

Study of the Fluoride Complexes of Tin(II) Using a Fluoride Ion Specific Electrode

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Prior to the development of the fluoride ion specific electrode by Frant and Ross (6) measurements of the stability or formation constants of fluoride complexes were usually made by the "ferri-method" (2, 4, 5) or by polarography and potentiometry (3, 10, 11). The work of Schaap, Davis, and Nebergall (11) was the first reported for the fluoride complexes of tin in aqueous solution. Later, Connick and Paul (3) using a potentiometric technique estimated the formation constant for the addition of the first fluoride ion to tin(II) in aqueous solution.

In a study similar to that to be reported here Hall and Slater (7) used the fluoride ion specific electrode to obtain the formation constants for SnF^+ , SnF_2 , and SnF_3^- . These authors, however, evidently did not take special care to exclude Sn(IV) from their solutions. Such a highly-charged positive ion would have a strong complexing tendency toward the fluoride ion.

Experimental Procedures

Because the crucial part of the present work which differentiates it from the similar work already published (7) is the preparation of the solutions, the experimental procedures will be described in some detail. The apparatus, similar to that described by Tobias (13), was designed to prepare tin(II) perchlorate solutions of known tin(II) concentration, ionic strength, and acidity under an oxygen-free atmosphere. This solution was then titrated potentiometrically at constant temperature with a solution of fluoride ion. A specific fluoride electrode (Model 94-09, Orion Research Inc.) and a commercial calomel electrode were used with a digital voltmeter (Orion Research Ionanalyzer, Model 605) to sense the concentration of uncomplexed fluoride ion during the titration.

All chemicals were of reagent-grade quality. The sodium fluoride was from the J. T. Baker Chemical Company. The sodium perchlorate (0.01% chloride and chlorate) to fix the ionic strength and the perchloric acid (70%, Double Vacuum Distilled, Lead-Free and 0.0001% chloride) were from the G. Frederick Smith Company. The tin metal foil was lead-free. The method of Tobias (13) was used to prepare the tin(II) perchlorate solutions. This procedure involves the reaction of metallic tin with an acid solution of copper(II) perchlorate under nitrogen atmosphere. The copper(II) perchlorate solutions were prepared by dissolving copper(II) oxide in a perchloric acid solution, the acidity of this final solution being determined by passing an aliquot through a cation-exchange column and titrating the total liberated hydrogen-ion content with sodium hydroxide solution. The nitrogen gas used to free

the solutions from oxygen and to maintain an inert atmosphere during the experiment was purified by the method of Meites and Meites (9).

The work reported here was carried out at a constant ionic strength of 3.0 and 25°C. The highest initial pH of the tin(II) perchlorate solution used was about 1.3, this being deemed sufficient to minimize formation of tin(II)-hydroxide complexes (13). Because of the high hydrogen-ion concentration, the formation of HF and HF_2^- had to be taken into consideration using the formation constants for the hydrogen-fluoride system reported by Kleboth (8). The response of the fluoride ion specific electrode to the concentration of free fluoride ion in the solution was checked before and after each experiment, and was found to be in agreement with the literature.

Results

The result for a typical experiment is shown in Figure 1. The ordinate, $\bar{n}$, as used by Bjerrum (1), is defined as the average number of fluoride ion bound to each tin(II) ion:

$$\bar{n} = \frac{\{[\text{F}^-]\text{total} - [\text{F}^-]\text{free} - [\text{HF}] - 2[\text{HF}_2^-]\}}{[\text{Sn}^{2+}]\text{total}} \quad (1)$$

where $[\text{F}^-]\text{total}$: total fluoride ion concentration corrected for dilution

$[\text{F}^-]\text{free}$: free fluoride ion concentration as measured by the ion-specific electrode.

$[\text{Sn}^{2+}]\text{total}$: total stannous ion concentration corrected for dilution.

$[\text{HF}]$ and $[\text{HF}_2^-]$: concentrations of the hydrogen ion/fluoride ion complexes calculated from the stability constants of Kleboth (8).

The presence of three reasonably distinct breaks in the curve of Figure 1 is indicative of the successive formation of the three complexes, SnF^+ ,

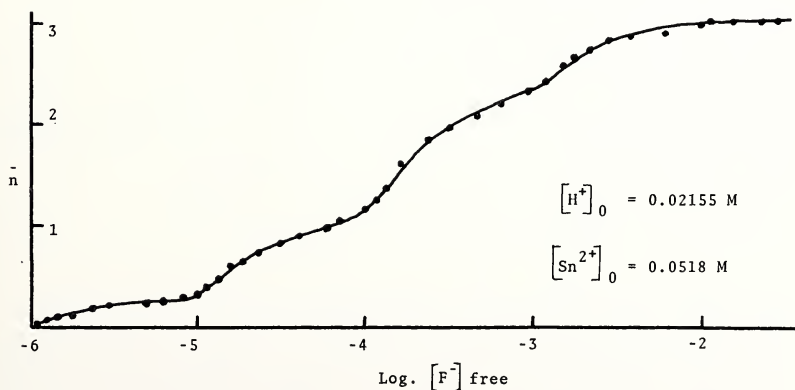


FIGURE 1. Graph of $\bar{n}$ versus logarithm of free fluoride ion concentration for a typical experiment.

SnF_2 , and SnF_3^- , with separated formation constants. Evidence from these experiments was inconclusive concerning the possibility of formation of SnF_4^{2-} .

The determination of the formation constant K_n for the complex SnF_n^{2-n} , where K_n is defined as

$$K_n = \frac{[\text{SnF}_n^{2-n}]}{[\text{SnF}_{n-1}^{3-n}] \cdot [\text{F}^-]} \quad (2)$$

was carried out as follows. Using the data from the region of $\bar{n}$ less than about 2, introduction of equations (2) into equation (1) yields

$$\bar{n} / (1-\bar{n}) [\text{F}^-] = K_1 + \{ (2-\bar{n}) K_1 K_2 [\text{F}^-] \} / (1-\bar{n}) \quad (3)$$

Hence K_1 and K_2 can be obtained from a graph such as Figure 2. Similarly, in a region of fluoride concentration where all three complexes are formed,

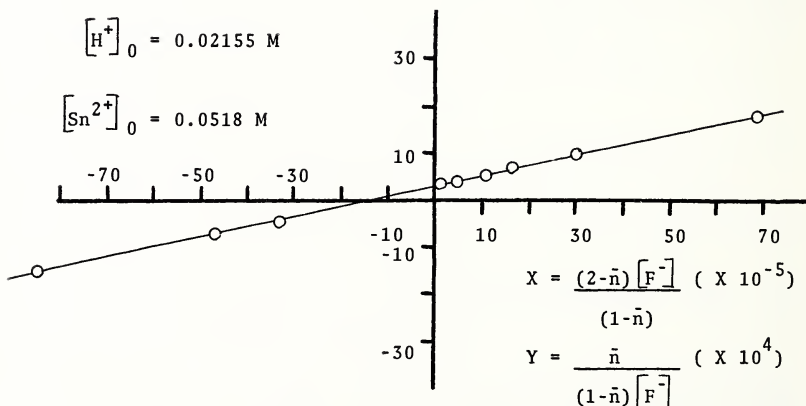


FIGURE 2. Graph for calculation of K_1 and K_2 from data of Figure 1.

$$\frac{\bar{n}}{n} = \frac{[\text{SnF}^+] + 2 [\text{SnF}_2] + 3 [\text{SnF}_3^-]}{[\text{Sn}^{2+}] + [\text{SnF}^+] + [\text{SnF}_2] + [\text{SnF}_3^-]} \quad (4)$$

which after the introduction of equations (2) for each complex yields upon rearrangement

$$\frac{\bar{n} - K_1 (1-\bar{n}) [\text{F}^-]}{(2-\bar{n}) K_1 [\text{F}^-]^2} = K_2 + \frac{(3-\bar{n}) K_2 K_3 [\text{F}^-]}{(2-\bar{n})} \quad (5)$$

A graph to determine K_2 and K_3 from equation (5) is shown in Figure 3. In all cases there were more experimental points than shown on the graphs. Data plotted according to equations (3) and (5) were subjected to least-squares analysis to obtain the formation constants. The results at an ionic strength of 3.0 with sodium perchlorate as the supporting electrolyte and at 25°C were as follows:

$$K_1 = (3.8 \pm 0.1) \times 10^4; K_2 = (5.8 \pm 0.5) \times 10^3;$$

$$K_3 = (9.4 \pm 0.5) \times 10^2.$$

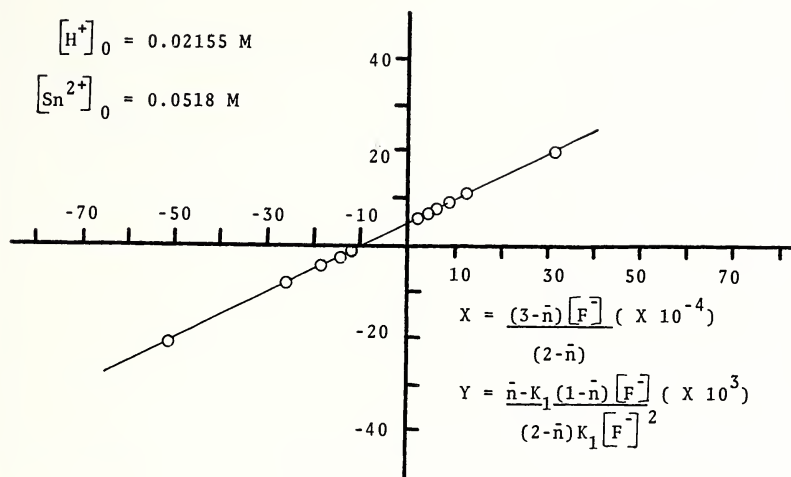


FIGURE 3. Graph for calculation of K_2 and K_3 from data of Figure 1.

Discussion

The results of the present work for the cumulative formation constant $B_3 (= K_1 \times K_2 \times K_3)$ of 2.1×10^{11} is in satisfactory agreement with the value of 9.1×10^{10} reported by Schaap, Davis, and Nebergall (11) who employed a polarographic technique. Moreover, they worked at a different ionic strength and supporting electrolyte. Hall and Slater (7), however, using a fluoride electrode in a work similar to the present one, report a value for B_3 of only 1.77×10^9 at an ionic strength of 0.85.

The logarithm of the formation constants for the halide complexes of various metal ions in aqueous solution has been found empirically to depend linearly on the standard potential of the halogen. Such a relationship is illustrated for several metal ions in Figure 4 for the formation constants for the addition of the first halide ion to the aquo metal ion. The result of the present work (Point V on Figure 4) is close to the expected value based on the long extrapolation from the chloride and bromide results. However, the value of Hall and Slater (7), Point IV on Figure 4, is some two orders of magnitude larger than the expected result, probably because of contamination by the more strongly-coordinating tin(IV) ion.

The results of the present study thus indicate that the formation constant for the addition of the first fluoride ion to the aquo tin(II) ion in aqueous solution is some two orders of magnitude smaller than that value previously reported (7) and confirm a linear relationship between the logarithm of the formation constant and the standard potential for the halogen for tin(II) in aqueous solution.

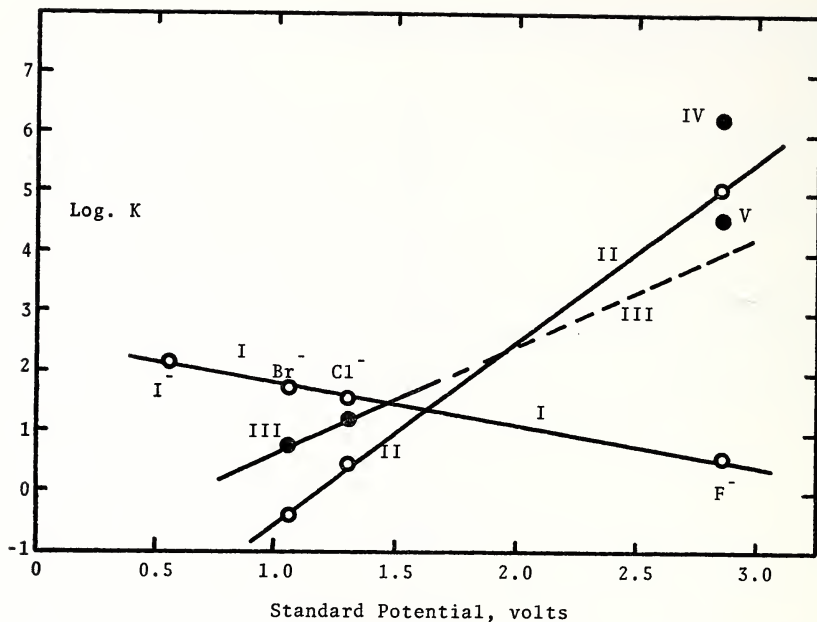


FIGURE 4. Logarithm of formation constant versus standard potential of the halogen, X^-/X_2 . All values at 25°C and at an ionic strength of 3.0 using sodium perchlorate as supporting electrolyte, except where indicated. Data for curves I, II, and III from Reference (12).

Curve I: $Cd^{2+} + X^- = CdX^+$

Curve II: $Fe^{3+} + X^- = FeX^{2+}$

(for clarity curve is displaced downward by 1 unit).

Curve III: $Sn^{2+} + X^- = SnX^+$.

Point IV: Reference (F), ionic strength 0.85.

Point V: Present Work.

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