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Speciation Analysis and Environment **AOC**

Speciation of organotin compounds in NaCl aqueous solution: interaction of mono-, di- and tri-organotin(IV) cations with nucleotide 5′ monophosphates

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Formation constants for complex species of mono-, di- and tri-alkyltin(IV) cations with some nucleotide 5′-monophosphates (AMP, UMP, IMP and GMP) are reported, at $T = 25\,^{\circ}\mathrm{C}$ and at $I = 0.16$ mol l^{-1} (NaCl). The investigation was performed in the light of speciation of organometallic compounds in natural fluids in the presence of nucleotides whose biological importance is well recognized. The simple and mixed hydrolytic complex species formed in all the systems investigated in the pH range 3–9 are (L = nucleotide; M = organotin cation $R_x\,Sn^{(4-x)+}$, with $x = 1$ to 3): ML^+, $ML(OH)^0$ and $ML(OH)_2{}^-$ for the system CH_3Sn^{3+}–L (L = AMP, IMP, UMP); ML^0 and $ML(OH)^-$ for the system $(C_2H_5)_2Sn^{2+}$–L (L = AMP, IMP, UMP); ML^-, $ML(OH)^{2-}$, MLH^0 and $M_2L(OH)^-$ for the system $(C_2H_5)_3Sn^+$–L (L = AMP); ML, $ML(OH)^{2-}$ and M_2L^0 for the system $(C_2H_5)_3Sn^+$–L (L = IMP, UMP). As expected, owing to the strong tendency of organotin(IV) cations to hydrolysis in aqueous solution, the main species formed in the pH range of interest of natural fluids are the mixed hydrolytic ones. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: nucleotides; organotin(IV) compounds; complex formation constants; chemical speciation

INTRODUCTION

The binding ability of nucleotides and nucleic acids towards metal ions has been extensively investigated for about 50 years, in the light of many biochemical and enzymatic processes involving biological systems. The occurrence of enzymatic reactions often requires the presence of essential metal ions; on the other hand, enzyme function is inhibited by the presence of toxic metals. Therefore, when studying biological and environmental processes where nucleotides are involved, the interactions of these substances with metal ions cannot be neglected. The solution chemistry of nucleotides depends mainly on the binding capacity of phosphate groups, in particular the terminal one; in some cases, also depending on the pH conditions, the nitrogen of the base, generally N-7, participates in metal complexation. Protonation constants and complex formation constants of nucleotides with most metal ions, determined in different experimental conditions are reported in many papers and different compilations.[1–9] In spite of this very large amount of literature data on the metal complex formation of nucleotides, there is a substantial lack of information on the interaction of nucleotides with some organic (such as polyamines, which act as cations in their protonated form at

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pH values of environmental and biological interest[10]) and organometallic aquatic pollutants. In particular, only very few data are reported in the literature on the interaction of nucleotides with organotin(IV) cations ($R_xSn^{(4-x)+}$, with R = alkyl group and $x = 1$ to 3),[11] whose presence in aquatic ecosystems is derived both from their industrial use (as fungicides in agriculture, as wood preservatives, as stabilizers and catalysts in PVC and in foam production, and as antifouling additives in paints for ships) and from microbial alkylation processes of the inorganic tin in the presence of detritus organic matter in sediments.[12,13] Organotin(IV) cations are considered as acids, in the Lewis sense, of different hardness, depending on the groups bonded to the tin(IV). Consequently, they show a strong tendency towards hydrolysis, in the order $RSn^{3+} >> R_2Sn^{2+} > R_3Sn^+$, as demonstrated by studies performed in our laboratories to investigate the aqueous solution chemistry of organotin(IV) compounds in different ionic media and at different ionic strengths.[14–17] By considering the acid–base behaviour of both nucleotides and organotin cations (i.e. by taking into account protonation constants of nucleotides and hydrolytic species formation of organotin(IV) cations), we report here the results of a potentiometric study on complex species formation between monomethyltin(IV), diethyltin(IV), and triethyltin(IV) cations and the nucleotides adenosine, uridine, inosine and guanosine 5′-monophosphates (AMP, UMP, IMP and GMP respectively) whose structures are reported in Scheme 1. The investigations have been performed in NaCl ionic medium, at $I = 0.16\ \text{mol}\ \text{l}^{-1}$ and in the pH range 3–9. Measurements have been carried out by $[H^+]$ glass electrode, at $T = 25\,°C$.

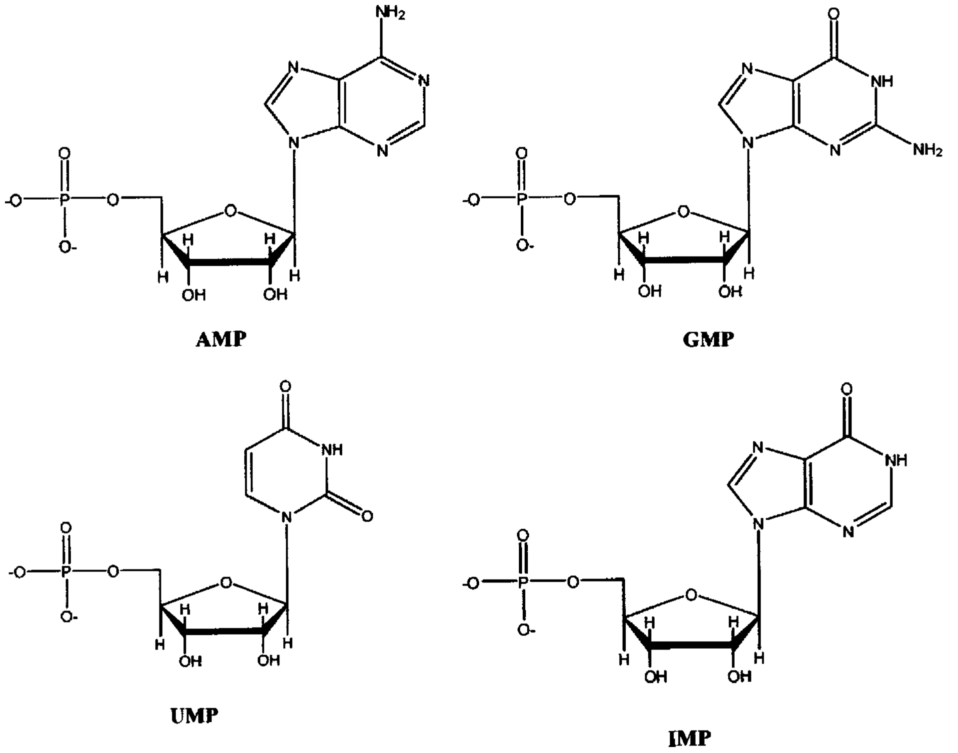
EXPERIMENTAL

Materials

Nucleotide 5′-monophosphates (AMP, GMP, IMP, UMP), all in the form of the disodium salts, were from Acros Organic. Their purity, ranging from 98 to 99%, was checked potentiometrically. The purity value of each nucleotide was taken into account in the calculations. Alkyltin(IV) compounds were used as chloride salts (from Alfa-Aesar). Hydrochloric acid and sodium hydroxide solutions were standardized against sodium carbonate and potassium biphthalate respectively. All the solutions were prepared by using twice-distilled, CO_2-free freshly prepared water ($R = 18\ \text{M}\Omega\ \text{cm}^{-1}$) and grade A glassware was always employed.

Apparatus and procedure

The measurements were carried out using a potentiometric apparatus consisting of a Metrohm model 665 automatic titrant dispenser coupled with a Crison model MicropH 2002 potentiometer and using a combination Orion-Ross 8172 glass electrode. The estimated accuracy of this system was



Scheme 1. Structures of nucleotide 5′-monophosphates.

±0.15 mV and ±0.003 cm^3 for e.m.f. and titrant volume reading respectively. Pure nitrogen was bubbled into the titration cell in order to avoid O_2 and CO_2 inside, and the solutions were stirred magnetically. A volume of 20–25 ml of solution containing the organotin(IV) chlorides (0.5–1.0 mmol l^{-1}, 2–5 mmol l^{-1} and 5–8 mmol l^{-1}, for mono-, di- and tri-alkyl derivatives respectively) and nucleotides (0.5–2.0 mmol l^{-1}, 4–15 mmol l^{-1} and 10–25 mmol l^{-1} respectively), in the presence of a slight excess of hydrochloric acid, was titrated with sodium hydroxide solutions in the pH range 3–9. NaCl was added as background salt in order to adjust the ionic strength value to 0.16 mol l^{-1}. In order to determine the electrode formal potential E^0, independent titrations of HCl (~10 mmol l^{-1}) with NaOH standard solution as titrant were performed under the same experimental conditions of ionic strength (0.16 mol l^{-1}, in NaCl) and temperature as the systems under investigation.

Calculations

The nonlinear least-squares computer program ESAB2M[18] was used in order to determine all the parameters of an acid–base titration (analytical concentration of the reagents, electrode potential, junction potential coefficient j_a, ionic product of water K_w). The following additional computer programs[19] were also used: BSTAC and STACO to calculate protonation and formation constants, and ES4ECI to draw distribution diagrams of the species in solution and to compute species formation. Formation constants are expressed as β_{pqr} according to the following equilibrium:

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

with $M = R_xSn^{(4-x)+}$; L = AMP, GMP, UMP or IMP. In Eqn (1), hydrolysis is also taken into account, and in this case $r < 0$.

RESULTS AND DISCUSSION

Protonation of nucleotides

Apparent protonation constants of nucleotides in NaCl ionic medium, used in this study, were taken from the literature.[1,10,20] For the ionic strength used in this study, $I = 0.16$ mol l^{-1}, we have: AMP, log $K_1^H = 6.16$, log $K_2^H = 3.8$; GMP, log $K_1^H = 6.19$; IMP, log $K_1^H = 6.17$; UMP, log $K_1^H = 6.03$, log $K[UMP(H)_{-1} + H^+ = UMP] = -6.4$.

Hydrolysis of organotin(IV) cations

All the investigations carried out on the aqueous solution chemistry of organotin(IV) compounds show that the hydrolytic species are by far the most important species formed in a wide range of pH. Therefore, in the studies of the interaction of organotin(IV) cations with different classes of ligands, in order to define their chemical speciation in natural fluids, the formation of hydrolytic species cannot be neglected.[14–17] In this study we used the hydrolysis constants values, previously determined,[14,17] reported in Table 1.

Table 1. Hydrolysis constants of $R_xSn^{(4-x)+}$ cations at $I = 0$ mol l^{-1} and $T = 25$ °C

	log β^{*a}		
Species (*pr*)	CH_3Sn^{3+b}	$(C_2H_5)_2Sn^{2+c}$	$(C_2H_5)_3Sn^{+c}$
1-1	−1.5	−3.09	−6.34
1-2	−3.46	−8.61	−18.17
1-3	−9.09	−20.08	–
1-4	−20.47	–	–
2-1		–	−4.77
2-2	–	−4.79	–
2-3	–	−9.95	–
2-5	−7.69	–	–

[a] log β^* hydrolysis constants refer to the reaction $pM + rH_2O = M_p(OH)_r + rH$ [M = alkyltin(IV) cation; charges omitted].

[b] Ref. 14.

[c] Ref. 17.

Complex species formation in the systems organotin(IV)–nucleotides

The formation constants of nucleotide 5′-monophosphates with mono-, di- and tri-alkyltin cations and their hydroxo species have been calculated using the STACO and BSTAC computer programs.[19] Results at $I = 0.16$ mol l^{-1} in NaCl and $T = 25$ °C are reported in Table 2. Different nucleotide 5′-monophosphates form the same species with CH_3Sn^{3+}, i.e. $(CH_3Sn)L^+$, $(CH_3Sn)LH^0_{-1}$ [or $(CH_3Sn)L(OH)^0$] and $(CH_3Sn)LH^-_{-2}$ [or $(CH_3Sn)L(OH)_2{}^-$]. The stability of these species is very high with mean formation constants [equilibrium (1)] log $\beta_{110} = 10.2 \pm 0.6$, log $\beta_{11-1} = 7.0 \pm 0.3$, and log $\beta_{11-2} = 1.0 \pm 0.3$.

The stability trend in the CH_3Sn^{3+}–XMP system is AMP > GMP > IMP < UMP for the (110) species and UMP > AMP > GMP > IMP for the (11-1) species. Analogous complexes are formed in the $(C_2H_5)_2Sn^{2+}$–XMP systems having the same stoichiometry as for monomethyltin(IV), but the (11-2) species is not formed. A more complicated formation model is shown by the triethyltin(IV) systems: in addition to the species (110) and (11-1), two further species (111 and 21-1) are formed in the presence of AMP, and for both IMP and UMP we found the species (210).

Speciation profiles of organotin(IV)–nucleotide systems

The speciation models proposed are valid for the experimental conditions of this investigation; however, it is quite probable that the formation of other species (in particular polynuclear species) will occur at higher reagent concentrations and that there will be a noticeable decrease in the formation of some species at very low reagent concentrations. In our experimental conditions, all the species proposed in

Table 2. Formation constants of complex species in the system $R_xSn^{(4-x)+}$–L (R = CH_3, C_2H_5; L = AMP, GMP, UMP, IMP), at $I = 0.16$ mol l^{-1} in NaCl and $T = 25$ °C

	$\log \beta_{pqr} \pm 3\,s$[a]					
L	$\log \beta_{110}$	$\log \beta_{11-1}$	$\log \beta_{11-2}$	$\log \beta_{210}$	$\log \beta_{111}$	$\log \beta_{21-1}$
CH_3Sn^{3+}						
AMP	10.79 ± 0.09	6.94 ± 0.08	1.2 ± 0.2	–	–	–
GMP	9.97 ± 0.15	6.91 ± 0.12	1.3 ± 0.2	–	–	–
IMP	9.40 ± 0.09	6.68 ± 0.06	0.7 ± 0.2	–	–	–
UMP	9.63 ± 0.07	7.24 ± 0.07	0.8 ± 0.2	–	–	–
$(C_2H_5)_2Sn^{2+}$						
AMP	5.24 ± 0.05	0.17 ± 0.05	–	–	–	–
IMP	5.29 ± 0.05	0.81 ± 0.05	–	–	–	–
UMP	5.07 ± 0.04	0.29 ± 0.04	–	–	–	–
$(C_2H_5)_3Sn^{+}$						
AMP	2.53 ± 0.05	−5.00 ± 0.15	–	–	7.54 ± 0.10	−1.86 ± 0.15
IMP	3.8 ± 0.2	−3.6 ± 0.2	–	7.4 ± 0.3	–	–
UMP	4.10 ± 0.15	−2.7 ± 0.2	–	7.7 ± 0.2	–	–

[a] Formation constants refer to the equilibrium $pM + qL + rH_2O = M_pL_q(OH)_r$ (M = alkyltin cation, L = nucleotide; charges omitted); s = standard deviation.

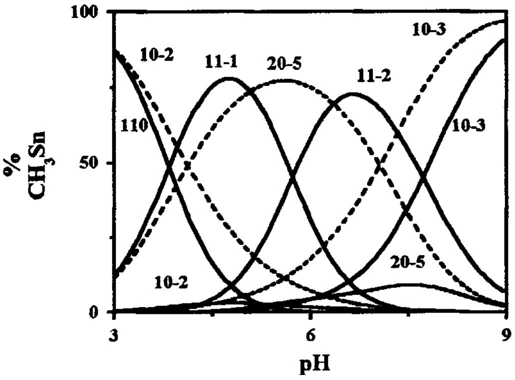


Figure 1. Distribution diagram of species for the system CH_3Sn^{3+}–AMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25$ °C. $C_{CH_3Sn} = 0.5$ mmol l^{-1}; $C_{AMP} = 1.0$ mmol l^{-1}. Dotted lines: simple hydrolytic species of monomethyltin(IV) cation in absence of AMP.

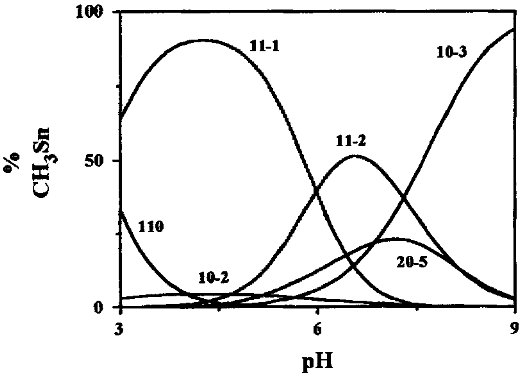


Figure 2. Distribution diagram of species for the system CH_3Sn^{3+}–IMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25$ °C. $C_{CH_3Sn} = 0.5$ mmol l^{-1}; $C_{IMP} = 1.0$ mmol l^{-1}.

the models are formed in significant amount as shown in the distribution diagrams reported in Figures 1–6.

In particular, we must pay attention to the behaviour of the CH_3Sn^{3+}–AMP system, where high yields are obtained with a very significant shift of hydrolytic species to higher pH values (Figure 1). In dilute conditions, where mononuclear species prevail, the stability of all nucleotide complexes of mono-, di- and tri-organotin(IV) compounds can be expressed by the following simple predictive relationship:

$$\log \beta = 3.3 + 0.25a^2 - 7.97b + 0.93ab \qquad (2)$$

with $a = \sqrt{z^3}$ and $b = \sqrt{r^3}$ (where z is the charge and r is the number of OH groups in the complex species). All mononuclear species in Table 2 are fitted by Eqn (2) with a mean deviation $\varepsilon = 0.4$.

In order to make uniform conditions and to compare formation data for all the systems under investigation, the formation percentages of species have been calculated, by means of the ES4ECI computer program,[19] at $I = 0.16$ mol l^{-1} (NaCl) in the pH range 6–9, of biological and environmental interest, by using the same following reagent concentrations: $C_{R_xSn^{(4-x)+}} = 0.5$ mmol l^{-1}; $C_{XMP} = 1$ mmol l^{-1}. Results are reported in Tables 3–5. Moreover, in order to compare the strength of interaction between organotin(IV) cations and nucleotide 5′-monophosphates with the hydrolysis processes, the formation percentages of the main simple hydrolytic species of organotin(IV) compounds which are formed in the same pH range[16–19] are also reported. As can be seen,

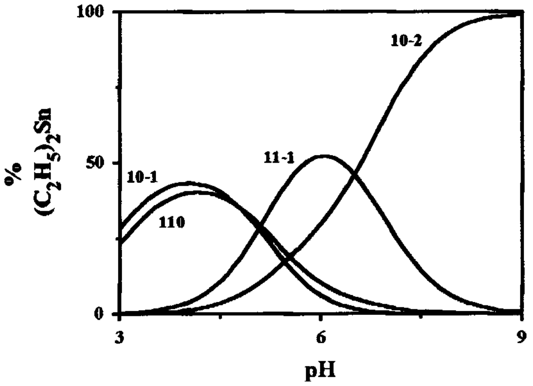


Figure 3. Distribution diagram of species for the system $(C_2H_5)_2Sn^{2+}$–AMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25\,°C$. $C_{(C_2H_5)_2Sn} = 3.0$ mmol l^{-1}; $C_{AMP} = 6.0$ mmol l^{-1}.

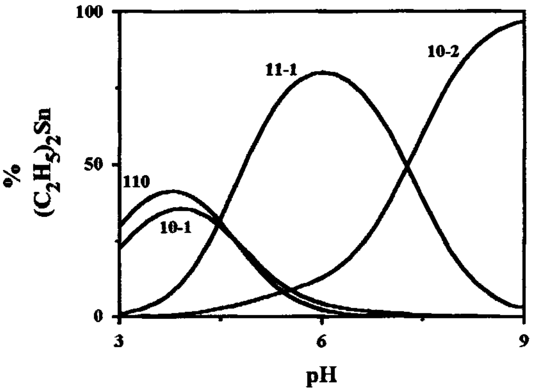


Figure 4. Distribution diagram of species for the system $(C_2H_5)_2Sn^{2+}$–IMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25\,°C$. $C_{(C_2H_5)_2Sn} = 3.0$ mmol l^{-1}; $C_{IMP} = 6.0$ mmol l^{-1}.

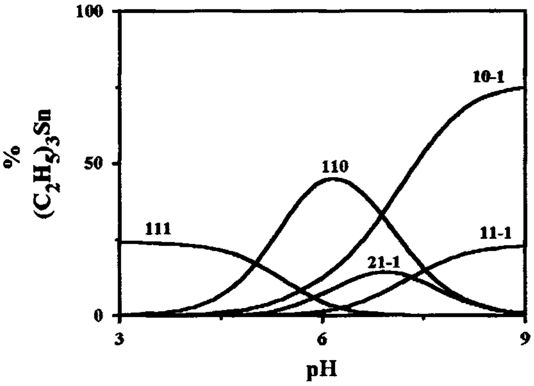


Figure 5. Distribution diagram of species for the system $(C_2H_5)_3Sn^{+}$–AMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25\,°C$. $C_{(C_2H_5)_3Sn} = 7.0$ mmol l^{-1}; $C_{AMP} = 15$ mmol l^{-1}.

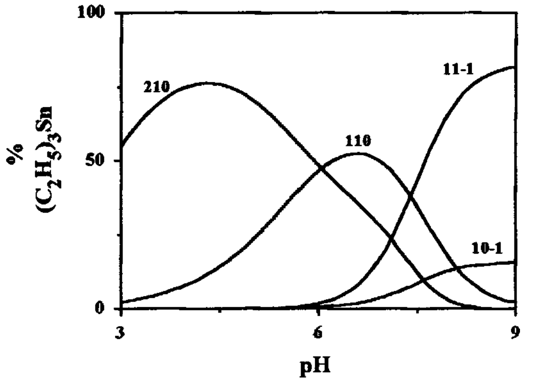


Figure 6. Distribution diagram of species for the system $(C_2H_5)_3Sn^{+}$–IMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25\,°C$. $C_{(C_2H_5)_3Sn} = 7.0$ mmol l^{-1}; $C_{IMP} = 15$ mmol l^{-1}.

for most of the systems investigated only mixed hydrolytic species are formed (in addition to the simple hydrolytic ones) in the pH range considered. In this range, the formation of simple organotin–XMP species is negligible, except for the triethyltin–UMP system (Table 5), where, in addition to the (110) species with yields of more than 49% at pH 6 and more than 28% at pH 7, a further $[(C_2H_5)_3Sn^+]_2UMP$ species is formed with a formation percentage ranging between about 25% and 5% at pH 6–7.

The high stability of hydroxo mixed species in the system CH_3Sn^{3+}–XMP (see Table 2) lowers considerably the formation of simple hydrolytic species of the monomethyltin(IV) cation, as shown in the distribution diagram of Figure 1, where, for comparison, the simple hydrolytic species of CH_3Sn^{3+} cation in the absence of the AMP ligand (dotted line) are also reported. In the CH_3Sn^{3+}–XMP system the main mixed species formed is $CH_3Sn(XMP)(OH)_2^-$ (species 11-2; see Table 3), which achieves about 70% formation at pH 7, which is in the region of interest for most biological fluids and natural fresh waters having a similar ionic strength value to that used in this investigation. The (11-2) species also shows a noticeable formation percentage at the typical pH conditions of seawater (pH 8), even if a lower formation percentage is obtained when considering the real ionic strength of seawater (~0.7 mol l^{-1}). In this case, in fact, owing to the higher concentration of sodium and chloride ions and the presence of other interacting components such as calcium, magnesium and sulfate ions, the free available concentration of both XMP and organotin(IV) cations, as well as their hydrolytic species, is lower, as shown in previous investigations on the chemical speciation of organotins[20] and nucleotides[21] in seawater.

The main mixed species in the system $(C_2H_5)_2Sn^{2+}$–XMP (see Table 4) is the (11-1) species $[(C_2H_5)_2Sn(XMP)(OH)^-]$, which is formed in a significant amount in the pH range 6–7.

Nevertheless, in this system, the simple hydrolytic species of diethyltin(IV) cation always shows a higher formation percentage in comparison with that of the mixed ones owing to their higher stability (see Table 2). Also in the case of $(C_2H_5)_2Sn^{2+}$–IMP, where a considerable amount

Table 3. Formation percentages of species in the system CH_3Sn^{3+}–XMP (XMP = AMP, GMP, UMP, IMP) in the pH range 6–9. $C_{CH_3Sn} = 0.5$ mmol l^{-1}; $C_{XMP} = 1$ mmol l^{-1}; $I = 0.16$ mol l^{-1} (NaCl)

Species	Formation percentages			
(*pqr*)[a]	pH 6	pH 7	pH 8	pH 9
AMP				
11-1	32.4 ± 0.1[b]	3.9 ± 0.1[b]	–	–
11-2	58.9 ± 0.1	70.8 ± 0.1	35.4 ± 0.1[b]	6.9 ± 0.1[b]
10-3	3.3 ± 0.1	16.1 ± 0.1	54.3 ± 0.1	89.8 ± 0.1
20-5	3.7 ± 0.1	8.6 ± 0.1	9.8 ± 0.1	2.7 ± 0.1
GMP				
11-1	26.4 ± 3.2	3.1 ± 0.5	–	–
11-2	64.7 ± 4.2	74.9 ± 3.2	40.2 ± 3.5	8.6 ± 1.2
10-3	3.5 ± 0.3	14.5 ± 1.4	50.8 ± 2.6	88.3 ± 1.1
20-5	4.00 ± 0.8	7.0 ± 1.3	8.6 ± 0.9	2.6 ± 0.1
IMP				
11-1	38.4 ± 2.6	4.4 ± 0.4	–	–
11-2	40.2 ± 4.1	45.7 ± 4.0	16.5 ± 2.1	2.5 ± 0.4
10-3	6.1 ± 0.3	26.0 ± 1.3	67.7 ± 1.4	93.9 ± 0.4
20-5	12.5 ± 1.3	22.7 ± 2.3	15.4 ± 0.7	2.9 ± 0.1
UMP				
11-1	66.7 ± 2.8	11.0 ± 0.8	–	–
11-2	24.2 ± 3.1	39.9 ± 3.8	14.2 ± 1.9	2.1 ± 0.3
10-3	3.5 ± 0.2	25.8 ± 1.1	69.2 ± 1.3	94.3 ± 0.3
20-5	4.1 ± 0.4	22.2 ± 1.9	15.9 ± 0.6	3.0 ± 0.1

[a] Indexes refer to the equilibrium reaction: $pR_xSn + qXMP + rH_2O = (R_xSn)_p(XMP)_q(OH)_r$.

[b] Plus/Minus standard deviation.

of mixed species (11-1) is formed at pH 6, the sum of simple hydrolytic species is higher. The distribution diagrams of species for the $(C_2H_5)_2Sn^{2+}$–XMP (XMP = AMP, IMP, UMP) systems in the pH range 3–9 are reported in Figure 7a–c.

The formation percentages of nucleotide monophosphate species with triethyltin(IV) cation are shown in Table 5. The speciation model for these systems is very different than that of the monomethyl and diethyl nucleotide systems because the hydrolysis processes of the triorganotin(IV) cation below pH 7 are much weaker than that of di-organotin and mono-organotin cations (see Table 1). For this reason, the formation of simple species (110) and (210) occurs up to pH 7 in significant percentages. Above pH 7 the mixed (11-1) species, together with the simple hydrolytic one (10-1), is formed in triethyltin(IV)–UMP and –IMP systems, where an inversion in the formation percentage of these species can be observed (see Figure 8).

Distribution diagrams for the $(C_2H_5)_3Sn^+$–UMP and –IMP systems at the concentration conditions reported in Table 5 are shown in Figure 8a and b.

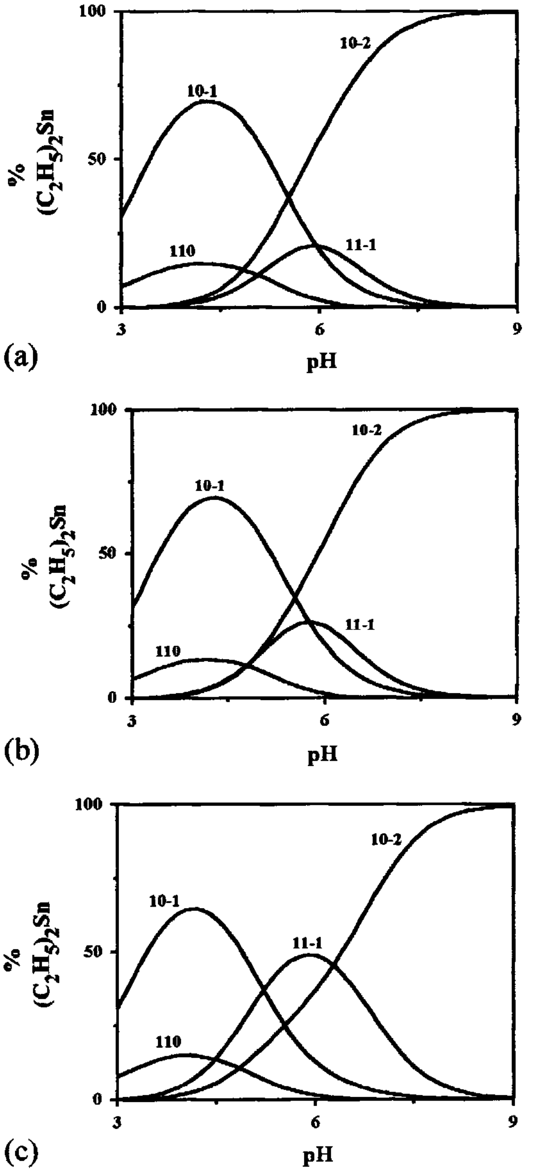


Figure 7. Distribution diagrams of species for the systems (a) $(C_2H_5)_2Sn^{2+}$–AMP, (b) –UMP, and (c) –IMP at $I = 0.16$ mol l^{-1} (NaCl) and $T = 25$ °C. $C_{(C_2H_5)_2Sn} = 0.5$ mmol l^{-1}; $C_{AMP} = C_{UMP} = C_{IMP} = 1$ mmol l^{-1}.

For much lower concentrations of both organotins and nucleotides, the formation percentages of species decrease considerably in favour of the formation of simple hydrolytic species of organotin cations. In spite of this, some species are still formed in a significant amount in the mono-organotin and triorganotin nucleotides systems; in particular, about 18% and 12% of the mixed hydrolytic species in the system CH_3Sn^{3+}–AMP [$CH_3Sn(OH)AMP^0$ and $CH_3Sn(OH)_2AMP^-$, in sum] is formed at pH 5 and pH 6 respectively, at 5×10^{-6} mol l^{-1} of both reagents; 15% formation of species $(C_2H_5)_3Sn(OH)UMP^{2-}$ is observed at pH 8–9 for a 5×10^{-5} mol l^{-1} concentration of triethyltin(IV) and uridine monophosphate reagents.

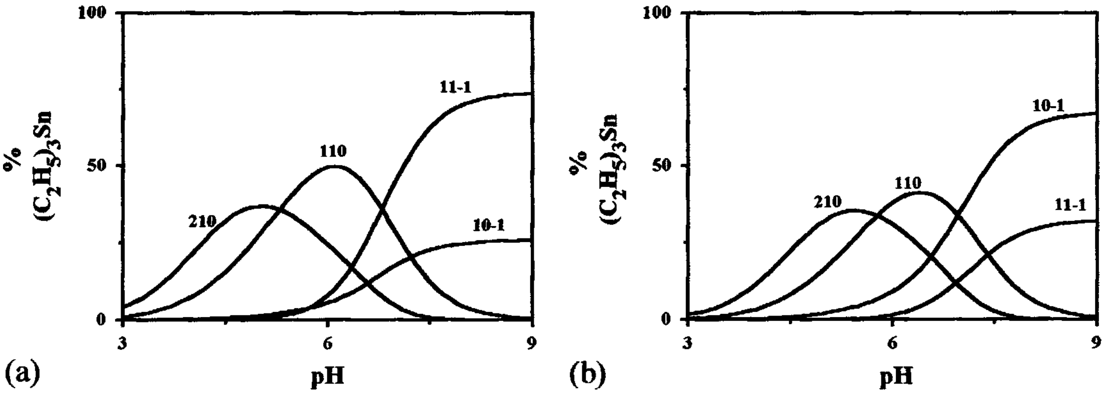


Figure 8. Distribution diagrams of species for the (a) $(C_2H_5)_3Sn^+$–UMP and (b) –IMP systems at $I = 0.16$ mol l^{-1} and $T = 25$ °C. $C_{(C_2H_5)_3Sn} = 0.5$ mmol l^{-1}; $C_{UMP} = C_{IMP} = 1$ mmol l^{-1}.

Table 4. Formation percentages of species in the system $(C_2H_5)_2Sn^{2+}$–XMP (XMP = AMP, IMP, UMP) in the pH range 6–9. $C_{(C_2H_5)_2Sn} = 0.5$ mmol l^{-1}; $C_{XMP} = 1$ mmol l^{-1}; $I = 0.16$ mol l^{-1} (NaCl)

Species	Formation percentages			
(*pqr*)[a]	pH 6	pH 7	pH 8	pH 9
AMP				
11-1	20.6 ± 0.4[b]	7.5 ± 0.2[b]	–	–
10-1	19.5 ± 0.1	3.1 ± 0.1	–	–
10-2	56.7 ± 0.3	89.2 ± 0.2	98.6 ± 0.1[b]	99.4 ± 0.1[b]
IMP				
11-1	48.7 ± 1.0	24.4 ± 0.8	4.1 ± 0.2	–
10-1	12.7 ± 0.3	2.5 ± 0.1	–	–
10-2	36.8 ± 0.7	72.9 ± 0.7	95.6 ± 0.2	99.1 ± 0.1
UMP				
11-1	24.8 ± 0.4	7.4 ± 0.2	–	–
10-1	18.7 ± 0.1	3.1 ± 0.1	–	–
10-2	54.3 ± 0.3	89.4 ± 0.2	98.7 ± 0.1	99.4 ± 0.1

[a] Indexes refer to the equilibrium reaction $pR_xSn + qXMP + rH_2O = (R_xSn)_p(XMP)_q(OH)_r$.

[b] Plus/Minus standard deviation.

Table 5. Formation percentages of species in the system $(C_2H_5)_3Sn^+$–XMP (XMP = AMP, IMP, UMP) in the pH range 6–9. $C_{(C_2H_5)_3Sn} = 0.5$ mmol l^{-1}; $C_{XMP} = 1$ mmol l^{-1}; $I = 0.16$ mol l^{-1} (NaCl)

Species	Formation percentages			
(*pqr*)[a]	pH 6	pH 7	pH 8	pH 9
AMP				
110	8.3 ± 0.3[b]	4.9 ± 0.2[b]	–	–
10-1	27.4 ± 0.1	75.5 ± 0.2	94.9 ± 0.3[b]	97.3 ± 0.3[b]
IMP				
110	37.9 ± 4.5	32.9 ± 3.6	7.2 ± 1.1	–
11-1	1.5 ± 0.3	13.1 ± 2.0	28.7 ± 3.0	32.0 ± 3.1
210	31.0 ± 4.7	10.6 ± 2.2	–	–
10-1	9.0 ± 0.6	35.3 ± 1.7	62.2 ± 2.6	67.0 ± 3.1
UMP				
110	49.5 ± 3.6	28.5 ± 3.2	4.4 ± 0.7	–
11-1	7.9 ± 1.3	45.2 ± 4.3	70.1 ± 3.1	73.7 ± 2.7
210	24.6 ± 3.2	4.6 ± 0.9	–	–
10-1	5.5 ± 0.3	17.7 ± 1.1	24.8 ± 2.4	25.8 ± 2.7

[a] indexes refer to the equilibrium reaction $pR_xSn + qXMP + rH_2O = (R_xSn)_p(XMP)_q(OH)_r$.

[b] Plus/Minus standard deviation.

COMPARISON OF COMPLEX STABILITY WITH ANALOGOUS SYSTEMS

Since stability data on the $R_xSn^{(4-x)+}$–XMP systems are reported here for the first time, we have no reference to compare our results. Therefore, we may compare the stability of the complex species found here with some selected formation constants relative to systems having the same ligand charge (dicarboxylates–$R_xSn^{(4-x)+}$)[22,23] and with other systems containing metal ions of similar binding capability as diorganotin(IV) cations (Cu^{2+}–XMP).[1] Results of comparison are reported in Table 6. As can be seen, the complex species formed by diethyltin cations with AMP and UMP are significantly more stable than those of Cu^{2+} (the differences are greater than two log units), due mainly to a greater charge availability for a smaller hydration caused by the presence of alkyl groups. With regard to other di-charged anions, mixed complexes of alkyltin with AMP, GMP, IMP and UMP are compared with those of malonate (mal^{2-}) and succinate ($succ^{2-}$). The values reported in parentheses are for $(CH_3)_xSn$–dicarboxylate complexes calculated approximately at $I = 0.16$ mol l^{-1} to make the data homogeneous. The results are obtained by using a Debye–Hückel-type equation for the dependence of formation constants on ionic strength for organotin(IV)–carboxylates complex species.[22,23] Also in

Table 6. Comparisons of Cu^{2+}–XMP and $R_nSn^{(4-n)+}$–dicarboxylate complexes with $R_nSn^{(4-n)+}$–XMP complexes at $T = 25\,°C$

log β comparison between cations						
pqr[a]	Cu^{2+}–AMP	$(C_2H_5)_2Sn^{2+}$–AMP	Cu^{2+}–UMP	$(C_2H_5)_2Sn^{2+}$–UMP		
110	3.22[b]	5.24[c]	2.90[b]	5.07[c]		
log β comparison between ligands						
pqr[a]	Malonate	Succinate	AMP	GMP	IMP	UMP
M = CH_3Sn^{3+}						
110	8.6[d] (7.3)[g]	8.94[d] (7.6)[g]	10.79[c]	9.97[c]	9.40[c]	9.63[c]
11-1	5.79 (4.5)	5.46 (4.2)	6.94	6.91	6.68	7.24
11-2	−0.07 (−1.2)	0.34 (−0.8)	1.2	1.3	0.7	0.8
M = $(CH_3)_2Sn^{2+}$			M = $(C_2H_5)_2Sn^{2+}$			
110	5.43[e] (4.5)[g]	4.98[d] (4.1)[g]	5.24[c]	5.29[c]	–	5.07[c]
11-1	−0.01 (−0.7)	0.05 (−0.6)	0.17	0.81	–	0.29
M = $(CH_3)_3Sn^{+}$			M = $(C_2H_5)_3Sn^{+}$			
110	2.73[d] (2.3)[g]	2.37[f] (1.9)[g]	2.53[c]	3.8[c]	–	4.10[c]
11-1	−3.70 (−3.7)	–	−5.00	−3.6	–	−2.7

[a] Indexes *pqr* refer to the equilibrium reaction $pM + qL + rH_2O = M_pL_q(OH)_r$; (M = Cu or R_nSn and L = XMP or dicarboxylate ligand).
[b] Ref. 1, at $I = 0.1\ mol\ l^{-1}$ (Me_4N^+).
[c] This work, at $I = 0.16\ mol\ l^{-1}$ (NaCl).
[d] Work in progress, $I = 0$.
[e] Ref. 22, at $I = 0$.
[f] Ref. 23, at $I = 0$.
[g] Values in parentheses calculated (approximately) at $I = 0.16\ mol\ l^{-1}$.

these cases there are very large differences, particularly for monomethyltin complexes.

CONCLUSIONS

The conclusions of this study can be summarized as follows:

- Stability data on the interaction between organotin cations and nucleotide 5′-monophosphates are reported here for the first time.
- Comparison with other analogous systems having the same metal and ligand charge shows a higher stability for these systems.
- The strength of stability for the various R_xSn–XMP systems follows the general trend RSn > R_2Sn > R_3Sn depending on the cation charge.
- In all systems investigated the main species formed are the hydrolytic mixed ones, confirming the strong tendency for the hydrolysis of organotin(IV) cations in aqueous solution.
- The results obtained in the investigation on the $(C_2H_5)_3Sn$–XMP system, where a non-negligible percentage formation of species is observed also at very low metal–ligand concentration, can be used for a realistic extrapolation to the tributyltin system, whose low solubility does not allow experimental potentiometric measurements. An extrapolation for the hydrolysis of the tributyltin(IV) cation has already been done in a previous paper[17] on the basis of results obtained from investigations on the hydrolysis of trimethyl, triethyl and tripropyltin(IV) cations.

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