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Spectrophotometric determination of the stability of tin(II) chloride complexes in aqueous solution up to 300°C

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Abstract—The aim of this study was to gain insight into the aqueous chemistry of tin at elevated temperatures and pressures. For this purpose, the spectra of chloridotin(II) complexes in the ultraviolet region were measured in acid chloride solutions containing 1.00×10^{-4} m tin, 1.00×10^{-2} m HCl and varying NaCl concentrations up to 2.936 m from 25 to 300°C and at the equilibrium saturated vapor pressure of the system. The thermodynamic cumulative and stepwise formation constants of the individual tin(II) chloride species were calculated from the spectrophotometric data using a nonlinear least squares routine. At 25°C, a scheme including five species of $SnCl_n^{2-n}$ $(0 \leq n \leq 4)$ best fitted the available data. At 300°C however, $SnCl_2^0$ and $SnCl_3^-$ are the predominant species at total chloride concentrations >0.1 m. The presence of $SnCl_4^{2-}$ in concentrated (up to 3 m) chloride solutions was not detected above 150°C. With increasing temperature, chloridotin(II) complex stability is characterized by quite large endothermic enthalpies and large positive entropies of formation. It was concluded that tin(II) chloride complexes could be important in the transport and deposition of tin by hydrothermal ore solutions of moderate to high salinity. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Hydrothermal ore deposition occurs when metal complexes become unstable within a particular temperature–pressure regime in the Earth's crust. The instability of a given metal complex in a migrating hydrothermal fluid arises from a complex interplay of tectonics and permeability with the physical and chemical behavior of the aqueous fluid and its reactivity with the rocks through which it is moving. Changes in temperature, pressure, pH, redox potential, and ligand activity, as well as phase separation and boiling and mineral precipitation reactions, can lead to metal complex instability and hence to ore mineral deposition. In this study, our goal was to gain insight into the hydrothermal chemistry of tin.

The majority of known tin deposits are of hydrothermal origin, and an extensive literature exists concerning their formation. Among the more recent studies are those by Taylor (1979), Kelly and Turneaure (1970), Patterson et al. (1981), Stemprok (1982), Haapala and Kinnunen (1982) Eadington (1983), Zaw and Thet (1983) Durasova et al. (1984, 1985, 1986, 1997), Eugster (1985), Jackson and Helgeson (1985a, 1985b), Solomon et al. (1986), Kwak (1987), Sun and Eadington (1987), Heinrich (1990), Ryzhenko et al. (1993, 1997), Schrön (1994) Linnen and Williams-Jones (1994), Halter et al. (1998a, 1998b) and Audétat et al. (2000). A number of these (e.g., Heinrich, 1990; Halter et al., 1998b) have emphasized not only the importance of the metal complex equilibria but also the redox and pH-dependent behavior of cassiterite precipitation in the formation of tin ore deposits. An understanding of the hydrothermal transport and deposition of tin is premised on a knowledge of the relevant metal complex equilibria in high temperature–high pressure aqueous systems. Hydrothermal ore fluids are multicomponent electrolyte solutions of generally low oxidation potential in which the dissolved tin is predominantly in the +2 oxidation state. Such natural fluids contain a number of ligands that are known to form stable complexes with Sn^{2+} at 25°C. Of particular interest are the simple halide complexes with fluoride and chloride, as well as hydrolyzed species with the hydroxyl ligand. At ambient temperature, the Sn(II) fluoride complexes are appreciably more stable than the equivalent species with chloride. For example, data on the equilibrium formation constants from Djokic-Konstantinovska and Zmbova (1985) and Samoilenko et al. (1976) for 1 mol/dm^3 Na/LiClO$_4$ media give $\beta_1 = 4.56$ (SnF^+) and $\beta_1 = 1.08$ ($SnCl^+$), thus demonstrating the more than three orders of magnitude difference in stability between simple monohalogenidotin(II) complexes at 25°C. However, hydrothermal ore solutions generally contain at least two to three orders of magnitude more chloride than fluoride, bearing in mind that the dominant electrolyte salt in crustal hydrothermal fluids is sodium chloride. Thus, there is a trade-off between complex stability and ligand availability in deciding which complexes may be most important in the formation of hydrothermal tin deposits. Furthermore, there is a dearth of experimentally based thermodynamic data pertaining to the stability of the halogenidotin(II) complexes at elevated temperatures and pressures. There also are few reliable measurements or estimates of the fluoride concentration of hydrothermal ore fluids. In this study, our aim was to obtain thermodynamic data on the stepwise formation of chloridotin(II) complexes up to 300°C at saturated vapor pressures as an approach toward gaining a better understanding of the processes defining the formation of hydrothermal tin deposits.

There have been numerous studies of tin(II) chloride complexes at ambient temperatures using potentiometric, conductance, and solubility methods to establish the equilibrium formation constants (i.e., Prytz, 1928a; Garrett and Heiks, 1941;

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Table 1. Stability Constants for Chloridotin(II) Complexes at 25°C.

Solution	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	Source
0.1–1 M HCl ($I = 0$)	1.51	2.25	2.02	1.50	1
2.03 M $NaClO_4$	1.05	1.76	1.14	1.14	2
3 M $NaClO_4$	1.14	1.70	1.68	—	3
2.03 M $NaClO_4$	1.06	1.72	1.50	—	4
3 M $HClO_4$	1.18	1.74	1.67	—	5
4.0 M HCl–2.0 M H_2SO_4	1.45	2.35	2.46	2.27	6
0.01–0.80 M HCl	1.05	1.71	1.69	—	7
0.5–6.0 M $NaClO_4$	1.87	2.38	1.93	—	8
2.03–3 M Na/$HClO_4$ ($I = 0$)	1.64	2.43	1.40	—	9
1 M $LiClO_4$	1.08	1.85	—	—	10
1 M $NaNO_3$	0.73	1.08	1.93	—	11

Note: (1) Prytz (1928a), (2) Duke and Courtney (1950), (3) Vanderzee and Rhodes (1952), (4) Rabideau and Moore (1961), (5) Tobias and Hugus (1961), (6) Haight et al. (1962), (7) Carpentier (1969), (8) Fedorov et al. (1975), (9) Vasilev et al. (1976); calculated from refs 2, 3, and 5), (10) Samoilenko et al. (1976), (11) Pettine et al. (1981).

M refers to mol/dm^3.

Duke and Courtney, 1950; Vanderzee and Rhodes, 1952; Rabideau and Moore, 1961; Tobias and Hugus, 1961; Haight et al., 1962; Fedorov et al., 1975; Pettine et al., 1981) and, to a lesser extent, spectrophotometric methods (Grant, 1935; Fromherz and Walls, 1936; Hüniger and Rudolph, 1940; Ishibashi et al., 1959; Illner, 1962; Hastie et al., 1969; Maya, 1978). Literature data pertaining to the equilibrium formation constants at 25°C are summarized in Table 1. Mixed hydroxo-chloride complexes have been studied by Smith (1928), Randall and Murakami (1930), Tobias (1958), Holleman and Wiberg (1976), and Pettine et al. (1981). In addition, fluoride and hydroxide complexes of Sn(II) have been studied at 25°C by Prytz (1928b), Gorman (1939), Schaap et al. (1954), Tobias (1958), Connick and Paul (1961), Haight and Johansson (1968), Hall and Slater (1968), Barsukov and Klintsova (1970), Bond and Taylor (1970), Pettine et al. (1981), Djokic-Konstantinovska and Zmbova (1985) and Djurdjevic et al. (1995).

At high temperatures and pressures, there are a number of experimental studies that provide information on the stability and stoichiometry of tin(II) chloride complexing. Dadze et al. (1981) measured the solubility of SnO_2 in KCl, HCl, and HNO_3 solutions at 200 to 400°C at 1000 bar. In addition, Nekrasov and Dadze (1973) measured the solubility of casseriterite in aqueous chloride solutions at 300 and 400°C but the oxidation potential in both of these two studies was unknown. More recently, Pabalan (1986) measured the solubility of SnO_2 in chloride solutions at 200 to 350°C and equilibrium vapor pressures and reported equilibrium constants for $SnCl_n^{2-n}$ ($1 \leq n \leq 4$). Wilson and Eugster (1990) measured the solubility of SnO_2 in HCl solutions from 400 to 700°C at 1500 bar and identified the complexes $SnCl^+$, $SnCl_2°$ and $SnCl_3^-$. The $SnCl_2°$ species was found to predominate at 700°C. From cassiterite solubility measurements at 700 to 800°C and 2000 bar, Taylor and Wall (1993) concluded that complexes such as $NaSnCl_3°$ accounted for the observed tin concentrations. A few experimental data for fluoride-containing systems by Klintsova et al. (1975), Kovalenko et al. (1992), and Kovalenko and Ryzhenko (1997) give information on the stability of SnFCl° and $SnF(OH)_2°$, as well as $SnCl(OH)_2°$ and $Sn(OH)_4^{2-}$ at 500°C and 1000 bar. Sn(IV) hydroxide and fluoride complex equilibria have also been studied at elevated temperatures by Kuril'chikova and Barsukov (1970), Kuril'chikova and Marov (1970), and Klintsova and Barsukov (1973). Sherman et al. (2000) recently performed X-ray absorption spectroscopic (EXAFS) measurements on chloride solutions containing Sn(II) and Sn(IV) from 25 to 350°C at equilibrium vapor pressures.

2. EXPERIMENTAL METHOD

The absorption spectra of Sn(II) chloride complexes were measured in the ultraviolet region using a Varian Cary4E UV-spectrophotometer. Data were collected at seven temperatures from 25 to 300°C at saturated vapor pressures on a series of 15 solutions having a 1.00 × 10 to 4 or 5.00 × 10 to 4 m tin concentration and total chloride concentrations (HCl + NaCl) ranging from 0.010 m to 2.936 m, where HCl was maintained constant at 0.010 m. The spectra were collected using a titanium alloy autoclave containing 6-mm-thick silica glass windows using an experimental setup similar to that described by Suleimenov and Seward (2000). Freshly prepared, deoxygenated solutions were pumped through the optical cell using an HPLC pump with pressures maintained at 15 bar above the saturated vapor pressure with a back pressure regulator. Measurements of the background absorbance (i.e., blank = window + solvent + chloride) for each solution at each temperature were carried out after the spectrum for each tin-containing solution was obtained.

The hydrolysis of Sn(II) solutions leads to the formation of simple hydroxotin(II) species such as $SnOH^+$, $Sn(OH)_2°$, and $Sn(OH)_3^-$ (Baes and Mesmer, 1976). At high tin concentrations, the hydroxyl-bridged polynuclear species, $Sn_2(OH)_2^{2+}$ and $Sn_3(OH)_4^{2+}$ were identified (Tobias, 1958). Mixed ligand species such as SnCl(OH)° have also been reported (Holleman and Wiberg, 1976). The hydrolysis of Sn(IV) solutions gives rise to species such as $Sn(OH)_6^{2-}$ and $SnCl_4(OH)_2^{2-}$ (Donaldson and Grimes, 1989; Jander and Blasius, 1983). To prevent hydrolysis, the tin-containing solutions in this study were prepared by addition of anhydrous $SnCl_2$ (Aldrich 99.99%) to NaCl (Merck Suprapur) solutions having a constant concentration of 0.010 m HCl (Merck Suprapur). Solutions containing tin in the +2 oxidation state are very sensitive to oxidation by atmospheric oxygen. It is important to avoid the formation of any Sn(IV) because Sn^{4+} readily hydrolyzes, and its chloride complexes also absorb strongly at ultraviolet wavelengths. Solutions were therefore prepared under a continuous flow of oxygen-free argon using Schlenk tube techniques. The deoxygenated argon was produced by passing high-purity argon through a column of copper filings at 420°C. The HCl was standardized by titration against recrystallized borax that had been equilibrated over a concentrated sucrose–salt solution.

3. EXPERIMENTAL RESULTS

Some typical spectra of chloride solutions containing 1.00×10^{-4} m total dissolved tin and corrected for solvent, chloride ion, and window absorbance are shown in Figures 1, 2, and 3. The chloride ion charge-transfer-to-solvent absorption bands occur in the vacuum ultraviolet region at 57,378 cm^{-1} and 60,995 cm^{-1} at 25°C (Fox et al., 1978) but with increasing temperature, these shift to lower energies (Seward, 1984). Inspection of Figures 1, 2, and 3 indicates that (1) with increasing chloride concentrations at constant temperature, the spectra alter significantly, thus reflecting changes in the coordination of Sn^{2+}; (2) with increasing temperature and at constant chloride concentration, the spectra also change considerably as a result of changes in the stability of various Sn(II) chloride complexes; and (3) with increasing temperature, the spectra also appear to undergo a red shift and associated decrease in absorbance. Parts of the Sn(II) chloride spectra overlap with the steep portion of the intense, chloride ion absorption edge, and all absorbances in

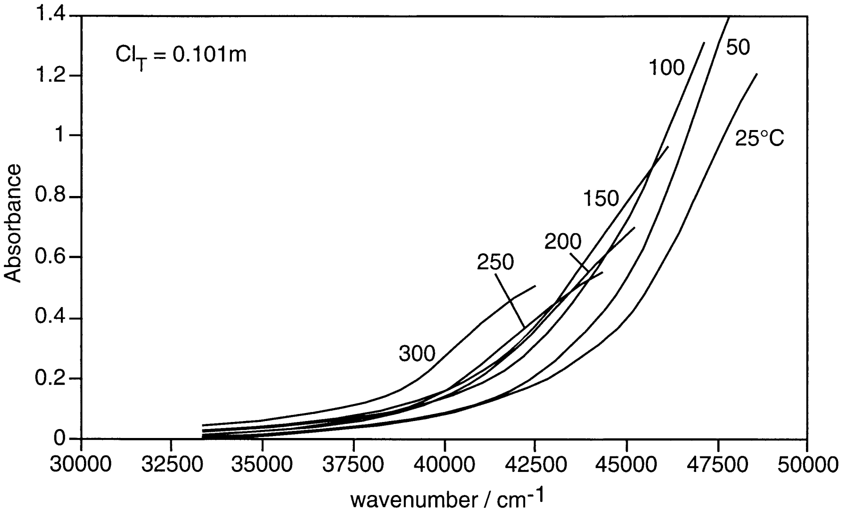

Fig. 1. Spectra of solution containing 1.00 × 10^{-4} m tin and 0.101 m total chloride at temperatures from 25 to 300°C; the spectra have been corrected for solvent, chloride and window absorbance.

excess of 1.5 were omitted from the data set. This commonly affected the spectral region below 210 nm. The spectra were corrected for water and chloride ion absorbance, as well as for window absorbance by subtracting the spectrum of the corresponding NaCl/HCl blank solution.

The absorbance of a solution at any given wavelength is defined by

$$A_\lambda = \sum_{o}^{n} [SnCl_n^{2-n}]\, \varepsilon_n l \qquad (1)$$

in accordance with Beer's law, where $[SnCl_n^{2-n}]$ is the molar concentration of a particular Sn(II) complex, ε_n is the corresponding molar absorptivity of each species, and l is the path length.

Eqn. (1) may be rewritten such that

$$A_\lambda = \sum_{o}^{n} \beta_n [Sn^{2+}]\,[Cl^-]^n\, \gamma_{Sn^{2+}} \gamma_{Cl^-}^{n} \gamma_n^{-1}\, \varepsilon_n l \qquad (2)$$

where β_n is the cumulative formation constant given by

$$\beta_n = \frac{[SnCl_n^{2-n}]\ \gamma_n}{[Sn^{2+}]\ \gamma_{Sn^{2+}}\ [Cl^-]^n\ \gamma_{Cl^-}^{n}} \qquad (3)$$

The individual ion activity coefficients, γ_n (and $\gamma_{Sn^{2+}}$) were obtained from an extended Debye-Hückel equation,

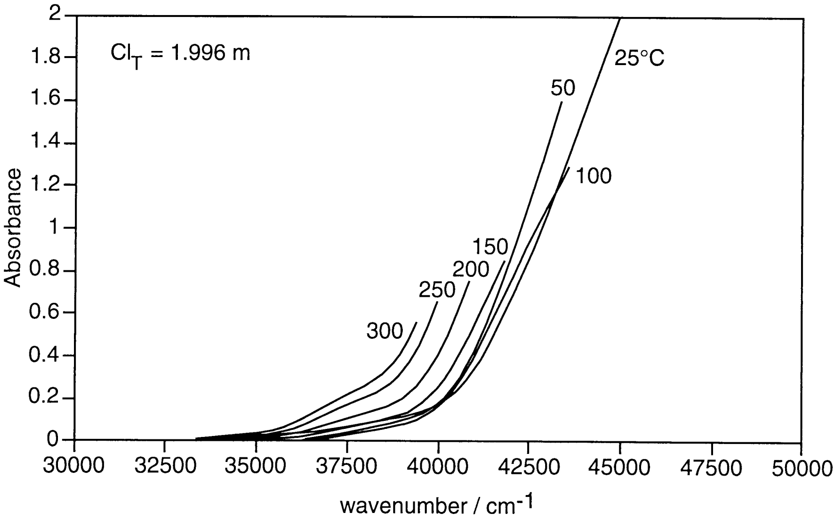

Fig. 2. Spectra of solution containing 1.00 × 10^{-4} m tin and 1.996 m total chloride at temperatures from 25 to 300°C; the spectra have been corrected for solvent, chloride and window absorbance.

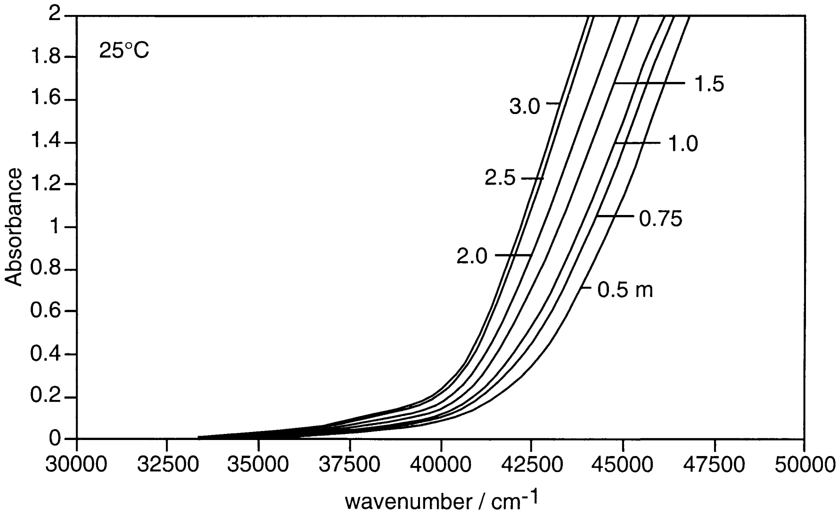

Fig. 3. Spectra of solutions containing 1.00×10^{-4} m tin and varying concentrations of total chloride at 25°C; the spectra have been corrected for solvent, chloride and window absorbance.

$$\log \gamma_n = -\frac{A|z_n|^2 I^{1/2}}{1 + B\mathring{a}_n I^{1/2}} + b°I \qquad (4)$$

where I is the ionic strength defined in the conventional way.

By analogy with the values given by Kielland (1937), the ion size parameters were taken as 6 for $n = 0$, 4 for $n = 1$ and $n = 3$, and 5 for $n = 4$ and were not considered to change significantly with temperature (Seward, 1984). The activity coefficient for $SnCl_2^0$ was assumed to be unity at all temperatures. b° is an empirical, temperature-dependent interaction parameter for aqueous NaCl solutions taken from Helgeson et al. (1981). A and B are the conventional molal Debye-Hückel coefficients, the high temperature values of which were taken from Helgeson and Kirkham (1974b). $\gamma_{Sn^{2+}}$ and γ_{Cl^-} are the individual ion activity coefficients for the free Sn^{2+} ion and the chloride ion, respectively.

To obtain γ_n, the ionic strength is required and hence the concentration of free chloride ion and charged tin species in solution. For each solution, the mass balance of tin is given by

$$[Sn]_T = \sum_{o}^{n} [SnCl_n^{2-n}] \qquad (5)$$

An expression defining the chloride ion mass balance is

$$[Cl]_T = [Cl]^- + [NaCl°] + [HCl°] + Q \qquad (6)$$

where Q is the total concentration of chloride bound as Sn(II) complexes,

$$Q = \sum_{n=1}^{n} n[SnCl_n^{2-n}] \qquad (7)$$

and $[Cl]_T$ is the total chloride in solution comprising that derived from sodium chloride, hydrogen chloride, and tin(II) chloride. As a simplifying assumption, let us consider that the solutions are comprised only of NaCl together with a small tin(II) chloride component.

The equilibrium dissociation constant for the sodium chloride ion pair is given by

$$K_d = \frac{[Na^+] \cdot [Cl^-]\gamma_{Na^+}\gamma_{Cl^-}}{[NaCl°]\gamma_u} \qquad (8)$$

The activity coefficient, γ_u, of the neutral ion pair is taken as unity. The mass balance of sodium ion can be expressed as

$$[Na^+] = [Cl]_T - [NaCl°] - 2M_T \qquad (9)$$

where M_T is the total tin concentration (added as $SnCl_2$).

Given values for γ_{Cl^-}, γ_{Na^+}, and M_T and combining Eqns. (8) and (9) with Eqn. (6) yields a quadratic expression from which $[Cl^-]$, the concentration of free chloride ion may be calculated; that is,

$$[Cl^-]^2 + [Cl^-] \cdot \left[\frac{K_d}{\gamma_{Cl^-}^2} + Q - 2M_T\right] + \left[(Q - [Cl]_T)\frac{K_d}{\gamma_{Cl^-}^2}\right] = 0 \qquad (10)$$

The individual ion activity coefficient, γ_{Cl}, for the chloride ion is taken as the mean ionic activity coefficient of sodium chloride, which may be calculated from

$$\gamma_{Cl^-} = \gamma_{st}\left[\frac{1 - \gamma_{st}^2[Cl]_T}{K_d\gamma_u}\right]^{-1} \qquad (11)$$

Values for γ_{st}, the stochiometric mean activity coefficient of sodium chloride, are from Silvester and Pitzer's (1977) treatment of literature data up to 300°C and data for K_d as a function of temperature are from Ho et al. (1994).

In the derivation above, we have considered the solutions to consist entirely of NaCl, that is, the small HCl component has been treated as NaCl. In these experiments, a series of solutions

Table 2. Values of the Equilibrium Cumulative Formation Constants. β_n for Chloridotin(II) Complexes.[a]

	25°C	50°C	100°C	150°C	200°C	250°C	300°C
$\log\beta_1$	1.42 (±0.05)	1.45 (±0.08)	1.43 (±0.10)	1.52 (±0.04)	1.58 (±0.07)	1.65	1.78
$\log\beta_2$	2.18 (±0.03)	2.25 (±0.08)	2.25 (±0.08)	2.52 (±0.09)	2.83 (±0.06)	3.06 (±0.05)	3.56 (±0.05)
$\log\beta_3$	2.33 (±0.04)	2.21 (±0.09)	2.39 (±0.06)	2.59 (±0.10)	3.13 (±0.04)	3.96 (±0.04)	4.66 (±0.03)
$\log\beta_4$	2.03 (±0.02)	1.98 (±0.10)	1.95 (±0.10)	1.97 (±0.14)	2.08		

Note: The terms in parantheses correspond to one standard deviation; values without standard deviations are extrapolated.

[a] Obtained from the measurements at different temperatures and at the saturated vapor pressure of the system.

having constant 0.010 m HCl concentration with varying NaCl concentrations up to 2.936 m were studied. It can be shown (e.g., Robinson and Stokes, 1968) that the activity coefficient of 0.010 m HCl in such a series of solutions of increasing NaCl concentration is essentially identical to that of pure NaCl, and our simplification is thus reasonable. Nevertheless, the activity coefficient relations for NaCl–HCl mixtures are quite well defined at 25°C (see Macaskill et al., 1977, and references therein). At 25°C, a rigorous treatment of the activity coefficients of both NaCl (0.015–2.926 m) and HCl (0.010 m) in the NaCl–HCl solutions yielded values of β_n for $SnCl_n^{2-n}$ identical to those given in Table 2. A more rigorous treatment of the NaCl–HCl activity relations at elevated temperatures seemed unjustified, given the small differences in the activity coefficients being considered, as well as the inherent uncertainties in estimating the values for mixed NaCl–HCl media. At elevated temperatures (i.e., $>$100°C), there is a paucity of data pertaining to mixed electrolyte solutions, although Lietzke et al (1965) reported activity coefficients for a limited range of NaCl–HCl mixtures from emf measurements up to 175°C. The relevant activity coefficients in NaCl–HCl solutions at elevated temperatures to 300°C may be estimated using the available Pitzer parameters (Pitzer and Kim, 1974) for the two 1-1 electrolytes from Silvester and Pitzer (1977, 1978) and Ruaya and Seward (1987). Unfortunately, there is a lack of suitable, experimentally based activity coefficient data for NaCl–HCl mixtures with which to compare (especially at temperatures $\geq$200°C); furthermore, uncertainties in the available activity coefficient data for pure HCl at elevated temperatures have been discussed by Ruaya and Seward (1987), Holmes et al. (1987) and Simonson et al. (1990). Bearing in mind that HCl is a minor component in the majority of the solutions studied and that the ion pair formation constants for NaCl and HCl are similar over the temperature range of our study at equilibrium vapor pressures (Ho et al., 1994, 2001), our somewhat simplified data treatment is considered to have a negligible effect on the derived values of β_n given in Table 2. Of course, this approach could have been circumvented by studying Sn(II) chloride complex equilibria in pure HCl solutions. However, photochemical or autoxidation reactions may occur with metal cations in concentrated HCl solutions as reported by Craig and Davidson (1951), Duke and Pinkerton (1951), Posner (1953), Bergh and Haight (1962), and Kodina et al. (1990). In addition, small concentrations of what are thought to be chlorine oxidation products form in concentrated HCl solutions at temperatures $>$200°C (perhaps photocatalyzed), and these species absorb intensely in the ultraviolet region (Heinrich and Seward, 1990), thus making UV spectra for $SnCl_n^{2-n}$ species uninterpretable.

The calculation of the equilibrium formation constants for $SnCl_n^{2-n}$ complexes and their associated molar absorptivities was performed with a modified version of the nonlinear least squares computer program, SQUAD (Leggett, 1985), using a strategy similar to that employed by Seward (1984), Heinrich and Seward (1990), and Bebié et al. (1998). To relate the molar concentration scale of Beer's law to the molal scale of standard thermodynamic convention, the measured absorbances, A_λ, were corrected for the isothermal variation of solution density with changing NaCl concentration at each temperature as described by Heinrich and Seward (1990). The required density data for NaCl solutions up to 300°C were taken from Ellis (1966) and Grant-Taylor (1981). The data at 25°C were treated before the other data sets for higher temperatures. Values of β_{mn} at 25°C were then employed as initial estimates in the treatment of the 50°C data. This procedure was repeated in the stepwise way up to 300°C such that each final set of refined β_{mn} provided the initial estimates for the data set at the next higher temperature. The βs reported here are related to the hypothetical 1 molal standard state.

4. EQUILIBRIUM FORMATION CONSTANTS AND COMPLEX STABILITY

At 25°C, the scheme of species that best fit the data was β_{mn}, where $m = 1$ and $1 \leq n \leq 4$; that is, five species, Sn^{2+}, $SnCl^+$, $SnCl_2^0$, $SnCl_3^-$, and $SnCl_4^{2-}$ are present in chloride solutions from 0.0106 to 2.936 m. There was no evidence for polynuclear species at 25°C or, in fact, at any higher temperature up to 300°C. The values of β_{mn} were evaluated simultaneously by treating all the data and these values are given in Table 2. At 50, 100, and 150°C, a scheme of five species also generated the best values of β_n. However, the concentration of $SnCl_4^{2-}$ in the solutions studied decreases with increasing temperature, and hence its contribution to the measured spectra is also diminished. This is reflected by increase in the standard deviation for β_4 (Table 2).

At 200°C and within the range of chloride concentrations studied in these experiments ($0.0106\ m \leq Cl_T \leq 2.936\ m$), the tetrachloridotin(II) species does not occur in high enough concentrations to permit evaluation of β_4. Thus, at 200°C, a scheme of only four species best fit the data. A model including five species (i.e., Sn^{2+}, $SnCl^+$, $SnCl_2^0$, $SnCl_3^-$, and $SnCl_4^{2-}$) yielded an unacceptably low value of β_4 with such a large standard deviation (more than three times the magnitude of β_4) and high minimized sum of squares that this model was rejected as meaningless. Therefore, a four-species model with improved standard deviations and minimized sum of squares was accepted. An extrapolated value of β_4 is included in Table 2 but should be regarded as approximate.

At 250°C and 300°C, some difficulties arose in obtaining reliable values of β_1 simultaneously with β_2 and β_3. This occurred in part because the stability of both Sn^{2+} and $SnCl^+$

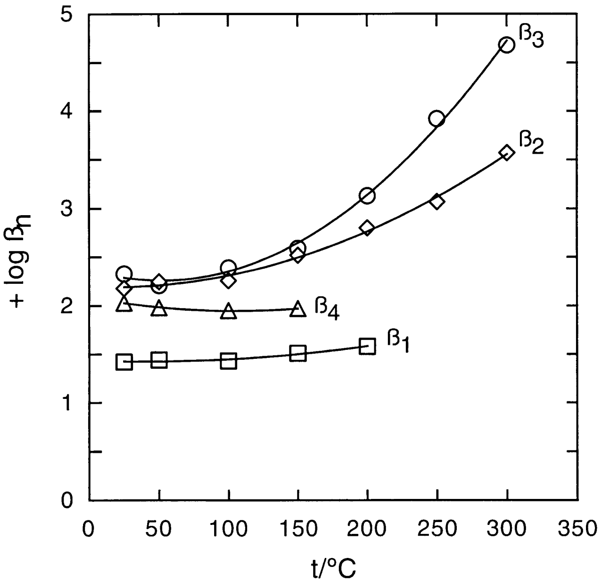

Fig. 4. The variation of the equilibrium cumulative formation constants, β_n, obtained in this study as a function of temperatures up to 300°C at the saturated vapor pressure of the system.

shifted to lower chloride concentrations. Furthermore, the lowest chloride concentration in these experiments was 0.0100 m, and at 300°C, only two solutions having chloride concentrations of 0.0106 and 0.0256 m contained significant contributions to the measured absorbances from both Sn^{2+} and $SnCl^{+}$. Hence, β_2 and β_3 were obtained by a refinement of the data for solutions having chloride concentrations ≥ 0.1 m. β_1 at 250 and 300°C was obtained by extrapolation of the lower temperature data. Similar values of β_1 were obtained by a nonlinear least squares refinement of all the data simultaneously to give values for, β_1, β_2, and β_3. However, the standard deviations associated with these values of β_1 were unacceptably large, and the graphically extrapolated values are considered more reliable. The overall variation of β_n with temperature is shown in Figure 4.

Using the values of β_n obtained in this study, together with the values of ε_n (molar absorptivity), generated at each wavelength at each temperature, the original measured spectra may be recalculated. This provides a simple criterion with which to assess the compatibility of β_n and ε_n with the experimental data from which they were derived. Figure 5 demonstrates the good agreement between the experimentally measured and calculated spectra. A comparison of the data obtained in this study at 25°C with those in the literature is complicated by the considerable scatter of previously published values of β_n. Much of the literature data for β_n ($1 \leq n \leq 4$) apply to high ionic strength media (Table 1); however, Prytz's (1928a) study in which β_1 to β_4 at 25°C and $I = 0$ are derived is available. The agreement between the value for β_1 and β_2 of this study with Prytz's values ($\log\beta_1 = 1.51$ and $\log\beta_2 = 2.25$), derived from potentiometric measurements, is quite good. However, the values for β_3 and β_4 obtained in Prytz' study are somewhat lower (i.e., $\log\beta_3 = 2.02$ and $\log\beta_4 = 1.14$). At 25°C, most of the other potentiometric studies have been carried out at higher ionic strength (see Table 1) and are thus not strictly comparable with the data obtained in this study.

Values of β_2, β_3, and β_4 at 25°C in the literature are also rather variable. (Table 1) and reflect the different ionic media associated with each set of experiments. For example, $\log\beta_2$ varies from 1.08 up to 2.25 and $\log\beta_4$ varies from 1.14 up to 1.50. However, only Prytz (1928) and Duke and Courtney (1950) found $SnCl_4^{2-}$ in their solutions and derived values of β_4. Fedorov et al. (1975) studied mixed bromido(chlorido)-complexes and chloro-complexes of tin at 25°C up to Cl_T = 6 m but did not report the presence of $SnCl_4^{2-}$.

After correction for solvent and chloride ion absorbance, measured spectra such as those given in Figures 1, 2, and 3, may be deconvoluted into their individual component gaussian bands as shown in Figure 6. The spectrum of an 0.101 m chloride solution at 25°C is mainly due to $SnCl^{+}$ with contributions from Sn^{2+}, $SnCl_2^0$, $SnCl_3^-$, and $SnCl_4^{2-}$, whereas at 300°C, the overall absorption envelope is due to $SnCl_2^0$ and $SnCl_3^-$ with a minor contribution from Sn^{2+} and $SnCl^{+}$. On the other hand, the spectrum of a 2.936 m chloride solution at 25°C is rather more simple with contributions from three species (i.e., $SnCl_4^{2-}$ with minor contributions from $SnCl_3^-$ and $SnCl_2^0$). However, the deconvoluted spectrum at 300°C is simply composed of absorption bands arising mainly from $SnCl_3^-$ with a smaller contribution from $SnCl_2^0$.

A better understanding of the complexities of these deconvoluted spectra may be obtained by examination of the individual spectra of the various chloridotin(II) species and free Sn^{2+} at 25°C. Earlier studies by Fromherz and Walls (1936) assigned a maximum of an $SnCl_2^0$ band at 46500 cm^{-1}; they also reported a band of $SnCl_4^{2-}$ at 45760 cm^{-1}. With the stepwise addition of chloride ligands, the absorption bands for each species as one proceeds from Sn^{2+} to $SnCl_2^0$ occur at increasingly longer wavelengths (see also Hüniger and Rudolph, 1940).

The dichlorido-, trichlorido-, and tetrachloridotin(II) species have intense bands at lower wave numbers (longer wavelengths) and there is also some indication that $SnCl_4^{2-}$ may have a higher energy band close to or within the vacuum ultraviolet region (Fernandez et al., 1986). All these results are in good agreement with the present study. The maximum absorption of $SnCl_2^0$ is around 47000 cm^{-1} at 25°C. At higher temperatures, the high-energy bands of the various chloridotin(II) species are obscured by the intense chloride ion charge-transfer-to-solvent absorption. The bands shift to lower wave numbers with increasing temperatures as the coordination sphere expands, causing the relevant electronic transitions to decrease in energy (see also Seward, 1984).

Tin(II) is characterized by a $4d^{10}\,5s^2$ configuration and the spectra of aquated Sn^{2+} and Sn(II) chloride complexes are hence dominated by intershell, central ion, $s^2 \rightarrow sp$ transitions rather than by electron (charge) transfer. The *d*-shells are not directly involved in bonding, whereas the outer s and p orbitals of the post-transition metal ions are the actual bonding orbitals (McClure, 1959). Thus the low energy bands for the free Sn^{2+} ion as well as the low energy bands of the tin(II)-chloride complexes may be tentatively assigned to the transition from the $^1S_0$ ground state to the $^3P_1$. The higher energy bands are

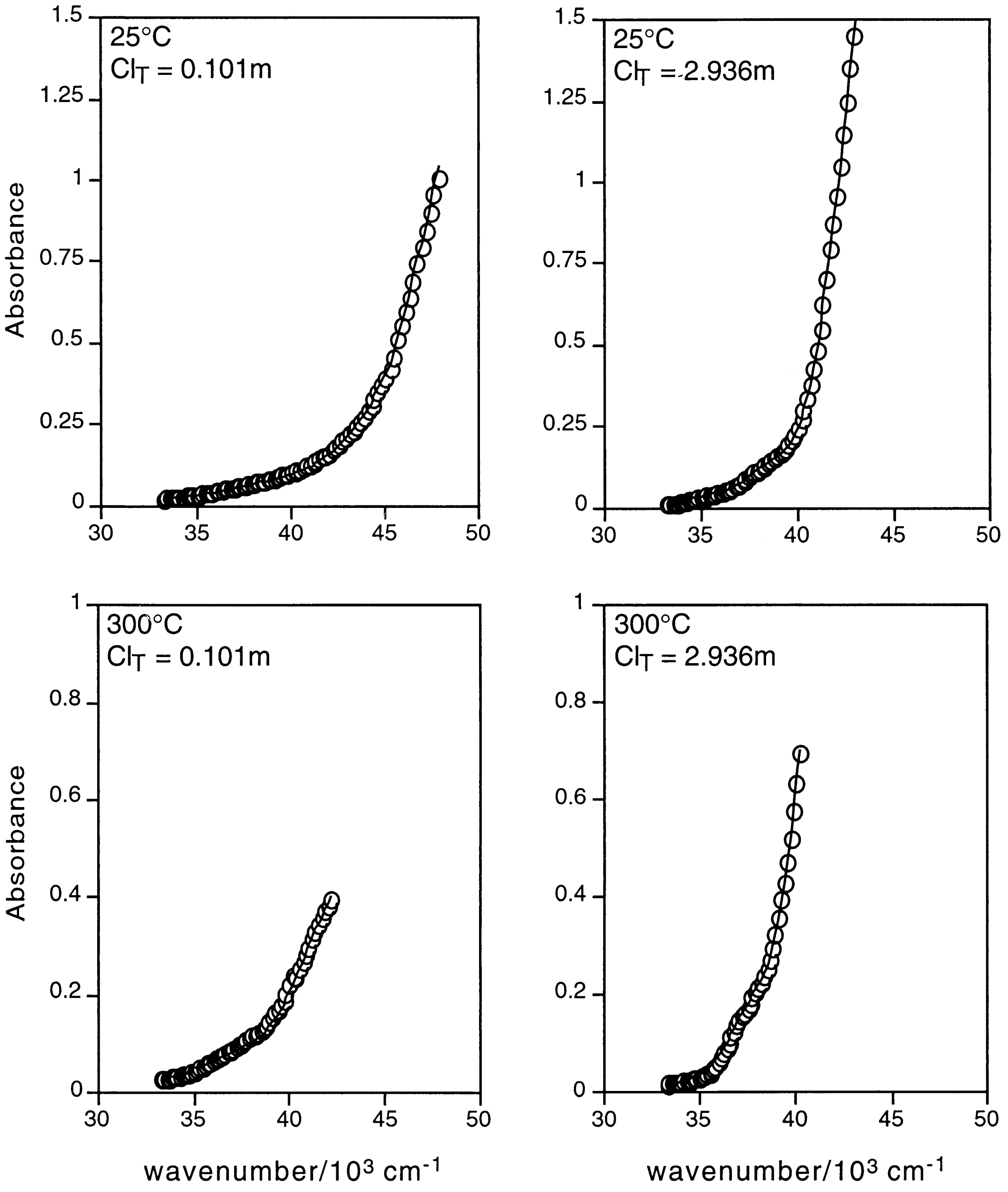

Fig. 5. Spectra demonstrating the agreement between calculated (solid lines) and experimental (circles) absorbances for solutions containing 1.00 × 10^{-4} m tin and having chloride concentrations of 0.101 m and 2.936 m at 25 and 300°C.

attributed to stronger spin allowed $^1S_0 \rightarrow {}^1P_1$. $^3P_2$ transitions could also occur within intermediate energy bands (McClure, 1959).

The distribution of chloridotin(II) complexes as a function of total chloride concentration and temperature may be calculated from the values of β_n obtained in this study (Fig. 7). At 25°C, the free Sn^{2+} ion predominates at chloride concentrations below 0.05 m, whereas at 300°C, Sn^{2+} is more complexed in dilute solutions and is a minor contributor to the overall speciation scheme at chloride concentrations higher than 0.025 m. With increasing temperature, there is also a decrease in the maximum coordination number of the species predominating in any given chloride solution. The tetrachloridotin(II) complex predominates in 3.0 m chloride solutions at 25°C (Fig. 7), but at 300°C, $SnCl_3^-$ is the dominant species. No significant concentration of $SnCl_4^{2-}$ occurs above 150°C for a range of chloride concentrations from 0.01 to 3.0 m. The $SnCl_3^-$ complex increases in stability and predominates at Cl_T >0.10 m at 300°C. All the above mentioned observations are consistent with trends reported by Suleimenov and Seward (2000), Bebié et al. (1998), Heinrich and Seward (1990), Ruaya and Seward (1986), and Seward (1976, 1984) for manganese(II), thallium(I), iron(II), zinc(II), lead(II), and silver(I) chloride complexes with increasing temperature.

Values of $\ln\beta_1$, $\ln K_2$, and $\ln K_3$ as a function of temperature were fitted to a number of equations of the type

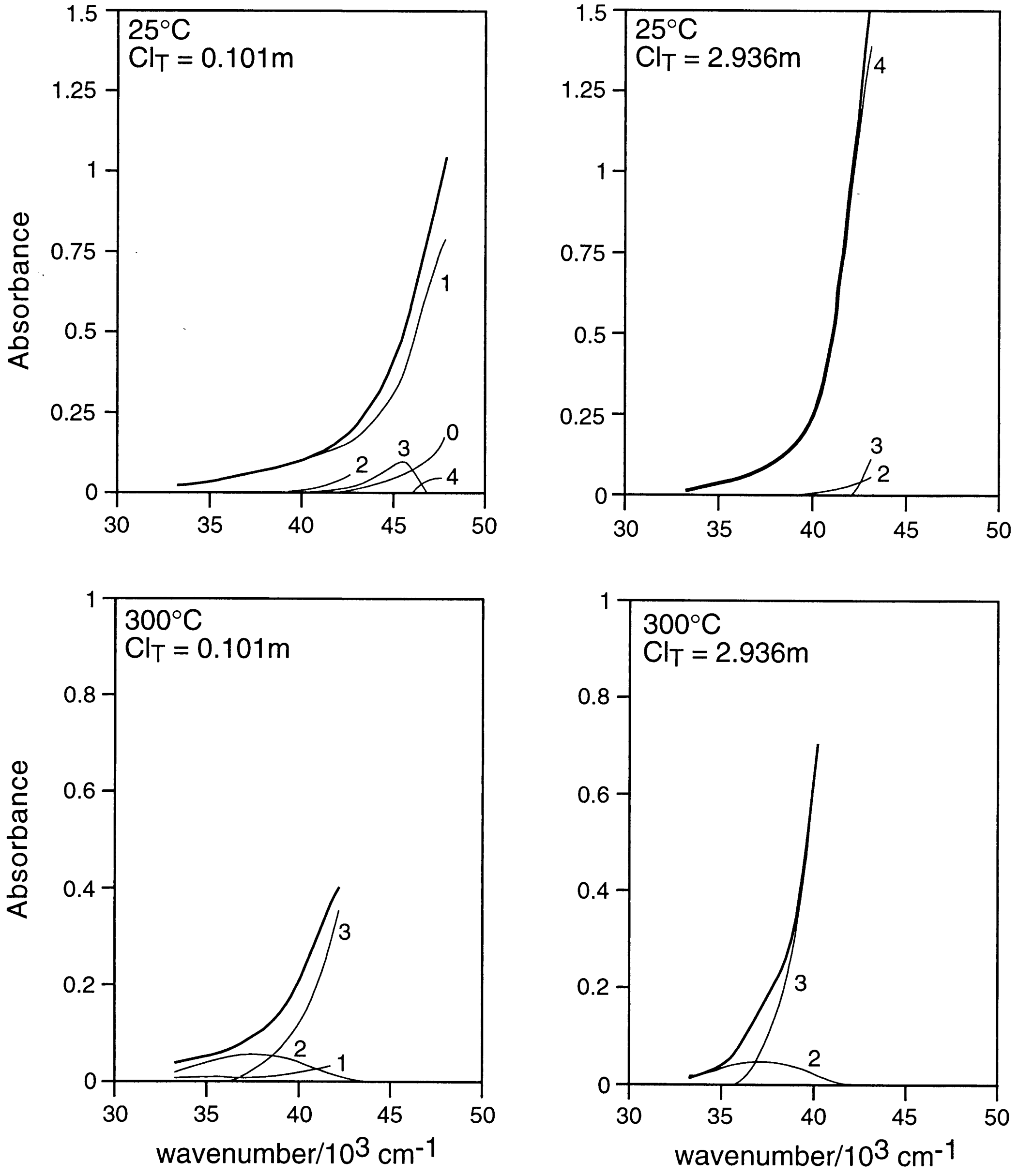

Fig. 6. Spectra of chloride solutions containing 1.00 × 10^{-4} m tin and having chloride concentrations of 0.101 m and 2.936 m at 25 and 300°C deconvoluted into their individual component bands; the bands attributable to each SnCl_n^{2-n} complex are defined according to the ligand number (e.g., curve labeled *2* refers to the SnCl_2^0 complex).

$$\ln K_n = A + BT + CT^2 + D/T + E \ln T \qquad (12)$$

where T is in Kelvin and K_n is the stepwise formation constant defined by,

$$K_n = \frac{\beta_n}{\beta_{n-1}} \qquad (13)$$

The values that best fit the temperature variation of each equilibrium constant together with appropriate constants are given in Table 3. Different forms of Eqn. (12), including terms varying as $1/T$ or $\ln T$, were attempted, but the quality of the fit did not improve significantly.

The equations describing the temperature variation of the stepwise formation constants (Table 3) were differentiated to give ΔH^0 for the formation of the different tin complexes at different temperatures. The entropy attending stepwise complex formation was then obtained in the conventional way from the associated Gibbs free energy and enthalpy of complex formation.

The formation of the monochloridotin(II) complex involves the interaction between a moderately "soft," class b (Donaldson, 1967) acceptor (Sn^{2+}) of $d^{10}s^2$ configuration and the moderately "soft" chloride ligand. Such metal–ligand bonds will have some covalent character with complex formation

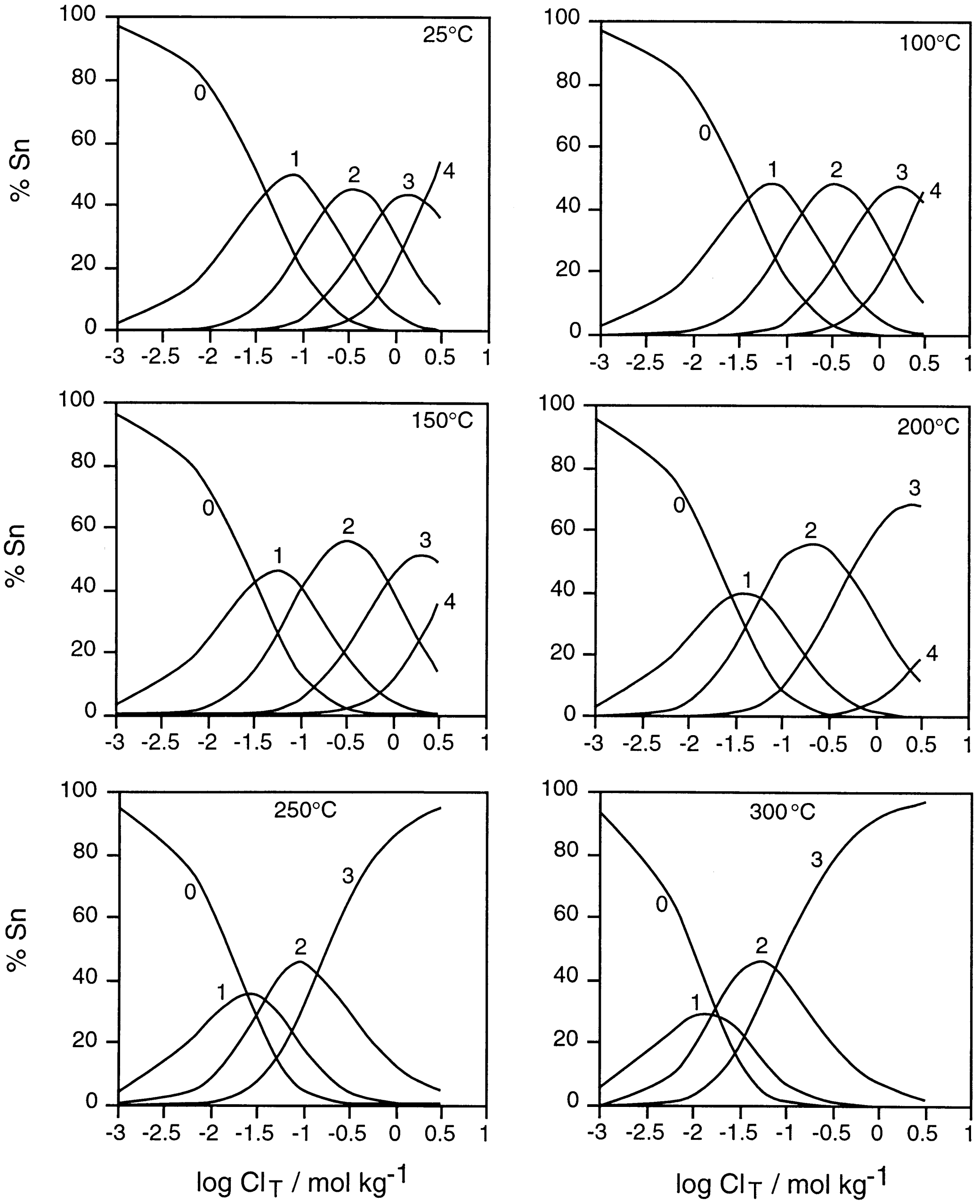

Fig. 7. The percentage distribution of tin as chloridotin(II) complexes as a function of total chloride concentration, Cl_T, up to 300°C at the saturated vapor pressure of the system; the curve for each complex is labeled according ligand number (e.g., curves labeled *2* refer to $SnCl_2^0$).

characterized by a negative or small positive enthalpy and a modest entropy of formation. With increasing temperature from 25° to 300°C and consequent decrease in the dielectric constant of water (Uematsu and Franck, 1980), ΔH^0 of formation of $SnCl^+$ increases from +0.10 to +15.6 kJ mol^{-1} with an accompanying large entropy change from 28 to 61 JK^{-1} mol^{-1} (Table 4). The endothermic enthalpies and positive entropies attending the monochlorotin(II) formation at elevated temperatures are the result of stronger electrostatic interactions between Sn^{2+} and chloride. The standard enthalpy and entropy of formation of $SnCl^+$ at 25°C and I = 0 ($\Delta H^0 = +0.10$ kJ mol^{-1} and $\Delta S^0 = +28$ JK^{-1} mol^{-1}; this study) are somewhat different from the calorimetrically based values of Vasilev et al.

Table 3. Coefficients in Eqn. (12) to Define the Variation of $\ln\beta_1$, ln K_2, and ln K_3 with Temperature up to 300°C.

	A	B	C
$\ln \beta_1$	+4.1523	-5.9524×10^{-3}	$+1.0187 \times 10^{-5}$
$\ln K_2$	+3.7022	-1.4290×10^{-2}	$+2.6030 \times 10^{-5}$
$\ln K_3$	+7.3819	-4.1145×10^{-2}	$+5.7661 \times 10^{-5}$

Table 4. Thermodynamic Data For the Stepwise Formation of $SnCl^+$, $SnCl_2^0$, and $SnCl_3^-$ as Described by the Equilibrium Constants β_1, K_2, and K_3 up to 300°C.

t/°C	ΔG^0/kJ mol^{-1}			ΔH^0/kJ mol^{-1}			ΔS^0/J K^{-1} mol^{-1}		
	$SnCl^+$	$SnCl_2^0$	$SnCl_3^-$	$SnCl^+$	$SnCl_2^0$	$SnCl_3^-$	$SnCl^+$	$SnCl_2^0$	$SnCl_3^-$
25	−8.10	−4.34	−0.86	+0.10	+0.91	−5.00	+28	+18	−14
50	−8.96	−4.95	+0.25	+0.55	+2.20	−3.37	+29	+22	−11
100	−10.2	−5.86	−1.00	+1.91	+5.95	+2.20	+32	+32	+8.6
150	−12.3	−8.10	−0.57	+3.97	+11.5	+11.4	+38	+46	+28
200	−14.3	−11.3	−2.72	+6.86	+19.1	+25.0	+45	+64	+59
250	−16.5	−14.1	−9.01	+10.7	+29.5	+43.7	+52	+83	+101
300	−19.5	−19.5	−12.1	+15.6	+42.5	+68.2	+61	+108	+140

(1976; i.e., $\Delta H^0 = +9.2$ kJ mol^{-1} and $\Delta S^0 = +62.3$ JK^{-1} mol^{-1}). This arises partly because their data treatment inherently includes values of β_n at $I = 0$, which were derived from potentiometric measurements conducted in high-ionic-strength perchlorate media by Duke and Courtney (1950), Vanderzee and Rhodes (1952), and Tobias and Hugus (1961) (Table 1).

With increasing temperature, the larger positive entropies arise from release of solvated water molecules into an increasingly more expanded water continuum. The large positive entropies also imply that inner sphere complex formation becomes more important at higher temperatures. At high temperatures, the favorable free energy of formation of $SnCl^+$ is therefore influenced by the positive entropy of complex formation.

5. DISCUSSION

The monochloridotin(II) complex is a moderately stable complex at 25°C and 1 bar. The results for β_1 and β_2 from this study at ambient temperature are in good agreement with the relevant literature data at zero ionic strength derived by Prytz (1928a). Her study as well as those of Duke and Courtney (1950) and Haight et al. (1962) are the only others that report the presence of $SnCl_4^{2-}$ in concentrated solution at ambient temperature.

The $SnCl_3^-$ complex becomes one order of magnitude more stable than $SnCl_2^0$ as temperature increases from 25 to 300°C at equilibrium saturated vapor pressures (see Table 2). In aqueous chloride solutions at $t \geq 200$°C, the coordination chemistry of tin(II) is dominated by $SnCl_2^0$ and $SnCl_3^-$, especially at high chloride concentration. The increase in stability of $SnCl_3^-$ is similar to that reported for $PbCl_3^-$ (Seward, 1984) at $t \geq 300$°, although all the lead(II) chloride complexes are rather more stable at high temperatures than the corresponding tin(II) species. In addition, the increase in stability of $SnCl_2^0$ and $SnCl_3^-$ in water solvent of diminished static permittivity at elevated temperature is consistent with the increased stability of $SnCl_n^{2-n}$ species observed in other protic solvents (e.g., ethanol) having lower dielectric constants at 25°C (Samoilenko et al., 1976).

Wilson and Eugster (1990) reported the presence of $SnCl_n^{2-n}$ ($1 \leq n \leq 3$) in acidic, chloride solutions and temperatures $\geq$400°C at 1500 bar. This is also in agreement with the conclusions of Patterson et al. (1981) and Jackson and Helgeson (1985). At $\geq$300°C, there could presumably be some ion pairing between Na^+ and $SnCl_3^-$. Taylor and Wall (1993) studied the solubility in sodium and potassium chloride solutions from 700 to 800°C at 2 kbar and suggested that alkali metal ion pairs such as $NaSnCl_3^0$ accounted for the measured solubilities. However, the stability of such species in hydrothermal solutions generally remains unknown.

EXAFS data (Yamaguchi et al., 1982) indicate that the aquated Sn^{2+} ion is coordinated by three to four first-shell water molecules at a distance of 2.25 Å at 25°C. Their X-ray scattering data indicate a similar number of solvated, nearest neighbor waters (~4) at a distance of 2.34 Å. More recently, Sherman et al. (2000) measured the Sn-EXAFS on two Sn(II) chloride solutions from 25 to 350°C at saturated vapor pressures. A comparison of the average ligand numbers obtained from their EXAFS data with our spectrophotometrically derived values is of interest. Despite the large (10–15%) inherent uncertainty in EXAFS-derived coordination numbers, their data show a systematic increase in the average number of bound chlorides at elevated temperature, suggesting that the Sn(II) solutions of Sherman et al. (2000) were partially oxidized. For example, in the case of their 2.92 M chloride solution at 250°C, the dominant species (from UV spectra) are $SnCl_2^0$ (5%) and $SnCl_3^-$ (95%), which leads to an average ligand number of about three. No $SnCl_4^{2-}$ was detected (see Fig. 7). The larger coordination number (4.2) reported by Sherman et al. (2000) probably reflects the presence of Sn(IV), which is known to form higher complexes such as $SnCl_6^{2-}$ in aqueous solutions as noted by earlier workers (e.g., Ishibashi et al. 1959; Everest and Harrison, 1957; Fatouros et al., 1978) as well as by Sherman et al. (2000).

Pabalan's (1986) detailed study of the solubility of cassiterite (SnO_2) in sodium chloride solutions (0.10–5.20 m) from 200 to 350°C comprises the only other attempt to measure the stepwise formation of Sn(II) chloride complexes at elevated temperatures. However, Pabalan (1986) also reported the presence of significant concentrations of $SnCl_4^{2-}$ in concentrated solutions up to 300°C. We were unable to detect the presence of this species in our nonlinear least squares analysis at the UV spectra at temperatures $\geq$250°C and chloride concentrations up to 2.936 m. For example, in a 3.00 m chloride solution at 300°C, Pabalan's (1986) data indicate that the total tin in solution is comprised of 4% $SnCl_2^0$, 48% $SnCl_3^-$, and 48% $SnCl_4^{2-}$, whereas we find for the same chloride concentration at 300°C, 3% $SnCl_2^0$ and 97% $SnCl_3^-$ (i.e., no $SnCl_4^{2-}$). The reason for this discrepancy probably arises from the presence of Sn(II) hydroxo- and mixed hydroxochloro-complexes in Pabalan's (1986) solutions, which were not explicitly dealt with in the data treatment. We note that many of the solutions used in his study, especially at higher chloride concentrations, had pHs in the range of 4 to 5.8, which would lead to the formation of hydrolyzed Sn(II) species.

Finally, it is of interest to briefly examine the role of Sn(II) chloride complexes in ore transport and deposition. In conjunction with our experimental study, we also carried out a reconnaissance study of fluid inclusion compositions in quartz from the hydrothermal veins in the Huanuni tin deposit (Bolivia). The results are reported by Müller et al. (2001) and are briefly summarized here for the purpose of discussion. For primary inclusions in quartz intimately associated with cassiterite, the mean homogenization temperature was found to be ~ 400°C with pressure estimated to be $\leq$500 bar. The fluids are saline with a mean, equivalent NaCl concentration of 4.2 m. The cassiterite-bearing, quartz-rich veins and associated wall rock alteration assemblages also contain potassium feldspar and muscovite. This leads to an estimated pH $\approx$2.4 from the relevant feldspar–mica equilibrium at the stated temperature and pressure.

Thus, for an ore fluid having 4.2 m NaCl and pH $\approx$2.4 at 400°C and 500 bar, the concentration of tin as $SnCl_n^{2-n}$ complexes may be calculated using the solubility product expression

$$SnO_2 + 2H^+ + H_{2(g)} = Sn^{2+} + 2H_2O_{(l)} \qquad (14)$$

Combining thermodynamic data from Wagman et al. (1982), Robie et al. (1978), and Jackson and Helgeson (1985) gives log $K_{sp} = -3.6$ for reaction (14) at 400°C and 500 bar. Inspection of Figure 7 indicates that the dominant chloridotin(II) complex in the above mentioned ore fluid will be $SnCl_3^-$. The estimated equilibrium formation constant for this complex under these conditions is, log $\beta_3 \approx 6.7$. We are therefore able to calculate the solubility of cassiterite in the Huanuni ore fluid using the equilibrium reaction

$$SnO_2 + 2H^+ + H_{2(g)} + 3Cl^- = SnCl_3{}^- + 2H_2O_{(l)} \qquad (15)$$

Choosing a value of hydrogen fugacity of 0.1 bar that is characteristic of many crustal hydrothermal ore fluids, the concentration of $SnCl_3^-$ in equilibrium with cassiterite is found to be 450 mg/kg. A similar calculation in terms of $SnCl_2^0$ gives a concentration of 4 mg/kg. The calculated value of ~450 mg/kg is in good agreement (perhaps fortuitously) with the measured tin concentration of 380 mg/kg which was obtained by direct analysis of the Huanuni saline inclusions with laser ablation ICP-MS.

This study of tin(II) chloride complexing to 300°C represents only a first step toward an understanding of the geochemistry of tin transport and deposition in hydrothermal ore forming systems. As mentioned previously, the hydrolysis of divalent tin in aqueous systems is important and also will play a role in the hydrothermal transport and precipitation chemistry of cassiterite. High-temperature data pertaining to the stability of tin(II) hydroxide and mixed hydroxide-chloride complexes are also required but are as yet unavailable. Furthermore, the role of fluoride will be important in some hydrothermal systems, but our current knowledge of the stability of Sn(II) fluoride complexes under hydrothermal conditions is sparse. There are few if any reliable data pertaining to the concentration of fluoride in hydrothermal ore solutions. The determination of fluoride concentrations in fluid inclusions associated with hydrothermal tin deposition is difficult and fraught with problems. The current lack of adequate experimental data defining the relevant Sn(II) complex equilibria and precipitation reactions involving cassiterite, stannite, and other tin-containing ore minerals under hydrothermal conditions comprises a significant barrier to further progress in the understanding of the formation of tin ore deposits.

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