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Hydrolysis of Monomethyl-, Dimethyl-, and Trimethyltin(IV) Cations in Fairly Concentrated Aqueous Solutions at I = 1 mol·L^{-1} (NaNO$_3$) and T = 298.15 K. Evidence for the Predominance of Polynuclear Species

Rosalia M. Cigala,[†] Concetta De Stefano,[†] Alba Giacalone,[‡] Antonio Gianguzza,[‡] and Silvio Sammartano[*,†]

[†]Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Viale Ferdinando Stagno d'Alcontres 31, I-98166, Messina (Vill. S. Agata), Italy

[‡]Dipartimento di Chimica "Stanislao Cannizzaro", Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy

ABSTRACT: The hydrolysis of methyltin(IV) cations at fairly high concentrations was investigated to evaluate the formation of polynuclear species in aqueous solution. The hydrolysis of monomethyltin(IV), dimethyltin(IV), and trimethyltin(IV) was studied by potentiometry at T = 298.15 K and at I = 1 mol·L^{-1} in NaNO$_3$ aqueous solutions. The results obtained gave evidence for the formation of the following polynuclear species, in addition to the mononuclear species already reported, which were also considered in the models proposed for the three systems investigated: $[(CH_3)Sn(OH)_3]^0$, $[(CH_3)Sn(OH)_4]^-$, $[((CH_3)Sn)_2(OH)_4]^{2+}$, $[((CH_3)Sn)_2(OH)_5]^+$, $[((CH_3)Sn)_2(OH)_7]^-$, $[((CH_3)Sn)_3(OH)_5]^{4+}$, $[((CH_3)Sn)_3(OH)_7]^{2+}$, $[((CH_3)Sn)_5(OH)_9]^{6+}$, and $[((CH_3)Sn)_5(OH)_{11}]^{4+}$ for the monomethyltin(IV) system; $[((CH_3)_2Sn)(OH)]^+$, $[((CH_3)_2Sn)(OH)_2]^0$, $[((CH_3)_2Sn)(OH)_3]^-$, $[((CH_3)_2Sn)_2(OH)_2]^{2+}$, $[((CH_3)_2Sn)_2(OH)_3]^+$, $[((CH_3)_2Sn)_3(OH)_4]^{2+}$, and $[((CH_3)_2Sn)_4(OH)_6]^{2+}$ for the dimethyltin(IV) system; $[((CH_3)_3Sn)(OH)]^0$, $[((CH_3)_3Sn)(OH)_2]^-$, $[((CH_3)_3Sn)_2(OH)]^+$, $[((CH_3)_3Sn)_2(OH)_2]^0$, and $[((CH_3)_3Sn)_2(OH)_4]^{2-}$ for the trimethyltin(IV) system. The formation constants β_{pq}^{OH} (relative to the equilibrium $p(CH_3)_nSn^{(4-n)+} + qOH^- = ((CH_3)_nSn)_p(OH)_q{}^{(p(4-n)-q)}$) can be expressed as a function of the cation charge z ($z = 4 - n$) by the general equation: $\log \beta_{pq}^{OH}/(p+q) = 1 + (2.50 \pm 0.05)z$, that allows the calculation of rough values of β_{pq}^{OH} for any (p,q) couple. The reliability of the proposed speciation models is discussed. As expected for a tricharged cation, by increasing the concentration of $(CH_3)Sn^{3+}$, the yield of polynuclear species becomes predominant; this behavior is less marked for $(CH_3)_2Sn^{2+}$ and $(CH_3)_3Sn^+$.

■ INTRODUCTION

Organotin(IV) compounds are used as active components in many industrial formulations for different purposes.[1−3] The most important applications are as pesticides in agriculture,[4,5] as antifouling preservatives in coatings for wood and stones and in paints for ships (see ref 6 and refs therein), as additives for thermal stabilization in the plastic industry,[7] and as catalysts for polyurethane and foams production[8,9] in the glass industry.[10] The wide distribution into the environment of organotin(IV) compounds, whose toxicity is well-recognized,[11−13] is a reason of great concern, also considering their high stability and, as a consequence, their accumulation in biota.[14−20] In spite of the policy adopted by many countries to reduce the use of organotin(IV) compounds in industrial applications,[21] especially as additives in antifouling paints,[22] these compounds, owing to their persistence, are still present in aquatic ecosystems.[23−26] Therefore, it is important to keep under control the environmental distribution and fate of organotins, as well as their reactivity in natural fluids. As a consequence of the acidic character of the organotin(IV) cations, hydrolysis is the most important reaction undertaken by this class of compounds in aqueous solution, often leading to the formation of polynuclear hydroxo-complexes in solution $(R_nSn)_p(OH)_q{}^{(p(4-n)-q)}$ with $p > 1$, depending on the organotin(IV) cation concentration. The hydrolysis of organotin(IV) cations has been subject of investigation for more than fifty years by different research groups,[27−46] using different techniques. To give a contribution to the speciation of organotin(IV) compounds in natural waters, the hydrolysis of the mono-,[47] di-,[48−50] and trimethyltin(IV)[50−52] cations has also been investigated in our laboratories in different ionic media and at different ionic strengths and temperatures. Moreover, some databases report quantitative data on the hydrolysis of organotin(IV) compounds,[53−55] and some recommended hydrolysis constants were given by Baes and Mesmer.[56]

Recently we were involved in the study of mixed metal hydrolytic species formation, in aqueous solution.[57,58] In these investigations, the use of rather high metal concentrations was necessary to evidence mixing effects, in particular the enhancement of hydrolysis. The results obtained in our previous studies show that the deviation of experimental data from those calculated, by considering only the hydrolysis constants determined for the single metal systems, is in general fairly small. Therefore, constants as precise as possible, determined under the same conditions for both single and mixed systems, are needed. We are now investigating some mixed metal systems that include the methyltin(IV) cation $[(CH_3)_nSn^{(4-n)+}]$. For this reason we need accurate values of hydrolysis constants for these cations determined at fairly high metal concentrations.

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Table 1. Experimental Conditions for Measurements at $I = (1.00 \pm 0.05)\ \mathrm{mol \cdot L^{-1}}$ and $T = 298.15$ K

methyltin(IV)	HNO_3		
mmol·L^{-1}	mmol·L^{-1}	pH range	runs[a]
	$(CH_3)Sn^{3+}$		
20−80	10−20	1−11	14
	$(CH_3)_2Sn^{2+}$		
20−80	10−15	1.5−7	13
	$(CH_3)_3Sn^{+}$		
60−85	5−10	2−12	13

[a] 40 to 70 titration points per run.

EXPERIMENTAL SECTION

Reagents and Materials. All reagents were of analytical grade, and the solutions were always prepared using CO_2-free freshly prepared distilled water ($R \geq 18\ \mathrm{M\Omega \cdot cm}$). Nitric acid and sodium hydroxide solutions were prepared by diluting concentrated solutions (Riedel-de Haën), and standardized by sodium carbonate (Aldrich) and potassium hydrogen phthalate (Fluka), respectively. Sodium nitrate (Aldrich), used as background salt, was always dried in a oven at 383.15 K before use. Monomethyltin(IV), dimethyltin(IV), and trimethyltin(IV), as chloride salts (by Aldrich), with purities of (> 97, 98, and 98) %, respectively, were used without further purification.

Safety Considerations. The effects of methyltin compounds' toxicity are skin and eye irritation, inflammation of the bile duct, hepatotoxicity, and neurotoxicity. Trimethyltin chloride, the most toxic, causes neuronal necrosis. Its ingestion or inhalation can cause lethal poisoning. Certain dialkyltin compounds have been shown to cause adverse effects on cell-mediated immunity, specifically on the T cell lymphocyte. Experimental studies have failed to reveal any evidence of carcinogenicity, mutagenicity, or teratogenicity. Direct contact with the skin must be avoided. Precautions and adequate clothing are absolutely necessary when manipulating the reagent. Disposal of all tin-containing waste from the experiment should be done in accordance with facility guidelines.

Apparatus and Procedure. Potentiometric titrations were carried out by using an apparatus consisting of a combination Orion-Ross 8172 glass electrode connected to a Crison pH2002 potentiometer coupled with a Metrohm mod. 665 automatic titrant dispenser. The equipment was connected to a personal computer, and a homemade computer program was used to control titrant delivery and data acquisition and to check for emf stability. The estimated precision of this system was ± 0.15 mV and ± 0.003 mL for electromotive force (emf) and titrant volume readings, respectively. All titrations were carried out at $T = (298.15 \pm 0.10)$ K, by using a HAAKE F3 digital thermocryostat, under magnetic stirring and bubbling purified presaturated N_2 through the solution to exclude O_2 and CO_2 inside the solution.

To determine the glass electrode formal potential ($E°$) and, when necessary, the junction potential ($E_j = j_a[H^+]$), independent titrations of acidic solutions (nitric acid) were performed with standard sodium hydroxide solutions in the same experimental conditions of ionic strength and temperature as the systems under study. The free hydrogen ion concentration scale was used for all measurements ($pH \equiv -\log[H^+]$). A solution volume of 25 mL containing monomethyltin(IV) trichloride, dimethyltin(IV) dichloride, or trimethyltin(IV) chloride, nitric acid, and sodium nitrate to adjust the ionic strength to the desired values (1 mol·L^{-1}), was titrated with standard CO_2-free sodium hydroxide solutions up to pH ~ 7 for dimethyltin(IV) and up to ~12 for the monomethyltin(IV) and trimethyltin(IV) cations, respectively. The experimental conditions used are reported in Table 1.

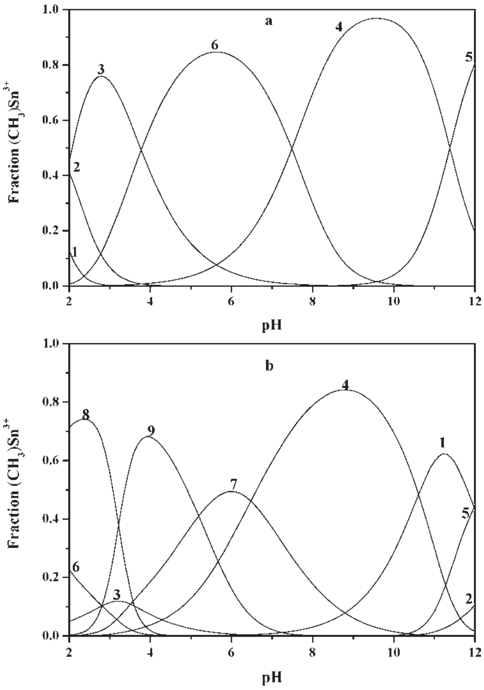

Figure 1. Distribution diagram of $(CH_3)Sn^{3+}$: (a) $c(CH_3)Sn^{3+}$ = 1 mmol·L^{-1}: **1** $(CH_3)Sn^{3+}$ free; **2** (1,1); **3** (1,2); **4** (1,3); **5** (1,4); **6** (2,5); (b) $c(CH_3)Sn^{3+}$ = 80 mmol·L^{-1}: **1** (1,3); **2** (1,4); **3** (2,4); **4** (2,5); **5** (2,7); **6** (3,5); 7 (3,7); **8** (5,9); **9** (5,11); in $NaNO_3$ I = 1.00 mol·L^{-1} at T = 298.15 K.

From separate titrations of strong acid in $NaNO_3$ media, the value $-\log K_w = 13.73 \pm 0.02$ at $I = (1.00 \pm 0.05)\ \mathrm{mol \cdot L^{-1}}$ and T = 298.15 K was obtained.

Calculations. To determine all of the parameters of an acid−base titration (analytical reagent concentrations, electrode formal potential $E°$, junction potential coefficient j_a) and to calculate complex formation constants (and $\log K_w$ values), the computer programs ESAB2M and BSTAC were used.[59,60] The ES4ECI[60] computer program was used to draw speciation diagrams and to compute the formation percentage of the species.

Hydrolysis constants are expressed according to the equilibrium 1:

$$p(CH_3)_nSn^{(4-n)+} + qH_2O = ((CH_3)_nSn)_p(OH)_q^{(p(4-n)-q)} + qH^+ \qquad \beta_{pq} \quad (1)$$

and $((CH_3)_nSn)_p(OH)_q^{(p(4-n)-q)}$ species formation constants are given by the equilibrium 2:

$$p(CH_3)_nSn^{(4-n)+} + q(OH^-) = ((CH_3)_nSn)_p(OH)_q^{(p(4-n)-q)} \qquad \beta_{pq}^{OH} \quad (2)$$

Table 2. Summary of Tested Speciation Models for the Hydrolysis of Monomethyltin(IV) [$I = (1.00 \pm 0.05)\ \mathrm{mol \cdot L^{-1}}$, $T = 298.15 \pm 0.10$ K]

$\log \beta_{pq}$[a]	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6	Model 7
1,2	-	-	-	−2.840(8)[b]	-	-	-
1,3	−9.912(5)[b]	−9.948(4)[b]	−9.961(5)[b]	−9.925(5)	10.567(13)[b]	−9.702(18)[b]	−9.767(15)[b]
1,4	−22.52(4)	-	−21.915(6)	−21.888(5)	-	-	−21.854(17)
2,4	−3.811(9)	−3.824(8)	−3.816(7)	-	−3.656(10)	−3.036(13)	−3.094(10)
2,5	−8.103(7)	−8.151(7)	−8.154(6)	−8.093(7)	−9.01(20)	−7.762(27)	−7.860(23)
2,7	−30.65(2)	−30.477(8)	-	-	−31.425(24)	−30.146(32)	-
3,5	−1.887(12)	−1.891(11)	−1.871(10)	−1.873(13)	−1.548(10)	−1.227(16)	−1.307(11)
3,7	−8.226(7)	−8.272(8)	−8.272(7)	−8.252(8)	−8.845(20)	−7.652(23)	−7.765(18)
5,9	−2.725(10)	−2.789(11)	−2.788(9)	−2.845(12)	-	−3.57(11)	-
5,11	−9.163(11)	−9.232(12)	−9.229(9)	−9.290(13)	−10.084(20)	-	-
σ^2/σ_0^2[c]	1.000	1.100	1.147	1.200	1.565	4.83	5.16

[a] β_{pq} refers to the equilibrium $p(CH_3)Sn^{3+} + qH_2O = [((CH_3)Sn)_p(OH)_q]^{(3p-q)} + qH^+$. [b] Standard deviation in the last figure(s) in parentheses. [c] σ^2 = variance in the fit; σ_0^2 = variance in the fit for the best speciation model.

RESULTS

Hydrolysis of $(CH_3)Sn^{3+}$. The hydrolysis of the monomethyltin(IV) cation in dilute aqueous solutions (≤ 1 $\mathrm{mmol \cdot L^{-1}}$) includes the formation of the mononuclear species (in parentheses the $\log \beta_{pq}$ at infinite dilution and T = 298.15 K, from refs 47 and 50):

$$[(CH_3)Sn(OH)]^{2+} \qquad (\log \beta = -1.5)$$

$$[(CH_3)Sn(OH)_2]^{+} \qquad (\log \beta = -3.46)$$

$$[(CH_3)Sn(OH)_3]^{0} \qquad (\log \beta = -9.09)$$

$$[(CH_3)Sn(OH)_4]^{-} \qquad (\log \beta = -20.47)$$

and the polynuclear species:

$$[((CH_3)Sn)_2(OH)_5]^{+} \qquad (\log \beta = -7.69)$$

As shown in Figure 1a, this cation undergoes strong hydrolysis, over the whole pH range 2 to 12, and at millimolar concentrations, the formation of polynuclear species is quite significant in the pH range 4 to 8. When higher concentrations are considered, as in our experiments [(20 to 80) $\mathrm{mmol \cdot L^{-1}}$], other polynuclear species are formed, namely, (p,q) = (2,4), (2,7), (3,5), (3,7), (5,9), and (5,11). Several speciation models were tested: in Table 2 seven models are summarized (other intermediate combinations of species were rejected by the computer program). The best model was chosen on the basis of lowest overall variance. The speciation diagram drawn in Figure 1b shows high yields for polynuclear species over the whole pH range 2 to 12, and in this range the amount of free cation is negligible.

Hydrolysis of $(CH_3)_2Sn^{2+}$. The hydrolysis of the dimethyltin(IV) cation in dilute aqueous solutions (≤ 1 $\mathrm{mmol \cdot L^{-1}}$) includes the formation of the mononuclear species (in parentheses the $\log \beta_{pq}$ at infinite dilution and T = 298.15 K, from refs 48 to 50):

$$[(CH_3)_2Sn(OH)]^{+} \qquad (\log \beta = -2.86)$$

$$[(CH_3)_2Sn(OH)_2]^{0} \qquad (\log \beta = -8.16)$$

$$[(CH_3)_2Sn(OH)_3]^{-} \qquad (\log \beta = -19.35)$$

and the polynuclear species:

$$[((CH_3)_2Sn)_2(OH)_2]^{2+} \qquad (\log \quad = -4.99)$$

$$[((CH_3)_2Sn)_2(OH)_3]^{+} \qquad (\log \beta = -9.06)$$

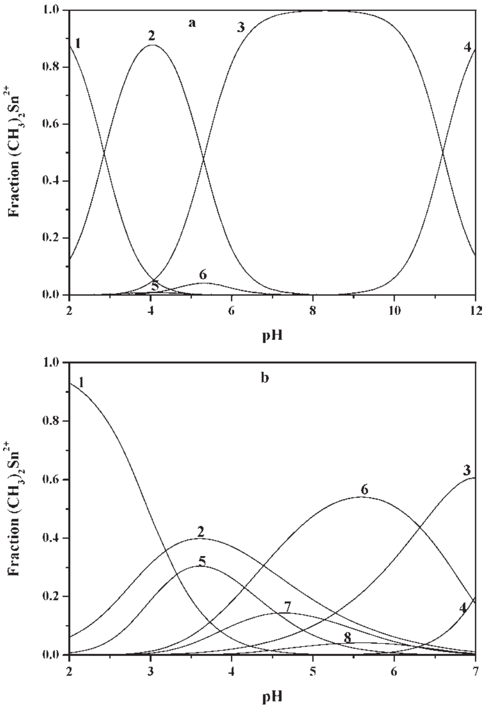

Figure 2. Distribution diagram of $(CH_3)_2Sn^{2+}$: (a) c$(CH_3)_2Sn^{2+}$ = 1 $\mathrm{mmol \cdot L^{-1}}$: **1** $(CH_3)_2Sn^{2+}$ free; **2** (1,1); **3** (1,2); **4** (1,3); **5** (2,2); **6** (2,3); (b) c$(CH_3)_2Sn^{2+}$ = 80 $\mathrm{mmol \cdot L^{-1}}$: **1** $(CH_3)_2Sn^{2+}$ free; **2** (1,1); **3** (1,2); **4** (1,3); **5** (2,2); **6** (2,3); **7** (3,4); **8** (4,6); in $NaNO_3$ I = 1.00 $\mathrm{mol \cdot L^{-1}}$ at T = 298.15 K.

This cation undergoes fairly strong hydrolysis, as shown in Figure 2a, over the pH range 2 to 12, and at millimolar concentrations the formation of polynuclear species is always

Table 3. Summary of Tested Speciation Models for the Hydrolysis of Dimethyltin(IV) [$I = (1.00 \pm 0.05)\ \mathrm{mol \cdot L^{-1}}$, $T = (298.15 \pm 0.10)$ K]

$\log \beta_{pq}$[a]	Model 1	Model 2	Model 3	Model 6	Model 5	Model 4
1,1	−3.185(2)[b]	−3.222(3)[b]	−3.248(3)	−3.181(6)[b]	−3.155(6)[b]	−3.179(3)[b]
1,2	−8.459(3)	−8.473(4)	−8.525(4)	−8.442(9)	−8.466(11)	−8.430(4)
1,3	−15.939(18)	-	-	-	−15.582(20)	-
2,2	−5.293(4)	−5.255(4)	−5.210(4)	−5.341(10)	−5.284(11)	−5.331(4)
2,3	−9.449(7)	−9.646(10)	−9.660(9)	−9.513(11)	−9.312(10)	−9.493(5)
3,4	−11.548(12)	−11.358(9)	−11.358(6)	−11.328(27)	-	−11.454(8)
4,6	−18.65(5)	−17.872(24)	−17.721(15)	-	-	-
4,7	-	-	-	−23.89(12)[d]	-	-
5,10	-	-	−36.426(24)[d]		-	-
σ^2/σ_0^2[c]	1.000	1.177	1.232	1.895	1.705	1.303

[a] β_{pq} refers to the equilibrium $p(\mathrm{CH_3})_2\mathrm{Sn}^{2+} + q\mathrm{H_2O} = [((\mathrm{CH_3})_2\mathrm{Sn})_p(\mathrm{OH})_q]^{(2p-q)} + q\mathrm{H}^+$. [b] Standard deviation in the last figure(s) in parentheses. [c] σ^2 = variance in the fit; σ_0^2 = variance in the fit for the best speciation model. [d] Very low formation percentages observed for this species.

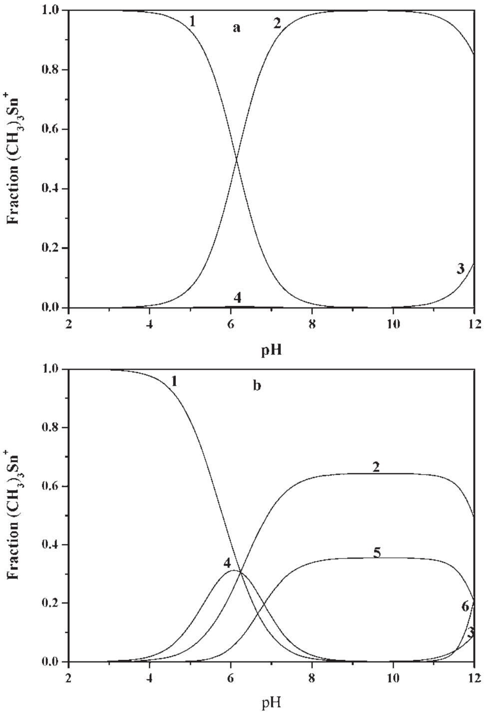

Figure 3. Distribution diagram of $(\mathrm{CH_3})_3\mathrm{Sn}^+$: (a) $c(\mathrm{CH_3})_3\mathrm{Sn}^+ = 1\ \mathrm{mmol \cdot L^{-1}}$: **1** $(\mathrm{CH_3})_3\mathrm{Sn}^+$ free; **2** (1,1); **3** (1,2); **4** (2,1); (b) $c(\mathrm{CH_3})_3\mathrm{Sn}^+ = 80\ \mathrm{mmol \cdot L^{-1}}$: **1** $(\mathrm{CH_3})_3\mathrm{Sn}^+$ free; **2** (1,1); **3** (1,2); **4** (2,1); **5** (2,2); **6** (2,4); in $\mathrm{NaNO_3}$ $I = 1.00\ \mathrm{mol \cdot L^{-1}}$ at $T = 298.15$ K.

lower than 0.05 (fraction of hydrolyzed cation). When higher concentrations are considered, as in our experiments [(20 to 80) $\mathrm{mmol \cdot L^{-1}}$], other polynuclear species are formed, namely, (p,q) = (3,4) and (4,6). As for the monomethyl derivative, several speciation models were tested: in Table 3 six models are considered (other intermediate combinations of species were rejected by the computer program), and the best model was chosen on the basis of lowest variance. The speciation diagram (80 $\mathrm{mmol \cdot L^{-1}}$) drawn in Figure 2b shows that high yields of polynuclear species are obtained, in the pH range 3 to 6. Note that for $(\mathrm{CH_3})_2\mathrm{Sn}^{2+}$ a shorter pH range was considered since at pH > 7 the solubility is lower than 10 $\mathrm{mmol \cdot L^{-1}}$. In the pH range 4 to 7 the dimethyltin(IV) cation is fully hydrolyzed.

Table 4. Summary of Tested Speciation Models for the Hydrolysis of Trimethyltin(IV) [$I = (1.00 \pm 0.05)\ \mathrm{mol \cdot L^{-1}}$, $T = (298.15 \pm 0.10)$ K]

$\log \beta_{pq}$[a]	Model 2	Model 1a[d]	Model 1	Model 2a[d]
1,1	−6.250(6)[b]	−6.280(16)[b]	−6.240(5)[b]	−6.177(5)[b]
1,2	−18.655(14)		−18.968(30)	
2,1	−4.958(9)	−4.969(20)	−4.932(7)	−5.156(10)
2,2	−11.81(8)	−11.75 (6)	−11.75	
2,4			−35.726(24)	
σ^2/σ_0^2[c]	1.150	1.000	1.000	1.179

[a] β_{pq} refers to the equilibrium $p(\mathrm{CH_3})_3\mathrm{Sn}^+ + q\mathrm{H_2O} = [((\mathrm{CH_3})_3\mathrm{Sn})_p(\mathrm{OH})_q]^{(p-q)} + q\mathrm{H}^+$. [b] Standard deviation in the last figure(s) in parentheses. [c] σ^2 = variance in the fit; σ_0^2 = variance in the fit for the best speciation model. [d] pH range < 8.

Hydrolysis of $(\mathrm{CH_3})_3\mathrm{Sn}^+$. The hydrolysis of the trimethyltin(IV) cation in dilute aqueous solutions ($\leq$ 10 $\mathrm{mmol \cdot L^{-1}}$) includes the formation of the mononuclear species (in parentheses the $\log \beta_{pq}$ at infinite dilution and T = 298.15 K, from refs 50 to 52):

$$[(\mathrm{CH_3})_3\mathrm{Sn(OH)}]^0 \qquad (\log \beta = -6.14)$$

$$[(\mathrm{CH_3})_3\mathrm{Sn(OH)_2}]^- \qquad (\log \beta = -18.88)$$

and the dinuclear species:

$$[((\mathrm{CH_3})_3\mathrm{Sn})_2(\mathrm{OH})]^+ \qquad (\log \beta = -5.19)$$

This cation undergoes fairly strong hydrolysis, as shown in Figure 3a, at pH > 4.5, and at millimolar concentrations the formation of polynuclear species is fairly negligible. When higher concentrations are considered, as in our experiments [(60 to 85) $\mathrm{mmol \cdot L^{-1}}$], other polynuclear species are formed, namely, (p,q) = (2,2) and (2,4). Also in this case, several speciation models were tested: in Table 4 four models are considered (other intermediate combinations of species were rejected by the computer program). The best model was chosen on the basis of lowest variance. The speciation diagram drawn in Figure 3b shows that at these concentrations high yields of polynuclear species are obtained, and at pH > 6.5 the trimethyltin(IV) cation is fully hydrolyzed.

DISCUSSION

Reliability of the Proposed Models. As above reported, the best model was chosen on the basis of a lower variance ratio (see Tables 2 to 4). Nevertheless, it must be emphasized that the reliability of quite complex hydrolysis models, for large pH ranges, can be different in acidic or in alkaline or even in small parts of these regions.

Models 1 to 4 reported in Table 2 for monomethyltin(IV) hydrolysis show statistical parameters that are not very different (even if the differences are significant at the 95 % level), and these models differ mainly for the presence/absence of species formed in the very acidic or alkaline ranges. Moreover, the analysis of residuals shows a small but significant worsening of the least-squares fit in these ranges. On the basis of this evidence we are able to define the reliability ranges:

$$\text{pH 4.5 to 10} = \text{good}$$

$$\text{pH 2 to 4.5 and 10 to 12} = \text{fairly good}$$

The model proposed for the dimethyltin(IV) cation is more robust and does not show worsening of the fit at low pH values, but the uncertainty for the equilibrium constant of $[(CH_3)_2Sn(OH)_3]^-$ species is significantly higher with respect to those of other species. In this case the reliability ranges are:

$$\text{pH 2 to 6} = \text{good}$$

$$\text{pH 6 to 7} = \text{fairly good}$$

Analogous observations for the hydrolysis of the trimethyltin(IV) cation allow definition of the reliability ranges:

$$\text{pH 5 to 10} = \text{good}$$

$$\text{pH 2 to 5 and 10 to 12} = \text{fairly good}$$

Relevance of Polynuclear Species. Quite high yields of polynuclear species are observed for the three methyl derivatives with, as expected, the trend:

$$(CH_3)Sn^{3+} > (CH_3)_2Sn^{2+} \gg (CH_3)_3Sn^+$$

and, in several conditions, these species are predominant, in particular for the monomethyltin(IV) cation. The mean ratio q/p of polynuclear species follows the opposite trend, and this indicates that the tendency to form these species is favored by the possibility to form hydroxo bridges. Moreover, we can observe that most of the q/p (for $p > 1$) values are lower than the charge of methyltin(IV) cations, that is, $q/p < z$, while for mononuclear species we observe the maximum values $q/p = z + 1$. This means that in the highly alkaline region mononuclear species become predominant. For example, $(CH_3)Sn^{3+}$ is characterized by a crossing pH point where the fraction of mononuclear species becomes higher than that of polynuclear ones, and this point is a positive function of the analytical cation concentration [pH ~ 8.4, (0.5 to 1) $\text{mmol}\cdot\text{L}^{-1}$; pH = 10, 20 $\text{mmol}\cdot\text{L}^{-1}$ and pH = 10.5, 80 $\text{mmol}\cdot\text{L}^{-1}$]. The formation of hydrolysis products with $p \gg 1$ has been recognized for some 2+ cations[56] and, in particular for 3+ cations, such as Al^{3+} and Fe^{3+}.[61−64]

Empirical Relationships. Another way to report equilibrium constants for the formation of hydrolytic species is given by eq 2 where the binding of OH^- by the cation is considered (β_{pq}^{OH}). In Table 5, we give these formation constants for the mono-, di-, and trimethyl cation derivates. The analysis of these data reveals that log β^{OH} is a fairly linear function of the sum of the stoichiometric coefficients p and q of eq 2, according to the relationship:

$$\log \beta_{pq}^{OH} = A(p + q) \tag{3}$$

Moreover, A can be expressed as a function of the cation charge z $[(CH_3)_nSn^{(4-n)+}, z = 4-n]$:

$$A = 1 + Bz$$

and therefore log β_{pq}^{OH} values for all methyltin(IV) derivatives can be expressed by the single parameter:

$$B = 2.50 \pm 0.05$$

Table 5. Formation Constants of $(CH_3)_nSn^{(4-n)+}$ Species [$I = (1.00 \pm 0.05)\ \text{mol}\cdot\text{L}^{-1}$, $T = (298.15 \pm 0.10)$ K]

	log β_{pq}^{OH}		
pq	$(CH_3)Sn^{3+}$	$(CH_3)_2Sn^{2+}$	$(CH_3)_3Sn^+$
1,1		10.54 ± 0.02[a]	7.49 ± 0.02[a]
1,2		19.00 ± 0.03	8.49 ± 0.07
1,3	31.28 ± 0.04[a]	25.25 ± 0.05	
1,4	32.40 ± 0.09		
2,1			8.80 ± 0.02
2,2		22.17 ± 0.03	15.71 ± 0.16
2,3		31.74 ± 0.04	
2,4	51.11 ± 0.04		19.19 ± 0.06
2,5	60.55 ± 0.05		
2,7	65.46 ± 0.07		
3,4		43.37 ± 0.05	
3,5	66.76 ± 0.05		
3,7	87.88 ± 0.05		
4,6		63.73 ± 0.11	
5,9	120.84 ± 0.06		
5,11	141.87 ± 0.07		

[a] ± 95 % C.I.

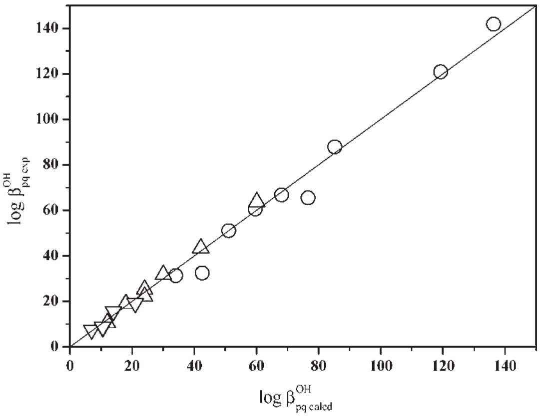

Figure 4. Experimental vs calculated log β_{pq}^{OH} values, according to eq 4. ○, monomethyltin(IV); △, dimethyltin(IV); ▽, trimethyltin(IV).

Table 6. Literature Data for the Formation of $(CH_3)_n Sn^{(4-n)+}-OH^-$ species at $I = 1\ mol \cdot L^{-1}$ and $T = 298.15$ K

		$\log \beta^{OH}$			
cation	species	NaCl	$NaNO_3$	$NaClO_4$	ref
$(CH_3)Sn^{3+}$	(1,2)	23.51	23.47		50
	(1,3)	31.89	31.88		50
	(1,4)	34.33	34.41		50
	(2,5)	59.93	59.61		50
$(CH_3)_2Sn^{2+}$	(1,1)	9.98	10.58	10.68	53
	(1,2)	18.15	18.98	19.02	53
	(1,3)	20.9	21.7	21.6	53
	(2,2)	21.8	22.4	22.5	53
	(2,3)	30.1	31.6	31.8	53
$(CH_3)_3Sn^{+}$	(1,1)	7.44	7.49		53

In Figure 4, we show $\log \beta^{OH}_{pq}$ (exp) vs $\log \beta^{OH}_{pq}$ (calcd), where one can see a quite good linearity ($R = 0.995$). The general equation:

$$\log \beta^{OH}_{pq}/(p+q) = 1 + 2.50z \tag{4}$$

allows the calculation of rough values of β^{OH}_{pq} for any (p,q) couple, that, in turn, can be useful in determining the extra stability of mixed hydrolytic species.[57,58] In fact, to calculate the quantitative parameters for the tendency to form mixed metal species, it is necessary to know the formation constants of some homopolynuclear species often not experimentally accessible.[57,58] Equations with more than one parameter can be obtained, such as that proposed by Brown et al.[63] for the hydrolysis of Al^{3+} ($-\log \beta_{pq} = 5.73 - 3.6p + 4.64q$). As an example, for the polynuclear species of $(CH_3)Sn^{3+}$, we have $-\log \beta_{pq} = 3.33 - 5.78p + 3.16q$.

FINAL REMARKS

To show the effect of the supporting electrolyte, we report in Table 6 some literature data in different salts at 1 mol·L^{-1} aqueous solutions. The differences are generally quite small, even if there is a systematic lowering for $\log \beta^{OH}_{pq}$ determined in NaCl. This means that the methyltin(IV) cations form very weak ion pairs with chloride ions. Attempts were already made to calculate the formation constants for these ion pairs,[47,48,50,51] with quite small constants resulting. Therefore we can affirm that the amount of Cl^-, deriving from methyltin(IV) chlorides, does not seriously affect the equilibrium constants reported in this work.

A comparison with literature data can be done only for the di- and trimethyl derivatives (data for the monomethyl derivative come from these laboratories). Formation constants reported in Tables 5 and 6 are in fairly good accordance, also taking into account that in the present investigation many other polynuclear species were found. These species are predominant, in particular for $(CH_3)Sn^{3+}$, over a large pH range, as shown in Figure 2. This result, together with the possibility of using the general empirical eq 4, is quite useful for the analysis of mixed metal systems. The formation of large amounts of homopolynuclear species, in particular those with $p > 2$, allows the prediction of the formation of heteropolynuclear species in mixed solutions containing different kinds of alkyltin(IV) compounds and other highly charged metal ions.

AUTHOR INFORMATION

Corresponding Author

*Silvio Sammartano. E-mail: ssammartano@unime.it. Fax: +39090392827.

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