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Interaction of methyltin(IV) compounds with carboxylate ligands. Part 2: formation thermodynamic parameters, predictive relationships and sequestering ability

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Thermodynamic data of mono-, di- and tri-methyltin(IV)-carboxylate complexes (acetate, malonate, succinate, oxydiacetate, diethylenetrioxydiacetate, malate, citrate, 1,2,3-tricarballylate, 1,2,3,4-butanetetracarboxylate, 1,2,3,4,5,6-benzenehexacarboxylate) in aqueous solution are reported at $t = 25\,^\circ\mathrm{C}$ and $I = 0$ mol l^{-1}. Thermodynamic parameters obtained were analysed to formulate empirical predictive relationships as a function of different parameters, such as the number of carboxylate groups of the ligand and the charge of the alkyltin(IV) cation. Sequestration diagrams of citrate and 1,2,3-tricarballylate towards alkyltin(IV) cations at different pH values are also reported and discussed. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: methyltin(IV) complexes; thermodynamic parameters; calorimetry; empirical relationships; speciation in aqueous solution

Introduction

Over the last decade, our research group had carried out an extensive study on the speciation of alkyltin(IV) cations in aqueous solution.[1–12] First, the hydrolysis processes of mono-, di- and tri-organotin cations in various ionic media and at different temperatures and ionic strengths were studied;[1–3] subsequently, the speciation of organotins in aqueous media, by simulating the composition of natural waters,[4–7] and the interactions with ligands of biological and environmental interest, such as carboxylate,[8–12] were investigated. In the first part[12] of this short series, we reported the stability data of complexes of mono-, di- and tri-methyltin(IV) cations with mono-, di-, tri-, tetra- and hexacarboxylate ligands obtained potentiometrically ($[\mathrm{H}^+]$-glass electrode) at $t = 25\,^\circ\mathrm{C}$ and $I \rightarrow 0$ mol l^{-1}. In order to improve the thermodynamic picture and to obtain more information on the nature and the extent of these interactions, it was necessary to determine enthalpy and entropy values for these complexation equilibria. In fact, for reactions in aqueous solution, formation enthalpies of the species metal–ligand give information on the breaking and formation of chemical bonds involving the metal ion, the ligand and the solvent. Entropies measure the order in the system and show the change in solvation between the uncomplexed and complexed states of metal ion and ligands.

Some papers[13–19] have appeared in the literature dealing with equilibria and structural aspects of complexes formed by the interaction of alkyltin(IV) cations with O-donor ligands, including amino acids. Only one of these gives thermodynamic data regarding dimethyltin(IV)-acetate, -malonate and -succinate species.[15]

In this paper, enthalpy and entropy data of mono-, di- and tri-methyltin(IV)-carboxylate complex species are reported. The measurements have been carried out by calorimetry at 25 °C in aqueous solution and the following ligands have been investigated: acetate (**ac**), malonate (**mal**), malate (**mala**), succinate (**succ**), oxydiacetate (**oda**), diethylenetrioxydiacetate (**toda**), 1,2,3-tricarballylate (**tca**), citrate (**cit**), 1,2,3,4-butanetetracarboxylate (**btc**) and 1,2,3,4,5,6-benzenehexacarboxylate (mellitate, **mlt**). Structures of all these ligands with the relative abbreviations are reported in Fig. 1. The large number of data (ΔG^0, ΔH^0 and $T\Delta S^0$) collected for the systems investigated and for the complex species formed (25 and 90, respectively), were analysed for the purposes of prediction, to find empirical relationships as a function of different parameters, such as the number of carboxylate groups of the ligand and the charge of the alkyltin(IV) cation.

Experimental

Materials

Monomethyl-, dimethyl- and trimethyl-tin(IV) compounds were used as chloride salts. The solutions were prepared from Aldrich commercial products twice re-crystalized before use. Carboxylate ligands (Fluka or Aldrich) were used without further purification. Their purity was checked by potentiometric titrations. Hydrochloric

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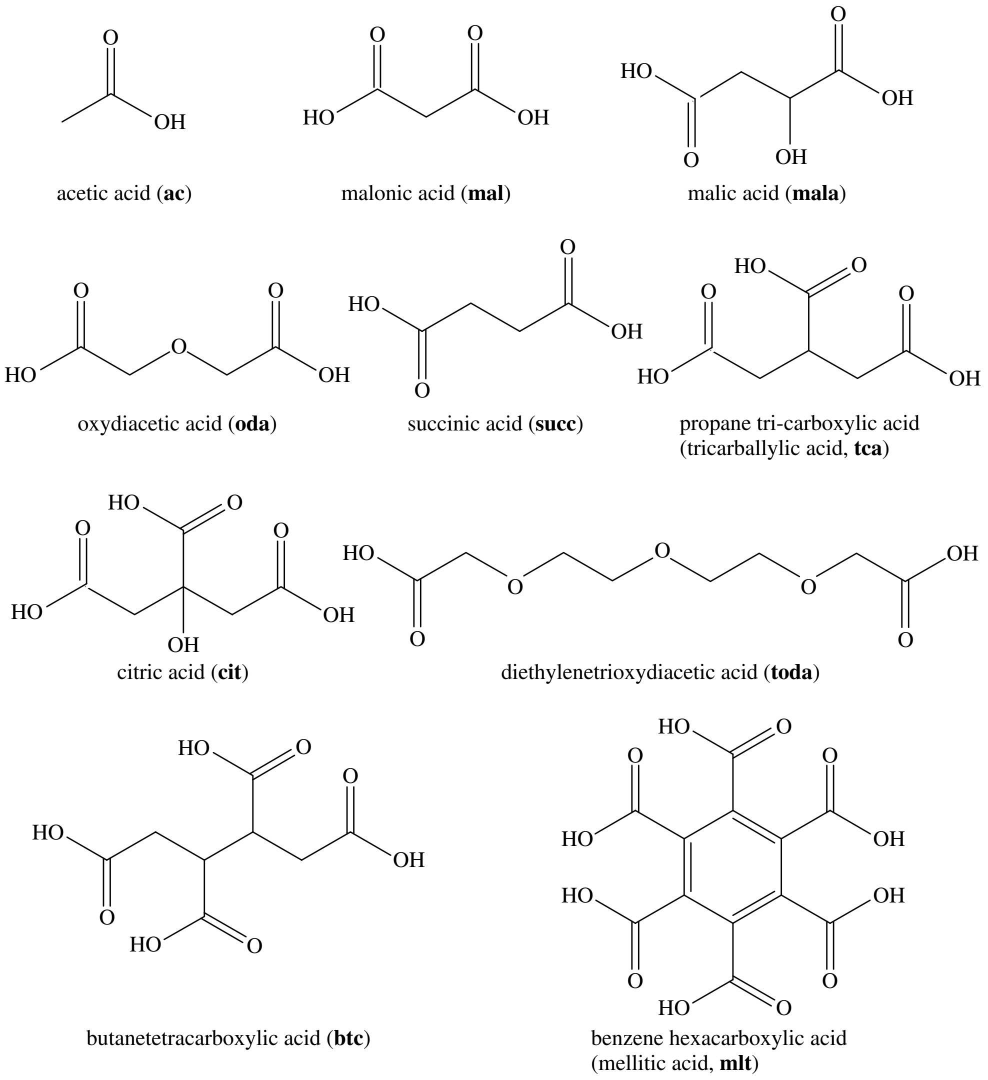

Figure 1. Structures of ligands.

acid and sodium hydroxide solutions were prepared by diluting concentrated Fluka ampoules and standardizing against sodium carbonate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical-grade water (resistivity = 18 MΩ cm), using grade A glassware.

Equipment and procedure

Calorimetric measurements were performed by titrating 50 ml of the solution containing the alkyltin(IV) cation under study with the carboxylate sodium salt at 25.000 ± 0.001 °C, by means of a model 450 Tronac Isoperibol Titration calorimeter, coupled with a Keithley 196 system Dmm digital multimeter. Details of experimental conditions are reported in Table 1. The titrant was delivered by a 2.5 ml capacity Hamilton syringe, model 1002TLL. A computer program was used for the acquisition of the calorimetric data. The system accuracy was checked by titrating a Tris [tris-(hydroxymethyl)amino-methane] buffer with HCl. The heat of dilution was measured before each experiment. The accuracy of calorimetric apparatus was $Q \pm 0.008$ J and $v \pm 0.001$ cm^3. The protonation enthalpies of **toda** were obtained titrating a solution of its sodium salt (2.5–5 mmol l^{-1}), with standard HCl. For the calculation of the hydrolysis enthalpies of monomethyltin(IV) cation, a solution containing this species (1–3 mmol l^{-1}) was titrated with standard NaOH.

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

	$C_{(CH_3)_xSnCl_{4-x}}$ ^{a}	C_L ^{a}	$I^{a,b}$	N_{tit} ^{c}
$(CH_3)SnCl_3$	0.001–0.003	0.085–0.26	0.008–0.010	28
$(CH_3)_2SnCl_2$	0.001–0.004	0.05–0.20	0.004–0.013	24
$(CH_3)_3SnCl$	0.003–0.010	0.16–0.3	0.010–0.017	28

^{a} Concentrations in mol l^{-1}; ^{b} range of ionic strength; ^{c} total number of titrations.

Calculations

The following computer programs were used: LIANA,[20] a linear and non-linear least squares program, to calculate relationships of dependence of thermodynamic parameters on charge; ES5CM,[21] to analyse calorimetric titration data, to deal with data obtained

Table 2. Hydrolysis enthalpies[a] of $(CH_3)_xSn^{(4-x)}$ cations at $I = 0$ mol l^{-1} and $t = 25$ °C

	$\Delta H^0{}_{pq}$		
pq	$(CH_3)Sn^{3+b}$	$(CH_3)_2Sn^{2+c}$	$(CH_3)_3Sn^{+d}$
1–1	-24 ± 2	33.1	25.8
1–2	-11 ± 3	62.1	80.8
1–3	15 ± 3	97.7	–
1–4	51 ± 3	–	–
2–2	–	60	–
2–3	–	84	–
2–5	9 ± 4	–	–

[a] $\Delta H^0{}_{pq}$ refers to the reaction: $pM + qH_2O = M_p(OH)_q + qH$ and is expressed in kJ mol^{-1}; [b] this work; [c] Foti *et al.*[4]; [d] De Stefano *et al.*[2]

in variable ionic strength conditions and to perform corrections to $I = 0$ mol l^{-1}. At $I < 0.05$ mol l^{-1}, the contribution of this extrapolation procedure to the total error is less than 0.2 kJ mol^{-1}.

Concentrations and thermodynamic parameters are given in the molar scale. Errors are given as standard deviations. The overall formation equilibria are expressed as (charges omitted)

$$pM + qL + rH = M_pL_qH_r \qquad (1)$$

where $r > 0$ for protonated species and $r < 0$ for hydrolytic species.

The hydrolysis enthalpies of di- and tri-methyltin(IV) have been reported in previous papers,[2,4] as well as the protonation enthalpies of the carboxylate ligands under investigation, also in relation to their association with metal ions.[22–25] Protonation enthalpies of **toda** and **mlt** and hydrolysis enthalpies of monomethyltin(IV) are determined and reported for the first time in this work. Hydrolysis enthalpies of mono-, di- and trimethyltin(IV) cations and protonation enthalpies of carboxylates used in this work are reported in Tables 2 and 3.

Results and Discussion

Enthalpy and entropy changes

The overall enthalpy changes, ΔH^0, determined by calorimetric measurements, are shown in the Tables 4–6, together with ΔG^0 and $T\Delta S^0$ values. Equilibrium thermodynamic parameters, reported in Tables 7–9, were calculated according to the following reactions:

$$M + LH_i = MLH_i \qquad (2)$$

$$M(OH)_j + L = ML(OH)_j \qquad (3)$$

$$L + ML = ML_2 \qquad (4)$$

$$M + ML = M_2L \qquad (5)$$

As organotin(IV) compounds are considered Lewis acids having different hardnesses [$CH_3Sn^{3+} \gg (CH_3)_2Sn^{2+} > (CH_3)_3Sn^{+}$], the interaction with hard base donors such as oxygen of carboxylate ligands is mainly driven by a favourable entropic factor, typical for hard–hard interactions, where free energy mainly results from the entropy gain, due to the change of orientation of water molecules of hydration.[26] On the whole, the results in Tables 4–9 confirm that the major contribution to the stability of these complex species is due to the entropic term.

On the other hand, enthalpy values are not too high and they are mostly of endothermic nature. This indicates that, as dehydration of the metal requires energy to break the cation–water and water–water bonding of the hydration layers, the energy required to break bonds with water is higher than the energy released during the formation of metal–ligand bonds.[27] This endoergic dehydration effect overcomes exoergic metal–oxygen interactions, except for some complex species of monomethyltin(IV) with **mal, succ, toda, tca, cit** and **btc** and some others of di- and trimethyltin(IV) with **cit**.

Moreover, thermodynamic results show that other factors influence the interaction: (i) charge effects – an increase in entropy values with increasing ligand charge, as well a decrease with decreasing cation charge is shown; (ii) structural effects – the presence of other potentially binding groups (alcoholic or ethereal) induces a significant lowering of $T\Delta S^0$ values. For example in the $(CH_3)_2Sn^{2+}$-bicarboxylate ligand systems, for the MLOH species, overall $T\Delta S^0 = 55.4$, 49.7, 22 and 14 kJ mol^{-1} for **mal, succ, oda** and **toda**, respectively; in the $(CH_3)_2Sn^{2+}$-tricarboxylate

Table 3. Protonation enthalpies[a] of carboxylate ligands, at $I = 0$ mol l^{-1} and $t = 25$ °C

	$\Delta H^0{}_j$						
Ligand	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$	Reference
ac	0						[22]
mal	5	4					[22]
succ	0.7	−1.7					[23]
oda	10	9.3					[23]
toda	4.2 ± 0.1^b	7.8 ± 0.1^b					this work
mala	0	−2					[22]
cit	1.6	−2.5	7.9				[24]
tca	3.4	3.7	−0.9				[25]
btc	6.6	5.7	4.4	0.4			[25]
mlt	13.0 ± 0.1^b	10.6 ± 0.1^b	8.2 ± 0.1^b	5.6 ± 0.1^b	3.4 ± 0.1^b	1.0 ± 0.1^b	this work

[a] $\Delta H^0{}_j$ refers to the equilibrium reaction: $L^{z-} + jH^+ = H_jL^{(j-z)}$ and are expressed in kJ mol^{-1}; [b] ±s = standard deviation.

Table 4. Overall thermodynamic parameters[a] for the formation of complex species in the CH_3Sn^{3+}-carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$

L	pqr[b]	$-\Delta G^0$	$\Delta H^0 \pm s$[c]	$T\Delta S^0$
ac	11−1	11.9	2.1 ± 0.5	14
	12−1	19.4	1.6 ± 0.5	21
	11−2	−3.2	1.2 ± 0.5	−2
	21−5	−24.5	22 ± 2	−25
mal	110	49.1	−1.4 ± 0.4	47.7
	11−1	33.0	−4.8 ± 0.3	28.2
	11−2	−0.4	14.4 ± 1.0	14
succ	110	50.8	−9 ± 1	41.8
	11−1	31.1	13.1 ± 0.8	44.2
	11−2	1.9	10.3 ± 0.6	12.2
oda	11−1	27.3	0.6 ± 0.2	27.9
	11−2	4.6	15.4 ± 0.4	20
	11−3	−22.3	15.8 ± 0.9	−6.5
toda	11−1	22.4	−2.7 ± 0.9	19.7
	11−2	3.4	12 ± 1	15.4
	11−3	−22.4	−9.5 ± 0.9	−31.9
mala	11−1	36.2	2.8 ± 0.7	39
	11−2	14.5	2.5 ± 0.8	17
	11−3	−23.4	1.4 ± 0.8	−22
tca	110	66.7	0.8 ± 0.5	67.5
	111	85.6	−8.6 ± 0.7	77
	11−1	41.8	4.6 ± 0.5	46.4
	11−2	8.2	17.4 ± 0.9	25.6
cit	110	73.1	−26.5 ± 0.4	46.6
	11−1	52.8	−19.2 ± 0.4	33.6
	11−2	21.9	−12.1 ± 0.8	9.8
	11−3	−20.3	9.8 ± 0.4	−10.5
btc	110	77.5	−3.8 ± 0.5	73.7
	111	101.6	−4.1 ± 0.5	97.5
	112	118.9	−4.9 ± 0.8	114
	11−1	47.5	−1.9 ± 0.4	45.6
	11−2	9.4	3.2 ± 0.9	12.6

[a] Values in kJ mol^{-1}; [b] indexes refer to the equilibrium reaction (1); [c] s = standard deviation.

ligand systems, for the ML species, overall $T\Delta S^0 = 82.9$ and 50 kJ mol^{-1} for **tca** and **cit**, respectively; in the $(CH_3)_3Sn^+$-bicarboxylate ligand systems, for the MLH species, overall $T\Delta S^0 = 66.1$, 69, 52 and 49 kJ mol^{-1} for **mal, succ, oda** and **toda**, respectively.

Using $\log \beta$ and ΔH^0 values at $t = 25\,^{\circ}C$, it is possible to calculate stability constants at any temperature using the Clarke and Glew equation,[28] which takes into account the temperature dependence of stability constants. As an example we chose the system dimethyltin(IV)-succinate; after calculating the stability constants of the species at $t = 5$ and $45\,^{\circ}C$, we plotted the speciation diagram shown in Fig. 2. As can be seen, with the increasing of the temperature beyond the growth of the formation percentage of the species, there is a shift of the maximum of the curve to lower pH values.

Empirical relationships

The formation reactions can also be expressed with the following equilibria (charges are omitted for simplicity):[10]

$$M(OH) + L + nH = M(OH)LH_n \quad \beta_n \tag{6}$$

$$M(OH)LH_n = M(OH)LH_{n-1} + H \quad K_n \tag{7}$$

Tables 10 and 11 show average values of stability constants and entropy, respectively calculated using the data with the same n_H value, according to the equilibrium 6. On the whole, these results indicate that the stability and the entropy of methyltin(IV)-carboxylate species is strictly dependent on n_H, as expressed by the following equations (R = correlation coefficient).

$$\begin{aligned}\log \beta_n &= 7.8 + 4.9\,n_H \quad \text{with} \quad R = 0.9997 \quad \text{for } CH_3Sn^{3+}\\ \log \beta_n &= 3.5 + 4.9\,n_H \quad \text{with} \quad R = 0.952 \quad \text{for } (CH_3)_2Sn^{2+}\\ \log \beta_n &= 1.1 + 7.0\,n_H \quad \text{with} \quad R = 0.9645 \quad \text{for } (CH_3)_3Sn^{+}\end{aligned}$$

Table 5. Overall thermodynamic parameters[a] for the formation of complex species in the $(CH_3)_2Sn^{2+}$-carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$

L	pqr[b]	$-\Delta G^0$	$\Delta H^0 \pm s$[c]	$T\Delta S^0$
ac	110	17.2	2.8 ± 0.5	20
	120	30	5 ± 0.5	35
	11−1	−5.3	5.3 ± 1.0	0
mal	110	31.0	27.1 ± 0.2	58.1
	111	44.5	17 ± 2	61.5
	11−1	0.1	55.3 ± 0.4	55.4
	120	41.2	8.8 ± 1.5	50
succ	110	28.4	30.1 ± 0.5	58.5
	111	48.9	15 ± 2	63.9
	11−1	0.3	49.4 ± 0.4	49.7
oda	110	34.3	10.7 ± 0.1	45.0
	111	43.9	24.1 ± 1.0	68
	11−1	−9.1	31.1 ± 1.5	22
toda	110	26.9	29.1 ± 0.2	56
	111	40.3	19.7 ± 0.5	60
	11−1	−2.9	16.9 ± 1.5	14
tca	110	38.2	44.7 ± 0.6	82.9
	111	63.4	30.7 ± 0.8	94.1
	112	82.1	26 ± 2	108
	11−1	5.8	45.1 ± 0.7	50.9
cit	110	44.0	5.6[d]	50
	111	70.5	5.0	75
	11−1	10.6	−2.6	8
	220	99.5	45	144
	21−1	48.2	54.5	103
	21−2	22.0	59.5	81
btc	110	46.8	35.6 ± 0.6	82.4
	111	76.1	27.3 ± 0.7	103.4
	112	99.7	15.0 ± 1.0	114.7
	113	116.4	18.6 ± 1.5	135
	11−1	10.3	30.8 ± 0.9	41.1

[a] Values in kJ mol^{-1}; [b] indexes refer to the equilibrium reaction (1); [c] s = standard deviation; [d] data from Cardiano *et al.*[11]

Table 6. Overall thermodynamic parameters[a] for the formation of complex species in the $(CH_3)_3Sn^+$ – carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^\circ$C

L	pqr[b]	$-\Delta G^0$	$\Delta H^0 \pm s$[c]	$T\Delta S^0$
mal	110	15.6	8.4 ± 0.6	24
	111	44.1	22 ± 1	66.1
	11−1	−21.1	23 ± 1	1.9
	11−2	−86.8	−95 ± 3	−8
succ	110	13.5	10.7 ± 0.3	24.2
	111	41.0	28 ± 3	69
oda	110	12.0	22.9 ± 0.6	34.9
	111	32.9	19.1 ± 1.0	52
	11−1	−25.0	35 ± 3	18
toda	110	12.9	7.8 ± 0.1	20.7
	111	34.1	14.9 ± 0.5	49
	11−1	−23.5	26.5 ± 1.0	3
	11−2	−90.2	59 ± 3	−31
tca	110	18.7	11.5 ± 0.3	30.2
	111	50.4	18 ± 1	68.4
	112	73.6	17 ± 3	91
cit	110	19.2	−2.7 ± 0.3	16.5
	111	50.8	7.0 ± 1.0	57.8
	112	75.8	3.2 ± 1.2	79
btc	110	21.1	5.0 ± 0.4	26.1
	111	58.5	26 ± 1	84.5
	112	87.6	10.4 ± 1.1	98
	210	39.5	−5 ± 1	34.5
mlt	110	36	11 ± 1	47
	111	73.4	1.6 ± 0.7	75
	112	102.6	−1.6 ± 0.8	101
	210	52.7	31 ± 2	84

[a] Values in kJ mol^{-1}; [b] indexes refer to the equilibrium reaction (1); [c] s = standard deviation.

Table 7. Thermodynamic parameters for the formation of complex species[a] in the CH_3Sn^{3+} – carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^\circ$C

L	Species	log K	$-\Delta G^{0}$[b]	ΔH^{0}[b]	$T\Delta S^{0}$[b]
ac	MLOH	3.6	20.5	11.4	31.9
	$ML(OH)_2$	2.9	16.6	8.7	25.3
mal	ML	8.6	49.1	4.9	54.0
	MLOH	7.3	41.6	12.2	53.8
	$ML(OH)_2$	3.4	19.4	12.3	31.7
succ	ML	8.9	50.9	0.9	51.8
	MLOH	7.0	39.7	20.7	60.4
	$ML(OH)_2$	3.8	21.7	17.1	38.8
mala	MLOH	7.8	44.8	7.5	52.3
	$ML(OH)_2$	6.0	34.2	7.5	41.7
	$ML(OH)_3$	5.0	28.5	5.6	34.1
oda	MLOH	6.3	35.8	16.7	52.5
	$ML(OH)_2$	4.3	24.4	17.9	42.3
	$ML(OH)_3$	5.2	29.6	1.5	31.1
toda	MLOH	5.7	32.7	16.9	49.6
	$ML(OH)_2$	4.0	23.1	17.5	40.6
	$ML(OH)_3$	5.2	29.5	−10.5	19.0
tca	ML	11.7	66.7	1.8	68.5
	MLH	8.5	48.6	0.8	49.4
	MLOH	8.8	50.4	15.5	65.9
	$ML(OH)_2$	4.9	28.0	21.4	49.4
cit	ML	12.8	73.1	−15.0	58.1
	MLOH	10.8	61.4	2.5	63.9
	$ML(OH)_2$	7.3	41.7	4.4	46.1
	$ML(OH)_3$	5.5	31.6	7.1	38.7
btc	ML	13.6	77.5	−1.5	76.0
	MLH	10.6	60.7	−0.7	60.0
	MLH_2	7.8	44.7	2.6	47.3
	MLOH	9.8	56.1	12.9	69.0
	$ML(OH)_2$	5.1	29.1	17.9	47.0

[a] Referring to the equilibria (2) and (3); [b] in kJ mol^{-1}.

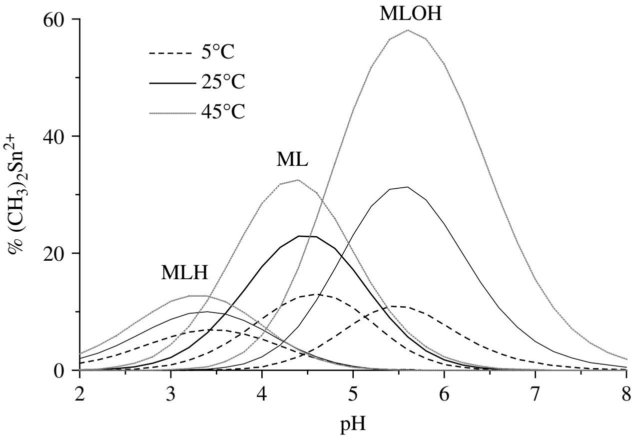

Figure 2. Speciation diagram of the species formed by dimethyltin(IV) (M) with succinate (L) at t = 5, 25 and 45°, C_M = 1 mmol l^{-1}; C_L = 5 mmol l^{-1}.

By considering all stability and entropy data, according to the equilibria (6) and (7), the following correlations, which, besides the n_H parameter, take into account the number of carboxylate groups of the ligand (n_{carbox}) and the charge of the alkyltin(IV) cation (z_{cation}), have been calculated:

$$Y = F_1 + F_2\, n_H + F_3\, n_{carbox} \qquad (8)$$

where for log β

$$\begin{aligned} F_1 &= -2.8(\pm 0.3) + 0.59(\pm 0.07)\, z^2{}_{cation} \\ F_2 &= 6.0(\pm 0.1) - 0.21(\pm 0.02)\, z^2{}_{cation} \\ F_3 &= 1.43(\pm 0.07) + 0.04(\pm 0.02)\, z^2{}_{cation} \end{aligned}$$

and for $T\Delta S^0$

$$\begin{aligned} F_1 &= -7(\pm 7) + 5(\pm 1)\, z^2{}_{cation} \\ F_2 &= 29(\pm 4) - 1.1(\pm 0.5)\, z^2{}_{cation} \\ F_3 &= 2(\pm 2) + 0.9(\pm 0.4)\, z^2{}_{cation} \end{aligned}$$

Figures 3 and 4 show the plots of log β_n and $T\Delta S_n{}^0$ values vs log β_n and $T\Delta S_n{}^0$ values calculated with equation (8).

Table 8. Thermodynamic parameters for the formation of complex species[a] in the $(CH_3)_2Sn^{2+}$ – carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$

L	Species	log K	$-\Delta G^{0b}$	ΔH^{0b}	$T\Delta S^{0b}$
ac	ML	3.0	17.2	8.3	25.5
	ML_2	2.2	12.8	7.6	20.4
	MLOH	1.9	11.0	6.6	17.6
mal	ML	5.4	31.0	15.8	46.8
	MLH	2.1	12.0	13.7	25.7
	MLOH	2.9	16.3	16.3	32.6
	ML_2	1.8	10.2	10.0	20.2
succ	ML	5.0	28.4	19.3	47.7
	MLH	2.9	16.8	13.0	29.8
	MLOH	2.9	16.6	13.4	30.0
oda	ML	6.0	34.3	8.2	42.5
	MLH	3.3	19.0	8.5	27.5
	MLOH	1.3	7.2	13.0	20.2
toda	ML	4.7	26.9	18.3	45.2
	MLH	2.8	16.0	8.6	24.6
	MLOH	2.4	13.5	10.0	23.5
tca	ML	6.7	38.2	23.5	61.7
	MLH	4.6	26.4	17.9	44.3
	MLH_2	3.0	17.0	16.0	33.0
	MLOH	3.9	22.1	13.1	35.2
cit	ML	7.7	44.0	6.5	50.5
	MLH	5.9	33.8	6.3	40.1
	MLOH	4.7	26.9	−0.7	26.2
btc	ML	8.2	46.8	21.4	68.2
	MLH	6.2	35.2	16.9	52.1
	MLH_2	4.5	25.5	10.7	36.2
	MLH_3	2.9	16.3	13.8	30.1
	MLOH	4.7	26.6	8.7	35.3

[a] Referring to the equilibria (2) and (3); [b] in kJ mol^{-1}.

The corresponding fits are fairly good, particularly for log β_n, as indicated by correlation coefficients ($R = 0.978$ and 0.903 for log β_n and $T\Delta S_n{}^0$, respectively), but there is a greater dispersion of data for the latter, which probably indicates a higher specificity of $T\Delta S^0$ with respect to ΔG^0.

Sequestering power of 1,2,3-propanetricarboxylate and citrate towards alkyltin(IV)

As stability constants are not enough by themselves to indicate the sequestering capacity of a ligand towards a metal, it can be expressed by the function $\Sigma(\%)$ vs pL, where $\Sigma(\%)$ is the total percentage of alkyltin(IV) cation complexed and $p\mathrm{L} = -\log[\mathrm{L}]_{\mathrm{tot}}$. Since this function is a typically sigmoidal curve (or a dose–response curve), increasing rapidly over a relatively small change in concentration, we can use the Boltzmann-type equation[29] (with asymptotes of 100 for $p\mathrm{L} \to -\infty$ and 0 for $p\mathrm{L} \to +\infty$):

$$\Sigma(\%) = 100 \times \left[\frac{1}{1 + e^{(p\mathrm{L} - p\mathrm{L}_{50})/S}} - 1\right] \qquad (9)$$

Table 9. Thermodynamic parameters for the formation of complex species[a] in the $(CH_3)_3Sn^{+}$ – carboxylate ligands (L) systems at $I = 0$ mol l^{-1} and $t = 25\,^{\circ}C$

L	Species	log K	$-\Delta G^{0b}$	ΔH^{0b}	$T\Delta S^{0b}$
mal	ML	2.7	15.6	10.0	25.6
	MLH	2.0	11.6	12.3	23.9
	MLOH	2.4	13.9	2.1	16.0
succ	ML	2.4	13.6	11.6	25.2
	MLH	1.5	8.8	17.2	26.0
oda	ML	2.1	12.0	18.1	30.1
	MLH	1.4	8.0	6.7	14.7
	MLOH	1.8	10.0	6.6	16.6
toda	ML	2.3	12.9	10.9	23.8
	MLH	1.7	9.9	5.8	15.7
	MLOH	2.0	11.5	6.0	17.5
tca	ML	3.3	18.8	13.4	32.2
	MLH	2.3	13.4	13.4	26.8
	MLH_2	1.5	8.4	9.5	17.9
cit	ML	3.4	19.2	5.3	24.5
	MLH	2.5	14.2	6.0	20.2
	MLH_2	2.1	12.0	9.4	21.4
btc	ML	3.7	21.1	13.2	34.3
	MLH	3.1	17.6	19.1	36.7
	MLH_2	2.3	13.3	15.4	28.7
	M_2L	3.2	18.4	−0.1	18.3
mlt	ML	6.3	36.0	35.3	71.3
	MLH	5.0	28.6	32.3	60.9
	MLH_2	3.7	20.9	29.7	50.6
	M_2L	2.9	16.7	26.8	43.5

[a] Referring to the equilibria (2) and (3); [b] in kJ mol^{-1}.

Table 10. Average values of stability constants[a] for species with different n_H values

$n_H{}^b$	CH_3Sn^{3+} log $\overline{\beta}_n \pm s/\sqrt{m}^c$	$(CH_3)_2Sn^{2+}$ log $\overline{\beta}_n \pm s/\sqrt{m}^c$	$(CH_3)_3Sn^{+}$ log $\overline{\beta}_n \pm s/\sqrt{m}^c$
4		23.26	
3	22.3	18.8 ± 1.5	21.0 ± 1.2
2	17.9 ± 1.4	12.6 ± 1.0	14.6 ± 0.8
1	12.6 ± 1.0	9.1 ± 0.5	9.4 ± 0.5
0	7.9 ± 0.6	3.2 ± 0.5	2.1 ± 0.2
−1	3.0 ± 0.5		−9.4 ± 0.3
−2	−2.35 ± 0.13		

[a] Referred to the equilibrium reaction (6); [b] n_H = number of protons in the complex species; [c] m = total number of stability data on species having equal n_H.

where $p\mathrm{L}_{50}$ and S are empirical parameters which define the ligand concentration necessary to sequester 50% of metal ion, while S is a measure of the slope in flex of the function $(\Sigma\%)$ vs pL. The $p\mathrm{L}_{50}$ parameter is very useful because it gives a representation of the binding ability of a ligand (L) towards a specific cation in the conditions investigated.

Figures 5(a–c) and 6(a, b) show sequestration diagrams of citrate and 1,2,3-propanetricarboxylate, respectively, towards

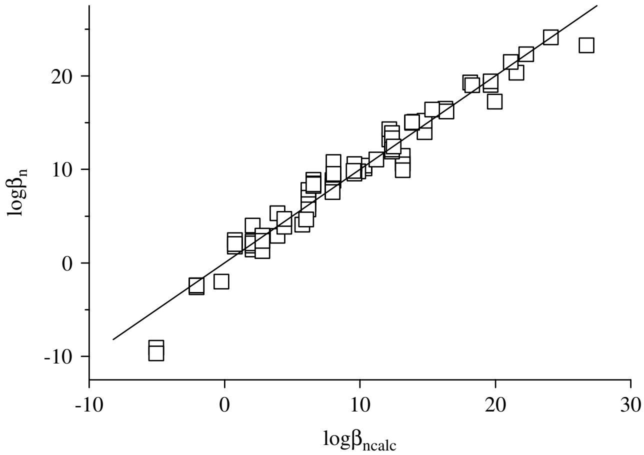

Figure 3. log β_n values according to the equilibrium 6 vs log β_n values calculated with equation (8).

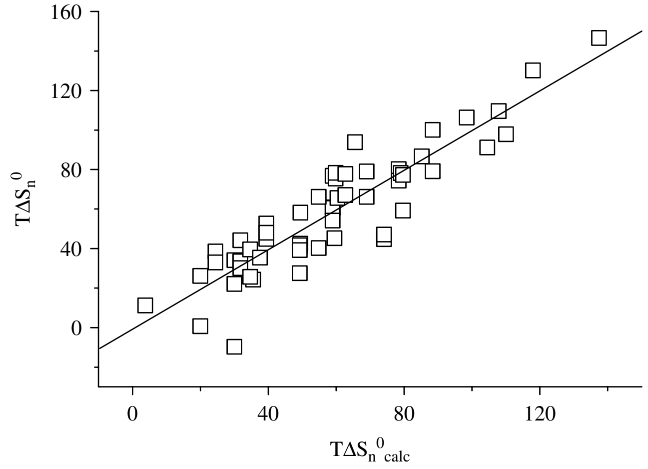

Figure 4. $T\Delta S_n{}^0$ values (kJ mol^{-1}) according to the equilibrium (6) vs $T\Delta S_n{}^0$ values (kJ mol^{-1}) calculated with equation (8).

Table 11. Average values of entropy[a] for species with different n_H values

n_H[b]	CH_3Sn^{3+} $\overline{T\Delta S_n{}^0} \pm s/\sqrt{m}$[c]	$(CH_3)_2Sn^{2+}$ $\overline{T\Delta S_n{}^0} \pm s/\sqrt{m}$[c]	$(CH_3)_3Sn^{+}$ $\overline{T\Delta S_n{}^0} \pm s/\sqrt{m}$[c]
4		118	101 ± 5
3	147	94 ± 3	74 ± 4
2	120 ± 10	58 ± 6	37 ± 3
1	88 ± 6	45 ± 6	17 ± 5
0	68 ± 3	18 ± 7	−10 ± 11
−1	48 ± 2		
−2	15 ± 6		

[a] Referred to the equilibrium reaction (6); [b] n_H = number of protons in the complex species; [c] m = total number of stability data on species having equal n_H.

Table 12. Empirical parameters of equation (9)[a]

Ligand	pH = 5 pL_{50}	pH = 6 pL_{50}	pH = 8 pL_{50}
		CH_3Sn^{3+}	
cit	6.150	6.309	5.613
tca	4.063	3.991	
		$(CH_3)_2Sn^{2+}$	
cit	3.962	3.598	2.004
tca	2.773	2.626	
		$(CH_3)_3Sn^{+}$	
cit	2.434	2.685	
tca	2.177	2.544	

[a] With S [slope of the function of equation (9)] = 0.434 for all systems at any pH value.

Table 13. Metal complexes of acetate butanetetracarboxylate at I = 0 mol L = 1 and *t* = 25 °C.

Species	log β $(CH_3)_2Sn^{2+}$	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Pb^{2+}	Ca^{2+}
M(**ac**)	3.01	2.21	1.44	1.97	1.38	2.58	1.18
M(**btc**)	8.20	–	–	–	–	–	4.50

alkyltin(IV) cations, at $C_{RSn} = 10^{-8}$ mol l^{-1} and $t = 25\,^{\circ}$C and at different pH values. The pL_{50} values referring to citrate and 1,2,3-propanetricarboxylate ligands toward mono-, di- and trimethyltin(IV) cations are reported in Table 12. At the three pH values examined, the trend of pL_{50} is mono-≫di-> trimethyltin(IV) cation. At the same pH value, the binding ability of citrate is significantly higher than that of 1,2,3-propanetricarboxylate. At pH = 5, $pL_{50\,\mathbf{cit}} - pL_{50\,\mathbf{tca}}$ = 2.087, 1.189, 0.257; at pH = 6, $pL_{50\,\mathbf{cit}} - pL_{50\,\mathbf{tca}}$ = 2.318, 0.972 and 0.141 for mono-, di- and trimethyltin(IV) cation, respectively. The pL_{50} value decreases with the increasing of the pH from 5 to 8, because the competition of the hydrolysis of alkyltin(IV) cations is relevant. This is particularly evident for trimethyltin–carboxylate systems where $(CH_3)_3Sn^+$ cation is present practically only as hydrolytic species over pH = 6.

Correlation with the stability of different metal ions

In the first part[12] of this short series, our stability data for species of mono- and di-methyltin(IV) cations with carboxylate ligands were compared with those published in the literature relative to the systems containing the same ligands with other metal ions having the same charge (tables 7 and 8 of the first part), at $t = 25\,^{\circ}$C, at various ionic strengths. Here we considered the stability constants regarding only the ML species of table 8 of the first part,[12] recalculated at $I = 0$ mol l^{-1}, according to the equation reported in Daniele *et al.*[30] The complexes considered are formed by divalent cations, such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+} and Ca^{2+} with several di- and tri-carboxylate ligands (**oda, toda, mal, succ, tca** and **cit**). In the calculations, the constant values from databasescited in Pettit and Powell[31] and Martell[32] regarding acetate and butanetetracarboxylate ligands at $t = 25\,^{\circ}$C and I = 0 mol l^{-1} have been also considered (Table 13).

We fitted all these data to the equation:

$$\log K_{(CH_3)_2Sn^{2+}-L} = a + b\log K_{M^{2+}-L} \qquad (10)$$

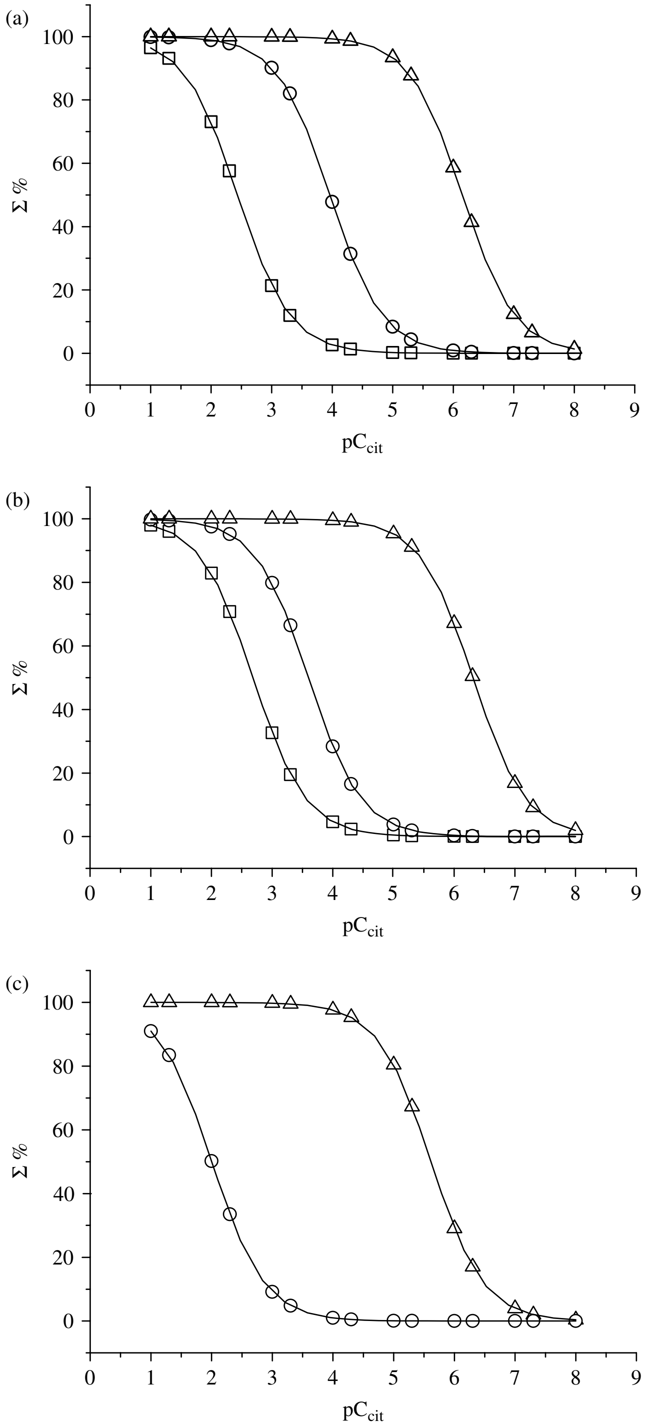

Figure 5. Sequestration diagrams of citrate towards alkyltin(IV) (RSn) at $t = 25\,^\circ C$ and $C_{RSn} = 10^{-8}$ mol l^{-1}. $\triangle = CH_3Sn^{3+}$; $\bigcirc = (CH_3)_2Sn^{2+}$; $\square = (CH_3)_3Sn^+$. (a) pH = 5; (b) pH = 6; (c) pH = 8.

and we obtained the value of $b = 0.87 \pm 0.03$, for all the considered metal ions. The equations for each metal considered are the following:

$$\log K_{(CH_3)_2Sn^{2+}-L} = 1.1(\pm 0.1) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Cu^{2+}$$

$$\log K_{(CH_3)_2Sn^{2+}-L} = 2.0(\pm 0.2) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Ni^{2+}$$

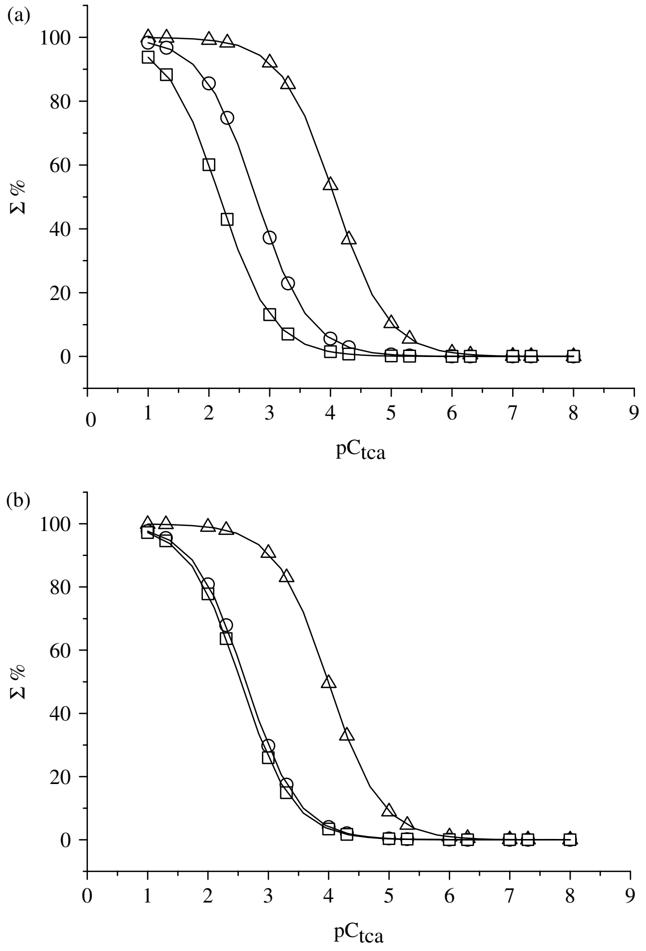

Figure 6. Sequestration diagrams of 1,2,3-tricarballylate towards alkyltin(IV) (RSn) at $t = 25\,^\circ C$ and $C_{RSn} = 10^{-8}$ mol l^{-1}. $\triangle = CH_3Sn^{3+}$; $\bigcirc = (CH_3)_2Sn^{2+}$; $\square = (CH_3)_3Sn^+$. (a) pH = 5; (b) pH = 6.

$$\log K_{(CH_3)_2Sn^{2+}-L} = 1.9(\pm 0.2) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Zn^{2+}$$

$$\log K_{(CH_3)_2Sn^{2+}-L} = 2.1(\pm 0.2) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Co^{2+}$$

$$\log K_{(CH_3)_2Sn^{2+}-L} = 1.4(\pm 0.3) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Pb^{2+}$$

$$\log K_{(CH_3)_2Sn^{2+}-L} = 3.2(\pm 0.2) + (0.87 \log K_{M^{2+}-L}) \quad \text{for } Ca^{2+}$$

These equations are useful to quantitatively predict the stability of $(CH_3)_2Sn{-}L$ complex species by using the stability data of complexes formed by the interaction of other and, in general, more investigated divalent metal ions with the same carboxylate ligands. Some examples confirm the validity of these relationships: using the $\log K_{Co(\mathbf{cit})} = 6.47$ ($I = 0$ mol l^{-1}) we obtain the corresponding $\log K_{(CH_3)_2Sn^{2+}-\mathbf{cit}} = 7.73$ calculated using the parameters of the above equation referring to the Co–L systems ($a = 2.1 \pm 0.2$ and $b = 0.87 \pm 0.03$), which is very close to the value of 7.71 experimentally determined,[11] and corrected for $I = 0$ mol l^{-1}. Again, the $\log K = 3.01$ for the $(CH_3)_2Sn{-}\mathbf{ac}$ system ($I = 0$ mol l^{-1}) is in excellent agreement with the value $\log K_{(CH_3)_2Sn-\mathbf{ac}} = 3.02$ calculated using the constant value of the Cu–**ac** system and the relative empirical parameters ($a = 1.1 \pm 0.1$ and $b = 0.87 \pm 0.03$) of the relationship reported above.

Conclusions

The results reported here give a comprehensive picture of the stability of the organotin–carboxylate systems. The large number of systems investigated allowed us to obtain relationships between the stability and (i) the number of both protonated and unprotonated carboxylic groups, and (ii) other potential O-donor ethereal or hydroxo groups present in the ligand molecules. The obtained equations show a good correlation between the experimental values of thermodynamic stability parameters and the calculated ones. Predictive relationships were also inferred to obtain stability data of diorganotin complexes from carboxylate systems containing other most common divalent metal ions. Finally, the sequestering capacity of carboxylate ligands towards organotin cations was defined as function of the ligand concentration in the pH range of interest of natural aqueous systems. Results reported here and in the first part[12] of this short series can be used for a better understanding of the speciation of carboxylate systems which are widely present in most of natural fluids.

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Appendix

List of symbols used in this work

$\log \beta$	log of overall formation constant
$\log \beta_n$	log of overall formation constant of the species *n* protonated
n_H	number of protons in the species
n_{carbox}	number of carboxylic groups of the ligand
z_{cation}	charge of the alkyltin(IV) cation
Y	in turn is $\log \beta$ or $T\Delta S^0$
F_1, F_2, F_3	empirical functions of equation (8)
$T\Delta S_n^0$	entropic factor of the species *n* protonated
$\sum\%$	total percentage of alkyltin(IV) cation complexed
L	symbol used to indicate ligands
pL	− log of analytical concentration of the ligand in solution
$p\mathrm{L}_{50}$	− log of analytical concentration of the ligand necessary to sequester 50% of the metal ion
S	slope in the flex of the function ($\sum\%$) vs pL
a, b	empirical parameters of equation (10)