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Hydrolysis of $(CH_3)_2Sn^{2+}$ in Different Ionic Media: Salt Effects and Complex Formation

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The hydrolysis of $(CH_3)_2Sn^{2+}$ was studied potentiometrically, in different aqueous media (sodium and tetramethylammonium chlorides, sodium nitrate, sodium perchlorate, and sodium sulfate), in a wide range of ionic strength, at $t = 25$ °C. Least squares calculations are consistent with the formation of the species $[M(OH)]^+$, $[M(OH)_2]^0$, $[M(OH)_3]^-$, $[M_2(OH)_2]^{2+}$, and $[M_2(OH)_3]^+$, with $M = (CH_3)_2Sn^{2+}$. The dependence on ionic strength for different salt solutions was taken into account by using a Debye−Hückel type equation. Medium effects were explained by considering the formation of the chloride and sulfate complexes, $[(CH_3)_2SnCl]^+$, $[(CH_3)_2SnCl_2]^0$, $[(CH_3)_2Sn(OH)Cl]^0$, $[(CH_3)_2Sn(OH)_2Cl]^-$, $[(CH_3)_2Sn(SO_4)]^0$, $[(CH_3)_2Sn(SO_4)_2]^{2-}$, $[(CH_3)_2Sn(OH)(SO_4)]^-$, and $[(CH_3)_2Sn(OH)_2(SO_4)]^{2-}$. Thermodynamic hydrolysis constants of $(CH_3)_2Sn^{2+}$ and formation constants of the complex species with chloride and sulfate ions are reported.

Introduction

Organotin(IV) compounds are used in a wide number of different industrial commodities, including production of poly(vinyl chloride) stabilizers, industrial catalyst, industrial and agricultural biocides, timber preservatives, antifouling paints and antimold agents, to mention only the major applications (Davies and Smith, 1982). Owing to the well-known toxicity, which is correlated to the number, to the kind of organic groups bonded to tin(IV) atom, and to their structure, organotin(IV) derivatives attracted the attention not only of environmental protection agencies but also of a number of research groups in all parts of the world. In particular, the cytotoxicity study of the organotin(IV) halides, oxides, and carboxylates and of many newly synthetized organotin(IV) complexes has been the aim of a number reports (Arakawa and Wada, 1993; Mansueto *et al.*, 1993; Mennie and Craig, 1993; Thayer, 1984; Vitturi *et al.*, 1994). In contrast, there are few data in literature about the chemical behavior of these compounds in aqueous solution. Organotin cations are considered to be acids, in the Lewis scale, of different hardnesses, depending on the groups bonded to the tin(IV) (Tobias, 1966). Consequently, they show a strong tendency to hydrolysis in aqueous solution, as demonstrated by Tobias and Friedline (1965). Other studies on the interactions of the dimethyltin(IV) cation with O-donor ligands (Arena *et al.*, 1989, 1990; Cucinotta *et al.*, 1992) have been recently reported, confirming the results previously obtained in the hydrolysis investigations. Unfortunately, thermodynamic parameters reported in all these studies refer to a single ionic medium and a single value of ionic strength. From these data, therefore, it is impossible to know the behavior of organotin compounds in a multicomponent solution, in order to describe the chemical speciation of these compounds in natural fluids. Since it is generally recognized that there is correlation between the biological activity and the chemical form of metal ions (free, complexed, hydrolyzed) present in the environment, some investigations on the chemical speciation of $(CH_3)_2Sn^{2+}$, as representative of diorganotin(IV) compounds, in different aqueous ionic media containing the main constituents of natural fluids (sodium, chloride, and sulfate ions), in a large ionic strength range, are under study in these laboratories.

In this paper we report a potentiometric investigation (H^+-glass electrode) on the hydrolysis of $(CH_3)_2Sn^{2+}$, at 25 °C and in the following aqueous media [in parentheses, the ionic strength range ($mol{\cdot}dm^{-3}$)]: $NaNO_3$ (0.01 to 3), $NaClO_4$ (0.01 to 3), NaCl (0.01 to 1.5), Me_4NCl (0.01 to 1), and Na_2SO_4 (0.03 to 1).

Experimental Section

Chemicals. Dimethyltin(IV) salt solutions have been prepared from dimethyltin oxide by reaction with stoichiometric amounts of the different acids (HCl, HNO_3, $HClO_4$, and H_2SO_4). Dimethyltin oxide was prepared, according to literature methods (Davies and Smith, 1982), from the reaction of the commercial $(CH_3)_2SnCl_2$ salt with ammonia in ethanol solution. After filtration, the oxide was dried in a oven at 40 °C. All other reagents were of analytical grade (from Fluka or C. Erba), with a purity always >99%. The commercial salt $NaClO_4$ (by Carlo Erba) was recrystallized before use. NaCl and Na_2SO_4 salts were used without further purification, their purity being checked by liquid chromatography with conductometric detection (by Dionex). Hydrochloric acid and sodium hydroxide stock solutions were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. Tetramethylammonium chloride (Me_4NCl) and tetramethylammonium hydroxide (Me_4NOH) were purified as recommended by Perrin *et al.* (1966). Hydrochloric, nitric, and perchloric acid solutions, used to react with dimethyltin oxide, were standardized against tris(hydroxymethyl)aminomethane or sodium carbonate. Concentrations of NaOH, Me_4NOH, and strong acids were also checked by cross titrations. All solutions were prepared with analytical grade water (R = 18 $M\Omega{\cdot}cm^{-1}$), using grade A glassware.

Apparatus. Measurements were performed by using an apparatus consisting of a potentiometer Metrohm model

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Table 1. Thermodynamic Equilibrium Constants ($I = 0$ mol·dm^{-3}) for the Hydrolysis of $(CH_3)_2Sn^{2+}$ (M^{2+}) at $t = 25$ °C

reaction[a]	$-\log \beta$[b]	reaction[a]	$\log K$
$M^{2+} = [M(OH)]^+ + H^+$	2.86 ± 0.05		
$M^{2+} = [M(OH)_2]^0 + 2H^+$	8.16 ± 0.05	$[M(OH)]^+ = [M(OH)_2]^0 + H^+$	-5.30
$M^{2+} = [M(OH)_3]^- + 3H^+$	19.35 ± 0.15	$[M(OH)_2]^0 = [M(OH)_3]^- + H^+$	-11.19
$2M^{2+} = [M_2(OH)_2]^{2+} + 2H^+$	4.99 ± 0.10	$2M(OH)^+ = [M_2(OH)_2]^{2+}$	0.73
$2M^{2+} = [M_2(OH)_3]^+ + 3H^+$	9.06 ± 0.08	$[M(OH)]^+ + [M(OH)_2]^0 = [M_2(OH)_3]^+$	1.96

reaction[c]	$-\log \beta$	reaction[c]	$\log K$
$M^{2+} + OH^- = [M(OH)]^+$	11.14		
$M^{2+} + 2OH^- = [M(OH)_2]^0$	19.84	$[M(OH)]^+ + OH^- = [M(OH)_2]^0$	8.70
$M^{2+} + 3OH^- = [M(OH)_3]^-$	22.65	$[M(OH)_2]^0 + OH^- = [M(OH)_3]^-$	2.81
$2M^{2+} + 2OH^- = [M_2(OH)_2]^{2+}$	23.01	$2[M(OH)]^+ = [M_2(OH)_2]^{2+}$	0.73
$2M^{2+} + 3OH^- = [M_2(OH)_3]^+$	32.94	$[M(OH)]^+ + [M(OH)_2]^0 = [M_2(OH)_3]^+$	1.96

[a] Hydrolysis reaction. [b] Uncertainties expressed as 3 times the standard deviation. [c] Formation reaction.

605, equipped with a combined glass electrode (Ross, from Orion) and by a motorized buret Metrohm model 654. The apparatus was connected to a PC, and automatic titrations were performed by using a suitable computer program (titrant delivery, data acquisition, check for the stability of emf). The measurement cells (25 or 50 cm^3) were thermostated at $t = (25.0 \pm 0.1)$ °C. All titrations were carried out by stirring magnetically and by bubbling purified and presaturated N_2 through the solution, in order to exclude O_2 and CO_2 inside.

Procedure. A 25 cm^3 aliquot of solution containing $(CH_3)_2SnX_2$ ($X = Cl^-$, NO_3^-, ClO_4^-) or $(CH_3)_2SnSO_4$ (5−15 mmol·dm^{-3}) and the background salt (sodium chloride, nitrate, sulfate or perchlorate), at different concentrations, were titrated with standard NaOH solution up to pH ~ 11−11.5 (60−80 points). Analogous titrations were carried out by using Me_4NCl as the background salt and Me_4NOH as titrant. For each experiment, independent titrations of acidic solutions (hydrochloric, nitric, sulfuric, or perchloric acids) with standard NaOH or Me_4NOH, in the same ionic strength conditions as the systems to be investigated, were carried out, in order to determine the 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 nonlinear least squares computer program ESAB2M (De Stefano *et al.*, 1987) 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 the calculation of complex formation constants, together with the parameters for the dependence on ionic strength, BSTAC (De Stefano *et al.*, 1993) and STACO (De Stefano et al., in press) computer programs were used. Statistical methods were used for the selection of species, as proposed by Vacca and Sabatini (1986). The ES4ECI (De Robertis *et al.*, 1986; De Stefano *et al.*, 1993) program was used to draw the distribution diagrams. Concentrations and formation constants are given in the molar scale.

Results and Discussion

Ionic Strength Dependence of Formation Constants. The general Debye−Hückel type equation (1) can be used to take into account the dependence on ionic strength of formation constants (β = generic equilibrium constant; ${}^{T}\beta$ = constant at infinite dilution)

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

with

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

where C, D, and E are empirical parameters, which can be obtained by fitting experimental data. Results of a series of investigations (Daniele *et al.*, 1991; De Stefano *et al.*, 1993) showed that, when all the interactions occurring in the solution are considered (or they are negligible, *i.e.* $K < 0.1$ dm^3·mol^{-1}), in the range $0 \le I \le 1$ mol·dm^{-3}, the above empirical parameters are dependent only on the stoichiometry of the formation reaction:

$$C = 0.10p^* + 0.23z^*; \qquad D = -0.10z^*; \qquad E = 0 \quad (2)$$

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

(the parameter E becomes relevant for $I > 1$ mol·dm^{-3}). When hydrolysis reactions are considered, the activity of water must be taken into account, too. For all the electrolytes here considered, the simple relationship $\log a_w = -0.015I$ (with a mean error $\epsilon \sim 0.002I$) can be used. Therefore

$$C = 0.085p^* + 0.23z^* \quad (3)$$

Hydrolytic Species. On the basis of literature data (Arena *et al.*, 1989; Yasuda and Tobias, 1963; Tobias and Yasuda, 1964; Tobias and Friedline, 1965; Natsume *et al.*, 1994), the formation of the following hydrolytic species has been hypothesized: $[(CH_3)_2Sn(OH)]^+$, $[(CH_3)_2Sn(OH)_2]^0$, $[(CH_3)_2Sn(OH)_3]^-$, $[((CH_3)_2Sn)_2(OH)_2]^{2+}$, $[((CH_3)_2Sn)_2(OH)_3]^+$, $[((CH_3)_2Sn)_3(OH)_4]^{2+}$, $[((CH_3)_2Sn)_2(OH)_4]^0$, $[((CH_3)_2Sn)_3(OH)_2]^{4+}$, $[((CH_3)_2Sn)_4(OH)_5]^{3+}$, and $[((CH_3)_2Sn)_4(OH)_6]^{2+}$. Least squares calculations are consistent with the formation of three mononuclear, $[(CH_3)_2Sn(OH)_q]^{2-q}$ (q = 1, ..., 3) and two binuclear, $[((CH_3)_2Sn)_2(OH)_q]^{4-q}$ (q = 2, 3), species. Mononuclear species are formed in high percentages (>70%), while binuclear species do not exceed 20−30%, in our experimental conditions.

Hydrolysis constants are expressed as [$M^{2+} = (CH_3)_2Sn^{2+}$]

$$\beta_{pq} = [M_p(OH)_q][H]^q[M]^{-p}$$

according to reaction 4

$$pM^{2+} = M_p(OH)_q^{\,p-q} + qH^+ \quad (4)$$

Curves $\log \beta_{pq} = f(I)$, for the various background salts (see also Tables 1*− 6* of supporting information), converge to a single value of $\log {}^{T}\beta_{pq}$, *i.e.* the thermodynamic constant (at $I = 0$ mol·dm^{-3}), which was calculated (Table 1) by a smoothing procedure. At $I \ne 0$ mol·dm^{-3}, the stability trend of hydroxo species is $NaClO_4 \sim NaNO_3 \gg NaCl \sim (CH_3)_4NCl > Na_2SO_4$. As an example, we report in Figure

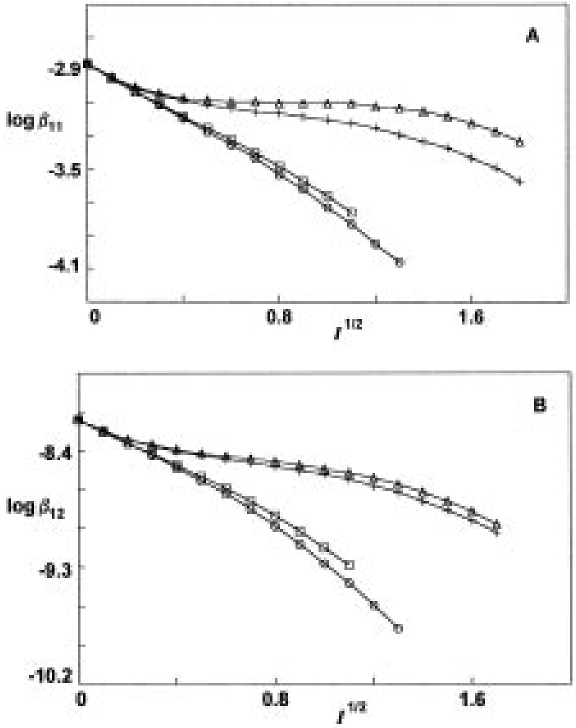

Figure 1. Dependence on ionic strength of (A) log β_{11} and (B) log β_{12} (t = 25 °C): (+) $NaNO_3$; (△) $NaClO_4$; (□) Me_4NCl; (○) NaCl.

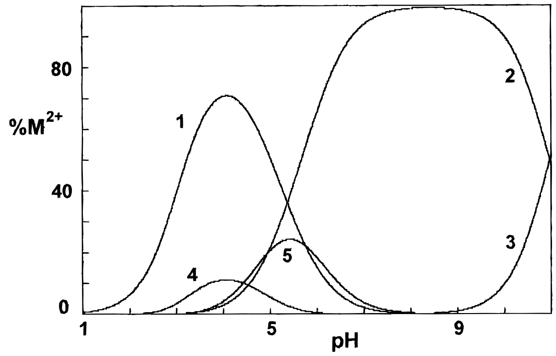

Figure 2. Distribution diagram of $(CH_3)_2Sn^{2+}$ (M^{2+}) hydrolytic species *vs* pH at t = 25 °C and I = 0.5 mol·dm^{-3} in $NaNO_3$. [M^{2+}]: 10 mmol·dm^{-3}. Species: (1) $[M(OH)]^+$; (2) $[M(OH)_2]^0$; (3) $[M(OH)_3]^-$; (4) $[M_2(OH)_2]^{2+}$; (5) $[M_2(OH)_3]^+$.

1 the dependence on ionic strength of the main species, $[(CH_3)_2Sn(OH)_2]^0$ and $[(CH_3)_2Sn(OH)]^+$, for the various background salts (except for Na_2SO_4). Formation constants $\beta_{pq}^{OH} = [M_p(OH)_q][M]^{-p}[OH]^{-q}$ can be obtained using the appropriate value of the ionic product of water, *i.e.* $\beta_{pq}^{OH} = \beta_{pq}pK_w^{\,q}$. The values obtained in this work for pK_w are expressed by the equation

$$pK_w = 14.00 - 2\sqrt{I}/(2 + 3\sqrt{I}) + CI + EI^2 \qquad (1a)$$

with $C = 0.242$, E = −0.005 ($NaClO_4$); $C = 0.160$, $E = 0$ ($NaNO_3$); $C = 0.159$, $E = 0$ (NaCl); and $C = 0.326$, $E = 0.010$ (Me_4NCl), in the considered ionic strength (I, mol dm^{-3}) ranges.

$NaNO_3$ and $NaClO_4$ Media. Hydrolysis constants in $NaNO_3$ and $NaClO_4$ are quite similar, and calculations for the determination of the parameters for the dependence on ionic strength were performed in two ways. (a) Data for the two background salts were analyzed separately, and the values of empirical parameters of eq 1 are reported in Table 2. (b) Since at $I \leq 1$ mol·dm^{-3}, curves of log $\beta_{pq} = f(I)$ are superimposed, within experimental errors, data for the two background salts were analyzed simultaneously (results are reported in Table 2). In all cases we assumed $D = -0.10z^*$; small deviations are counterbalanced in the parameters C and E. Moreover, for $NaNO_3$ and $NaClO_4$, at $I \leq 1$ mol dm^{-3}, we have

$$C = 0.081p^* + 0.216z^* \qquad (D = -0.10z^*, E = 0) \qquad (5)$$

with an estimated error ≤0.05 log units. Equation 5 can be compared with eq 3: as can be seen (Table 2), empirical parameters calculated with the two equations are quite similar. This indicates that interactions of $(CH_3)_2Sn^{2+}$ with NO_3^- and ClO_4^- can be considered as negligible. In Figure 2 we report the distribution *vs* pH of the hydrolytic species (I = 0.5 $NaNO_3$). The mononuclear complex $[(CH_3)_2Sn(OH)]^+$ is the predominant species in the acidic pH range (at pH = 4, ~70%), and the complex $[(CH_3)_2Sn(OH)_2]^0$ shows ~100% formation in the pH range 7.5−9.5. The species $[(CH_3)_2Sn(OH)_3]^-$ becomes predominant at pH > 11. Binuclear species are formed in fairly low percentages, depending on the concentration of $(CH_3)_2Sn^{2+}$. In the conditions of Figure 2, the species $[((CH_3)_2Sn)_2(OH)_2]^{2+}$ and $[((CH_3)_2Sn)_2(OH)_3]^+$ show a maximum formation percentage at pH ~ 4 (~10%) and at pH ~ 5.5 (~25%), respectively.

NaCl, Me_4NCl, and Na_2SO_4 Media. Hydrolysis constants in NaCl and Me_4NCl are much lower with respect to those determined in nitrate or perchlorate media (Figure 1). The parameters for the dependence on ionic strength are reported in Table 3. Also in this case, at low ionic strength values ($I \leq 1$ mol·dm^{-3}), the data obtained in NaCl and Me_4NCl media can be analyzed simultaneously. Empirical parameters for the ionic strength dependence of hydrolysis constants in chloride media (Table 3) are very different with respect to those in nitrate or perchlorate media, clearly indicating that quite strong interactions between $(CH_3)_2Sn^{2+}$ and Cl^- occur and must be taken into consideration. As regards measurements in Na_2SO_4 medium, calculations performed without considering the formation of SO_4^{2-} complexes (*i.e.*, calculations of apparent hydrolysis constants) do not give results.

Chloride and Sulfate Complexes. Hydrolytic species of $(CH_3)_2Sn^{2+}$ are much less stable in chloride than in

Table 2. Dependence on Ionic Strength[a] of Hydrolysis Constants of $(CH_3)_2Sn^{2+}$ in $NaNO_3$ and $NaClO_4$, at t = 25 °C

			C			
p	q^b	z^*	$NaNO_3$ (I = 0.02−3)	$NaClO_4$ (I = 0.04−3)	$NaNO_3 + NaClO_4$ (I = 0.01−1)	c
1	1	2	0.246	0.358	0.305	0.375
1	2	2	0.163	0.220	0.242	0.29
1	3	0	−0.22	−0.31	−0.24	−0.25
2	2	2	0.41	0.47	0.54	0.375
2	3	4	0.56	0.80	0.705	0.75
			$D = -0.10z^*$	$D = -0.10z^*$	$D = -0.10z^*$	$D = -0.10z^*$
			$E = 0.007z^*$	$E = 0.001z^*$	$E = 0$	$E = 0$

[a] Empirical parameters C, D, and E (and z^*) of eq 1. [b] See reaction 4. [c] C values from eq 3.

Table 3. Dependence on Ionic Strength of Hydrolysis Constants of $(CH_3)_2Sn^{2+}$ in NaCl and Me_4NCl, at $t = 25$ °C

			C^a		
p	q^b	$z*$	NaCl ($I = 0.01-1.5$)	Me_4NCl ($I = 0.01-1$)	NaCl + Me_4NCl ($I = 0.01-1$)
1	1	2	−0.485	−0.425	−0.601
1	2	2	−0.725	−0.609	−0.886
1	3	0	−0.895	−1.11	−1.03
2	2	2	−0.57	−0.54	−0.64
2	3	4	−1.20	−0.93	−1.40
			$D = 0$	$D = 0.011z*$	$D = 0.050z*$
			$E = 0.010z*$	$E = 0$	$E = 0$

[a] Empirical parameters *C*, *D*, and *E* (and *z**) of eq 1. [b] See reaction 4.

Table 4. Formation Constants of M − Cl⁻ and M − SO_4^{2-} Complex Species at $I = 0$ mol·dm^{-3} and at $t = 25$ °C [M = $(CH_3)_2Sn^{2+}$]

species	$\log \beta \pm 3s^a$	$z*$	C^b	reacn	$\log K$
$[MCl]^+$	0.92 ± 0.07	4	0.83		
$[MCl_2]^0$	1.07 ± 0.12	6	1.26	$[MCl]^+ + Cl^-$	0.15
$[MCl(OH)]^0$	−2.60 ± 0.05	4	0.80	$[M(OH)]^+ + Cl^-$	0.26
$[MCl(OH)_2]^-$	−8.85 ± 0.12	2	0.37	$[M(OH)_2]^0 + Cl^-$	−0.7
$[M(SO_4)]^0$	2.53 ± 0.05	8	1.93		
$[M(SO_4)_2]^{2-}$	2.98 ± 0.15	8	2.01	$[M(SO_4)]^0 + SO_4^{2-}$	0.45
$[M(SO_4)(OH)]^-$	−1.22 ± 0.04	6	1.38	$[M(OH)]^+ + SO_4^{2-}$	1.64
$[M(SO_4)(OH)_2]^{2-}$	−8.27 ± 0.12	2	0.38	$[M(OH)_2]^0 + SO_4^{2-}$	−0.11

[a] Overal formation constants (according to reaction 6); values at other ionic strengths can be calculated by using eq 1, with *C* values (reported in this table) and $D = -0.1z*$ and $E = 0$, in the ionic strength range $0 \leq I \leq 1$ mol·dm^{-3} (see also Tables 6* and 7* of supporting information. [b] See eq 1.

nitrate or perchlorate media (see Figure 1). This behavior can be explained by assuming that chloride complexes are formed with both free and hydrolyzed dimethyltin cations. This is still more evident for experimental data in Na_2SO_4 medium. Calculations, performed under the assumption that, in the ionic strength range $0 \leq I \leq 1$ mol·dm^{-3}, $NaNO_3$ and $NaClO_4$ media represent the reference baseline (no interactions between the anion of background salt and the dimethyltin(IV) cation), are consistent with the formation of four complex species with both Cl⁻ and SO_4^{2-}: $[(CH_3)_2SnCl]^+$, $[(CH_3)_2SnCl_2]^0$, $[(CH_3)_2Sn(OH)Cl]^0$, $[(CH_3)_2Sn(OH)_2Cl]^-$, $[(CH_3)_2Sn(SO_4)]^0$, $[(CH_3)_2Sn(SO_4)_2]^{2-}$, $[(CH_3)_2Sn(OH)(SO_4)]^-$, $[(CH_3)_2Sn(OH)_2(SO_4)]^{2-}$. In the calculation relative to sulfate complexes, we considered the formation of HSO_4^- and $NaSO_4^-$ species, using the stability constant values already reported (De Robertis *et al.*, 1994, De Stefano *et al.*, 1988). In Table 4 we report the formation constants of these species according to the reaction

$$M^{2+} + iX^{z-} = MX_i(OH)_q^{\ 2-z-q} + qH^+ \qquad (6)$$

Chloride species are fairly weak ($K < 10$ dm^3·mol^{-1}), while sulfate ones, in particular $[(CH_3)_2Sn(SO_4)]^0$ and $[(CH_3)_2Sn(OH)(SO_4)]^-$, are quite stable. In Figure 3, the distribution of the complex species *vs* pH is shown, for a NaCl−Na_2SO_4 mixture: in the experimental conditions reported, both chloride and sulfate species are present in highly significant percentages. It is interesting to note that mono- and bihydrolytic species of Cl⁻ and SO_4^{2-} complexes alter drastically the formation percentages of hydrolytic species of $(CH_3)_2Sn^{2+}$ obtained in a not interacting medium such as $NaNO_3$ (Figure 2).

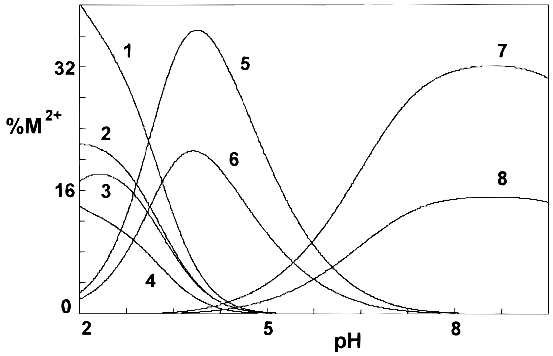

Figure 3. Distribution diagram of $(CH_3)_2Sn^{2+}$ (M^{2+}) hydrolytic species with Cl⁻ and SO_4^{2-} *vs* pH at $t = 25$ °C. [Simple hydrolytic species are not reported for the sake of simplicity.] $[M^{2+}] = 10$, $[Na^+] = 480$, $[Cl^-] = 560$, $[SO_4^{2-}] = 30$ mmol·dm^{-3} (I adjusted to ~0.7 mol·dm^{-3}). Species: (1) $[MCl_2]^0$; (2) $[M(SO_4)]^0$; (3) $[M(SO_4)_2]^{2-}$; (4) $[MCl]^+$; (5) $[M(OH)(SO_4)]^-$; (6) $[M(OH)Cl]^0$; (7) $[M(OH)_2Cl]^-$; (8) $[M(OH)_2(SO_4)]^{2-}$.

Literature Comparison. Few quantitative data can be found in the literature on the hydrolysis of $(CH_3)_2Sn^{2+}$ (Arena *et al.*, 1989; Yasuda and Tobias, 1963; Tobias and Yasuda, 1964; Tobias and Friedline, 1965; Natsume *et al.*, 1994): in Table 5 we report the most significant findings. Only *constant medium* hydrolytic constants have been reported ($I = 0.1$ mol·dm^{-3}), and the values in Table 5 are in fairly good agreement. Tobias and Yasuda (1964) reported also hydrolysis constants at $I = 3$ mol·dm^{-3} ($NaClO_4$): also in this case the agreement with present values is fairly good. Minor polynuclear species, such as $[((CH_3)_2Sn)_4(OH)_6]^{2+}$ and others, have been proposed, but accurate statistical analysis of residuals performed in this work showed that mononuclear and binuclear species are sufficient to explain experimental data. Nevertheless, we must emphasize that the formation of polynuclear hydroxo species is strictly dependent on the cation concentration: our hypothesis, according to which only two polynuclear species are formed, is correct for $(CH_3)_2Sn^{2+} \leq 15$ mmol·dm^{-3}. As concerns Cl⁻ complexes, Tobias and Yasuda (1964) estimated, at $I = 0.1$ mol·dm^{-3}, $\log K = 1.4$ for the interaction of $(CH_3)_2Sn^{2+}$ with Cl⁻ from the difference of $\log \beta_{11}$ in NaCl and in KNO_3; by taking into account that this estimate includes contributions of both $[(CH_3)_2SnCl]^+$ and $[(CH_3)_2Sn(OH)Cl]^0$ complexes, we have a substantial agreement with present findings in terms of order of magnitude. No investigations on SO_4^{2-} complexes and on medium effects have been reported till now.

Table 5. Literature Comparisons for the Hydrolysis Constants of $(CH_3)_2Sn^{2+}$, at $t = 25$ °C and $I = 0.1$ (or 3) mol·dm^{-3}

medium	$-\log \beta_{11}{}^a$	$-\log \beta_{12}{}^a$	$-\log \beta_{13}{}^a$	$-\log \beta_{22}{}^a$	$-\log \beta_{23}{}^a$	ref
KNO_3	3.12	8.43	19.45	5.05	9.75	Arena *et al.* (1989)
NaCl	3.25	8.54		5.05	9.81	Tobias and Yasuda (1964)
KNO_3	3.2			4.6		Yasuda and Tobias (1963)
$NaNO_3$	3.18	8.42		4.69	9.64	Natsume *et al.* (1994)
$NaNO_3$	3.06	8.36	19.36	5.16	9.44	this work
NaCl	3.12	8.45	19.48	5.2	9.7	this work
$NaClO_4{}^b$	3.54	8.98		4.60	9.76	Tobias and Yasuda (1964)
$NaNO_3{}^b$	3.52	9.07	20.1	5.1	10.2	this work
$NaClO_4{}^b$	3.30	9.08	20.3	5.1	9.7	this work

[a] See reaction 4. [b] $I = 3$ mol·dm^{-3}.

Concluding Remarks. The main conclusions can be summarized as follows: (a) dimethyltin(IV) cation forms five hydrolytic species, and the mononuclear ones show very high formation percentages; (b) the presence of NaCl and Na_2SO_4 influences the speciation picture of $(CH_3)_2Sn^{2+}$ owing the formation of chloride and sulfate complexes; (c) results reported in this work, *i.e.* thermodynamic hydrolysis and formation constants of $(CH_3)_2Sn^{2+}$, together with parameters for the ionic strength dependence of formation constants, allow the speciation of $(CH_3)_2Sn^{2+}$ in very different aqueous systems containing the main components of natural fluids, such as sodium, chloride, and sulfate ions, to be studied. For example, for the concentration values of chloride and sulfate similar to that of sea water (35 ‰ salinity, Figure 3), $(CH_3)_2Sn^{2+}-Cl^-$ and $(CH_3)_2Sn^{2+}-SO_4^{2-}$ complex species show a relevant formation in the pH range of natural fluids (*e.g.* seawater, pH = 8.2).

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Supporting Information Available:

Tables (1*−8*) containing smoothed hydrolysis constants at different ionic strengths, in various background salts, and formation constants for chloride and sulfate complexes are available as supporting information (8 pages). Ordering information is given on any current masthead.

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