

# The Sn<sup>4+</sup>/Sn<sup>2+</sup> redox couple, a neglected problem in aqueous tin chemistry

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## Introduction

The redox couple Sn<sup>4+</sup>/Sn<sup>2+</sup> is thermodynamically the connecting link between aqueous tin(IV) and tin(II) chemistry as pointed out by Séby et al. (2001), see Fig. 1. Surprisingly limited reliable thermodynamic data are available in the literature for aqueous chemistry of tin(IV). Until recently values of the standard electrode potential  $E^\circ$  (Sn<sup>4+</sup>/Sn<sup>2+</sup>) were reported in four papers only. All of them suffering under major deficiencies, see Fig. 2. Clearly the mixed chloride and sulphate medium of Despić et al. (1972) obscures the extrapolation to zero ionic strength, and thus the value of Vasil'ev et al. (1979) seemed to confirm the generally accepted result of Huey & Tartar (1934). As the value of Forbes & Bartlett (1914) deviates less than 10 mV from the mean value of the former ones, Latimer's (1952) selection  $E^\circ$  (Sn<sup>4+</sup>/Sn<sup>2+</sup>) = (150 ± 10) mV seemed amply justified. Re-evaluation of Vasil'ev et al.'s data, however, shows that those are flawed by two numerical mistakes.

(1) While the equations used for extrapolation to ionic strength  $I = 0$  are quite correct and similar to those of the SIT approach,  $-\psi(I)$  has erroneously been ascribed a negative value, see Fig. 3. This sign error was detected by Hummel et al., see NAGRA review (2002).

(2) In the Table containing the experimental values some data must be exchanged.

In order to carry out an SIT analysis based on molality as composition variable the corrected data were transformed accordingly, see Fig. 4. Correctly calculated Vasil'ev et al.'s standard electrode potential of the Sn<sup>4+</sup>/Sn<sup>2+</sup> couple differs by more than 120 mV from the value generally accepted.

Now the question arises how Vasil'ev et al. dealt with Sn(II) and Sn(IV) hydroxo and chloro complexes in order to find out the concentrations of free Sn<sup>2+</sup> and Sn<sup>4+</sup> ions. Sn(II) hydroxo complexes can be neglected in 2 to 4 M HClO<sub>4</sub> solutions, but only the single experimental study of Nazarenko et al. (1971) is available on the hydrolysis of tin(IV) under acidic conditions. Because several experimental details are debatable the results of this investigation can be regarded as approximate estimates only.

In addition Vasil'ev et al. assume that no Sn(IV) chloro complexes form in the pertinent medium. This has been concluded from experiments of Vasil'ev & Glavina (1976) and (1977) where SnCl<sub>4</sub> and ammonium hexachlorostannate seemed to dissociate completely in 0.6–2.0 M HClO<sub>4</sub>. The conclusion drawn from these surprising observations clearly contradicts the

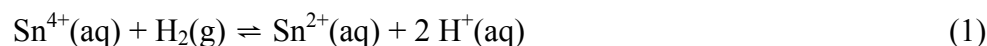
results of Fatouros *et al.* (1978) who based their study of Sn(IV) chloro complexes on a symmetric cell without liquid junction, see Fig. 5. Fatouros et al. found the complete series from  $\text{SnCl}_3^+$  to  $\text{SnCl}_6^{2-}$  in 5 M  $\text{HClO}_4$  solutions, where Sn(IV) hydroxo complex formation should essentially be suppressed. The stability constants of the Sn(IV) chloro complexes range from  $3 < \lg \beta^\circ < 11$ .

A rationale of these seemingly contradictory experimental results could be that hydrolysis, which certainly is effective in 0.6 to 2 M  $\text{HClO}_4$ , and dissociation cannot be distinguished by measurements with Vasil'ev & Glavina's cells.

Thus, in fact the link between aqueous tin(IV) and tin(II) chemistry is missing! This prompted Gajda et al. (2009) to perform potentiometric and spectrophotometric studies to determine  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  and the formation constants of tin(IV)-chloro complexes in strongly acidic solution. The latter condition is necessary to suppress as far as possible hydrolytic processes leading to Sn(IV) hydroxo complexes of unknown stability.

*First estimation of  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  from measurements in  $\text{Cl}^-$ -free systems*

At first it was attempted to determine the standard electrochemical potential of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple for reaction (1)



in chloride-free systems with electrochemical cell (I), see Fig. 6.

For the initial experiments, 1 mM tin(II) perchlorate in 5 M  $\text{HClO}_4$  and 0.5 mM tin(IV) perchlorate in 5 M  $\text{HClO}_4$  solutions were used. Although, high purity  $\text{H}_2$  and Ar were permanently bubbled through the reference and measuring compartments, respectively, but the potential of the above cell was not stable. Moreover, the reproducibility of routine titrations, when tin(IV) perchlorate was titrated by tin(II) perchlorate solution, was not acceptable ( $\pm 25$  mV), and the slopes of these plots were found to be 28 – 38 mV. These spurious potentiometer readings were associated with the low concentration of the potential determining cations, which was dictated by the low solubility of tin(IV) in perchlorate containing media. The sub-millimolar tin(IV) and tin(II) concentrations make the electrochemical cell poorly buffered, and probably extremely oxygen sensitive, because even traces of oxygen could significantly change the relative concentrations of Sn(IV) and thus the cell potential. Therefore, the standard potential determined under these conditions ( $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) \approx 0.3$  V) can be considered at most as first approximation.

Obviously the solubility of tin(IV) under strongly acidic conditions can significantly be enhanced by the presence of chloride ion, due to the formation of various tin(IV) chloro complexes. The higher concentration of potential determining ions is expected to reduce the above mentioned uncertainties. However, the evaluation of  $E^\circ (\text{Sn}^{4+}/\text{Sn}^{2+})$  in chloride containing media requires the knowledge of the stepwise formation constants of tin(II) and tin(IV) chloro complexes. Such data for tin(IV) chloro complexes under the conditions relevant to these studies have not been available from the literature.

#### *The stepwise formation constants of $\text{SnCl}_x^{4-x}$ complexes*

First the determination of the stepwise formation constants of tin(IV) chloro complexes from the potentials of the following, almost symmetrical concentration cell (II), see Fig. 6 was attempted. In spite of all efforts, the preparation of Ag/AgCl electrodes which are stable in concentrated perchloric acid solutions has failed.

UV spectroscopy has been successfully applied to determine the stability of tin(II)-chloro complexes by Müller & Seward (2001). Therefore, the UV spectra of tin(IV) were studied as a function of the chloride concentration at five different ionic strengths. Fig.7 shows the background and dilution corrected UV spectra of tin(IV) detected at different chloride concentration in 8 M  $\text{HClO}_4$  solution.

With increasing  $[\text{Cl}^-]_{\text{TOT}}$  significant spectral changes were observed, reflecting changes in the coordination sphere of tin(IV), which provided sufficient information to derive the formation constants of the tin(IV)-chloro complexes. The observed spectral changes can be best described by the formation of 5 species ( $\text{SnCl}^{3+}$ ,  $\text{SnCl}_2^{2+}$ ,  $\text{SnCl}_4(\text{aq})$ ,  $\text{SnCl}_5^-$  and  $\text{SnCl}_6^{2-}$ ) at all ionic strengths. The formation of  $\text{SnCl}_3^+$  was not detected. Since  $^{119}\text{Sn}$  NMR spectra of concentrated tin(IV) chloride solution seem to prove the existence of this species, our observation is probably due to the high similarity of the individual spectra of  $\text{SnCl}_3^+$  and  $\text{SnCl}_4(\text{aq})$ , which prevents their differentiation by the method used. The individual spectra of the chloro complexes formed in 8 M  $\text{HClO}_4$  are shown in Fig. 8.

The formation constants determined at different ionic strengths have been used to extrapolate to zero ionic strength by weighted linear regression and error propagation assuming Gaussian probability distribution applying the Specific Ion interaction Theory (SIT). The ionic strength dependences of  $\lg\beta_1$  and  $\lg\beta_6$  are depicted in Figs. 9 and 10. Obviously, the extrapolation to  $I_m = 0$  using data for  $I_m \geq 5.55 \text{ mol kg}^{-1}$  results in higher uncertainties than predicted for the range of ionic strengths where the actual measurements were carried out. Therefore, it is preferable to define an additional key ionic strength within the range covered.

The interpolated formation constants at  $I_m = 6.41 \text{ mol kg}^{-1}$  (5 M HClO<sub>4</sub>) have a considerably lower uncertainty.

#### *Determination of $E^\circ$ from measurements in Cl<sup>-</sup>-containing systems*

For the electrochemical measurements involving chloride containing mixed background electrolyte the electrochemical cell (III) was employed, see Fig. 11.

Only a limited ionic strength range ( $I-1$ ) M HClO<sub>4</sub> + 1M HCl was available for the potentiometric measurements, since at  $(I-1) > 5$  some greyish precipitate on the mercury surface resulted in unstable potentials, while at  $(I-1) < 3$  the chloride content of the background electrolyte is too high, and cannot be regarded as ‘perchlorate medium’. Under such conditions, the experimental complications mentioned with cell (I) were not experienced: the electrode potentials were found to be stable within  $\pm 0.2$  mV after 30-60 minutes (as the system is relatively “well buffered” against O<sub>2</sub>-traces). The reproducibility of the parallel runs were found to be reasonable ( $\pm 4$  mV, see Fig. 12), the slope of the experimental plots was found to be close to the theoretical value (29.58 mV/decade), i.e. this experimental setup, should provide a reliable Sn<sup>4+</sup>/Sn<sup>2+</sup> redox potential.

The evaluation of the experimental data requires the knowledge of the formation constants of tin (II) and tin(IV) chloro complexes at a given ionic strength  $I$ . Since a mixed background electrolyte has been used, the true formation constants are not available. In the case of tin(IV) the constants determined as described previously for HClO<sub>4</sub> background were used to extra/interpolate to the given ionic strength. In the case of tin(II) the data set for NaClO<sub>4</sub> background electrolyte, evaluated by the OECD/NEA Tin Review Team, has been used. As a mixed background electrolyte was used, it seemed reasonable to assume similar ionic strength dependence in NaClO<sub>4</sub> and HClO<sub>4</sub>/HCl background electrolytes.

The experimentally observed potential values as a function of the logarithmic mole ratio  $\lg [r(\text{Sn}^{4+}_{\text{free}}/\text{Sn}^{2+}_{\text{free}})]$  are depicted in Fig. 12. The extrapolation to  $\lg[r(\text{Sn}^{4+}_{\text{free}}/\text{Sn}^{2+}_{\text{free}})] = 0$  resulted in the formal potentials  $E^{\circ'}(\text{Sn}^{4+}/\text{Sn}^{2+})$  at the different ionic strengths applied. Considering the uncertainties related to the formation constants of the chloro complexes and the mixed background electrolyte, the uncertainties of  $E^{\circ'}(\text{Sn}^{4+}/\text{Sn}^{2+})$  have been assigned three times the mean deviation between the measured and calculated  $E$  values of cell (III). The extrapolation of the determined standard potentials to zero ionic strength by linear regression and error propagation assuming Gaussian probability distribution applying the SIT approach (Fig. 14, dotted line) resulted in  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.396 \pm 0.011) \text{ V}$ . However, at  $m(\text{HClO}_4) > 3 \text{ mol kg}^{-1}$  the activity coefficients deviate strongly from those calculated by the

simple SIT approach. Therefore, the use of extended SIT is more appropriate in our case, see Fig. 13. There are two accepted ways to extend the validity of SIT to high ionic strengths. For the sake of brevity only one is shown here, see Fig. 13, Eq. (2). From Eq. (2) (Fig. 14, solid line)  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = (0.385 \pm 0.011) \text{ V}$  can be calculated.

The above  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  value is more positive than the so far generally accepted value of 0.15 V. The latter value was based on measurements conducted in HCl media, however the formation of chloro complexes was neglected. Since tin(IV) forms much more stable chloro complexes than tin(II), and therefore the mole ratio  $r(\text{Sn}^{4+}_{\text{free}}/\text{Sn}^{2+}_{\text{free}}) \ll r[\text{Sn(IV)}/\text{Sn(II)}]$ , the considerably more positive value determined by us is understandable. Indeed, assuming identical ionic strength dependence of tin(II)- and tin(IV)-chloro complexes in perchlorate and chloride media,  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) \approx 0.36 \text{ V}$  can be estimated from Huey & Tartar's data, which validates the high positive value derived by us.

The relatively high uncertainty of  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  originates from the uncertainties associated with both formation constants and the applied mixed background electrolyte. The extrapolation to ionic strength = 0 poses the same problem as mentioned above for the formation constants of chloro complexes, therefore we define a formal potential  $E^{\circ'}(\text{Sn}^{4+}/\text{Sn}^{2+}, 5 \text{ M HClO}_4) = (0.318 \pm 0.011) \text{ V}$ . For the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  standard electrode potential we estimate a larger uncertainty, because of the long extrapolation to zero ionic strength which has to be taken into account, thus

$$E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}, 298.15 \text{ K}) = (0.384 \pm 0.020) \text{ V}.$$

### *Conclusions*

Although, several intelligent guesses had to support this evaluation, the first reliable data on the standard redox potential of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple have been reported. In addition, the first detailed solution equilibrium study on the tin(IV)-chloro complexes has been performed. The results will contribute to the basic knowledge on aqueous tin(IV) chemistry.