APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 89–98
Main Group Metal Compounds
Published online 28 November 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.1012

Interaction of methyltin(IV) compounds with carboxylate ligands. Part 1: formation and stability of methyltin(IV)–carboxylate complexes and their relevance in speciation studies of natural waters

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Received 6 August 2005; Revised 31 August 2005; Accepted 30 September 2005

Quantitative data on the stability of mono-, di- and trimethyltin(IV)-carboxylate complexes (acetate, malonate, succinate, malate, oxydiacetate, diethylenetrioxydiacetate, tricarballylate, citrate, butanetetracarboxylate and mellitate) are reported at $t = 25\,^{\circ}C$ and $I \rightarrow 0\ mol\ l^{-1}$. Several mononuclear, mixed proton, mixed hydroxo and polynuclear species are formed in these systems. As expected, the stability trend is mono- > di- > trimethyltin(IV) and mono < di < tri < tetra < hexa for the organotin moieties and carboxylate ligands investigated, respectively. Moreover, ligands containing, in addition to carboxylic,–O–and—OH groups show a significantly higher stability with respect to analogous ligands with the same number of carboxylic binding sites. The results obtained from all the systems investigated allowed us to formulate the following empirical predictive equation for correlation between complex stability and some simple structural parameters,

$$\log \beta = -6.0 + 1.63 n_{carb} + 1.4 n_{OH} + 4.58 r + 3.9 z_{cat}$$

where n_{carb} and n_{OH} are the number of carboxylic and alcoholic groups in the ligand, respectively, r is the stoichiometric coefficient of H^+ (positive) or OH^- (negative) and z_{cat} is the methyltin cation charge $(CH_3)_x Sn^{z+}$ ($z^+ = 4 - x$). Distribution diagrams for some representative systems are also reported and are discussed in the light of speciation studies in natural waters. A literature data comparison is made with carboxylate complexes of other metal ions with the same charge as the organotin cations investigated here. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: methyltin(IV) cations; carboxylate ligands; methyltin(IV)–carboxylate complexes; speciation

INTRODUCTION

Organotin(IV) compounds are present in aquatic systems and derive from industrial uses,[1] mainly as anti-bacterial and wood and stone preservative agents or as catalysts for the production of plastics, as well as from the bioalkylation processes of inorganic tin.[2,3] The toxicity of organotin(IV) compounds, which largely depends on the nature and number of alkyl or phenyl groups, has been extensively documented in several papers and reports,[4,5] and triorganotin(IV) derivatives are well recognized to show the highest toxicity towards living organisms, including humans, as shown by recent investigations into their presence in blood[6] and the liver[7] and their behaviour as hormone disrupters in prostate cancer cells.[8] Most of

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Contract/grant sponsor: ARPA Sicilia.

the interaction processes of organotin(IV) cations occur in the aquatic environment, where they behave as acids of differing hardnesses on the Lewis scale,[9] and, for this reason, undergo hydrolysis following the trend $RSn^{3+} \gg R_2Sn^{2+} > R_3Sn^{+}$. After the pioneering studies into the hydrolysis of organotin cations of Tobias and co-workers,[10–14] the dependence of hydrolysis and complex formation constants of organotins on ionic strength and medium was neglected and few investigations of their binding ability toward various ligands in aqueous solution were carried out.[15,16] A systematic study of the hydrolytic processes of mono-, di- and tri-organotin(IV) cations in different aqueous media at different ionic strengths and temperatures[9,17,18] has been carried out over the past few years by our research group. Moreover, with the aim of defining the speciation of organotin compounds in natural waters, we also performed investigations in aqueous media by simulating the composition of natural waters[19–22] containing ligands of biological and environmental interest,[23–26] with particular reference to the carboxylate ligands which are by far the most common binding sites in the molecular components of natural organic matter, such as acidic polysaccharides, linear and aromatic poly-carboxylic and amino-poly-carboxylic acids, humic and fulvic substances, etc.

As an extension of previous investigations, this paper furnishes new data on the stability of mono-, di- and tri-organotin(IV)–carboxylate complexes in aqueous solution. Investigations into organotin systems with malonate (mal), succinate (succ), oxydiacetate (oda) and diethylenetrioxydiacetate (toda) ligands were carried out potentiometrically ($[H^+]$-glass electrode) at $t = 25\,^{\circ}C$. The hydrolysis of organotin cations and the protonation of carboxylate ligands were always taken into account in the calculations. Based on the new stability data and previous data[23–25] obtained from investigations into organotin systems with acetate (ac), malate (mala), citrate (cit), propane tricarboxylate (tricarballylate, tca), butane tetracarboxylate (btc) and benzene hexacarboxylate (mellitate, mlt), a relationship between complex stability and ligand charge and structure is proposed with the aim of providing a predictive interaction model. Structures of all the ligands with the relative abbreviations are reported in Fig. 1. The stability of these systems is compared with that of other carboxylate complexes with metal ions having the same organotin(IV) cation charges.

EXPERIMENTAL

Materials

Mono-, di- and trimethyltin compounds were used as chloride salts. The solutions were prepared from Aldrich commercial products twice re-crystallized before use. Carboxylate ligands (Fluka or Aldrich) were used without further purification. Their purity (always >99.5%) was checked by potentiometric titration. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical-grade water ($R = 18\,M\Omega$), using grade A glassware.

Equipment and procedure

Potentiometric titrations were carried out (at $25.0 \pm 0.1\,^{\circ}C$) using apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combined glass electrode (Ross type 8102, from Orion) and a model 765 Metrohm motorized burette. Estimated accuracy was ±0.2 mV and ±0.003 mL for e.m.f. 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 e.m.f. stability. All titrations were carried out under magnetic stirring and presaturated N_2 was bubbled through the purified solution in order to exclude O_2 and CO_2 inside. A volume of 25 ml of the solution containing the carboxylic ligand and the organotin cation under study was titrated with standard NaOH up to pH ≈ 11. Details of experimental measurements are reported in Table 1. Independent titrations of HCl with standard NaOH were carried out to determine standard electrode potential E^0 and to obtain $pH = -\log[H^+]$ readings.

Calculations

The following computer programs[27] were used: (i) BSTAC and STACO to refine all the parameters of an acid–base titration (such as analytical concentration of reagent and E^0) and to calculate complex formation constants; (ii) ES4ECI to draw distribution diagrams and calculate the formation percentage of each species; (iii) LIANA, a linear and nonlinear least-squares program, to calculate relationships of stability dependence on charge and structure. No background salt was added to the solutions under study in order to avoid interferences. The interactions of alkyltin(IV) with small amounts of Cl^- from the alkyltin(IV) chlorides and carboxylate ligands with small amounts of Na^+ from the standard NaOH titrant were taken into account in the calculations. The dependence of formation constants on ionic strength was taken into account using the Debye–Hückel[28] type equation:

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

where

$$C = c_0 p^* + c_1 z^*; \quad D = d_1 z^*; \quad p^* = \Sigma p_{\text{reactants}} - \Sigma p_{\text{products}};$$
$$z^* = \Sigma z^2_{\text{reactants}} - \Sigma z^2_{\text{products}}$$

(β is the formation constant; ${}^{T}\beta$ is the formation constant at zero ionic strength; p and z are stoichiometric coefficients and charges, respectively). For the calculations performed in this study we used the values $c_0 = 0.11$, $c_1 = 0.20$ and $d_1 = -0.075$. Both BSTAC and STACO computer programs

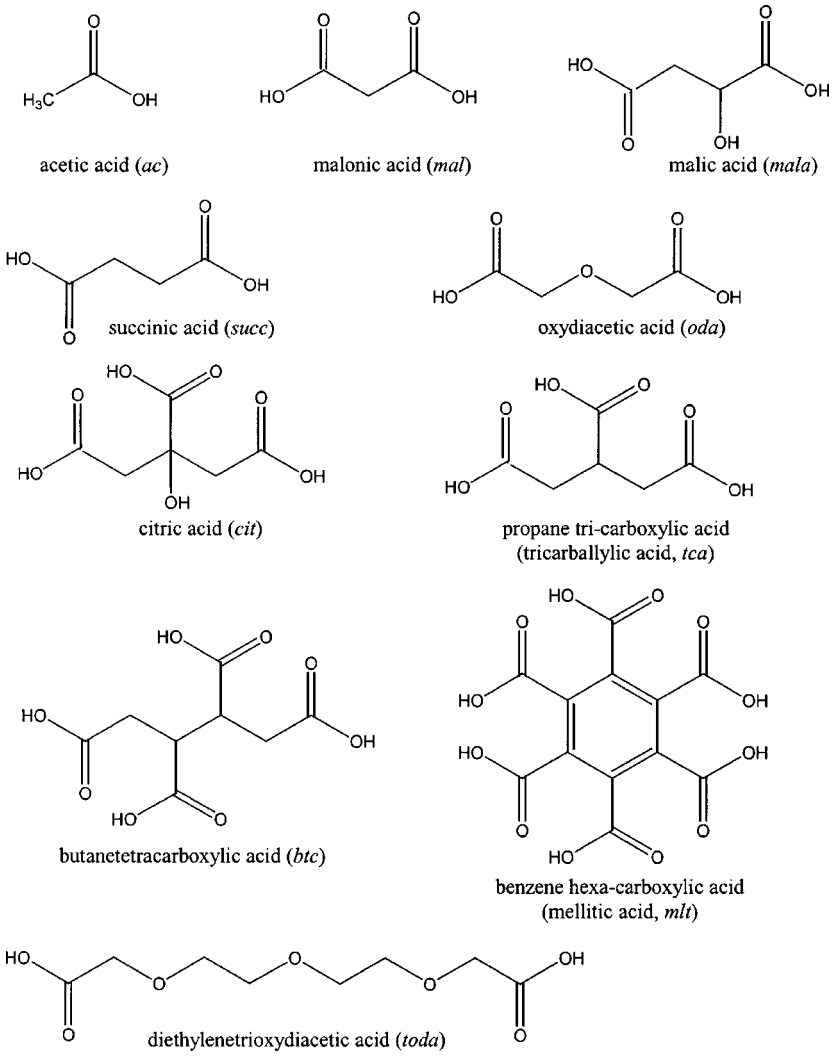

Figure 1. Structures of the carboxylic acids.

Table 1. Experimental conditions for potentiometric measurements ($t = 25\,^{\circ}C$)

Ligand	$C_{(CH_3)_xSnCl_{4-x}}$ [a]	C_L [a]	I [a,b]	N_{tit} [c]	N_{pts} [d]
	$(CH_3)SnCl_3$				
mal	1, 2	3, 4	8	4	325
succ	1, 2	3, 4	8	4	297
oda	1, 2	3, 4	10	4	320
toda	1, 2	3, 4	8	4	350
	$(CH_3)_2SnCl_2$				
succ	2, 4	3, 5	10	4	315
oda	2, 4	3, 5	8	4	292
toda	2, 4	3, 5	6	4	284
	$(CH_3)_3SnCl$				
mal	5, 10	5, 10	12	4	295
oda	5, 10	5, 10	16	4	319
toda	5, 10	5, 10	18	4	379

[a] Concentrations in mmol l^{-1}; [b] mean value of ionic strength; [c] total number of titrations; [d] total number of points.

can deal with potentiometric data obtained in variable ionic strength conditions and can be used to perform corrections to $I = 0$ mol l^{-1}. At $I < 0.05$ mol l^{-1}, σ $(\log\beta) \approx 0.15I$ and therefore, since the ionic strength in our measurements was always less than 0.020 mol l^{-1}, the contribution of this extrapolation procedure to the total error is less than 0.003.

Since alkyltin cations show a strong tendency to hydrolysis, hydroxo species formed by mono-, di- and trimethyltin(IV) cations must be considered when studying interactions with ligands. Analogously, the protonation of the carboxylate ligands used in this work must be taken into account. The hydrolysis constants of organotins have been extensively reported in previous papers,[9,17–19,21] along with the protonation constants of the carboxylate ligands under investigation, also in relation to their association with metal ions.[28,29] Equilibrium constants for hydrolysis and Cl^- complex formation of mono-, di- and trimethyltin(IV) cations and protonation and Na^+ carboxylate complexes used in this work are reported in Tables 2 and 3, respectively.

Table 2. Equilibrium constants[a] for hydrolysis and Cl^- complexes of $(CH_3)_xSn^{(4-x)}$ cations at $I = 0$ mol l^{-1} and $t = 25\,^\circ C$

	log β_{pqr}		
p q r	$(CH_3)Sn^{3+}$[b]	$(CH_3)_2Sn^{2+}$[c]	$(CH_3)_3Sn^{+}$[d]
1–1 0	−1.5	−2.86	−6.14
1–2 0	−3.46	−8.16	−18.88
1–3 0	−9.09	−19.35	—
1–4 0	−20.47	—	—
2–2 0	—	−4.99	—
2–3 0	—	−9.06	—
2–5 0	−7.69	—	—
1 0 1	—	0.78	−0.60
1–1 1	—	−3.17	—
1–2 1	−2.45	—	—
2–5 1	−6.03	—	—

[a] β_{pqr} refer to the reaction: $pM^{z+} + qH_2O + rCl^- \overleftrightarrow{} M_p(OH)_qCl_r^{zp-q-r} + qH^+$. [b] References 18 and 21; [c] references 9 and 21; [d] references 17 and 21.

RESULTS AND DISCUSSION

Complexes of mono-, di- and trimethyltin(IV) cations with carboxylates and empirical relationships

Complex formation constants of mono-, di- and trimethyltin (IV) (M) with carboxylates (L) are expressed as log β_{pqr}, according to the equilibrium reaction (charges omitted for simplicity):

$$pM + qL + rH_2O \rightleftharpoons M_pL_q(OH)_r + rH \qquad (2)$$

Table 3. Equilibrium constants[a] for the protonation and Na^+ complexes of carboxylate ligands, at $I = 0$ mol l^{-1} and $t = 25\,^\circ C$

	log β_{pqr}			
pqr	mal[b]	succ[b]	oda[b]	toda[c]
011	5.70	5.64	4.36	4.25
012	8.56	9.85	7.33	7.56
110	0.91	0.85	0.71	1.01
111	5.66	5.79	4.04	4.67

[a] β_{pqr} refers to the equilibrium reaction: $pNa^+ + qL^{2-} + rH^+ \overleftrightarrow{} Na_pL_qH_r^{(p+r-2q)}$. [b] Reference 28; [c] reference 29.

The formation constant values of organotin–carboxylate species, calculated at infinite dilution by means of Eq. (1) are reported in Tables 4 and 5. In order to give a complete picture of stability in mono-, di- and triorganotin–carboxylate systems, the same tables also include the previously determined formation constants of organotin–carboxylate species.[23–25] The errors associated with experimental data are given as standard deviations. Analysis of the results for the ML and MLOH species formed between CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$ and $(CH_3)_3Sn^+$ and the same carboxylic ligand showed, as expected, a decrease in stability with decreasing cation charge. For example, the stability constants of the ML(OH) species [L = *oda* ligand, M = mono-, di-, trimethyltin(IV) cation] are 4.78, −1.6 and −4.38, respectively and the corresponding $\Delta \log \beta_{[CH_3Sn-oda-((CH_3)_2Sn-oda)]} = 6.4$ and $\Delta \log \beta_{[((CH_3)_2Sn-oda)-((CH_3)_3Sn-oda)]} = 2.8$. Other observations can be made if we consider the interaction of the same organotin cation with different carboxylate ligands. For example, the stability constants of the mixed hydroxo

Table 4. Formation constants of complexes of $(CH_3)_xSn^{(4-x)}$ cations with mono- and dicarboxylate ligands at $I = 0$ mol l^{-1} and $t = 25\,^\circ C$

		log β_{pqr}[a]					
M	Species	ac	mal	succ	mala	oda	toda
$(CH_3)Sn$	ML		8.6 ± 0.1[b]	8.911 ± 0.007[b]			
	MLOH	2.09[c]	5.79 ± 0.05	5.457 ± 0.004	6.35[c]	4.78 ± 0.01[b]	4.23 ± 0.01[b]
	$ML(OH)_2$	−0.56	−0.07 ± 0.09	0.341 ± 0.005	2.54	0.81 ± 0.01	0.58 ± 0.01
	$ML(OH)_3$				−4.06	−3.90 ± 0.01	−3.92 ± 0.01
	$M_2L(OH)_5$	−4.29					
	ML_2OH	3.39					
$(CH_3)_2Sn$	ML	3.01[d]	5.43[d]	4.984 ± 0.003		6.011 ± 0.001	4.709 ± 0.008
	MLH		7.81	8.58 ± 0.01		7.69 ± 0.01	7.06 ± 0.07
	ML_2	5.25	7.21				
	MLOH	−0.925	−0.01	0.051 ± 0.003		−1.6 ± 0.2	−0.50 ± 0.02
$(CH_3)_3Sn$	ML		2.74 ± 0.01	2.374[e]		2.099 ± 0.004	2.268 ± 0.007
	MLH		7.74 ± 0.02	7.182		5.766 ± 0.008	5.98 ± 0.01
	MLOH		−3.7 ± 0.2			−4.382 ± 0.008	−4.12 ± 0.01
	$ML(OH)_2$		−15.21 ± 0.01				−15.81 ± 0.01

[a] Logβ values refer to the equilibrium: $pM + qL + rH_2O \overleftrightarrow{} M_pL_q(OH)_r + rH$. [b] Standard deviation. [c] Reference 25; [d] reference 23; [e] reference 24.

Table 5. Formation constants of complexes of $(CH_3)_xSn^{(4-x)}$ cations with tri-, tetra- and hexacarboxylate ligands at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$

		$\log \beta_{pqr}$ [a]			
M	Species	tca	cit	btc	mlt
$(CH_3)Sn$[b]	ML	11.69	12.81	13.58	
	MLH	15.01		17.81	
	MLH_2			20.84	
	MLOH	7.33	9.26	8.32	
	$ML(OH)_2$	1.44	3.84	1.64	
	$ML(OH)_3$		−3.56		
$(CH_3)_2Sn$	ML	6.69[c]	7.71[d]	8.20[c]	
	MLH	11.12	12.348	13.34	
	MLH_2	14.38		17.47	
	MLH_3			20.40	
	MLOH	1.01	1.85	1.80	
	M_2L_2		17.43		
	M_2LOH		8.44		
	M_2LOH_2		3.854		
$(CH_3)_3Sn$[e]	ML	3.288	3.367	3.70	6.31
	MLH	8.831	8.908	10.264	12.86
	MLH_2	12.89	13.281	15.345	17.97
	M_2L			6.93	9.23

[a] Logβ values refer to the equilibrium: $pM + qL + rH_2O \rightleftarrows M_pL_q(OH)_r + rH$. [b] Reference 25; [c] reference 23; [d] data from work in progress; [e] reference 24.

species ML(OH) formed by the interaction of monomethyltin cation with simple carboxylate ligands, such as malonate and succinate, are quite similar, whilst the species formed by the same cation with a hydroxocarboxylate ligand, such as malate, shows higher stability. This is probably due to the influence of the alcoholic group, which further stabilizes the complex. These results show a clear dependence of species stability on charge and also demonstrate that other factors, such as ligand structure, are also involved. Taking into account the differences in stability values observed for different carboxylate ligands with the same charge, we assumed thermodynamic parameters to be dependent on ligand structure. Similarly to other classes of complexes, such as alkali and alkaline earth–carboxylate[30] and open chain ammonium and polyammonium cation–carboxylate complexes,[31] it is possible to find linear relationships between thermodynamic and other parameters. In fact, by considering some structural variables, such as the number of carboxylic groups and the presence of alcoholic groups, we found the following relationship for all the $\log \beta$ values in Tables 4 and 5:

$$\log \beta = -6.0 + 1.63n_{carb} + 1.4n_{OH} + 4.58r + 3.9z_{cat} \qquad (3)$$

where n_{carb} and n_{OH} are the number of carboxylic and alcoholic groups in the ligand, the number of H^+ in the species formed was identified as $r > 0$ and the number of OH^- as $r > 0$, and

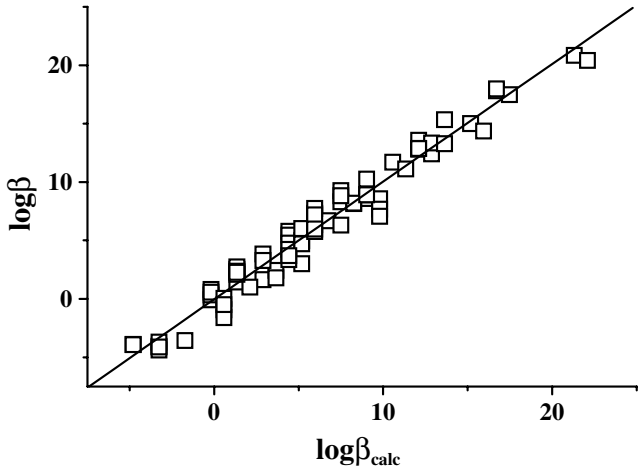

Figure 2. Logβ values of Tables 4 and 5 vs $\log \beta$ values calculated using Eq. (3).

z_{cat} is the charge on the methyltin cation $(CH_3)_xSn^{z+}$ ($z^+ = 4 - x$). Figure 2 plots $\log \beta$ vs $\log \beta_{calc}$ [calculated according to Eq. (3)] for all the organotin–carboxylate complexes. As can be seen, there is a slight dispersion of data (for a total number equal to 74), with a linear correlation coefficient = 0.984.

Speciation profiles of monomethyltin(IV)–dicarboxylate ligand complexes

Based on the stability data relative to the systems under investigation (Tables 4 and 5), distribution diagrams of complex species were drawn as a function of pH. Figure 3(a, b) and (c, d) shows distribution diagrams vs pH for CH_3Sn^{3+}—malonate and CH_3Sn^{3+}—oxydiacetate complexes, respectively, at two different organotin : ligand (M : L) concentration ratios (M:L = 1 : 1 and M:L = 1 : 10). Analysis of the speciation diagrams for these systems allows us to make the following observations:

1. The CH_3Sn–mal system behaves differently from the corresponding system with the oda ligand, where the species $ML(OH)_3^{2-}$, which is not present in the former, was identified. This species achieves a formation percentage of around 90% in both CH_3Sn-oda and CH_3Sn-toda systems, and is the main species in the pH range 6–9.
2. The formation percentages of complex species in the system CH_3Sn-oda [Fig. 3(c, d)] are generally much higher than the corresponding percentages for the same species in the CH_3Sn–mal system [Fig. 3(a, b)].
3. As expected, for higher M : L ratios [Fig. 3(a, c)], the formation of simple hydrolytic species of monomethyltin(IV) cation predominates, whilst lower M : L concentration ratios [Fig. 3(b, d)] generally favour the formation of simple and mixed $ML(OH)_x$ ($x = 0$, 1, 2, 3) complex species.

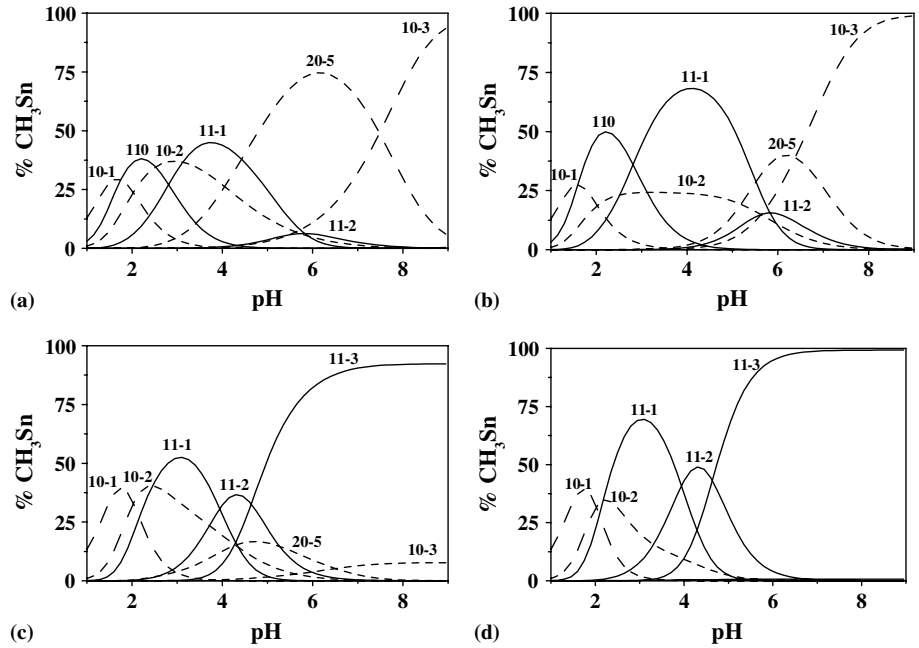

Figure 3. Speciation diagrams for CH_3Sn^{3+} (M)–carboxylic acid (L = mal, oda) at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$. Indexes refer to reaction (2). Dotted lines: simple hydrolytic species of monomethyltin(IV) cation. L = mal (a, b); L = oda (c, d). $C_M = 1$ mmol l^{-1} (a, c); $C_M = 0.1$ mmol l^{-1} (b, d); $C_L = 1$ mmol l^{-1}.

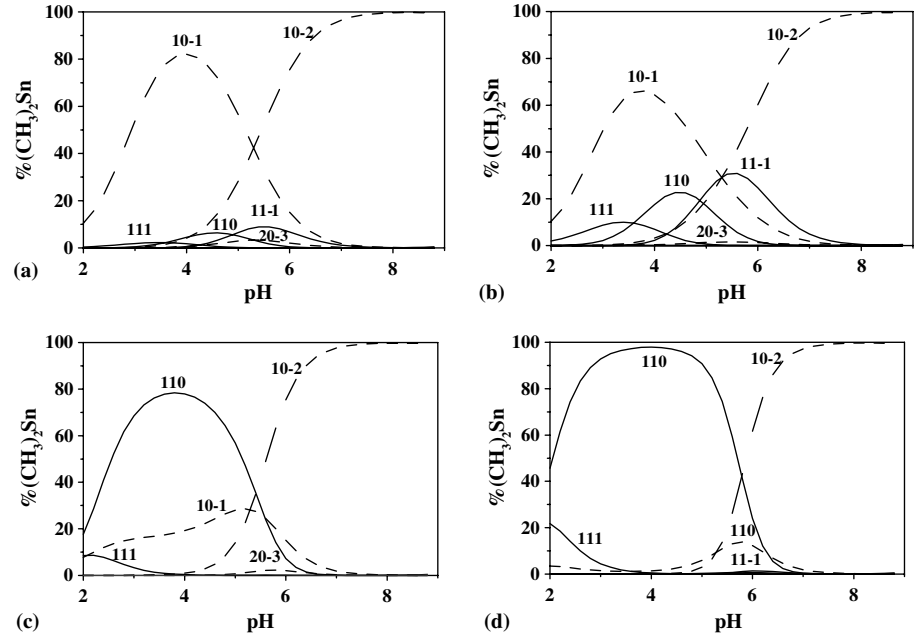

Figure 4. Speciation diagrams for $(CH_3)_2Sn^{2+}$ (M)-carboxylic acid (L = succ, oda) at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$. Indexes refer to reaction (2). Dotted lines: simple hydrolytic species of dimethyltin(IV) cation. L = succ (a, b); L = oda (c, d). $C_M = 1$ mmol l^{-1}; $C_L = 1$ mmol l^{-1} (a, c); $C_L = 5$ mmol l^{-1} (b, d).

Speciation profiles of dimethyltin(IV)–dicarboxylate ligand complexes

Figure 4(a, b) and (c, d) shows the distribution diagrams of complex species for the $(CH_3)_2Sn^{2+}$—succ, and $(CH_3)_2Sn^{2+}$—oda systems, respectively (stability data in Table 4). Here too, speciation diagrams are drawn at two different M : L concentration ratios: M:L = 1 : 1 and M:L = 1 : 5 [Fig. 4(a, c) and (b, d) for the two systems, respectively].

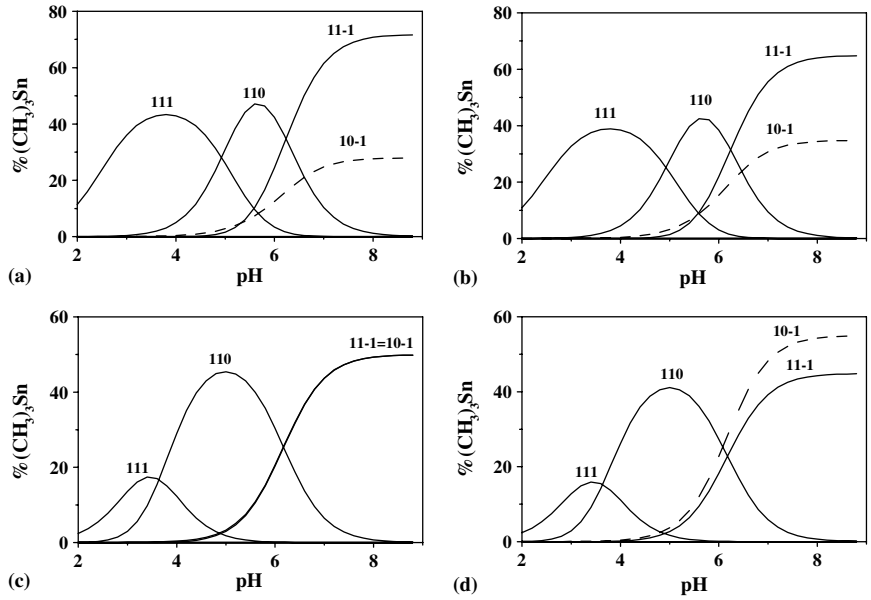

Figure 5. Speciation diagrams for complex species in the $(CH_3)_3Sn^+$ (M)–carboxylate ligand (L = mal, toda) systems, at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$. Indexes refer to reaction (2). Dotted lines: simple hydrolytic species of trimethyltin(IV) cation. L = mal (a, b); L = toda (c, d). $C_M = 1$ mmol l^{-1} (a, c); $C_M = 5$ mmol l^{-1} (b, d); $C_L = 10$ mmol l^{-1}.

A comparison of these two systems clearly shows that ML is a very significant species in the oda system: the formation percentage at pH = 3.5 is about 80% for $C_L : C_M = 1$ [$C = 1$ mmol l^{-1}, Fig. 4(c)] and over 90% for $C_L : C_M = 5$ [Fig. 4(d)]. On the other hand, formation percentages for complex species in the dimethyltin(IV)–succinate system are low even for the higher ligand : organometal cation concentration ratio: the highest formation percentage of complex species in the $(CH_3)_2Sn^{2+}$—succ system is achieved by the $ML(OH)^-$ species, which reaches about 30% formation at pH = 5.5 for $C_L/C_M = 5$ [Fig. 4(b)]. It must be noted that, for both systems, the simple $(CH_3)_2Sn(OH)_2$ hydrolytic species is the only species present in the pH range (6.5–8.5) of interest for natural waters.

Speciation profiles of trimethyltin(IV)–dicarboxylate ligand complexes

Figure 5 shows distribution diagrams for complex species in the $(CH_3)_3Sn^+$—mal and $(CH_3)_3Sn^+$—toda systems (stability data in Table 4). The differences between them are not too large if we consider the different M : L concentration ratios [M:L = 1 : 10 and M:L = 1 : 2 in Fig. 5(a, c) and (b, d) for M(mal) and M(toda), respectively]. In comparison with the monomethyl(IV)–and dimethyltin(IV)–carboxylate systems, the most significant difference is the very high formation of MLOH species [over 60% of formation percentage in the trimethyl–malonate system, Fig. 4(a)] in the pH range 6.5–8.5 that is of interest for natural waters. This is a very important result if we consider that, among organotin derivatives, triorganotin(IV) compounds are the most toxic towards mammals and fish. Moreover, as we showed in a previous work,[32] trimethyltin(IV) behaves similarly to the tributhyltin(IV) cation. Therefore the speciation model described here for trimethyltin(IV)–dicarboxylate ligands can be assumed to also be valid for tributhyltin(IV)–carboxylate systems.

Speciation profiles of organotin–carboxylates in seawater

When dealing with multicomponent solutions, such as natural waters, interactions between all components must be carefully considered in order to build up an accurate picture of the speciation of the system under investigation. In these cases, the number of interactions is often very high and this increases calculation difficulties. In some cases, the interactions classified as weak interactions between the components of the ionic medium must also be taken into consideration owing to the high concentration of the interacting species. In a number of previous works[19–22] we reported results for the speciation of organotin compounds in seawater using an artificial seawater made up of six major components (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}) as the ionic medium for our equilibrium studies (SSWE).[33] Details of the SSWE composition are reported in Table 6. More recently, in order to facilitate calculations, a new chemical model for seawater was used where the above-mentioned macrocomponents are represented by a single salt, BA,[34] B^{z+} and A^{z-} ($z = \pm 1.117$) being representative of all the cations and anions in SSWE, respectively. Table 6 shows equilibrium constants for the species in the BA system. Using these equilibrium constants, together with previously reported[21,22] formation constants of species formed by the interaction of organotin compounds with the anion $A^{1.117-}$, we calculated the distribution of species in the

organotin–carboxylate systems in SSWE as a single salt BA. As an example, in Fig. 6 we show the species distribution diagram for $(CH_3)_3Sn$–toda in SSWE as BA. In addition to the interaction for $(CH_3)_3Sn$–toda species formation, interactions for BA and $(CH_3)_3Sn$–A species formation, trimethyltin(IV) cation hydrolysis and trioxydiacetate protonation were also considered. As can be seen, the main species at the pH value of natural seawater (8.1 ± 0.2) is the trimethyltin(IV) hydrolytic species, but a significant percentage of the mixed $(CH_3)_3Sn$(toda)(OH) species is also formed. The formation of both these species confirms that the aqueous solution chemistry of organotin compounds is primarily regulated by the process of hydrolysis. The formation of simple $(CH_3)_3Sn$(toda) species occurs at lower pH values.

Literature data comparison

An extensive study of the interaction between trimethyltin(IV) cation and carboxylate ligands was carried out by Hynes and O'Dowd[16] and the results of that investigation can be used for comparison with our own results. For the $(CH_3)_3Sn$–mal system, the authors reported the formation of only species M_2L

Table 6. Composition of artificial seawater (SSWE) at 35‰ salinity[a] and at $t = 25\,^{\circ}C$

Component	Concentration (mol l^{-1})
NaCl	0.4221
Na_2SO_4	0.0288
KCl	0.0110
$CaCl_2$	0.0111
$MgCl_2$	0.0548
BA[b]	0.5751 (0.717)[c]
Single salt equilibria	log K[d]
$B^{z+} + A^{z-} = BA^0$	−0.03
$H^+ + A^{z-} = HA^{(1-z)}$	0.24
$B^{z+} = B(OH)^{(z-1)} + H^+$	−12.75

[a] Reference 33; [b] seawater single salt;[34] [c] ionic strength (mol l^{-1}); [d] at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$.

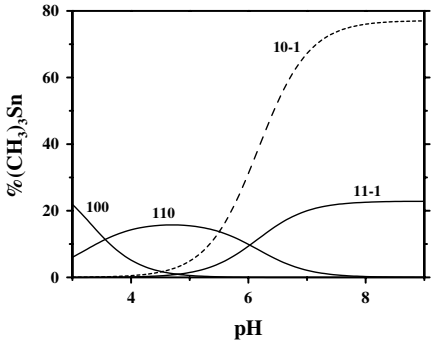

Figure 6. Speciation diagram for complex species in the $(CH_3)_3Sn^+$ (M)–toda (L) system, in SSWE 35‰ and at $t = 25\,^{\circ}C$. Indexes refer to reaction (2). Dotted lines: simple hydrolytic species of trimethyltin(IV) cation. $C_M = 5$ mmol l^{-1}; $C_L = 15$ mmol l^{-1}.

Table 7. Literature data comparisons, at $t = 25\,^{\circ}C$

	logβ					
Species	$(CH_3)Sn^{3+}$	Al^{3+}	Bi^{3+}	Cr^{3+}	Fe^{3+}	La^{3+}
M(mal)	8.6	6.711[a]	—	7.06[b]	8.04[c]	4.01[d]
M(succ)	8.911	3.63[e]	8.76[f]	6.42[g]	7.89[h]	3.09[i]
M(cit)	11.69	7.85[j]	11.80[k]	—	11.2[l]	6.41[m]
M(cit)OH	7.33	4.27	—	—	—	—
M(cit)$(OH)_2$	1.44	−1.77	—	—	—	—
M(cit)H	15.01	—	—	—	9.9	10.22

[a] Reference 35 at $I = 0.1$ mol l^{-1} in KCl; [b] reference 36 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [c] reference 37 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [d] reference 38 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [e] reference 39 at $I = 0.2$ mol l^{-1} in KCl; [f] reference 40 at $I = 0.2$ mol l^{-1} in $NaClO_4$; [g] reference 41 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [h] reference 42 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [i] reference 43 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [j] reference 44 at $I = 0.2$ mol l^{-1} in KCl; [k] reference 45 at $I = 0.1$ mol l^{-1} in KNO_3; [l] reference 46 at $I = 0.15$ mol l^{-1} in NaCl; [m] reference 47 at $I = 0.25$ mol l^{-1} in $NaNO_3$.

Table 8. Literature data comparisons, at $t = 25\,^{\circ}C$

	log β						
Species	$(CH_3)_2Sn^{2+}$	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Pb^{2+}	Ca^{2+}
M(toda)	4.709	2.85[a]	2.39[a]	2.60[a]	2.29[a]	—	—
M(oda)	6.011	3.97[b]	2.81[b]	3.65[b]	3.07[c]	4.41[b]	4.28[d]
M(oda)H	7.69	5.36	4.78	—	—	5.86	7.12
M(mal)	5.43	5.04[e]	3.28[f]	3.0[g]	2.37[h]	2.6[g]	—
M(mal)H	7.81	—	7.17	—	5.86	—	—
M(succ)	4.98	3.98[i]	1.62[k]	2.47[l]	1.71[k]	—	1.45[m]
M(succ)H	8.58	6.66[j]	5.79[h]	1.51	—	—	5.96
M(tca)	6.69	3.35[n]	2.70[o]	—	—	3.17[p]	3.17[q]
M(tca)H	11.12	8.03	4.26	—	—	7.91	—
M(tca)H_2	14.38	11.53	—	—	—	11.59	—
M(tca)OH	1.01	−3.34	—	—	—	—	—
M(cit)	7.71	5.67[r]	5.51[s]	5.02[t]	4.83[u]	5.98[v]	4.91[d]
M(cit)H	12.35	9.29[n]	8.87	8.71	8.02	—	9.23
$M_2(cit)_2$	17.43	14.10	—	—	—	—	—

[a] Reference 48 at $I = 0.1$ mol l^{-1} in KNO_3; [b] reference 49 at $I = 0.1$ mol l^{-1} in KCl; [c] reference 50 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [d] reference 51 at $I = 0$ mol l^{-1}; [e] reference 52 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [f] reference 53 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [g] reference 54 at $I = 0.1$ mol l^{-1}; [h] reference 55 at $I = 0.5$ mol l^{-1} in NaCl; [i] reference 56 at $I = 0.1$ mol l^{-1} in $NaClO_4$; [j] reference 57 at $I = 1$ mol l^{-1} in $NaClO_4$; [k] reference 58 at $I = 0.1$ mol l^{-1} in KNO_3; [l] reference 28 at $I = 0$ mol l^{-1}; [m] reference 28 at $I = 0.25$ mol l^{-1} in R_4NX; [n] reference 59 at $I = 0.2$ mol l^{-1} in KCl; [o] reference 60 at $I = 0.15$ mol l^{-1}; [p] reference 61 at $I = 1$ mol l^{-1} in $NaClO_4$; [q] reference 62 at $I = 0$ mol l^{-1}; [r] reference 63 at $I = 0.5$ mol l^{-1} in $NaClO_4$; [s] reference 64 at $I = 0.25$ mol l^{-1} in KNO_3; [t] reference 65 at $I = 0.1$ mol l^{-1} in KNO_3; [u] reference 66 at $I = 0.1$ mol l^{-1}; [v] reference 67 at $I = 0.1$ mol l^{-1} in $NaClO_4$.

with $\log\beta = 3.37$ at $I = 0.3\ \text{mol l}^{-1}$ ($NaClO_4$) and $t = 25\,^{\circ}\text{C}$. For the same system we found the species ML, MLH, MLOH and $ML(OH)_2$ with $\log\beta = 2.74$, 7.74, −3.7 and −15.21, respectively, at $I = 0\ \text{mol l}^{-1}$ and $t = 25\,^{\circ}\text{C}$. The different interaction model proposed is dictated by two main factors: (i) Hynes and O'Dowd did not consider the formation of mixed (hydroxo and protonated) species; and (ii) in their experimental conditions they used a higher concentration of trimethyltin(IV) cation ($C_M = 5$–$50\ \text{mmol l}^{-1}$) than that used here ($C_M = 5$–$10\ \text{mmol l}^{-1} = C_L$), a different concentration ratio ($C_M : C_L = 1$–$2/3$) and a maximum pH value equal to 6.5.

Furthermore, we compared our stability data for species of mono- and dimethyltin cations with carboxylate ligands and those published in literature[35–67] relative to the same ligands with other metals having the same charge. These literature comparisons are reported in Tables 7 and 8 at $t = 25\,^{\circ}\text{C}$, at various ionic strengths and in a range of ionic media. If we consider the ML species formed with trivalent cations (data from Table 7), stability decreases in the order $(CH_3)Sn^{3+} \approx Bi^{3+} > Fe^{3+} > Cr^{3+} \gg Al^{3+} > La^{3+}$. A comparison of stability data for divalent cations with carboxylate ligands (data from Table 8), however, shows that $(CH_3)_2Sn^{2+}$ forms more stable complexes than other metals, and those with Cu^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} show fairly equivalent stabilities, probably because they have rather similar chemical characteristics as regards electronic configuration and electronegativity.

Acknowledgement

This study has been carried out with funds from ARPA Sicilia (Decreto n. 214 of 19-04-04).

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