

## Solubility Studies on Substituted Ammonium Salts of Halide Complexes

### II. Tetramethylammonium Trichlorostannate(II)

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Tetramethylammonium trichlorostannate(II) has been found to form a single phase in equilibrium with chloride ion in hydrochloric acid from 2.0 to 9.0 M in concentration. The single phase is also present at ion concentration of 4.0 maintained with mixtures of  $\text{H}(\text{HSO}_4)$  and  $\text{HCl}$ . Solubility equilibria have been studied assuming the validity of the equations for the formation constants of  $\text{SnCl}_n^{2-n}$  complexes:

$$K_n = [\text{SnCl}_n^{2-n}]/[\text{SnCl}_{n-1}^{3-n}] [\text{Cl}^-]$$

and for the solubility product:

$$K_s = [(\text{CH}_3)_4\text{N}^+] [\text{SnCl}_3^-]$$

Analysis of data obtained at  $[\text{HCl}] + [\text{H}_2\text{SO}_4] = 4.0$  using the equations of paper I gave consistent results for the various  $K_n$  values and a single value for  $K_s$ . Analysis of data in varying hydrochloric acid concentration (no other large source of ions present), substituting activity of chloride ion for  $[\text{Cl}^-]$  also gave consistent results for the various  $K_n$  values and the same single value for  $K_s$ .

The results of this study confirm the suitability of using  $\text{H}_2\text{SO}_4$  as an inert 1:1 electrolyte for maintaining constant ion normality.

Stannous ions are found to coordinate with a maximum of four chloride ions in solutions containing up to 6.0 M hydrochloric acid. A comparison of the distribution of various  $\text{SnCl}_n^{2-n}$  with kinetic data on reactions employing  $\text{Sn}(\text{II})$  as a reducing agent indicates that  $\text{SnCl}_3^-$  is the most active reducing agent among the various chlorotin(II) complexes.

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The frequent employment by one of us (GPH) of stannous ion as a reducing agent in kinetic studies<sup>2</sup> of oxidation-reduction reactions has prompted us to investigate further the nature of Sn(II) species in chloride media. Studies reported in the literature describe complexes with ligand number up to four<sup>3-5</sup> and also with ligand number reaching a maximum of three<sup>6</sup>, while recently data of Duke and Courtney<sup>5</sup> have been reanalyzed using computer techniques<sup>7</sup> and found to be consistent with a maximum of three chloride ligands per stannous ion. Our discovery that tetramethylammoniumtrichlorostannate(II) is formed in high purity from hydrochloric acid solutions of tetramethylammonium chloride and stannous chloride over wide ranges of chloride ion concentration provided a useful method for settling the question of the presence or absence of a tetrachloro complex and for checking the complexity constants in the literature. A preliminary study of the solubility of the salt *vs.* concentration of hydrochloric acid revealed a sharp minimum at 3.0 M acid. This meant that at higher concentrations of chloride the tetrachloro complex and perhaps higher complexes would become the dominant Sn(II) species present. A careful study of the solubility at constant ion strength of 4.0 using sulfuric acid as 1:1 electrolyte has provided a test of the proposition<sup>1</sup> that sulfuric acid could be so used and enabled us to determine the relative concentrations of the various chloro-tin(II) complex species over a wide range of chloride ion concentrations. In the absence of sulfuric acid, activity of hydrochloric acid *vs.* solubility gives the same information up to an activity of 29 (6 molar).

#### EXPERIMENTAL

Eastman white label tetramethylammonium salts were analyzed argentometrically for halide content and found suitable for use without further purification. Analytical grade hydrochloric and sulfuric acids were diluted with distilled water. Hydrochloric acid was standardized by titration of weighed sodium carbonate using methyl orange indicator and by potentiometric titration with silver nitrate. Sulfuric acid was standardized with sodium carbonate and by measuring its density. All other reagents were of analytical grade and used without further purification.

*Preparation of tetramethylammonium trichlorostannate (II).* This salt can be precipitated in high yields and high purity simply by mixing solutions of the two ions in 3.0 M hydrochloric acid and cooling to 0°C in an ice bath. The concentration of acid is not critical, salts of the same composition being prepared from solutions 1.0 to 9.0 M in hydrochloric acid. The solubility studies indicate that the concentration of trichlorostannate(II) ion is a maximum in 3.0 M acid, and that hydrolysis may occur if the chloride and hydrogen ion concentrations each are as low as 2.0 M. Commercial stannous chloride gave preparations which were 98.5 to 99.0 % pure, the chief contaminant probably being tin(IV). If stannous chloride solutions are prepared by passing solutions of cupric chloride in hydrochloric acid through a tin reductor in an inert atmosphere, very pure preparations of salt always result. The salt has a large temperature coefficient of solubility and may be recrystallized by dissolving in hot hydrochloric acid and cooling. The salt is washed with alcohol and ether and dried in the absence of oxygen. The dry salt is non-hygroscopic, stable to oxidation by air at room temperature and might well be a good primary standard as a reducing agent. Once in aqueous solution, however, it is as susceptible as stannous chloride to air oxidation. Analysis for tin(II) was made by permanganate titration, chloride was determined by potentiometric titration with silver nitrate after oxidizing tin(II) to tin(IV). Often tin(II) and chloride were determined consecutively on the same sample. Microanalyses for carbon, hydrogen and nitrogen were performed by the Clark Microanalytical Laboratory. The difficult to analyze quaternary nitrogen generally gave poor results. Results on a typical preparation showed: Sn 40.06;

Cl 35.9; C 16.26; H 3.99; N 4.83 %. Calc. for  $C_4H_{12}NSnCl_3$ : Sn 39.6; Cl 35.6; C 16.1; H 4.04; N 4.68 %.

Solubility studies on the chloro-salt were carried out with solutions from which oxygen had been removed by bubbling through nitrogen or hydrogen scrubbed with chromous sulfate solution. Reproducible results were obtained only when the salt was covered with solution in a wax sealed, completely filled and stoppered weighing bottle. The bottle was placed in a constant temperature bath and shaken at  $25.0^\circ$  for 24 h, equilibrium being reached well within this time. Samples were withdrawn with a filter pipette immediately on breaking the seal and added to a solution containing an excess of standard permanganate solution in dilute sulfuric acid. The permanganate was back titrated with standard sodium oxalate solution. Difficulty was encountered occasionally with colloid formation. Samples that did not become *very* clear shortly after shaking ceased gave slightly high results. Despite the fact that commercial stannous chloride containing 10 to 20 % tin(IV) gave rather good preparations of the complex stannous salt, the presence of the smallest air bubble in a reaction bottle led to low solubilities. Evidently the hydrolyzed stannic chloro complexes do not precipitate the tetramethylammonium ion, but oxidation in a solubility study frees tetramethylammonium ions which suppress the solubility of the stannous salt. This difficulty could be minimized in future work by using a large excess of tetramethylammonium ion in the solvent.

Except for a few measurements on solubility in various hydrochloric acid concentrations, all studies were made with a concentration of 4.0 M hydrogen ion to suppress hydrolysis, and to permit chloride ion concentrations well in excess of that corresponding to the minimum in the curve obtained for hydrochloric acid (Fig. 1). Ion concentrations were maintained using sulfuric acid as a 1:1 electrolyte. (Perchloric acid could not be used owing to the insolubility of tetramethylammonium perchlorate). A nearly exact correspondence exists between concentration and activity properties of  $H(HSO_4)$  and  $HClO_4$  in the region of 4.0 M concentration<sup>8</sup>.

Analysis of data has been carried out by

(a) Assuming activity coefficients remain constant at constant ion normality,  $[H(HSO_4)] + [HCl] = 4.0$ , and using concentrations in expressions for equilibrium constants

$$K_n = \frac{[SnCl_n^{2-n}]}{[SnCl_{n-1}^{3-n}][Cl^-]}$$

and

(b) Assuming  $K_n = \frac{[SnCl_n]}{[SnCl_{n-1}]a_{HCl}}$ , where  $a$  is activity, in hydrochloric acid solutions

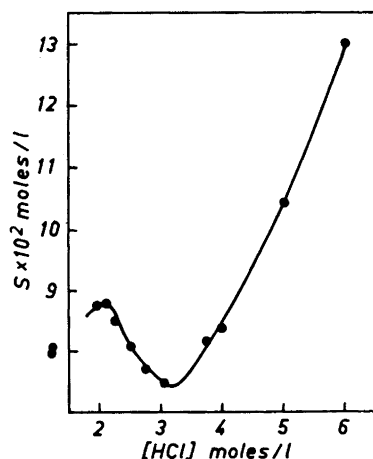


Fig. 1. Solubility curve of tetramethylammonium trichlorostannate(II) vs. concentration of hydrochloric acid showing minimum at 3.0 M.

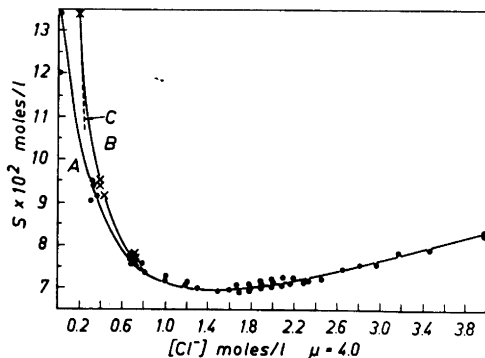


Fig. 2. Solubility of tetramethylammonium trichlorostannate(II) vs. added chloride at  $H^+ = 4.0$  (curve A). Curve B shows corrections for chloride derived from dissolved salt. The broken line C shows the theoretical limiting slope for the point corresponding to no added chloride. Dots represent raw data. Crosses show corrected chloride concentrations for curve B.

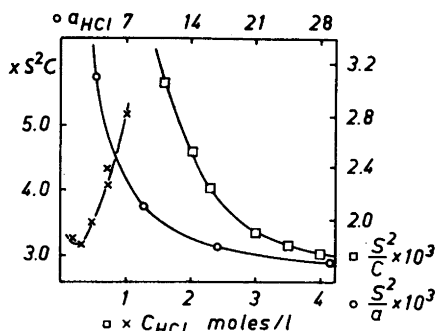


Fig. 3. Plots used in search of evidence for the presence of pentachloro and monochloro complexes in the solutions studied. The minimum at left requires the presence of  $SnCl^+$  and/or  $Sn^{2+}$ . The absence of a minimum on the right suggests the absence of  $SnCl_3^-$  but does not prove it.

in which ion strength is varied and which contain no other substance than hydrochloric acid in large concentration and small concentrations of  $(CH_3)_4NSnCl_3$ .

## RESULTS

The solubility curves vs. hydrochloric acid concentration are shown in Figs. 1 and 2. The line drawn through the points in Fig. 2 favors the points deemed most reliable by virtue of increasing experience with the technique. All points which could not definitely be ruled out as having been subject to oxidation, or involving obvious colloid formation are included. At the lower concentrations the correction of the curve for chloride ions derived from the solution of the salt is shown together with the corrected points. This curve with the theoretical limiting slope of  $0.5^1$  at zero added chloride is the curve upon which calculation of constants was based, and corresponds nearly identically to a curve calculated from the constants reported. The maximum at 2.0 M acid in the curve obtained in hydrochloric acid alone (Fig. 1) corresponds to a change in the solid phase. The salt became gelatinous in appearance suggesting hydrolysis with the formation of stannous hydroxide or basic chloride. This is consistent with the detection of hydrolysis by Vanderzee and Rhodes<sup>6</sup> at 3.0 M hydrogen ion and low chloride ion concentrations. The data used in calculating constants are summarized in Tables 1 and 2.

*Analysis of data. Detection of species present.* The minimum of the solubility curve shows clearly the presence of  $SnCl_2$ ,  $SnCl_3^-$ , and  $SnCl_4^{2-}$ . Fig. 3 shows plots designed to locate minima corresponding to average ligand numbers ( $\bar{n}$ ) of two and four<sup>1</sup>. There is an apparent minimum for the  $S^2[Cl^-]$  vs.

Table 1. Solubility data at ion normality = 4.0.

[HCl] <sub>0</sub> m/l	[H <sub>2</sub> SO <sub>4</sub> ] m/l	[Cl <sup>-</sup> ] m/l	<i>S</i> m/l	<i>S</i> <sup>2</sup> × 10 <sup>3</sup>	$\bar{n}^a$
0.00	4.0	0.18	0.1340	17.9	1.70
0.30	3.7	0.38	0.0939	8.8	2.20
0.36	3.64	0.43	0.0912	8.3	2.25
0.67	3.33	0.71	0.0757	5.72	2.52
0.80	3.20	0.83	0.0738	5.43	2.70
1.00	3.00	1.00	0.0722	5.20	2.80
1.60	2.40	1.60	0.0698	4.88	3.00
2.00	2.00	2.00	0.0707	5.00	3.27
2.30	1.70	2.30	0.0717	5.12	3.39
3.00	1.00	3.00	0.0755	5.70	3.56
3.50	0.50	3.50	0.0792	6.25	3.66
4.00	0.00	4.00	0.0832	6.91	3.77

<sup>a</sup> from slope of *S* vs. [Cl<sup>-</sup>]. Corrected for [Cl<sup>-</sup>] produced by or added to dissolved salt, using eqn.

$$[\text{Cl}^-] = \frac{[\text{Cl}^-]_0}{1 + 2dS/d[\text{Cl}^-]} \text{ (Ref. }^1\text{)}.$$

[Cl<sup>-</sup>] plot very near to the lowest attainable chloride concentration. This corresponds to a maximum concentration of SnCl<sub>2</sub>, and indicates that SnCl<sup>+</sup> must be a minor factor at every experimental point, the fact that Sn<sup>2+</sup> is the only species present at total chloride concentration equal to zero can be used to extend the data to lower chloride concentrations than the measurements alone allow. At the highest chloride concentration no minimum for *S*<sup>2</sup>/[Cl<sup>-</sup>] is observed even at activity 29. Complete conversion to  $\overline{\text{SnCl}_4^{2-}}$  without the formation of any SnCl<sub>5</sub><sup>3-</sup> is apparently the situation, although the failure to reach a minimum corresponding to  $\bar{n} = 4.0$  cannot be used to rule out a pentachloro complex. It must be recalled that the data of Duke and Courtney<sup>5</sup> and of Vanderzee and Rhodes<sup>6</sup> did not warrant introduction of SnCl<sub>4</sub><sup>2-</sup> into their calculations simply because the data did not extend to high enough chloride concentrations. We could fit our data by assuming an SnCl<sub>5</sub><sup>3-</sup> complex, but could fit it equally well without so assuming.

Table 2. Solubility data in hydrochloric acid solution.

[HCl] m/l	$\alpha_{\text{HCl}}$ m/l	<i>S</i> m/l	<i>S</i> <sup>2</sup> × 10 <sup>3</sup>	$\bar{n}^a$
6.00	29.0	0.130	17.0	3.90
5.00	17.0	0.1045	10.9	3.82
4.00	8.7	0.0832	6.9	3.77
3.75	6.67	0.0813	6.67	3.75
3.00	4.17	0.0750	5.60	3.00
2.75	3.72	0.0775	6.00	2.92
2.50	3.40	0.0814	6.60	2.85
2.25	2.78	0.0854	7.28	2.70
2.10	2.37	0.0878	7.70	2.57

<sup>a</sup> From slope of *S* vs.  $\alpha_{\text{HCl}}$  curve.

Attempts to extract  $\text{HSnCl}_3$  from aqueous solutions in which  $\text{SnCl}_3^-$  is a prominent species into chloroform ( $\text{HCCl}_3$ ) gave negative results. This provides qualitative evidence for the absence of molecular  $\text{HSnCl}_3$  indicating that it is a very strong acid contrary to the conclusions of Lachman and Tompkins<sup>10</sup>.

*Determination of complexity constants.* Given the species present, and using the notation of the previous paper<sup>1</sup>, substituting  $\text{Sn}^{2+}$  for M, and  $(\text{CH}_3)_4\text{N}^+$  or  $\text{A}^+$ , the equation for the solubility is:

$$S = [(\text{CH}_3)_4\text{N}^+] = \sum_0^4 [\text{SnCl}_n^{2-n}] \quad (1)$$

where  $S$  is the solubility in moles per liter and  $n$  the number of chloride ions bound to  $\text{Sn}^{2+}$ .

If we define a solubility product:

$$K_s = [(\text{CH}_3)_4\text{N}^+] [\text{SnCl}_3^-] \quad (2)$$

it follows that

$$S^2 = K_s \sum_0^4 \frac{\beta_n [\text{Cl}^-]^n}{\beta_3 [\text{Cl}^-]^3} \quad (3)$$

and

$$\frac{d \ln S^2}{d \ln [\text{Cl}^-]} = \bar{n} - 3 \quad (4)$$

Eqn. 4 is the Bjerrum equation for finding the formation function<sup>11a</sup> modified for the use of solubility data. In Fig. 4 the formation curve obtained through application of this equation is shown. We have chosen to plot  $\bar{n}$  vs.  $[\text{Cl}^-]$  rather than  $\log[\text{Cl}^-]$  in order to make use of the point at the origin. The log plot gives the familiar inflected curve for the last three steps in the formation of  $\text{SnCl}_4^{2-}$ . From the curve vs.  $[\text{Cl}^-]$  it is possible to obtain first estimates of the formation constants by applying the rules:

$$K_n = \frac{1}{[\text{Cl}^-]_{\bar{n}=\bar{n}-0.5}} \quad \text{and} \quad K_n K_{n+1} = \frac{1}{[\text{Cl}^-]_{\bar{n}=n}^2}$$

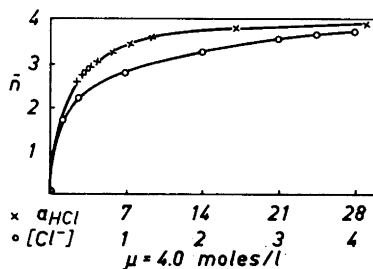


Fig. 4. Formation curves for  $\text{SnCl}_n^{2-n}$  complexes as a function of chloride concentration at ion normality = 4.0 and of activity of hydrochloric acid in variable ion strength. Note the usefulness of the 0, 0 point when the plot is made in this way.

Table 3. Results of calculations based on Tables 1 and 2.

	Using [Cl <sup>-</sup> ] in 4 M ([HCl] + [H <sub>2</sub> SO <sub>4</sub> ])		Using $\alpha_{\text{HCl}}$ in HCl of varying concentration	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
$K_1$	—	~28		
$K_2$	8.00	8.0	5.00	~5.0 <sup>c</sup>
$K_3$	0.90	1.3	0.30	~1.2 <sup>c</sup>
$K_4$	0.65	0.7	0.25	0.40
$F_4 = K_s K_4 [\text{Cl}^-]$	$1.15 \times 10^{-3} / [\text{Cl}^-]$		$0.5 \times 10^{-3} / \alpha_{\text{HCl}}$	0.24
$F_3 = K_s / K_3 [\text{Cl}^-]$	$2.0 \times 10^{-3} / [\text{Cl}^-]$		$6.5 \times 10^{-3} / \alpha_{\text{HCl}}$	
$F_2 = K_s / K_2 K_3 [\text{Cl}^-]^2$	$0.25 \times 10^{-3} / [\text{Cl}^-]^2$		$11.0 \times 10^{-3} / \alpha_{\text{HCl}}^2$	
$K_s = [(\text{CH}_3)_4\text{N}^+] [\text{SnCl}_3^-]$	$1.7 \times 10^{-3}$		$1.7 \times 10^{-3}$	

a. Using *F* values.

b. Using  $\bar{n}$  values.

c. From formation curve. Not reliable, unimproved.

As first approximations

$$K_1 \sim 33, K_2 = 6.0, K_3 = 1.4, \text{ and } K_4 = 0.36$$

$$K_3 K_4 = 0.65, K_2 K_3 = 9.0, \text{ and } K_1 K_2 \sim 230.$$

The approximate values have been improved by applying the method of Bjerrum<sup>11b</sup> to the experimental points on the formation curve using the formula

$$K_n = \frac{1}{[\text{Cl}^-]} \frac{\sum_{t=0}^{i=n-1} \frac{\bar{n} - n + 1 + t}{[\text{Cl}^-]^t K_{n-1} K_{n-2} K_{n-3} \dots K_{n-t}}}{\sum_{t=0}^{i=N-n} (n - \bar{n} + t) [\text{Cl}^-]^t K_{n+1} K_{n+2} \dots K_{n+t}} \quad (5)$$

Eqn. (5) is useful only in the region of the formation curve where the species involved in the expression for a particular  $K_n$  are present in appreciable concentrations. The improved values of the constants are summarized in Table 3. It is interesting to note that only the approximate value of  $K_4$  is seriously different from the improved value reported in the table. The values in the table are averages of six or seven points improved by application of eqn. (5) except for values of  $K_1$  where only the three points at lowest chloride gave reasonable results. This implies that significant concentrations of  $[\text{Sn}^{2+}]$  are present at these points.

Values of constants were also estimated by graphical successive approximations similar to those employed by Leden<sup>12</sup> and Ahrlund<sup>13</sup>. This method employs the equation:

$$S^2 = K_s \left[ 1 + K_4 [\text{Cl}^-] + \frac{1}{K_3 [\text{Cl}^-]} + \frac{1}{K_3 K_2 [\text{Cl}^-]^2} + \frac{1}{K_3 K_2 K_1 [\text{Cl}^-]^3} \right] \quad (6)$$

Plotting  $S^2$  vs.  $[\text{Cl}^-]$ , one obtains  $F_4 = K_s K_4 [\text{Cl}^-]$  from the limiting slope at high  $[\text{Cl}^-]$ . Plotting  $S^2 - F_4$  vs.  $1/[\text{Cl}^-]$ , one obtains from the slope  $F_3 = K_s / K_3 [\text{Cl}^-]$ . Plotting  $S^2 - F_3$  vs.  $[\text{Cl}^-]$  gives improved values of  $F_4$  and so

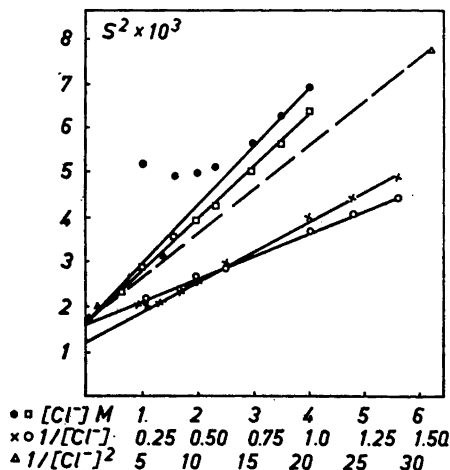


Fig. 5. Analysis of solubility data at ion normality of 4.0 by the method of Leden and Ahrlund. Improved plots using  $F$  values converge on intercept at  $1.7 \times 10^{-3} = K_s$ . Curves given by ● and × are used for first approximations for  $F_4$  and  $F_3$  values. Plots given by □, △, and ○ represent best fits of data to eqn. (6).

on. Each plot should give an intercept for  $S^2 = K_s$ . Successive improvements lead to the convergence of intercepts on the best value of  $K_s$ . An illustration of the use of this method to estimate  $K_n$  values at ion normality of 4.0 is found in Fig. 5.

The available data cannot give  $K_1$  by this method, but new data at lower  $[\text{Cl}^-]$  and high  $(\text{CH}_3)_4\text{N}^+$  could conceivably do so. The two methods of calculation give comparable results as shown in Table 3 which summarizes values for constants and final  $F_n$  values used in the second method of calculation. The Bjerrum method suffers from the need to determine  $\bar{n}$  values from the slopes of curves, while the Leden method places too much reliance on extrapolated values of  $K_s$  which must be determined to calculate  $K_n$  values. Application of the Leden method should reveal departures from constancy of  $K_s$  values at different ligand concentrations, and the Bjerrum method permits estimation of  $K_n$  values derived from data at ligand concentrations lower than the limitations of experiment will normally allow.

*Use of activity of hydrochloric acid in place of concentration.* This substitution gives consistent results only if sulfuric acid is absent. Molal activity coefficients for hydrochloric acid were obtained from published tables<sup>8</sup> and converted to molar activity coefficients. By substituting molar activities for concentration of chloride in the equations previously employed,  $K_n$  values may be calculated as before, assuming the formula

$$K_n = \frac{[\text{SnCl}_n]}{[\text{SnCl}_{n-1}] a_{\text{HCl}}} \quad (7)$$



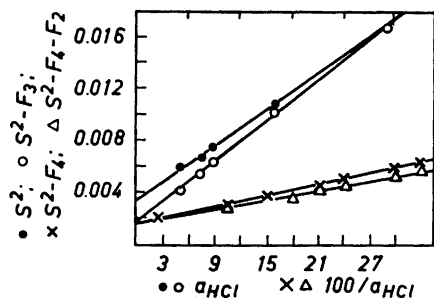


Fig. 6. An illustration of the application of the method of Leden and Ahrlund to solubility data at varying activity of hydrochloric acid. Plot for finding  $F_2$  is not shown. Note the convergent intercept corresponding to  $K_s = 1.7 \times 10^{-3}$ . Activities of hydrochloric acid were used assuming eqn. (7) is applicable.

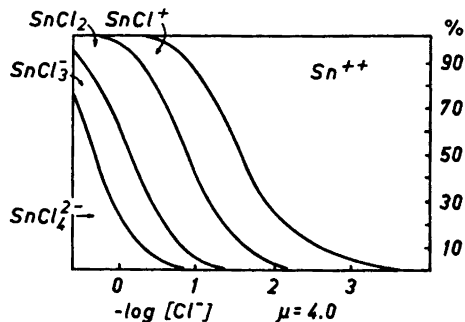


Fig. 7. The distribution of various  $\text{SnCl}_n^{2-n}$  complexes at ion strength 4.0 and varying chloride ion concentrations.

is valid. The formation curve derived by the Bjerrum method is given in Fig. 4. Fig. 6 illustrates the results of using the Leden technique for calculating  $K_4$  and  $K_3$ . Rather surprisingly, the improved  $F$  values give not only straight lines, but a common intercept at the same value of  $K_s$  which was found in the analysis of data at constant ion normality of 4.0. The results of this analysis of data are summarized in Table 3. In Table 4 a comparison of constants obtained at different ion normalities by various techniques is made. It is seen that the values of the constants divided by the molar activity coefficient of hydrochloric acid when its concentration is equal to the total ion normality give values in fair agreement with those obtained employing eqn. (7).

Table 4. Comparison of  $K_n$  from different studies.

	$\mu = 2.0 \text{ M}^a$	$\mu = 3.0 \text{ M}^a$	$\mu = 4.0 \text{ M}^*$	
			a	b
$K_1$	11.4	14		28
$K_2$	4.6	3.5	8	8
$K_3$	0.6	0.95	0.9	1.3
$K_4$	—	—	0.65	0.70
$K_1/\gamma_{\text{HCl}}$	10.6	9.3		11
$K_2/\gamma_{\text{HCl}}$	4.1	2.3	3.6	3.6
$K_3/\gamma_{\text{HCl}}$	0.4	0.6	0.4	0.6
$K_4/\gamma_{\text{HCl}}$	—	—	0.3	0.3

$$\mu = [\text{HCl}] + [\text{H}_2\text{SO}_4]$$

$\gamma$  is mean activity coefficient for pure  $[\text{HCl}] = \mu$ .

\* Present work.

a. Using  $F$  values.

b. Using  $\bar{n}$  values.

The relative concentrations of the various  $\text{SnCl}_n^{2-n}$  species have been determined and are presented graphically for ion normality of 4.0 in Fig. 7. Disagreements with previous studies arise as follows:

(a) Vanderzee and Rhodes<sup>6</sup> did not have sufficient data to include  $K_4$  in their calculations.

(b) Prytz<sup>3</sup> applied Debye-Hückel activity corrections at ion concentrations too high for them to be valid and apparently ignored hydrolysis effects. In a subsequent publication<sup>14</sup> she reported studies on  $\text{Sn(II)-OH}$  complexes. Her distribution of  $\text{SnCl}_n$  species in 3.0 M hydrochloric acid agrees remarkably well with ours.

(c) The only serious disagreement appears in the work of Riccobini *et al.*<sup>4</sup> and this too may be attributed to his use of activity corrections based on the Debye-Hückel theory in solutions of high ion normality.

All in all, the agreement between the different methods is excellent and will probably be improved when an adequate theory is available for more concentrated electrolyte solutions, or by simply employing a standard set of assumptions for calculating values of  $K_n$  from available data.

#### DISCUSSION

The results obtained by using eqn. (7) require comment. The analysis indicates not only that eqn. (7) holds within the accuracy of the experimental data, but that  $K_s$  is not affected by large changes in ion concentration. There is one precedent for employing eqn. (7) in the work of Bjerrum<sup>15</sup> on the complexes of  $\text{CuCl}_n^{2-n}$ . Bjerrum assumed the existence of a mean activity coefficient:

$$F = \frac{f_{\text{CuCl}_n} f_{\text{Cl}^-}}{f_{\text{CuCl}_{n+1}}}$$

He also noted that for a number of electrolytes at molarities  $> 3$

$$\log f_{\pm} = A + BC$$

where A and B are constants and C is molar concentration. Assuming that F has similar properties to  $f_{\pm}$ , Bjerrum found for studies in hydrochloric acid that B for the mean activity coefficient, F, was the same as B for HCl and that his data could be fitted to a smooth curve if the A values corresponding to  $f_{\pm}$  and F were also the same. Examining his data one finds that eqn. (7) with Cu substituted for Sn would describe the  $\text{CuCl}_n^{2-n}$  system very well.

Another interesting result of the present study is the apparent constancy of  $K_s$  over wide ranges of chloride ion concentration and of total ion normality. The assumption that there is little effect on the activities of minor constituents is put to a rather severe test since concentrations of tetramethylammonium ion rise as high as 0.13 M, yet the  $K_s$  obtained by extrapolation remains  $1.7 \times 10^{-3}$  (moles/liter)<sup>2</sup> within a few percent. It may appear that the constancy of  $K_s$  has been assumed and built in to the analysis of the data. Insofar as the slopes of plots of F functions are multiples of  $K_s$  this is true. The constancy of the intercept and straight lines for F functions are experimental results

Table 5. Comparison of rate constants and  $\frac{[\text{SnCl}_3^-]}{[\text{Sn(II)}]} = \alpha$ 

Conc. $[\text{Cl}^-]$	$k^*$	$\alpha$
2.0	0.008	30
3.0	0.020	60
4.0	0.002	10
6.0	$3 \times 10^{-6}$	<1

<sup>a</sup> Ref.<sup>16</sup>

which we doubt could be obtained if  $K_s$  were to vary considerably at different ion strength. The apparent constancy of  $K_s$  coupled with the apparent validity of eqn. (7) imply that the assumption that the activity coefficients of ions present in low concentration in solutions of high ion normality are not much affected by changes in the ion normality. The only other reasonable possibility is that this assumption introduces a startling combination of cancelling errors.

The failure to find evidence for formation of  $\text{SnCl}_5^{3-}$  implies only that its formation constant is extremely low. In preliminary results on the solubility of tetramethylammonium tetrachloroantimonate(III) definite evidence for the existence of  $\text{SbCl}_5^{3-}$  has been obtained<sup>16</sup>. The higher charge on  $\text{Sb}^{3+}$  over that on  $\text{Sn}^{2+}$  means that formation constants will be higher for the antimony complexes. The detection of a higher maximum ligand number for  $\text{SbCl}_n^{3-n}$  reflects this. It is thus apparent that  $\text{SnCl}_4^{2-}$  represents an upper limit for ligand numbers for reasons of stability rather than for reasons of structure.

*Relative reactivity of the various  $\text{SnCl}_n^{2-n}$  complexes.* It has been observed that the rate constant for the molybdate catalyzed reduction of hydroxylamine by stannous ions varies with hydrochloric acid concentration, having a sharp maximum at 3.0 M hydrochloric acid<sup>17</sup>. Since this maximum corresponds to maximum concentration of  $\text{SnCl}_3^-$  relative to other chlorotin(II) complexes as shown in this study, the conclusion seems inescapable that  $\text{SnCl}_3^-$  is the most reactive of the chlorotin(II) species. Table 5 shows the qualitative correlation between the relative amount of  $\text{SnCl}_3^-$  present and observed rate constants. Duke and Peterson<sup>18</sup> came to the same conclusion as a result of their study of the rate of reduction of methyl orange by stannous ions. This finding is interesting when compared to the finding of Gerischer<sup>19</sup> that  $\text{Cd}(\text{CN})_3^-$  is the most easily reduced of the cadmium cyanide complexes during electrolysis of their solutions, and the observations of Vlcek<sup>20</sup> showing that complexes of the type  $\text{MX}_5\text{Y}$  are the most reducible of mixed complexes of the octahedral type. There seems to be a strong suggestion that maximum asymmetry leads to maximum reactivity. If  $\text{SnCl}_3^-$  is in fact  $\text{Sn}(\text{Cl}_3\text{H}_2\text{O})^-$ , its reactivity is understandable in similar terms.

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## The Effect of the Solvent on the Base Catalyzed Conjugation-Isomerisation of Poly-unsaturated Fatty Acid Compounds

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The rate of the conjugation-isomerisation of linseed oil in a solution of K-butoxide in butanol is increased enormously by the presence of an excess of dimethylsulfoxide, dimethylformamide or tetramethylurea. The reaction may thereby be caused to proceed rapidly at room temperature.

In the literature concerning the effect of the solvent on the rate of organic reactions most authors have tried to correlate the effect to the polar properties of the solvent. This theory has led to equations which, for each type of reaction, postulate a certain relationship between the rate and the dielectric constant of the solvent. In two recent publications we discussed these problems<sup>1,2</sup>, and gave several examples of reactions where there seems to be no such correlation. In many cases special types of interaction between the reactants and the nearest neighbour solvent molecules seem to outweigh the integral electrostatic effect of the polar forces. As an example of this type of effect we have described briefly some types of base-catalyzed reactions. One of the reactions mentioned was the conjugation-isomerisation of poly-unsaturated fatty acid compounds. In the present paper some of the preliminary results of these investigations are described.

When analyzing a fatty acid compound for the content of different poly-unsaturated fatty acids, conjugation of the double bonds is usually brought about by treatment of the compound at 180°C with a solution of KOH or K-alcoholate in alcohol. From the amount of conjugated diene, triene *etc.*, as determined from UV absorption spectra, the content of the original poly-unsaturated fatty acids may be estimated.

As will be shown below, we have found that the conjugation-isomerisation proceeds rapidly even at 25°C when using a mixture of K-alcoholate in alcohol and an excess of dimethylsulfoxide, dimethylformamide or tetramethylurea as the reaction medium for the conjugation process.