Studies on the Hydrolysis of Metal Ions

21. The Hydrolysis of the Tin(II) Ion, Sn^{2+}

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The hydrolysis of Sn(II) has been studied in a constant ionic medium (3 M ClO_4^-) at 25°C by two series of electrometric titrations. In one series, $[\text{H}^+] = h$ was measured with a glass electrode, and in the other $[\text{Sn}^{2+}] = b$ was measured with a tin amalgam electrode.

A mathematical analysis has been made of the two families of curves $Z(\log h)_B$ and $\eta(\log h)_B$, where Z is the average number of ligands (hydroxyl groups) bound per tin(II), B is the total Sn concentration, and $\eta = \log B/b$. The main product of the hydrolysis reaction is $\text{Sn}_3(\text{OH})_4^{2+}$, and the equilibrium constant of the reaction $3 \text{Sn}^{2+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Sn}_3(\text{OH})_4^{2+} + 4 \text{H}^+$ was found to be $\log K_{43} = -6.77 \pm 0.03$. Deviations at low values of Z , η , and B indicate the presence of $\text{Sn}_2(\text{OH})_2^{2+}$ and SnOH^+ . The following equilibrium constants were found: $2 \text{Sn}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Sn}_2(\text{OH})_2^{2+} + 2 \text{H}^+$, $\log K_{22} = -4.45 \pm 0.15$; $\text{Sn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{SnOH}^+ + \text{H}^+$, $\log K_{11} = -3.92 \pm 0.15$.

The first attempt to determine the products of the hydrolysis of tin(II) solutions and the equilibrium constants for their formation was made by Prytz¹ in 1928. Solutions of tin(II) salts were prepared in various ionic media and titrated at 25°C with NaOH. A hydrogen electrode was used to follow the change in the hydrogen ion concentration; an attempt was also made to follow the change in $[\text{Sn}^{2+}]$ using a tin electrode. The data could not be explained by a simple reaction giving SnOH^+ , but equilibrium constants were calculated on the basis of the following reaction

since such measurements cannot determine the number of solvent molecules involved. The following values of the equilibrium constant ($= K_{22}$ below) were given. SnCl_2 in 0.5 M KCl, 8×10^{-5} , in water, 2×10^{-3} ; SnBr_2 in 0.5 M KBr, 5.8×10^{-4} , in water, 8.3×10^{-3} ; $\text{Sn}(\text{ClO}_4)_2$ in water and 0.5 M NaClO_4 , 1.8×10^{-3} .

Randall and Murakami² studied the hydrolysis of Sn^{2+} in chloride solution. The equilibrium constant for the reaction $\text{Sn}^{2+} + 2 \text{H}_2\text{O} + \text{Cl}^- \rightleftharpoons$

$\text{Sn}(\text{OH})\text{ClH}_2\text{O}(\text{s}) + \text{H}^+$ was obtained from solubility measurements. The constant was given as $\log K = 2.75$.

In 1939, Gorman³ titrated tin(II) perchlorate solutions with NaOH and measured the hydrogen ion concentration with a hydrogen electrode at 25°C. The data were interpreted in terms of the reaction

The data were extrapolated to zero ionic strength to obtain the equilibrium constant, and a value $\log K_{11} = -1.70$ was given for 25°C.

Garrett and Heiks⁴ measured the solubility of SnO in HCl solutions and interpreted the results in terms of the mononuclear species Sn^{2+} , SnOH^+ , and $\text{Sn}(\text{OH})_2(\text{aq})$. From their data, we may obtain the following constants: $\log K_{11} = -2.1$, $\log K_{21} = -7.06$.

More recently, Vanderzee and Rhodes^{5,6} have estimated equilibrium constants for the reaction giving SnOH^+ at 0°, 25°, 35°, and 45°C, assuming this to be the only hydrolysis reaction occurring in solutions with high concentrations of halide ions. The values for $\log K_{11}$ range from -1.8 at 0° to -1.6 at 40°C.

Since the hydrolysis of many metal ions has been found to yield polynuclear complexes, it is essential to study the equilibria at a number of different total tin concentrations. The aim of this work was, therefore, to investigate the hydrolysis of tin(II) by the methods developed in this laboratory⁷⁻¹⁰ in order to elucidate the mechanism of the hydrolysis and to calculate the various equilibrium constants.

Symbols and formulas

The symbols adopted are mainly those used in the previous papers in this series.

b	concentration of free Sn^{2+}
B	total concentration of $\text{Sn}(\text{II})$
B	normalized value of B (27)
E_A	-emf, E_A° -constant, E_{jA} -liquid junction potential, all for cell A (3)
E_B	-emf, E_B° -constant, E_{jB} -liquid junction potential, all for cell B (4)
F_q	function of experimental data defined by (22)
$g(u) =$	$\sum_n k_n u^n$
h	concentration of free H^+
j_A, j_B	constants in $E_j = jh$
k_n	equilibrium constant for $(n+1)\text{Sn}^{2+} + nt\text{H}_2\text{O} \rightleftharpoons \text{Sn}[(\text{OH})_t\text{Sn}]_n^{(2n+2-tn)+} + nt\text{H}^+$
k, k_0	constants in $k_n = k^N$, hypothesis II; $k_n = k_0 k^n$, hypothesis IIIa; $k_n = k_0 n k^n$, hypothesis IIIb; $k_n = k_0 k^n (n!)^{-1}$, hypothesis IIIc (AB II 28a, b, c) ⁸
K_{pq}	equilibrium constant for the reaction $q\text{Sn}^{2+} + p\text{H}_2\text{O} \rightleftharpoons \text{Sn}_q(\text{OH})_p^{(2q-p)+} + p\text{H}^+$
n	number of links per complex
$\bar{n}$	average number of links per complex (11)

N	number of $\text{Sn}(\text{OH})_t$ links in a unique complex
P_1, P_2	normalizing constants (28), (29)
p	number of OH^- in $\text{Sn}_q(\text{OH})_p$
q	number of Sn^{2+} in $\text{Sn}_q(\text{OH})_p$
R	ratio K_{43}/K_{22}^2
t	number of hydroxyl groups per link
u	$= h^{-t}b$
x	$= \log B - t \log h$
$x_{1/2}$	value of x at $y = 1/2$
X	normalized $x = x + \log 2 - x_{1/2}$ (AB II 10) ^s
y	$= Z/t$
Z	average number of (OH) bound per $\text{Sn}(\text{II})$
α	normalized h (29)
β	normalized b (28)
γ_+, γ_{2+}	activity factors of H^+ and Sn^{2+}
δ	residual integral in (17)
η	$= \log B/b$
ξ	normalized x

All species may be combined with the medium ions, Na^+ and ClO_4^- , or with the solvent. The mole l^{-1} , M , is the standard unit of concentration used in all equilibrium constants. In some cases, the convenient mM unit is used in the text and headings.

METHOD

The hydrolysis of tin(II) was studied by two series of potentiometric titrations at 25°C . These will be referred to, in the following discussion, as the Z and η titrations. The free concentrations of H^+ and Sn^{2+} will be denoted by

$$[\text{H}^+] = h \quad [\text{Sn}^{2+}] = b$$

B is the total concentration of tin in the solution, and H is the analytical excess of hydrogen ion, assuming no hydrolysis, *i. e.* all tin(II) in the form Sn^{2+} . H is therefore negative in the latter parts of the titrations. The quantities B and H are known from the analytical data.

In each Z and η titration, B was maintained constant while H was varied and h measured. The average number of OH^- bound per $\text{Sn}(\text{II})$, Z , could then be calculated.

$$Z = (h - H) / B \quad (1)$$

The data are most conveniently plotted in the form $Z(\log h)_B$.

In the η titrations, the free tin concentration, $[\text{Sn}^{2+}] = b$, was also measured. One can then calculate

$$\eta = \log B/b \quad (2)$$

These data are presented in the form $\eta (\log h)_B$.

The acidity of the solutions was increased by adding H^+ClO_4^- and decreased by adding $\text{Na}^+\text{HCO}_3^-$. The use of $\text{Na}^+\text{HCO}_3^-$ as a base has been recommended

by Hedström¹¹ to avoid the formation of a precipitate which would be only slowly redissolved to give true equilibrium.

In both types of cells used, the reference electrode was

The hydrogen ion concentration was determined with the cell

Solution S had the initial composition

The measured emf is related to h by the following equation

$$E_A = E_A^\circ - 59.16 \log h - E_{jA} - 59.16 \log \gamma_+ \quad (3)$$

The equilibrium tin(II) concentration was measured using the following cell.

The equilibrium tin (II) concentration, b , is related to the emf of cell (B) by the equation

$$E_B = E_B^\circ - \frac{59.16}{2} \log b - \frac{59.16}{2} \log \frac{\gamma_{2+}}{a_{\text{Sn}}} - E_{jB} \quad (4)$$

In the two cells (A) and (B), E_A° and E_B° are constants characteristic of each cell. NaClO_4 was added to make all solutions 3 M in ClO_4^- with no other anions present. The activity coefficients, γ_+ and γ_{2+} , are defined so that $\lim_{c \rightarrow 0} a/c = 1$ in the solvent 3 M NaClO_4 . Since the concentrations of tin(II) and hydrogen ions were quite low compared to the 3 000 mM ClO_4^- (Sn(II)-maximum 40 mM; H^+ -maximum 70 mM), it can be assumed to a close approximation that activity factors remain constant and can be included in the E° for the cell¹² so that true stoichiometric equilibrium constants are obtained. The tin activity in the amalgam is maintained constant by the use of the mercury-rich phase of the 2-phase amalgam. At these low concentrations E_{jA} and E_{jB} are linear functions of the hydrogen ion concentration. If these junction potentials are written in the form $j_A h$ and $j_B h$, j_A has a value of -0.017 ± 0.001 mV/mM as reported earlier¹². The value of j_B varied somewhat between titrations with different B , and the value was determined for each titration by measurements in a region where no hydrolysis occurred. j_B varied from -0.022 to -0.028 mV/mM. It seems probable that the liquid junction potentials are the same and that the difference between E_{jA} and E_{jB} is caused by the inclusion of a small correction term for minute deviations of the amalgam electrode from the Nernst equation. At any rate, the magnitude of the effect is so small that it has no significant influence on the amalgam electrode data.

When E_A° and j_A are known and E_A is measured, h may be obtained using equation (3). Similarly, b is obtained from E_B° , j_B , and measured values of E_B applying eqn. (4).

EXPERIMENTAL DETAILS

One especially difficult problem encountered during the study of the hydrolysis of tin(II) solutions is that the tin(II) ion is very easily oxidized in solution to the 4-valent state. It is almost impossible to store and handle tin(II) solutions for any length of time without having small amounts of tin(IV) formed by reaction with atmospheric oxygen, a reaction that is greatly accelerated by light. Since the reduction of tin(IV) to tin(II) by metallic tin is a very slow process, it is quite difficult to reduce tin(IV) to the +2 state quantitatively. Halide ions are also particularly undesirable when the hydrolysis of tin(II) is to be investigated, since strong complexes are formed between these ions and Sn^{2+} . The following experimental procedure was developed to circumvent these experimental difficulties.

Tin(II) perchlorate solutions were prepared by a modification of the method first described by Noyes and Toabe¹³. Standard copper(II) perchlorate solutions were prepared by dissolution of Merck (p.a.) CuO in warm dilute perchloric acid. No traces of Cl^- could be found in the solutions which were then filtered and diluted.

The copper(II) content of the solutions was determined by electrodeposition of Cu using HNO_3 as a depolarizing agent and adding a small excess of urea just before the completion of the electrolysis to destroy any accumulated nitrous acid. The accuracy was better than $\pm 0.1\%$.

The total ClO_4^- content of the stock solution was determined by passing a definite volume through the cation exchange resin Duolite C 3 and titrating the eluate with standard NaOH . The analytical excess of H^+ in the stock solution was calculated from $[\text{H}^+] = [\text{ClO}_4^-] - 2[\text{Cu}^{2+}]$.

Standard solutions for the titrations were prepared by dilution of the stock solution with standard NaClO_4 and HClO_4 .

The tin(II) solutions were prepared just before each titration to the concentration 2B in a modification of the apparatus described by Lingane and Pecsok¹⁴ for the production of solutions of strong reducing agents. Hopkins and Williams' "Analar" metallic tin was used to displace copper(II) from the solutions. It was found that the hydrogen overvoltage on a pure tin surface was sufficient to prevent any reduction of H^+ so long as the solutions were free of any dissolved oxygen. Dissolved oxygen was flushed from the solutions by bubbling N_2 through them for about one hour. The tin was cleaned with dilute HCl before use, washed with water and ethanol, and dried under vacuum. Iodometric determinations of the tin(II) content of the most concentrated solution prepared (80 mM) agreed within $\pm 0.3\%$ of the value calculated on the basis of the copper displaced.

Tin amalgams were prepared in the two-limbed vessel described by Biedermann¹⁵ by warming freshly cleaned Merck (p.a.) tin and triple distilled mercury in an atmosphere of CO_2 . The two phase amalgam formed was thermostated at $25^\circ \pm 0.1^\circ \text{C}$ for about 20 h before use. Since the liquid phase of the tin amalgam contains 1.263 mole % tin at 25°C ¹⁶, amalgams with a constant tin activity could be easily prepared. The two phases were separated by passing the amalgam through a capillary tube just before the amalgam was introduced into the titration vessel.

Perchloric acid solutions were prepared by dilution of Kebo (p.a.) HClO_4 and standardized against KHCO_3 dried under CO_2 and also against standard NaOH solutions. The *sodium hydroxide solutions* were in turn standardized against potassium acid phthalate. The determinations agreed to $\pm 0.1\%$.

Sodium hydrogen carbonate solutions were prepared from Merck (p.a.) NaHCO_3 containing less than 0.01% Cl^- .

Sodium perchlorate solutions were prepared by neutralizing a solution of HClO_4 (p.a.) with Merck (p.a.) NaHCO_3 . The solutions were filtered to remove silicates and analyzed by evaporation and drying to a constant weight. The analysis was checked by passing portions of the solution through the hydrogen form of an ion exchanger and titrating the perchloric acid with NaOH . Good agreement was found between the two methods. No chloride, chlorate, or iron could be detected in the final product.

Silver perchlorate solutions were prepared by evaporating Merck (p.a.) AgNO_3 with a large excess of HClO_4 until no nitrate could be detected in the product. The remaining HClO_4 was neutralized with Ag_2O , the solution filtered, and the silver determined gravimetrically as AgCl .

Fig. 1. Arrangement for the preparation of tin(II) solutions.

Nitrogen gas was purified by washing with 10 % H_2SO_4 , 10 % NaOH , distilled water, and finally 3 M NaClO_4 . Both the nitrogen and carbon dioxide gases were freed of oxygen by passage over hot activated copper.

Apparatus

A titration cell of the "Wilhelm" type as described by Forsling, Hietanen, and Sillén⁷ was used. All measurements were made in a paraffin oil thermostat at $25^\circ \pm 0.1^\circ\text{C}$ which was located in a room thermostated at approximately 25°C .

The silver reference electrode was prepared as described by Brown¹⁷ and was coated with AgCl by electrolysis for half of an hour with a current of 0.3 mA.

The glass electrode was a Radiometer, Copenhagen, type G-102 AK. The potential of the cell

was constant to ± 0.1 mV indicating that eqn. (3) is valid. The emf values of the glass electrode cell (A) were read to 0.1 mV using a Radiometer PHM3 valve potentiometer. The emf values of the amalgam cell (B) were read to 0.01 mV with a Leeds and Northrup K-2 potentiometer.

The solution in the titration vessel was agitated with nitrogen gas while CO_2 was introduced over the surface of the liquid to prevent the entry of any atmospheric oxygen.

Titration procedure

Almost all of the titrations were carried out in the following manner. The preparation train illustrated in Fig. 1 was flushed with carbon dioxide for about 2 h. Approximately 100 ml of standard Cu(II) solution was introduced into the reservoir A containing the metallic tin. A strong flow of CO_2 was maintained during the addition to prevent the

entry of oxygen into the system. The flask was gently agitated for 10–15 min after which samples of the solution were withdrawn at C and tested for Cu^{2+} . When the solution gave no test for copper using $\text{Fe}(\text{CN})_6^{4-}$ in dilute HCl , it was transferred to the reservoir B. The burette D could be filled by pressing the solution up with CO_2 admitted through the 3-way stopcock G. The tin solution was thus completely protected from the atmosphere during the preparation. Stopcock F was used to meter the solution during the titration.

25.00 ml of 3 M NaClO_4 solution was pipetted into the titration flask. About 100 g of tin amalgam was introduced into the cell from the two limbed vessel. A strong stream of CO_2 was passed over the surface of the NaClO_4 solution, while N_2 was bubbled into the solution. A platinum needle was used to make electrical contact with the amalgam. 25.00 ml of the tin solution T_1 (concentration 2 B) was then added. This mixture, solution S, was titrated with equal volumes v_1 of NaHCO_3 solution (T_2) and solution T_1 . In this way, the total concentration of tin was maintained constant at B. The values of the cell constants E_A° and E_B° were obtained as illustrated in Table 1 by titration at hydrogen ion concentrations where hydrolysis was negligible.

The one exception to the above procedure was for the titration with $B = 2.5$ mM. In this case T_1 had a concentration of 4 B. Therefore, 75.00 ml of NaClO_4 (3 M) was added together with 25.00 ml of T_1 . Titration was with equal volumes v_1 of T_1 and T_2 plus $2v_1$ ml of 3 M NaClO_4 .

At the end of the titrations with 5 and 2.5 mM $\text{Sn}(\text{II})$, the emf values of both cells were noted. CO_2 was passed into the solution for one hour and N_2 bubbled through the solution again for 2 min. No change in either the glass or amalgam electrode potentials was observed, so that it can be assumed that there was no significant formation of complexes between tin(II) and carbonate ion even at the lowest value of $h \sim 1.0$ mM.

Steady values of both potentials were attained rapidly, usually within 15 min, and remained constant for 10 h. At $\eta > 0.3$ the amalgam surface apparently became contaminated, since variations of 0.1 mV could be obtained by agitation of the amalgam. The glass electrode potentials were reproducible within ± 0.2 mV and the amalgam potentials within ± 0.05 mV.

A back titration was performed at the lowest value of B, and the points for both $Z(\log h)$ and $\eta(\log h)$ fell on the same curve, indicating that true equilibria had been obtained even in this region.

At tin(II) concentrations of less than 2.5 mM, the amalgam electrode potentials became very sensitive to agitation of the amalgam pool even at low values of η , and hence no measurements were made for $B < 2.5$ mM.

Table 1. Standardization of electrodes for $B = 20$ mM.

$B = 20.00$ mM, $H = 60.00$ mM, $[\text{ClO}_4] = 3$ M		50.00 ml					
$B = 40.00$ mM, $H = 120.00$ mM, $[\text{ClO}_4] = 3$ M		v_1 ml					
$[\text{NaHCO}_3] = 272.5$ mM, $[\text{ClO}_4] = 3$ M		v_1 ml					
		$E_A^\circ = 316.1 \pm 0.05$ mV					
		$E_B^\circ = 777.26 \pm 0.01$ mV					
v_1 ml	E_A mV	E_B mV	H mM	E_A°	E_B°	E_{jA}	E_{jB}
0.00	211.9	740.10	60.00	316.1	777.30	1.00	1.28
0.50	213.0	740.00	57.33	316.0	777.25	0.96	1.23
1.00	241.1	739.94	54.77	316.1	777.25	0.91	1.17
1.75	215.8	739.88	51.08	316.0	777.27	0.85	1.09
2.50	217.7	739.80	47.62	316.2	777.26	0.79	1.02
3.00	218.8	739.74	45.39	316.0	777.25	0.76	0.97
3.50	220.0	739.70	43.26	316.1	777.26	0.72	0.92
4.00	221.3	739.65	41.21	315.9	777.25	0.69	0.88
5.00	223.6	739.57	37.30	316.4	777.25	0.62	0.80
6.00	226.7	739.53	33.63	316.0	777.29	0.56	0.72
7.00	229.0	739.43	30.19	316.0	777.26	0.50	0.65
8.00	231.8	739.38	26.97	316.1	777.28	0.45	0.58

Fig. 2. Data from glass electrode measurements. Average number, Z , of OH bound per Sn as a function of $\log h$ (molar scale), B as a parameter. Full curves calculated for $K_{11} = K_{22} = 0$, $\log K_{43} = -6.69$. Broken curves calculated for $\log K_{11} = -3.92$, $\log K_{22} = -4.45$, $\log K_{43} = -6.77$. Points $\bullet$ adjusted upward by $\frac{1}{2}0.02$ units.

Fig. 3. Data from amalgam electrode measurements, $\eta = \log B/b$ as a function of $\log h$ (molar scale), B as a parameter. Curves calculated for the same sets of constants as in Fig. 2.

THE MAIN PRODUCTS OF HYDROLYSIS

Fig. 2 gives the data $Z(\log h)_B$ as calculated from the emf values of the cell (A), using eqns. (1) and (3). Fig. 3 gives the data $\eta(\log h)_B$ calculated using eqns. (2) and (4) together with the emf values of cells (A) and (B). Table 2 gives the values of $\log h$, Z , and η for each titration.

It is seen from Figs. 2 and 3 that Z and η are functions of both B and h , which indicates that at least one polynuclear species is formed during the hydrolysis of tin(II) solutions. If only mononuclear complexes were formed, Z and η would be functions of the single variable h .

In order to evaluate the data, several different approaches will be tried in the following discussion.

"Core + links" approach

The systematic treatment developed by Sillén^{8,18} will be closely followed in this discussion. It has frequently been observed that the products formed by the hydrolysis of metal ions can be described by a general "core + links"

Table 2. Experimental data Z , η , $\log h$.

Titration 1. $B = 40$ mM			Titration 2. $B = 20$ mM		
Z	η	$-\log h$	Z	η	$-\log h$
0.01	0.0000	1.391	0.001 ₅	0.0008	1.569
0.01 ₅	0.0000	1.425	0.002	0.0025	1.622
0.01 ₈	0.0003	1.460	0.001 ₅	0.0028	1.675
0.02	0.0014	1.496	0.01	0.0038	1.731
0.02 ₂	0.0014	1.533	0.01	0.0049	1.761
0.02 ₅	0.0024	1.573	0.01	0.0066	1.795
0.025	0.0034	1.612	0.01	0.0072	1.830
0.032	0.0058	1.650	0.02	0.0092	1.861
0.038	0.0071	1.693	0.02	0.0116	1.898
0.042	0.0098	1.732	0.03	0.0140	1.932
0.054	0.0108	1.771	0.04	0.0174	1.966
0.054	0.0145	1.817	0.052	0.0211	2.003
0.068	0.0173	1.856	0.066	0.0258	2.037
0.085	0.0227	1.893	0.074	0.0312	2.080
0.10	0.0277	1.930	0.119	0.0437	2.140
0.115	0.0341	1.964	0.164	0.0616	2.204
0.135	0.0412	1.996	0.220	0.0836	2.256
0.157	0.0470	2.021	0.276	0.1076	2.305
0.177	0.0538	2.048	0.333	0.1332	2.351
0.219	0.0720	2.097	0.392	0.1627	2.390
0.261	0.0950	2.138	0.452	0.1942	2.427
0.304	0.1143	2.173	0.506	0.2229	2.469
0.344	0.1342	2.204	0.562	0.2523	2.506
0.384	0.1559	2.229	0.616	0.2851	2.544
0.429	0.1748	2.268	0.670	0.3189	2.579
0.473	0.1995	2.295	0.722	0.3477	2.611
0.513	0.2208	2.324	0.772	—	2.645
0.552	0.2421	2.348	0.820	—	2.681
0.587	0.2634	2.375	0.867	—	2.719
0.622	0.2813	2.935	0.912	—	2.758

Table 2. Continued

0.956	—	2.799	0.402	0.1780	2.699
0.998	—	2.841	0.542	0.2524	2.792
1.040	—	2.880	0.690	—	2.887
			0.838	—	2.992
			0.986	—	3.118
<i>Titration 3. B = 10 mM</i>					
<i>Z</i>	η	$-\log h$			
0.00	0.0000	1.731			
0.01	0.0007	1.768			
0.00	0.0024	1.812			
0.02	0.0027	1.852			
0.01	0.0037	1.900			
0.03	0.0054	1.945			
0.028	0.0085	2.001			
0.041	0.0108	2.057			
0.050	0.0145	2.121			
0.069	0.0220	2.187			
0.102	0.0314	2.251			
0.143	0.0477	2.317			
0.195	0.0646	2.380			
0.261	0.0926	2.432			
0.329	0.1248	2.484			
0.396	0.1616	2.544			
0.511	0.2164	2.611			
0.548	0.2360	2.637			
0.625	0.2782	2.682			
0.661	—	2.709			
0.700	—	2.730			
0.738	—	2.757			
0.776	—	2.780			
0.810	—	2.814			
0.847	—	2.841			
0.885	—	2.866			
0.922	—	2.894			
<i>Titration 5. B = 5 mM</i>					
<i>Z</i>	η	$-\log h$			
—0.02	0.0016	1.808			
—0.02	—0.0004	1.839			
—0.02	—0.0001	1.869			
—0.02	0.0002	1.898			
—0.04	—0.0008	1.934			
—0.02	—0.0001	1.966			
—0.02	0.0009	2.006			
—0.01	0.0029	2.043			
—0.02	0.0046	2.087			
—0.02	0.0063	2.133			
—0.02	0.0097	2.184			
—0.006	0.0124	2.233			
0.02	0.0164	2.283			
0.024	0.0249	2.348			
0.056	0.0344	2.407			
0.094	0.0459	2.469			
0.158	0.0655	2.518			
0.216	0.0902	2.579			
0.288	0.1179	2.633			
0.368	0.1524	2.681			
0.442	—	2.743			
0.530	—	2.789			
0.612	—	2.844			
0.700	—	2.896			
0.784	—	2.959			
<i>Titration 4. B = 5 mM</i>					
<i>Z</i>	η	$-\log h$			
0.01	—0.0008	1.563			
0.04	0.0002	1.592			
0.00	—0.0001	1.628			
0.00	—0.0004	1.660			
0.00	0.0002	1.695			
—0.01	0.0002	1.732			
0.02	0.0002	1.768			
0.00	0.0009	1.813			
0.02	0.0009	1.854			
—0.02	0.0022	1.905			
—0.02	0.0029	1.957			
0.01 ₄	0.0039	2.010			
0.01 ₄	0.0043	2.074			
0.024	0.0087	2.143			
0.026	0.0141	2.226			
0.046	0.0232	2.317			
0.096	0.0425	2.412			
0.172	0.0729	2.512			
0.274	0.1179	2.610			
<i>Titration 6. B = 2.5 mM</i>					
<i>Z</i>	η	$-\log h$			
—0.04	0.0010	1.800			
—0.04	0.0017	1.822			
—0.04	0.0020	1.844			
0.00	0.0020	1.862			
0.00	0.0017	1.883			
0.00	0.0024	1.906			
0.00	0.0034	1.930			
—0.04	0.0044	1.954			
—0.04	0.0051	1.977			
—0.02 ₄	0.0064	2.003			
—0.004	0.0074	2.026			
—0.004	0.0078	2.052			
—0.01 ₂	0.0085	2.080			
—0.01 ₂	0.0091	2.108			
—0.004	0.0108	2.136			
0.004	0.0112	2.165			
0.008	0.0132	2.199			
—0.004	0.0142	2.231			
0.02 ₄	0.0159	2.260			

Table 2. Continued

0.01 ₂	0.0186	2.299	0.08	0.0047	1.901
0.02 ₀	0.0210	2.336	0.04	0.0054	1.925
0.03 ₂	0.0233	2.375	0.08	0.0057	1.945
0.03 ₃	0.0270	2.419	0.04	0.0064	1.972
0.060	0.0318	2.459	-0.004	0.0071	2.001
0.068	0.0395	2.508	0.004	0.0085	2.025
0.088	0.0473	2.556	-0.02	0.0091	2.054
0.124	0.0588	2.603	0.01	0.0101	2.077
0.164	0.0744	2.652	-0.02	0.0115	2.109
0.228	0.0953	2.699	-0.02	0.0125	2.138
0.264	0.1170	2.750	-0.01	0.0135	2.167
0.320	0.1487	2.802	-0.004	0.0159	2.196
0.384	0.1792	2.850	0.004	0.0179	2.229
0.460	0.2113	2.897	-0.008	0.0199	2.266
0.528	0.2529	2.951	-0.008	0.0227	2.304
0.616	—	2.988	-0.004	0.0264	2.342
			0.008	0.0294	2.381
			0.02	0.0335	2.422
			0.03	0.0395	2.468
			0.048	0.0507	2.515
			0.080	0.0588	2.559
			0.15	0.0886	2.657
			0.096	0.0669	2.581 *
			0.064	0.0507	2.513 *
			0.036	0.0379	2.452 *
			0.03	0.0318	2.395 *
			0.01	0.0308	2.348 *
<hr/>					
Titration 7. $B = 2.5$ mM					
Z	η	$-\log h$			
	0.0010	1.737			
	0.0017	1.758			
	0.0024	1.778			
	0.0027	1.798			
	0.0027	1.819			
	0.0037	1.840			
	0.0030	1.862			
0.03	0.0044	1.881			

* Back titrations

formula, *i. e.* $\text{Me}[(\text{OH})_t\text{Me}]_n$, where t is a constant and n may be a constant or have several integral values ^{15,19-22}. If all of the complexes can be described by the "core + links" hypothesis, the curves $Z(\log h)_B$ and $\eta(\log h)_B$ must form a family of parallel curves with a constant spacing along the $\log h$ axis. The value of t , the number of hydroxyl groups per "link", may be obtained from (5).

$$\left(\frac{\partial \log B}{\partial \log h}\right)_Z = \left(\frac{\partial \log B}{\partial \log h}\right)_\eta = t \quad (5)$$

It is seen that the data for the hydrolysis of tin(II), given in Figs. 2 and 3, form approximately parallel curves. The spacing between the curves gives the difference quotients

$$\left(\frac{\Delta \log B}{\Delta \log h}\right)_Z = \left(\frac{\Delta \log B}{\Delta \log h}\right)_\eta = 2.0 \quad (5a)$$

It follows from eqn. (5) that the value of t may be obtained directly from the slope of the curves $\log B(\log h)_Z$ and $\log B(\log h)_\eta$ given in Figs. 4 and 5. Neglecting the slight deviations at low B , the data form straight lines with slopes of 2.0.

The value of t obtained may be tested by plotting Z and η versus $\log B - t \log h$. Since the limitation to "core + links" species requires Z and η

Fig. 4. $\log B$ as a function of $\log h$, Z as a parameter. Full curves calculated for $K_{11} = K_{22} = 0$, $\log K_{43} = -6.69$. Broken curves calculated for $\log K_{11} = -3.92$, $\log K_{22} = -4.45$, $\log K_{43} = -6.77$.

to be functions of the single variable $u = (bh^{-t})$ and $Bh^{-t} = f(u)$, Z and η are functions of the variable (Bh^{-t}) . The data are most conveniently plotted as

$$\begin{aligned} y &= Z/2 \text{ versus } x = \log (Bh^{-t}) \\ \eta &\text{ versus } x = \log (Bh^{-t}) \end{aligned}$$

These data are given in Figs. 6 and 7.

Since all of the experimental points seem to describe the same curve within the range $40 \text{ mM} \geq B \geq 5 \text{ mM}$, the "core + links" hypothesis may be considered a good explanation of the data. A significant discrepancy occurs for $B = 2.5 \text{ mM}$ in the plot $\eta(x)$. Deviations in this direction are to be expected if mononuclear species are formed in addition to the "core + links" complexes. Although this deviation appears to be beyond the experimental error, a discussion of the effect will be postponed until the data have been evaluated in the region where the $y(x)$ and also the $\eta(x)$ curves coincide for $t = 2$.

Direct analysis of the curves $y(x)$ and $\eta(x)$

As outlined by Sillén in AB II⁸, it is possible to calculate the equilibrium constants for the "core + links" complexes directly from the experimental data $y(x)$ and $\eta(x)$.

Fig. 5. $\log B$ as a function of $\log h$, η as a parameter. Curves calculated for the same sets of constants as in Fig. 4.

If k_n is defined as the equilibrium constant for the reaction

then

$$B = b + \sum (n+1) [\text{Sn}[(\text{OH})_2\text{Sn}]_n^{2+}] = b + \sum (n+1) k_n h^{-2n} b^{n+1} \quad (6)$$

Substituting $u = (h^{-2}b)$ into (6)

$$B = b (1 + \sum (n+1) k_n u^n) \quad (7)$$

if $g = \sum k_n u^n$, $\frac{dg}{du} = g'$, substitution into (7) gives

$$B = b \frac{d}{du} (u + ug) = b(1 + g + ug') \quad (8)$$

From (8) it is seen that

$$(1 + g) = u^{-1} \int_0^u B b^{-1} du = u^{-1} \int_0^u 10^\eta du \quad (9)$$

It follows directly from the definitions of u , x , and η that

$$\log u = x - \eta. \quad (10)$$

Fig. 6. Z or $y = Z/2$ as a function of $x = \log B - 2 \log h$. All experimental points are shown using the same symbols as in Fig. 2. Full curve calculated for $K_{11} = 0$, $\log K_{23} = -4.43$, $\log K_{43} = -6.74$. Broken curve calculated for $\log K_{43} = -6.69$.

Therefore $g(u)$ may be obtained from the amalgam electrode data $\eta(x)$, using (9) and (10).

One may also calculate the average number of links in the complexes (average degree of polymerization) defined by

$$\bar{n} = \frac{\sum n c_n}{\sum c_n} = \frac{u g'}{g} \quad (11)$$

Substituting from (8)

$$\bar{n} = \frac{B b^{-1} - g - 1}{g} \quad (12)$$

η can also be obtained as a function of u from the glass electrode data $y(x)$ using the eqn. (15) given by Sillén in AB II⁸. In the present case $y = Z/t = Z/2$.

$$\eta = y \log e + \int_{-\infty}^x y dx \quad \text{together with} \quad (13)$$

$$\log u = x - \eta \quad (10)$$

Although $g(u)$ may then be obtained from (9) as with the amalgam electrode data, it is simpler to apply a relation obtained from eqns. (5a) and (8a) in AB II⁸.

$$\log (1 + g) = \eta + \log (1 - y) \quad (14)$$

Equation (14) may be easily derived in the following way. The total number of bound OH groups per liter of solution is given by the following equation (comparing with equations (6) to (8)).

$$BZ = \sum 2n[\text{Sn}[(\text{OH})_2\text{Sn}]_n^{2+}] = 2b \sum nk_n u^n = 2bug' \quad (15)$$

Inserting $Z = 2y$, $Bb^{-1} = (1 + g + ug')$ (8), and $Bb^{-1} = 10\eta$ (definition) and eliminating Bb^{-1} and ug' gives $(1 + g) = 10\eta(1 - y)$. Upon taking logarithms we obtain (14).

Substituting (14) into (12) we obtain

$$\bar{n} = \frac{y}{1 - y - bB^{-1}} \quad (16)$$

Using (13), (10), and (14), one may obtain $\eta(x)$ and $g(u)$ from the glass electrode data $y(x)$.

In order to calculate $g(u)$ from the amalgam electrode data, a smooth curve was drawn through the data $\eta(x)$ using the lowest values of η where slight deviations occurred at low values of η . η was then read off for a number of values of x . Using eqn. (10), a new curve was constructed for B/b as a function of u . The integration in eqn. (9) was made graphically. The data for g , u , and $\bar{n}$ calculated from eqn. (12) are given in Table 4. Since from eqn. (11) $\bar{n} = u g'/g = d \log g / d \log u$, $\bar{n}$ may also be obtained from a plot of $\log g$ versus $\log u$. This is given in Fig. 8. In order to evaluate the polynuclear complexity constants, the function $gu^{-1} = k_1 + k_2u + \dots$ was plotted versus u in Fig. 9.

In a similar fashion, a smooth curve was drawn through the glass electrode data $y(x)$. Again when deviations occurred at low values of y , the lowest values were chosen for each x . The values of B/b , $\log g$, and $\log u$ were calculated using

Table 3. Direct analysis of curve $y(x)$.

y	x	$\int_{-\infty}^x y \, dx$	B/b	$\log u$	$\log g$	$\bar{n}$
0.104	2.800	0.0339	1.199	2.7212	-1.1308	1.68
0.135	2.900	0.0458	1.272	2.7953	-1.0000	1.71
0.166	3.000	0.0609	1.358	2.8671	-0.8761	1.69
0.201	3.100	0.0792	1.468	2.9333	-0.762	1.70
0.240	3.200	0.1013	1.605	2.9945	-0.6576	1.75
0.274	3.300	0.1270	1.762	3.0539	-0.5544	1.73
0.319	3.400	0.1566	1.972	3.1052	-0.4647	1.83
0.364	3.500	0.1908	2.233	3.1510	-0.3768	1.94
0.397	3.600	0.2288	2.519	3.1987	-0.2848	1.93
0.427	3.700	0.2704	2.856	3.2442	-0.1965	1.91
0.454	3.800	0.3144	3.248	3.2885	-0.1118	1.91
0.480	3.900	0.3611	3.712	3.3304	-0.0315	1.91
0.506	4.000	0.4104	4.268	3.3698	0.0444	1.95

Table 4. Direct analysis of curve $\eta(x)$.

B/b	u	$\frac{1}{u} \int_0^u B/b \, du$	$\log u$	$\log g$	$\bar{n}$
1.042	200	1.0173	2.3010	-1.7620	1.44
1.073	300	1.0307	2.4771	-1.5129	1.37
1.118	400	1.0469	2.6021	-1.3288	1.51
1.171	500	1.0664	2.6990	-1.1778	1.58
1.236	600	1.0893	2.7782	-1.0491	1.65
1.316	700	1.1159	2.8451	-0.9359	1.72
1.408	800	1.1467	2.9031	-0.8335	1.80
1.505	900	1.1810	2.9542	-0.7423	1.79
1.611	1 000	1.2187	3.0000	-0.6601	1.79
1.719	1 100	1.2592	3.0414	-0.5864	1.77
1.832	1 200	1.3000	3.0792	-0.5229	1.77
1.958	1 300	1.3463	3.1139	-0.4605	1.77
2.068	1 400	1.3939	3.1461	-0.4056	1.71
2.222	1 500	1.4440	3.1761	-0.3526	1.75

eqns. (10) and (14), performing the integration in (13) graphically. These data together with the values of $\bar{n}$ calculated with eqn. (16) are given in Table 3. The data are plotted as $\log g$ versus $\log u$ together with the amalgam electrode data in Fig. 8. The function gu^{-1} is also plotted versus u in Fig. 9 together with the amalgam data.

In performing the integration in eqn. (13), it was assumed that the residual integral

$$\delta = \int_{-\infty}^{x=1.7} y \, dx = 0 \quad (17)$$

It is seen from the data in Tables 3 and 4 and the slope of the curve in Fig. 8 that $\bar{n}$ rises from approximately 1.7 to 2.0, indicating that the trimer $\text{Sn}[(\text{OH})_2\text{Sn}]_2^{2+}$ predominates at high values of y and η . It is seen from the $y(x)$ data that $\bar{n}$ approaches 2.0 as a limit, *i. e.* $d\bar{n}/du = 0$ at high values of u . This indicates that no complexes higher than the trimer are present in significant amounts.

The data were also used to calculate the number of hydroxyl groups bound per complexed metal atom. This quantity $BZ(B-b)^{-1}$ had an average value 1.30 ± 0.03 for $2.6 \leq x \leq 3.5$ indicating the complex is primarily $\text{Sn}_3(\text{OH})_4^{2+}$.

The values of the equilibrium constants for the dimer and trimer "core + links" complexes may be obtained from the slope and intercept of the curve in Fig. 9. The following values were obtained

$$\begin{aligned} \log K_{22} &= -4.4_3 \pm 0.15 \\ \log K_{43} &= -6.74 \pm 0.04 \end{aligned}$$

The solid lines in Figs. 6 and 7 were calculated with these constants.

Fig. 7. η as a function of $x = \log B - 2 \log h$. All experimental points are shown using the same symbols as in Fig. 3. Curves calculated for the same sets of constants as in Fig. 6.

Comparison with simple reaction mechanisms

The experimental curves $y(x)$ and $\eta(x)$ were compared with the families of curves $y(X)$ and $\eta(\xi)$ calculated for the simple reaction mechanisms outlined in [†]AB II⁸ and part 8¹⁹ of this series.

† No agreement was found between the experimental curves and those calculated on the basis of hypothesis I. This hypothesis assumes that no soluble complexes occur and only a precipitate is formed.

‡ Good agreement was obtained between the experimental and theoretical curves calculated for hypothesis II with $N = 2$. This hypothesis assumes the formation of a single soluble complex where n has the single value N . This again indicates that the trimer $\text{Sn}[(\text{OH})_2\text{Sn}]_2^{2+}$ is the main complex formed by the hydrolysis of solutions of tin(II). The equilibrium constant for the reaction may be obtained in the following way. The constant k is defined by

$$k_n = k^N, \quad (18)$$

when n has the single value N and where k_n is the equilibrium constant for the reaction

Fig. 8. Direct analysis of the curves $y(x)$ (Fig. 6) $\circ$, and $\eta(x)$ (Fig. 7) $\square$: $\log g$ as a function of $\log u$, together with the best straight line of slope 1.92.

By moving the calculated curves $y(X)$ and $\eta(\xi)$ across the experimental points, the differences $(X-x)$ and $(\xi-x)$ can be read off at the position of best fit. The value of k is then obtained directly from one of the relations

$$(X-x) = \log 2 - x_{1/2} = -\log 2 + \log k \quad [(24), (25) \text{ AB II}^8] \quad (19)$$

where $x_{1/2}$ = value of x at $y = 1/2$, or from

$$(\xi-x) = \log k + \frac{1}{2} \log 3 \quad [(59) \text{ AB II}^8] \quad (20)$$

Fig. 9. $[gu^{-1}]$ as a function of u . $y(x)$ data $\circ$, $\eta(x)$ data $\square$. Straight line drawn for $\log K_{43} = -6.74$, $\log K_{22} = -4.43$.

The best overall fit between the curves $y(X)$ and $y(x)$ gave $\log k = -3.36$. If the deviations at low values of y were ignored and the curves matched so the best fit was obtained at high values of y where effects due to complexes lower than the trimer would be small, $\log k = -3.37$. The value of the equilibrium constant for the reaction

is related to k by

$$K_{43} = k^N = k^2 \quad (18a)$$

The best overall fit is obtained with $\log K_{43} = -6.72$ or for the best fit at high values of y , $\log K_{43} = -6.74$.

The curves $\eta(x)$ and $\eta(\xi)$ were compared in the same way. The best overall fit was obtained with $\log k = -3.34$, which corresponds to $\log K_{43} = -6.68$. From the best fit at high values of η , $\log k = -3.37$ which again corresponds to $\log K_{43} = -6.74$.

The curves $y(X)$ and $\eta(\xi)$ were also calculated for the repeated mechanisms (AB II⁸), III-a, -b, -c for different values of k_0 . A satisfactory agreement could not be obtained between these curves and the experimental data $y(x)$ and $\eta(x)$ using any of these hypotheses. In particular, large deviations occurred for $y > 0.3$, as the theoretical curves all rose too sharply. This is caused by the consideration of polymers higher than the trimer in all of these hypotheses.

Comparison with these simple mechanisms has verified the information obtained from the direct analysis of the experimental data, *i. e.* there seems to be no evidence for the formation of complexes higher than the trimer $\text{Sn}_3(\text{OH})_4^{2+}$ during the hydrolysis.

If one views both sets of data $y(x)$ and $\eta(x)$ simultaneously, the best overall fit is with $\log K_{43} = -6.69 \pm 0.04$; however, significant deviations occur at both high and low values of y and η . The full lines in Figs. 2, 3, 6, and 7 are calculated for $\log K_{43} = -6.69$. The best fit to both sets of data at high values of y and η is obtained with $\log K_{43} = -6.74 \pm 0.04$, a value which is identical with that obtained by direct analysis of the data.

Secondary reactions

Although it appears that the main parts of the curves $y(x)$ and $\eta(x)$ are compatible with the formation of a single complex $\text{Sn}_3(\text{OH})_4^{2+}$, there are definite deviations at low values of Z, η , and B indicating the presence of small amounts of other complexes.

In an attempt to establish the formulas of the secondary products, an approach similar to that used by Kakihana and Sillén²² will be used.

It is first assumed that only one other complex besides $\text{Sn}_3(\text{OH})_4^{2+}$ is formed. The equilibrium constants for the two species will be written as K_{pq} and K_{43} . Charges will be omitted in the following equations.

$$\begin{aligned} B &= [\text{Sn}^{2+}] + q[\text{Sn}_q(\text{OH})_p] + 3 [\text{Sn}_3(\text{OH})_4] \\ &= b + qb^qh^{-p}K_{pq} + 3 b^3h^{-4}K_{43} \\ BZ &= pb^qh^{-p}K_{pq} + 4 b^3h^{-4}K_{43} \\ BZ b^{-3}h^4 &= 4K_{43} = pb^{(q-3)}h^{(4-p)}K_{pq} \end{aligned} \quad (21)$$

Fig. 10. $\log F_1$, $\log F_2$, and $\log F_3$ (eqn. 22) versus $\log h$. Straight line ($\log F_2$) calculated using $\log K_{22} = -4.30$. The experimental points are given for $40 \text{ mM} > B > 5 \text{ mM}$.

$$\text{Let } (BZ b^{-3}h^4 - 4K_{43})b^{(3-q)} = F_q \quad (22)$$

$$\log F_q = \log pK_{pq} + (4-p) \log h \quad (23)$$

The function F_q was calculated for $q = 1, 2$, and 3 , assuming $K_{43} = -6.74$, using the data from the glass and amalgam electrodes for $5 \text{ mM} \leq B \leq 40 \text{ mM}$, and plotted versus $\log h$. If the deviations from the single complex curve can be attributed primarily to one other complex, one should obtain a straight line with slope $(4-p)$ and intercept $\log pK_{pq}$ when the correct value of q has been chosen.

The data are shown in Fig. 10. For $q = 2$ the data form a good approximation to a straight line with a slope of 2 . The data for $q = 1$ and 3 both exhibit a greater spread. In agreement with the result of the direct analysis, the hydrolysis data can be well explained for the range $5 \text{ mM} \leq B \leq 40 \text{ mM}$ by the formation of two polynuclear complexes $\text{Sn}_2(\text{OH})_2^{2+}$ and $\text{Sn}_3(\text{OH})_4^{2+}$. A value of $\log K_{22} = -4.3 \pm 0.2$ is obtained from the position of the best straight line in Fig. 10.

It is still necessary to explain the deviations at the lowest value of B , 2.5 mM . The only reasonable explanation of these deviations is, besides experimental errors, the presence of mononuclear complexes. The method of Hedström²⁴ was used to obtain values for the mononuclear constants. Using data for both b and h , we may calculate

$$\begin{aligned} \frac{B-b}{b} &= (K_{11}h^{-1} + K_{21}h^{-2} + K_{31}h^{-3} + \dots) + \\ &2b (K_{12}h^{-1} + K_{22}h^{-2} + K_{32}h^{-3} + \dots) + \\ &3b^2 (K_{13}h^{-1} + K_{23}h^{-2} + \dots) + \dots \end{aligned} \quad (24)$$

Plots were made of (a) $[(B-b)/b]h$ and (b) $[(B-b)/b]h^2$ versus b . Because the main complex is a trimer, the functions vary essentially as the square of b . This renders the extrapolation to $b = 0$, required to determine the mononuclear constant, quite inaccurate. If a single complex SnOH^+ is formed, the intercept of plot (a) should be K_{11} , while if $\text{Sn}(\text{OH})_2$ (aq) is formed the intercept of (b) should be K_{21} . The data appear to be best satisfied by the formation of a mononuclear complex SnOH^+ with $K_{11} = 1.2 \times 10^{-4}$. The determination of K_{11} is quite inaccurate, since the extrapolation is governed almost entirely by the set of points for $B = 2.5$ where the experimental errors are greatest.

If the proper mononuclear constant has been chosen, a plot of $\left[\left(\frac{B-b}{b}\right)h - K_{11}\right] h/b$ versus b should give a straight line with intercept $2K_{22}$ and $3K_{43}h^{-2}$ as slope. Values of $K_{11} = 1.1, 1.2$, and 1.3×10^{-4} were tried, and the best family of straight lines was obtained with $K_{11} = 1.2 \times 10^{-4}$ and gave a value of $\log K_{22} = -4.5 \pm 0.15$. The value of K_{43} obtained in this way is quite inaccurate, $\log K_{43} = -6.7 \pm 0.2$.

Calculation of equilibrium constants with normalized projection maps

Since the effects due to mononuclear and dinuclear complexes are slight, it is best to refine the values of the constants using the method of projection maps.

In the present work, the quantities b, h, B, H are known. The presence of the two polynuclear species may be considered established by the previous discussion; however, there is still some question as to the composition of the mononuclear complex(es).

For this reason projection maps were constructed for the two extreme cases (a) one mononuclear complex SnOH^+ (b) one mononuclear complex $\text{Sn}(\text{OH})_2$.

In the first case (a)

$$B = b + K_{11}bh^{-1} + 2K_{22}b^2h^{-2} + 3K_{43}b^3h^{-4} \quad (25)$$

$$\eta = \log (1 + K_{11}h^{-1} + 2K_{22}bh^{-2} + 3K_{43}b^2h^{-4}) \quad (26)$$

$$BZ = K_{11}bh^{-1} + 2K_{22}b^2h^{-2} + 4K_{43}b^3h^{-4} \quad (27)$$

It is convenient to prepare two different projection maps of the variables

$$\log B = f(\log h)_Z$$

$$\log B = f(\log h)_\eta$$

and to compare these with the calculated, normalized projection maps $\log B$ ($\log \alpha$)_Z and $\log B$ ($\log \alpha$)_η. The normalized variables β and α are defined by the following equations.

$$\beta = b \cdot 10^{P_1} \quad B = B \cdot 10^{P_2} \quad (28)$$

$$\alpha = h^{-1} 10^{P_1} \quad (29)$$

where P_1 and P_2 are constants.

The two constants P_1 and P_2 may be obtained by the displacement of the curve $\log B (\log \alpha)_Z$ with respect to $\log B (\log h)_Z$ and also by the displacement of $\log B (\log \alpha)_\eta$ with respect to $\log B (\log h)_\eta$, since

$$\begin{aligned} P_1 &= \log \alpha - \log h \\ P_2 &= \log B - \log B \end{aligned}$$

In order to obtain simple equations for calculation, the constants P_1 and P_2 are chosen so that all equilibrium constants will be eliminated from the equations. This necessitates the assumption of some relation between two of the constants. Since the data at high Z and η are well satisfied by the two constants for $\text{Sn}_2(\text{OH})_2^{2+}$ and $\text{Sn}_3(\text{OH})_4^{2+}$ (cf. Figs. 6, 7), a relation will be chosen between K_{22} and K_{43} which satisfies the values obtained by direct analysis.

$$R = K_{43}K_{22}^{-2} = 10^{2.13}$$

By the proper choice of the constants P_1 and P_2 , we may make the following equations, analogous to (25)–(27), valid.

$$B = B \cdot 10^{P_1} = (\beta + \beta\alpha + 2\beta^2\alpha^2 + 3R\beta^3\alpha^4) \quad (30)$$

$$\eta = \log (1 + \alpha + 2\beta\alpha^2 + 3R\beta^2\alpha^4) \quad (31)$$

$$BZ = (\beta\alpha + 2\beta^2\alpha^2 + 4R\beta^3\alpha^4) \quad (32)$$

Inserting (28) and (29) into (30)–(32) and comparing with (25)–(27), gives the necessary condition that

$$\begin{aligned} \log K_{11} &= P_1 \\ \log K_{22} &= 2P_1 + P_2 \\ \log K_{43} &= 2 \log K_{22} + 2.13 \end{aligned} \quad (33)$$

The diagram $\log B (\log \alpha)_\eta$ was constructed by solution of (31) for β using various values of η and α . The values of β were then substituted into (30). The diagrams $\log B (\log \alpha)_Z$ were constructed by solution of eqn. (34) for β (eqn. (34) is obtained by eliminating B from (30) and (32))

$$(3Z-4)\alpha^4 R \beta^2 + 2\alpha^2(Z-1)\beta + Z(1+\alpha) - \alpha = 0 \quad (34)$$

This was done for several values of α for each Z giving β . As before, substitution of β into (30) gives B .

The construction of the maps for $\text{Sn}(\text{OH})_2$ was done in the same manner as for SnOH^+ . The predominance of an uncharged species cannot be considered unlikely, since the predominating mononuclear complex formed by the hydrolysis of Be^{2+} is apparently²² $\text{Be}(\text{OH})_2$. Also in the hydrolysis of $\text{Hg}(\text{II})$ ²⁵, the predominating product is $\text{Hg}(\text{OH})_2$ (aq). In this case the equations are

$$B = b + K_{21}bh^{-2} + 2K_{22}b^2h^{-2} + 3K_{43}b^3h^{-4} \quad (35)$$

$$\eta = \log (1 + K_{21}h^{-2} + 2K_{22}bh^{-2} + 3K_{43}b^2h^{-4}) \quad (36)$$

$$BZ = 2K_{21}bh^{-2} + 2K_{22}b^2h^{-2} + 4K_{43}b^3h^{-4} \quad (37)$$

Using the same normalized variables,

$$B = B \cdot 10^{P_1} = \beta + \beta\alpha^2 + 2\beta^2\alpha^2 + 3R\beta^3\alpha^4 \quad (38)$$

$$\eta = \log (1 + \alpha^2 + 2\beta\alpha^2 + 3R\beta^2\alpha^4) \quad (39)$$

$$BZ = 2\beta\alpha^2 + 2\beta^2\alpha^2 + 4R\beta^3\alpha^4 \quad (40)$$

and

$$\begin{aligned} \log K_{12} &= 2 P_1 & \log K_{22} &= 2 P_1 + P_2 \\ \log K_{43} &= 2 \log K_{22} + 2.13 \end{aligned} \quad (41)$$

In the position of best fit for the two sets of maps calculated for SnOH^+ ,

$$\begin{aligned} P_1 &= \log \alpha + \log h = -3.925 \\ P_2 &= \log B - \log B = 3.40 \pm 0.02. \end{aligned} \quad (42)$$

Thus from eqns. (33)

$$\begin{aligned} \log K_{43} &= -6.77 \pm 0.03 \\ \log K_{22} &= -4.45 \pm 0.15 \\ \log K_{11} &= -3.92 \pm 0.15 \end{aligned}$$

Comparing the experimental data $\log B (\log h)_\eta$ with the curves $\log B (\log \alpha)_\eta$ calculated assuming the mononuclear complex $\text{Sn}(\text{OH})_2$ a good fit could be obtained for $P_1 = -3.23$ and $P_2 = 2.01$. The agreement between the curves $\log B (\log \alpha)_z$ and the experimental data $\log B (\log h)_z$ was, however, extremely bad for these values of P_1 and P_2 , the deviations being far greater than the experimental error. In this case, the advantages of having the complete set of data (B b H h) are apparent, since it allows the rejection of faulty hypotheses which appear to satisfy one of the individual sets (B b h) or (B H h).

Since the projection maps allow the simultaneous determination of the polynuclear and mononuclear constants, the above values will be taken as final.

Fig. 11. Distribution of complexes for total tin(II) concentrations $B = 2.5, 40 \text{ mM}$ as a function of $\log h$, calculated using the constants determined in this work. If a vertical line is drawn for a given value of h , the segment of the line falling in a given area, e. g. $\text{Sn}_2(\text{OH})_2^{2+}$, represents the concentration of $\text{Sn}(\text{II})$ present as this complex in the solution at equilibrium.

The broken lines in Figs. 2 and 3 are calculated with this final set of constants. The projection maps for the final set of constants are given by the broken lines in Figs. 4 and 5.

Fig. 11 shows the distribution of the total tin(II) over the various species as a function of $\log h$ and for the total concentrations $B = 2.5$ mM, 40 mM.

DISCUSSION

Potentiometric measurements giving the set of data (B H b h) for 40 mM $\geq B \geq 2.5$ mM have shown that the hydrolysis of tin(II) solutions gives the trimer $\text{Sn}_3(\text{OH})_4^{2+}$ as the predominating product. In addition, as would be expected, small amounts of the lower complexes $\text{Sn}_2(\text{OH})_2^{2+}$ and SnOH^+ also are formed. Precipitation occurs shortly above $Z = 1.0$, and no evidence has been found for the existence of higher polymers than the trimer.

As evidence that the trimer is the primary product, one may cite the good agreement of the values of the equilibrium constant for the reaction

calculated by different methods.

Direct analysis of $y(x)$ and $\eta(x)$ curves	-6.74 ± 0.04
Curve fitting of data $y(x)$, $y > 0.2$ and $\eta(x)$, $B \geq 5.0$ mM	-6.74 ± 0.04
Projection maps $\log B$ ($\log h$) $_Z$ and $\log B$ ($\log h$) $_\eta$	-6.77 ± 0.03

The equilibrium constant for the reaction

was determined primarily from the data $\eta(\log h)$ for the single value of $B = 2.5$ mM. Unfortunately, K_{11} could not be obtained from data at concentrations lower than 2.5 mM as Z , h , and η could not be measured with sufficient accuracy.

Since the data can be explained by the following equilibria

it would perhaps be suitable at this time to critically examine the earlier work on the hydrolysis of tin(II) solutions.

As was mentioned earlier, the preparation and handling of solutions of tin(II) presents a rather serious problem, because of the ease with which these solutions become contaminated by small amounts of the much stronger aquo-acid Sn(IV). Milda Prytz, working in N. Bjerrum's laboratory, has the reputation of having been a very careful worker. In her work on tin(II), great care was taken to avoid the oxidation of tin(II), and it is therefore of interest to recalculate these data assuming $\text{Sn}_3(\text{OH})_4^{2+}$ to be the hydrolysis product. Because of the nature of the experiments, the values obtained can be considered only roughly approximate. The data, recalculated to give K_{43} , may be summarized as follows.

Mol. conc. NaClO ₄	B mM	Z	—log h	log K ₄₃
0	54.5	0.26	1.85	—5.9
0	43.6	0.29	1.89	—5.7
0	5.45	0.44	2.62	—6.4
0	4.36	0.47	2.68	—6.4
0.5	54.5	0.23	1.91	—6.2

It is seen that the value of K_{43} for the two lowest concentrations of tin(II) and the measurement in 0.5 M NaClO₄ agree fairly well with the value calculated above. In this work, the small number of data and their limited accuracy made it impossible to choose the correct reaction.

Gorman³, also working with perchlorate solutions, obtained a value of $\log K_{11} = -1.70$, corrected to infinite dilution. These data indicate that tin(II) is a much stronger aquo-acid than the work of Prytz does, and if recalculated to give K_{43} , give a constant which is too large by a factor of about 10^2 . In this work, the wrong hydrolysis reaction was chosen for the calculations, and a large part of the effect measured was probably caused by tin(IV).

The experiments of Garrett and Heiks⁴ were also performed quite carefully to prevent oxidation of tin(II); however, the value of the constant for the reaction

given in this work is actually the sum of a series of constants $K_s + 2K_s^2K_{22} + 3K_s^3K_{43}$, since solubility measurements cannot distinguish between species with the same charge. The hydrolysis constant K_{11} for the monomeric species cannot be obtained with any accuracy when the concentration of the species is very much lower than that of ions with higher charges, as occurs in this case.

In the work of Vanderzee and Rhodes⁵, the value of K_{11} was estimated from a term correcting the deviations in the tin(II) halide complexity constants at different hydrogen ion concentrations. Since the effect was quite small, it would be greatly influenced by traces of tin(IV), and the values cannot be considered reliable.

The relatively large value of the constant K_{43} determined in this work and the fact that the data give no indication that species with more than three atoms are formed in any significant concentration makes it unlikely that the complex $\text{Sn}_3(\text{OH})_4^{2+}$ has an open chain structure. A ring structure would be more plausible, *e. g.*

● tin atoms

⊙ oxygen atoms below plane of paper

○ oxygen atoms above plane of paper

The complex may also contain fewer water molecules such as $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$, for the equilibrium measurements give no information about the number of solvent molecules bound in the complex. Since equilibrium measurements can give no proof of a structure and there are no crystallographic data available for basic salts of tin(II), no definite conclusions can be drawn.

It may be noted here that a large number of the hydrolysis products of cations may be written in the form $\text{Me}[(\text{OH})_2\text{Me}]_n$, i. e. the "core + links" form with $t = 2$. Among others, $\text{Fe(III)}^{(11,19)}$, Cu(II)^{26} , $\text{VO}^{2+ (27)}$, $\text{Sc}^{3+ (28,29)}$, $\text{In(III)}^{(15)}$, $\text{UO}_2^{2+ (21)}$, and Sn(II) appear to exhibit this behavior. When the cation is divalent as in the case of tin(II), the link is uncharged, and the ratio of hydroxide groups to metal ions is the same as in the precipitate.

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