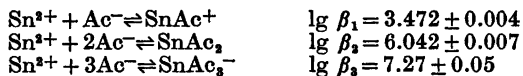


The Complex Formation between Tin(II) Ions and Acetate Ions

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The equilibria between tin(II) and acetate ions have been studied by means of potentiometric titrations at 25 °C in 3 M NaClO₄ medium. The titrations were performed in the approximate pH range 2.0–4.2 at total acetate concentrations varying within the limits 80 mM < c_{Ac} < 145 mM. Tin(II) ions were introduced stepwise into the test solution, by constant current coulometry. This study covers the [Sn(II)] range 0.2 to 0.9 mM. The concentrations of the free tin(II) and hydrogen ions were measured with tin amalgam and glass electrodes, respectively. The emf data, which were evaluated with the generalized least squares program LETAGROP, version ETITR, were consistent with the following reactions and equilibrium constants:



Since the hydrolysis of tin(II) was found to interfere with the complex formation, allowance was made for the presence of SnOH⁺ and Sn₂(OH)₄²⁺.

It would appear that there have been no quantitative studies on tin(II) complexes with acetate ions or other carboxylate ions. Donaldson *et al.*^{1–5} have prepared and studied the properties of triacetatostannate(II) compounds with alkali metal, ammonium and alkaline earth metal ions and have found evidence for the existence of SnCH₂COO⁺, Sn(CH₂COO)₂, Sn₂(CH₂COO)₇⁻, Sn₂(CH₂COO)₅⁻, and Sn(CH₂COO)₃⁻ in solution from potentiometric and polarographic measurements.^{1,3} Potentiometric and polarographic measurements on the corresponding triformatostannate(II) compounds indicated the presence of SnHCOO⁺, Sn(HCOO)₂, Sn₂(HCOO)₅⁻ and Sn(HCOO)₃⁻ in solution.⁴ Donaldson *et al.* have studied bond-

ing and structural properties in compounds containing SnX₃⁻ ions from Mössbauer data (*e.g.* Ref. 5). The expected pyramidal environment of tin has been confirmed by the crystal structure determination of KSn(HCOO)₃, in which the three unidentate formate groups form covalent bonds with the tin atom.⁶

SYMBOLS

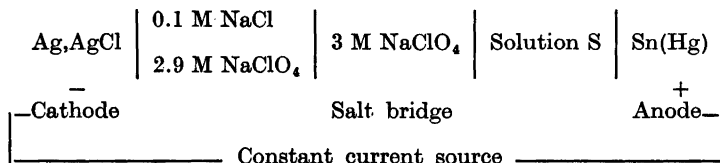
The following notation is used:

lg	log ₁₀
H	total concentration of hydrogen ions, proton excess over H ₂ O and Ac ⁻ .
h	concentration of H ⁺ .
B	total concentration of Sn(II).
b	concentration of Sn(II).
C	total concentration of Ac ⁻ .
c	concentration of Ac ⁻ .
η	lg B/b
E_B	emf of the cell with amalgam electrode (in mV) (3).
E_H	emf of the cell with glass electrode (in mV) (4).
DA	$H_{\text{cal}} - H$ (Table 1).
DEB	$E_{\text{cal}} - E_B$ (Table 1), where E_{cal} is the calculated value of E_B .
H_0	analytical hydrogen ion concentration in the starting solution, S ₀ .
H_T	analytical hydrogen ion concentration in the titrant solution, T.
B_0	analytical tin(II) concentration in the starting solution S ₀ .
B_T	analytical tin(II) concentration in the titrant solution, T.
C_0	analytical acetate concentration in the starting solution, S ₀ .
C_T	analytical acetate concentration in the titrant solution, T.

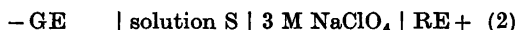
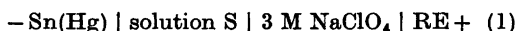
S_0 starting solution.
 T titrant solution.
 V_0 volume of S_0 .
 V_T added volume of T.

METHOD OF INVESTIGATION

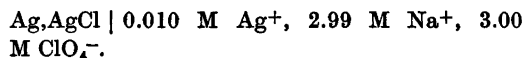
The measurements were performed at 25 °C as potentiometric titrations using the automatic titrator described previously.⁷ The constant



The equilibrium concentrations of Sn^{2+} and H^+ were measured with another tin amalgam electrode and a glass electrode, respectively, in the following cells



where GE is a glass electrode and RE the reference electrode:



The emfs of cells (1) and (2) are related to the concentrations of Sn^{2+} and H^+ , b and h , respectively, by the equations

$$E_B = E_B^0 - \frac{1}{2} \times 59.16 \lg b + E_j \quad (3)$$

$$E_H = E_H^0 - 59.16 \lg h + E_j \quad (4)$$

where E_j is the liquid junction potential formed between the test solution S and the 3 M NaClO_4 of the salt bridge. According to previous investigations,¹⁰ E_j may be assumed to vary linearly with the hydrogen ion concentration. In this work the value determined by Biedermann and Sillén,¹¹ $E_j = 0.017h$ mV, was used (h in mM).

It has been found that for acetic acid, boric acid and ascorbic acid¹²⁻¹⁵ in 3 M NaClO_4 , E_H^0 is a linear function of the total concentration of the acid. Since the total acetate concentration was kept constant in each titration, E_H^0 was assumed to be constant and was calculated for each titration from the measured value of E_H in an acid solution containing no tin ions.

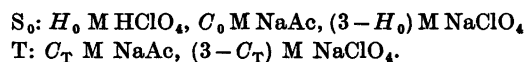
The reduction of Sn(IV) in the presence of tin $\text{Sn(IV)} + \text{Sn(s)} \rightleftharpoons 2\text{Sn(II)}$

ionic medium method^{9,10} was applied using 3 M NaClO_4 to keep the activity factors constant. The equilibrium conditions can thus be expressed in terms of concentrations instead of activities. The test solutions, S, were obtained by adding tin(II) ions to a solution containing sodium acetate, perchloric acid, and sodium perchlorate.

The tin(II) ions were generated in the test solution by constant current electrolysis.⁸ A tin amalgam electrode⁷ was used as anode in the following circuit

is highly favoured in acid solution,¹⁶ but the process is slow. It was thus important to avoid formation of Sn(IV) in the experiments. To prevent oxidation of the amalgam and tin(II) ions, the solutions and titration vessels were pretreated with argon or nitrogen and the test solutions were kept under argon atmosphere.

The solutions used in the titrations had the following compositions



V_0 ml of S_0 was titrated with V_T ml of T, forming the test solution denoted by S. The tin(II) ions were generated directly into S_0 and S. In order to suppress the hydrolysis of tin and possible complex formation in the starting solution, S_0 , the value of H_0 was chosen so that $H_0 - C_0$ was about 10 mM. The titrations thus started at approximately pH = 2. C was kept constant in each titration ($C = C_0 = C_T$) and was chosen sufficiently high to favour the formation of complexes between tin(II) and acetate ions.

In each titration the emf value of the glass electrode, E_H , was first measured in V_0 ml of S_0 in the absence of tin ions. From this value E_H^0 was calculated. The two tin amalgam electrodes, which were to be used to generate and measure the concentration of the tin(II) ions, were then inserted into the solution. The tin ions were added step-wise by constant current electrolysis, until a desired concentration had been attained. The equilibrium value of the amalgam electrode, E_B , was registered after each addition. Using eqn. (3) an approximate value of E_B^0 was thus obtained. V_T ml of the titrator T were then added, and tin ions were generated to compensate for the dilution. The equilibrium values of E_B and E_H were measured for each addition. From

Table 1. Experimental data $\eta(\lg h)$ at different B and C concentrations. For each point E_B , E_G , pH , η , $DH = (H_{cal} - H)$ (in mM), and $DEB = (E_{B,cal} - E)$ (in mV) are given. In calculating H_{cal} and E_{cal} the mean values (Table 3) of the equilibrium constants obtained have been used. The values of E_H^0 and $E_B^0 \pm 3\sigma$ are given at the head of each titration.

SATS 9.		H = 109.7	B = 0.773	C = 99.95	SATS 14.	H = 155.2	B = 0.367	C = 144.3			
E = 821.10 ± 0.05		E = 821.10 ± 0.05	B = 0	C = 100.0	E = 818.07 ± 0.04	E = 150.000	B = 0.411	C = 144.3			
EA (mV)	EB (mV)	PH	ETA	DH	DEB	EA (mV)	EB (mV)	PH	ETA	DH	DEB
117.20	916.48	1.977	0.1135	0.51	-0.20	273.30	923.33	1.947	0.1459	0.14	-0.19
120.74	917.09	2.038	0.1286	0.42	-0.17	275.52	923.68	1.984	0.1570	0.14	-0.15
122.68	917.45	2.071	0.1376	0.37	-0.14	277.88	924.10	2.024	0.1702	0.12	-0.10
124.70	917.82	2.105	0.1476	0.33	-0.13	280.45	924.57	2.068	0.1856	0.09	-0.07
126.83	918.24	2.141	0.1586	0.30	-0.10	283.26	925.13	2.115	0.2038	0.06	-0.03
129.14	918.70	2.180	0.1717	0.27	-0.09	286.32	925.78	2.167	0.2253	0.05	0.01
131.61	919.23	2.222	0.1865	0.24	-0.06	289.52	926.57	2.226	0.2519	0.01	0.03
134.26	919.82	2.267	0.2037	0.22	-0.04	293.82	927.54	2.290	0.2834	0.01	0.09
137.17	920.51	2.317	0.2239	0.19	-0.02	298.06	928.81	2.366	0.3257	-0.05	0.12
140.37	921.31	2.371	0.2482	0.16	0.0	302.99	930.35	2.450	0.3770	-0.05	0.16
143.98	922.27	2.430	0.2771	0.14	0.04	308.70	932.34	2.547	0.4439	-0.05	0.19
147.76	923.39	2.496	0.3122	0.12	0.06	315.62	935.05	2.654	0.5358	-0.09	0.20
152.09	924.75	2.569	0.3554	0.10	0.08	323.14	938.42	2.791	0.6498	-0.09	0.21
156.91	926.41	2.651	0.4088	0.08	0.11	331.20	942.46	2.928	0.7885	-0.08	0.16
162.33	928.46	2.743	0.4751	0.06	0.12	339.18	946.96	3.063	0.9426	-0.07	0.11
168.24	930.94	2.843	0.5560	0.04	0.15	346.50	951.52	3.196	1.0984	-0.05	0.07
174.64	933.89	2.951	0.6536	0.02	0.14	353.74	956.77	3.294	1.2451	-0.04	-0.01
181.01	937.14	3.059	0.7612	0.01	0.15	358.77	959.97	3.394	1.3890	-0.06	-0.05
187.25	940.59	3.164	0.8766	0.0	0.12	363.45	963.49	3.473	1.5088	-0.05	-0.08
193.03	944.06	3.262	0.9923	-0.01	0.10	367.55	966.65	3.542	1.6175	-0.04	-0.12
198.21	947.36	3.350	1.1028	-0.01	0.06	371.15	969.59	3.603	1.7156	-0.03	-0.09
202.87	950.51	3.429	1.2076	-0.02	0.05	374.33	972.16	3.658	1.8042	-0.01	-0.13
207.05	953.46	3.499	1.3058	-0.02	0.02	377.00	974.56	3.708	1.8856	0.00	-0.14
210.74	956.16	3.562	1.3956	-0.03	0.0	379.84	976.81	3.760	1.9616	0.01	-0.13
214.03	958.66	3.617	1.4780	-0.03	0.0	382.34	978.99	3.792	2.0345	-0.02	-0.10
217.04	961.01	3.668	1.5531	-0.03	0.0	384.48	980.89	3.829	2.0976	0.01	-0.06
219.76	963.18	3.714	1.6265	-0.03	0.0	386.51	982.67	3.863	2.1579	0.02	-0.06
222.24	965.20	3.756	1.6925	-0.03	0.0	388.38	984.35	3.895	2.2139	0.03	-0.04
224.55	967.11	3.795	1.7549	-0.04	0.0	390.16	985.90	3.925	2.2675	0.03	-0.07
226.68	968.90	3.831	1.8131	-0.04	0.0	391.80	987.40	3.952	2.3172	0.04	-0.04
228.67	970.58	3.865	1.8668	-0.05	-0.01	393.51	988.89	3.981	2.3693	-0.02	-0.08
230.51	972.16	3.896	1.9193	-0.05	0.0	394.94	990.22	4.005	2.4129	0.00	-0.04
232.25	973.68	3.925	1.9682	-0.05	0.0	396.32	991.49	4.029	2.4552	0.01	-0.02
233.87	975.09	3.953	2.0141	-0.05	-0.01	397.62	992.70	4.051	2.4952	0.02	0.02
235.41	976.46	3.979	2.0579	-0.06	0.0	398.87	993.84	4.072	2.5337	0.03	0.02
						400.13	994.98	4.093	2.5725	0.01	0.02
						401.27	996.04	4.112	2.6077	0.01	0.04
						402.43	997.11	4.132	2.6436	-0.02	0.05
						403.47	998.07	4.150	2.6758	-0.01	0.06
						404.48	999.01	4.167	2.7071	-0.00	0.08
						405.47	999.88	4.183	2.7377	-0.01	0.05
						406.43	1000.78	4.200	2.7675	-0.02	0.07
						407.37	1001.59	4.216	2.7966	-0.04	0.02
						408.23	1002.38	4.230	2.8232	-0.03	0.01
						409.10	1003.16	4.245	2.8501	-0.04	0.01

SATS 11.		H = 89.71	B = 0.823	C = 79.13	SATS 18.	H = 93.25	B = 0.537	C = 101.9			
E = 819.48 ± 0.03		E = 171.51	B = 0.835	C = 79.45	E = 816.14 ± 0.04	E = 160.3	B = 174.82	C = 100.0			
EA (mV)	EB (mV)	PH	ETA	DH	DEB	EA (mV)	EB (mV)	PH	ETA	DH	DEB
287.73	913.35	1.962	0.0900	0.12	0.10	409.25	972.72	3.946	2.0194	-0.16	0.13
288.99	913.48	1.983	0.0982	0.12	-0.22	407.05	971.77	3.926	1.9853	-0.15	0.13
290.31	913.62	2.005	0.0987	0.12	-0.20	405.81	970.78	3.905	1.9502	-0.14	0.11
291.65	913.78	2.028	0.1035	0.13	-0.19	404.54	969.78	3.883	1.9145	-0.13	0.10
293.03	913.95	2.052	0.1088	0.14	-0.16	403.22	968.76	3.861	1.8776	-0.12	0.11
294.53	914.13	2.077	0.1147	0.13	-0.14	401.90	967.73	3.839	1.8409	-0.12	0.10
296.12	914.33	2.104	0.1214	0.11	-0.12	400.54	966.67	3.816	1.8033	-0.12	0.09
297.76	914.54	2.132	0.1285	0.11	-0.11	399.15	965.57	3.792	1.7652	-0.12	0.06
299.47	914.79	2.161	0.1364	0.11	-0.10	397.71	964.43	3.768	1.7261	-0.12	0.01
301.32	915.06	2.193	0.1454	0.09	-0.07	396.20	963.26	3.742	1.6853	-0.12	-0.01
303.31	915.36	2.226	0.1557	0.07	-0.06	394.80	962.00	3.719	1.6479	-0.16	-0.17
305.38	915.70	2.262	0.1670	0.06	-0.06	393.06	960.82	3.689	1.6018	-0.13	-0.11
307.55	916.08	2.298	0.1797	0.04	0.04	391.29	959.56	3.659	1.5555	-0.12	-0.06
309.89	916.52	2.336	0.1942	0.05	-0.03	389.43	958.27	3.628	1.5075	-0.11	0.01
312.39	917.01	2.380	0.2108	0.05	-0.01	387.56	956.90	3.596	1.4598	-0.11	-0.01
315.09	917.59	2.426	0.2301	0.05	0.0	385.67	955.45	3.564	1.4124	-0.12	-0.12
318.01	918.27	2.476	0.2526	0.04	0.02	383.57	954.02	3.529	1.3605	-0.11	-0.07
321.18	919.05	2.529	0.2769	0.04	0.04	381.64	952.54	3.496	1.3136	-0.14	-0.22
324.63	919.94	2.586	0.3100	0.04	0.06	379.40	951.00	3.458	1.2602	-0.14	-0.25
328.40	921.08	2.651	0.3470	0.03	0.08	376.81	949.43	3.415	1.1999	-0.12	-0.09
332.53	922.39	2.722	0.3914	0.03	0.08	374.15	947.80	3.370	1.1395	-0.10	0.01
336.97	923.95	2.797	0.4435	0.03	0.11	371.44	946.09	3.324	1.0797	-0.10	0.01
341.77	925.77	2.878	0.5054	0.02	0.10	368.59	944.41	3.276	1.0187	-0.09	0.07
346.84	927.88	2.964	0.5769	0.02	0.10	365.70	942.71	3.227	0.9588	-0.09	0.08
352.03	930.25	3.051	0.6569	0.02	0.11	362.70	940.98	3.176	0.8989	-0.09	0.07
357.20	932.79	3.139	0.7432	0.02	0.10	359.64	939.26	3.124	0.8401	-0.10	0.03
362.22	935.43	3.224	0.8334	0.01	0.08	356.42	937.54	3.070	0.7808	-0.09	0.0
366.89	938.08	3.303	0.9288	0.01	0.08	353.14	935.85	3.014	0.7231	-0.08	0.06
371.17	940.66	3.378	1.0293	0.02	0.09	348.77	933.90	2.940	0.6505	-0.07	0.08
375.15	943.12	3.442	1.1333	0.02	0.08	344.51	932.11	2.870	0.5860	-0.06	0.12
382.10	947.69	3.560	1.2489	0.02	0.06	340.71	930.48	2.804	0.5296	-0.05	0.08
385.14	949.77	3.611	1.3200	0.01	0.04	337.06	929.14	2.742	0.4802	-0.05	0.12
387.96	951.75	3.659	1.3876	0.01	0.02	333.71	927.97	2.685	0.4379	-0.04	0.13
390.48	953.58	3.702	1.4492	0.01	0.02	330.59	926.91	2.633	0.4009	-0.03	0.08
392.64	955.30	3.741	1.5080	0.01	0.01	327.74	926.03	2.584	0.3692	-0.03	0.06
395.05	956.93	3.779	1.5639	0.00	-0.02	325.22	925.33	2.542	0.3428	-0.03	0.07
397.10	958.48	3.814	1.6165	-0.00	-0.02	323.44	924.86	2.512	0.3250	-0.04	0.07
399.00	959.94	3.846	1.6658	-0.00	-0.02	321.76	924.40	2.483	0.3089	-0.04	0.02
400.75	961.33	3.875	1.7117	0.00	0.02	320.14	923.99	2.456	0.2940	-0.03	0.0
402.40	962.64	3.903	1.7553	0.01	0.04	318.54	923.67	2.429	0.2798	-0.02	0.04
403.96	963.90	3.929	1.7969	0.01	0.07						
405.46	965.07	3.955	1.8371	0.01	0.05						
406.89	966.21	3.979	1.8757	0.01	0.05						
408.28	967.30	4.002	1.9135	-0.00	0.02						
409.60	968.33	4.025	1.9495	-0.01	-0.01						
410.83	969.33	4.046	1.9831	-0.01	-0.01						
412.00	970.27	4.065	2.0153	-0.01	-0.02						
413.10	971.18	4.084	2.0459	-0.00	0.0						
414.19	972.06	4.102	2.0757	-0.01	-0.01						
415.23	972.90	4.120	2.1045	-0.01	-0.02						

Table 2. Survey of the compositions of the solutions used in the titrations. In titrations Nos. 1–17 $H_T=0$ and in titrations Nos. 18–19 $B_T=0$.

Titr. No.	H_0	B_0	C_0	B_T	C_T
1	110.0	0.535	99.95	0.549	101.5
2	109.9	0.525	99.95	0.541	101.0
3	109.9	0.812	99.95	0.827	100.0
4	110.0	0.862	99.95	0.862	100.0
5	109.7	0.773	99.95	0	100.0
6	108.8	0.213	99.0	0.234	100.0
7	109.0	0.216	99.0	0.241	102.0
8	88.14	0.338	78.37	0.362	78.37
9	88.19	0.884	78.37	0.917	78.37
10	89.48	0.572	79.13	0.578	79.45
11	89.71	0.823	79.13	0.835	79.45
12	89.63	0.337	79.13	0.350	79.45
13	155.4	0.562	144.3	0.590	144.3
14	155.2	0.387	144.3	0.411	144.3
15	152.2	0.798	144.3	0.800	146.0
16	155.1	0.248	144.3	0.305	144.3
17	109.9	0.327	99.92	0.321	101.0
H_T					
18	93.25	0.537	101.9	160.3	100.0
19	93.05	0.290	101.9	160.3	101.0

these experimental data, the equilibrium model was calculated. Since the amount of data was very large (19 titrations with a total of 690 measuring points), the experimental data from only 4 titrations (Nos. 5, 11, 14, and 18) are represented in Table 1.* The composition of the investigated solutions are given in Table 2. About one third of the experimental points from 9 titrations (Nos. 3–5, 10–14 and 16) are shown in Fig. 1. Back titrations (Nos. 18, 19) showed that the equilibria were reversible. The reproducibility was tested by varying the tin concentration in some titrations (Nos. 5, 18, 19).

The amalgam electrodes normally attained a steady potential almost instantaneously which remained constant within ± 0.02 mV for several hours. For each experimental point, the value of E_B was not, however, accepted to correspond to equilibrium, until it had been ascertained that this value was constant within 0.02 mV during 15 minutes. This was an important criterion, because accidental errors in the titrations (e.g. a gas bubble in the salt bridge, stop of the gas flow, a poor electrical contact, leakage currents, change in temperature) often appeared as a very slow drift in the

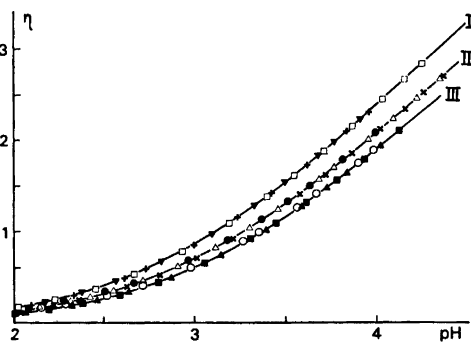


Fig. 1. Survey of measurements: $\eta = \lg(B/b)$ as a function of pH. The theoretical curves have been calculated with the equilibrium constants given in the text. I: $B=0.248-0.562$ mM II: $B=0.639-0.862$ mM III: $B=0.337-0.823$ mM

$C=144$ mM	$C=100$ mM	$C=79.2$ mM
Symbol Tit.	Symbol Tit.	Symbol Tit.
No.	No.	No.
+ 13	× 3	▲ 10
□ 14	△ 4	■ 11
▼ 16	● 5	○ 12

* 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.

emf-values. The glass electrode attained its equilibrium value almost as rapidly as the amalgam electrode.

EXPERIMENTAL DETAILS

The measurements were carried out in a paraffin oil thermostat at 25.00 ± 0.01 °C, the room temperature being 25 °C. The thermostating equipment was the same as described in Ref. 7. The titration cell and the cell used for the generation of the tin ions were of the "Wilhelm" type.¹⁷

Several glass electrodes were tested in order to find electrodes which gave stable emf-values that were not influenced by the magnetic stirrer or other external disturbances. Finally Beckmann 39004 and Jena 9201/71 were chosen. The glass electrodes were checked with hydrogen electrodes in solutions of high buffer capacity in the approximate pH range 2–8. These tests were made as titrations with hydroxide ions as described by Olin.¹⁸ The amalgam electrodes were prepared by dissolving tin metal (Mallinckrodt, analytical reagent, granular, 20 mesh) in mercury (Merck, *p.a.*). The surface of the tin was first cleaned with diluted HCl, washed with water and dried between filter papers. The tin and mercury were mixed with a magnetic stirrer in a 40 ml wash bottle, under *ca.* 10 mM HClO₄, through which nitrogen gas was bubbled to exclude oxygen. With this efficient stirring the amalgam obtained a homogeneous composition almost instantaneously. The amalgam was transferred to the titration vessel by nitrogen gas. It was passed through a capillary tube and to avoid "plugs" only liquid amalgam was used. The solubility of tin in mercury is 1.263 mol % at 25 °C,¹⁹ and the tin content in both electrodes was kept, generally, at ~ 1.25 mol %. In some experiments lower concentrations of tin (*e.g.* 0.5, 0.3, 0.03 mol %) were used in the measuring amalgam. The amalgam was then prepared either from strips of thin tin foil (Merck, *p.a.*) which were dissolved in mercury or by electrolytic reduction of Sn²⁺ in a chloride solution on a mercury cathode. Neither the stability of the electrode potential nor the time required to attain equilibrium seemed to vary with the tin content of the amalgam. In the titration vessel the amalgam was kept in teflon holders. The electrical connection to an amalgam electrode was *via* a platinum wire sealed through a glass tube. This tube also carried the whole electrode. The device was held above the solution when it was filled with amalgam to prevent the platinum needle from coming into contact with the solution, in which case unstable emf-values might be obtained.

It was sometimes difficult to obtain stable, reliable E_B values especially at the lower tin concentrations. In some titrations this was

due to a poor contact between the platinum wire and the amalgam in the measuring electrode. The best way of obtaining a good amalgamation of the platinum was to heat the cleaned wire momentarily in a flame and insert it immediately into a small pool of mercury. The small Hg-drop adhered to the Pt gave a perfect contact with Sn(Hg). The generating electrode was inserted into the solution only during the electrolysis and then withdrawn. As the titrations were fairly time-consuming (*ca.* 20 h) the generating amalgam was held above the test solution when not in use. The electrode surface was carefully rinsed by dipping the electrode once or twice into the solution. When the electrode holder was made of a platinum net a slow emf drift, indicating a spontaneous Sn²⁺-generation, was noticed as soon as the electrode came in contact with the solution. This was due to a lowering of the hydrogen overvoltage on the amalgam where this was in contact with the platinum. On increasing the acidity of the solution it was even possible to see evolution of gas from one or two points on the borderline.

30–35 g of *ca.* 1.25 mol % Sn(Hg) was used in the generating electrode, the surface of which was about 2.5 cm². The current density was approximately 1.2 mA/cm², it not being possible to vary the current strength. The anodic oxidation was carried out stepwise in order to avoid a local excess of tin ions.

The test solution was protected from atmospheric oxygen by the passage of a slow stream of argon, which had been purified by passage through a column filled with an activated copper catalyst (BASF-catalyst R3-11) through wash bottles with 10 % H₂SO₄, 10 % NaOH, 3 M NaClO₄²⁰ and finally through a bottle containing S₂ solution or a mixture of S₂ and T to resemble the test solution. Glass filters were used in some bottles to increase the contact area of the gas. Diffusion-tight high pressure polythene tubing (Samuel Moore "P" Tubing 6 mm) was used to connect the gas cylinder with the titration vessel *via* the wash bottles. The test solution was stirred with a magnetic stirrer, which proved to be more efficient than gas stirring and did not cause any splashing on the glass walls. The digital voltmeter, the constant current source and other instruments in the computerised titrator were those used previously.⁷ The reference silver-silver chloride electrode was prepared according to Brown^{20,21} and the hydrogen gas electrode as described in Ref. 20.

Chemicals

Sodium perchlorate stock solutions were prepared from recrystallized Na₂CO₃ (Merck, *p.a.*) and *ca.* 70 % HClO₄ (Merck, *p.a.*) as described by Biedermann.²² Using a mixture of bromocresol-green and methyl red²⁰ as indicator it

was possible to prepare an almost neutral solution. The proton excess was determined by a coulometric titration with hydrogen ions using a Gran plot.²⁵ The oxygen gas was generated on a cylindrical platinum net anode. The metal content was checked with Eriochrome Black T.²³

Sodium acetate stock solutions were prepared from recrystallized $\text{NaOCOCH}_3 \cdot 3\text{H}_2\text{O}$ (Merck, *p.a.*). The sodium content was determined as NaCl by evaporating a known amount of the solution with concentrated HCl.²⁴ The acetate content was determined by a cation exchanger in the hydrogen form, the resulting eluate being titrated with sodium hydroxide. The results of the two methods agreed to within 0.2%. The stock solutions were kept in polythene bottles with thick walls. The sodium acetate solution was tested for proton excess by titrating equimolar solutions of HClO_4 and NaAc (0.1 M) with HClO_4 in 3 M NaClO_4 until a suitable proton excess was obtained. The original excess was determined by a Gran extrapolation.²⁵

Perchloric acid solutions were prepared by diluting ~70% HClO_4 (Merck, *p.a.*) and were standardized against tris(hydroxymethyl)-aminomethane (Merck, *p.a.*).²⁶ They were also titrated against recrystallized Ti_2CO_3 (BDH, *p.a.*).²⁰ The results of the two methods agreed to within 0.1%. The Sn^{2+} ions were generated by constant current electrolysis and the concentration was calculated from the amount of electricity that had passed through the solution.⁷

CALCULATIONS AND RESULTS

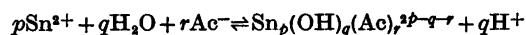
From the experimental values of E_H , E_B , V_T and the analytical composition of the test solutions a series of data sets $\eta(\lg h)_{B,C}$ or $\eta(\lg h)_C$ were calculated (Table 1). The analytical concentrations of H , B , and C for each point in Table 1 were calculated. The titrations can be divided into three groups, each with a different acetate concentration, $C = C_0 = C_T = 79, 100, \text{ and } 144 \text{ mM}$, respectively. Experimental values of $\eta(\lg h)_{B,C}$ or $\eta(\lg h)_C$ for some of these titrations are shown in Fig. 1. For the sake of clarity, only about a third of the points from each titration have been included.

E_H^0 was calculated at the beginning of each titration using eqn. (4), assuming h to be known from the composition of the acid solution S_0 . By generating tin ions into the solution and neglecting both the hydrolysis and complex formation, an ap-

proximate value of E_B^0 could be calculated from eqn. (3), for values of B from about 0.05 mM to the desired value, which was then generally kept constant in the titration. Later, this constant, E_B^0 , was adjusted for the presence of SnAc^+ and SnOH^+ (see Fig. 2).

The titration was interrupted when a black precipitate of SnO became visible on the generating electrode. This compound was identified from its Guinier powder photograph. It was difficult to ascertain when the tin oxide was first formed since there was no sudden change in the emf-values nor any effect on the time required to attain equilibrium. However, the neglect of the precipitate introduced an error which caused the $\eta(\lg h)_{B,C}$ curves to deviate in a non-reproducible way. This generally occurred when $\text{pH} > 4$. Points from this region were not therefore included in the calculations.

The complex formation in the solution may be described in terms of the reactions



and



The corresponding equilibrium constants are

$$\beta_{qrp} = \frac{[\text{Sn}_p(\text{OH})_q(\text{Ac})_r] h^q}{[\text{Sn}^{2+}]^p [\text{Ac}^-]^r}$$
 (the charge of the

complex being omitted)

and

$$K_{\text{HAc}} = \frac{[\text{HAc}]}{[\text{H}^+][\text{Ac}^-]}$$

It is assumed that under given conditions the sum of all species $[\text{Sn}^{2+}(\text{H}_2\text{O})_i(\text{Na}^+)_m(\text{ClO}_4^-)_n]$ may be written $[\text{Sn}^{2+}]$.²⁷ K_{HAc} was determined by performing titrations in different acetate solutions in the absence of tin ions, evaluation of the data with the Letagrop program yielding

$$\lg K_{\text{HAc}} = 5.018 \pm 0.010$$

This value agrees well with those previously reported under the same conditions.^{28,29} For the pure hydrolysis products the values

$$\lg \beta_{101} = -3.70 \pm 0.02$$

$$\lg \beta_{403} = -6.81 \pm 0.03$$

as determined in a separate titration^{30,31} (cf. Ref. 32) were used.

When $\eta = \lg(B/b)$ was plotted as a function of $\lg h$ at a constant C level the curves obtained were independent, within the experimental errors, of the metal ion concentration (Fig. 1). As a consequence the concentrations of $\text{Sn}_3(\text{OH})_4^{2+}$ and other possible polynuclear complexes were ignored. Some titrations in which B was varied (Table 1, titrations Nos. 5, 18, 19) were carried out to verify the coincidence of the $\eta(\lg h)_C$ curves with the $\eta(\lg h)_{B,C}$ curves (Fig. 1). In this way a check of the assumed 100 % efficiency of the tin generating electrode was obtained.

The mass balance for total tin, B , hydrogen, H (over H_2O , Ac^- and Sn^{2+}), and acetate, C , gives

$$B = b + \sum_{p,q,r} p \beta_{qrp} b^p h^{-q} c^r \quad (5)$$

$$H = h + K_{\text{HAc}} h c - \sum_{p,q,r} q \beta_{qrp} b^p h^{-q} c^r \quad (6)$$

$$C = c + K_{\text{HAc}} h c + \sum_{p,q,r} r \beta_{qrp} b^p h^{-q} c^r \quad (7)$$

Inserting into (5) and neglecting polynuclear and possible mixed complexes

$$B/b = 1 + \beta_{101} h^{-1} + \sum_r \beta_{0r1} c^r = 1 + \beta_{101} h^{-1} + \sum_r \beta_{0r1} K_{\text{HAc}}^r [\text{HAc}]^r h^{-r}$$

Since $C \gg B$ an approximate value of $[\text{HAc}]$ and $[\text{Ac}^-] = c$ could be calculated from (6) neglecting the b -containing terms. Thus the value of the function

$$F(c) = B/b - 1 - \beta_{101} h^{-1} = \sum_r \beta_{0r1} c^r$$

could be calculated approximately from the corresponding measured values of b and h (eqns. 3 and 4) and the coefficients β_{0r1} could be evaluated by, e.g., Leden's method.⁹ According to, e.g., Donaldson¹ the highest mononuclear complex is SnAc_3^- . With estimated values of β_{011} , β_{021} and β_{031} - denoted β_1 , β_2 and β_3 in the following - the final equilibrium model was calculated with the generalized least squares program Letagrop, version ETITR³²⁻³⁵ without any of the approximations used in the graphical treatment.

Assuming that E_H , B and C are correct, any errors lie in E_B . Equilibrium constants which minimized the error squares sum $U = \sum w(E_{\text{cal}}$

$- E_B)^2$, where E_{cal} is the calculated value of E_B were thus sought. The same weight was assigned to all points ($w=1$). Using the option denoted *Typ*=3, *Val*=5 in Ref. 35, the program calculated b and c from eqns. 5 and 6 by successive approximations using the known or estimated values of E_H^0 , E_B^0 , β_{qrp} and K_{HAc} . The value of H was not utilized for these calculations but $H_{\text{cal}} - H = \text{DH}$ (Table 1), where H_{cal} was calculated from eqn. 6, was useful as a check of the proposed equilibrium model. The agreement between the calculated and experimental E_B , $E_{\text{cal}} - E_B = \text{DEB}$ is shown in Table 1.

The formation constants of the tin-acetate complexes were chosen as adjustable common parameters, assuming that K_{HAc} , β_{SnOH^+} and $\beta_{\text{Sn}_3(\text{OH})_4^{2+}}$ were known. E_B^0 was used as adjustable group parameter, since, as discussed earlier, only an approximate value of this constant was known. By assuming small errors in H , E_H^0 and C and varying these as group parameters systematic errors may be compensated for. Since these parameters are interrelated they could not be varied simultaneously. In the version of Letagrop used it was not possible to vary C . Therefore only H or E_H^0 was varied, which resulted in a closer agreement between experimental and calculated values in some of the titrations. To reduce the risk of systematic errors due to accidental impurities in the reagents, several different batches of the recrystallized salts and several stock solutions of sodium acetate, sodium perchlorate, and perchloric acid had been used.

Since not more than 200 data could be treated at a time with this version of Letagrop, the 690 points were divided into 4 groups. The results of these calculations are shown in Table 3.

The uncertainties provided by the program correspond to three times the "standard deviation" of the constant.^{36,37} The standard deviation of the mean values were calculated from

$$\sigma = \frac{\sum_i \sigma_i^2 f_i}{\sum_i f_i}$$

where

σ_i = the standard deviation for each group
 f_i = the number of experimental points minus the number of unknown constants for each group.

Table 3. Equilibrium constants, $\lg \beta_i$, for the formation of SnAc_i^{2-i} , $i=1, 2, 3$.

Titration No.	$\lg \beta_1 \pm 3\sigma$	$\lg \beta_2 \pm 3\sigma$	$\lg \beta_3 \pm 3\sigma$
1-4	3.471 ± 0.004	6.046 ± 0.006	7.25 ± 0.03
5-10	3.474 ± 0.004	6.038 ± 0.012	7.30 ± 0.10
11-15	3.471 ± 0.003	6.041 ± 0.005	7.26 ± 0.03
16-19	3.472 ± 0.003	6.041 ± 0.004	7.27 ± 0.03
Mean value	3.472 ± 0.004	6.042 ± 0.007	7.27 ± 0.05

In Table 1 the "best" value of E_B° for each group is given together with three times its standard deviation $\sigma(E_B^\circ)$. The fit between the experimental and calculated data is illustrated in Fig. 1. For the sake of clarity

only a fraction of the titration points have been included. The distribution of the complexes as a function of pH, as calculated with the Haltfall program,^{38,39} is shown in Fig. 2. The plotting was carried out on an IBM 370/145 computer.⁴⁰

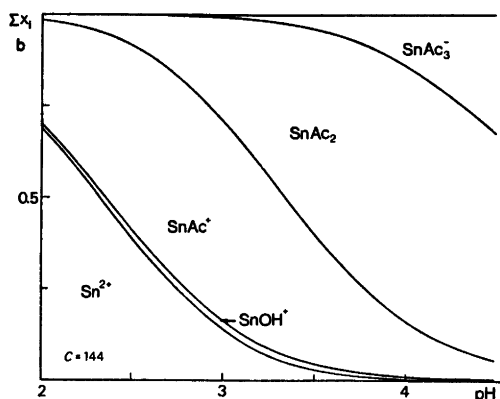
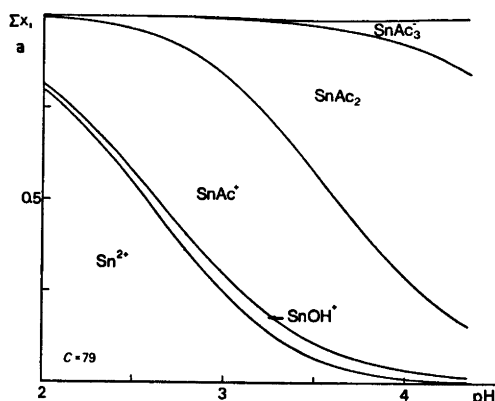


Fig. 2. Distribution diagrams for the tin(II)-acetate system at different acetate concentrations, *i.e.* a, $C=79$ and b, $C=144$ mM, respectively. The mol fraction of the total Sn(II) is plotted as a function of pH at constant values of C .

DISCUSSION

The present investigation gives evidence for the formation of the three mononuclear complexes SnAc^+ , SnAc_2 and SnAc_3^- . The agreement between the calculated and experimental values

$$\text{DH} = H_{\text{cal}} - H$$

$$\text{DEB} = E_{\text{cal}} - E_B$$

is good, although there are systematic trends in some of the titrations (*cf.* Table 1).

The species SnAc^+ , SnAc_2 and SnAc_3^- were also found in the investigation made by Donaldson *et al.*³ Using the formation constants from the present work, these complexes should, however, not have been formed, in appreciable amounts, in the strongly acid solutions (2 M H_2SO_4) used in their potentiometric and polarographic titrations. Since their experimental data are not given, it is difficult to suggest another interpretation of their measurements. Polarographic and potentiometric studies have been carried out by Elbourne and Buchanan^{41,42} on the reactions between Sn(II) and some organic acids, *e.g.* acetic acid. Their calculations seem, however, to have been based on the assumption that only one complex was formed in each solution. The reported values of the mean ligand number for some different compositions do not agree with the equilibrium model given in the present work.

Table 4. Equilibrium constants, $\lg \beta_i$, for the formation of InAc_i^{3-i} ($i=1, 2, 3$), PbAc_i^{2-i} ($i=1, 2, 3, 4$) and SnAc_i^{2-i} ($i=1, 2, 3$).

Metal	Medium	$\lg \beta_1$	$\lg \beta_2$	$\lg \beta_3$	Ref.
In^{3+}	2 M NaClO_4	3.50	5.95	7.90	46
Sn^{2+}	3 M NaClO_4	3.47	6.04	7.26	This work
Pb^{2+}	3 M NaClO_4	2.33	3.60	3.59	30

The magnitudes of the formation constants obtained agree well with that expected from consideration of the principle of hard and soft acids and bases.⁴³⁻⁴⁶ The hard acid character of, e.g. In^{3+} , Sn^{2+} , and Pb^{2+} should decrease in the given order. Thus the stabilities of the complexes with hard bases, such as the acetate ion, is expected to decrease in the same order. The stability constants of the first three mononuclear complexes are given in Table 4 and the complex formation as a function of pAc

is visualized in Fig. 3. It is clear that the harder the acid the lower the acetate concentration at which the third complex starts to dominate.

The titrations were terminated when a precipitate of black SnO became visible on the generating electrode. This might have indicated the presence of hydrolysed tin-acetate complexes in the solutions. The SnO was, however, only formed on the surface of the electrode, where a temporary excess of Sn^{2+} ion is inevitably built up. As is seen from Fig. 2 a lower acetate concentration would be necessary in order to favour the possible formation of mixed complexes in this pH and $[\text{Sn(II)}]$ range.

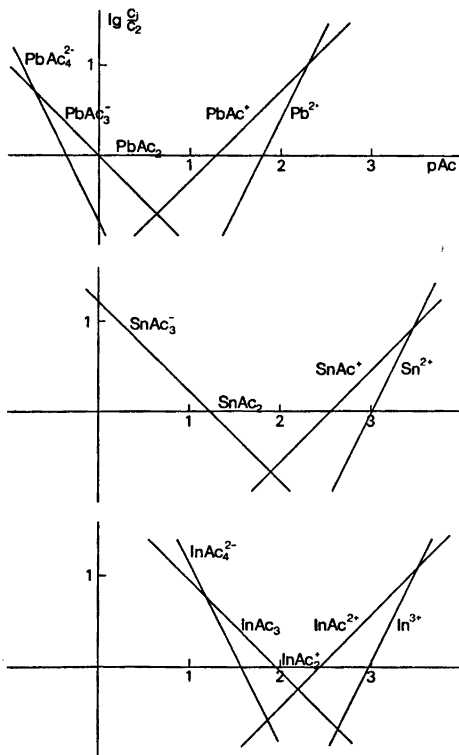


Fig. 3. Distribution diagrams for the $\text{Pb}^{2+}-\text{Ac}^-$, $\text{Sn}^{2+}-\text{Ac}^-$ and $\text{In}^{3+}-\text{Ac}^-$ complexes. $\lg(c_i/c_{\text{ref}})$ is plotted as a function of pAc.

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