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Hydrolysis and chemical speciation of $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ in aqueous media simulating the major composition of natural waters

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The hydrolysis of $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ and $(n\text{-}C_3H_7)_3Sn^+$ has been studied, by potentiometric measurements ($[H^+]$-glass electrode), in $NaNO_3$, NaCl, NaCl/Na_2SO_4 mixtures and in a synthetic seawater (SSWE), as an ionic medium simulating the major composition of natural seawater, at different ionic strengths ($0 \leq I \leq 5$ mol dm^{-3}) and salinities ($15 \leq S \leq 45$), and at $t = 25\,°C$. Five hydrolytic species for $(C_2H_5)_2Sn^{2+}$, three for $(C_2H_5)_3Sn^+$ and two for $(C_3H_7)_3Sn^+$ are found. Interactions with the anion components of SSWE, considered as single-salt seawater, are determined by means of a complex formation model. A predictive equation for the calculation of unknown hydrolysis constants of trialkyltin(IV) cations, such as tributyltin(IV), in $NaNO_3$, NaCl, and SSWE media at different ionic strengths is proposed. Equilibrium constants obtained are also used to determine the interaction parameters of Pitzer equations. **Copyright © 2001 John Wiley & Sons, Ltd.**

KEYWORDS: alkyltin(IV); hydrolysis constants; ionic strength dependence; speciation; Pitzer parameters; predictive relationships

INTRODUCTION

Since trialkyltin(IV)'s biocide activity was first demonstrated in the 1950s, worldwide production of organotin(IV) compounds have increased from 5000 t year^{-1} in 1960 to over 65000 t year^{-1} in 1986, and now they are the most industrially used organometallic compounds. The wide spectrum of applications has raised the number of input sources to the environment and their wide presence in natural fluids has attracted the attention of many scientists.[1] Toxicity towards living organisms is correlated to the number and to the nature of organic groups bonded to the central atom; the most toxic are triorganotin(IV) species and, *e.g.* for mammals, ethyl derivatives [$(C_2H_5)_2Sn^{2+}$ and $(C_2H_5)_3Sn^+$] are the most active.[2] Cations of this class of compounds are considered to be Lewis acids of different hardness and, in general, show a strong tendency to hydrolysis in aqueous solutions. In order to contribute to the knowledge of the chemical speciation of organotin(IV) cations, we thought that soluble compounds of this class may be considered as models for all others. So, during the last few years, we have undertaken a systematic investigation, in different ionic media and for a wide range of ionic strengths, on the aqueous chemistry of $(CH_3)_nSn^{(4-n)+}$ cations[3–8] showing a very high solubility both in distilled water and in seawater.[9] Data obtained on the hydrolysis and complex formation of soluble organotin cations can be useful to make predictions about the aqueous chemistry of similar homologous systems, such as $(C_4H_9)_nSn^{(4-n)+}$, whose data are not accessible owing to their very low solubility. For this reason, we had to limit our research to $(C_2H_5)_3Sn^+$ and $(n\text{-}C_3H_7)_3Sn^+$, whose solubilities, though low (in seawater they are estimated to be lower than 25 mg dm^{-3} and 50 mg dm^{-3} respectively), allow us to perform thermodynamic studies by potentiometric measurements on the hydrolysis processes and complex formation. In this paper, we extended our investigations to the hydrolytic processes of $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$, and $(C_3H_7)_3Sn^+$, carrying out studies in different ionic media, with the aim of establishing the salt effect of the most important components of natural fluids. Moreover, we studied the hydrolysis in synthetic seawater for

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Table 1. Composition of artificial seawater (SSWE) at 35 salinity[a] and at $t = 25\,^{\circ}\mathrm{C}$

Component	Concentration	
	mol dm^{-3}	mol (kg H_2O)$^{-1}$
NaCl	0.4221	0.427 40
Na_2SO_4	0.0288	0.029 19
KCl	0.0110	0.011 12
$CaCl_2$	0.0111	0.011 21
$MgCl_2$	0.0548	0.055 52
BA[b]	0.5751	0.582 40
I	0.717	0.726

[a] Concentrations in the molal scale at different salinities are given by: $m_s = m_{35}27.565\,72S/(1000 - 1.005\,714S)$.
[b] Seawater single salt.

equilibrium studies (SSWE)[10] as an ionic medium simulating the major composition of natural seawater. Interactions of the organotin cations under investigation with the major constituents of seawater have been calculated using a complex formation model according to which SSWE is considered as of single-salt (BA) seawater, where cation B and anion A are representative of all major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^- and SO_4^{2-}) respectively.[11]

Potentiometric investigations ([H^+]-glass electrode) of $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ have been performed in $NaNO_3$, NaCl, NaCl–Na_2SO_4 mixtures and SSWE, at different ionic strengths ($0 \leq I \leq 5$ mol dm^{-3}) and salinities ($15 \leq S \leq 45$), and at $t = 25\,^{\circ}\mathrm{C}$. The equilibrium constants obtained have been used to determine the interaction parameters of Pitzer equations.[12]

EXPERIMENTAL

Chemicals

Alkyltin(IV) compounds were used in the form of chloride salts (from Alfa-Aesar). Purities were checked potentiometrically. Hydrochloric and nitric acids and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Fluka). Solutions of acids and hydroxide were standardized against sodium carbonate and potassium hydrogen phthalate respectively. Sodium nitrate, sodium chloride, sodium sulfate, magnesium chloride, potassium chloride and calcium chloride were prepared by weighing the pure salts (Fluka) previously dried in an oven at 110 °C. Solutions of magnesium and calcium chloride were standardized against EDTA standard solutions. SSWE solutions at different salinities ($15 \leq S \leq 45$) were prepared by mixing different salts, as reported in Table 1. All solutions were prepared with analytical-grade water ($R = 18$ MΩ cm^{-1}), using grade A glassware.

Apparatus

Potentiometric titrations were carried out (at $25.0 \pm 0.1\,^{\circ}\mathrm{C}$) using apparatus consisting of a Model 713 Metrohm potentiometer, equipped with a combination glass electrode (Ross type 8102, from Orion) and a Model 715 Metrohm motorized burette. Estimated accuracy was ±0.2 mV and ±0.003 cm^3 for emf and titrant volume readings respectively. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery, data acquisition and to check for emf stability. All titrations were carried out with magnetic stirring and with purified presaturated nitrogen bubbling through the solution in order to exclude oxygen and CO_2 inside.

Procedure

Potentiometric measurements were carried out by titrating 25 cm^3 of the solution containing the organotin(IV) chloride [0.8–5 mmol dm^{-3}, but 0.8–1 mmol dm^{-3} for $(C_3H_7)_3SnCl$], an excess of hydrochloric or nitric acid (1.5–7.5 mmol dm^{-3}) and the background salt in order to obtain pre-established ionic strength values [$(C_2H_5)_2Sn^{2+}$: $0.1 \leq I \leq 3.0$ mol dm^{-3}; $(C_2H_5)_3Sn^+$: $0.1 \leq I \leq 5.0$ mol dm^{-3}; $(C_3H_7)_3Sn^+$: $0.1 \leq I \leq 1.0$ mol dm^{-3}] or salinities ($15 \leq S \leq 45$) with standard NaOH solution up to pH 11.5 (pH 9 in SSWE). For each experiment, independent titrations of strong acid solution with standard NaOH were carried out under the same ionic strength conditions as the systems to be investigated, with the aim of determining the electrode potential E^0_{ext} 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

BSTAC[13] and STACO[14] computer programs were used in the refinement of all the parameters of an acid–base titration (E^0, pK_w, coefficient of junction potential j_a, analytical concentration of reagents) and in the calculation of complex formation constants. The ES4ECI[15] program was used to draw distribution diagrams and to calculate species formation percentages. The LIANA[16] program was used to test the dependence of log K on ionic strength using different equations.

Dependence on ionic strength was taken into account by the Debye–Hückel type equation in Eqn. (1):[17]

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

with

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

where K is the formation constant, $^{\mathrm{T}}K$ is the formation constant at infinite dilution and C, D, E are empirical parameters. The E parameter can be neglected when $I < 1$ mol dm^{-3}. The activity of water was taken into account by the simple relationship $\log a_w = -0.015I$. Both the STACO and BSTAC computer programs can deal with measurements at different ionic strengths and can refine empirical parameters for Eqn. (1).

Dependence on ionic strength was also taken into account by considering the Pitzer equations.[12] According to the Pitzer equations, for electrolytes 1–1, 1–2 and 2–1, the activity coefficients of cation M or anion X can be expressed by Eqns (2a) and (2b):

$$\begin{aligned}\ln\gamma_{\mathrm{M}} = {} & Z_{\mathrm{M}}^{2}f^{\gamma} + 2\sum\nolimits_{\mathrm{a}} m_{\mathrm{a}}(B_{\mathrm{Ma}} + EC_{\mathrm{Ma}}) \\ & + \sum\nolimits_{\mathrm{a}}\sum\nolimits_{\mathrm{c}} m_{\mathrm{c}}m_{\mathrm{a}}(Z_{\mathrm{M}}^{2}B'_{\mathrm{ca}} + Z_{\mathrm{M}}C_{\mathrm{ca}}) + \sum\nolimits_{\mathrm{c}} m_{\mathrm{c}}(2\Theta_{\mathrm{Mc}} \\ & + \sum\nolimits_{\mathrm{a}} m_{\mathrm{a}}\Psi_{\mathrm{Mca}}) + \sum\nolimits_{\mathrm{a}}\sum\nolimits_{\mathrm{a'}} m_{\mathrm{a}}m_{\mathrm{a'}}\Psi_{\mathrm{Maa'}} \qquad (2a)\end{aligned}$$

$$\begin{aligned}\ln\gamma_{\mathrm{X}} = {} & Z_{\mathrm{X}}^{2}f^{\gamma} + 2\sum\nolimits_{\mathrm{c}} m_{\mathrm{c}}(B_{\mathrm{Xc}} + EC_{\mathrm{Xc}}) \\ & + \sum\nolimits_{\mathrm{a}}\sum\nolimits_{\mathrm{c}} m_{\mathrm{c}}m_{\mathrm{a}}(Z_{\mathrm{X}}^{2}B'_{\mathrm{ca}} + Z_{\mathrm{M}}C_{\mathrm{ca}}) + \sum\nolimits_{\mathrm{a}} m_{\mathrm{a}}(2\Theta_{\mathrm{Xa}} \\ & + \sum\nolimits_{\mathrm{c}} m_{\mathrm{c}}\Psi_{\mathrm{Xca}}) + \sum\nolimits_{\mathrm{c}}\sum\nolimits_{\mathrm{c'}} m_{\mathrm{c}}m_{\mathrm{c'}}\Psi_{\mathrm{Xaa'}} \qquad (2b)\end{aligned}$$

and for neutral species by Eqn. (3):

$$\ln\gamma_{\mathrm{MX}}^{0} = 2\lambda I \qquad (3)$$

where m_i is the molality of the cation (c) and anion (a) in the solution, Z the charge, E the equivalent molality ($E = 1/2\sum_i m_i|Z_i|$), I the ionic strength in molal scale, and:

$$B_{\mathrm{MX}} = \beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(1)}(2I)^{-1}f_1 \qquad (4)$$

$$B'_{\mathrm{MX}} = \beta_{\mathrm{MX}}^{(1)}(2I^2)^{-1}f_2 \qquad (5)$$

$$C_{\mathrm{MX}} = C_{\mathrm{MX}}^{(\phi)}(2|Z_{\mathrm{M}}Z_{\mathrm{X}}|^{1/2})^{-1} \qquad (6)$$

$$f^{\gamma} = -0.392[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667\ln(1 + 1.2I^{1/2})] \qquad (7a)$$

$$f_1 = 1 - (1 + 2I^{1/2})\exp(-2I^{1/2}) \qquad (7b)$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2}) \qquad (7c)$$

$\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite signs, Θ is the interaction parameter between two ions of the same sign, Ψ is a triple interaction parameter ($+ - +$, $- + -$) and λ is the interaction parameter for neutral species. At $I < 3$ mol kg^{-1}, the Θ and Ψ parameters can generally be neglected.[12]

RESULTS AND DISCUSSION

Hydrolysis of $(C_2H_5)_2Sn^{2+}$

The formation of hydrolytic species of diethyltin(IV) cation was studied in $NaNO_3$, NaCl and NaCl–Na_2SO_4 mixtures in the ionic strength range $0.1 \le I \le 3$ mol dm^{-3}. The formation of three mononuclear [$(C_2H_5)_2Sn(OH)^+$, $(C_2H_5)_2Sn(OH)_2^0$ and $(C_2H_5)_2Sn(OH)_3^-$] and two binuclear [$((C_2H_5)_2Sn)_2(OH)_2^{2+}$ and $((C_2H_5)_2Sn)_2(OH)_3^+$] species was found in NaCl and $NaNO_3$ media. In the experimental conditions used in NaCl-Na_2SO_4 mixtures ($C_{(C_2H_5)_2Sn^{2+}} \le 1$ mmol dm^{-3}), only mononuclear species were found. Hydrolysis constants relative to the reaction

$$\begin{aligned} & p(C_2H_5)_2Sn^{2+} + qH_2O \\ & \quad = [(C_2H_5)_2Sn]_p(OH)_q^{(2p-q)+} + qH^+ \qquad (8) \\ & \beta_{pq} \end{aligned}$$

are shown in Tables 2 and 3. Table 4 shows hydrolysis constants extrapolated to $I = 0$ mol dm^{-3}, also converted to β^{OH} formation constants for the reaction

$$\begin{aligned} & p(C_2H_5)_2Sn^{2+} + qOH = [(C_2H_5)_2Sn]_p(OH)_q^{(2p-q)+} \\ & \beta_{pq}^{\mathrm{OH}} \end{aligned} \qquad (9)$$

by using appropriate pK_w values, at different ionic strengths[3] ($\beta_{pq}^{\mathrm{OH}} = \beta_{pq}/qK_w$). The importance of hydrolytic species is illustrated in Fig. 1, which shows the distribution diagram versus pH. As can be seen, binuclear species are not very significant, but they must be considered when $C_{(C_2H_5)_2Sn^{2+}} > 1$ mmol dm^{-3} and pH <6.5; at the pH of seawater (pH 8.2), diethyltin(IV) is present only in hydrolytic form $(C_2H_5)_2Sn(OH)_2^0$.

Hydrolysis constants proved fairly dependent on the medium and on the ionic strength, as can be seen in Figs 2 and 3, where log K for $(C_2H_5)_2Sn(OH)^+$ species are reported *versus* I in NaCl and in $NaNO_3$, and *versus* sulfate concentration in NaCl–Na_2SO_4 mixtures respectively. The combined effect of ionic strength and of medium produces a shift in the pH of hydrolysis of about one unit. This is due to the interaction between the diethyltin(IV) cation and chloride and sulfate anions. The strength of these interactions can be calculated by considering the differences in β_{pq}, as in other works.[3–8]

In order to give a complete picture of hydrolytic species formation, some measurements were made in SSWE containing six components (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^2; see Table 1). In our experimental conditions, only two species were found: $(C_2H_5)_2Sn(OH)^+$ and $(C_2H_5)_2Sn(OH)_2^0$. Hydrolysis constant values at different salinities ($15 \le S \le 45$), reported in Table 5 and shown in Fig. 4, can be expressed as a function of salinity by Eqn. (10):

$$\log\beta = \log^{\mathrm{T}}\beta + aS^{1/2} + bS \qquad (10)$$

with $a = -0.096 \pm 0.011$, $b = -0.006 \pm 0.002$ and $a = -0.058 \pm 0.027$, $b = -0.018 \pm 0.005$ for the first and the second hydrolysis constants respectively. The same values were calculated using: (i) hydrolysis constants at $I = 0$ mol dm^{-3}; (ii) dependence on ionic strength in non-interacting media ($NaNO_3$, Table 2); (iii) formation constants for Cl^- and SO_4^{2-} ion pairs. As can be seen in Table 6, there are some slight differences between experimental and calculated data, probably due to the formation of very weak mixed complexes between $(C_2H_5)_2Sn^{2+}$ and chloride and sulfate.

Hydrolysis of $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$

The hydrolysis of $(CH_3)_3Sn^+$ in different media and at different ionic strengths was studied in previous papers.[4,5,8]

Table 2. Hydrolysis constants[a] of $(C_2H_5)_2Sn^{2+}$ in $NaNO_3$ and in NaCl, at different ionic strengths (mol dm^{-3}) and at $t = 25\,°C$

I	$\log K_{11}$	$\log \beta_{12}$	$\log \beta_{13}$	$\log \beta_{22}$	$\log \beta_{23}$
			$NaNO_3$		
0.10	−3.15 ± 0.03[b]	−8.60 ± 0.02[b]	−19.98 ± 0.02[b]	−4.90 ± 0.03[b]	−10.09 ± 0.04[b]
0.15	−3.19 ± 0.06	−8.65 ± 0.03	−20.02 ± 0.03	−4.96 ± 0.03	−10.18 ± 0.05
0.25	−3.24 ± 0.03	−8.71 ± 0.03	−20.04 ± 0.03	−5.03 ± 0.04	−10.28 ± 0.05
0.50	−3.38 ± 0.03	−8.93 ± 0.03	−20.23 ± 0.05	−5.24 ± 0.04	−10.61 ± 0.04
0.75	−3.49 ± 0.03	−9.11 ± 0.04	−20.39 ± 0.08	−5.39 ± 0.05	−10.86 ± 0.04
1.00	−3.57 ± 0.03	−9.25 ± 0.04	−20.50 ± 0.10	−5.48 ± 0.06	−11.03 ± 0.04
1.50	−3.70 ± 0.03	−9.48 ± 0.05	−20.69 ± 0.13	−5.63 ± 0.07	−11.30 ± 0.05
2.00	−3.79 ± 0.03	−9.63 ± 0.06	−20.82 ± 0.14	−5.69 ± 0.07	−11.45 ± 0.06
2.50	−3.83 ± 0.03	−9.71 ± 0.08	−20.88 ± 0.12	−5.68 ± 0.06	−11.49 ± 0.06
3.00	−3.86 ± 0.06	−9.77 ± 0.13	−20.95 ± 0.10	−5.66 ± 0.06	−11.49 ± 0.09
			NaCl		
0.10	−3.50 ± 0.03	−8.91 ± 0.04	−19.96 ± 0.10	−4.92 ± 0.07	−10.2 ± 0.1
0.15	−3.57 ± 0.03	−8.98 ± 0.05	−19.97 ± 0.10	−4.96 ± 0.09	−10.2 ± 0.1
0.25	−3.67 ± 0.04	−9.12 ± 0.05	−20.04 ± 0.11	−5.04 ± 0.08	−10.4 ± 0.2
0.50	−3.83 ± 0.04	−9.36 ± 0.05	−20.20 ± 0.13	−5.19 ± 0.07	−10.7 ± 0.2
0.75	−3.93 ± 0.04	−9.54 ± 0.06	−20.37 ± 0.14	−5.31 ± 0.06	−10.9 ± 0.2
1.00	−4.02 ± 0.04	−9.69 ± 0.07	−20.51 ± 0.15	−5.39 ± 0.06	−11.1 ± 0.2
1.50	−4.20 ± 0.06	−9.98 ± 0.07	−20.83 ± 0.17	−5.56 ± 0.09	−11.4 ± 0.3
2.00	−4.36 ± 0.06	−10.23 ± 0.06	−21.10 ± 0.16	−5.68 ± 0.12	−11.7 ± 0.3
2.50	−4.48 ± 0.06	−10.38 ± 0.06	−21.21 ± 0.14	−5.70 ± 0.16	−11.8 ± 0.3
3.00	−4.68 ± 0.06	−10.71 ± 0.06	−21.54 ± 0.20	−5.87 ± 0.24	−12.0 ± 0.5

[a] Relates to the reaction: $pM^{2+} + qH_2O = M_p(OH)_q^{(2p-q)} + qH^+$.

[b] $\pm 3\sigma$.

In order to complete speciation studies of trialkyltin(IV) cations, here we describe a study of the hydrolysis of $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ in $NaNO_3$, NaCl and NaCl–Na_2SO_4 mixtures in the ionic strength range $0.1 \le I \le 5$ mol dm^{-3} [for $(C_3H_7)_3Sn^+$ only the ionic strength range $0.1 \le I \le 1$ mol dm^{-3} was considered]. For both cations, the formation of two mononuclear [$M(OH)^0$ and $M(OH)_2^-$] species was found. For the $(C_2H_5)_3Sn^+$ cation a binuclear

Table 3. Hydrolysis constants[a] of $(C_2H_5)_2Sn^{2+}$ in NaCl–Na_2SO_4 mixtures at different ionic strengths (mol dm^{-3}) and at $t = 25\,°C$

I	C_{SO_4}	$\log K_{11}$	$\log \beta_{12}$	$\log \beta_{13}$
1	0.05	−4.10 ± 0.09[b]	−10.00 ± 0.09[b]	−21.23 ± 0.15[b]
1	0.10	−3.98 ± 0.03	−9.73 ± 0.03	−21.26 ± 0.12
1	0.20	−3.93 ± 0.03	−9.75 ± 0.03	−21.14 ± 0.09
1	0.30	−3.82 ± 0.03	−9.67 ± 0.03	−21.47 ± 0.18
2	0.10	−4.26 ± 0.06	−10.17 ± 0.09	−21.52 ± 0.18
2	0.20	−4.19 ± 0.06	−10.17 ± 0.09	−21.38 ± 0.15
2	0.40	−4.10 ± 0.09	−10.11 ± 0.09	−21.32 ± 0.14
2	0.50	−4.04 ± 0.15	−10.00 ± 0.12	−21.20 ± 0.14
3	0.10	−4.58 ± 0.09	−10.78 ± 0.12	−22.04 ± 0.14
3	0.20	−4.52 ± 0.09	−10.63 ± 0.12	−21.69 ± 0.14
3	0.40	−4.39 ± 0.06	−10.64 ± 0.09	−22.03 ± 0.24
3	0.60	−4.30 ± 0.09	−10.76 ± 0.12	−22.43 ± 0.30

[a] Relates to the reaction: $pM^{2+} + qH_2O = M_p(OH)_q^{(2p-q)} + qH^+$

[b] $\pm 3\sigma$.

Table 4. Hydrolysis and formation constants of $(C_2H_5)_2Sn^{2+}$ species at $I = 0$ mol dm^{-3} and $t = 25\,°C$

Reaction	$\log \beta$
$M^{2+} + H_2O = M(OH)^+ + H^+$	−3.09 ± 0.02[a]
$M^{2+} + 2H_2O = M(OH)_2^0 + 2H^+$	−8.61 ± 0.03
$M^{2+} + 3H_2O = M(OH)_3^- + 3H^+$	−20.08 ± 0.05
$2M^{2+} + 2H_2O = M_2(OH)_2^{2+} + 2H^+$	−4.79 ± 0.04
$2M^{2+} + 3H_2O = M_2(OH)_3^+ + 3H^+$	−9.95 ± 0.04
$M^{2+} + OH^- = M(OH)^+$	10.91 ± 0.02
$M^{2+} + 2OH^- = M(OH)_2^0$	19.39 ± 0.02
$M^{2+} + 3OH^- = M(OH)_3^-$	21.92 ± 0.05
$2M^{2+} + 2OH^- = M_2(OH)_2^{2+}$	23.21 ± 0.02
$2M^{2+} + 3OH^- = M_2(OH)_3^+$	32.05 ± 0.02

[a] $\pm 3\sigma$.

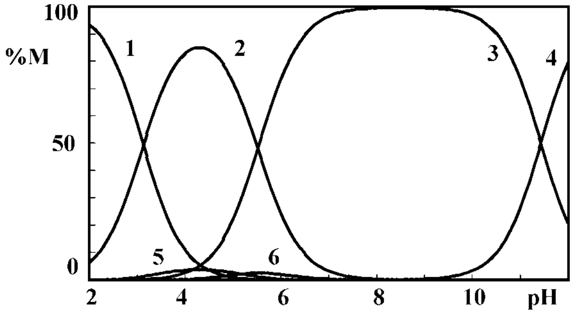

Figure 1. Distribution diagram of $(C_2H_5)_2Sn^{2+}$ *versus* pH, at $t = 25$ °C ($C_M = 1$ mmol dm^{-3}) Species: (1) M^{2+}; (2) $M(OH)^+$; (3) $M(OH)_2{}^0$; (4) $M(OH)_3^-$; (5) $M_2(OH)_2{}^{2+}$; (6) $M_2(OH)_3^+$ [$M = (C_2H_5)_2Sn^{2+}$].

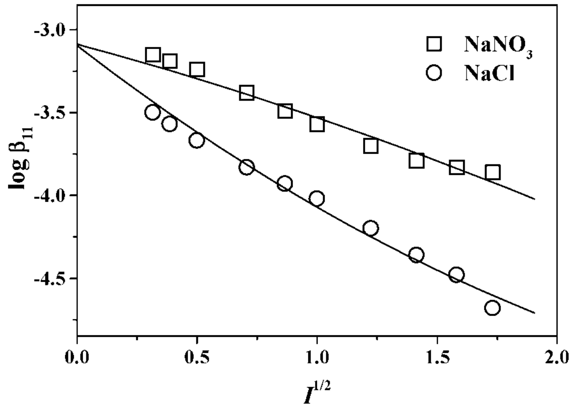

Figure 2. Hydrolysis constants of $(C_2H_5)_2Sn(OH)^+$ species in $NaNO_3$ and in NaCl *versus* *I* (mol dm^{-3}), at $t = 25$ °C.

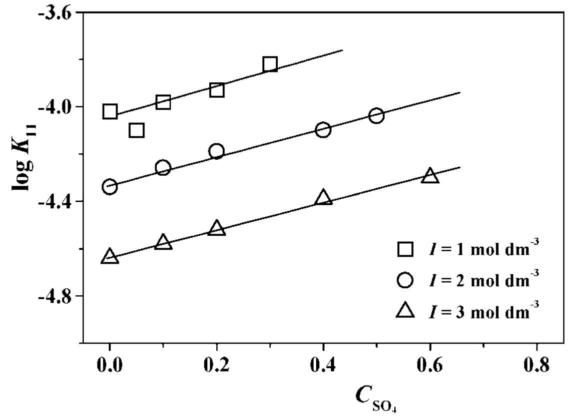

Figure 3. Hydrolysis constants of $(C_2H_5)_2Sn(OH)^+$ species in NaCl–Na_2SO_4 mixtures, at different ionic strengths *versus* sulfate concentration (mol dm^{-3}), at $t = 25$ °C.

Table 5. Hydrolysis constants[a] of $(C_2H_5)_2Sn^{2+}$ in SSWE at different salinities and at $t = 25$ °C

S	log K_{11}	log β_{12}
15	-3.54 ± 0.01[b]	-9.05 ± 0.02[b]
25	-3.72 ± 0.03	-9.34 ± 0.03
35	-3.92 ± 0.02	-9.67 ± 0.03
45	-3.98 ± 0.02	-9.73 ± 0.03

[a] Relates to the reaction: $pM^{2+} + qH_2O = M_p(OH)_q^{(2p-q)} + qH^+$.
[b] $\pm 3\sigma$.

$M_2(OH)^+$ species was also found. Hydrolysis constants for $M(OH)^0$, the most significant species, at different ionic strengths are reported in Tables 7 and 8, according to the reaction in Eqn. (11):

$$M^+ + H_2O = M(OH)^0 + H^+ \tag{11}$$

[$M^+ = (C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$]. Table 9 shows hydrolysis constants at $I = 0$ mol dm^{-3}. The dependence of the

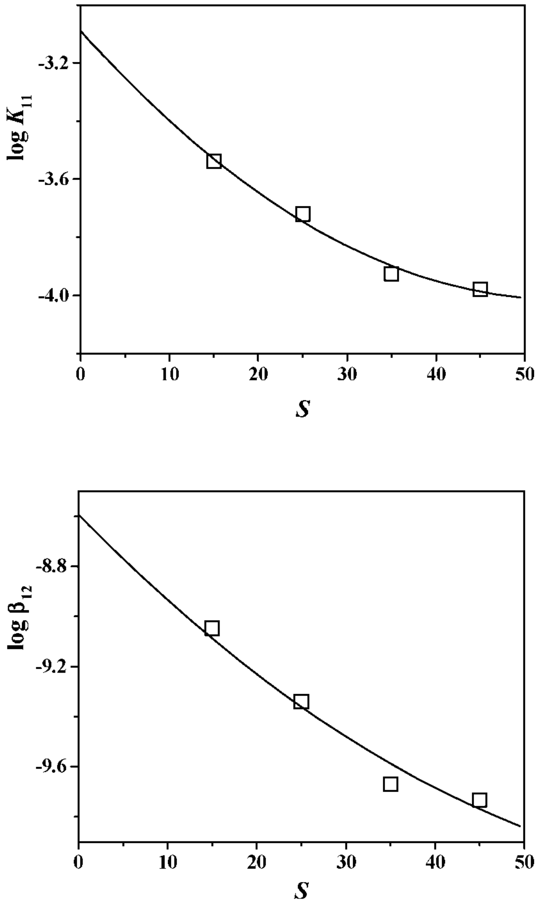

Figure 4. Hydrolysis constants of $(C_2H_5)_2Sn^{2+}$ in SSWE *versus* *S*, at $t = 25$ °C

Table 6. Comparison between experimental and calculated hydrolysis constant values for $(C_2H_5)_2Sn^{2+}$, in SSWE ($S = 35$), and at $t = 25\,°C$

	Calculated	Experimental	Δ
$\log K_{11}$	−3.75	−3.92	0.17
$\log \beta_{12}$	−9.63	−9.67	0.04

hydrolysis constants on the medium and on the ionic strength is shown in Figure 5, for both $(C_2H_5)_3Sn(OH)^0$ and $(C_3H_7)_3Sn(OH)^0$ species.

We also determined the hydrolysis constants of trialkyltin(IV) cations in SSWE at different salinities ($15 \leq S \leq 45$). Only $(C_2H_5)_3Sn(OH)^0$ and $(C_3H_7)_3Sn(OH)^0$ species were found. Values at different salinities are reported in Table 10, and can be expressed by Eqn. ((10)) with $a = -0.012 \pm 0.006$, $b = -0.0033 \pm 0.0009$, and $a = 0.024 \pm 0.010$, $b = -0.009 \pm 0.002$, for $(C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$ respectively.

Table 8. Hydrolysis constants of $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ in NaCl–Na_2SO_4 mixtures at $I = 1$ mol dm^{-3} and at $t = 25\,°C$

C_{SO_4}	$\log K$[a]	
	$(C_2H_5)_3Sn^+$	$(C_3H_7)_3Sn^+$
0.05	−6.70 ± 0.03[b]	−6.61 ± 0.03[b]
0.10	−6.66 ± 0.03	−6.63 ± 0.03
0.20	−6.66 ± 0.03	−6.59 ± 0.03
0.30	−6.68 ± 0.03	−6.57 ± 0.03

[a] Relates to the reaction: $M^+ + H_2O = M(OH)^0 + H^+$.

[b] $\pm 3\sigma$.

Table 9. Hydrolysis constants of $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ at $I = 0$ mol dm^{-3} and at $t = 25\,°C$

Reaction	$\log\beta$
$(C_2H_5)_3Sn^+ + H_2O = (C_2H_5)_3Sn(OH)^0 + H^+$	−6.34 ± 0.01[a]
$(C_2H_5)_3Sn^+ + 2H_2O = (C_2H_5)_3Sn(OH)_2^- + 2H^+$	−4.77 ± 0.14
$2(C_2H_5)_3Sn^+ + H_2O = [(C_2H_5)_3Sn]_2(OH)^+ + H^+$	−18.17 ± 0.06
$(C_3H_7)_3Sn^+ + H_2O = (C_2H_5)_3Sn(OH)^0 + H^+$	−6.28 ± 0.01
$(C_3H_7)_3Sn^+ + 2H_2O = (C_2H_5)_3Sn(OH)_2^- + 2H^+$	−18.18 ± 0.05

[a] $\pm 3\sigma$.

Single-salt (BA) synthetic seawater

The speciation of alkyltins(IV) in SSWE was also studied using the single-salt (BA) approximation.[11] In recent years, in order to simplify equilibrium calculations, we have described the composition of SSWE in terms of a single salt BA ($C_{BA} = 1/2 \sum c_i$, where c_i is the concentration of anions and cations of artificial seawater) with an ionic charge ±1.117 ($z = \sqrt{I/C_{BA}}$). BA concentration (mean ionic concentration) is reported in Table 1. Use of the single-salt approximation considerably reduces the complexity of the system. In fact, only three species, deriving from internal ionic medium interactions, need be considered: BA^0 (with $\log K = -0.03$, at $I = 0$ mol dm^{-3} and $t = 25\,°C$), $HA^{(1-z)}$ (with $\log K = 0.24$, at $I = 0$ mol dm^{-3} and $t = 25\,°C$) and $B(OH)^{(z-1)}$

Table 7. Hydrolysis constants[a] of $(CH_3)_3Sn^+$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ in $NaNO_3$ and in NaCl aqueous solutions, at different ionic strengths (mol dm^{-3}) and at $t = 25\,°C$

I	$(CH_3)_3Sn^+$ [b]		$(C_2H_5)_3Sn^+$		$(C_3H_7)_3Sn^+$	
	$NaNO_3$	NaCl	$NaNO_3$	NaCl	$NaNO_3$	NaCl
0.10	6.189	6.120	−6.36 ± 0.01[c]	−6.37 ± 0.02[c]	−6.29 ± 0.02[c]	−6.31 ± 0.02[c]
0.15	–	–	–	–	−6.30 ± 0.01	−6.32 ± 0.02
0.20	6.169	6.178	–	–	–	–
0.25	–	–	−6.37 ± 0.02	−6.40 ± 0.01	−6.31 ± 0.01	−6.36 ± 0.01
0.50	6.218	6.226	−6.40 ± 0.03	−6.46 ± 0.01	−6.35 ± 0.03	−6.43 ± 0.02
0.75	6.278	6.307	−6.42 ± 0.05	−6.51 ± 0.02	−6.38 ± 0.02	−6.51 ± 0.03
1.00	6.280	6.323	−6.44 ± 0.06	−6.57 ± 0.02	−6.42 ± 0.02	–
1.50	6.340	6.460	−6.48 ± 0.08	−6.68 ± 0.02	–	–
2.00	–	–	−6.51 ± 0.10	−6.79 ± 0.03	–	–
2.50	–	–	−6.54 ± 0.10	−6.90 ± 0.03	–	–
3.00	–	–	−6.55 ± 0.10	−7.01 ± 0.04	–	–
5.00	–	–	−6.56 ± 0.07	−7.45 ± 0.06	–	–

[a] Relates to the reaction: $M^+ + H_2O = M(OH)^0 + H^+$.

[b] Ref. 4.

[c] $\pm \sigma$.

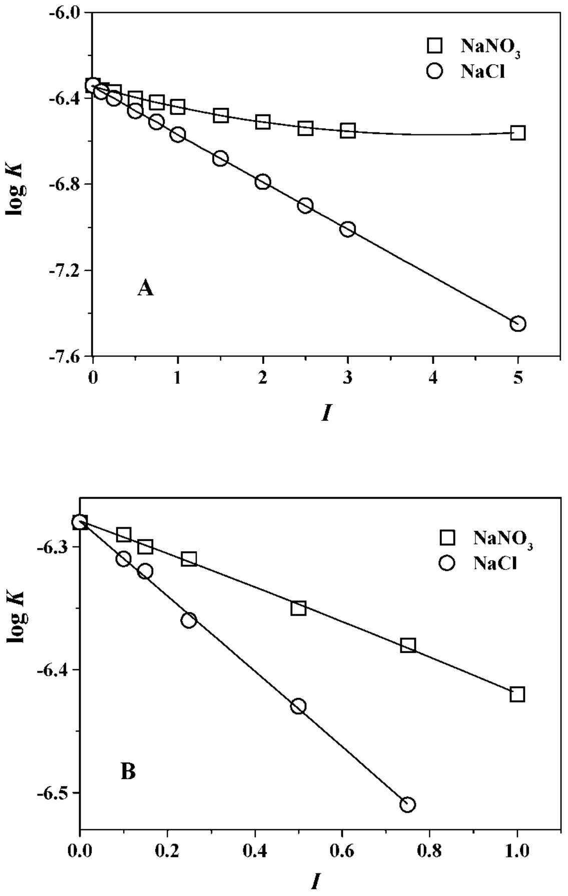

Figure 5. Hydrolysis constants of $(C_2H_5)_3Sn(OH)^0$ (A) and $(C_3H_7)_3Sn(OH)^0$ (B) species, in $NaNO_3$ and in NaCl *versus* I (mol dm^{-3}), at $t = 25$ °C.

(log $K = -12.75$, relative to the reaction: $B^{z+} + H_2O = B(OH)^{(z-1)} + H^+$, at $I = 0$ mol dm^{-3} and $t = 25$ °C). Equilibrium constants for these species are included in the calculations carried out in order to determine quantitatively the interactions between alkyltin(IV) cations and the seawater salt. Least-squares calculations showed the formation of $MA^{(z-1.117)}$ species, according to the reaction in Eqn. ((12)):

$$M^{z+} + A^{-1.117} = MA^{(z-1.117)} \tag{12}$$

[$M^{z+} = (C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$]. Formation constant values at different salinities are shown in Table 11. For the $(C_2H_5)_2Sn^{2+}$ cation, a hydrolytic species was also found:

$$(C_2H_5)_2Sn^{2+} + A^{-1.117} + H_2O = ((C_2H_5)_2Sn(OH)A)^{0.117-} + H^+ \tag{13}$$

with log $\beta = -3.32 \pm 0.04$ ($I = 0$ mol dm^{-3}, $t = 25$ °C).

The distribution diagrams of the cations in SSWE considered to be a single salt are shown in Figure 6. As can be seen, at the pH of natural fluids, the alkyltin(IV) cations are present as neutral hydrolytic species $[M(OH)_2^0$ for $(C_2H_5)_2Sn^{2+}$, and $M(OH)^0$ for $(C_2H_5)_3Sn^+$ and $(C_3H_5)_7Sn^+]$. The $MA^{(z-1.117)}$ species is formed only in the acidic pH range, with a maximum percentage formation of ~70% for the $(C_2H_5)_2Sn^{2+}$ cation.

Table 10. Hydrolysis constants of $(CH)_3Sn^+$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ in SSWE at different salimities and at $t = 25$ °C

S	I/mol dm^{-3}	log$K$[a]		
		$(CH_3)_3Sn^+$ [b]	$(C_2H_5)_3Sn^+$	$(C_3H_7)_3Sn^+$
5	0.1	−6.15	–	–
10	0.2	−6.18	–	–
15	0.3	–	−6.44 ± 0.01[c]	−6.31 ± 0.02[c]
20	0.4	−6.22	–	–
25	0.51	−6.26	−6.47 ± 0.02	−6.42 ± 0.02
35	0.72	−6.26	−6.53 ± 0.02	−6.47 ± 0.02
45	0.93	−6.30	−6.57 ± 0.01	−6.54 ± 0.02

[a] Relates to the reaction: $M^+ + H_2O = M(OH)^0 + H$.
[b] Ref. 8.
[c] ±3σ.

Table 11. Formation constants of $MA^{(z-1,117)}$ species [$M^{z+} = (C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$], at different salinities and $t = 25$ °C

S	log$K$		
	$(C_2H_5)_2Sn^{2+}$	$(C_2H_5)_3Sn^+$	$(C_3H_7)_3Sn^+$
0	1.09 ± 0.01[a]	0.12 ± 0.02[a]	0.27 ± 0.02[a]
15	0.33 ± 0.03	−0.13 ± 0.04	−0.47 ± 0.08
25	0.03 ± 0.04	−0.08 ± 0.01	−0.13 ± 0.01
35	−0.03 ± 0.05	−0.11 ± 0.02	−0.22 ± 0.02
45	0.12 ± 0.03	−0.17 ± 0.02	−0.26 ± 0.02

[a] ±3σ.

Predictive relationship for trialkyltin(IV) hydrolysis

The similar behaviours of the different trialkyltin cations studied suggest it might be possible to predict quantitatively the hydrolysis of tributyltin(IV), for which no experimental data are available owing to its very low solubility. The hydrolysis constants of $(C_nH_{2n+1})_3Sn^+$ ($n = 1,2,3$) in $NaNO_3$, NaCl and SSWE in the ionic strength range $0 \leq I \leq 1$ mol dm^{-3} can be expressed by the general equation in Eqn. (14):

$$\log K = p_1 + p_2 I + p_3 I/n + p_4/n \tag{14}$$

where p_1, p_2, p_3 and p_4 are empirical parameters. A good fit for Eqn. (14) ($\sigma = 0.034$, where σ is the standard deviation on the fit) was obtained by making the p_1, p_3 and p_4 parameters equal for all cations and ionic media ($p_1 = 6.37 \pm 0.03$; $p_3 = -0.22 \pm 0.03$; $p_4 = -0.12 \pm 0.06$), whilst the p_2 parameter

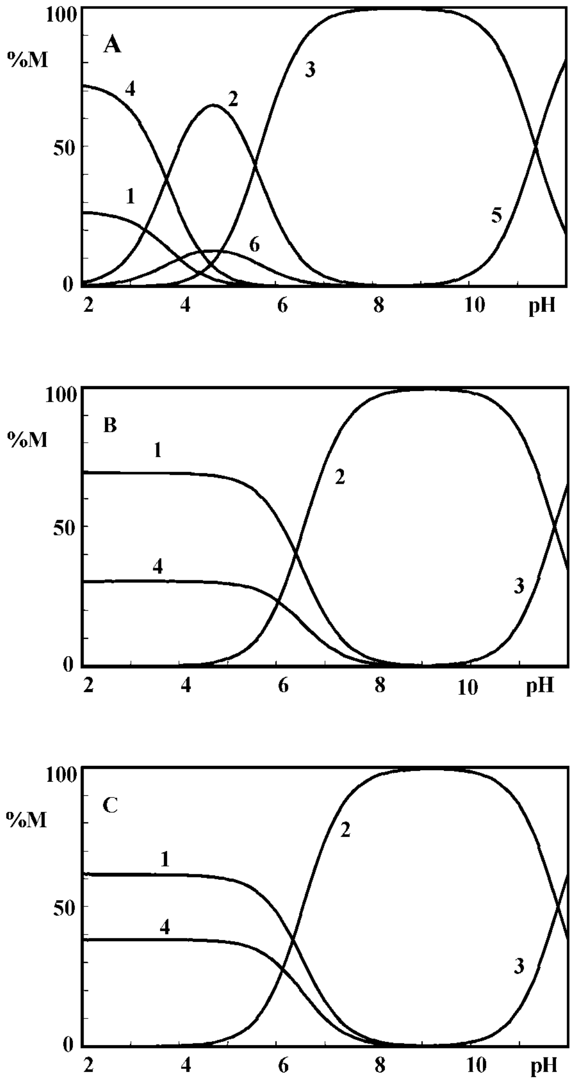

Figure 6. Distribution diagrams of $(C_2H_5)_2Sn^{2+}$ (A), $(C_2H_5)_3Sn^+$ (B) and $(C_3H_7)_3Sn^+$ (C) species *versus* pH in SSWE as a single salt, at $S = 35$ and $t = 25$ °C. Analytical conditions: $C_{AB} = 0.57$ mol dm^{-3}, $C_M = 1$ mmol dm^{-3}. Species; (1) M; (2) M(OH); (3) $M(OH)_2$; (4) MA; (5) $M(OH)_3$; (6) M(OH)A [M = $(C_2H_5)_2Sn^{2+}$ or $(C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$; charges omitted for the sake of simplicity].

was different for each ionic medium ($NaNO_3$: 0.24 ± 0.04; NaCl: 0.34 ± 0.05; SSWE: 0.32 ± 0.05). Using Eqn. (14) we can calculate the hydrolysis constants of $(C_4H_9)_3Sn^+$, which are reported in Table 12.

Table 12. Calculated hydrolysis constants of $(C_4H_9)_2Sn^+$ in $NaNO_3$, NaCl and SSWE

I/mol dm^{-3}	log K^a		
	$NaNO_3$	NaCl	SSWE
0	-6.31 ± 0.02^b		
0.1	-6.33 ± 0.02	-6.34 ± 0.02^b	-6.34 ± 0.02^b
0.5	-6.42 ± 0.01	-6.47 ± 0.01	-6.46 ± 0.01
1	-6.53 ± 0.02	-6.62 ± 0.02	-6.60 ± 0.02

[a] Relates to the reaction: $M^+ + H_2O = M(OH)^0 + H^+$.

[b] $\pm 3\sigma$.

Pitzer interaction parameters

Pitzer equations[12] have been widely used in speciation studies and extensive databases of interaction parameters have been set up to include Pitzer interaction parameters for sea salts,[12,18] metal[19] and organometal cations,[5,7,8,20] and some ligand classes as carboxylates,[21–24] amines[25,26] and amino acids.[27,28] In order to contribute to further extension of the database, we determined the interaction parameters of Pitzer equations [Eqns ((2)–(7))] for $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$, using hydrolysis constants in NaCl and $NaNO_3$ media (converted into molal scale) over a wide range of ionic strengths. The hydrolysis constants measured (ln β_{pq}) for the reaction in Eqn. (15)

$$pM^{z+} + qH_2O = M_p(OH)_q^{(pz-q)} + qH^+ \qquad (15)$$

[$M^{z+} = (C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ or $(C_3H_7)_3Sn^+$] are related to the thermodynamic values (ln $^T\beta_{pq}$) and the activity coefficients (ln γ) of the ionic species by Eqn. (16):

$$\ln\beta_{pq} = \ln^T\beta_{pq} + \ln\gamma_{M_p(OH)_q} + q\ln\gamma_H - p\ln\gamma_M - q\ln a_{H_2O} \qquad (16)$$

To determine the Pitzer parameters, we combined Eqns ((2)–(16)) and, in the resulting expressions, we assumed the activity coefficient of neutral species to be equal to zero and we allowed for the known Pitzer parameters ($\beta^{(0)}_{H,Cl} = 0.1775$, $C^{(\phi)}_{H,Cl} = 0.00080$, $\beta^{(1)}_{H,Cl} = 0.2945$, $C^{(\phi)}_{Na,Cl} = 0.00127$, $\beta^{(1)}_{Na,Cl} = 0.2664$, $\beta^{(0)}_{H,NO_3} = 0.1168$, $C^{(\phi)}_{H,NO_3} = -0.00539$, $\beta^{(1)}_{H,NO_3} = 0.3546$, $C^{(\phi)}_{Na,NO_3} = -0.00072$, $\beta^{(1)}_{Na,NO_3} = 0.1783$, $\Theta_{H,Na} = 0.036$, $\Psi_{H,Na,Cl} = -0.004$).[12] The parameter values calculated are reported in Table 13. In some cases, the $C^{(\phi)}$ term was not needed and the results could be adequately represented using only the $\beta^{(0)}$ and $\beta^{(1)}$ terms. Moreover, the $C^{(\phi)}$ term can be neglected when $I < 2$ mol kg^{-1}.

Comparisons with literature

Few quantitative data regarding the hydrolysis of $(C_2H_5)_2Sn^{2+}$ and $(C_2H_5)_3Sn^+$ can be found in the literature.[29–34] Most studies were performed in an $NaClO_4$ medium and some in KNO_3, but there are no data for variable ionic strengths. As regards $(C_3H_7)_3Sn^+$, no data are available. As can be seen in Table 14, literature data are fairly consistent with the data included here. Results for di- and tri-metyltin(IV) hydrolysis are also included in Table 14. These data are also useful for making comparisons between homologous alkyltin(IV) compounds, in order to establish whether there is any difference in their behaviour.

Table 13. Pitzer interaction parameters

M	X	$\beta^{(0)}_{MX}$	$C^{(\Phi)}_{MX}$	$\beta^{(1)}_{MX}$	σ^a
$(C_2H_5)_2Sn^{2+}$	Cl^-	0.28 ± 0.02^b	0	-0.75 ± 0.09^b	0.022
$(C_2H_5)_2Sn(OH)^+$	Cl^-	-0.49 ± 0.08	0.23 ± 0.03	1.74 ± 0.24	0.032
$(C_2H_5)_2Sn^{2+}$	NO_3^-	-1.24 ± 0.21	0.77 ± 0.12	5.46 ± 0.64	0.047
$(C_2H_5)_2Sn(OH)^+$	NO_3^-	-0.52 ± 0.27	0.23 ± 0.10	1.84 ± 0.82	0.072
$(C_2H_5)_2Sn(OH)_3^-$	Na^+	-0.12 ± 0.01	0	0.90 ± 0.08	0.090
$(C_2H_5)_3Sn^+$	Cl^-	-0.007 ± 0.002	0.0056 ± 0.0004	0.241 ± 0.007	0.003
$(C_2H_5)_3Sn^+$	NO_3^-	0.092 ± 0.004	0.0143 ± 0.0008	0.249 ± 0.015	0.004
$(C_3H_7)_3Sn^+$	Cl^-	-0.119 ± 0.012	–	0.326 ± 0.033	0.004
$(C_3H_7)_3Sn^+$	NO_3^-	-0.008 ± 0.008	–	0.419 ± 0.003	0.003

[a] standard deviations on Pitzer equation fits.

[b] $\pm\sigma$.

Table 14. Comparison with literature data

Cation	I/mol dm^{-3}	log β_{11}	log β_{12}	log β_{13}	log β_{22}	log β_{23}	Ref.
$(CH_3)_2Sn^{2+}$	0	−2.86	−8.16	−19.35	−4.99	−9.06	3
	0.1 $NaNO_3$	−3.05	−8.36	−19.4	−5.2	−9.5	3
	3.0 $NaNO_3$	−3.50	−9.06	−20.0	−5.1	−10.1	3
	3.0 $NaClO_4$	−3.30	−9.00	−20.2	−5.1	−9.6	3
$(C_2H_5)_2Sn^{2+}$	0	−3.09	−8.61	−20.08	−4.79	−9.95	this work
	0.1 KNO_3	−3.102	−8.563	–	−5.07	−10.26	31
	0.1 $NaNO_3$	−3.15	−8.60	–	−4.90	−10.09	this work
	3.0 $NaClO_4$	−3.40	–	–	–	–	32
	3.0 $NaClO_4$	−3.50	–	–	−4.34		33
	3.0 $NaNO_3$	−3.86	−9.77	−20.95	−5.66	−11.49	this work
$(C_3H_7)_2Sn^{2+}$	3.0 $NaClO_4$	−2.92					32
$(CH_3)_3Sn^+$	0	−6.14	−12.74				4
$(C_2H_5)_3Sn^+$	0	−6.34	−18.17				this work
	3.0 $NaClO_4$	−6.81					32
	3.0 $NaClO_4$	−6.81					34
	3.0 $NaNO_3$	−6.55					this work
$(C_3H_7)_3Sn^+$	0	−6.28	−18.18				this work

CONCLUDING REMARKS

Since the biological and chemical behaviour of alkyltin(IV) compounds is strictly related to the form in which they are present in the environment, speciation in natural waters represents the basis of our understanding of their biochemistry. Our main conclusions on $(C_2H_5)_2Sn^{2+}$, $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ cations may be summarized as follows.

(a) The $(C_2H_5)_2Sn^{2+}$ cation forms five hydrolytic species; the mononuclear ones show very high formation percentages, whereas the binuclear ones can be neglected when $C_{(C_2H_5)_2Sn^{2+}}$ is <1 mmol dm^{-3}.

(b) $(C_2H_5)_3Sn^+$ and $(C_3H_7)_3Sn^+$ form two mononuclear hydrolytic species, and $(C_2H_5)_3Sn^+$ also forms a binuclear species, but in a negligible percentage.

(c) The most important hydrolytic species at the pH of natural fluids (6–8) for all the alkyltin(IV) cations are the neutral ones.

(d) Comparisons with the behaviour of other organotin(IV) compounds in aqueous solution demonstrate many similarities between the interactions of all $R_n(Sn)^{(4-n)+}$, making simulations of the conditions of natural fluids containing these cations possible. This is significant for $(C_4H_9)_nSn^{(4-n)+}$ compounds, whose data can be predicted using the simple empirical relation in Eqn. (14).

(e) Hydrolysis and complex formation in synthetic seawater using the single-salt approximation make it possible to characterize the speciation of organotin(IV) compounds in this ionic medium.

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