

The Complex Formation of Tin(II) with Iodide in Aqueous Solution*

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The complex formation between tin(II) and iodide has been studied at 25°C in a 4 M perchlorate medium. Solubility measurements of $\text{SnI}_2(\text{s})$ and $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ are consistent with the formation of the series of mononuclear complexes $\text{SnI}_n^{(2-n)+}$, $n = 1, 2, 3, 4, 6,$ and 8 , with the stability constants $\beta_n = 5.0, 13.5, 135, 200, 390,$ and 120 , respectively. It is shown that no ion pair formation takes place between $(\text{CH}_3)_4\text{N}^+$ and I^- or between $(\text{CH}_3)_4\text{N}^+$ and $\text{SnI}_n^{(2-n)+}$. The results are compared with those of earlier measurements on the tin(II) chloride¹ and bromide² systems.

Tin holds an interesting position in the periodic system with respect to the (a) and (b) classification of metal acceptors.³ In order to assign the proper classification, a considerable amount of quantitative data on the complex formation between tin and various ligands is required. The information available⁴ is, however, rather incomplete, for tin(II) as well as for tin(IV). This paper presents an investigation of the tin(II) iodide system, with the aim to complete the picture of the tin(II) halide systems. The chloride and bromide systems have earlier been subject to detailed studies,^{1,2,5,6} and data are also available on the fluoride system.⁴

Earlier studies of tin(II) iodides include the measurements by Young⁷ in 1897 of the solubility of $\text{SnI}_2(\text{s})$ as a function of iodide concentration, and the spectrophotometric study of tin(II) iodide solutions by Fromhertz-Walls⁸ in 1937. No attempts to describe the findings quantitatively in terms of complex formation were made in either of these studies.

However, Young's study shows, that $\text{SnI}_2(\text{s})$ is well suited for solubility measurements. Therefore, in the present study, the major part of the data are obtained from measurements of the solubility of $\text{SnI}_2(\text{s})$ over a range of iodide concentrations. When $[\text{I}^-] > 1 \text{ M}$, $\text{SnI}_2(\text{s})$ is too soluble to give easily

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interpreted results. We have, therefore, prepared and studied the solubility of *bis*-(tetramethylammonium)-tetraiodostannate(II) in the range $0.5 \text{ M} < [\text{I}^-] < 4 \text{ M}$. Reports that tetramethylammonium ion and iodide ions form ion pairs⁹ required that we also study the solubility of tetramethylammonium iodide *versus* $[\text{I}^-]$ to ascertain to what extent ion pair formation affected our data.

DATA ANALYSES

Notation

M denotes Sn^{2+}

A denotes I^-

T denotes $(\text{CH}_3)_4\text{N}^+$

Brackets, [], indicate equilibrium concentrations of free ions. Initial, total concentrations are denoted by an indexed C .

Solubility of $\text{SnI}_2(\text{s})$

The solubility, S , is measured for various ligand concentrations, C_A . The soluble species are the free central ion, M, and the complexes MA_n , $n = 1, 2, \dots, N$. It is assumed that only mononuclear complexes are formed. Thus, the solubility of $\text{MA}_2(\text{s})$ is

$$S = [\text{M}] + [\text{MA}] + \dots + [\text{MA}_N]$$

The solubility product being $K_s = [\text{M}][\text{A}]^2$, and the stability constants of the complexes being $\beta_n = [\text{MA}_n]/[\text{M}][\text{A}]^n$, the following equation for the solubility is obtained¹⁰

$$S = K_s [\text{A}]^{-2} (1 + \beta_1[\text{A}] + \dots + \beta_N[\text{A}]^N) \quad (1)$$

The expression within parenthesis is denoted X . We also introduce \bar{n} , the complex formation function

$$\bar{n} = \frac{\sum_1^N n\beta_n[\text{A}]^n}{X} = \frac{\text{d} X}{\text{d} [\text{A}]} \frac{[\text{A}]}{X} = \frac{\text{d} \log X}{\text{d} \log [\text{A}]} \quad (2)$$

From eqns. (1) and (2) we get

$$\frac{\text{d} \log S}{\text{d} \log [\text{A}]} = \bar{n} - 2 \quad (3)$$

C_A and $[\text{A}]$ are connected by the equation

$$C_A + 2S = [\text{A}] + \bar{n}S$$

or

$$[\text{A}] = C_A - (\bar{n} - 2)S \quad (4)$$

$[\text{A}]$ is found by iteration: $\log S$ is plotted *versus* $\log [\text{A}]$, with some approximate value of $[\text{A}]$. $\bar{n} - 2$ is obtained from the slope (eqn. (3)) and inserted into eqn. (4), giving a better $[\text{A}]$, which is used for correcting the plot, etc.

The expression $K_s X$ is now known as a function of $[A]$ and, by graphical extrapolations,¹⁰ $K_s, K_s \beta_1, \dots, K_s \beta_N$, and hence also β_1, \dots, β_N , are obtained. Now, S and \bar{n} can be back-calculated and compared with the experimental values. If any systematic deviations occur, the constants can be refined to give a better comparison.

Solubility of $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$

With a ternary salt, the concentrations of two of the components can be varied independently, and the concentration of the third measured as a function of these two. In this case it is suitable to vary the ligand and the tetramethylammonium ion concentrations and regard as the solubility, the resulting total tin(II) concentration in solution.

Then the following equations apply for the solubility S'

$$2S' + C_T = [T] \quad (5)$$

$$S' = [M]X$$

Hence, if $K_s' = [T]^2[M][A]^4$,

$$S'(C_T + 2S')^2 = K_s' X [A]^{-4} \quad (6)$$

Two important possibilities emerge

(a) C_T is varied, but $[A]$ is constant. According to its definition, X is also constant, and eqn. (6) reads

$$S'(C_T + 2S')^2 = \text{const.}; \quad [A] = \text{const.} \quad (6')$$

(b) $C_T = 0$, $[A]$ (C_A) is varied.

Eqn. (6) reduces to

$$4(S')^3 = K_s' X [A]^{-4} \quad (6'')$$

The following equation corresponds to eqn. (3):

$$\frac{d \log S'}{d \log [A]} = \frac{\bar{n}-4}{3} \quad (7)$$

Now, the constants can be elucidated in the same way as in the previous section.

Some important assumptions have been made:

First, it is assumed that only mononuclear complexes are formed. It is a known fact (Ref. 10, p. 191) that with solubility measurements of a salt between the central ion and the ligand only, like SnI_2 , it is generally not possible to decide whether the complexes are mononuclear or not. With a ternary salt, on the other hand, the formation of polynuclear complexes should show up. For instance, eqn. (6') would be invalid, if a polynuclear complex existed to an appreciable extent at the ligand concentration in question.

Second, it is assumed that the tetramethylammonium ion behaves ideally, *i.e.*, it does not form complexes (ion pairs) with the iodostannate ions, nor with the iodide ion.

The formation of any complex of the type TMA_n , to an appreciable extent, would necessarily result in a variation in the product on the left side of eqn. (6'), when C_T is varied.

The formation of, say, the complex TA, with the stability constant K would have the following effects: Eqn. (5) would be

$$2S' + C_T = [T] + [TA] = [T](1 + K[A])$$

which changes eqn. (6) to

$$S'(C_T + 2S')^2 = K_s'X (1 + K[A])^2[A]^{-4}$$

Hence, eqn. (6'') would contain, instead of X , the product $X(1 + K[A])^2$, while eqn. (6') would remain true (with some other constant, though). This means that X cannot be determined from the described measurements alone. Some independent determination of K , or, some good evidence for the absence of this ion pair formation, is necessary.

The required information is obtained from measurements of the solubility, S'' , of $(CH_3)_4NI(s)$, in solutions of varying iodide concentration. If no ion pairs are found,

$$S''(C_A + S'') = [T][A] = K_s'' \quad (8)$$

If, on the other hand, an ion pair TA were formed,

$$S''[A] = K_s''(1 + K[A])$$

i.e., the product $S''[A]$ would increase with increasing $[A]$.

EXPERIMENTAL

Chemicals. Sodium perchlorate was prepared from analytical grade perchloric acid and sodium carbonate. Solutions were standardized by evaporating and weighing samples. Analytical grade sodium iodide (Baker or Mallinckrodt) was used without purification. Solutions were analyzed for iodide by precipitation as silver iodide. A weighed sample of tetramethylammonium iodide (Eastman) was found to contain the calculated amount of both ions, as determined by the silver iodide and tetraphenyl boron methods, respectively. Solutions of this salt were therefore prepared by weighing calculated amounts.

Solids for solubility studies. To prevent the oxidation of Sn(II) (and iodide), preparation and handling of solutions and solids were performed with very careful exclusion of air, by means of oxygen free carbon dioxide.

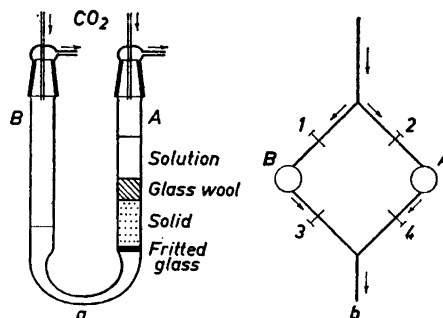
A tin(II) chloride solution was prepared from an acidified copper(II) solution, which was allowed to run through a bed of tin metal. The bright orange colored $SnI_2(s)$ was formed when an excess of iodide was added to this tin(II) chloride, in the saturator. $[(CH_3)_4N]_2SnI_4(s)$ (light yellow) was formed when a slurry of $(CH_3)_4NI$ in water was added to SnI_2 , dissolved in *ca.* 4 M sodium iodide solution.

The solids were washed with large amounts of sodium iodide solution, in order to remove all traces of chloride, and other unwanted ions.

A sample of the tin iodide was washed free from excess iodide with perchloric acid and then analyzed for tin(II) as described below (*Analyses*). After the tin titration the iodide was precipitated as silver iodide; the extra iodide added by the titration, was determined separately. The molar ratio of iodide to tin of 1.98 was found, *i.e.*, very near the expected value 2.

Samples of the tetramethylammonium compound were washed with alcohol and ether and dried, in the absence of air. Various analyses gave the following results (values calculated for $[(CH_3)_4N]_2SnI_4$ within parenthesis):

Fig 1. (a). The saturator; the volume of either compartment is about 10 ml, the diameter 10 mm. (b). Schematic view from above (see text).



Oxidation to SnO_2 : 14.7 % Sn (15.2); Ce(IV) titration: equiv. wt. 131 (129); $\text{S}_2\text{O}_3^{2-}$ titration: equiv. wt. 202 (194); elementary analyses (CLARK Microanalytical Lab., Urbana, Illinois) C: 12.47 % (12.41), H: 2.97 % (3.10), N: 3.57 % (3.75).

The commercially available tetramethylammonium iodide was used directly in the saturator, after washing with oxygen free sodium iodide solution.

Apparatus, equilibration. The solutions were equilibrated, with the solid under investigation, in a modified solubility column (Brønsted saturator;¹⁰ Fig. 1) immersed in a water bath maintained at $25.0 \pm 0.1^\circ\text{C}$.

The CO_2 gas served the double purpose to prevent oxidation and supply pressure in either compartment to push the solution through the solid: With the screw clamps 1 and 4 partially shut, an excess pressure in compartment A pushed the solution over to B, whereupon 2 and 3 could be tightened and the solution pushed back to A. A stream of gas was maintained in both compartments all the time. Solutions (oxygen free) were introduced in A with pipettes; though the cap had to be lifted, the intrusion of air was avoided as the CO_2 stream was maintained all the time. Equilibrated samples were withdrawn from B, also with a pipette.

Some measurements were performed without the glass wool holding down the solid. A glass rod was then kept in compartment A, and the solution-solid mixture was stirred each time the solution was in A. This resulted in quicker equilibration, especially with $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4$, which had a tendency to develop "channels" for the solution, if not stirred.

Often a solution was found to be at equilibrium after one to three passes through the bed. Several passes were usually employed, however, and the complete equilibration of every solution was ascertained by frequent checks.

Analyses. Equilibrated solutions, to be analyzed for tin(II), were transferred to an oxygen free iodine-iodide solution in a titration vessel flushed with CO_2 . The excess of iodine was back-titrated with sodium thiosulphate, using starch as indicator. A 10^{-4} M tin(II) concentration could be determined to better than 5 %.

In a preliminary series of measurements on $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4$, polarographic determination of tin was employed, giving the same trend in the solubilities, though with much less accuracy.

Tetramethylammonium ion concentrations were determined by adding sodium tetraphenyl boron which precipitated $[(\text{CH}_3)_4\text{N}][(\text{C}_6\text{H}_5)_4\text{B}](\text{s})$. As tested with known amounts of tetramethylammonium ion, the method worked satisfactorily (errors ≤ 1 %) for the range of solubilities studied ($S'' \approx 40$ mM).

Concentration ranges. The ionic strength was kept constant at 4 M by addition of perchloric acid and sodium perchlorate. For the SnI_2 measurements, the acidity 1 M was chosen in order to prevent Sn(II) hydrolysis¹¹ at the lower ligand concentrations, where Sn(II) is present as free Sn^{2+} to a considerable extent. Thus, the solutions were made up of 1 M HClO_4 , C_A M NaI and $(3 - C_A)$ M NaClO_4 . C_A ranged from 0 to 1 M, the upper limit chosen for two reasons: the solubility starts to be inconveniently high, and very rapidly increasing. Moreover, solutions of this high acidity and high iodide concentrations, seemed to evolve iodine, slowly, despite the most careful exclusion of the air.

The $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4$ measurements were performed with a much lower acidity, 0.010 M, where the iodide oxidation was negligible. In order to avoid hydrolysis, these measurements were not extended below $C_A = 0.5$ M. At the highest ligand concentration employed, 3.99 M, the solubility was measured as a function of the tetramethylammonium ion concentration. C_T was varied between 0 and 10 mM, higher concentrations giving too low solubilities.

These solutions, thus, had the general composition 0.010 M HClO_4 , C_T M $(\text{CH}_3)_4\text{NI}$, $(C_A - C_T)$ M NaI , $(3.99 - C_A)$ M NaClO_4 .

The acidity 0.010 M was also chosen for the $(\text{CH}_3)_4\text{NI}$ measurements. Here, C_A could be varied only between ≈ 3.3 M and 3.99 M. At lower iodide concentrations (higher perchlorate concentrations) $(\text{CH}_3)_4\text{NI}(s)$ was converted to some perchlorate-containing compound, as was clearly indicated by a sharp break in the solubility curve. This solid gave no simple solubility product $S[\text{ClO}_4^-]$, as one would have expected for $(\text{CH}_3)_4\text{NClO}_4(s)$. It could, however, be converted back to the iodide, at higher iodide concentrations.

Reproducibility. With each solution, at least two samples were always equilibrated. The solubilities of SnI_2 could all be reproduced within 2%. Two different samples of the solid gave the same result, within these limits of error. Also, the $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4$ solubilities, with $C_T = 0$, could be reproduced within 2%, except for the two lowest C_A , where the deviations were somewhat higher. As to the series with varying C_T , great care was taken to make the measurements as accurate as possible, so that even the lowest solubility could be reproduced within 2%.

The solubilities of $(\text{CH}_3)_4\text{NI}(s)$ could be reproduced within 1%. A solid, converted to the perchlorate, and then converted back to the iodide again, gave the same solubilities as the original iodide.

RESULTS

| $\text{SnI}_2(s)$ and $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(s)$ solubilities

The solubilities of $\text{SnI}_2(s)$, for various C_A , are given in Table 1. The free ligand concentration $[A]$ is obtained by eqns. (3) and (4).

Table 1. The measured solubility, S , of $\text{SnI}_2(s)$. "calc" indicates values calculated from the final set of constants.

C_A M	$[A]$ M	$S \times 10^3$ M	$S_{\text{calc}} \times 10^3$ M	\bar{n}_{calc}
0	0.0260	13.96	13.92	0.14
0.0400	0.0480	4.60	4.61	0.27
0.0800	0.0828	1.931	1.910	0.54
0.1200	0.1213	1.170	1.165	0.92
0.1600	0.1606	0.890	0.906	1.30
0.240	0.240	0.797	0.794	2.05
0.320	0.320	0.874	0.875	2.62
0.400	0.399	1.033	1.051	3.05
0.500	0.498	1.412	1.393	3.51
0.600	0.596	1.912	1.890	3.91
0.800	0.791	3.57	3.57	4.61
1.000	0.980	6.60	6.65	5.20

Table 2 gives the solubilities of the tetramethylammonium salt. With these low solubilities, the change in ligand concentration is negligible, *i.e.* $[A] = C_A$.

Table 2. The solubility, S' , of $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ as a function of iodide ion concentration. "calc" indicates values calculated from the final set of constants.

$C_A = [\text{A}]$ M	$S' \times 10^3$ M	$S'_{\text{calc}} \times 10^3$ M	\bar{n}_{calc}
0.50	0.34	0.348	3.51
1.00	0.38	0.377	5.25
1.50	0.472	0.480	
2.00	0.614	0.616	6.86
2.50	0.776	0.772	
3.00	0.945	0.945	7.42
3.50	1.117	1.130	
3.99	1.327	1.325	7.62

In Fig. 2, $\log S$ and $\log S'$ are plotted against $\log [\text{A}]$, and the best curves drawn. From the slopes of these curves, \bar{n} is calculated by eqns. (3) and (7), and plotted against $\log [\text{A}]$ in Fig. 3. \bar{n} ranges from 0.1 to about 5 for SnI_2 and from 4 to 7.7 for the tetramethylammonium salt. Although the range of $[\text{I}^-]$ common to the two studies is not extensive, it seems clear that there is no systematic difference in the values obtained with the two methods. Further, it is seen from this figure, that it is necessary to include a complex with at least 8 ligands, in the explanation of the results. The \bar{n} -curve, however, shows a marked tendency to level off at $\bar{n} = 8$. It is highly probable, therefore, that $N = 8$ is the limiting co-ordination number.

N can also be found in the following way: $K_s' X \cdot [\text{A}]^{-n}$ is plotted against $[\text{A}]^{-1}$, for various values of n . Obviously, if $n > N$, a zero intercept will be obtained on extrapolation to $[\text{A}]^{-1} = 0$, while, if $n = N$, a positive intercept will be obtained. In other words, the highest value of n giving a positive intercept is $n = N$. Also with this approach, $N = 8$ was found.

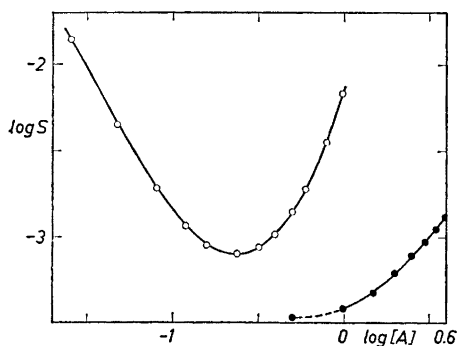


Fig. 2. Solubility curves for $\text{SnI}_2(\text{s})$ (O) and $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ (●). Best curves are drawn through the experimental points.

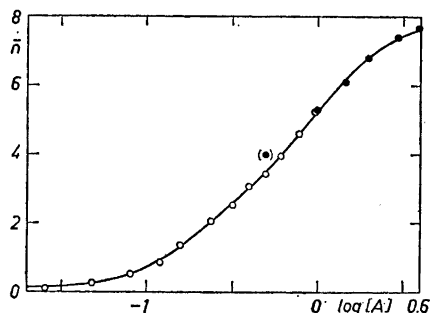


Fig. 3. \bar{n} , from the slopes in Fig. 2, for $\text{SnI}_2(\text{s})$ (O) and $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ (●). Curve: calculated from the final set of constants.

When $K_s'X[A]^{-8}$ was plotted against $[A]^{-1}$, the shape of the curve indicated that $\beta_7 = 0$. Therefore, the same function was plotted against $[A]^{-2}$, with an approximately straight line as the result. The intercept is $K_s'\beta_8$, and from the slope a preliminary value of $K_s'\beta_6$ was obtained.

Now the $\text{SnI}_2(\text{s})$ data were analyzed beginning in the region of low $[\text{I}^-]$, yielding K_s , β_1 – β_4 , and β_6 . (As to β_5 the best value appeared to be 0.) As \bar{n} only reaches a value 5.2, it was not possible to draw any definite conclusions about the maximum coordination number from these data, nor to assign any value to β_8 . Therefore, the value of β_6 from these data must be regarded as tentative.

However, it was assumed that the stability constants, or at least their ratios, do not change much for the change in acidity between the two series (see page 965). Then, approximate values of K_s' and β_8 could be calculated from the preliminary β_6 , $K_s'\beta_6$, and $K_s'\beta_8$. This β_8 was used as a correction for the SnI_2 data, to yield a better value of β_6 . Also, the $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4$ data could be corrected for the presence of the fourth (and lower) complexes, to give a better ratio between β_8 and β_6 . This procedure was repeated to obtain a best fit for a single set of constants to all experimental data. Solubilities and \bar{n} values calculated from the constants (see Tables 1 and 2, Fig. 3) are in close agreement with observed values.

The final set of stability constants obtained in this way, is given in Table 5. As to the solubility products, $K_s = (0.83 \pm 0.02) \times 10^{-5}$ and $K_s' = (2.5 \pm 0.3) \times 10^{-13}$ were used as final values.

Fig. 4 shows the distribution of tin(II) among the various species. It may be noted that for some ligand concentrations, as many as six species are present in the solution in appreciable concentrations. The range for each individual species is consequently narrow, and the uncertainties in the computed constants necessarily large. Especially the intermediate constants, β_2 – β_5 , are subject to large uncertainties. The absence of the fifth complex is thus by no means proved; the data could be fitted equally well with a low, positive β_5 . However, this lack of accuracy is not due to the actual choice of computation method, obviously, because the experimental data are fitted as well as they could reasonably be (Tables 1 and 2). With the prevailing "crowded" situation, only a considerable increase in the accuracy of the measured solubilities could diminish the uncertainties in the computed constants.

It should also be strongly emphasized that, as the data are interpreted here (*i.e.*, with the assumption that the solubility changes are due only to the formation of mononuclear complexes), postulation of the existence of the eight coordinated SnI_8^{6-} is required.

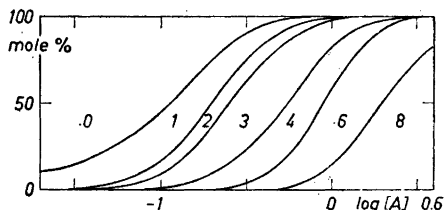


Fig. 4. Distribution of Sn(II) among the various species $\text{SnI}_n^{(2-n)+}$ (n indicated in the figure).

Behavior of the tetramethylammonium ion

Table 3 shows the solubility of $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ as found when C_T was varied at a constant ligand concentration. The product $S'(C_T + 2S')^2$ was found constant, as expected from eqn. (6'). Thus, the assumptions of mononuclear complexes and of the absence of interaction between T and the prevailing Sn(II) complexes seem valid.

Table 3. The solubility of $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ as a function of C_T at constant $[A] = 3.99 \text{ M}$.

$C_T \times 10^3$ M	$S' \times 10^3$ M	$S'(C_T + 2S')^2 \times 10^9$
0	1.327	9.3
2.96	0.564	9.4
4.94	0.305	9.4
9.87	0.093	9.4

Table 4 shows the solubility of $(\text{CH}_3)_4\text{NI}(\text{s})$ as a function of the iodide concentration, and the subsequently calculated solubility product (eqn. (8)).

Table 4. The solubility of tetramethylammonium iodide.

C_A M	$[A]$ M	$S'' \times 10^3$ M	$S'' \times [A]$ M^2
3.99	4.03	35.7	0.1439
3.70	3.74	38.5	0.1440
3.50	3.54	40.5	0.1434
3.30	3.34	43.3	0.1448

No variation of K_s'' is shown, implying that the ion pair formation between T and I^- is negligible. This is not in agreement with the results of Azzari and Kraus,⁸ who find, from an interpretation of conductivity measurements at low $[\text{I}^-]$, a value of $K \approx 3$.

It may be noted that this disagreement could be avoided, if it is assumed that both perchlorate and iodide ions form ion pairs with the tetramethylammonium ion: If ion pair formation constants for TA and TClO_4 are equal, their effects on the solubility will balance each other. As a net result, $[\text{T}][\text{A}]$ will still be constant. Such an exact cancellation seems somewhat improbable, however; the most reasonable interpretation of our data is still that neither I^- nor ClO_4^- forms any ion pairs. Of most importance, however, is the fact that even if such a cancellation takes place, it would not change our interpretation of the $[(\text{CH}_3)_4\text{N}]_2\text{SnI}_4(\text{s})$ measurements, naturally, as a cancellation would also result in that case. It may also be noted that in all measurements at constant ionic strength, the assumption is always made, that the medium

ions do not take part in the complex formation, or if they do, their constants are incorporated in those of the studied system.

Thus, it seems to be confirmed that the formation of mononuclear tin iodide complexes is the only reaction occurring in the solutions studied, and that the solubility changes reflect this complex formation only.

DISCUSSION

Although the data presented in this paper are reliable, it is obviously desirable to study the region of high iodide concentration with other methods, before the existence of SnI_8^{6-} can be said to be established. Examples of eight coordinated ions are quite common, however, especially in the crystalline state.¹² Most examples occur among the lanthanides and actinides, and in the transition series. Some of the ions, studied in crystals, exist in aqueous solution as well, like $\text{Mo}(\text{CN})_8^{4-}$. Also in aqueous solution, the ions BiBr_8^{5-} and $\text{Pb}(\text{SCN})_8^{6-}$ have been reported, from data similar to ours,¹³ and from potentiometric data¹⁴, respectively.

For the arrangement of eight ligands around a central ion, various configurations are possible. Among these, the square antiprism and the dodecahedron are the most common. Normally, these two configurations have the lowest energies.¹⁵ As to SnI_8^{6-} , the application of formal ionic radii¹⁶ shows that the iodide ions are a little too big for either of these configurations. It is doubtful, however, if this fact is of any importance in this case with the highly polarizable iodide ions.

One might also speculate about a possible configuration with two coordination shells, *e.g.* with six iodides in an octahedral inner sphere, and two iodides in an outer sphere.

Table 5 shows the stability constants for tin(II) halides. The chloride and bromide systems were studied in 4 M hydrogen sulphate, while the iodide system was studied in 4 M perchlorate. Disregarding these medium differences, it can be judged that tin(II) forms moderately strong halide complexes, which,

Table 5. Stability constants, $\beta_n \text{ M}^{-n}$, for the tin(II) chloride,¹ bromide,² and iodide systems.

\bar{n}	Cl^-	Br^-	I^-
1	28	7.9	5.0 ± 0.5
2	225	53	13.5 ± 2
3	290	130	135 ± 10
4	200	45	200 ± 20
5	—	(95)	0 ± 30
			(—)
6	—	—	390 ± 20
7	—	—	0 ± 20
			(—)
8	—	—	120 ± 10

when compared with each other, are roughly of the same strength. The strongest first complex is the chloride one, while the iodide complexes tend to be stronger for $n \geq 3$.

This indicates an intermediate position, for tin(II), between (a) and (b) acceptors.³ Of special interest therefore is the fluoride system. The data available⁴ show the fluoride complexes to be stronger than the other halides, thus favoring the (a) acceptor classification. The limited data on Sn(IV)⁴ indicate a more pronounced (a) character. For organotin(IV) halide complexes, class (a) character has been reported.¹⁷

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REFERENCES

1. Haight, Jr., G. P., Zoltewicz, J. and Evans, W. *Acta Chem. Scand.* **16** (1962) 311.
2. Haight, Jr., G. P. *Proc. 7 ICCO* (1962) 318.
3. Ahrland, S., Chatt, J. and Davies, N. R. *Quart. Rev. (London)* **12** (1958) 265.
4. Martell, A. E. and Sillén, L. G. *Stability Constants*, The Chemical Society, London 1964.
5. Vanderzee, C. E. and Rhodes, D. E. *J. Am. Chem. Soc.* **74** (1952) 3552.
6. Vanderzee, C. E. *J. Am. Chem. Soc.* **74** (1952) 4806.
7. Young, S. W. *J. Am. Chem. Soc.* **19** (1897) 845.
8. Fromhertz, H. and Walls, H. J. *Z. physik. Chem. (Leipzig)* **A 178** (1937) 29.
9. Azzarri, M. and Kraus, C. A. *Proc. Natl. Acad. Sci. U.S.* **42** (1956) 590.
10. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York 1961.
11. Tobias, R. S. *Acta Chem. Scand.* **12** (1958) 198.
12. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry*, 2nd Ed., Wiley, London 1966.
13. Preer, J. R. and Haight, Jr., G. P. *Inorg. Chem.* **5** (1966) 656.
14. Golub, A. M. and Romanenko, L. I. *Ukr. Khim. Zh.* **27** (1961) 11.
15. Parish, R. V. and Perkins, P. G. *J. Chem. Soc.* **A 1967** 345.
16. Ahrens, L. H. *Geochim. Cosmochim. Acta* **2** (1952) 155.
17. Cassol, A., Magon, L. and Barbieri, R. *Inorg. Nucl. Chem. Letters* **3** (1967) 25.

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