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Interaction of Alkyltin(IV) Compounds with Ligands of Interest in the Speciation of Natural fluids: Complexes of $(CH_3)_2Sn^{2+}$ with Carboxylates

Concetta De Stefano,[1]* Antonio Gianguzza,[2]* Francesca Marrone[2] and Daniela Piazzese[2]

[1] Dipartimento di Chimica Inorganica, Analitica e Chimica Fisica, Università, Salita Sperone 31, I-98166 Messina, Italy

[2] Dipartimento di Chimica Inorganica, Università, Via Archirafi 26-28, I-90123 Palermo, Italy

Complex formation by $(CH_3)_2Sn^{2+}$ with acetate (ac), malonate (mal), 1,2,3-propanetricarboxylate (tricarballylate, tca) and 1,2,3,4-butanetetracarboxylate (btc) ligands in aqueous solution is reported. The study has been performed by potentiometry ($[H^+]$–glass electrode) at $T = 25$ °C, and in the $0 \leq I \leq 1$ mol dm^{-3} ionic strength range. In order to evaluate the salt effects on the formation constants of the complex species, and to contribute to the definition of the chemical speciation of diorganotin(IV) compounds in natural waters where carboxylic ligands are naturally present, interactions of NaCl (which is the major component of all natural fluids), with the components of the systems under investigation have also been considered. A model for the ionic strength dependence of the formation constant was used in order to calculate the values of thermodynamic constants, at infinite dilution, for all the proposed species, by considering hydrolytic species too. A relationship between the charges on the different ligands considered and the stabilities of the complex species formed is also discussed. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Owing to the well-known toxicity of organotin(IV) compounds,[1,2] it is very important to check their presence in natural fluids both as regards their total content and their chemical behaviour towards other components of these fluids, by considering suitable chemical speciation models. Several studies[3] have been recently reported in the literature on the analytical methodologies useful for detecting the relative amounts of the different mono-, di- and tri-organotin(IV) derivatives in the aquatic environment, in order to evaluate their fate and transformation, both in water and in sediments. In contrast there are few and fragmentary data in the literature about the chemical interactions of these compounds in aqueous solution,[4–9] where they behave as Lewis acids of different hardnesses.[10] In particular, there are no data on their chemical behaviour in a multicomponent aqueous solution such as natural waters, where different interacting ions are present simultaneously. Having this situation in mind, we planned a systematic study of the interactions of alkyltin(IV) compounds with different potential ligand molecules in aqueous solution containing the ions which are the principal (macro) components of natural waters. In a recent paper[11] we reported a comprehensive study on the hydrolysis of the $(CH_3)_2Sn^{2+}$ cation

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* Correspondence to: Concetta De Stefano and Antonio Gianguzza.

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in different aqueous media ($NaNO_3$, $NaClO_4$, $NaClO_4$, NaCl and Na_2SO_4), over a wide ionic strength range. A model based on the dependence on ionic strength of formation constants was used to calculate both the thermodynamic hydrolysis constants ($I=0$ mol dm^{-3}) of the $(CH_3)_2Sn^{2+}$ cation and the formation constants of chloride and sulphate complex species. The data obtained allowed us to propose a chemical base model accounting for the network of interactions of $(CH_3)_2Sn^{2+}$ in the presence of the major constitutents of natural fluids (i.e. chloride and sulphate ions), and can be used as definitive results in subsequent speciation studies.

In this paper we extended our investigations to the study of the interactions of $(CH_3)_2Sn^{2+}$ with other ligands occurring naturally in natural fluids. Among these, low- and high-molecular-weight ligands containing carboxylic groups, such as amino acids (mostly, acidic amino acids), polysaccharides (such as uronic acids, pectin and its derivatives), linear and aromatic polycarboxylic acids, and humic substances derived from degradation of vegetable matter are always present in natural waters.[12] The great variability of the compositions of organic dissolved matter in natural waters do not permit us to indicate a definite concentration for each class of organic compounds. However, estimate values have been reported by some authors[13–16] in terms of functional group content. In particular, as far as –COOH groups are concerned, a content of 7.1–8.9 and 9.6–16.6 meq g^{-1} in the water humic (WHA) and fulvic (WFA) fractions, respectively, has been reported.

In spite of the irrelevant total concentration of carboxylic groups in natural waters, nevertheless, their generally high complexing capacity renders it necessary to study their possible interactions with other microcomponents such as metallic and organometallic cations, which are, generally, present at very low concentrations.

For the above reasons, and with the aim to add further elements for a more complete picture of the chemical speciation of diorganotin(IV) compounds in natural fluids, we report here a study on the interactions of the $(CH_3)_2Sn^{2+}$ cation with mono-, di-, tri- and tetra-carboxylic ligands in different aqueous ionic media, by considering all the possible interactions between components both of the background salts and of the systems under investigation. In particular, acetate (ac), malonate (mal), 1,2,3-propanetricarboxylate (tricarballylate, tca) and 1,2,3,4-butane-tetracarboxylate (btc) ligands have been considered.

The investigation has been carried out by potentiometry ([H^+]–glass electrode), in the ionic stength range $0 \leqslant I \leqslant 1$ mol dm^{-3}, at $T=25$ °C, in aqueous $NaNO_3$, Me_4NCl and NaCl ionic media.

EXPERIMENTAL

Chemicals

Dimethyltin(IV) salt solutions were prepared from dimethyltin oxide by reaction with stoichiometric amounts of the different acids (HCl, HNO_3). Dimethyltin oxide was prepared, according to the literature method,[17] from the reaction of the commercial $(CH_3)_2SnCl_2$ salt with ammonia in ethanol solution. After filtration, the oxide was dried in an oven at 40 °C. All the other reagents were of analytical grade (from Fluka or Merck), with a purity always $>99.5\%$. Carboxylic ligands were used without further purification, their purity being checked both by liquid chromatography equipped with conductometric detection (by Dionex), and by potentiometric titrations. Hydrochloric acid and sodium hydroxide stock solutions were standardized against sodium carbonate and potassium hydrogenphthalate, respectively. Tetramethylammonium chloride (Me_4NCl) and tetramethylammonium hydroxide (Me_4NOH) were purified as recommended by Perrin *et al.*[18] Hydrochloric and nitric acid solutions, used to dissolve dimenthyltin 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 ($R=18$ MΩ cm^{-1}), using grade A glassware.

Apparatus

Measurements were performed on an apparatus consisting of a Metrohm model 605 potentiometer equipped with a combination glass electrode (Ross, from Orion) and with a Metrohm model 654 motorized burette. 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 e.m.f.). The measurement cells (25 or 50 cm^3) were thermostatted at $T=(25.0\pm0.1)$ °C. All titrations were carried out with magnetical stirring and with purified and pre-saturated N_2 bubbling through the solution in order to exclude O_2 and CO_2 from it.

Procedure

Solution (25 cm^3) containing $(CH_3)_2SnX_2$ (5–15 mmol dm^{-3}, with X=Cl or NO_3), obtained by adding a slight excess of the corresponding acid to $(CH_3)_2SnO$, and the carboxylic ligand (acetate, malonate, tricarballylate and butanetetracarboxylate) in NaCl, $NaNO_3$ or Me_4NCl, as background salts to adjust the ionic strength to different values, were titrated with standard NaOH or Me_4NOH solutions up to pH ~11 to 11.5 (60 to 80 points). For each experiment, independent titrations of acidic solutions (hydrochloric or nitric acid) with standard NaOH or Me_4NOH in the same conditions of ionic strength 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. Some experimental details of the potentiometric measurements are reported in Table 1.

Calculations

The non-linear least-squares computer program ESAB2M[19] was used for the refinement of all the parameters of an acid–base titration (E^0, 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[20] and STACO[21] computer programs were used. The ES4ECl[20, 22] program was used to draw the distributions diagrams and to calculate the percentage formation of the species. Concentrations and formation constants are given in the molar scale.

RESULTS

Carboxylic ligands form protonated species H_jL ($j=1\ldots m$, m=no. of carboxylic groups) and Na_pH_qL weak complexes [$p=1\ldots(n-1)$, $q=0, 1), \ldots (m-1)$]; both protonation constants and Na^+ complex formation constants have already been determined,[23–26] together with their dependence on ionic strength, and they are reported in Table 2. Protonation constants of different carboxylic ligands are always $<10^8$, and therefore, in the natural fluids pH range, it is expected that fairly stable free-anion/cation complexes would exist. Sodium complexes are quite weak for carboxylic anions bearing low charges (acetate and malonate), whilst fairly stable species are formed with tri- and tetra-charged anions. Dimethyltin(IV) cation forms five hydrolytic species and four chloride complexes (two mixed OH^-–Cl^- species) whose equilibrium constants[11] are reported in Table 3. The hydrolysis of $(CH_3)_2Sn^{2+}$ is almost complete in the neutral pH range, in the absence of complexing ligands, and Cl^- species are sufficiently stable to play an important role in the speciation of this organotin(IV) compound in natural fluids.

Calculations on the determination of dimethyltin(IV)–carboxylic ligand complexes have

Table 1 Experimental details of potentiometric measurements (T=25 °C)

Ligand	Ionic medium	C_L[a] (mol dm^{-3})	C_M[b, c] (mol dm^{-3})	Ionic strength (mol dm^{-3})	No. of titrations	No. of exptl points
ac^-	$NaNO_3$	10–25	5–8	0.1–1	30	933
mal^{2-}	$NaNO_3$	5–25	3–15	0.1–1	40	2227
	NaCl	5–25	4–15	0.1–1	37	1825
	Me_4NCl	5–25	5–15	0.1–1	20	1130
tca^{3-}	$NaNO_3$	6–20	5–8	0.1–1	15	605
btc^{4-}	$NaNO_3$	6–20	5–8	0.1–1	15	553

[a] L=carboxylic ligands.
[b] $M=(CH_3)_2Sn^{2+}$.
[c] Concentration ratios varied from C_L(min)/C_M(max) to C_L(max)/C_M(min).

Table 2 Protonation and Na^+ complex formation constants of carboxylic ligands at $I = 0$ mol dm^{-3} and $T = 25$ °C

System[a]			log β			
p	q	r	ac	mal	tca	btc
0	1	1	4.75	5.71	6.49	7.18
0	1	2	—	8.55	11.41	13.01
0	1	3	—	—	15.09	17.54
0	1	4	—	—	—	20.92
1	1	0	− 0.1	0.91	1.40	1.82
1	1	1	—	5.66	7.31	8.67
1	1	2	—	—	11.56	13.94
1	1	3	—	—	—	17.76
2	1	0	—	—	1.98	3.45
2	1	1	—	—	6.96	9.31
3	1	0	—	—	—	3.30

[a] Indices refer to the reaction: $p\mathrm{Na}^+ + q\mathrm{L}^{z-} + 2\mathrm{H}^+ \rightarrow \mathrm{Na}_p\mathrm{L}_q\mathrm{H}_r^{(p+r-zq)}$.

been performed in two ways: (a) by neglecting the formation of Cl^-–$(CH_3)_2Sn^{2+}$ and Na^+–L^{z-} (L^{z-} = carboxylic ligand) complexes, and (b) by considering the complete speciation of the different systems, i.e. by including weak species in the model also. In the first case the so-called ‘apparent’ formation constants are used in describing the system [protonation constants of ligands, hydrolysis constants of dimethyltin(IV) formation constants of carboxylic complexes], whilst in the second case the so-called ‘effective’ formation constants are used.

To take into account the dependence on ionic strength of formation constants, a Debye–Hückel-type equation has been used[20, 23–30] (Eqn [1]):

$$\log \beta = \log ({}^{\mathrm{T}}\beta) - z^* G(I) + L(I) \qquad [1]$$

where

$$G(I) = \sqrt{I}/(2 + 3\sqrt{I}) \qquad [1a]$$

$$L(I) = CI + DI^{3/2} \qquad [1b]$$

and

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

with β = generic constant; ${}^{\mathrm{T}}\beta$ = formation constant at infinite dilution; C and D = empirical parameters. It has been shown[20, 23–30] that, when effective formation constants are used, the

Table 3 Hydrolysis constants and Cl^- complex formation constants of $(CH_3)_2Sn^{2+}$ at $I = 0$ mol dm^{-3} and $T = 25$ °C

Hydrolytic species[a]				Chloride species[a]			
p	q	r	log β	p	q	r	log β
1	0	− 1	− 2.86 ± 0.05	1	1	0	0.92 ± 0.07
1	0	− 1	− 8.16 ± 0.05	1	2	0	1.07 ± 0.12
1	0	− 3	− 19.35 ± 0.15	1	1	− 1	− 2.60 ± 0.05
2	0	− 2	− 4.99 ± 0.10	1	1	− 2	− 8.85 ± 0.12
2	0	− 3	− 9.06 ± 0.08	—	—	—	—

[a] Indices refer to the reaction: $p\mathrm{M}^{2+} + q\mathrm{Cl}^- + r\mathrm{H}^+ \rightarrow \mathrm{M}_p\mathrm{Cl}_q\mathrm{H}_r^{(2p+r-q)}$ negative r values refer to the hydrolysis reaction: $p\mathrm{M}^{2+} + q\mathrm{Cl}^- \rightarrow \mathrm{M}_p\mathrm{Cl}_q(OH)_r + r\mathrm{H}^+$.

Table 4 Formation constants of $(CH_3)_2Sn^{2+}$–carboxylic ligands complexes at $I=0$ mol dm^{-3} and a $T=25$ °C

	log K[b]			
Reaction[a]	ac	mal	tca	btc
$M+L \rightarrow ML$	3.01 ± 0.03	5.43 ± 0.05	6.69 ± 0.08	8.20 ± 0.10
$M+L+H \rightarrow MLH$	—	7.81 ± 0.10	11.12 ± 0.03	13.34 ± 0.08
$M+L+2H \rightarrow MLH_2$	—	—	14.38 ± 0.07	17.47 ± 0.05
$M+L+3H \rightarrow MLH_3$	—	—	—	20.40 ± 0.06
$M+2L \rightarrow ML_2$	5.25 ± 0.07	7.21 ± 0.10	—	—
$M+L+H_2O \rightarrow ML(OH)+H^+$	−0.925 ± 0.025	−0.01 ± 0.10	1.01 ± 0.11	1.80 ± 0.11
$M+L+OH \rightarrow ML(OH)$	13.075	13.99	15.01	15.80
$M+LH \rightarrow MLH$	—	2.11	4.63	6.16
$M+LH_2 \rightarrow MLH_2$	—	—	2.97	4.46
$M+LH_3 \rightarrow MLH_3$	—	—	—	2.86
$ML+L \rightarrow ML_2$	2.24	1.78	—	—
$ML+OH \rightarrow ML(OH)$	10.07	8.56	8.32	7.60
$M(OH)+L \rightarrow ML(OH)$	1.94	2.85	3.87	4.66

[a] Charges omitted for simplicity.
[b] ±3 SD.

empirical parameters can be expressed as Eqn [1c]:

$$C=c_0p^*+c_1z^* \qquad \text{and} \qquad D=d_1z^* \qquad [1c]$$

where

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

with c_0, c_1 and d_1 ($c_0=0.1$, $c_1=0.23$, $d_1=-0.1$) independent of the system.[30] Equation [2], which is simpler, was used for calculating the dependence on ionic strength of both apparent and effective formation constants.

$$\log\beta=\log{}^{T}\beta-z^*[G(I)+0.1\,I^{3/2}]+CI \qquad [2]$$

When hydrolysis reactions $pM+L+qH_2O=M_pL(OH)_q$ are considered, the activity of water must be also considered,[11] which can be expressed simply by $\log a_w=-0.015I$.

Potentiometric measurements were performed at different ionic strengths in the range $0.1 \leqslant I$

Table 5 Dependence of formation constants on ionic strength ($T=25$ °C)

Ligand	Medium	C (empirical parameter)[a]					
		ML	MLH	MLH_2	MLH_3	ML_2	ML(OH)
ac	$NaNO_3$	0.80	—	—	—	0.86	0.99
		1.12	—	—	—	0.96	1.22
mal	$NaNO_3$	1.08	1.17	—	—	0.81	0.76
		1.93	2.06	—	—	1.67	1.53
	NaCl	0.41	0.96	—	—	−0.061	−0.056
		2.02	2.50	—	—	2.35	1.20
	Me_4NCl	0.83	1.01	—	—	0.71	0.41
		1.83	2.28	—	—	1.90	1.17
tca	$NaNO_3$	1.47	1.78	1.95	—	—	0.85
		2.95	3.30	3.45	—	—	2.27
btc	$NaNO_3$	1.67	2.37	2.54	2.84	—	0.82
		3.79	4.70	4.95	5.07	—	2.57

[a] Empirical parameter of Eqn [2]. First row: values calculated using apparent formation constants. Second row: values calculated using effective formation constants.

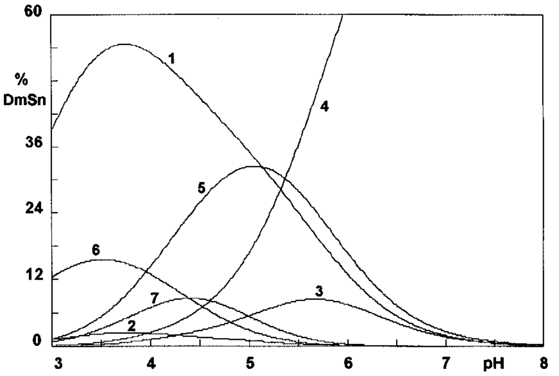

Figure 1 Distribution of the species vs pH for the system $(CH_3)_2Sn^{2+}$–acetate [C_{ac}=25 mmol dm^{-3}; C_M=5 mmol dm^{-3}; I=0.1 ($NaNO_3$)]. Curves: 1, $[M(OH)]^+$; 2, $[M_2(OH)_2]^{2+}$; 3, $[M_2(OH)_3]^+$; 4, $[M(OH)_2]^0$; 5, $[M(ac)(OH)]^0$; 6, $[M(ac)]^+$; 7, $[M(ac)_2]^0$, with M=$(CH_3)_2Sn^{2+}$ and ac=(acetate)$^-$.

(mol dm^{-3}) $\leq$ 1 using $NaNO_3$ as background salt, for all the carboxylic ligands. The study of malonate complexes was extended by considering also Me_4NCl and NaCl as background salts, in order to include the effect of Cl^-.

The analysis of potentiometric data relative to the $(CH_3)_2Sn^{2+}$–ac^- system showed that the species ML^+, ML_2^0 and $ML(OH)^0$ are formed. In the system $(CH_3)_2Sn^{2+}$–mal^{2-} formation of the species ML^0, ML_2^{2-}, MLH^+ and $ML(OH)^-$ takes place. In the system $(CH_3)_2Sn^{2+}$–tricarballylate^{3-} and –butanetetracarboxylate the species ML^{2-z} MH_iL^{2-z+i} (i=1, 2 for tca; and 1,2,3 for btc) and $ML(OH)^{1-z}$ are formed. Different

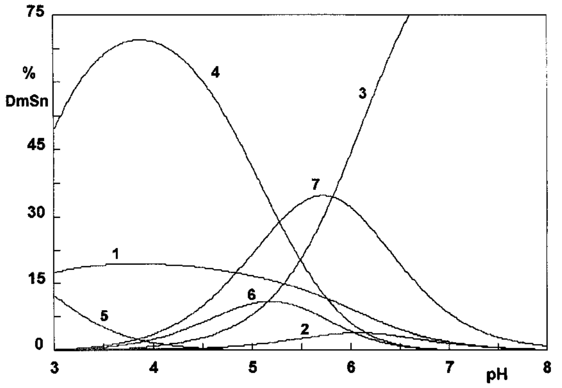

Figure 2 Distribution of the species vs pH for the system $(CH_3)_2Sn^{2+}$–malonate [C_{mal}=15 mmol dm^{-3}; C_M=5 mmol dm^{-3}; I=0.1 ($NaNO_3$)]. Curves: 1, $[M(OH)]^+$; 2, $[M_2(OH)_3]^+$; 3, $[M(OH)_2]^0$; 4, $[M(mal)]^0$; 5, $[M(mal)H]^+$; 6, $[M(mal)_2]^{2-}$; 7, $[M(mal)(OH)]^-$, with M=$(CH_3)_2Sn^{2+}$, mal=(malonate)$^{2-}$.

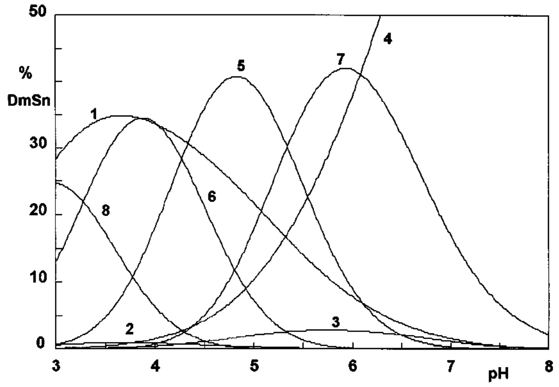

Figure 3 Distribution of the species vs pH for the system $(CH_3)_2Sn^{2+}$–tricarballylate [C_{tca}=10 mmol dm^{-3}; C_M=5 mmol dm^{-3}; I=0.1 ($NaNO_3$)]. Curves: 1, $[M(OH)]^+$; 2, $[M_2(OH)_2]^{2+}$; 3, $[M_2(OH)_3]^+$; 4, $[M(OH)_2]^0$; 5, $[M(tca)]$; 6, $[M(tca)H]^0$; 7, $[M(tca)(OH)]^{2-}$; 8, $[M(tca)(OH)_2]^{3-}$, with M=$(CH_3)_2Sn^{2+}$ and tca=(1,2,3-propanetricarboxylate)$^{3-}$.

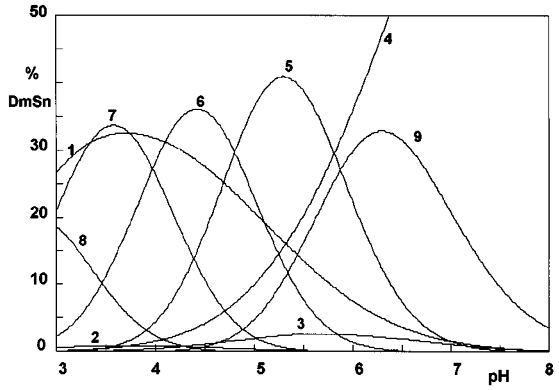

Figure 4 Distribution of the species vs pH for the system $(CH_3)_2Sn^{2+}$–butanetetracarboxylate [C_{btc}=7.5 mmol dm^{-3}; C_M=5 mmol dm^{-3}; I=0.1 ($NaNO_3$)]. Curves: 1, $[M(OH)]^+$; 2, $[M_2(OH)_2]^{2+}$; 3, $[M_2(OH)_3]^+$; 4, $[M(OH)_2]^0$; 5, $[M(btc)]^{2-}$; 6, $[M(btc)H]^-$; 7, $[M(btc)H_2]^0$; 8, $[M(btc)H_3]^+$; 9, $[M(btc)OH]^{3-}$, with M=$(CH_3)_2Sn^{2+}$ and btc=(1,2,3,4-butanetetracarboxylate)$^{4-}$.

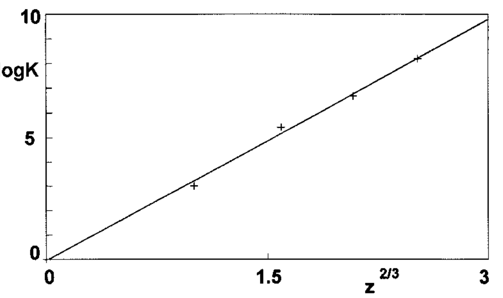

Figure 5 Dependence of complex stability on the carboxylate ligand charge.

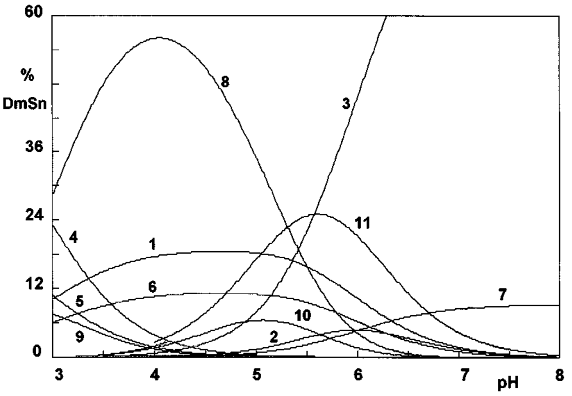

Figure 6 Distribution of the species vs pH for the system $(CH_3)_2Sn^{2+}$–malonate [$C_{mal}=15$ mmol dm^{-3}; $C_M=5$ mmol dm^{-3}; $I=0.5$ (NaCl)]. Curves: 1, $[M(OH)]^+$; 2, $[M_2(OH)_3]^+$; 3, $[M(OH)_2]^0$; 4, $[M(Cl)]^+$; 5, $[M(Cl)_2]^0$; 6, $[M(Cl)(OH)]^0$; 7, $[M(Cl)(OH)_2]^-$; 8, $[M(mal)]^0$; 9, $[M(mal)(H)]^+$; 10, $[M(mal)_2]^{2-}$; 11, $[M(mal)OH]^-$, with $M=(CH_3)_2Sn^{2+}$ and mal = (malonate)$^{2-}$.

speciation schemes were tested and that reported above was the best in terms of statistical considerations. It is noteworthy that in the experimental conditions used in this work no polynuclear species is formed for either tca or btc complex systems. In Table 4 we report the relative formation constants at infinite dilution. For the neutral and protonated species the stability is similar to that of copper(II)–carboxylic ligand complexes [for the species ML, $\log K=2.2$ and 5.7 for ac and mal respectively; $\log K=4.2$ (ML) and $\log \beta=7.2$ (M_2L) for tca (unpublished results from this laboratory)], whilst hydrolytic species $(ML(OH)^{1-z}$ are definitely stronger than those of any divalent transition metal, according to the fairly strong acid characteristics of alkyltin compounds.[10] The dependence on ionic strength, characterized by the empirical parameter C of Eqn [2], is reported in Table 5 for both apparent and effective formation constants. Note that owing to the interference of Na^+ and Cl^-, values relating to the apparent formation constants are much lower than those for effective constants.

DISCUSSION

Stability of $(CH_3)_2Sn^{2+}$–carboxylate ligand complexes

As already seen, the stability of these complexes is comparable with (or somewhat higher than) that of analogous copper(II) complexes, except the hydrolytic species. In order to give a picture of the formation of these species as a function of pH, in Figs 1–4 we report the distribution diagrams for the four systems investigated. As regards the mono- and di-carboxylic ligand anions, only the mixed complex species $[(CH_3)_2Sn(OH)(ac)]^0$ and $[(CH_3)_2Sn(OH)(mal)]^-$ are formed, in a very low percentage, in the neutral pH range (Figs 1 and 2, curves 5 and 7, respectively), the hydrolysis of $(CH_3)_2Sn^{2+}$ being predominant in both cases. In Figs 3 and 4 it is evident that the formation of M(L)(OH), with L = 1,2,3-propanetricarboxylate and 1,2,3,4-butanetetracarboxylate (curves 7 and 9, respectively) is higher than that of homologous species formed in the acetate and malonate systems. This must be attributed to the higher charges of anions, and therefore, to stronger interactions. In all cases, the predominant species is always the hydrolytic one, $[(CH_3)_2Sn(OH)_2]$, in the pH range of interest in natural fluids.

As can be seen from the analysis of data reported in Table 4, the stability of $(CH_3)_2Sn^{2+}$–carboxylic ligand complexes is a positive function of ligand charge. If we consider the reaction: $M^{2+}+L^{z-}=ML^{2-z}$, the relative formation constant can be expressed by the linear relationship (Fig. 5):

$$\log K=3.25\, z^{2/3} \qquad [3]$$

and analogously, for the reaction: $M(OH)+L^{z-}=ML(OH)^{1-z}$, the relationship is

$$\log K=1.87\, z^{2/3} \qquad [4]$$

Formation constants are fitted by Eqns [3] and [4] with a mean deviation $\varepsilon<0.2$ log units. The relationships have a good predictive value and indicate a partial electrostatic nature of the bonds (pure electrostatic bonds should show a dependence on z).

Dependence on ionic strengh and on medium of formation constants

Parameters C (Eqn [2]) for the dependence of formation constants on ionic strength (Table 5) can be used to obtain $\log \beta$ values at different ionic strengths using either effective or apparent models. If we consider effective formation constants, the parameter C can be expressed by Eqn [1c], and calculations, performed using the values in Table 5, giving $c_0=0.09\pm0.02$ and

Table 6 Literature comparison

Reaction	Log β	
	This work[a]	Literature data[b]
$(CH_3)_2Sn^{2+} + ac^- \rightarrow [(CH_3)_2Sn(ac)]^+$	2.65	2.81
$(CH_3)_2Sn^{2+} + ac^- + OH^- \rightarrow [(CH_3)_2Sn(ac)(OH)]^0$	−1.26	−1.32
$(CH_3)_2Sn^{2+} + 2ac^- \rightarrow [(CH_3)_2Sn(ac)_2]^0$	4.67	4.62
$(CH_3)_2Sn^{2+} + mal^{2-} \rightarrow [(CH_3)_2Sn(mal)]^0$	4.65	4.54
$(CH_3)_2Sn^{2+} + mal^{2-} \} + H^+ \rightarrow [(CH_3)_2Sn(mal)^+H]^+$	7.06	6.95
$(CH_3)_2Sn^{2+} + mal^{2-} + OH^- \rightarrow [(CH_3)_2Sn(mal)(OH)]^-$	−0.60	−0.74
$(CH_3)_2Sn^{2+} + 2mal^{2-} \rightarrow [(CH_3)_2Sn(mal)_2]^{2-}$	6.41	6.14

[a] $I = 0.1$ mol dm^{-3} ($NaNO_3$), $T = 25$ °C [values calculated using Eqn [2], with C parameters from Table 5 (first row)].
[b] Data from Ref. 8; $I = 0.1$ mol dm^{-3} (KNO_3), $T = 25$ °C.

$c_1 = 0.229 \pm 0.002$.

These values are in very good agreement with those already obtained[30] using formation data for several systems under the assumption that all significant interactions have been taken into account. As expected, C values calculated using apparent formation constants are rather lower, and the difference $C_{\text{effective}} - C_{\text{apparent}} = \Delta C$ is proportional to the stability of weak Na^+ and Cl^- species. In fact, ΔC, calculated in $NaNO_3$ medium, follows the trend btc > tca > mal > ac, which is the same trend shown by the log K values for $Na^+ + L^{z-} = NaL^{1-z}$ reaction (L = carboxylate ligands; see Table 2). The lowering effect (for malonate) is higher in Me_4NCl than in $NaNO_3$, since chloride complexes of $(CH_3)_2Sn^{2+}$ are stronger than Na^+–carboxylate ligand complexes (see Tables 2 and 3). Finally, the lowering effect in NaCl medium is close to the sum $\Delta C_{(NaNO_3)} + \Delta C_{(Me_4NCl)}$. Taking into account weak interactions, this leads to the complete picture of the speciation of $(CH_3)_2Sn^{2+}$–carboxylic ligand in a particular medium. As an example, we report in Fig. 6, the distribution of the species vs pH for the $(CH_3)_2Sn^{2+}$–malonate system in the presence of NaCl, by considering the interactions of both Na^+ and Cl^-. As can be seen, when interactions of chloride ions are also considered, the formation of the mixed species $[(CH_3)_2Sn(Cl)(OH)_2]^-$ contributes to lower the percentage of $[(CH_3)_2Sn(OH)(mal)]^-$ complex formed (Fig. 6, curve 7) in comparison with that of the same species obtained in $NaNO_3$ ionic medium (Fig. 2, curve 7).

Literature comparisons

A study on the interactions $(CH_3)_2Sn^{2+}$ with acetate and malonate ligands, at $I = 0.1$ mol dm^{-3} (KNO_3) and $T = 25$ °C, has been already reported.[8] Data reported there are comparable with those obtained in this work for the same systems, using $NaNO_3$ ionic medium. In both cases, hydrolytic species have been considered in describing the chemical base model represented by Me(ac), $Me(ac)_2$, Me(ac)(OH), Me(mal), Me(mal)H, Me(mal)(OH) and $Me(mal)_2$ complex species. Formation constant values reported here [at $I = 0.1$ mol dm^{-3} ($NaNO_3$), and $T = 25$ °C] are in good agreement with previous finding (see Table 6). No comparison can be made, as far as the dependence on ionic medium is concerned, for malonate species or for tricarballylate and butanetetracarboxylate complex species of $(CH_3)_2Sn^{2+}$, these last being reported for the first time in this work.

Concluding remarks

(1) Dimethyltin(IV) forms quite stable complexes with carboxylic ligands with formation constants comparable with those of transition metals [rather higher than copper(II)], except for the hydrolytic species $ML(OH)^{1-z}$.
(2) Both simple hydrolytic species $Mp(OH)_q^{2p-q}$ and mixed species $ML(OH)^{1-z}$ are very important for the speciation of $CH_3)_2Sn^{2+}$.
(3) Medium effects are quite significant, in particular when both Na^+ (interferences with

carboxylic ligand) and Cl^- [interference with $(CH_3)_2Sn^{2+}$] are present simultaneously.

(4) The stability of $(CH_3)_2Sn^{2+}$–carboxylic ligand species follows a regular trend as a function of $z^{2/3}$ and this makes it possible to estimate formation constants of other systems.

(5) All data reported in this work, i.e. formation constants together with medium effects, allow us to have a complete picture of the speciation of $(CH_3)_2Sn^{2+}$ in the presence of carboxylic ligands in electrolyte solutions containing different anions and cations.

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REFERENCES

1. J. S. Thayer, *Organometallic Compounds and Living Organisms*, Academic Press, New York, 1984.
2. Y. Arakawa and O. Wada, Biological properties of alkyltin compounds. In: *Metal Ions in Biological Systems*, Vol. 29, Siegel, H. and Siegel, A. (eds), Marcel Dekker, New York, 1993, pp. 101–133.
3. D. Mennie and P. J. Craig, Analysis of organometallic compounds in the environment. In: *Metal Ions in Biological Systems*, Vol 29, Siegel, H. and Siegel, A. (eds), Marcel Dekker, New York, 1993, pp. 37–72.
4. M. Yashuda and R. S. Tobias, *Inorg. Chem.* **2**, 207 (1963).
5. R. S. Tobias and C. E. Friedline, *Inorg. Chem.* **4**, 215 (1965).
6. R. S. Tobias and M. Yashuda, *Can. J. Chem.* **42**, 781 (1964).
7. G. Arena, A. Gianguzza, L. Pellerito, R. Purrello and R. Rizzarelli, *J. Chem. Soc., Dalton Trans.* 773 (1989).
8. G. Arena, A. Gianguzza, S. Musumeci, L. Pellerito, R. Purrello and R. Rizzarelli, *J. Chem. Soc., Dalton Trans.* 2603 (1990).
9. V. Cucinotta, A. Gianguzza, G. Maccarrone, L. Pellerito, R. Purrello and R. Rizzarelli, *J. Chem. Soc., Dalton Trans.* 2299 (1992).
10. R. S. Tobias, *Chem. Rev.* **1**, 93 (1966).
11. C. De Stefano, C. Foti, A. Gianguzza, M. Martino, L. Pellerito and S. Sammartano, *J. Chem. Eng. Data* **41**, 511 (1996).
12. J. Buffle, in: *Complexation Reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood Series in Analytical Chemistry, Ellis Horwood, Chichester, 1988, Chapter 4.
13. M. A. Wilson, P. F. Barron and A. H. Gillam, *Geochim. Cosmochim. Acta* **45**, 1743 (1981).
14. K. C. Beck, J. H. Reuter and E. M. Purdue, *Geochim. Cosmochim. Acta* **38**, 341 (1974).
15. J. H. Reuter and E. M. Perdue, *Geochim. Cosmochim. Acta* **41**, 325 (1977).
16. E. M. Thurmann and R. L. Malcom, in: *Aquatic and Terrestrial Humic Materials*, Christman, R. F. and Gjessing, E. T. (eds), Ann Arbor Science, 1983, Chapter 1.
17. A. J. Davies and P. J. Smith, Tin. In: *Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structure of Organometallic Compounds*, Wilkinson, G., Stone, F. G. A. and Abe, E. W. (eds), Pergamon, New York, 1982.
18. D. D. Perrrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1966).
19. C. De Stefano, P. Princi, C. Rigano and S. Sammartano, *Ann. Chim. (Rome)* **77**, 643 (1987).
20. C. De Stefano, G. Mineo, C. Rigano and S. Sammartano, *Ann. Chim. (Rome)* **83**, 243 (1993).
21. C. De Stefano, C. Foti, P. Mineo, C. Rigano and S. Sammartano, *Ann. Chem. (Rome)* **86**, 257 (1996).
22. A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, *Anal. Chim. Acta* **191**, 385 (1986).
23. P. G Daniele, A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, *J. Chem. Soc., Dalton Trans.* 2355 (1985).
24. A. De Robertis, C. De Stefano, C. Rigano, S. Sammartano and R. Scarcella, *J. Chem. Res. (S)* **42**, (M) 629 (1985).
25. C. De Stefano, C. Foti and A. Gianguzza, *Talanta* **41**, 1715 (1994).
26. A. De Robertis, C. Foti and A. Gianguzza, *Ann. Chim. (Rome)* **83**, 485 (1993).
27. A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, *J. Solut. Chem.* **19**, 569 (1990).
28. P. G. Daniele, A. De Robertis, C. De Stefano and S. Sammartano, in: *Miscellany of Scientific Papers Offered to Enric Casassas*, Alegret, S., Arias, J. J., Barcelò, D., Casal, J. and Router, G. (eds), Barcelona, 1991.
29. A. De Robertis, C. De Stefano, A. Gianguzza and S. Sammartano, *Chem. Spec. Bioavail.* **6**, 65 (1994).
30. A. Casale, P. G. Daniele, A. De Robertis and S. Sammartano, *Ann. Chim. (Rome)* **78**, 249 (1988).