APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 805–811 (1999)

Hydrolysis of Methyltin(IV) Trichloride in Aqueous NaCl and NaNO$_3$ Solutions at Different Ionic Strengths and Temperatures

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The hydrolysis of methyltin(IV) trichloride (CH_3SnCl_3) has been studied in aqueous NaCl and $NaNO_3$ solutions ($0 < I$/mol dm$^{-3} \leq 1$), at different temperatures ($15 \leq T/°C \leq 45$) by potentiometric measurements (H^+-glass electrode). By considering the generic hydrolytic reaction $pCH_3Sn^{3+} + qH_2O = (CH_3Sn)_p(OH)_q{}^{3p-q} + qH^+$ ($\log\beta_{pq}$), we have the formation of five species and $\log\beta_{12} = -3.36$, $\log\beta_{13} = -8.99$, $\log\beta_{14} = -20.27$ and $\log\beta_{25} = -7.61$. The first hydrolysis step is measurable only at very low pH values and was not determined: a rough estimate of the hydrolysis constant is $\log\beta_{11} = -1.5\ (\pm\ 0.5)$. The dependence on ionic strength of $\log\beta_{pq}$ is quite different in $NaNO_3$ and NaCl solutions, and the formation at low pH values of the species $CH_3Sn(OH)Cl^+$ has been found with $\log\beta = -1.40$. Hydrolysis constants strongly depend on temperature and from the relationships $\log\beta_{pq} = f(T)$, $\Delta H°$ values have been calculated. Speciation problems of CH_3Sn^{3+} in aqueous solution are discussed. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: methyltin(IV) trichloride; hydrolysis; ionic strength; speciation

Received 18 August 1998; accepted 18 January 1999

INTRODUCTION

In speciation studies of organotin(IV) compounds in aqueous solutions, hydrolysis processes play an important role, as shown by recent studies performed on dimethyltin(IV) and trimethyltin(IV) in different aqueous media.[1–4] Various hydrolysed species of these cations are formed over a wide pH range: in particular, the divalent cation $(CH_3)_2Sn^{2+}$ forms five species, $(CH_3)_2Sn(OH)^+$, $(CH_3)_2Sn(OH)_2{}^0$, $(CH_3)_2Sn(OH)_3{}^-$, $[(CH_3)_2Sn]_2(OH)_2{}^{2+}$ and $[(CH_3)_2Sn]_2(OH)_3{}^+$, while the monovalent cation $(CH_3)_3Sn^+$ forms only the two species $(CH_3)_3Sn(OH)^0$ and $(CH_3)_3Sn(OH)_2{}^-$.

Mono-organotin(IV) compounds have not achieved as much commercial application as diorgano and triorgano derivatives, and are considered as the least toxic among organotin(IV) derivatives ($R_3Sn^+ > R_2Sn^{2+} > RSn^{3+} > Sn^{4+}$, on the toxicity scale). However, they are often used as hydrophobic agents for building materials and cellulosic matter[5] and can be present in the aquatic environment as the first step in the alkylation of inorganic tin.[6] Therefore, in order to draw a complete picture of the chemical speciation of mono-, di- and tri-organotin(IV) compounds, the hydrolysis processes involved in the $RSnX_3$ aqueous chemistry must also be taken into account.

The behaviour of mono-organotin(IV) compounds in aqueous solution has been little investigated. Most studies concern complex formation with N-donor molecules[7] and with chloro[8–10] and fluoro ions.[11,12] Raman measurements by Kriegsmann and Pauly[8] showed the formation of $CH_3SnCl_2(OH)_2{}^-$ in the presence of high concentrations of chloride ions. Van den Beaghe and Van der Kelen,[10] by NMR measurements performed in

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Contract/grant sponsor: Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST).
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CCC 0268–2605/99/110805–07 $17.50

very concentrated solutions of CH_3Sn^{3+} (from 210 up to 830 mmol dm^{-3}), reported the formation of mixed chloro–hydroxo complexes $CH_3SnCl_x(OH)_y$[3] with x decreasing in the more dilute solutions. Analogous behaviour was found by Tobias[13,14] and more recently by De Stefano *et al.*[3] in studying the interactions of $(CH_3)_2Sn^{2+}$ in chloride solutions. Investigations on the hydrolysis products of ethyl-, butyl- and octyl-tin trichlorides have been performed by Luijten,[15] who reported their properties and preparation in the solid state. Some potentiometric studies on hydrolysis[16–18] and complex formation with sulphide[19] of ethyl tin(IV) trichloride in mixed water/methanol solution, have been performed by Devaud and co-workers, in the concentration range of the organometallic compound, around 6–60 mmol dm^{-3}. Results obtained by these authors are partially in contrast with findings for methyltin trichloride (Van der Kelen), probably owing to the different solvent and concentration ranges used. Results of ^{1}H-and ^{119}Sn-NMR and ^{119}Sn Mossbauer spectroscopy studies on the hydrolysis of methyl-and butyl-tin trichloride (0.5 mol dm^{-3}) have been reported by Blunden and co-workers.[20,21]

From literature data it can be affirmed that, in general, investigations on the hydrolysis of mono-organotin(IV) derivatives have been performed by using high concentrations of monoalkytin trichloride. As a consequence, the formation of mixed hydroxo–chloride polynuclear complexes cannot be avoided, and the determination of hydrolysis constants of simple species, most importantly in dilute solutions such as natural fluids, becomes quite difficult.

In order to define a general scheme for the speciation of organotin(IV) compounds in aqueous solution, we report here some results on the hydrolysis of methyltin trichloride in $NaNO_3$ and NaCl media in the ionic strength range $0 \leq I/\text{mol dm}^{-3} \leq 1$, at different temperatures ($15 \leq T/°C \leq 45$).

EXPERIMENTAL

Chemicals

Monomethyltin(IV) cation was used in the form of the trichloride salt (Aldrich; purity = 98%). All the other reagents were of analytical grade (from Fluka or Merck), with purity always >99.5%. Sodium nitrate and sodium chloride were used without purification. Hydrochloric acid and sodium hydroxide stock solutions were standardized against sodium carbonate and potassium hydrogenphthalate, respectively. Concentrations of NaOH and strong acids were also checked by cross-titrations. All solutions were prepared with analytical-grade water (R = 18 MΩ cm^{-1}), using grade A glassware.

Apparatus

Measurements were performed using an apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combination glass electrode (Ross model, 8102, from Orion) and a model 654 Metrohm motorized burette. The estimated accuracy was ± 0.2 mV and ± 0.003 cm^3 for emf. and titrant volume readings, respectively. Titrations were performed automatically using a suitable computer program which allows evaluation of equilibrium potential values and determination of the amount of titrant to be added when the emf. was stable within 0.1 mV for 3 min. The measurement cells (25 or 50 cm^3) were thermostatted at the required temperature with an uncertainty of ± 0.1 °C. All titrations were carried out with magnetic stirring, and bubbling purified and pre-saturated N_2 through the solution in order to exclude O_2 and CO_2 from it.

Procedure

A solution (25 cm^3) containing $(CH_3)SnCl_3$ (1, 2, 5 and 10 mmol dm^{-3}) in NaCl or $NaNO_3$ as background salts to adjust the ionic strength to different values (in turn, 0.1, 0.25, 0.5, 0.75 and 1.0 mol dm^{-3}) was titrated with standard NaOH solution up to pH ~11 (80 to 110 points). For each experiment, independent titrations of acidic solutions (hydrochloric or nitric acids) with standard NaOH, in the same ionic strength conditions as the systems to be investigated, were carried out in order to determine the formal electrode potential ($E°$) and the acidic junction potential ($E_j = j_a [H^+]$). The reliability of the calibration in the alkaline range was checked by calculating pK_W values.

Calculations

The non-linear least-squares computer program ESAB2M[22] was used for the refinement of all parameters of an acid–base titration ($E°$, K_W, coefficient of junction potential, j_a, analytical concentration of reagents). For calculation of hydrolysis and complex formation constants, together with parameters for dependence on ionic strength, BSTAC[23] and STACO[24] computer programs were used. Concentrations, and hydrolysis and formation constants, are given on the molar scale. The LIANA[25] program was used to test the dependence of log*K* on ionic strength and temperature by different equations; the ES4ECI[26] program was used to draw the distribution diagrams. The hydrolysis reactions may written as Eqns [1] and [2]; Throughout the paper we indicate, for simplicity, aquo–chloro and aquo–chloro–hydroxo complexes as $(\mathrm{CH_3})\mathrm{Sn}^{3+}$ and $[(\mathrm{CH_3})\mathrm{Sn}]_p(\mathrm{OH})_q{}^{(3p-q)}$, respectively.

$$p\mathrm{CH_3Sn}^{3+} + q\mathrm{H_2O} = (\mathrm{CH_3Sn})_p(\mathrm{OH})_q{}^{(3p-q)} + q\mathrm{H}^+ \qquad (\beta_{pq}) \qquad [1]$$

$$p\mathrm{CH_3Sn}^{3+} + q\mathrm{OH}^- = (\mathrm{CH_3Sn})_p(\mathrm{OH})_q{}^{(3p-q)} \qquad (\beta_{pq}{}^{\mathrm{OH}}) \qquad [2]$$

Dependence of formation constants on ionic strength

Dependence on ionic strength was taken into account by using a Debye–Hückel type equation (Eqn [3])[26,27]

$$\log K = \log{}^{\mathrm{T}}K - z^* I^{1/2}(2 + 3I^{1/2})^{-1} + CI + DI^{3/2} + EI^2 \qquad [3]$$

with

$$z^* = \sum(\text{charges})^2_{\text{reactants}} - \sum(\text{charges})^2_{\text{products}}$$

(K = formation constant; ${}^{\mathrm{T}}K$ = formation constant at infinite dilution; z = charge; C, D and E = empirical parameters). The parameter E can be neglected at $I < 1\ \mathrm{mol\ dm^{-3}}$. Results of a series of investigations[27,28] showed that, when all interactions are taken into account, the empirical parameters of Eqn [3] are given by Eqn [4]:

$$C = 0.1p^* + 0.23z^*; \quad D = -0.10z^* \qquad [4]$$

with

$$p^* = \sum(\text{moles})_{\text{reactants}} - \sum(\text{moles})_{\text{products}}$$

The activity of water was taken into account by the simple relationship $\log a_{\mathrm{w}} = -0.015\ I$. Both STACO and BSTAC computer programs can deal with measurements at different ionic strengths and can refine the empirical parameters of Eqn [3] in addition to formation constants.

Table 1 Equilibrium constants for the hydrolysis of $\mathrm{CH_3Sn}^{3+}$ at 25 °C and $I = 0\ \mathrm{mol\ dm^{-3}}$

Reaction	$\log\beta \pm$ S.D.
$\mathrm{M}^{3+} + \mathrm{H_2O} = \mathrm{M(OH)}^{2+} + \mathrm{H}^+$	$-1.5 \pm 0.5^{\mathrm{a}}$
$\mathrm{M}^{3+} + 2\ \mathrm{H_2O} = \mathrm{M(OH)_2}^{+} + 2\mathrm{H}^+$	-3.36 ± 0.05
$\mathrm{M}^{3+} + 3\ \mathrm{H_2O} = \mathrm{M(OH)_3}^{0} + 3\mathrm{H}^+$	-8.99 ± 0.04
$\mathrm{M}^{3+} + 4\ \mathrm{H_2O} = \mathrm{M(OH)_4}^{-} + 4\mathrm{H}^+$	-20.27 ± 0.06
$2\ \mathrm{M}^{3+} + 5\ \mathrm{H_2O} = \mathrm{M_2(OH)_5}^{+} + 5\mathrm{H}^+$	-7.61 ± 0.08
$\mathrm{M}^{3+} + \mathrm{OH}^- = \mathrm{M(OH)}^{2+}$	13.5^{a}
$\mathrm{M}^{3+} + 2\mathrm{OH}^- = \mathrm{M(OH)_2}^{+}$	22.64^{b}
$\mathrm{M}^{3+} + 3\mathrm{OH}^- = \mathrm{M(OH)_3}^{0}$	33.01^{b}
$\mathrm{M}^{3+} + 4\mathrm{OH}^- = \mathrm{M(OH)_4}^{-}$	35.73^{b}
$2\mathrm{M}^{3+} + 5\mathrm{OH}^- = \mathrm{M_2(OH)_5}^{+}$	62.38^{b}

[a] Estimated value.
[b] $\mathrm{p}K_{\mathrm{W}} = 14.00 \pm 0.01$.

RESULTS

Hydrolysed species

The monomethyltin(IV) cation undergoes strong hydrolysis, even at very low pH values. The first hydrolysis step cannot be studied quantitatively since the species $\mathrm{CH_3Sn(OH)}^{2+}$ is neutralized to give the free cations at $[\mathrm{H}^+]/[\mathrm{CH_3Sn}^{3+}] \gg 1$ ratios, and in these conditions quite small errors in analytical concentrations produce unacceptable errors in the determination of hydrolysis constants. Three other hydrolysis steps are observed, giving the species $\mathrm{CH_3Sn(OH)_2}^{+}$, $\mathrm{CH_3Sn(OH)_3}^{0}$ and $\mathrm{CH_3Sn(OH)_4}^{-}$, in the pH range 2–10.5. Between the second and third hydrolysis steps there is experimental evidence for the formation of a polymeric species $(\mathrm{CH_3Sn})_p(\mathrm{OH})_q{}^{(3p-q)}$. Least-squares calculations were consistent with the formation of the hydrolytic product $\mathrm{CH_3Sn(OH)_{2.5}}$, which can be expressed as $(\mathrm{CH_3Sn})_2(\mathrm{OH})_5{}^{+}$, $(\mathrm{CH_3Sn})_4(\mathrm{OH})_{10}{}^{2+}$, etc. The comparison between different fits does not give significant differences and therefore we decided in favour of the simplest species. Therefore the speciation scheme for the hydrolysis of $\mathrm{CH_3Sn}^{3+}$ includes four mononuclear species $\mathrm{CH_3Sn(OH)}_q{}^{(3-q)}$ (q = 1–4), and the polynuclear species $(\mathrm{CH_3Sn})_2(\mathrm{OH})_5{}^{+}$. Calculations performed at low ionic strength values, and the extrapolation to zero of equilibrium constants determined at higher ionic strength, allowed us to obtain $\log\beta_{pq}$ values in pure water, reported in Table 1. As already mentioned, the hydrolysis constant for the species $\mathrm{CH_3Sn(OH)}^{2+}$ cannot be determined but it can be estimated to be

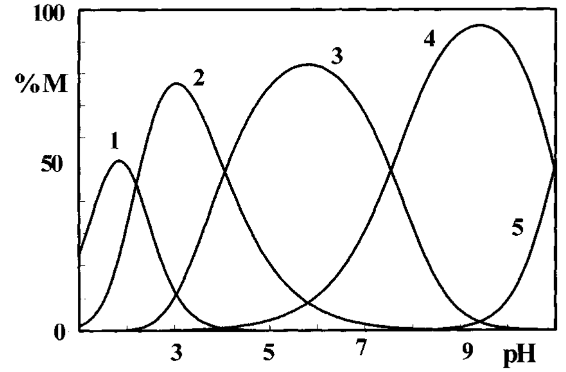

Figure 1 Distribution diagram vs pH for the hydrolysis of CH_3Sn^{3+} (M) [$c_M = 10^{-3}$ mol dm^{-3}, $I = 0.5$ mol dm^{-3} ($NaNO_3$)]. Species: **1**, $(CH_3)Sn(OH)^{2+}$; **2**, $(CH_3)Sn(OH)_2{}^+$; **3**, $[(CH_3)Sn]_2(OH)_5{}^+$; **4**, $(CH_3)Sn(OH)_3{}^0$; **5**, $(CH_3)Sn(OH)_4{}^-$.

$\log\beta_{11} = -1.5 \pm 0.5$; this is a rough estimate which can be calculated by using the predictive equation $\log K_1 \sim 0.4\ \log K_2 - 1$, obtained from literature data for hydrolysis of di- and tri-valent cations. Equilibrium constants reported in Table 1 demonstrate quantitatively the strong tendency of monomethyltin(IV) to hydrolyse. A comparison (see also discussion) can be made with iron(III): hydrolysis constants of that cation are significantly lower than those of CH_3Sn^{3+}. In Fig 1 we report the speciation diagram in $NaNO_3$ ($I = 0.5$ mol dm^{-3}). For pH >2 monomethyltin(IV) is fully hydrolysed (only a small percentage of free cation is present) and in the pH range 5–9, which is of interest for natural fluids, the main species are $CH_3Sn(OH)_3{}^0$ and $(CH_3Sn)_2(OH)_5{}^+$, in the experimental condition $C_{(CH_3Sn^{3+})} = 1$ mmol dm^{-3}.

Ionic strength and medium effects

Potentiometric measurements performed in $NaNO_3$ and NaCl, at different ionic strengths, show quite different behaviour, in particular at low pH values. This can be explained by the tendency of the chloride ion to form ion pairs with alkyltin(IV) cations and with their hydrolysed species. In the pH range 2–3 we were able to calculate the formation constant of the species $(CH_3)Sn(OH)Cl^+$, whose formation percentages are quite high at $I \geq 0.5$ mol dm^{-3} (NaCl). It is likely that also for pH >3, other Cl^- mixed species are formed, but only semiquantitative values can be obtained for the formation constants. Therefore we prefer to give ‘apparent’ hydrolysis constants in NaCl, which can be used in the speciation studies as well as ‘effective’ formation constants coupled with ion-pair formation constants for Cl^- species. In Fig. 2 we report $\log\beta_{13}$ *vs* $I^{1/2}$ in both aqueous $NaNO_3$ and NaCl solutions. In Table 2, we report empirical parameters (Eq. [1]) for the dependence on ionic strength of hydrolysis constants. In Table 3, we report thermodynamic parameters for the formation of the mixed species $CH_3Sn(OH)Cl^+$. The problems of determining the formation of mixed OH–Cl species, and of calculating the relative formation constants, are quite difficult since many species can be taken into account. Moreover, when anionic hydroxo species, such as $CH_3Sn(OH)_4{}^-$, are formed one must take into account also the possibility of interaction with the cation of the background salt (Na^+ in this case). As a general rule, we attribute a lowering of formation or hydrolysis constants, with respect to the values determined in a non-interacting medium (such as nitrate or perchlorate), to the interaction between the cation under study and the anion of the background salt; on the contrary, a rise is observed when the hydroxo species forms ion

Table 2 Empirical parameters (Eqn [1]) for the hydrolysis constants of CH_3Sn^{3+} at 25 °C

			C^a	
p	q^b	z^*	$NaNO_3$	NaCl
1	2	6	1.83	1.63
1	3	6	1.52	2.08
1	4	4	1.35	2.00
2	5	12	3.37	2.99

[a] With $D = -0.1\ z^*$; $E = 0$.
[b] Refer to Eqn [1].

Table 3 Thermodynamic parameters for the formation of the mixed species $CH_3Sn(OH)Cl^+$ at 25 °C and $I = 0$ mol dm^{-3}

Reaction	$\log\beta \pm$ S.D.	$\Delta G° \pm$ S.D.	$\Delta H° \pm$ S.D.	$T\Delta S° \pm$ S.D.
$M^{3+} + H_2O + Cl^- = M(OH)Cl^+ + H^+$	-1.40 ± 0.04	—	—	—
$M^{3+} + OH^- + Cl^- = M(OH)Cl^+$	12.60 ± 0.05	-71.9 ± 0.3	-31.5 ± 2.5	40 ± 3

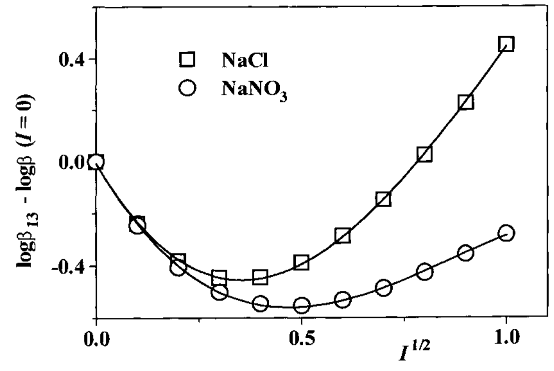

Figure 2 Dependence on ionic strength of $\log\beta_{13}$ in NaCl and NaNO$_3$ aqueous solution at 25°C.

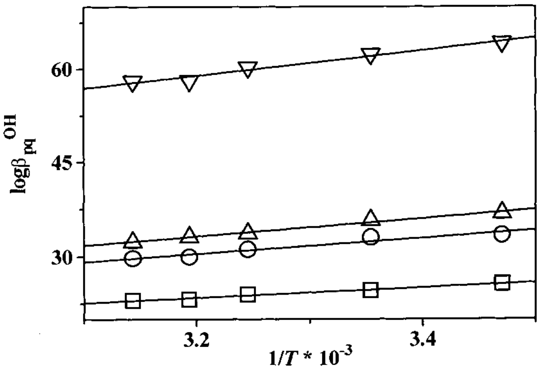

Figure 3 Values of $\log\beta_{pq}^{OH}$ vs $1/T$ (T/K): □, $\log\beta_{12}^{OH}$; ○, $\log\beta_{13}^{OH}$; △, $\log\beta_{14}^{OH}$; ▽, $\log\beta_{25}^{OH}$.

pairs with the anion (or cation) of the salt. As an example, if we indicate by K and K^* the hydrolysis constant of the species M(OH), K is calculated by considering the formation of the species $M(OH)Cl^+$ [$M(OH)^{2+} + Cl^- = M(OH)Cl^+$] and K^* by neglecting this interaction, in which case $\log K^* = \log K + \log (1 + K^{Cl}[Cl])$. When dealing with multiple simultaneous equilibria, the equation becomes much more complicated but the trend is the same. (In this paper we calculated the formation constants for the species $M(OH)Cl^+$ alone, and we considered the apparent hydrolysis constants which account for other interactions. However, in mixed electrolytes, such as seawater, where dications and dianions are present in high concentration, the formation of such mixed species may be relevant.) The dependence on ionic strength reported in Fig. 2 indicates that $\log\beta_{13}(NaCl) > \log\beta_{13}(NaNO_3)$, and therefore it is expected that a weak species $CH_3Sn(OH)_3Cl^-$ is formed.

Temperature dependence of hydrolysis constants

Hydrolysis constants strongly depend on temperature, as shown in Fig. 3, where the variation of $\log\beta_{pq}^{OH}$ is reported *vs* $1/T$ (T = absolute temperature/K). From the dependence on temperature one can obtain $\Delta H°$ values (Eqn [5]), where

$$\log \beta_{pq}^{OH} = \log \beta_{pq}^{OH}(\theta) + \Delta H° F(T) \times 52.23 \quad [5]$$

$$F(T) = (1/T) - (1/\theta]$$

θ = reference temperature = 298.15 K. As $\log\beta_{pq}^{OH}$ values are affected by fairly large uncertainties, and the temperature range is quite small, $\Delta H°$ values (Table 4) must be considered only as indicative. As one can see, $\log\beta_{pq}^{OH}$*v* s $1/T$ is linear and therefore we can write for the different species the simple equations [5a]–[5d].

$$\log \beta_{12}^{OH} = 24.6 - 7.9(\pm 0.4)F(T) \times 10^4 \quad (5a)$$

$$\log \beta_{13}^{OH} = 33.0 - 15.6(\pm 0.6)F(T) \times 10^4 \quad (5b)$$

$$\log \beta_{14}^{OH} = 35.7 - 16.2(\pm 0.6)F(T) \times 10^4 \quad (5c)$$

$$\log \beta_{25}^{OH} = 62.4 - 20.6(\pm 0.9)F(T) \times 10^4 \quad (5d)$$

Table 4 Thermodynamic parameters for the formation of hydrolysed species of CH_3Sn^{3+} at 25 °C and I = 0 mol dm^{-3}

Reaction	$\Delta G° + $ S.D.	$\Delta H° \pm$ S.D.	$T\Delta S° \pm$ S.D.
$M^{3+} + 2\ OH^- = M(OH)_2^+$	−140.6 ± 0.3	−152 ± 5	−11 ± 6
$M^{3+} + 3\ OH^- = M(OH)_3^0$	−188.4 ± 0.2	−233 ± 15	−45 ± 15
$M^{3+} + 4\ OH^- = M(OH)_4^-$	−203.9 ± 0.4	−260 ± 10	−56 ± 10
$2M^{3+} + 5\ OH^- = M_2(OH)_5^+$	−351.1 ± 0.5	−369 ± 16	−13 ± 7

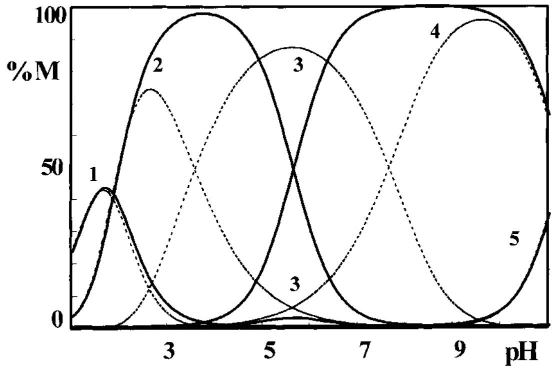

Figure 4 Distribution of the species vs pH for the hydrolysis of CH_3Sn^{3+} (M) at $I \cong 0$ mol dm^{-3}. Species: **1**, $(CH_3)Sn(OH)^{2+}$; **2**, $(CH_3)Sn(OH)_2^{+}$; **3**, $[(CH_3)Sn]_2(OH)_5^{+}$; **4**, $(CH_3)Sn(OH)_3^{0}$; **5**, $(CH_3)Sn(OH)_4^{-}$. ——, $c_M = 10^{-6}$ mol dm^{-3}; – – –, $c_M = 10^{-3}$ mol dm^{-3}.

Errors and reliability of the speciation of $(CH_3)Sn^{3+}$

Standard deviations reported in Table 1 for hydrolysis constants are fairly large. However, the complexity of the systems does not allow us to obtain better results. In fact we have to work with quite low monomethyltin(IV) concentrations, to avoid the formation of higher polynuclear species. Nevertheless, as the various species in our experimental conditions, in the pH range 4–10, are well separated, errors in the formation percentages are compatible with the correct speciation of the system. As an example, at pH = 8, we have $(CH_3)Sn(OH)_2^{+}$ content = 34 ± 5% and $[(CH_3)Sn]_2(OH)_5^{+}$ content = 64 ± 5%.

DISCUSSION

The main characteristic of the $(CH_3)Sn^{3+}$–H_2O system is the very strong tendency of monomethyltin(IV) to form hydrolysed species over a wide range (see Fig. 1). This cation also shows the ability to give polynuclear species of the type $[M(OH)_y^{3-y}]_n$ with $2 < y < 3$, such as those observed for other trivalent cations. Iron(III) forms the species $Fe_{12}(OH)_{34}^{2+}$ ($y = 2.83$)[28,29] and aluminium(III) forms $Al_{13}(OH)_{32}$ ($y = 2.46$).[30] For chromium(II), recent experimental results (P. G. Daniele and S. Sammartano, unpublished results) indicate the formation of polynuclear species with $y \simeq 2.5$–2.8. Devaud[16–18] found (in mixed aqueous organic solvent) the formation of the species $[(CH_3)Sn]_{10}(OH)_{28}$ ($y = 2.8$) and $[(CH_3)Sn]_8(OH)_{23}$ ($y = 2.87$). In this work, we found, in low-concentration conditions, the formation of the polynuclear species $[(CH_3)Sn]_2(OH)_5^{+}$. It is likely that at higher $(CH_3)Sn^{3+}$ concentrations, higher polynuclear species are formed, with general formulae $[M(OH)_3]_{p-1}M(OH)_x$, with $p > 2$ and $1 \leq x < 3$. The formation of polynuclear species becomes less significant at very low concentrations, as can be seen in Fig. 4, where the distribution of $(CH_3)Sn^{3+}$ hydrolysed species is reported at 10^{-3} and 10^{-6} mol dm^{-3}. At a higher monomethyltin(IV) concentration the dimeric species, at pH 6, reaches a formation percentage >80%, whilst at a lower concentration the yield of this species is below 10%. Among trications, monomethyltin(IV) is one of the most hydrolysed one,[30] and it undergoes hydrolysis at lower pH values than iron(III) and aluminium(III).

The dependence on temperature given by Eqn [5], together with explicit functions (Eqns [5a–5d]), and the dependence on ionic strength (Eq. [3] and values of *C* in Table 2), allow us to draw a corrected speciation of $(CH_3)Sn^{3+}$, in the ranges $0 \leq I/\text{mol dm}^{-3} \leq 1$ and $15 \leq T/°C \leq 45$, in aqueous NaCl and $NaNO_3$ solutions. No comparison can be made with the literature, since these data for the hydrolysis of $(CH_3)Sn^{3+}$ in aqueous solution at different temperatures and ionic strength are the first so far reported.

Acknowledgements We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR) for financial support.

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