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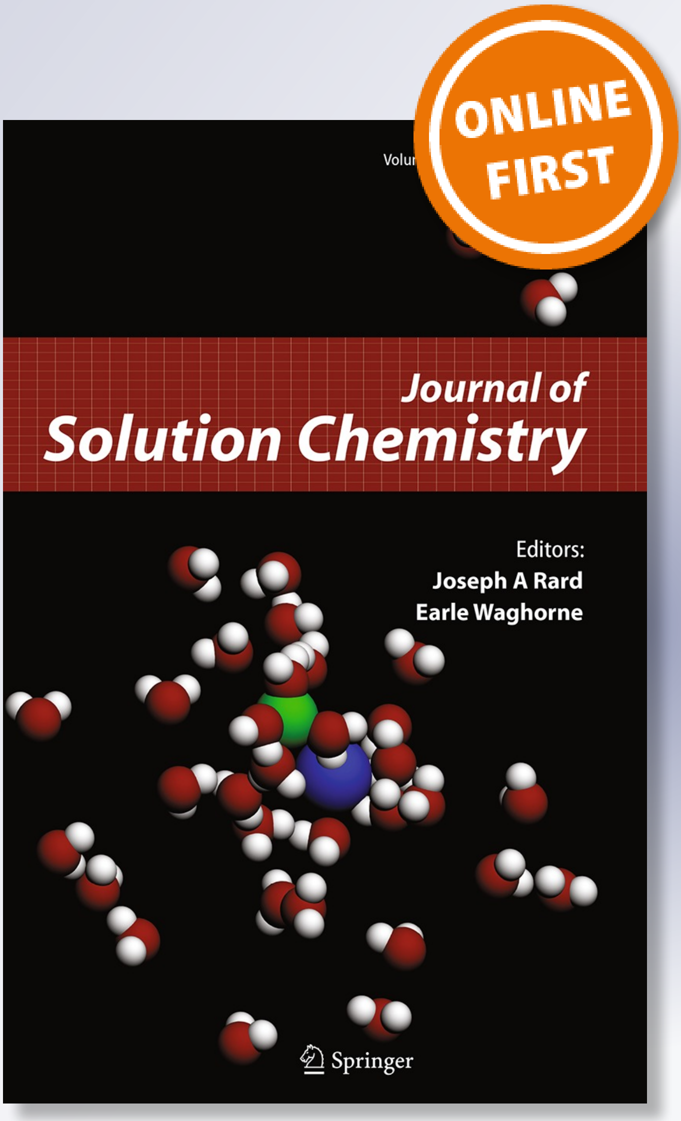

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Modelling the Hydrolysis of Mixed Mono-, Di- and Trimethyltin(IV) Complexes in Aqueous Solutions

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Abstract The formation of mixed hydrolytic species obtained by the interaction of dimethyltin(IV) $\{(CH_3)_2Sn^{2+}$ or DMT or $M2^{2+}\}$ with the monomethyltin(IV) (CH_3Sn^{3+} or MMT or $M1^{3+}$) and trimethyltin(IV) $\{(CH_3)_3Sn^{+}$ or TMT or $M3^{+}\}$ cations was studied in aqueous solutions of $NaNO_3$, at $I = 1.00 \pm 0.05\ \text{mol·dm}^{-3}$ and $T = (298.15 \pm 0.1)$ K, by the potentiometric technique. The formation of several mono- and polynuclear hydrolytic mixed species was observed in the two mixed systems. For the $(M1)_p(M2)_q(OH)_r$ mixed species we have: $(p, q, r) = (1, 1, 3), (1, 1, 4), (1, 1, 5), (2, 1, 5), (2, 1, 7), (1, 3, 6)$ and $(2, 3, 11)$; for $(M2)_p(M3)_q(OH)_r$: $(p, q, r) = (1, 1, 2), (1, 1, 3), (1, 2, 3), (1, 2, 4), (2, 1, 4), (3, 1, 4)$ and $(3, 1, 5)$. The stability of these species, expressed by the following general equilibrium:

$$p\text{Mi}^{n+} + q\text{Mj}^{j+} + r\text{OH}^- \rightleftharpoons (\text{Mi})_p(\text{Mj})_q(\text{OH})_r^{(np+jq-r)} \quad \beta_{pqr}^{\text{OH}}$$

can be modelled by the empirical relationship that depends on the stoichiometry of the species:

$$\log_{10}\beta_{pqr}^{\text{OH}} = a_1p + a_2q + a_3r - y$$

For the $(M1)_p(M2)_q(OH)_r$ species: $a_1 = 6.98$, $a_2 = 2.73$, $a_3 = 9.93$ and $y = 1.14$, while for the $(M2)_p(M3)_q(OH)_r$ species: $a_1 = 5.03$, $a_2 = 1.00$, $a_3 = 8.04$ and $y = 1.71$. By using the equilibrium constant X_{pqr} relative to the formation reactions:

$$p(\text{M1})_{(p+q)}(\text{OH})_r + q(\text{M2})_{(p+q)}(\text{OH})_r \rightleftharpoons (p+q)(\text{M1})_p(\text{M2})_q(\text{OH})_r$$

and

$$p(\text{M2})_{(p+q)}(\text{OH})_r + q(\text{M3})_{(p+q)}(\text{OH})_r \rightleftharpoons (p+q)(\text{M2})_p(\text{M3})_q(\text{OH})_r$$

Previous contributions to this series: Refs. 8, 10 and 11.

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we found that the formation of hetero-metal mixed species is thermodynamically favored and the extra stability can be expressed as a function of the difference in the stability of the parent homo-metal species. This leads, in turn, to a significant enhancement of hydrolysis. The general stability and extra stability behavior of mixed-metal (or organometal) species is discussed while also considering previous findings from this laboratory.

Keywords Alkyltin(IV) cations · Hydrolysis · Mixed hetero-cation species · Stability constants · Potentiometry

1 Introduction

Natural waters and biological fluids are solutions containing a high number of components (see, for example, Ref. [1]), and whose composition can be very complicated, depending on several variables such as: (i) the number of components; (ii) the concentrations and the molar ratio among them; (iii) the negative or positive charge of the components; and (iv) the acid–base properties and the binding ability of the ligands and metals dissolved in such systems. In these conditions, the formation of both binary and ternary species can be observed, although in many cases the formation of species of high complexity can be neglected.

Generally, when two components such as two metal cations are simultaneously present in solution and can react with a third component, two conditions may occur: (a) the system behaves ideally, i.e. the metal cations interact independently with the third component, or (b) more complex interactions occur between components, with the formation of mixed species.

The mixing effects can be explained simply as deviations from ideality or by considering the formation of ternary or quaternary complex species; these aspects have been already studied in this laboratory for many different mixed systems [2–12]. The mixing effects on the protonation of carboxylic ligands [4, 6, 7] and phytic acid [9] in concentrated solutions of mixtures of alkali metal salts were interpreted in terms of deviation from ideality or by a model which implies the formation of weak mixed alkali metal complexes [13]. The same criteria were used when investigating the hydrolysis in aqueous solutions of two different metal or organometal cations; the deviations from the ideality were interpreted in terms of hetero-polynuclear species formation [2–4, 6–8, 10–12]. In these investigations particular attention was devoted to recognizing the extra stability of mixed species.

In this work, a study on the hydrolysis of two aqueous mixed systems {$M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$, where $M1^{3+}$ = monomethyltin(IV); $M2^{2+}$ = dimethyltin(IV) and $M3^{+}$ = trimethyltin(IV)} is reported. The stability of hypothesized hetero-polynuclear species and their extra-stability was modelled by empirical relationships.

2 Experimental Section

2.1 Chemicals

The mono-, di- and trimethyltin(IV) solutions were purchased from Aldrich in the form of their chloride salts and were used without further purification; the purity of the single salt was >97 for the monomethyltin(IV) and 98 % for the di- and trimethyltin(IV) salts, respectively. Sodium nitrate (Aldrich) solutions, used as supporting electrolyte, were prepared by weighing the pure salt, previously dried in an oven at $T = (383.15 \pm 0.1)$ K for at least 2 h. Nitric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Riedel-deHaën), and standardized against sodium carbonate (Aldrich) and potassium hydrogen phthalate, respectively. All solutions were prepared using doubly distilled water and using grade A glassware. NaOH solutions were preserved from atmospheric CO_2 by means of soda lime traps.

2.2 Procedure

Potentiometric measurements were carried out in termostatted cells at $T = (298.15 \pm 0.1)$ K, using a 809 Metrohm Titrando apparatus equipped with an half cell glass electrode (Orion glass electrode, 8101 Ross type) coupled with an Ag/AgCl/KCl reference electrode (from Metrohm). This apparatus was connected to a computer and automatic titrations were performed using the Metrohm TiAMO 1.2 software for automatic data acquisition, to control the titrant delivery and e.m.f. stability. The estimated accuracy for titrant volume and e.m.f. readings are ± 0.003 cm^3 and ± 0.15 mV, respectively.

In order to minimize systematic errors and to check the repeatability of the measurements, as already reported in previous works [10, 11, 14], the measurements for the hetero-cation systems were carried out, in an independent way, by using two different experimental systems. The second apparatus used for the potentiometric measurements consisted by a Metrohm potentiometer (model 713) equipped with a combined glass electrode; a Metrohm motorized burette (model 765) was employed to add the standard solution titrant in the sample cell.

In a total volume of 25 cm^3 of aqueous solution, different aliquots of two alkyltin(IV) salts, namely monomethyltin(IV) ($M1^{3+}$) and dimethyltin(IV) ($M2^{2+}$) or dimethyltin(IV) ($M2^{2+}$) and trimethyltin(IV) ($M3^+$) were mixed, in a wide range of concentration and molar ratios (see Table 1), together with strong acid (nitric acid) and $NaNO_3$ to obtain the desired ionic strength value, $I = 1.00$ mol·dm^{-3}; these solutions were titrated with CO_2-free sodium hydroxide, generally up to pH $\sim$ 8–9, under magnetic stirring and bubbling with purified pre-saturated N_2 through the solution in order to exclude O_2 and CO_2 from the solution.

Table 1 Experimental conditions for the measurements of the $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^+$ systems in $NaNO_3$ aqueous solutions at $I = 1.00$ mol·dm^{-3} and $T = (298.15 \pm 0.1)$ K

$M1^{3+}/M2^{2+}$ system[a]		$M2^{2+}/M3^+$ system[b]	
C_{M1Cl3}[c]	C_{M2Cl2}[c]	C_{M2Cl2}[c]	C_{M3Cl}[c]
0.0102	0.0502	0.0399	0.0200
0.0200	0.0400	0.0302	0.0303
0.0303	0.0302	0.0201	0.0401
0.0499	0.0102	0.0401	0.0198
0.0602	0.0200	0.0549	0.0052
0.0499	0.0302	0.0501	0.0099
0.0299	0.0502	0.0250	0.0350
0.0200	0.0600	0.0099	0.0502
0.0102	0.0702	0.0052	0.0549
		0.0467	0.0496

[a] 0.0196 mol·dm^{-3} of HNO_3 added in each titration of this system

[b] 0.0098 mol·dm^{-3} of HNO_3 added in each titration of this system

[c] Concentration values are expressed in the molar scale, mol·dm^{-3}

For each titration 80–100 points were collected and the equilibrium state during titrations was checked using the usual precautions [15].

The formal glass electrode potential ($E°$) and the junction potential ($E_j = j_a$ [H^+]) were determined by independent titrations of acidic solutions (nitric acid) with standard sodium hydroxide solutions, in the same experimental conditions of ionic strength as the mixed alkyltin(IV) measurements. The free proton concentration scale was used, i.e. $\text{pH} \equiv -\log_{10} [\text{H}^+]$.

2.3 Calculations

The formal electrode potential $E°$, the coefficient j_a relative to acidic junction potential, $E_j = j_a$ [H^+], and the ionic product of water, K_w, were determined by means of the non-linear least-squares ESAB2M computer program [16], whereas the formation constants of the hydrolytic mixed alkyltin(IV) species were determined by means of the BSTAC computer program [17]. The ES4ECI [18] computer program was used to draw distribution diagrams of the species and to compute their formation percentages. The formation constants of the mixed M1^{3+}/M2^{2+} and M2^{2+}/M3^{+} species are expressed according to the following equilibria:

$$p\text{M1}^{3+} + q\text{M2}^{2+} + r\text{OH}^- \rightleftharpoons (\text{M1})_p(\text{M2})_q(\text{OH})_r^{(3p+2q-r)} \quad \beta_{pqr}^{\text{OH}} \tag{1}$$

and

$$p\text{M2}^{2+} + q\text{M3}^{+} + r\text{OH}^- \rightleftharpoons (\text{M2})_p(\text{M3})_q(\text{OH})_r^{(2p+q-r)} \quad \beta_{pqr}^{\text{OH}} \tag{2}$$

The formation of such species can be also expressed by means of the hydrolytic constants, taking into account the following equilibria:

$$p\text{M1}^{3+} + q\text{M2}^{2+} + r\text{H}_2\text{O} \rightleftharpoons (\text{M1})_p(\text{M2})_q(\text{OH})_r^{(3p+2q-r)} + r\text{H}^+ \quad \beta_{pqr} \tag{3}$$

and

$$p\text{M2}^{2+} + q\text{M3}^{+} + r\text{H}_2\text{O} \rightleftharpoons (\text{M2})_p(\text{M3})_q(\text{OH})_r^{(2p+q-r)} + r\text{H}^+ \quad \beta_{pqr} \tag{4}$$

If $p = 0$ or $q = 0$, the equilibria refer to the formation of the single alkyltin(IV) hydrolytic species (Eqs. 1 and 2) or to the hydrolysis of the single alkyltin(IV) cations (Eqs. 3 and 4).

The conversion from the molar to the molal concentration scale can be obtained using the ratio c/m (c = molar concentration; m = molal concentration). When $I = 1$ mol·dm^{-3} NaNO_3, I(molal) = 1.03 and $\log_{10} \beta$ (molal) = $\log_{10} \beta$ (molar) − $0.015p^*$, where, for the single alkyltin(IV) cations, $p^* = p + r - 1$ for equilibria (1) and (2), or $p^* = p - r - 1$ for equilibria (3) and (4) [8]; in the case of the mixed alkyltin(IV) species: $p^* = p + q + r - 1$ for equilibria (1) and (2) or $p^* = p + q - r - 1$ for equilibria (3) and (4).

3 Results and Discussion

3.1 Hydrolysis of M1^{3+}, M2^{2+} and M3^{+}

The hydrolysis of M1^{3+}, M2^{2+} and M3^{+} cations were already reported in a previous work [14]. Table 2 reports the stability constants of the hydrolytic species of each alkyltin(IV) cation, expressed taking into account the equilibria (1) and (2). The formation of several

Table 2 Formation constants[a] of $(CH_3)_nSn^{(4-n)+}$ species in $NaNO_{3(aq)}$ at $I = 1.00 \pm 0.05\ mol{\cdot}dm^{-3}$ and $T = (298.15 \pm 0.1)$ K

Species	$\log_{10} \beta_{pq}^{OH}$	Species	$\log_{10} \beta_{pq}^{OH}$	Species	$\log_{10} \beta_{pq}^{OH}$
$[(CH_3)Sn(OH)_3]^0$	31.28	$[((CH_3)_2Sn)(OH)]^+$	10.54	$[((CH_3)_3Sn)(OH)]^0$	7.49
$[(CH_3)Sn(OH)_4]^-$	32.40	$[((CH_3)_2Sn)(OH)_2]^0$	19.00	$[((CH_3)_3Sn)(OH)_2]^-$	8.49
$[((CH_3)Sn)_2(OH)_4]^{2+}$	51.11	$[((CH_3)_2Sn)(OH)_3]^-$	25.25	$[((CH_3)_3Sn)_2(OH)]^+$	8.80
$[((CH_3)Sn)_2(OH)_5]^+$	60.55	$[((CH_3)_2Sn)_2(OH)_2]^{2+}$	22.17	$[((CH_3)_3Sn)_2(OH)_2]^0$	15.71
$[((CH_3)Sn)_2(OH)_7]^-$	65.46	$[((CH_3)_2Sn)_2(OH)_3]^+$	31.74	$[((CH_3)_3Sn)_2(OH)_4]^{2-}$	19.19
$[((CH_3)Sn)_3(OH)_5]^{4+}$	66.76	$[((CH_3)_2Sn)_3(OH)_4]^{2+}$	43.37		
$[((CH_3)Sn)_3(OH)_7]^{2+}$	87.88	$[((CH_3)_2Sn)_4(OH)_6]^{2+}$	63.73		
$[((CH_3)Sn)_5(OH)_9]^{6+}$	120.84				
$[((CH_3)Sn)_5(OH)_{11}]^{4+}$	141.87				

[a] The formation constants refer to the equilibrium: $p(CH_3)_nSn^{(4-n)+} + q\mathrm{OH}^- \rightleftharpoons \left\{(CH_3)_nSn)_p(OH)_q^{\{p(4-n)-q\}}\right\}$, from Ref. [14]

homo-polynuclear hydrolytic species is observed for each alkyltin cation, since measurements were carried out at high cation concentrations, as was done in a previous investigation [19]. The formation of species with high poly-nuclearity allowed us to propose the formation of hetero-cation hydrolytic species in mixed alkyltin(IV) solutions.

In our previous paper [14], we already proposed predictive equations to calculate the hydrolysis constants, β (or the formation constants, β^{OH}), of the different alkyltin(IV) cations as a function of the stoichiometric coefficients. Taking into account the equilibria (1) and (2) (remembering that if $p = 0$ or $q = 0$, the equilibria refer to simple $\mathrm{M1}^{3+}$, $\mathrm{M2}^{2+}$ and $\mathrm{M3}^{+}$ hydrolytic species, respectively), formation of the hydrolytic species can be expressed by:

$$\log_{10} \beta_{sr}^{\mathrm{OH}} = A(s + r) \tag{5}$$

where $s = p$ or q. The parameter A is a linear function of the charge (z) of the cations, i.e. $A = 1 + B \cdot z$, where for a generic $(\mathrm{CH_3})_n\mathrm{Sn}^{(4-n)+}$ ion, $z = 4 - n$. By using the $\log_{10} \beta_{sr}^{\mathrm{OH}}$ values of the hydrolytic species of all the methyltin(IV) cations, we calculated, for the parameter B, a mean value of 2.50 ± 0.05 [14], that substituted in the Eq. 5 gives:

$$\log_{10} \beta_{sr}^{\mathrm{OH}} = (1 + 2.50z)(s + r) \tag{6}$$

The $\log_{10} \beta^{\mathrm{OH}}$ values calculated by Eq. 5 have an accuracy of ±0.5 log units, a value that can be considered suitable for predicting purposes. Other empirical stability relationships were also given in a recent review [20]. Moreover, other reviews on alkyltin(IV) complexes have been reported by El-Sherif and Pellerito et al. [21, 22].

3.2 Formation of Hetero-Cation Hydrolytic Species

The analysis of the potentiometric data was done by least-squares calculation using the BSTAC computer program. The formation of several mixed metal species was checked, and the best model was selected taking into account the criteria of selection already used in previous papers [5, 8, 10, 11, 23].

The criteria used to select the best chemical model are: (a) analysis of the variance ratio values; (b) the simplicity of the model (the addition of other species formed in low amounts can complicate the model); c) the likelihood of occurrence of the proposed species, in particular in relation to homo-polynuclear species. As a further check, during calculations, we also refined these species together with mixed hydrolytic ones, without sensibly altering the values of hydrolysis constants for each species. The consistency of the values demonstrates that the formation of mixed species during calculations by the computer programs is not a fictitious improvement in fittings coming out from a simple minimization of experimental errors.

Table 3 reports the equilibrium constants calculated according to equilibria 1 and 2 or 3 and 4 for each species in the selected speciation model of the $\mathrm{M1}^{3+}/\mathrm{M2}^{2+}$ and $\mathrm{M2}^{2+}/\mathrm{M3}^{+}$ systems.

The conversion of the hydrolytic constants, calculated by means of the BSTAC computer program, to formation constants was made by using the equation:

$$\log_{10} \beta_{pqr}^{\mathrm{OH}} = \log_{10} \beta_{pqr} + 13.73r \tag{7}$$

where 13.73 is the ionic product of water (K_{w}) valid at $I = 1.00\ \mathrm{mol \cdot dm^{-3}}$, $T = (298.15 \pm 0.1)$ K in $\mathrm{NaNO_3}$. The formation constant of each mixed hydrolytic species

Table 3 Experimental and calculated formation constants of the $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$ species in $NaNO_3$ aqueous solutions at $I = 1.00\ mol{\cdot}dm^{-3}$ and $T = (298.15 \pm 0.1)$ K

p	q	r	$\log_{10}\beta_{pqr}^{OH}$(expt.)[a]	$\log_{10}\beta_{pqr}^{OH}$(calcd.)[b]	$\log_{10}\beta_{pqr}$[c]
$(M1)_p(M2)_q(OH)_r$					
1	1	3	38.5 ± 0.2[d]	38.3	−2.7
1	1	4	49.1 ± 0.3	48.3	−5.8
1	1	5	57.5 ± 0.4	58.2	−11.1
2	1	5	65.2 ± 0.2	65.2	−3.5
2	1	7	84.8 ± 0.3	85.0	−11.3
1	3	6	73.3 ± 0.4	73.6	−9.1
2	3	11	130.5 ± 0.4	130.2	−20.5
$(M2)_p(M3)_q(OH)_r$					
1	1	2	20.4 ± 0.2	20.4	−7.1
1	1	3	28.5 ± 0.2	28.4	−12.7
1	2	3	29.8 ± 0.3	29.4	−11.4
1	2	4	37.2 ± 0.3	37.5	−17.8
2	1	4	41.4 ± 0.2	41.5	−13.5
3	1	4	46.3 ± 0.3	46.5	−8.6
3	1	5	55.0 ± 0.3	54.6	−13.6

[a] According to Eqs. 1 and 2 for $(M1)_p(M2)_q(OH)_r$ and $(M2)_p(M3)_q(OH)_r$, respectively

[b] Calculated by Eq. 10

[c] According to Eqs. 3 and 4 for $(M1)_p(M2)_q(OH)_r$ and $(M2)_p(M3)_q(OH)_r$, respectively

[d] ±95 % C.I

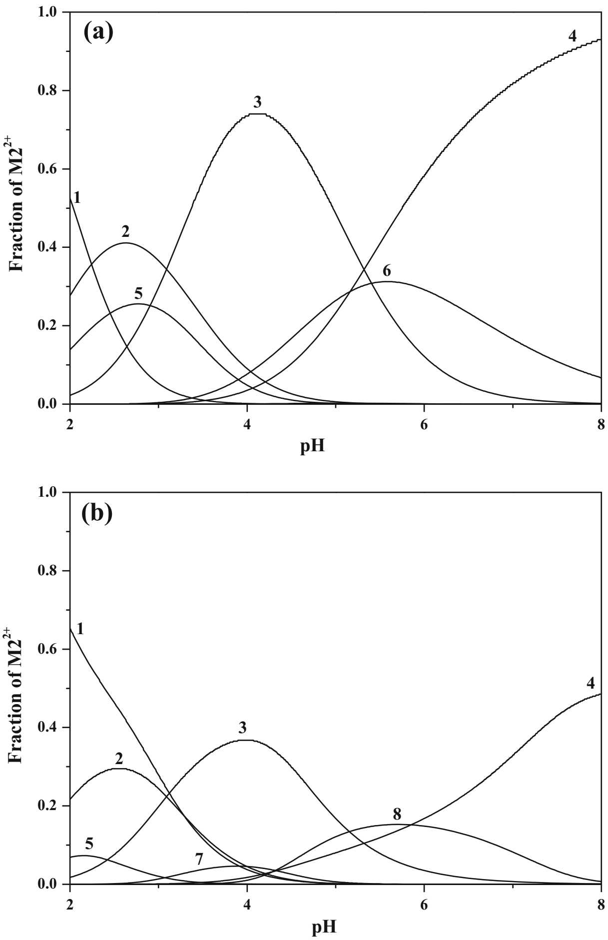
is reported in the first column of Table 3. By using the hydrolytic constant values of the homo- and hetero-metal species, some distribution diagrams were drawn: Fig. 1a, b shows the distribution of the $(M1)_p(M2)_q(OH)_r$ species at two different molar ratios (M1:M2), (a) = 2:1 and (b) = 1:2. The comparison of the two diagrams, (a) and (b), shows a significant lowering of the formation percentages of the hydrolytic species (fraction expressed with respect to $M2^{2+}$) when the M1:M2 = 1:2 molar ratio was used. Instead, when the distribution diagram is drawn by using the M1:M2 = 2:1 molar ratio, we observe that, despite the high stability of the mixed species, the formation of the species having high stoichiometric coefficients for $M2^{2+}$, i.e. $(M1)(M2)_3(OH)_6$ and $(M1)_2(M2)_3(OH)_{11}$ species, are hindered; in case (b), these species reach the fraction 0.05 and 0.15, respectively.

Similarly, Fig. 2a, b shows the distribution of the $(M2)_p(M3)_q(OH)_r$ hydrolytic species at the same molar ratios of Fig. 1a, b. In this case the formation percentages of the hetero-cation hydrolytic species decrease when the molar ratio M2:M3 is 1:2. A comparison of the two graphs, 2a and 2b, highlights that the $(M2)(M3)(OH)_3$ species is predominant, independent of the experimental conditions.

Analysis of the formation constants of the mixed species reveals that the $\log_{10}\beta_{pqr}^{OH}$ values are a function of the stoichiometric coefficients, as is also observed for the homo-cation hydrolytic species of $M1^{3+}$, $M2^{2+}$ and $M3^{+}$. By means of least-squares analysis, the following relationships were obtained for $M1^{3+}/M2^{2+}$:

$$\log_{10}\beta_{pqr} = 6.98p + 2.73q + 9.93r - 1.14 \qquad (8)$$

Fig. 1 Distribution diagram of the $(M1)_p(M2)_q(OH)_r$ species in aqueous solution of $NaNO_3$ at $I = 1.00$ mol·dm^{-3} and $T = (298.15 \pm 0.1)$ K. Concentration conditions: **a** $c_{M1} = 0.040$ mol·dm^{-3} and $c_{M2} = 0.020$ mol·dm^{-3}; **b** $c_{M1} = 0.020$ mol·dm^{-3} and $c_{M2} = 0.040$ mol·dm^{-3}. Species: *1* free $M2^{2+}$; *2* $(M1)(M2)(OH)_{32}^{+}$; *3* $(M1)(M2)(OH)_4^{+}$; *4* $(M1)(M2)(OH)_5$; *5* $(M1)_2(M2)(OH)_5^{3+}$; *6* $(M1)_2(M2)(OH)_7^{+}$; *7* $(M1)(M2)_3(OH)_6^{3+}$; *8* $(M1)_2(M2)_3(OH)_{11}^{+}$



with a predicted error ε = 0.35 (ε = 95 % confidence interval), and for $M2^{2+}/M3^{+}$:

$$\log_{10} \beta_{pqr} = 5.03p + 1.00q + 8.04r - 1.71 \tag{9}$$

with ε = 0.21. Moreover, the coefficients of Eqs. 8 and 9 can be expressed as a function of the charge of each metal ion, allowing us to propose the general equation:

$$\log_{10} \beta_{\mathrm{pqr}} = 2.373 z_1 p + 1.300 z_2 q + \frac{z_2 25 r}{(z_1 z_2)} - \frac{5}{z_1} \tag{10}$$

where z_1 and z_2 are the charges of the cations involved in the formation reaction and the indexes (1 and 2) refer to higher and lower charge in the mixed metal system. This equation fits quite well to the experimental data, with a linear correlation coefficient $r = 0.999$, indicating that it can be used as a predictive/descriptive model. The formation constants of $(M1)_p(M2)_q(OH)_r$ and $(M2)_p(M3)_q(OH)_r$, calculated by Eq. 10, are reported in Table 3. As an example, Fig. 3 reports the correlation between the formation constants $\log_{10} \beta_{pqr}^{\mathrm{OH}}$(calcd.) calculated by applying Eq. 10 versus the experimental ones

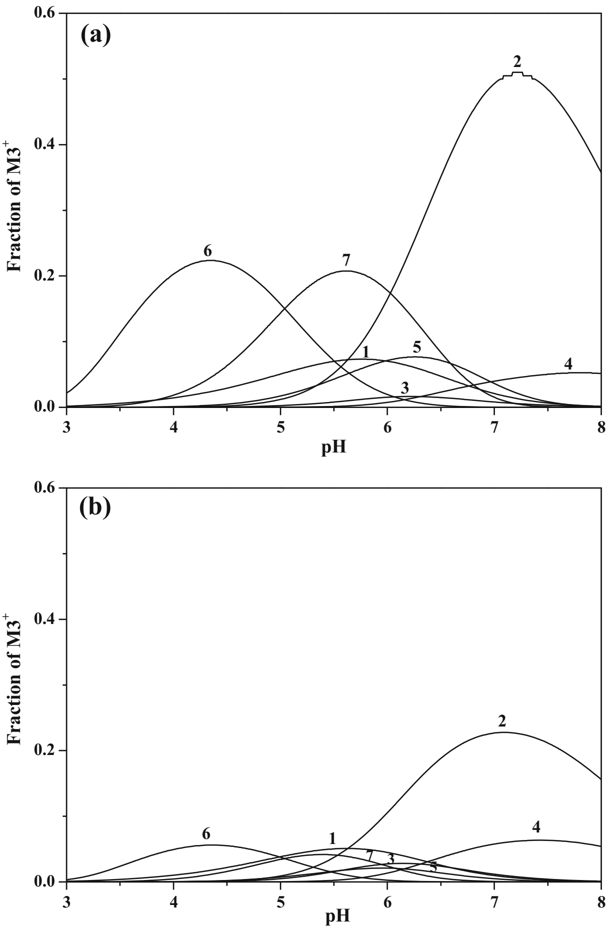


Fig. 2 Distribution diagram of the $(M2)_p(M3)_q(OH)_r$ species in aqueous solution of $NaNO_3$ at $I = 1.00\ mol{\cdot}dm^{-3}$ and $T = (298.15 \pm 0.1)$ K. Concentration conditions: **a** $c_{M2} = 0.040\ mol{\cdot}dm^{-3}$ and $c_{M3} = 0.020\ mol{\cdot}dm^{-3}$; **b** $c_{M2} = 0.020\ mol{\cdot}dm^{-3}$ and $c_{M3} = 0.040\ mol{\cdot}dm^{-3}$. Species: *1* $(M2)(M3)(OH)_2^+$; *2* $(M2)(M3)(OH)_3$; *3* $(M2)(M3)_2(OH)_3^+$; *4* $(M2)(M3)_2(OH)_4$; *5* $(M2)_2(M3)(OH)_4^+$; *6* $(M2)_3(M3)(OH)_4^{3+}$; *7* $(M2)_3(M3)(OH)_5^{2+}$

$\log_{10} \beta_{pqr}^{OH}$(expt.); it is possible to observe a fairly linear correlation between them, with a predicted error $\varepsilon = 0.32$.

Taking into account the charge of each cation and the parameters reported in the above Eqs. 8–10, simple predictive equations can be proposed for each mixed system. In the case of the mixed $M1^{3+}/M2^{2+}$ system we have:

$$\log_{10} \beta_{pqr} = 7.12p + 2.60q + 10.00r - 1.67 \tag{11}$$

and for the $M2^{2+}/M3^+$ one:

$$\log_{10} \beta_{pqr} = 4.75p + 1.30q + 8.33r - 2.50 \tag{12}$$

Mixed formation constants obtained by Eqs. 11 and 12 are very close to those calculated by Eqs. 8 and 9.

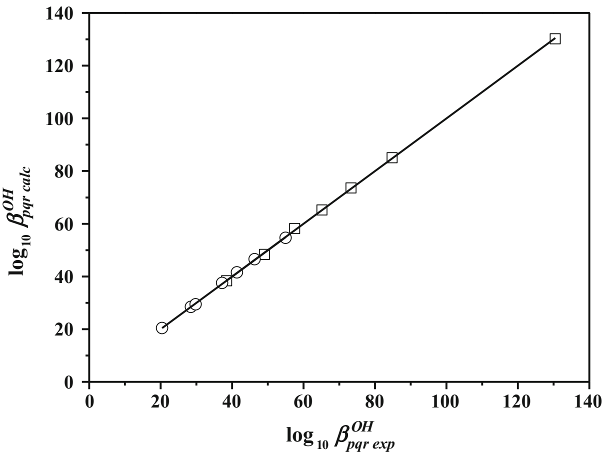


Fig. 3 Calculated versus experimental formation constant values according to Eq. 10: *square* $M1^{3+}/M2^{2+}$ and *circle* $M2^{2+}/M3^{+}$ systems

The empirical Eq. 10 is very important since it allows calculation of the formation constants of species formed under experimental conditions not yet investigated. For example, we can predict the stability constants of mixed complexes for the hetero-cation systems $M1^{3+}/M3^{+}$. The application of the Eq. 10 to this system, allowed us to obtained the following Eq. 13:

$$\log_{10} \beta_{pqr} = 7.12p + 1.30q + 6.25r - 1.67 \tag{13}$$

Moreover, taking into account that the complexing ability of the different alkyltin(IV) compounds (ethyl, propyl, etc.) are quite similar or follow smooth linear trends [24], the possible applications of Eq. 10 become very large.

By analyzing the stoichiometric coefficients of the mixed species listed in Table 3, we can observe the approximate constancy of the ratio $r/(p + q)$ for each system studied. This ratio is (± mean deviation) 1.96 ± 0.34 and 1.20 ± 0.20, for $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$, respectively. By dividing this ratio for the sum of the charges of each cation, in turn, the constant value $r/(p + q)/(z_1 + z_2) = 0.40 \pm 0.07$ is calculated. Similar calculations were carried out on the data obtained for other two hetero-metal systems containing one alkyltin(IV) cation, namely $M1^{3+}/Al^{3+}$ [8] and $M2^{2+}/UO_2^{2+}$ [11]. In this case, by dividing the ratio of the stoichiometric coefficients by the sum of the charges, a fairly constant value: $r/(p + q)/(z_1 + z_2) = 0.35 \pm 0.02$ was obtained for both systems; this value can be considered, within the error, to be in very good agreement with that obtained for the two mixed alkyltin(IV) systems ($M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$) here investigated. By considering simultaneously all the ratios of the above systems, we obtained a mean value of 0.37 ± 0.05; this indicates a regularity in the formation of the mixed hydrolytic species, taking into account the significant number of mixed species (29) reported in the speciation models of the different systems, the very different stoichiometry of the species and the different charge and acid–base properties of each metal/organometal cation.

3.3 Extra Stability of Hetero-Metal Hydrolytic Species

The stability of mixed complexes can be compared with that of parent complexes by considering the equilibrium constants [8, 10, 11, 25]:

$$\log_{10} X_{pqr} = (p+q)\log_{10}\beta^{\mathrm{OH}}_{pqr} - p\log_{10}\beta^{\mathrm{OH}}_{(p+q)0r} - q\log_{10}\beta^{\mathrm{OH}}_{0(p+q)r} \tag{14}$$

whose statistical value can be calculated by:

$$X_{\mathrm{stat}} = [(p+q)!/(p!q!)]^{(p+q)} \tag{15}$$

In several cases the values of formation constants for the parent complexes are not available experimentally (see Table 2), but they can be estimated using Eq. 6. The values of $\log_{10} X$ and $\log_{10} X_{\mathrm{stat}}$ are reported in Table 4: we can observe that the $\log_{10} X$ values are always higher than the corresponding $\log_{10} X_{\mathrm{stat}}$, highlighting the significant extra stability in the formation of mixed species. Also, for $\log_{10} X$, we can model the experimental values as a function of their stoichiometric coefficients.

For the $M1^{3+}/M2^{2+}$ system:

$$\log_{10} X_{pqr} = 19.25(pq) - 14(p+q) + 4.26r \tag{16}$$

and for $M2^{2+}/M3^{+}$:

$$\log_{10} X_{pqr} = 11.69(pq) - 14(p+q) + 8.44r \tag{17}$$

Equations 16 and 17 can be expressed as a function of the charges of the cations by the general equation:

$$\log_{10} X_{pqr} = 6.39z_1(pq) - 14(p+q) + 17.23\frac{\mathrm{r}}{z_1 + z_2 - 1} \tag{18}$$

The extra stability ($\log_{10} X - \log_{10} X_{\mathrm{stat}}$) term is proportional to the difference in stability of the parent complexes $\left(\Delta_{\mathrm{parent}} = \left|\log_{10}\beta_{(p+q)0r} - \log_{10}\beta_{0(p+q)r}\right|\right)$ as observed in some previous investigations [8, 26]. In Fig. 4 we plot ($\log_{10} X - \log_{10} X_{\mathrm{stat}}$) versus Δ_{parent}. The extra stability can be expressed by the equation:

Table 4 Experimental and statistical values of the $\log_{10} X$ of the $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$ species

p	q	r	$\log_{10} X$	$\log_{10} X_{\mathrm{stat}}$	Δ_{parent}
$(M1)_p(M2)_q(OH)_r$					
1	1	3	3.6	0.6	12.5
1	1	4	9.1	0.6	15
1	1	5	14.6	0.6	17.5
2	1	5	11.5	1.4	20
2	1	7	25.5	1.4	25
1	3	6	28.0	2.4	25
2	3	11	91.8	5.0	40
$(M2)_p(M3)_q(OH)_r$					
1	1	2	2.4	0.6	10
1	1	3	9.6	0.6	12.5
1	2	3	11.5	1.4	15
1	2	4	23.5	1.4	17.5
2	1	4	16.3	1.4	17.5
3	1	4	13.4	2.4	20
3	1	5	25.2	2.4	22.5

$$(\log_{10} X - \log_{10} X_{\text{stat}}) = 0.45\Delta_{\text{parent}} - 0.064\left(\Delta_{\text{parent}}\right)^2 \quad (19)$$

The higher $\log_{10} X_{pqr}$ values with respect to the corresponding statistical values, Eq. 15, indicate that formation of the mixed species is strongly favored and that similar species cannot be neglected in the studies of speciation of metals in multicomponent systems.

Another tool for highlighting the importance and the influence of these species, on the speciation of a given system and on the distribution of the species, is to calculate the conditional stability constants as introduced by Schwarzenbach [27]; this approach was already used in a previous investigation [23], confirming the experimental evidences.

By means of Eq. 20 and according to Schwarzenbach, the conditional formation constants were calculated taking into account the total and free metal concentration and the hydroxide concentration:

$$K_{\text{cond}} = \left(\frac{[\text{M}]_{\text{TOT}} - [\text{M}]_{\text{free}}}{[\text{M}]_{\text{free}}[\text{OH}^-]}\right) \quad (20)$$

Table 5 reports the $\log_{10} K_{\text{cond}}$ both for the simple and the mixed systems, at different pH values. It is possible to observe that, independent of the metal, the conditional formation constants of the mixed species are always higher than the simple system. This is an indication that the formation of the mixed species is favored. In our case, the higher difference were observed between the system M1^{3+} and the mixed $\text{M1}^{3+}/\text{M2}^{2+}$, with difference at high pH values of about 4 log units.

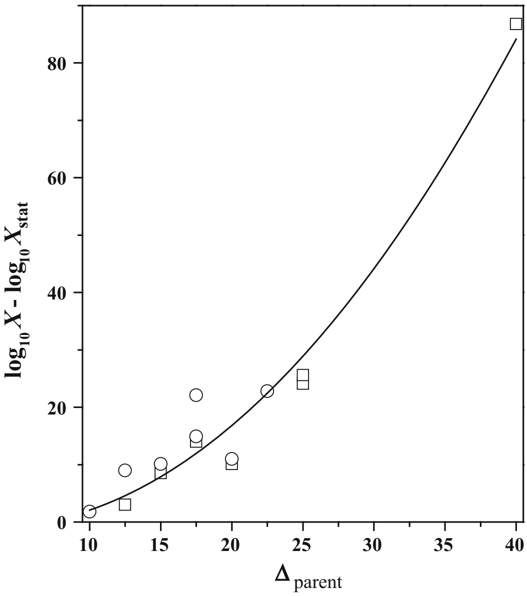


Fig. 4 The extra-stability values ($\log_{10} X - \log_{10} X_{\text{stat}}$) of the mixed species versus Δ_{parent}: *square* extra-stability of the $(\text{M1})_p(\text{M2})_q(\text{OH})_r$ species, and *circle* extra-stability of the $(\text{M2})_p(\text{M3})_q(\text{OH})_r$ species

Table 5 Conditional formation constants, calculated by Eq. 20, of the simple $M1^{3+}$ and $M2^{2+}$ systems and mixed $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$ systems

$\log_{10} K_{cond}$				
pH	$M1^{3+a}$	$M1^{3+}/M2^{2+b}$	$M2^{2+c}$	$M2^{2+}/M3^{+d}$
2.00	13.39	13.69	10.55	10.55
3.00	14.22	15.49	10.59	10.60
4.00	15.32	17.42	10.67	10.77
5.00	16.59	19.45	10.92	11.13
6.00	17.95	21.61	11.47	11.83
7.00	19.39	23.50	12.42	12.91
8.00	20.87	24.90	13.91	14.18

[a] 0.010 $mol\cdot dm^{-3}$

[b] 0.010 $mol\cdot dm^{-3}$ $M1^{3+}$/0.040 $mol\cdot dm^{-3}$ $M2^{2+}$

[c] 0.010 $mol\cdot dm^{-3}$

[d] 0.010 $mol\cdot dm^{3}$ $M2^{2+}$/0.040 $mol\cdot dm^{-3}$ $M3^{+}$

4 Final Remarks

The main results of this investigation can be summarized as follows:

i) The formation constants of the hydrolytic species of the three alkyltin(IV) cations were determined at a constant ionic strength value of $I = 1.00$ $mol\cdot dm^{-3}$ in $NaNO_3$ and $T = (298.15 \pm 0.1)$ K. From the speciation model of each system and from the stoichiometry of the species it has been possible to propose some empirical equations (Eqs. 5 and 6) for the dependence of the stability constants on the p, q indexes and on the charge of the cations.

ii) By using usual criteria of selections, different speciation models were obtained for the different hetero-metal systems ($M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$).

iii) Similarly to the homo-metal systems, also for the hetero-metal ones, some descriptive/predictive Eqs. 8 and 9, dependent on the stoichiometry of each species, were proposed; in this case, a general Eq. 10 was also used to model the dependence of the stability of the species of each system on the stoichiometric coefficients and on the charge of the cations.

iv) A very satisfactory correlation between the experimental formation constants and the formation constants calculated by using Eq. 10 was found, Fig. 3; this allows to also calculate the formation constants of species not experimentally determined or the formation constants of species of systems not investigated.

v) Analyzing the stability constants and the stoichiometric coefficients, a constancy of the ratio $r/(p + q)$ was observed; in particular values of 1.96 ± 0.34 and 1.20 ± 0.20 were obtained for the $M1^{3+}/M2^{2+}$ and $M2^{2+}/M3^{+}$ systems, respectively.

vi) Taking into account all the species of the two hetero-cation systems, we observed that dividing the ratio $r/(p + q)$ by the sum of the charge of the cations $(z_1 + z_2)$, a constant value of 0.40 ± 0.07 is found.

vii) If similar calculations are done by also considering the $[r/(p+q)]/(z_1+z_2)$ values of the systems $M1^{3+}/Al^{3+}$ [8] and $M2^{2+}/UO_2^{2+}$ [11], together with those calculated here, a value of 0.37 ± 0.02 is obtained.

viii) A significant extra stability was observed in the formation of the hetero-cation species; this value is proportional to the difference between the stability of the parent species and the mixed ones; also the extra stability was modeled in dependence on the stoichiometric coefficients and on the charge of the cations.

ix) The extra stability in the formation of the mixed species was also quantified calculating the conditional formation constants of the species at different pH values by using Eq. 20; independent of the pH, the conditional formation constants of the mixed species are always higher than the homo-metal ones.

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