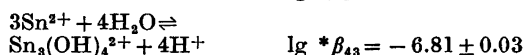
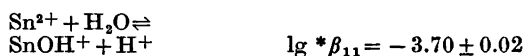


The Hydrolysis of the Tin(II) Ion

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The hydrolysis of Sn(II) has been studied by means of potentiometric titrations at low Sn(II) concentrations, ranging from 0.02 to 2.3 mM, in the pH range 2.7–3.7. Tin amalgam and glass electrodes were used as sensors and all measurements were carried out at 25 °C, using 3 M NaClO₄ as ionic medium. The emf data could be explained by the following reactions and equilibrium constants.



The formation constants were calculated with the least squares program LETAGROP.

This work can be considered as an extension of the study of the tin(II) hydrolysis by Tobias,¹ in which potentiometric titrations of tin(II) perchlorate solutions were carried out in a 3 M NaClO₄ medium with tin concentrations varying from 2.5 mM to 40 mM. In the pH range investigated (1.5–3.0 for the lowest and 1.5–2.4 for the highest tin concentration) Tobias found that Sn₃(OH)₄²⁺ predominated, small amounts of SnOH⁺ and Sn₂(OH)₂²⁺ also being present. A summary and discussion of the results of hydrolytic tin(II) studies made before 1958 is given in Tobias' paper,¹ and very few studies have been reported since. The existence of SnOH⁺, in the concentration range used in Tobias' investigation, has, however, been questioned by Liang Chia-Ch'ang and Tu Yu-Ming.² After new calculations based on Tobias' data they concluded that the main hydrolysis products were Sn₃(OH)₄²⁺ and Sn₂(OH)₂²⁺ with minor amounts of Sn₂(OH)₂²⁺. Mesmer and Irani³ measured the solubility of SnO at 25 °C in 1 M perchloric acid—sodium

perchlorate mixtures, and, using the equilibrium model proposed by Tobias, calculated the constant for the hydrolysis reaction SnO(s) + H₃O⁺ ⇌ SnOH⁺ + H₂O, *i.e.* $\lg K_{s1} = -0.28$.

Because of the extensive hydrolysis of tin(II), it is necessary to know the composition and the formation constants of the hydrolytic species when studying complexes with other ligands in aqueous solutions. The formation of Sn₃(OH)₄²⁺ is well established by Tobias.¹ The mononuclear SnOH⁺ suggested by Tobias,¹ was not formed according to the calculations due to Liang *et al.*, Sn₂(OH)₂²⁺ being introduced instead. The aim of the present work was to investigate the possible formation of SnOH⁺. For this reason a concentration range in which the formation of SnOH⁺ ought to be favoured was examined. The results of this work were to be used in a study of acetato—tin(II) complexes in 3 M NaClO₄.

SYMBOLS

The following notation is used:

lg	log ₁₀
H	analytical hydrogen ion concentration
h	free hydrogen ion concentration
B	analytical concentration of Sn(II)
b	free concentration of Sn(II)
η	lg B/b
E _H	measured emf of the glass electrode (4)
E _B	measured emf of the amalgam electrode (3)
Q	number of ampere-seconds passed through the test solution during anodic oxidation
DEH	E _{H,cal} - E _H (Table 1), where E _{H,cal} denotes the calculated value of E _H .
DEB	E _{B,cal} - E _B (Table 1), where E _{B,cal} denotes the calculated value of E _B .

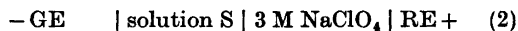
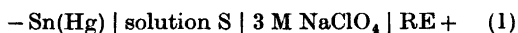
Emf values are given in mV and equilibrium constants on the molar scale.

METHOD OF INVESTIGATION

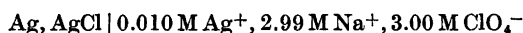
The measurements were performed as potentiometric titrations in a paraffin oil thermostat at 25 °C, using the automatic titrator described earlier.⁷

Since a concentration range favouring the formation of SnOH^+ was to be used, solutions with a much lower Sn(II) content than that used by Tobias had to be prepared. It thus proved convenient to generate the tin ions by constant current electrolysis. When larger amounts of Sn(II) are required the method used by Tobias, in which a solution of $\text{Cu}(\text{ClO}_4)_2$ is passed through a tin column, yielding an equivalent amount of tin(II) ions, is, however, preferable.

The free concentrations of Sn^{2+} and H^+ , b and h , were measured with a tin amalgam and a glass electrode, respectively. The cells were of the following types



where GE is the glass electrode and RE the reference half cell:



In some titrations (Nos. 1 and 6, Table 1) sodium chloride was used instead of silver perchlorate in the reference half cell (since an investigation of the tin(II) hydrolysis in alkaline solution was carried out simultaneously).⁸ No difference in the stability of the two types of reference half cells could be detected.

The emfs of cells (1) and (2) can be written

$$E_B = E_B^\circ - \frac{1}{2} \times 59.16 \lg b + E_j \quad (3)$$

and

$$E_H = E_H^\circ - 59.16 \lg h + E_j \quad (4)$$

It was assumed that the activity factors were constant and could thus be included in the constants E_B° and E_H° , respectively. E_j , the liquid junction potential between the test solution and the 3 M NaClO_4 in the salt bridge was calculated from $E_j = jh$ mV, $j = 0.017$ mV/mM, according to earlier studies by Biedermann and Sillén.⁹

A description of the electrodes and the equipment used for the coulometric addition of tin ions and other experimental details are given in Ref. 6.

The hydrolysis of tin(II) was studied by introducing tin(II) ions into an acidified solution of 3 M NaClO_4 , the H level being kept constant

in each titration. The initial solution, 3 M NaClO_4 containing a slight excess of protons, was prepared from freshly prepared stock solutions. The proton excess was determined by titration with hydrogen ions, generated electrolytically in the solution. A platinum gauze was used as an anode, the other parts of the electrolysis circuit being the same as described in Ref. 6. This type of coulometer was introduced by Biedermann and Ciavatta.¹⁰ Gran's extrapolation method¹¹ was used to calculate the original H . The stepwise addition of H^+ was continued, until the desired H level was reached, and for each addition the constant E_H° (4) was calculated. The platinum gauze was then replaced by a tin amalgam anode, and the tin ions were generated in steps of ca. 0.5 μmol , with a current density of ca. 1.2 mA/cm². After each step of electrolysis the equilibrium emf's of the measuring tin amalgam electrode and glass electrode, E_B and E_H , were registered (Table 1). A graphical survey of the concentration ranges covered in these experiments is given in Fig. 1.

Chemicals and analysis

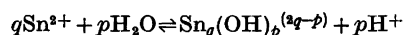
Sodium perchlorate solutions were prepared as described by Biedermann.¹²

Tin amalgams were prepared as described in Ref. 6.

The analytical tin(II) concentration was calculated from the known amount of ampere-seconds that passed through the solution during electrolysis.

CALCULATIONS AND RESULTS

The hydrolytic equilibria can be described by the general reaction



with the equilibrium constants $^*\beta_{qp}$. The mass balances for B and H give

$$B = b + \sum_{pq} q^* \beta_{qp} b h^{-p} \quad (5)$$

$$h = H + \sum_{pq} p^* \beta_{qp} b h^{-p} \quad (6)$$

The equilibrium constants were determined from 223 experimental points obtained from six different titrations. Part of the data (Q , E_B , E_H) are listed in Table 1,* and the con-

* A complete list of the experimental data is available from the Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden.

Table 1. Experimental data. Part of computer output for 6 titrations. For each point Q (coulomb), E_H (\equiv EH), E_B (\equiv EB), pH, DEH = $E_{H,cal} - E_H$ and DEB = $E_{B,cal} - E_B$ are given. H_0 and B_0 are the initial concentrations of H^+ and Sn^{2+} , respectively. All concentrations are given in mM. $V_0 = 49.98$ ml. In the calculations the equilibrium constants $\lg \beta_{11} = -3.70$ and $\lg \beta_{43} = -6.81$ were used. E_B and E_H in the table correspond to E_B° and E_H° in eqns. (3) and (4).

SATs 1. E = 423.56 ± 0.03 H = 0.1934 B = 0						SATs 5. E = 819.44 ± 0.03 H = 1.138 B = 0					
O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB	O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB
0.197	1.36	571.28	3.6908	-0.05	0.05	0.764	171.63	942.89	2.9394	-0.10	0.06
0.247	1.03	568.38	3.6852	-0.04	0.01	0.860	171.61	941.40	2.9388	-0.09	0.08
0.296	0.71	565.97	3.6796	-0.03	-0.07	0.956	171.57	940.06	2.9383	-0.09	0.09
0.345	0.48	564.00	3.6739	-0.08	-0.09	1.051	171.59	938.84	2.9377	-0.04	0.09
0.395	0.05	562.38	3.6682	-0.01	-0.02	1.242	171.52	936.68	2.9368	-0.04	0.08
0.444	-0.17	560.91	3.6624	0.10	-0.01	1.433	171.48	934.83	2.9354	-0.01	0.06
0.493	-0.52	559.61	3.6567	0.09	0.01	1.624	171.42	933.20	2.9342	0.0	0.03
						1.816	171.35	931.78	2.9330	0.0	0.03
						2.007	171.30	930.49	2.9318	0.02	0.02
						2.198	171.23	929.32	2.9306	0.02	0.0
						2.389	171.17	928.25	2.9293	0.04	-0.01
						2.674	171.06	926.80	2.9274	0.04	-0.02
						2.962	170.96	925.49	2.9255	0.05	-0.04
						3.249	170.86	924.32	2.9235	0.07	-0.05
						3.536	170.76	923.25	2.9214	0.09	-0.05
						3.918	170.61	921.96	2.9186	0.11	-0.06
						4.300	170.47	920.80	2.9156	0.14	-0.06
						4.682	170.29	919.73	2.9126	0.14	-0.07
						5.160	170.08	918.53	2.9087	0.16	-0.06
						5.638	169.87	917.44	2.9047	0.19	-0.06
						6.211	169.61	916.25	2.8998	0.22	-0.06
						6.784	169.32	915.18	2.8947	0.23	-0.05
						7.453	168.99	914.03	2.8886	0.26	-0.05
						8.122	168.64	912.98	2.8824	0.28	-0.05
						8.887	168.24	911.90	2.8753	0.30	-0.04
						9.747	167.78	910.78	2.8672	0.32	-0.03
						10.607	167.33	909.77	2.8591	0.35	-0.01
						11.562	166.82	908.73	2.8501	0.37	0.0
						12.614	166.27	907.68	2.8404	0.39	0.01
						13.760	165.67	906.62	2.8299	0.41	0.02
						15.003	165.04	905.57	2.8187	0.44	0.03
						16.340	164.36	904.53	2.8070	0.46	0.04
						17.774	163.65	903.50	2.7948	0.47	0.06
						19.303	162.91	902.48	2.7822	0.47	0.06
						21.023	162.11	901.43	2.7685	0.48	0.08
						22.838	161.14	900.40	2.7547	0.33	0.10

SATs 2. E = 816.81 ± 0.03 H = 0.2302 B = 0						SATs 6. E = 423.69 ± 0.02 H = -217.29 B = 0					
O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB	O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB
0.287	370.58	948.87	3.5823	0.14	-0.03	0.296	565.91	3.6603	0.05		
0.334	370.32	948.00	3.5778	0.14	0.02	0.345	563.95	3.6550	0.05		
0.430	369.78	946.40	3.5690	0.12	0.07	0.395	562.25	3.6497	0.04		
0.526	369.23	945.00	3.5601	0.10	0.12	0.444	560.77	3.6443	0.04		
0.621	368.69	943.66	3.5514	0.07	0.08	0.493	559.43	3.6390	0.02		
0.717	368.15	942.48	3.5426	0.05	0.07	0.543	558.24	3.6336	0.02		
0.812	367.61	941.38	3.5340	0.02	0.05	0.592	557.16	3.6282	0.02		
0.908	367.09	940.35	3.5255	0.0	0.01	0.642	556.14	3.6228	-0.01		
1.003	366.57	939.43	3.5171	-0.02	0.01	0.691	555.24	3.6175	0.01		
1.099	366.05	938.55	3.5088	-0.05	-0.02	0.740	554.40	3.6121	0.02		
1.194	365.56	937.74	3.5007	-0.06	-0.02	0.789	553.60	3.6067	0.02		
1.238	364.86	936.58	3.4888	-0.05	-0.05	0.839	552.83	3.6014	0.0		
1.481	364.12	935.54	3.4772	-0.11	-0.05	0.888	552.13	3.5961	0.01		
1.624	363.43	934.56	3.4659	-0.13	-0.07	0.938	551.45	3.5909	0.0		
1.768	362.77	933.65	3.4549	-0.14	-0.07	0.987	550.85	3.5857	0.03		

SATs 3. E = 818.51 ± 0.02 H = 0.4731 B = 0						SATs 4. E = 818.90 ± 0.02 H = 0.7674 B = 0					
O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB	O(C)	EH(MV)	EB(MV)	pH	-DEH	-DEB
0.191	353.06	949.31	3.3103	-0.13	0.16	9.142	173.09	912.40	2.9741	-0.19	0.05
0.287	352.94	947.12	3.3077	-0.09	0.11	9.810	172.52	911.40	2.9639	-0.16	-0.07
0.334	352.88	946.15	3.3063	-0.07	0.08	10.479	171.97	910.54	2.9539	-0.12	-0.10
0.430	352.74	944.42	3.3035	-0.05	0.04	11.244	171.34	909.65	2.9429	-0.10	-0.11
0.526	352.57	942.91	3.3007	-0.05	0.02	12.199	170.59	908.63	2.9296	-0.06	-0.11
0.621	352.40	941.56	3.2978	-0.05	0.0	13.155	169.87	907.71	2.9168	-0.03	-0.07
0.717	352.24	940.36	3.2949	-0.04	0.0	14.110	169.17	906.84	2.9045	0.0	-0.05
0.812	352.17	939.81	3.2934	-0.02	0.0	15.257	168.36	905.87	2.8904	0.03	-0.02
0.908	352.02	938.77	3.2904	0.01	-0.01	16.404	167.58	904.96	2.8768	0.05	0.0
0.956	351.88	937.80	3.2874	0.0	-0.02	17.359	166.96	904.24	2.8659	0.07	0.01
1.051	351.69	936.90	3.2844	0.04	-0.04	18.506	166.22	903.43	2.8534	0.07	0.03
1.147	351.49	936.08	3.2813	0.02	-0.03	19.461	165.63	902.77	2.8433	0.08	0.03
1.242	351.31	935.31	3.2781	0.02	-0.03	20.417	165.06	902.16	2.8336	0.08	0.04
1.338	351.11	934.59	3.2750	0.01	-0.03	21.372	164.53	901.57	2.8242	0.11	0.05
1.433	350.97	933.90	3.2718	0.06	-0.04	22.232	163.99	900.97	2.8160	0.06	-0.03
1.529	350.76	933.26	3.2685	0.04	-0.04	22.423	163.90	900.90	2.8142	0.07	0.01
1.624	350.61	932.64	3.2653	0.08	-0.05	22.615	163.80	900.81	2.8124	0.08	0.04

centration ranges covered are visualized in Fig. 1 as curves $\lg B$ ($\lg b$)_H. The evaluation was carried out by means of the least squares computer program LETAGROP ETITR.¹³⁻¹⁵ The analytical concentrations of tin and hydrogen ions, B and H , respectively, were as-

sumed to be correct, and the parameters $T'yp = 3$ and $val = 6$ in the Letagrop program¹⁵ were chosen. The free concentrations, b and h , were calculated by successive approximation from eqns. (5) and (6), using the measured value of E_H° and the estimated values of β_{pq} and E_B° .

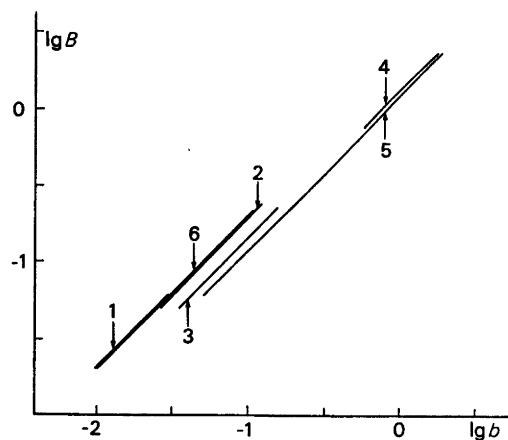


Fig. 1. Survey of concentration ranges studied in 6 titrations, $\lg B$ ($\lg b$)_H. B and b are expressed in mM (Table 1).

Table 2. Literature survey of hydroxy-tin(II) complexes in 3 M NaClO₄.

	Tobias	Liang <i>et al.</i> ^a	This work
$\lg \beta_{11}^*$	-3.92 ± 0.15	—	-3.70 ± 0.02
$\lg \beta_{22}^*$	-4.45 ± 0.15	-4.58 ± 0.41	—
$\lg \beta_{43}^*$	-6.77 ± 0.03	-6.85 ± 0.04	-6.81 ± 0.03
$\lg \beta_{32}^*$	—	-6.66 ± 0.18	—

^a Recalculation of Tobias data.

As starting values of the equilibrium model, Tobias' values (Table 2) for β_{11}^* , β_{22}^* and β_{43}^* were used. These constants were varied (common parameters) together with E_B° (group parameter) to minimize the errors squares sum $U = \sum (E_{B,cal} - E_B)^2$. In these calculations the species $\text{Sn}_2(\text{OH})_2^{2+}$ was rejected, and the lowest errors squares sum was obtained for

$$\lg \beta_{11}^* = -3.70 \pm 0.02 \quad (7)$$

$$\lg \beta_{43}^* = -6.81 \pm 0.03 \quad (8)$$

The uncertainties furnished by the program correspond to three times the "standard deviation" of the constant.^{16,17} The agreement between the calculated and experimental values $\text{DEB} = E_{B,cal} - E_B$ and $\text{DEH} = E_{B,cal} - E_B$ is given in the last two columns in Table 1.

To illustrate the complex formation the distribution diagrams $\sum_{i=1}^3 x_i = f(\text{pH})_B$, $i=1, 2, 3$ were constructed (Fig. 2), where x_i represents the fraction of the total amount of tin present in the three species, Sn^{2+} ($i=1$), SnOH^+ ($i=2$), and $\text{Sn}_3(\text{OH})_4^{2+}$ ($i=3$). The distribution of the complexes was calculated with the Haltafall program^{18,19} and plotted²⁰ with an IBM 370/145 computer.

The diagrams in Fig. 2a–2d cover the concentrations studied in the present work. In Fig. 2e the curves have been extrapolated to the highest concentration used in Tobias' measurements to enable a comparison between the two investigations.

The agreement of the present results with the equilibrium model proposed by Liang *et al.*² was also tested. Theoretical curves, using their values, were compared with the experimental values $\eta(\text{pH})_B$ from Tobias' and the $\lg B(\lg b)_H$ data from the present work. At low values of B , the theoretical curves deviated markedly from the experimental points, indicating that SnOH^+ should not be neglected or replaced by $\text{Sn}_2(\text{OH})_3^+$. Letagrop calculations using the equilibrium constants found by Liang *et al.*, as initial values, were also carried out. When these constants and E_B° were varied to find the "best" values, the error squares sum became much higher than that obtained with (7) and (8). This was due to deviations between the calculated and measured E_B values, which were larger the lower the value of B . The "best" value of $\lg \beta_{43}^*$ also differed considerably from the starting value (*ca.* 0.25 units) and $\sigma(\beta_{43}^*)$ became *ca.* ten times higher than the value reported in Table 2.

Attempts to interpret the present data in terms of the formation of SnOH^+ , $\text{Sn}_2(\text{OH})_3^+$ and $\text{Sn}_3(\text{OH})_4^{2+}$ also failed. On the other hand, an accurate determination of the polynuclear species formed, would require study of a wider range of B . The simplest interpretation of the present data is, however, obtained, by assuming the formation of the single polynuclear complex $\text{Sn}_3(\text{OH})_4^{2+}$.

DISCUSSION

In this investigation the formation of the hydrolysis products $\text{Sn}_3(\text{OH})_4^{2+}$ and SnOH^+

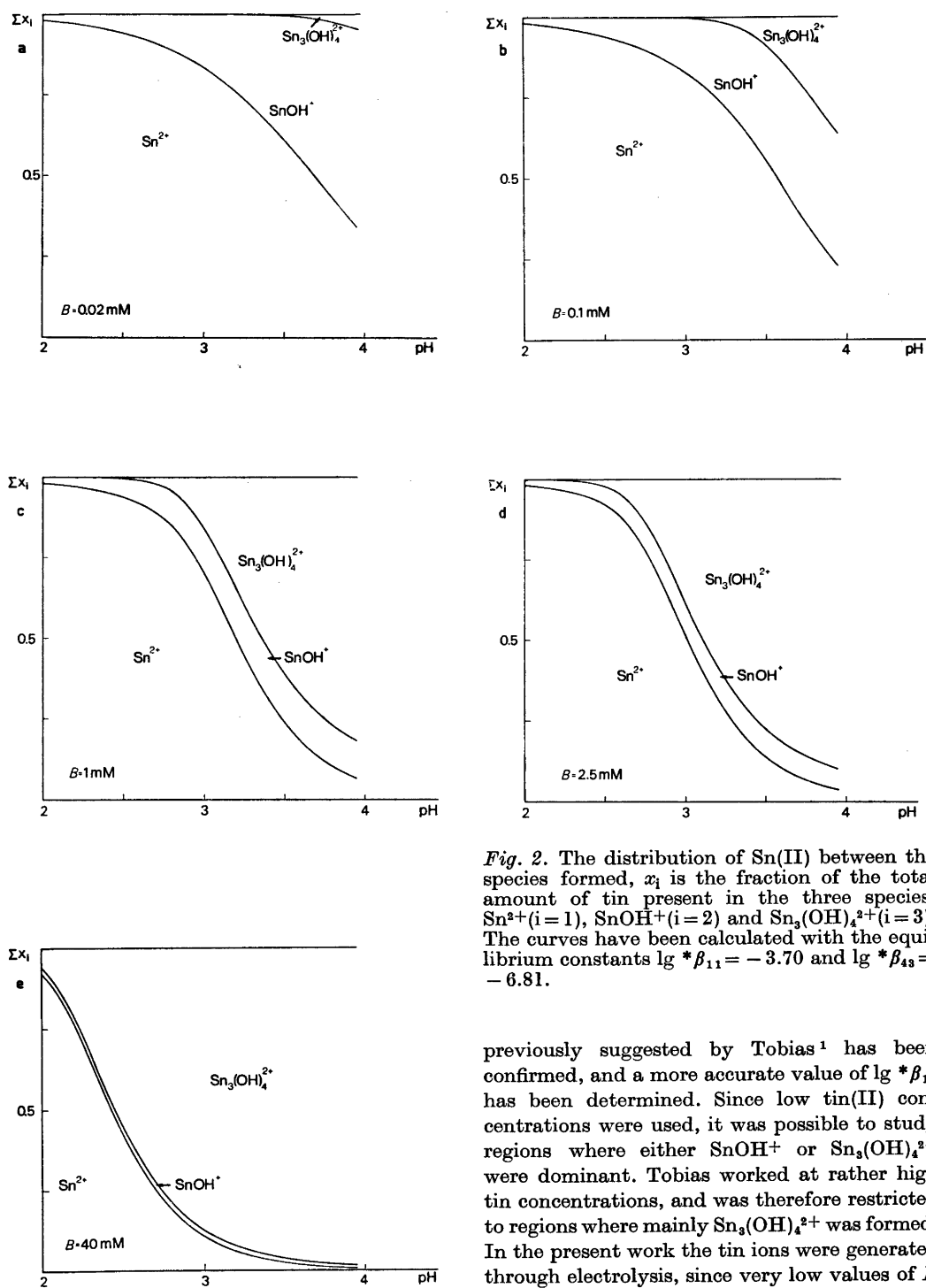


Fig. 2. The distribution of Sn(II) between the species formed, x_i is the fraction of the total amount of tin present in the three species, Sn^{2+} ($i=1$), SnOH^+ ($i=2$) and $\text{Sn}_3(\text{OH})_4^{2+}$ ($i=3$). The curves have been calculated with the equilibrium constants $\lg^* \beta_{11} = -3.70$ and $\lg^* \beta_{43} = -6.81$.

previously suggested by Tobias¹ has been confirmed, and a more accurate value of $\lg^* \beta_{11}$ has been determined. Since low tin(II) concentrations were used, it was possible to study regions where either SnOH^+ or $\text{Sn}_3(\text{OH})_4^{2+}$ were dominant. Tobias worked at rather high tin concentrations, and was therefore restricted to regions where mainly $\text{Sn}_3(\text{OH})_4^{2+}$ was formed. In the present work the tin ions were generated through electrolysis, since very low values of B

were required. The titration techniques in the present investigation also differed from those used by Tobias. In Tobias' measurements solutions of NaHCO_3 were added, the tin(II) concentration being kept constant. In the present work the titrations were performed at constant H levels, the tin(II) ions being generated *in situ* by electrolysis. In view of the differences between the methods of investigation, the agreement between the values for $\lg \beta_{42}$ is satisfactory.

Whereas SnOH^+ was present only in minor amounts in Tobias' work, in the present study it was the predominant complex, especially at low values of B (Fig. 2a-d). It is thus reasonable that $\lg \beta_{11}$ should be obtained with better accuracy in the present work. The lowest tin(II) concentration studied by Tobias was $B = 2.5$ mM, and he has reported experimental values $\eta(\text{pH})_B = 2.5$ from two titrations.¹ If these experimental data are compared with the theoretical curves obtained, using the values in Table 2, a poor fit is obtained, for $\text{pH} < 2.7$, for all the models proposed. On the other hand, a reasonably good fit is obtained for one of his titrations, when $\text{pH} < 2.2$, if the equilibrium model from the present work is used. Tobias has, however, reported that the amalgam electrodes did not function satisfactorily for $B < 2.5$ mM. Even for $B = 2.5$ mM one might suspect erroneous emf values, since there was a marked deviation between the experimental values $\eta(\text{pH})_B = 2.5$ in the two titrations reported. Tobias completed one of these titrations with a back titration. Even here the deviation from the forward titration is evident for $\text{pH} < 2.4$. The problems entailed in working with amalgam electrodes at low Sn(II) concentrations have been overcome in the present work. A possible explanation of these difficulties is given in Ref. 6.

Dimerization of mononuclear monohydroxo complexes is fairly common, and in accordance with earlier investigations¹ $\text{Sn}_2(\text{OH})_2^{2+}$ was expected to be formed. When $\lg \beta_{22}$ was varied in the Letagrop calculations, $\text{Sn}_2(\text{OH})_2^{2+}$ was, however, rejected. If $\text{Sn}_3(\text{OH})_3^{2+}$ was formed, its concentration was too low to evaluate its stability constant.

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