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D-Glucuronate complexes of mono-, di- and triorgano tin(IV) compounds: potentiometric and Mössbauer spectroscopic investigations

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Complex species formation of glucuronate with mono-, di- and trimethyltin(IV) cations has been studied potentiometrically in a wide range of ionic strength (0.1 to 1 mol l^{-1}, NaCl medium), at 25 °C. By a suitable complex formation model, according to which all the interactions are considered, the formation constants at infinite dilution have been calculated by using a well-tested equation for the ionic strength dependence. The following complex species have been found ($R = CH_3$): $[RSn(gluc)(OH)]^+$, $[RSn(gluc)(OH)_2]^0$ and $[(RSn)_2(gluc)(OH)_5]^0$ for the monomethyltin(IV)–glucuronate system; $[R_2Sn(gluc)]^+$ and $[R_2Sn(gluc)(OH)]^0$ for the dimethyltin(IV)–glucuronate system; and $[R_3Sn(gluc)]^0$ for the trimethyltin(IV)–glucuronate system. Mössbauer investigations, carried out in quickly frozen solution, confirmed the species formation and led us to propose their structural configuration. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: organotin compounds; D-glucuronate ligand; aqueous solution complexes; formation constants; structural investigations

INTRODUCTION

In a previous paper[1] we reported a study on the complex species formation of D-glucuronate (5-carboxy-D-pyranose) acid with cadmium(II) and zinc(II) ions. The results obtained were in good agreement with literature data and showed the binding capacity of D-glucuronic ligand towards toxic metal ions, confirming its important role—as a component of some natural polysaccharides, such as hemicelluloses, heparin, pectin and alginyc acid, the latter being present in different marine algae—in the detoxification processes in living organisms.[2] The binding capacity of the D-glucuronate ligand has been relatively little investigated, either in aqueous solution,[1,3–6] or in the solid state.[5–7] The donor ability of the D-glucuronate ligand is mainly due to the carboxylate oxygen atoms; also, some authors[6,8] have reported the behaviour of D-glucuronate as a bidentate ligand, both through the oxygen atoms of one alcohol hydroxy group and through the carboxylate one (Fig. 1).

In this paper we extend our investigations on complex formation between the D-glucuronate ligand and organotin(IV) compounds, of which the environmental toxicity is well known.[9–16] Mono-, di- and triorganotin(IV) compounds are widely distributed in the aquatic environment as a consequence of their industrial use[17,18] and the bio-alkylation of inorganic tin compounds.[19–22] Organotin cations show a strong acidity in the Lewis scale.[23] Their reactivity

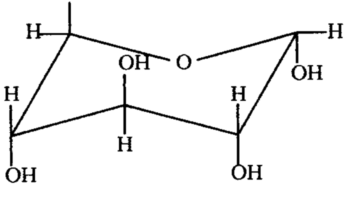

Figure 1. D-Glucuronic acid.

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Table 1. Details of experimental conditions for potentiometric measurements

System	$(CH_3)_xSn^{(4-x)+}$/mM	NaGluc/mM	I/mol l^{-1}
$(CH_3)_3Sn$–Gluc	1, 2, 5	5, 10, 20	0.1, 0.25, 0.5, 0.75, 1
$(CH_3)_2Sn$–Gluc	2, 4	5, 10, 20	0.1, 0.25, 0.5, 0.75, 1
$(CH_3)Sn$–Gluc	2, 4	5, 10	0.1, 0.25, 0.5, 0.75, 1

towards carboxylate ligands has been extensively investigated,[24–27] as have their hydrolysis processes in different aqueous media and in a wide range of ionic strengths.[28–40]

With the aim of contributing further to chemical speciation studies on toxic organometallic compounds in the presence of naturally occurring ligands, we report here a study on the interaction of mono-, di- and trimethyltin cations with the glucuronate ligand in NaCl ionic medium, in the ionic strength range $0.1 \leq I \leq 1$ mol l^{-1}. Formation constants of complex species have been determined by potentiometric measurements ([H$^+$]-glass electrode) at 25 °C. Structural investigations, performed to confirm species formation, have been carried out by Mössbauer spectroscopy in quickly frozen solutions.

MATERIAL AND METHODS

Reagents

Mono-, di- and trimethyltin(IV) (Aldrich and Fluka products) have been used as chloride salts. Sodium glucuronate (Fluka) was used without further purification and its purity, checked potentiometrically, was found to be >99%. NaCl was used as an anhydrous salt and always dried in a stove at 140 °C before use. HCl and NaOH stock solutions were standardized against sodium carbonate and potassium hydrogen phthalate respectively. All solutions were prepared with analytical-grade water, using grade A glassware.

Potentiometric measurements and procedure

Potentiometric measurements were carried out using an apparatus consisting of a Metrohm model 605 potentiometer, equipped with an Orion combination glass electrode (Ross type 8102) and a motorized burette (Metrohm model 654). The estimated accuracy was ±0.15 mV and ±0.003 ml for e.m.f. and titrant volume readings respectively. The apparatus was connected to a personal computer, and automatic titrations were carried out using a suitable home laboratory designed and made computer program (titrant delivery, data acquisition, check for the stability of e.m.f.). All titrations were carried out by stirring magnetically and by bubbling purified and pre-saturated nitrogen through the solution, in order to exclude oxygen and carbon dioxide.

A volume of 25 ml of solution containing the glucuronate ligand as sodium glucuronate, to which a small excess of HCl was added, and the organotin(IV) compound (in turn, mono-, di- and trimethyltin chloride) was titrated with standard NaOH solution up to *ca* pH 9.5. NaCl was added to adjust the ionic strength to the desired value. Details of the experimental conditions used for each system are shown in Table 1.

For each experiment, an independent titration of a corresponding solution (at the same ionic strength) without the components of the system under investigation was carried out in order to determine the electrode potential $E^\circ_{ext}$and the acidic junction potential ($E_j = j_a[H^+]$).

Mössbauer spectroscopic measurements and procedure

The ^{119}Sn Mössbauer spectra of quickly frozen solutions were measured at liquid-nitrogen temperature with a multichannel analyser [TAKES Mod. 269, Ponteranica, Bergamo (Italy)] and the following Wissenschaftliche Elektronik system [MWE, München (Germany)]: an MR250 driving unit, an FG2 digital function generator and an MA250 velocity transducer, moved at linear velocity, constant acceleration, in a triangular waveform. The organotin(IV) samples, contained in cylindrical polyethylene sample holders (≅1 ml, 1 cm^2 section, corresponding to ^{119}Sn = 0.025–0.050 mg cm^{-2}), were maintained at liquid-nitrogen temperature in a model NDR-1258-MD Cryo liquid nitrogen cryostat (Cryo Industries of America, Inc., Atkinson, NH, USA) with a Cryo sample holder. The 77.3 ± 0.1 K temperature was controlled with an ITC 502 temperature controller from Oxford Instruments (Oxford, UK). The multichannel calibration was performed with an enriched iron foil [^{57}Fe = 95.2%, thickness 0.06 mm; Dupont, MA (USA)], at room temperature, by using a ^{57}Co–Pd source [10 mCi; Ritverc GmbH, St Petersburg (Russia)], and the zero point of the Doppler velocity scale was determined, at room temperature, through absorption spectra of natural $CaSnO_3$ (^{119}Sn = 0.5 mg cm^{-2}) and a $Ca^{119}SnO_3$ source [10 mCi; Ritverc GmbH, St Petersburg (Russia)].

In order to determine the geometry of the species discussed below (see Mössbauer spectroscopic investigations section), and according to the distribution curves obtained by potentiometric investigations, ^{119}Sn Mössbauer spectroscopic measurements of quickly frozen solutions were performed at selected pH values. Depending on the concentration of different insoluble products, by increasing the pH precipitates are formed, thus preventing further measurements. As a consequence, the experimental conditions reported in Table 2 were used.

Table 2. Details of the experimental conditions used in the Mössbauer measurements

System	$(CH_3)_xSn^{(4-x)+}$/mM	NaGluc/mM	I/mol l^{-1}	pH
$(CH_3)Sn$–Gluc	25	100	0.25	2.07, 4.41, 6.54, 11.3
$(CH_3)_2Sn$–Gluc	25	100	0.25	3.04, 4.52
$(CH_3)_3Sn$–Gluc	25	100	0.25	4.45

Table 3. Formation constants[a] for the species in the system $(CH_3)_xSn^{(4-x)+}$–gluc$^-$, at $I = 0$ mol l^{-1}, $T = 25\,°C$

System	log β_{pqr}[b]			
	110[c]	11-1	11-2	21-5
CH_3Sn–gluc	–	3.017 ± 0.009	-0.252 ± 0.009	-4.96 ± 0.06
$(CH_3)_2Sn$–gluc	2.431 ± 0.006	-1.193 ± 0.004	–	–
$(CH_3)_3Sn$–gluc	1.605 ± 0.005	–	–	–

[a] From Eqn. (1).

[b] Equilibria refer to the general reaction (R = CH_3): $pR_xSn^{(4-x)+} + q\text{gluc}^- + rH_2O \rightleftharpoons [(R_xSn)_p(\text{gluc})_q(OH)_r{}^{p(4-x)-q-r}] + rH^+$.

[c] pqr, see equilibrium reaction.

CALCULATIONS

Potentiometric data

For the refinement of the parameters of acid–base titrations (E^0, pK_w, coefficient of junction potential j_a, analytical concentration of reagents) and to calculate the hydrolysis and complex formation constants, the BSTAC and STACO computer programs were used.[41] STACO refines formation constants by minimizing the weighted error squares sum of titrant volumes, *i.e.* $\sum w(v - v_{calcd})^2$, whilst BSTAC minimizes $\sum w(E - E_{calcd})^2$. Weights may be kept constant ($w = 1$) or proportional to the potentiometric curve gradient using error propagation. Moreover, STACO and BSTAC are able to perform calculations for non-constant ionic strength conditions (in particular, at low ionic strength there may be significant variations in I during the same titration) and to calculate the thermodynamic constant values (at infinite dilution, *i.e.* for $I \to 0$ mol l^{-1}, see below concerning the dependence on ionic strength). The ES4ECI program[41] was used to draw distribution diagrams and to calculate formation percentages of species. The dependence on ionic strength was considered by using the following Debye–Hückel-type equation:[42]

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

with

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

where K is the formation constant, ${}^{T}K$ is the formation constant at infinite dilution and C and D are empirical parameters. From previous results on the interactions between organotin cations with carboxylic ligands,[24,25] in this work the following values of empirical parameters have been used.

$$C = c_0 p^* + c_1 z^* \qquad \text{with } c_0 = 0.1, c_1 = 0.22 \qquad (2)$$

where

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

and

$$D = d_1 z^* \qquad \text{with } d_1 = -0.1 \qquad (3)$$

Mössbauer spectroscopic data

The 5×10^5 count spectra obtained were refined with the proper software[43] to obtain the isomer shift δ (mm s^{-1}), the nuclear quadrupole splitting Δ (mm s^{-1}), and the width at half-height of the resonant peaks reported in Tables 4–6 below.

RESULTS AND DISCUSSION

Potentiometric investigations

Investigations performed by different authors[23–33,35–40] on the aqueous chemistry of organotin(IV) compounds have previously demonstrated that these cations show strong tendency to hydrolysis, the trend being $CH_3Sn^{3+} > (CH_3)_2Sn^{2+} > (CH_3)_3Sn^+$, over a wide pH range. Therefore, hydrolysis species formation cannot be neglected when determining the formation constants of complex species. The general picture of organotin(IV) cation speciation, including their hydrolysis and chloride species formation, has recently been reported.[34] Analogously, the protonation

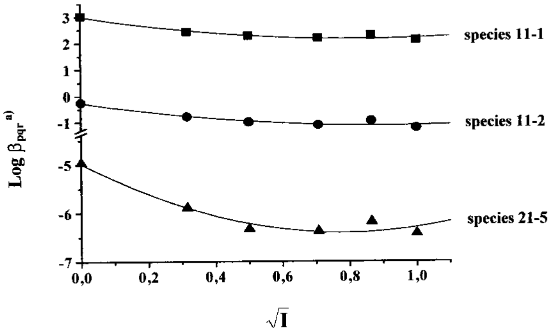


Figure 2. Ionic strength dependence [Eqn. (1)] for complex species in the CH_3Sn–gluc–NaCl system.
The log β_{pqr} values refer to the general reaction:
$p(CH_3)_xSn^{(4-x)+} + q\text{gluc}^- + rH_2O \rightleftharpoons [((CH_3)_xSn)_p(\text{gluc})_q(OH)_r{}^{(p(4-x)-q-r)}] + rH^+$.

of the ligand has to be considered,[1] whilst the weak interaction between glucuronate ligand and Na^+ from the ionic medium can be neglected. By following the above scheme, we studied the interactions between mono-, di- and trimethyltin(IV) cations and D-glucuronic ligand in the $0.1 \leq I$ mol $l^{-1} \leq 1$ ionic strength range (NaCl ionic medium). As expected, the formation of a single simple 1:1 species was only found in the trimethyltin–glucuronic system; in the other systems, mixed hydroxo species are always formed and, in particular, in the monomethyltin–glucuronate system only mixed species are formed, owing to the very strong tendency to hydrolysis of the triply charged organotin cation.

By using the values of the empirical parameters for the ionic strength dependence from Eqns (2) and (3), the formation constants at $I = 0$ mol l^{-1} have been calculated using Eqn. (1), and are reported in Table 3.

As an example, the plots of log β *vs* $I^{1/2}$ in Fig. 2 show the ionic strength dependence for the species formed in the CH_3Sn–gluc system.

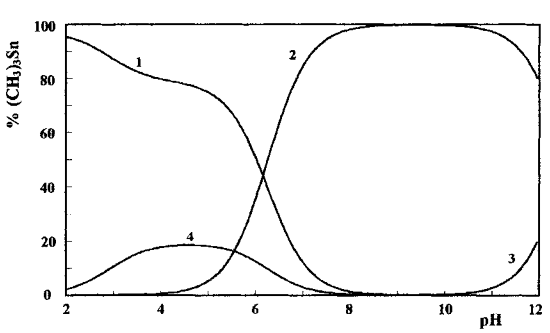


Figure 3. Distribution diagram of complex species in the system $(CH_3)_3Sn$–gluc–NaCl (chloride and other minor species are not reported for the sake of simplicity). Experimental conditions: $(CH_3)_3Sn$ = 5 mM; gluc = 20 mM; NaCl = 0.16 M.
Curves: (1) $[(CH_3)_3Sn]^+$; (2) $[(CH_3)_3Sn(OH)]^0$;
(3) $[(CH_3)_3Sn(OH)_2]^-$; (4) $[(CH_3)_3Sn(Gluc)]^0$.

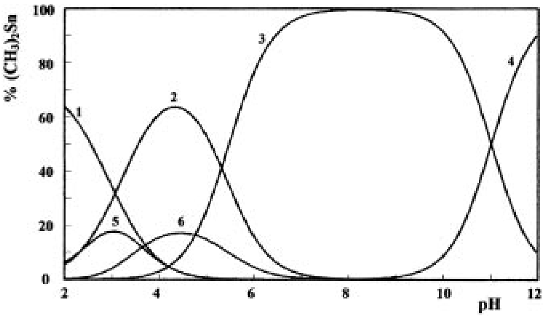


Figure 4. Distribution diagram of complex species in the system $(CH_3)_2Sn$–gluc–NaCl (chloride and other minor species are not reported for the sake of simplicity). Experimental conditions: $(CH_3)_2Sn$ = 5 mM; gluc = 20 mM; NaCl = 0.16 M.
Curves: (1) $(CH_3)_2Sn^{2+}$; (2) $[(CH_3)_2Sn(OH)]^+$;
(3) $[(CH_3)_2Sn(OH)_2]^0$; (4) $[(CH_3)_2Sn(OH)_3]^-$;
(5) $[(CH_3)_2Sn(Gluc)]^+$; (6) $[(CH_3)_2Sn(Gluc)(OH)]^0$.

By means of the ES4ECI computer program,[41] distribution diagrams have been drawn for the simple and mixed hydroxo species formed over a wide pH range for all the $(CH_3)_xSn$–gluc–NaCl ($x = 1$, 2, 3) investigated (Figs 3–5). Formation percentages of the species refer to the following experimental conditions: $[(CH_3)_xSnCl_{4-x}]$ = 5 mM and [gluc–Na] = 20 mM. To draw diagrams, the ionic strength values of most biological fluids (0.16 mol l^{-1}) have been considered. Neverthless, as the investigations have been performed in the $0.1 \leq I$ mol $l^{-1} \leq 1$ ionic strength range, the considerations reported below can also be extended to most natural waters.

The values of hydrolysis constants and chloride complex formation constants for all organotin(IV) systems were taken

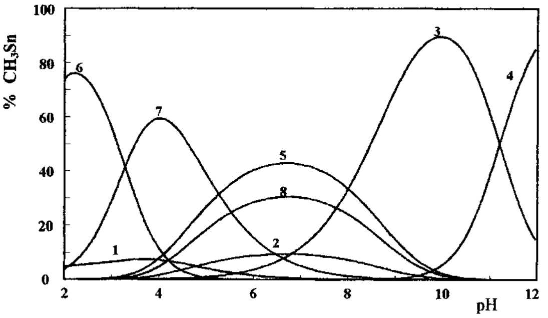


Figure 5. Distribution diagram of complex species in the system CH_3Sn–gluc–NaCl. Experimental conditions: CH_3Sn = 5 mM; gluc = 20 mM; NaCl = 0.16 M.
Curves: (1) $[CH_3Sn(OH)_2]^+$; (2) $[(CH_3Sn)_2(OH)_5]^+$;
(3) $[CH_3Sn(OH)_3]^0$; (4) $[CH_3Sn(OH)_4]^-$; (5) $[(CH_3Sn)_2Cl(OH)_5]^0$;
(6) $[CH_3Sn(gluc)(OH)]^+$; (7) $[CH_3Sn(gluc)(OH)_2]^0$;
(8) $[(CH_3Sn)_2(gluc)(OH)_5]^0$.

Table 4. Pqs values used for Δ calculations[a]

Donor atom or group	Structure			
	Tet	Tba	Tbe	Oct
−Me	−1.37	−0.94	−1.13	−1.03
−OH (alcohol) and OH^-	−0.20	−0.13	0.02	−0.14
H_2O	0.27	0.18	0.43	0.09
COO^- unidentate	−0.18	−0.10	0.06	−0.11
COO^- bridging	0.11	0.075	0.29	0.083

[a] Data obtained from Refs 44–50 and calculated from these for the missing values.

from the paper by Foti *et al.*[34] Owing to their low percentage formation, mixed chloride species are neglected in the trimethyltin- and dimethyltin–glucuronate systems. In the $(CH_3)_3Sn$–gluc–NaCl system (Fig. 3) the simple 1:1 species (curve 4) is formed, with a maximum 20% formation, over the pH range of interest for natural and biological fluids. Analogously, in the $(CH_3)_2Sn$–gluc–NaCl system (Fig. 4) both the simple and the mixed hydroxy glucuronate species (curves 5 and 6 respectively), achieving no more than maximum 20% formation, are formed in the range pH 2–6, whereas only the hydrolytic species of the dimethyltin cation predominate in the pH range of interest for natural fluids.

Table 5. Mössbauer data and proposed structures of complex species in the monomethyltin (IV)–glucuronate system

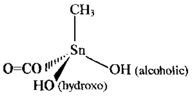
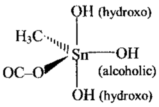
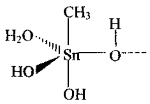
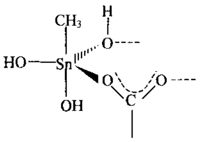
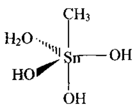
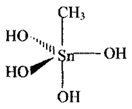
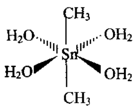
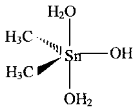
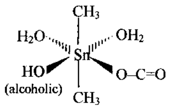
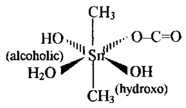
pH	Complex formed	δ (mm s^{-1})	Δ (mm s^{-1})	Proposed structure
2.07 and 4.41	$[CH_3Sn(gluc)(OH)]^+$ (species 11-1)	0.70	2.45	 (A) $\Delta_{calc.} = 2.35$
4.41	$[CH_3Sn(gluc)(OH)_2]^0$ (species 11-2)	0.53	1.97	 (B) $\Delta_{calc.} = 2.10$
6.54	$[(CH_3Sn)_2(OH)_5]^+$ (species 20-5)	0.54	1.56	 (C) $\Delta_{calc} = 1.35$
	$[(CH_3Sn)_2(gluc)(OH)_5]$ (species 21-5)	0.60	2.22	 (D) $\Delta_{calc} = 2.52$
9.95 and 11.30	$[CH_3Sn(OH)_3]$ (species 10-3)	0.54	1.56	 (E) $\Delta_{calc} = 1.35$
11.30	$[CH_3Sn(OH)_4]^-$ (species 10-4)	0.58	2.23	 (F) $\Delta_{calc} = 2.20$

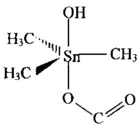
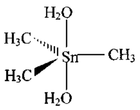
Table 6. Mössbauer data and proposed structures of complex species in the dimethyltin(IV)–glucuronate system

pH	Complex formed	Species	δ (mm s^{-1})	Δ (mm s^{-1})	Proposed structure
3.04	$[(CH_3)_2Sn(H_2O)_4]^{2+}$	100	1.43	4.34	 (G) $\Delta_{calc.}$ = 4.92
3.04 and 4.52	$[(CH_3)_2Sn(OH)]^+$	10-1	1.33	3.41	 (H) $\Delta_{calc.}$ = 3.56
3.04	$[(CH_3)_2Sn(gluc)]^+$	110	1.43	4.14	 (I) Δ_{calc} = 4.27
4.52	$[(CH_3)_2Sn(gluc)(OH)]^+$	111	1.34	4.32	 (L) Δ_{calc} = 3.98

As expected, the monomethyltin(IV)–glucuronate system shows a different behaviour (Fig. 5). Because hydrolysis of the monomethyltin(IV) cation can also occur in the very acidic pH range,[30] no simple CH_3Sn^{3+}-$gluc^-$ species is formed.

Calculations performed in all the pH ranges investigated experimentally show the formation of three mixed hydroxo species: $[CH_3Sn(gluc)(OH)]^+$, $[CH_3Sn(gluc)(OH)_2]^0$ and $[(CH_3Sn)_2(gluc)(OH)_5]^0$ the first two (curves 6 and 7) achieve their maximum percentage formation at acidic pH values (75% and 60% at pH 2.4 and pH 4 respectively), and the third

Table 7. Mössbauer data and proposed structures of complex species in the trimethyltin(IV)–glucuronate system

pH	Complex formed	Species	δ (mm s^{-1})	$\|\Delta\|$ (mm s^{-1})	Proposed structure
	$[(CH_3)_3Sn(gluc)]^0$	110	1.40	3.18	 (M) $\Delta_{calc.}$ = 2.93
4.55	and $[(CH_3)_3Sn(H_2O)_2]^+$	100	1.43	3.80	 (N) $\Delta_{calc.}$ = -3.54

one (curve 8) is formed, together with the corresponding hydroxo-chloride species (curve 5), in the pH range of interest for natural and biological fluids, with a maximum 30% formation at *ca* pH 7.

Mössbauer spectroscopic investigations

The partial quadrupole splitting (p.q.s.) values of the different functional groups used in calculations were taken from the literature[44–50] and are reported in Table 4.

Comparison of the experimental Δ values with those calculated on the basis of the point-charge model (p.c.m.)[44] enabled us to propose the steric arrangements of the complex species formed. Results obtained for the mono-, di- and trimethyltin(IV)–glucuronate systems are summarized in Tables 5–7 below.

Monomethyltin(IV)–glucuronate system

The Mössbauer spectra for the system monomethyltin(IV)–glucuronate were measured in the acidic pH region. The spectrum at pH 2.07, containing one doublet, characteristic of a single tin(IV) absorbing atom, which, following the rationalization of the experimental nuclear quadrupole splitting according to the p.c.m. formalism, can be attributed to the species 11-1, $[CH_3Sn(gluc)(OH)]^+$ in a tetrahedral environment [Table 5, (A)], in which the glucuronate behaves as a monoanionic bidentate ligand through the monodentate carboxylate and an alcohol hydroxo group. At pH 4.41, two overlapping doublets are present in the spectrum, which can be assigned, on the basis of the distribution diagram (see Fig. 5), and according to the p.c.m. formalism, to the monohydroxo–monomethyltin(IV)–glucuronate cation (species 11-1), $[CH_3Sn(gluc)(OH)]^+$ [Table 5, (A)] and to the dihydroxo–monomethyltin(IV)–glucuronate species 11-2, $[CH_3Sn(gluc)(OH)_2]^0$. In $[CH_3Sn(gluc)(OH)_2]^0$, the tin(IV) is embedded in a trigonal bipyramidal environment, with the methyl group, the unidentate carboxylate group and the alcohol OH in the equatorial plane, whereas the two hydroxo groups are in the axial positions [Table 5, (B)]. A two-doublet spectrum was obtained at pH 6.54, from which two Δ values have been extracted, characteristic of the hydrolytic dimeric species (20-5) bis-[monometyltin(IV)] pentahydroxo cation, $[(CH_3Sn)_2(OH)_5]^+$ [Table 5, (C)], and of the complex (species 21-5) bis-[monometyltin(IV)] pentahydroxo–glucuronate, $[(CH_3Sn)_2(gluc)(OH)_5]^0$ [Table 5, (D)]. In both the complexes the two tin atoms are in a trigonal bipyramidal configuration with bridging hydroxo groups. Furthermore, in $[(CH_3Sn)_2(gluc)(OH)_5]^0$, a second bridge is constituted by a bidentate carboxylate [Table 5, (D)]. At pH 9.95 and pH 11.30, the Δ values could be explained only as a result of Mössbauer-monitored hydrolysis of $[\text{monomethyltin(IV)}]^{3+}$, leading to $[CH_3Sn(OH)_3]^0$ and $[CH_3Sn(OH)_4]^-$ anion. In particular, at pH 9.95, the occurrence of a doublet and the comparison of experimental and calculated Δ values indicated that the species formed contained only an absorbing species with the tin(IV) atom in a trigonal bipyramidal configuration [Table 5, (E)], with composition 1–3, $[CH_3Sn(OH)_3]^0$. The fifth coordination site should be occupied by a water molecule [Table 5, (E)]. At pH 11.3, two overlapping doublets may be superimposed in the Mössbauer spectrum, according to which the two experimental Δ values would strongly suggest the occurrence of the previously described neutral trihydroxo–monomethyltin(IV) species, 1-3, and of an anionic trigonal bipyramidal tetrahydroxo–monomethyltin(IV) species, 1-4, [Table 5, (E) and (F) respectively].

Dimethyltin(IV)–glucuronate system

The Mössbauer spectrum of the dimethyltin(IV)–glucuronate system in the acidic pH range (pH 3.04) contained three doublets, which, on the basis of the distribution curves (Fig. 3), could be assigned to the hydrated dimethyltin(IV) cation, 100, $[(CH_3)_2Sn(H_2O)_4]^{2+}$, to the dimethyltin(IV)–glucuronate (species 110), $[(CH_3)_2Sn(gluc)]^+$, both in *trans*-Me_2 octahedral structures, and, finally, to the hydrolysis product with composition 10-1, $[(CH_3)_2Sn(OH)]^+$, whose structure is likely to be trigonal bipyramidal *cis*-Me_2 in the equatorial plane [Table 6, (G)–(I)]. The $|\Delta|$ value found for the species 110 is very similar to that published by Barbieri and Silvestri[48] as a result of Mössbauer-monitored hydrolysis of $\text{dimethyltin(IV)}^{2+}$. The two doublets, present in the Mössbauer spectrum at pH 4.52 were due to the hydrolysis product with composition 10-1, $[(CH_3)_2Sn(OH)]^+$, described previously, and to the hydroxo–dimethyltin(IV)–glucuronate complex, 11-1, in a *trans*-Me_2 octahedral configuration [Table 6, (L)].

Trimethyltin(IV)–glucuronate

The experimental Mössbauer spectrum of the trimethyltin(IV)–glucuronate system, determined at pH 4.55, can be deconvoluted for two doublets representing the aquocation $[(CH_3)_3Sn(H_2O)_2]^+$ (species 100) and the trimethyltin(IV)-glucuronato complex $[(CH_3)_3Sn(gluc)]^0$ (species 110). According to their $|\Delta|$ values, they should be five-coordinated tin(IV) compounds, in which the methyl groups are displaced in the equatorial plane of the trigonal bipyramidal structure [Table 7, (M) and (N)].

CONCLUSIONS

The results obtained allow us to make the following conclusion.

(1) Concerning complex formation, it must be pointed out that, owing to the strong tendency to hydrolysis of all the organotin cations investigated, no simple species is formed in the trimethyl–glucuronate system; the mixed hydroxo–glucuronate species formed generally achieve their maximum percentage formation in the

acidic pH range. In the monomethyl–glucuronate system, the species $[CH_3Sn(gluc)(OH)_2]^0$ shows a more than 30% maximum formation in the pH range of interest for natural and biological fluids.

(2) Mössbauer spectroscopic investigations confirm the complex species formation and enable us to propose a hypothetical structure for each of them. Mössbauer data, first here reported, also confirm the formation of the hydroxo species $[(CH_3Sn)_2(OH)_5]^+$, whose formation was found by potentiometric investigations and reported previously.[30,34]

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