ± 0.2*	(Pettine et al., 1981)
	DPASV	NaCl	0.5	17.8 ± 0.2*	(Pettine et al., 1981)
	<i>Recommended value</i>			$-\log^{\text{m}}K^{\circ} = 17.5 \pm 0.2^*$	( <i>this work</i> )
$2\text{Sn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn}_2(\text{OH})_2^{2+} + 2\text{H}^+$	pot(H)	Sn(ClO <sub>4</sub> ) <sub>2</sub>	dil	2.74	(Sillén, 1964)
	pot(H)	SnCl <sub>2</sub>	dil	2.70	(Sillén, 1964)
	pot(H)	NaClO <sub>4</sub>	0.5	2.96	(Sillén, 1964)
	pot(H)	KCl	0.5	4.10	(Sillén, 1964)
	pot(H)	KBr	0.5	3.24	(Sillén, 1964)
	pot(gl,Sn)	NaClO <sub>4</sub>	3	4.45 ± 0.15	(Tobias, 1958)
	calc <sup>b</sup>	NaClO <sub>4</sub>	3	4.58 ± 0.41	(Chia-ch'ang and Yu-ming, 1964)
	pot(gl)	NaClO <sub>4</sub>	0.5	4.59 ± 0.08	(Dokic et al., 1991)
	<i>Recommended value</i>			$-\log^{\text{m}}K^{\circ} = 2.4 \pm 0.3$	( <i>this work</i> )
	calc <sup>b</sup>	NaClO <sub>4</sub>	3	6.66 ± 0.18	(Chia-ch'ang and Yu-ming, 1964)
	$3\text{Sn}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Sn}_3(\text{OH})_4^{2+} + 4\text{H}^+$	pot	NaClO <sub>4</sub>	3	6.77 ± 0.03
calc <sup>b</sup>		NaClO <sub>4</sub>	3	6.85 ± 0.04	(Chia-ch'ang and Yu-ming, 1964)
pot(gl,Sn)		NaClO <sub>4</sub>	3	6.87 ± 0.09	(Salvatore et al., 1997)
pot(gl)		NaCl	3	2.70	(Djurdjevic et al., 1995)
pot(gl,Sn)		NaClO <sub>4</sub>	3	6.81 ± 0.03	(Gobom, 1976)
pot(gl)		NaClO <sub>4</sub>	0.5	6.30 ± 0.10	(Dokic et al., 1991)
<i>Recommended value</i>				$-\log^{\text{m}}K^{\circ} = 5.6 \pm 0.1$	( <i>this work</i> )
sol		NaOH	0	11.11	(Barsukov and Klintsova, 1970)
$\Delta G^{\text{c}}$			0	23.47	(Pourbaix, 1964)
<i>Precipitation Reactions</i>					
<i>Sn(II)</i>					
$\text{Sn(OH)}_2(\text{s}) \rightleftharpoons \text{Sn}^{2+} + 2\text{OH}^-$	sol	var	0 <sub>corr</sub>	25.80	(Garret and Heiks, 1941)
	$\Delta G^{\text{c}}$		0	26.5	(Pourbaix, 1964)
$\text{SnO}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Sn}^{2+} + 2\text{OH}^-$	sol		0 <sub>corr</sub>	26.24	(Garret and Heiks, 1941)
	pot(H)	Sn(ClO <sub>4</sub> ) <sub>2</sub>	dil	25.10	(Sillén, 1964)
	pot(H)	SnCl <sub>2</sub>	dil	25.47	(Sillén, 1964)
	pot(H)	NaClO <sub>4</sub>	0.5	24.97	(Sillén, 1964)
	pot(H)	KCl	0.5	25.50	(Sillén, 1964)
	pot(H)	KBr	0.5	25.70	(Sillén, 1964)
	pol,pH		0 <sub>corr</sub>	28.1**	(Sillén, 1964)
	lit		0	26.2	(Sillén, 1964)
	pot(gl)	NaCl	3	27.9 ± 0.1	(Djurdjevic et al., 1995)
	$\Delta G^{\text{c}}$		0	26.93	(Pourbaix, 1964)
	<i>Sn(IV)</i>				
$\text{Sn(OH)}_4(\text{s}) \rightleftharpoons \text{Sn}^{4+} + 4\text{OH}^-$	$\Delta G^{\text{c}}$		0	57.02	(Pourbaix, 1964)
	sol	H <sub>2</sub> O	0	57.28	(Barsukov and Klintsova, 1970)
$\text{SnO}_2(\text{s}) \rightleftharpoons \text{Sn}^{4+} + 4\text{OH}^-$	$\Delta G^{\text{c}}$		0	63.68	(Pourbaix, 1964)

<sup>a</sup> pot: potentiometry, gl: glass electrode, sol: solubility, Sn: tin amalgam electrode, DPASV: Difference Pulse Cathodic Stripping Voltammetry, H: hydrogen(g) electrode, calc: recalculation of stability constants from published data,  $\Delta G$ : combination of thermodynamic formation data, lit: from critical survey of literature data, pol: polarography, F: fluoride ion specific electrode, Cl: Ag,AgCl electrode, spe: spectrophotometry.

<sup>b</sup> Stability constants recalculated from the experimental data of Tobias (1958).

<sup>c</sup> Stability constants calculated from free-energy values without quotation of the source used.

0<sub>corr</sub> = Constants corrected to zero ionic strength by the authors.

var = Ionic medium varied.

\* Stability constant determined at 20°C and \*\* at 22°C.

concentrations (between 0.001 and 0.02 mol L<sup>-1</sup>), and these complex species could correspond to reaction intermediates that appear just before tin(II) oxide precipitates (Stumm and Morgan, 1996). Gobom (1976) has shown that the amount of the trinuclear complex decreased in favour of SnOH<sup>+</sup> when the Sn(II) concentration decreased from 0.02 to 2.3 × 10<sup>-3</sup> mol L<sup>-1</sup>. For more diluted tin(II) solutions (5 × 10<sup>-7</sup> mol L<sup>-1</sup>), no polynuclear complexes were found and only the SnOH<sup>+</sup>, Sn(OH)<sub>2</sub><sup>0</sup> and Sn(OH)<sub>3</sub><sup>-</sup> mononuclear species were identified (Pettine et al., 1981).

Garret and Heiks (1941) and Djurdjevic et al. (1995) have shown that solid tin (II) hydroxide (Sn(OH)<sub>2</sub>(s)) is not stable and is easily dehydrated to SnO(s). These experimental results are consistent with values compiled by Pourbaix (1964).

Table 1 shows that several complex formation constants have been obtained in one medium with various ionic strengths for most of the Sn(II) hydrolysis equilibria. To recommend stability constants for these reactions at I = 0, we estimated the molal activity coefficients using the SIT methodology. For the formation of mononuclear complex species (SnOH<sup>+</sup>, Sn(OH)<sub>2</sub><sup>0</sup>, Sn(OH)<sub>3</sub><sup>-</sup>), we more specifically used the original data obtained in a NaNO<sub>3</sub> medium at 20°C (Pettine et al., 1981). For the polynuclear complex species (Sn<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> and Sn<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup>), we used the stability constants obtained in NaClO<sub>4</sub> medium at 25°C. Such an evaluation cannot be done for the formation of Sn<sub>2</sub>(OH)<sub>3</sub><sup>+</sup> because only one constant value is available. An example of the application of SIT methodology to these different equilibria for the formation of SnOH<sup>+</sup> is given below.

For the equilibrium Sn<sup>2+</sup> + H<sub>2</sub>O ⇌ SnOH<sup>+</sup> + H<sup>+</sup>, the formation constant at the molal scale, <sup>m</sup>K determined in an ionic medium of ionic strength I<sub>m</sub> is related to the corresponding value at zero ionic strength <sup>m</sup>K<sup>o</sup> by the following equation:

$$\log^m K = \log^m K^o + \log a_{\text{H}_2\text{O}} + \log \gamma_{\text{Sn}^{2+}} - \log \gamma_{\text{SnOH}^+} - \log \gamma_{\text{H}^+} \quad (2)$$

The substitution of the log  $\gamma_i$  values in Eqn. 2 with the corresponding forms of the Eqn. 1 and further rearrangement leads to Eqn. 3:

$$\log^m K + 2D - \log a_{\text{H}_2\text{O}} = \log^m K^o - \Delta \varepsilon I_m \quad (3)$$

$$\text{where } \Delta \varepsilon = \varepsilon_{(\text{SnOH}^+, \text{NO}_3^-)} + \varepsilon_{(\text{H}^+, \text{NO}_3^-)} - \varepsilon_{(\text{Sn}^{2+}, \text{NO}_3^-)} \quad (4)$$

In the presence of an ionic medium NX in dominant concentration, the contribution of all minor species, i.e., the reacting ions, can be neglected (Grenthe et al., 1992). Hence, the activity of water (a<sub>H<sub>2</sub>O</sub>) for a 1:1 electrolyte of ionic strength I<sub>m</sub> can be calculated using Eqn. 5:

$$\log a_{\text{H}_2\text{O}} = \frac{-2I_m \Phi}{\ln(10) \times 55.51} \quad (5)$$

$\Phi$ , the osmotic coefficient, was calculated in each medium by using compiled data in Robinson and Stokes (1959). By plotting  $\log^m K + 2D - \log a_{\text{H}_2\text{O}}$  as a function of I<sub>m</sub> both  $\log^m K^o$  (intercept of the curve with the y-axis) and  $\Delta \varepsilon$  (slope of the curve) were obtained.

The different hydrolysis constants corrected to zero ionic strength ( $-\log^m K^o$ ) by this method are given in Table 1. Reported experimental data and theoretical curves for NaNO<sub>3</sub>

ionic medium for the formation of both SnOH<sup>+</sup> (Fig. 1a) and Sn(OH)<sub>2</sub><sup>0</sup> (Fig. 1b) were plotted as a function of ionic strength and showed a good fit despite the low number of data, particularly for Sn(OH)<sub>2</sub><sup>0</sup>.

For these two equilibria, the SIT methodology seems to be a good approach to describe the influence of ionic strength, and similar results have been obtained for the other tin(II) hydrolysis equilibria. For SnOH<sup>+</sup>, equilibrium constants are also available in NaClO<sub>4</sub> at a concentration of 3 mol L<sup>-1</sup>. From these values and those obtained previously at I = 0 from values determined in NaNO<sub>3</sub>, the behaviour of the SnOH<sup>+</sup> hydrolysis constant as a function of I<sub>m</sub> was modeled in NaClO<sub>4</sub> with satisfactory results (dashed curve of Fig. 1a).

After substitution of the known ion interaction parameters ( $\varepsilon_{(\text{H}^+, \text{NO}_3^-)} = (0.07 \pm 0.01)$  kg mol<sup>-1</sup> and  $\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} = (0.14 \pm 0.02)$  kg mol<sup>-1</sup> (Grenthe et al., 1992)) and combination of the  $\Delta \varepsilon$  obtained by applying SIT methodology to the different hydrolysis equilibria, we estimated the ion interaction parameters of the different charged hydrolytic products in the presence of the H<sup>+</sup>, ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> counter-ions (Table 2). In the case of H<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, the ion interaction parameters were assessed from data given in Table 1, and for ClO<sub>4</sub><sup>-</sup>, these parameters were calculated using both data from Table 1 and complexation stability constants of tin(II) with halide ions reported in Table 4.

A comparison of the ion interaction parameters given in Table 2 with other values is impossible to perform. However, this kind of data can be useful for the calculation of activity coefficients and stability constants at I = 0, when the constant value is available for only one ionic strength value in nitrate or perchlorate media. Because these ion interaction parameters were evaluated from a very low number of data, a large uncertainty is assigned to them.

With regard to the solubility product constants of tin(II) oxide (SnO(s)) and hydroxide (Sn(OH)<sub>2</sub>(s)), homogeneous values were obtained no matter what medium and experimental method were used (Table 1). Because of the wide diversity of ionic media used, a rigorous extrapolation to zero ionic strength is difficult to perform, and the pK<sub>s</sub> value recommended herein corresponds to a mean value calculated from data obtained at I = 0 (Table 1).

From the tin(II) hydrolysis constants selected in this study, a modeling of the distribution of the different species as a function of pH was performed both in the absence and presence of solid tin(II) oxide. These calculations were carried out assuming that the difference in constant values is minor over the temperature range of 20 to 25°C. The results are reported in Figure 2 and Figure 3, respectively.

As the concentration levels of tin are generally very low in natural waters, only mononuclear hydrolytic products were considered when constructing Figure 2. As we have assumed that tin(II) oxide does not precipitate, the Sn(II) distribution is only valid for tin concentrations <10<sup>-6</sup> mol L<sup>-1</sup> (see Fig. 3).

The influence of Sn(II) hydrolysis on the solubility of tin(II) oxide is shown in Figure 3, considering mononuclear and polynuclear hydrolytic products. This distribution shows that SnO(s) solubility is affected mainly by Sn<sup>2+</sup> for pH < 4, by Sn(OH)<sub>2</sub><sup>0</sup> for pH ranging from 4 to 10, and by Sn(OH)<sub>3</sub><sup>-</sup> at higher pH.

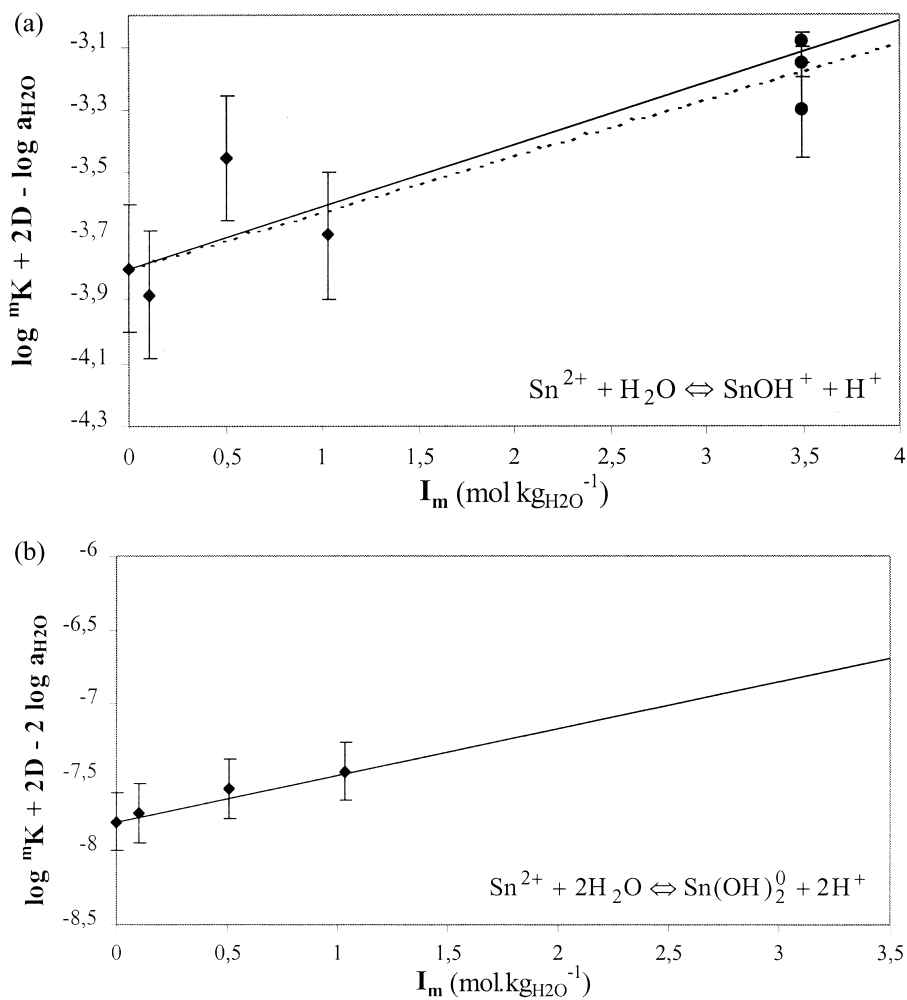


Fig. 1. Plot of  $\log^m K + 2D - \log a_{H_2O}$  for  $\text{Sn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{SnOH}^+ + \text{H}^+$  (a) and plot of  $\log^m K + 2D - 2 \log a_{H_2O}$  for  $\text{Sn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn}(\text{OH})_2^0 + 2\text{H}^+$  (b) vs.  $I_m$  in different ionic media: (solid line) theoretical function in  $\text{NaNO}_3$ ; ( $\blacklozenge$ ) experimental values in  $\text{NaNO}_3$ ; (broken line) theoretical function in  $\text{NaClO}_4$ ; ( $\bullet$ ) experimental values in  $\text{NaClO}_4$ .

### 3.1.2. Sn(IV) hydrolysis reactions

As shown in Table 1, few data are available in literature to describe Sn(IV) hydrolysis. According to the Pourbaix (1964) study, only the soluble species  $\text{SnO}_3^{2-}$  are present in alkaline medium. The study of the solubility of cassiterite ( $\text{SnO}_2(\text{s})$ ) in alkaline medium ( $\text{NaOH}$  0.2–2.5 mol  $\text{L}^{-1}$ ) showed the presence of  $\text{Sn}(\text{OH})_5^-$  in solution (Barsukov and Klintsova, 1970). Macchi and Pettine (1980) have identified the following Sn(IV) hydrolytic products by DPASV:  $\text{SnO}(\text{OH})^+$  and  $\text{SnO}^{2+}$  for  $2 \leq \text{pH} \leq 6$ ,  $\text{SnO}(\text{OH})_2^0$  for  $6 \leq \text{pH} \leq 7$ , and  $\text{SnO}(\text{OH})_3^-$  for  $\text{pH} \geq 8$ . However, no stability constant is given for these reactions. The  $\text{SnO}^{2+}$  formation was also considered in the work of Brubaker (1954, 1955). From so disparate results, it is difficult to draw conclusions about the presence and the identification of the Sn(IV) hydrolysed species. Because of this lack of characterisation, we have only retained  $\text{Sn}^{4+}$  and  $\text{SnO}_3^{2-}$  as Sn(IV) soluble form in this study.

For the precipitation of solid tin(IV) hydroxide and oxide, solubility product constants were estimated by Pourbaix (1964) (Table 1). For the solid tin(IV) hydroxide, the value obtained is

similar to one determined by Barsukov and Klintsova (1970). For the two solids, the solubility constants are high with an instability of  $\text{Sn}(\text{OH})_4(\text{s})$  in favour of  $\text{SnO}_2(\text{s})$  (Barsukov and Klintsova, 1970).

### 3.2. Standard Potentials of Inorganic Tin

Standard potential values available in literature for the simplest tin redox reactions are reported in Table 3.

Whatever the standard potential source is, all the values are in good agreement for all the tin redox reactions considered. Most of the values were calculated from standard thermodynamic Sn species formation data (Pourbaix, 1964; Latimer, 1952; Galus, 1985) selected by the National Bureau of Standards (Wagman et al., 1982). In the case of the  $\text{Sn}^{2+}/\text{Sn}$  redox couple, a value directly derived from experimental measurements is available (Galus, 1985) and is very close to the one calculated in other studies. Assuming that the difference in constant values is minor over the temperature range of 20 to 25°C, we also calculate the standard potential values of Sn(II)/

Table 2. Ion interaction coefficients calculated by applying the SIT methodology to tin(II) stability constants reported in the literature

Ion Interaction parameter	Value (L mol <sup>-1</sup> )
<i>Hydrolysis Reactions</i>	
$\epsilon_{(\text{Sn}^{2+}, \text{NO}_3^-)}$	$(0.4 \pm 0.1)$
$\epsilon_{(\text{SnOH}^+, \text{NO}_3^-)}$	$(0.2 \pm 0.1)$
$\epsilon_{(\text{Sn}(\text{OH})_2^0, \text{NO}_3^-)}$	$(0.3 \pm 0.2)$
$\epsilon_{(\text{SnOH}^+, \text{ClO}_4^-)}$	$(-0.14 \pm 0.08)^a$
$\epsilon_{(\text{Sn}_2(\text{OH})_2^{2+}, \text{ClO}_4^-)}$	$(0.5 \pm 0.2)^a$
$\epsilon_{(\text{Sn}_3(\text{OH})_4^{2+}, \text{ClO}_4^-)}$	$(-0.04 \pm 0.05)^a$
<i>Reactions of Tin(II) with Halide Ions</i>	
$\epsilon_{(\text{Sn}^{2+}, \text{ClO}_4^-)}$	$(0.19 \pm 0.05)^b$
	$(0.18 \pm 0.05)^c$
	$(0.11 \pm 0.05)^d$
$\epsilon_{(\text{SnF}^+, \text{ClO}_4^-)}$	$(0.07 \pm 0.05)$
$\epsilon_{(\text{SnF}_2^+, \text{Na}^+)}$	$(0.16 \pm 0.05)$
$\epsilon_{(\text{SnCl}^+, \text{ClO}_4^-)}$	$(0.05 \pm 0.05)$
$\epsilon_{(\text{SnCl}_2^+, \text{Na}^+)}$	$(-0.003 \pm 0.050)$
$\epsilon_{(\text{SnBr}^+, \text{ClO}_4^-)}$	$(-0.01 \pm 0.05)$
$\epsilon_{(\text{SnBr}_2^+, \text{Na}^+)}$	$(-0.04 \pm 0.07)$

<sup>a</sup> Ion interaction parameters calculated using  $\epsilon_{(\text{Sn}^{2+}, \text{ClO}_4^-)} = (0.18 \pm 0.05)$ .

<sup>b</sup> Ion interaction parameters calculated with data obtained in the system Sn (II)-fluoride ions.

<sup>c</sup> Ion interaction parameters calculated with data obtained in the system Sn(II)-chloride ions.

<sup>d</sup> Ion interaction parameters calculated with data obtained in the system Sn(II)-bromide ions.

Sn(0) and Sn(IV)/Sn(II) with  $\text{SnOH}^+$ ,  $\text{Sn}(\text{OH})_2^0$ ,  $\text{Sn}(\text{OH})_3^-$  and  $\text{SnO}(\text{s})$  as Sn(II) species and  $\text{SnO}_3^{2-}$  and  $\text{SnO}_2(\text{s})$  as Sn(IV) species (Table 3). These data were evaluated using the hydrolysis stability constants and the solubility product values previously recommended at 20 and 25°C, respectively.

From all these values, pe-pH stability fields diagrams were drawn for an Sn activity of  $10^{-10}$  mol L<sup>-1</sup>, this low concen-

tration being more suitable to describe the behaviour of tin in real systems.

Figure 4 shows that under strongly reducing conditions, elemental Sn and particularly  $\text{SnH}_4(\text{g})$  are thermodynamically stable. Under moderate redox potential range, tin(II) is the predominant form and can exist under the  $\text{Sn}^{2+}$ ,  $\text{SnOH}^+$ ,  $\text{Sn}(\text{OH})_2^0$  or  $\text{Sn}(\text{OH})_3^-$  species, depending on the pH. For higher redox potentials, Sn(IV) is predominant mainly under the form of  $\text{SnO}_2(\text{s})$ .

### 3.3. Complexation of Tin with Halide Ions

#### 3.3.1. Sn(II) complexation reactions with halide ions

Dissociation constants ( $K_d$ ) associated with these reactions are given in Table 4.

Interactions between tin(II) and halide ions have been studied by several authors usually at low pH to minimise tin(II) hydrolysis. For all the halide ions considered, most of the dissociation constant values have been obtained by potentiometry with tin amalgam electrodes (Vanderzee and Rhodes, 1952; Vanderzee, 1952; Hall and Slater, 1968; Connick and Paul, 1961; Tobias and Hugus, 1961; Duke and Courtney, 1950; Duke and Pinkerton, 1951; Fedorov et al., 1969). More recently, potentiometry with ion-selective electrodes has been used to monitor the uncomplexed fluoride ion concentration (Hall and Slater, 1968; Djokic-Konstantinovska and Zmbova, 1985). Literature reports also the use of electrochemical techniques such as polarography for the tin(II)-fluoride system (Schaap et al., 1954; Bond and Taylor, 1970; Haight et al., 1962) and DPASV for the tin(II)-chloride and tin(II)-bromide systems (Pettine et al., 1981). Complexation of tin(II) with iodide ions has only been followed by analysis of the species appearing after solubilisation of  $\text{SnI}_2(\text{s})$  and modeling of the data (Haight and Johansson, 1968).

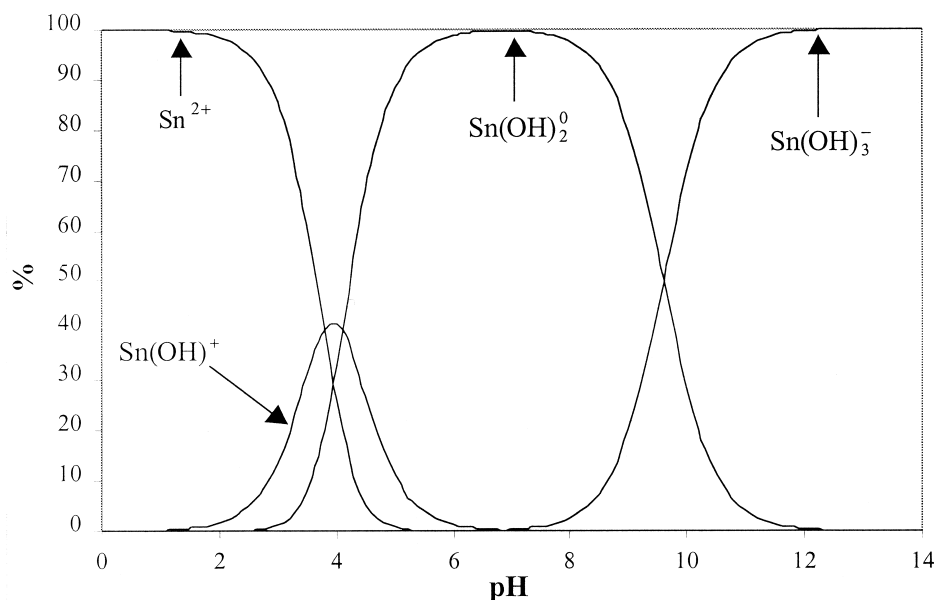


Fig. 2. Distribution of various species of tin(II) as a function of pH.

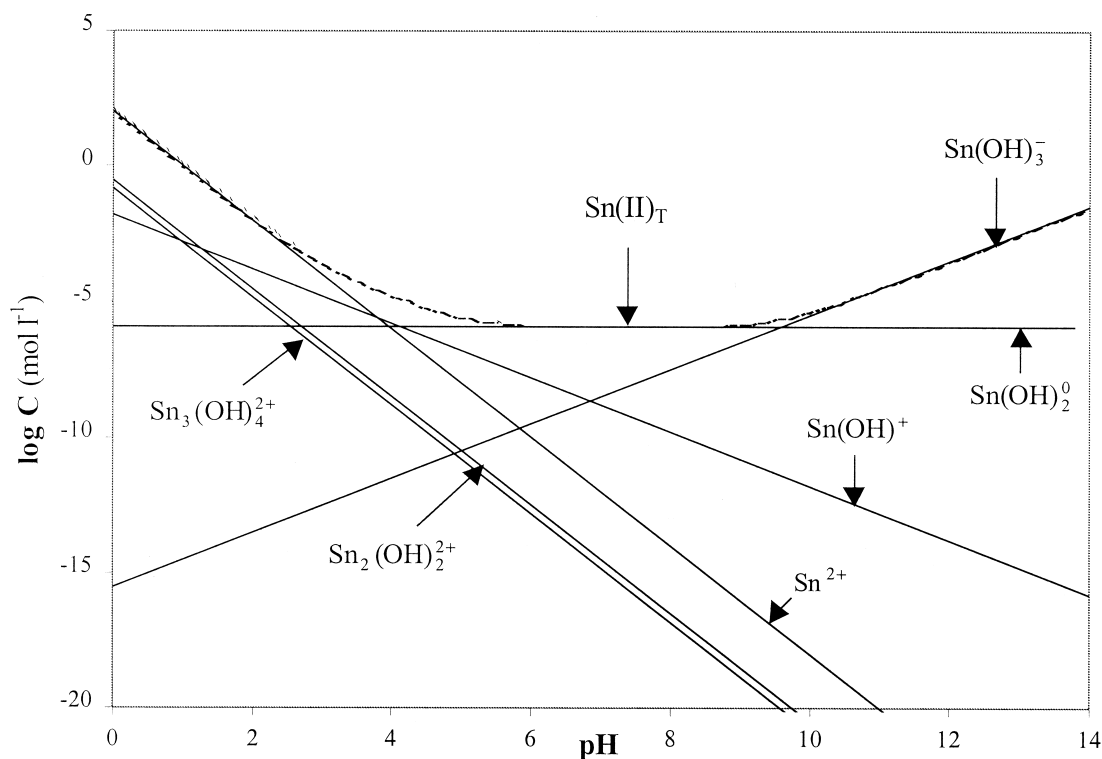


Fig. 3. Distribution of hydrolysis products in solution saturated with SnO(s).

Except for the Connick and Paul (1961) study, which suggested the existence of polymers such as  $\text{Sn}_2\text{F}^{3+}$  at low fluoride concentration, the formation of polynuclear complexes with halide ions is rejected in most of the studies. Only the  $\text{SnX}_n^{(2-n)}$  complex species are formed, the number of ligands ( $n$ ) varying according to the halide ion considered ( $\text{X}^-$ ). With fluoride ions,

only complexes with ligands numbering from one to three were identified (Hall and Slater, 1968; Djokic-Konstantinovska and Zmbova, 1985; Bond and Taylor, 1970). In the case of chloride ions, studies describe complexes with ligands numbering up to four (Duke and Courtney, 1950; Haight et al., 1962), and also with ligand numbers reaching a maximum of three (Vanderzee

Table 3. Standard potentials of tin redox couples (relative to normal hydrogen electrode)

Chemical equilibrium	Method <sup>a</sup>	E° (V)	Source
$\text{Sn} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{SnH}_4(\text{g})$	<i>Sn(0)/Sn(-IV) couple</i> $\Delta G^b$	-1.074	(Pourbaix, 1964)
$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$	<i>Sn(II)/Sn(0) couple</i> $\Delta G^b$ $\Delta G^c$ pot	-0.136 -0.136 $-0.1375 \pm 0.0005$	(Latimer, 1952; Galus, 1985) (Pourbaix, 1964) (Galus, 1985)
<i>Recommended value</i>			
$\text{SnOH}^+ + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn} + \text{H}_2\text{O}$		-0.136	(this work)
$\text{Sn(OH)}_2^0 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn} + 2\text{H}_2\text{O}$		-0.024	(this work)
$\text{Sn(OH)}_3^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn} + 3\text{H}_2\text{O}$		0.097	(this work)
$\text{SnO}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn} + \text{H}_2\text{O}$		0.381	(this work)
		-0.077	(this work)
$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$	<i>Sn(IV)/Sn(II) couple</i> $\Delta G^a$ $\Delta G^b$	0.15 0.15	(Latimer, 1952; Galus, 1985) (Pourbaix, 1964)
$\text{SnO}_2(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{SnO}(\text{s}) + \text{H}_2\text{O}$		-0.136	(this work)
$\text{SnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+} + 2\text{H}_2\text{O}$		-0.077	(this work)
$\text{SnO}_2(\text{s}) + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{SnOH}^+ + \text{H}_2\text{O}$		-0.189	(this work)
$\text{SnO}_2(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn(OH)}_2^0$		-0.310	(this work)
$\text{SnO}_2(\text{s}) + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Sn(OH)}_3^- + \text{OH}^-$		-1.008	(this work)
$\text{SnO}_3^{2-} + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn(OH)}_3^-$		0.326	(this work)

<sup>a</sup> See footnote (a) of Table 1 for the meaning of the abbreviation.<sup>b</sup> Stability constants calculated from free-energy values selected by the National Bureau of Standards (Wagman et al., 1982).<sup>c</sup> Stability constants calculated from free-energy values without quotation of the source used.

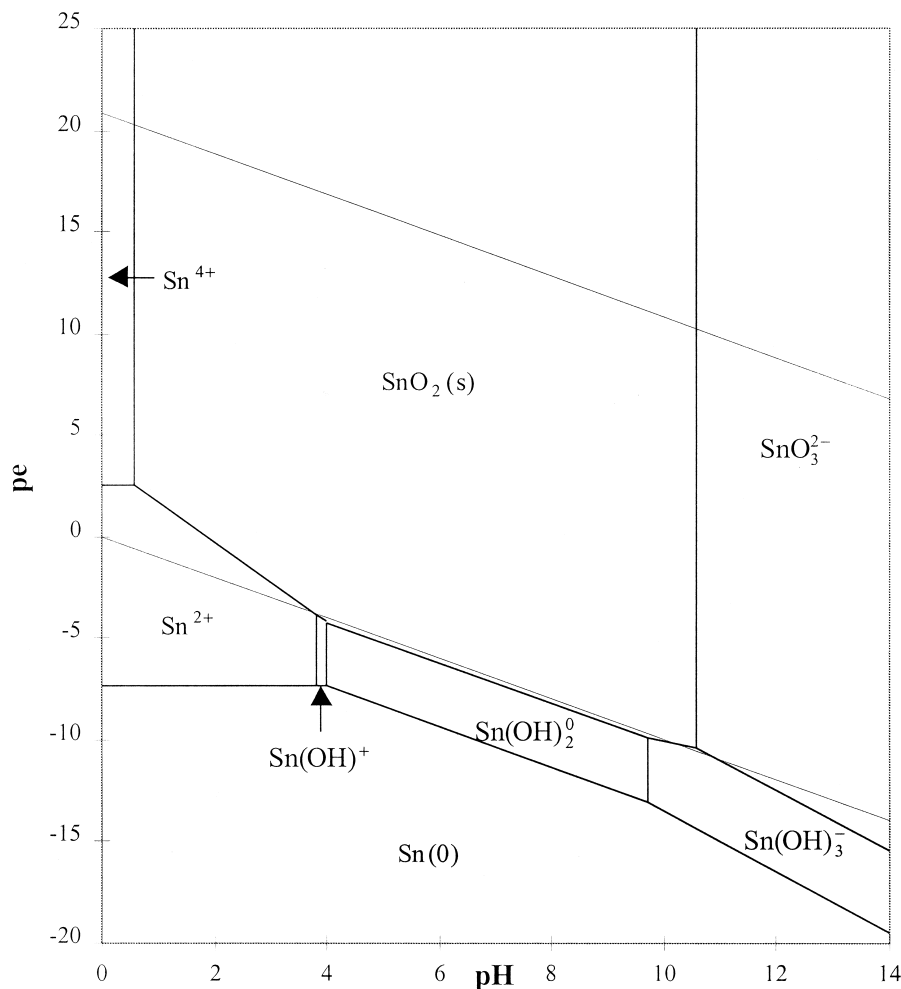


Fig. 4. Tin pe-pH diagram for a dissolved tin activity of  $10^{-10} \text{ mol L}^{-1}$ .

and Rhodes, 1952; Tobias and Hugus, 1961). However, it seems that  $\text{SnCl}_4^{2-}$  represents an upper limit for ligand numbers for stability reasons rather than for structural reasons (Haight et al., 1962). By using a low chloride ion concentration, Pettine et al. (1981) did not find it necessary to introduce the formation of  $\text{SnCl}_3^-$  in calculations to fit their data. For bromotin(II) complexes, the maximum number of ligands is three (Vanderzee and Rhodes, 1952; Sillén, 1964), except in the study of Fedorov et al. (1969) who showed that the number of bromo groups attached to  $\text{Sn}^{2+}$  increases with an increase in ionic strength. In the case of the complexation of tin(II) with iodide ions, the only available study showed that ligands numbering eight are required to model the results (Haight and Johansson, 1968). However, the authors thought it desirable to study the region of high iodide concentrations with other methods before the existence of  $\text{SnI}_8^{6-}$  can be definitive.

To obtain complex dissociation constants at zero ionic strength for the reactions of tin(II) with halide ions, SIT methodology was applied to some of the equilibria listed in Table 4. These calculations have been done for all the complexes with a number of ligands ranging from one to three. Above  $n = 3$ , the number of data is insufficient or corresponds to data obtained at ionic strengths  $>3.5 \text{ mol kg}_{\text{H}_2\text{O}}^{-1}$ , which is the limit of the

validity of SIT methodology. In the case of fluoride ions, the more reliable data are those obtained at 22°C (Djokic-Konstantinovska and Zmbova, 1985). Therefore, only these values have been retained for the calculations. For the chlorotin(II) and bromotin(II) complexes, all the data obtained at 25°C with a ionic strength  $<3.5 \text{ mol kg}_{\text{H}_2\text{O}}^{-1}$  have been used. An extrapolation to zero ionic strength is impossible to perform for the iodotin(II) complexes, because all the data compiled in Table 4 were obtained in  $\text{NaClO}_4$  with only one ionic strength value.

The complex dissociation constants extrapolated to zero ionic strength recommended herein are given in Table 4. For all the equilibria considered, SIT methodology was applied with good accuracy, the correlation coefficients of the curves  $\log^m K - \Delta z^2 D = \log^m K^\circ - \Delta \epsilon I_m$  being all higher to 0.960. Complex dissociation constants recommended in this study for interactions between Sn(II) and chloride ions or bromide ions are very close to those reported in the compilation of Sillén (1964) at zero ionic strength (Table 4), showing that SIT methodology is perfectly adequate to obtain data at  $I = 0$ . From the combination of the different slopes of the curves ( $\Delta \epsilon$ ) and substitution of the known ion interaction parameters ( $\epsilon_{(\text{Na}^+, \text{Cl}^-)} = 0.03 \pm 0.01 \text{ kg mol}^{-1}$ ,  $\epsilon_{(\text{Na}^+, \text{Br}^-)} = 0.05 \pm 0.01 \text{ kg mol}^{-1}$  ( $\epsilon_{(\text{Na}^+, \text{F}^-)} = 0.02 \pm 0.02 \text{ kg mol}^{-1}$ , (Grenthe et al., 1992)), the



Table 4. Complex dissociation constants of inorganic tin with halide ions

Chemical equilibrium	Method <sup>a</sup>	Medium	I (mol L <sup>-1</sup> )	pK <sub>d</sub>	Source
<i>Fluoride Ions</i>					
<i>Sn(II)</i>					
SnF <sup>+</sup> ⇌ Sn <sup>2+</sup> + F <sup>-</sup>	pol	NaClO <sub>4</sub>	1	4	(Bond and Taylor, 1970)
	pot(Sn,F)	NaClO <sub>4</sub>	0.85	6.25	(Hall and Slater, 1968)
	pot(Sn)	HClO <sub>4</sub>	2	4	(Connick and Paul, 1961)
	pot(F)	NaClO <sub>4</sub>	0.1	4.789**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	0.5	4.606**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	1	4.557**	(Djokic and Zmbova, 1985)
<i>Recommended value</i>				$-\log^m K^o = 5.22 \pm 0.01^{**}$	( <i>this work</i> )
SnF <sub>2</sub> <sup>o</sup> ⇌ Sn <sup>2+</sup> + 2F <sup>-</sup>	pol	NaClO <sub>4</sub>	1	6.68	(Bond and Taylor, 1970)
	pot(Sn,F)	NaClO <sub>4</sub>	0.85	8.76	(Hall and Slater, 1968)
	pot(F)	NaClO <sub>4</sub>	0.1	8.256**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	0.5	8.013**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	1	7.940**	(Djokic and Zmbova, 1985)
<i>Recommended value</i>				$-\log^m K^o = 8.90 \pm 0.05^{**}$	( <i>this work</i> )
SnF <sub>3</sub> <sup>o</sup> ⇌ Sn <sup>2+</sup> + 3F <sup>-</sup>	pol	NaClO <sub>4</sub>	1	9.5	(Bond and Taylor, 1970)
	pol	NaNO <sub>3</sub>	0.8	9.92	(Schaap et al., 1954)
	pol	KNO <sub>3</sub>	2.5	10.96	(Schaap et al., 1954)
	pot(Sn,F)	NaClO <sub>4</sub>	0.85	9.25	(Hall and Slater, 1968)
	pot(F)	NaClO <sub>4</sub>	0.1	12.235**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	0.5	11.974**	(Djokic and Zmbova, 1985)
	pot(F)	NaClO <sub>4</sub>	1	11.799**	(Djokic and Zmbova, 1985)
<i>Recommended value</i>				$-\log^m K^o = 12.9 \pm 0.1^{**}$	( <i>this work</i> )
<i>Sn(IV)</i>					
SnF <sub>6</sub> <sup>2-</sup> ⇌ Sn <sup>4+</sup> + 6F <sup>-</sup>	pol	var		25	(Schaap et al., 1954)
<i>Chloride Ions</i>					
<i>Sn(II)</i>					
SnCl <sup>+</sup> ⇌ Sn <sup>2+</sup> + Cl <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	3	1.18 ± 0.01	(Tobias and Hugus, 1961)
	pot(Sn)	var	0 <sub>corr</sub>	1.51	(Sillén, 1964)
	pot(Sn)	ClO <sub>4</sub> <sup>-</sup>	2.03	1.05 ± 0.01	(Duke and Courtney, 1950)
	pot	HClO <sub>4</sub>	2	1.11	(Djokic and Pinkerton, 1951)
	pot(Sn)	NaClO <sub>4</sub>	3	1.15	(Vanderzee and Rhodes, 1952)
	pol	H <sub>2</sub> SO <sub>4</sub>	4	1.45	(Haight et al., 1962)
	DPASV	NaNO <sub>3</sub>	1	0.73 ± 0.10*	(Pettine et al., 1981)
<i>Recommended value</i>				$-\log^m K^o = 1.54 \pm 0.02$	( <i>this work</i> )
SnCl <sub>2</sub> <sup>o</sup> ⇌ Sn <sup>2+</sup> + 2Cl <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	3	1.74 ± 0.02	(Tobias and Hugus, 1961)
	pot(Sn)	var	0 <sub>corr</sub>	2.24	(Sillén, 1964)
	pot(Sn)	ClO <sub>4</sub> <sup>-</sup>	2.03	1.76 ± 0.01	(Duke and Courtney, 1950)
	pot(Sn)	NaClO <sub>4</sub>	3	1.7	(Vanderzee and Rhodes, 1952)
	pol	H <sub>2</sub> SO <sub>4</sub>	4	2.35	(Haight et al., 1962)
	DPASV	NaNO <sub>3</sub>	1	1.08 ± 0.10*	(Pettine et al., 1981)
<i>Recommended value</i>				$-\log^m K^o = 2.3 \pm 0.1$	( <i>this work</i> )
SnCl <sub>3</sub> <sup>-</sup> ⇌ Sn <sup>2+</sup> + 3Cl <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	3	1.67 ± 0.04	(Tobias and Hugus, 1961)
	pot(Sn)	var	0 <sub>corr</sub>	2.03	(Sillén, 1964)
	pot(Sn)	ClO <sub>4</sub> <sup>-</sup>	2.03	1.14 ± 0.01	(Duke and Courtney, 1950)
	pot(Sn)	NaClO <sub>4</sub>	3	1.68	(Vanderzee and Rhodes, 1952)
	pol	H <sub>2</sub> SO <sub>4</sub>	4	2.46	(Haight et al., 1962)
<i>Recommended value</i>				$-\log^m K^o = 1.97 \pm 0.05$	( <i>this work</i> )
SnCl <sub>4</sub> <sup>o</sup> ⇌ Sn <sup>2+</sup> + 4Cl <sup>-</sup>	pot(Sn)	var	0 <sub>corr</sub>	1.48	(Sillén, 1964)
	pot(Sn)	ClO <sub>4</sub> <sup>-</sup>	2.03	1.14 ± 0.01	(Duke and Courtney, 1950)
	pol	H <sub>2</sub> SO <sub>4</sub>	4	2.27	(Haight et al., 1962)
SnOHCl <sup>o</sup> ⇌ SnOH <sup>+</sup> + Cl <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	3	1.04	(Vanderzee and Rhodes, 1952)
	DPASV	NaCl	0.5	1.14*	(Pettine et al., 1981)
<i>Sn(IV)</i>					
SnCl <sub>3</sub> <sup>+</sup> ⇌ Sn <sup>4+</sup> + Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	3.71 ± 0.03	(Fatouros et al., 1978)
SnCl <sub>2</sub> <sup>2+</sup> ⇌ Sn <sup>4+</sup> + 2Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	6.46 ± 0.02	(Fatouros et al., 1978)
SnCl <sub>3</sub> <sup>+</sup> ⇌ Sn <sup>4+</sup> + 3Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	8.78 ± 0.02	(Fatouros et al., 1978)
SnCl <sub>4</sub> <sup>o</sup> ⇌ Sn <sup>4+</sup> + 4Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	9.48 ± 0.09	(Fatouros et al., 1978)
SnCl <sub>5</sub> <sup>-</sup> ⇌ Sn <sup>4+</sup> + 5Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	11.23 ± 0.06	(Fatouros et al., 1978)
SnCl <sub>6</sub> <sup>2-</sup> ⇌ Sn <sup>4+</sup> + 6Cl <sup>-</sup>	pot(Cl)	HClO <sub>4</sub>	5	12.40 ± 0.05	(Fatouros et al., 1978)

Continued

$\varepsilon_{(\text{Sn}^{2+}, \text{ClO}_4^-)}$  ion interaction parameter and those between tin(II) complexed with halide ions and ClO<sub>4</sub><sup>-</sup> or Na<sup>+</sup> have been calculated; they are listed in Table 2. The values obtained for  $\varepsilon_{(\text{Sn}^{2+}, \text{ClO}_4^-)}$  from the study of the systems Sn<sup>2+</sup> – Cl<sup>-</sup> and Sn<sup>2+</sup> – F<sup>-</sup> are in very good agreement. Considering the uncer-

tainty, this same value obtained from the Sn<sup>2+</sup> – Br<sup>-</sup> system is lower but consistent.

Speciation calculations have been done to represent the distribution of tin(II) species as a function of pH in presence of chloride ([Cl<sup>-</sup>] = 10<sup>-2</sup> mol L<sup>-1</sup>).

Table 4. (Continued)

<i>Bromide Ions</i>					
<i>Sn(II)</i>					
$\text{SnBr}^+ \rightleftharpoons \text{Sn}^{2+} + \text{Br}^-$	pot(Sn)	var	$0_{\text{corr}}$	1.11	(Sillén, 1964)
	pot	HClO <sub>4</sub>	2	0.43	(Duke and Pinkerton, 1951)
	pot(Sn)	NaClO <sub>4</sub>	3	0.73	(Vanderzee, 1952)
	DPASV	NaNO <sub>3</sub>	1	0.60 ± 0.10*	(Pettine et al., 1981)
	pot(Sn)	NaClO <sub>4</sub>	1	0.74 ± 0.04	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	2	0.56 ± 0.06	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	3	0.78 ± 0.02	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	4	0.84 ± 0.02	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	6	1.18 ± 0.03	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	8	1.6 ± 0.04	(Fedorov et al., 1969)
<i>Recommended value</i>				$-\log^{\text{m}}K^{\circ} = 1.07 \pm 0.06$	( <i>this work</i> )
$\text{SnBr}_2^0 \rightleftharpoons \text{Sn}^{2+} + 2\text{Br}^-$	pot(Sn)	var	$0_{\text{corr}}$	1.81	(Sillén, 1964)
	pot(Sn)	NaClO <sub>4</sub>	3	1.14	(Vanderzee, 1952)
	DPASV	NaNO <sub>3</sub>	1	1.13 ± 0.1*	(Pettine et al., 1981)
	pot(Sn)	NaClO <sub>4</sub>	1	0.90 ± 0.05	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	2	1.19 ± 0.01	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	3	1.17 ± 0.01	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	4	1.43 ± 0.06	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	6	2.1 ± 0.1	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	8	2.74 ± 0.04	(Fedorov et al., 1969)
<i>Recommended value</i>				$-\log^{\text{m}}K^{\circ} = 1.88 \pm 0.07$	( <i>this work</i> )
$\text{SnBr}_3^- \rightleftharpoons \text{Sn}^{2+} + 3\text{Br}^-$	pot(Sn)	var	$0_{\text{corr}}$	1.46	(Sillén, 1964)
	pot(Sn)	NaClO <sub>4</sub>	3	1.34	(Vanderzee, 1952)
	pot(Sn)	NaClO <sub>4</sub>	3	1.09 ± 0.02	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	4	1.48 ± 0.04	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	6	2.18 ± 0.07	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	8	3.7 ± 0.1	(Fedorov et al., 1969)
<i>Recommended value</i>				$-\log^{\text{m}}K^{\circ} = 1.5 \pm 0.1$	( <i>this work</i> )
$\text{SnBr}_4^{2-} \rightleftharpoons \text{Sn}^{2+} + 4\text{Br}^-$	pot(Sn)	NaClO <sub>4</sub>	3	0.40 ± 0.05	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	4	1.00 ± 0.05	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	6	2.2 ± 0.2	(Fedorov et al., 1969)
	pot(Sn)	NaClO <sub>4</sub>	8	3.30 ± 0.04	(Fedorov et al., 1969)
$\text{SnBr}_5^{3-} \rightleftharpoons \text{Sn}^{2+} + 5\text{Br}^-$	pot(Sn)	NaClO <sub>4</sub>	8	2.4 ± 0.1	(Fedorov et al., 1969)
$\text{SnBr}_6^{4-} \rightleftharpoons \text{Sn}^{2+} + 6\text{Br}^-$	pot(Sn)	NaClO <sub>4</sub>	8	2.3 ± 0.1	(Fedorov et al., 1969)
<i>Iodide Ions</i>					
<i>Sn(II)</i>					
$\text{SnI}^+ \rightleftharpoons \text{Sn}^{2+} + \text{I}^-$	sol	NaClO <sub>4</sub>	4	0.70 ± 0.5	(Haight and Johansson, 1968)
$\text{SnI}_2^0 \rightleftharpoons \text{Sn}^{2+} + 2\text{I}^-$	sol	NaClO <sub>4</sub>	4	1.13 ± 0.07	(Haight and Johansson, 1968)
$\text{SnI}_3^- \rightleftharpoons \text{Sn}^{2+} + 3\text{I}^-$	sol	NaClO <sub>4</sub>	4	2.13 ± 0.03	(Haight and Johansson, 1968)
$\text{SnI}_4^{2-} \rightleftharpoons \text{Sn}^{2+} + 4\text{I}^-$	sol	NaClO <sub>4</sub>	4	2.3 ± 0.05	(Haight and Johansson, 1968)
$\text{SnI}_6^{4-} \rightleftharpoons \text{Sn}^{2+} + 6\text{I}^-$	sol	NaClO <sub>4</sub>	4	2.6 ± 0.04	(Haight and Johansson, 1968)
$\text{SnI}_8^{6-} \rightleftharpoons \text{Sn}^{2+} + 8\text{I}^-$	sol	NaClO <sub>4</sub>	4	2.08 ± 0.04	(Haight and Johansson, 1968)
$\text{SnI}_2(\text{s}) \rightleftharpoons \text{Sn}^{2+} + 2\text{I}^-$	sol	NaClO <sub>4</sub>	4	5.08 ± 0.01	(Haight and Johansson, 1968)

<sup>a</sup> See footnote (a) of Table 1 for the meaning of the abbreviation.

$0_{\text{corr}}$  = Constants corrected to zero ionic strength by the authors.

var = Ionic medium varied.

\* Stability constant determined at 20°C and at \*\* 22°C.

Figure 5 shows that the presence of chloride ions influences tin(II) speciation only in acid medium (pH < 4). For higher pH values, the tin(II) hydrolytic products predominate. For a chloride concentration of 10<sup>-3</sup> mol L<sup>-1</sup>, only SnCl<sup>+</sup> as chlorotin(II) complex species is present at low pH with a proportion close to 4%. For lower concentrations, the presence of chlorotin(II) complexes is negligible.

### 3.3.2. Sn(IV) complexation reactions with chloride ions

Only one study is available in literature for the complexation of stannate ion with chloride ions (Fatouros et al., 1978). The method used is based on the potentiometric determination of free Cl<sup>-</sup> ions by means of Ag, AgCl electrodes. The statistical treatment of the data by the least squared method allowed them

to identify the SnCl<sub>n</sub><sup>(4-n)</sup> chlorotin(IV) complexes with *n* ranging from 1 to 6 in HClO<sub>4</sub> at a concentration of 5 mol L<sup>-1</sup>.

### 3.4. Inorganic Tin Reactions With Other Inorganic Compounds

Tin(II) and tin(IV) can also react with other inorganic compounds such as chalcogenides (sulphide, selenide, telluride), sulphate, phosphate, or thiocyanate ions to form complex species or solid phases. All the stability constants of these equilibria reported in literature are listed Table 5.

#### 3.4.1. Tin(II) precipitation reactions with chalcogenide ions

Due to the very low solubility of tin(II)-chalcogenide solid phases, few solubility products directly determined by experi-

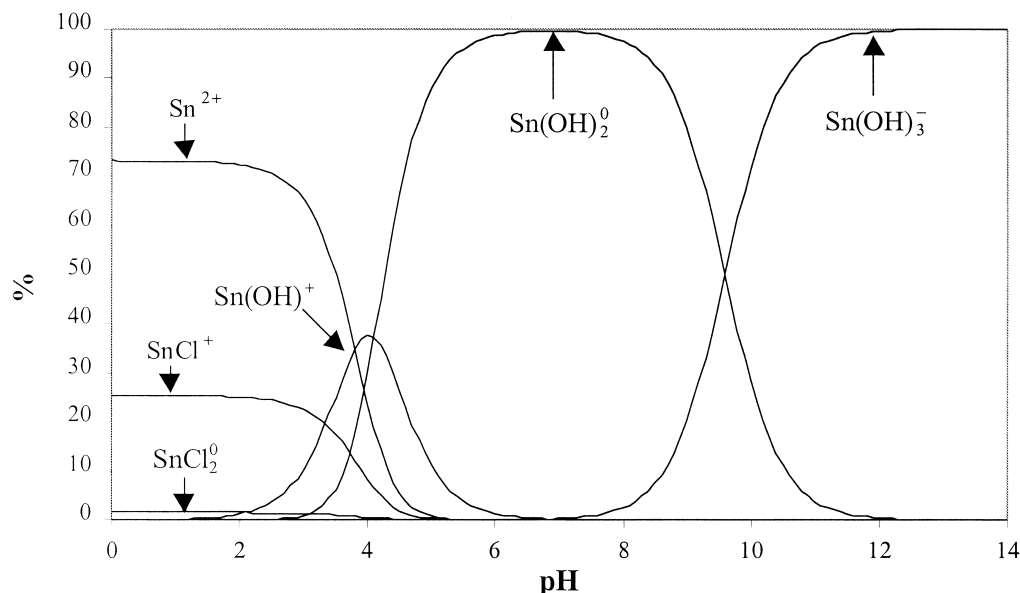


Fig. 5. Distribution of various species of tin(II) in presence of  $[\text{Cl}^-] = 10^{-2} \text{ mol L}^{-1}$  as a function of pH.

mental methods are available in the literature. For SnSe(s) and SnTe(s), the solubility products were estimated by means of approximate thermodynamic calculations (Buketov et al., 1964) from heats of formation, entropies, free energies, and heats of hydration of ions given by Latimer (1952). As no entropy values are available in the literature for these two solid phases, they recalculated them by an approximate method based on the entropy values of SnS(s) (Buketov et al., 1964). In the case of solubility products of selenium-containing phases, we have shown previously that the values obtained by Buketov et al. (1964) are very often in agreement with values obtained by solubility measurements (Séby et al., 2001); thus the data given in Table 5 can be considered as reliable. For the precipitation of SnS(s), the  $\text{p}K_s$  values obtained directly by experimental methods are consistent with values calculated by the combination of thermodynamic formation data selected most of the time in the compilation of the National Bureau of Standards (Wagman et al., 1982). By rejecting the value given by Pourbaix (1964) that seems too low compared to other solubility product values, a  $\text{p}K_s$  close to 26 can be recommended for this equilibrium.

### 3.4.2. Tin(II) complexation reactions with phosphate and thiocyanate ions

Only Cilley (1968) has studied the chemical interactions between tin(II) and phosphate ions and shown the formation of a precipitate with  $\text{HPO}_4^{2-}$ . The study of its solubility in phosphate solutions with different concentrations showed the formation of the  $\text{SnHPO}_4^0$  and  $\text{Sn}(\text{HPO}_4)_3^{4-}$  complex species. The first complex is predominant for phosphate concentrations  $< 0.03 \text{ mol L}^{-1}$ ; for higher concentrations, the second compound is the major species.

Two different studies, reported in the compilations of Sillén (1964, 1971) were devoted to reactions between stannous ions

and thiocyanate ions. In each case, complex species are formed with a number of ligands ranging from one to three.

### 3.4.3. Tin(IV) reactions with sulphate ions

Stability constants describing interactions between tin(IV) species and sulphates were determined by spectrophotometry (Brubaker, 1954, 1955). If sulphuric acid with concentrations  $> 3 \text{ mol L}^{-1}$  is added to Sn(IV) solutions, the  $\text{Sn}(\text{SO}_4)_2^0$  complex species would be formed. In more diluted medium ( $[\text{H}_2\text{SO}_4] < 0.8 \text{ mol.l}^{-1}$ ), only  $\text{SnSO}_4^{2+}$  would appear.

## 4. CONCLUSIONS

The objective of this work was to evaluate the sources of published inorganic tin thermodynamic data to determine the most reliable values that can be recommended. Whenever possible, we used the Guggenheim-Scatchard Specific Interaction Theory for the extrapolation of experimental data to zero ionic strength in the data evaluation process. The chemical equilibria considered in this study are hydrolysis reactions, precipitation reactions, redox reactions, and complexation reactions with halide, thiocyanate, phosphate, and sulphate ions for the Sn(II) and Sn(IV) inorganic species.

The study of the hydrolytic behaviour of tin(II) has shown that the main species formed are  $\text{SnOH}^+$ ,  $\text{Sn}(\text{OH})_2^0$  and  $\text{Sn}(\text{OH})_3^-$ . If tin(II) is present with high concentration, the  $\text{Sn}_2(\text{OH})_2^{2+}$  and  $\text{Sn}_3(\text{OH})_4^{2+}$  polynuclear species are predominant and have to be taken into account. Because of the high stability of  $\text{SnO}_2(\text{s})$ , few studies are available in the literature to understand the hydrolysis mechanisms of Sn(IV). This study has also enabled us to propose the most well-adapted standard potentials for the tin redox reactions.

Tin(II) can also react with other inorganic compounds such as halide or chalcogenide ions. In the presence of the latter compounds, the stannous ions form very stable solid phases.

Table 5. Equilibrium constants of inorganic tin with chalcogenide, sulphate, phosphate and thiocyanate ions

Chemical equilibrium	Method <sup>a</sup>	Medium	I (mol L <sup>-1</sup> )	pK <sub>s</sub>	Source
<i>Chalcogenide Ions</i>					
<i>Sn(II)</i>					
<i>Sulphide ions</i>					
SnS(s) ⇌ Sn <sup>2+</sup> + S <sup>2-</sup>	pot(Sn)		0 <sub>corr</sub>	26.94	(Sillén, 1964)
	lit		0 <sub>corr</sub>	26	(Sillén, 1964)
	lit		0 <sub>corr</sub>	25	(Sillén, 1964)
	sol	HCl 0.1	0 <sub>corr</sub>	26.6*	(Geyer and Mücke, 1963)
	ΔG <sup>b</sup>		0	20	(Pourbaix, 1964)
<i>Selenide ions</i>					
SnSe(s) ⇌ Sn <sup>2+</sup> + Se <sup>2-</sup>	ΔG <sup>c</sup>		0	38.4	(Buketov et al., 1964)
<i>Telluride ions</i>					
SnTe(s) ⇌ Sn <sup>2+</sup> + Te <sup>2-</sup>	ΔG <sup>c</sup>		0	44.7	(Buketov et al., 1964)
<i>Sulphate Ions</i>					
<i>Sn(IV)</i>					
Sn(SO <sub>4</sub> ) <sub>2</sub> <sup>0</sup> ⇌ Sn <sup>4+</sup> + 2SO <sub>4</sub> <sup>2-</sup>	spe	H <sub>2</sub> SO <sub>4</sub>	var	-0.85	(Brubaker, 1954)
SnSO <sub>4</sub> <sup>2+</sup> + 2H <sub>2</sub> O ⇌ SnO <sub>2</sub> (aq) + 2H <sub>2</sub> SO <sub>4</sub>	spe	H <sub>2</sub> SO <sub>4</sub> dil	0 <sub>corr</sub>	1.55**	(Brubaker, 1955)
<i>Phosphate Ions</i>					
<i>Sn(II)</i>					
SnHPO <sub>4</sub> <sup>0</sup> · 0.5H <sub>2</sub> O(s) ⇌ Sn <sup>2+</sup> + HPO <sub>4</sub> <sup>2-</sup> + 0.5H <sub>2</sub> O	sol	NaClO <sub>4</sub>	0.2	12.8 ± 0.1	(Cilley, 1968)
SnHPO <sub>4</sub> <sup>0</sup> ⇌ Sn <sup>2+</sup> + HPO <sub>4</sub> <sup>2-</sup>	sol	NaClO <sub>4</sub>	0.2	7.8 ± 0.1	(Cilley, 1968)
Sn(HPO <sub>4</sub> ) <sub>3</sub> <sup>4-</sup> ⇌ Sn <sup>2+</sup> + 3HPO <sub>4</sub> <sup>2-</sup>	sol	NaClO <sub>4</sub>	0.2	10.0 ± 0.1	(Cilley, 1968)
<i>Thiocyanate Ions</i>					
<i>Sn(II)</i>					
SnSCN <sup>+</sup> ⇌ Sn <sup>2+</sup> + SCN <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	2.2	1.17*	(Sillén, 1964)
	pot(Sn)	NaClO <sub>4</sub>	1.6	1.02	(Sillén, 1971)
Sn(SCN) <sub>2</sub> <sup>0</sup> ⇌ Sn <sup>2+</sup> + 2SCN <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	2.2	1.77*	(Sillén, 1964)
	pot(Sn)	NaClO <sub>4</sub>	1.6	1.54	(Sillén, 1971)
Sn(SCN) <sub>3</sub> <sup>-</sup> ⇌ Sn <sup>2+</sup> + 3SCN <sup>-</sup>	pot(Sn)	NaClO <sub>4</sub>	2.2	1.72 or 1.76*	(Sillén, 1964)
	pot(Sn)	NaClO <sub>4</sub>	1.6	1.46	(Sillén, 1971)

<sup>a</sup> See footnote (a) of Table 1 for the meaning of the abbreviation.

<sup>b</sup> Stability constants calculated from free-energy values without quotation of the source used.

<sup>c</sup> Stability constants calculated from thermodynamic data extrapolated from that of the corresponding sulphides.

0<sub>corr</sub> = Constants corrected to zero ionic strength by the authors.

var = Ionic medium varied.

\* Stability constant determined at 20°C and at \*\* 18°C.

With halide ions, the reactions appear well known but the complexes formed are only present when halide concentration is  $> 10^{-3}$  mol L<sup>-1</sup> and at pH generally  $< 4$ .

Although this work allowed the authors to identify the species formed and assign stability constants to the dominant inorganic tin reactions, additional thermodynamic data are necessary, particularly with carbonates, sulphates, or phosphates. Furthermore, to obtain reliable data, it seems necessary now to develop analytical methods for the speciation of inorganic tin at trace levels. These methods will allow future research to study tin mobility in the relevant conditions of a deep repository of nuclear waste and to compare results with those obtained by speciation calculations.

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