Thermodynamics of Hydroxo Complex Formation of Dialkyltin(IV) Ions in Aqueous Solution†

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The hydrolysis of $[SnMe_2]^{2+}$ and $[SnEt_2]^{2+}$ has been investigated, both potentiometrically and calorimetrically, at 25 °C and I = 0.1 mol dm^{-3} (KNO_3). The species formed, together with their stability constants, have been determined by analysing a total of 550 and 300 potentiometric data points, for dimethyltin and diethyltin respectively, using two different computer programs. The results are critically compared with literature data obtained under analogous experimental conditions. In addition, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values for the main species formed at the concentrations investigated have been obtained by means of calorimetric measurements. Bonding details of the hydroxo species have been inferred on the basis of the enthalpic and entropic changes.

Although it is known that many elements are able to form organometallic cations of the type MR_n^{Z+} which are stable in aqueous solutions,[1,2] very few quantitative studies have been carried out to determine the formation, stability, and structure of the species existing in solution. By contrast, extensive work on the synthesis of organometallic compounds has been carried out.[3] Organotin compounds are now among the most studied organometallic systems in terms of industrial and agricultural applications.[4] As a consequence of ever increasing quantities of organotin entering the environment through biocidal applications, or as antifouling agents that release these compounds into natural waters, the question of the fate of organometallic species has been raised.[5] Further interest in the speciation of organotin cations is due to evidence that di- and tri-alkyltin compounds, containing donor ligands bound to tin, are effective against P-388 leukaemia[6,7] and to the implications of organotin compounds in cancer prophylaxis and other physiological processes.[8,9]

Since water is a crucial part of the cellular organization of all terrestrial life, we decided to study the interaction of SnR_2^{2+} ions with a number of biofunctional ligands in aqueous solution. Since the organometallic cations are strong Lewis acids, it follows that the hydrolytic equilibria should be examined in the presence of non-complexing anions prior to the study of the interactions of organometallic cations with other ligands.

Thus, here we report the study of hydrolytic species formed by SnR_2^{2+} (R = Me or Et) in aqueous solution at 25 °C and I = 0.1 mol dm^{-3} (KNO_3).

In addition to the potentiometric investigation, we have carried out calorimetric measurements, under the same experimental conditions, to obtain information on both the contribution of enthalpy and entropy changes to the stability, and on the structural features of different organometallic complexes formed in solution by SnR_2^{2+} ions and OH^-.

Experimental

Chemicals.—Dialkyltin nitrates were obtained using dialkyltin oxides as a starting material. The oxide (ICN Biomedical Inc.) was suspended in water and vigorously stirred for a couple of hours to eliminate the dialkyltin chloride. The suspension was then filtered and dried. The powder thus obtained was dissolved in nitric acid (C. Erba R.P.E.). Brownish impurities were eliminated by extraction with benzene. Dialkyltin oxide was then precipitated from the nitric acid solution using concentrated ammonia; it was filtered by suction using a gooch and repeatedly washed. The dissolution–precipitation procedure was repeated until no chloride could be detected in the mother liquor. The white powder was dried and used to make up dialkyltin nitrate solutions by adding a calculated amount of HNO_3. The excess of nitric acid was checked potentiometrically using the computer program SUPERQUAD (see Calculations) for the data treatment. Virtually no difference was observed between the calculated and observed excess. The ionic strength of all solutions was adjusted to 0.1 mol dm^{-3} by adding KNO_3. Grade A glassware was used throughout.

E.M.F. Measurements.—The potentiometric measurements were carried out by means of two semi-automatic meters (Amel 232 and Analog Devices AD 2072B) using glass electrodes (Metrohm EA109) and single saturated calomel electrodes (Metrohm EA404). Values of $E^{\ominus}$ and nernstian slope of the electrode system were determined by titrating 20—25 cm^3 of HNO_3 with CO_2-free KOH. The concentration of dialkyltin investigated ranged from 2 to 12 and from 5 to 12 mmol dm^{-3} for $[SnMe_2]^{2+}$ and $[SnEt_2]^{2+}$, respectively. Checks on the pH stability of each solution to be titrated showed no detectable drift in e.m.f. over a period of 2 h. Other details were as previously described.[10] Experimental details for the potentiometric titrations are reported in Table 1.

Calorimetric Measurements.—The calorimetric measurements were performed at 25.000 ± 0.001 °C using a Tronac 450 isoperibolic calorimeter equipped with a 25 cm^3 titration Dewar. Essentially, two sets of experiments were performed.

(*a*) Dialkyltin solutions at a pH of *ca.* 7.5 were titrated with standard HNO_3.

(*b*) Dimethyltin solutions at a pH of *ca.* 7.0 were titrated with standard CO_2-free KOH. The titration data thus obtained (a total of 700 points), corrected for all non-chemical energy terms determined in separate experiments, were refined simultaneously to obtain the final $\Delta H^{\ominus}$ values. Procedure (*b*) was adopted to mimimize water formation which would 'mask' the actual heat

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† *Non-S.I. unit employed:* cal = 4.148 J.

Table 1. Experimental conditions of potentiometric measurements at 25 °C and I = 0.1 mol dm^{-3} (KNO_3)

M	C°_{M} (mmol dm^{-3})	Titrant, KOH (mol dm^{-3})	pH Range
$[SnMe_2]^{2+}$	2.070	0.099 60	2.6—10.7
	2.070	0.099 49	2.6—10.7
	4.020	0.100 98	2.5—10.7
	4.020	0.100 57	2.5—10.7
	4.308	0.099 60	2.5—10.7
	4.308	0.099 49	2.5—10.7
	7.997	0.100 98	2.5—10.7
	7.997	0.100 57	2.5—10.7
	9.031	0.100 98	2.5—10.6
	9.031	0.100 57	2.5—6.1
	10.072	0.100 98	2.4—10.4
	10.072	0.100 57	2.4—6.1
	12.021	0.099 60	2.4—10.4
	12.021	0.099 49	2.4—6.1
$[SnEt_2]^{2+}$	4.477	0.101 00	2.6—5.5
	4.477	0.100 70	2.6—5.5
	4.956	0.099 60	2.5—5.5
	4.956	0.099 49	2.5—5.5
	6.352	0.101 00	2.4—5.5
	6.352	0.100 70	2.4—5.5
	7.506	0.101 00	2.4—5.5
	7.506	0.100 70	2.4—5.0
	9.001	0.099 60	2.4—4.6
	9.001	0.099 49	2.4—4.4
	12.004	0.101 00	2.4—4.4
	12.004	0.100 70	2.4—4.2

Table 2. Experimental conditions of calorimetric measurements at 25 °C and I = 0.1 mol dm^{-3} (KNO_3)

M	C°_{M} (mmol dm^{-3})	Titrant (mol dm^{-3})	pH Range
$[SnMe_2]^{2+}$	5.987	HNO_3 1.0052	5.0—2.4
	6.017		5.5—2.4
	8.032		6.2—2.5
	9.003		6.0—2.4
	9.037		6.0—2.4
	8.983	HNO_3 0.3728	6.0—2.4
	2.570	HNO_3 0.4058	6.5—2.5
	4.931		6.5—2.5
	4.952		6.0—2.5
	11.966	HNO_3 0.5998	5.0—2.5
	2.894	KOH 0.1002	8.0—10.4
	5.549		8.5—10.4
	8.046		8.5—10.4
$[SnEt_2]^{2+}$	5.050	HNO_3 0.5998	4.2—2.5
	5.994		4.0—2.5
	7.920		4.0—2.5
	8.002		4.2—2.5
	11.948		4.2—2.5
	11.998		4.2—2.5
	12.001		4.0—2.5

evolved during the reaction. Experimental details for the calorimetric titrations are reported in Table 2.

Calculations.—The calculations concerning the calibration of the electrode system as well as the slope were performed using the computer program ACBA [11] which refines the parameters of an acid–base titration by using a non-linear least-squares method minimizing the function $U = \Sigma(V_{exp.} - V_{calc.})^2$ where V is the volume of titrant added. The programs MINIQUAD 76A [12] and SUPERQUAD [13] were used to handle all other data. MINIQUAD minimizes the function $U = \Sigma(T_1 - T_{1,calc.})^2$, where T is the analytical concentration of the ith component, whereas SUPERQUAD minimizes the error-square sum based on measured electrode potentials. As to the analysis of residuals, the procedure recommended by Vacca *et al.*[14] was followed.

The calorimetric data were treated by using the computer program DOEC.[15] The distribution diagrams were obtained by means of the computer program DISDI.[16]

Results

Metal ions generally hydrolyse to form a series of mono- and poly-nuclear hydroxo complexes. The general equation is (1).

$$xM^{n+} + yH_2O \rightleftharpoons M_x(OH)_y^{n-y} + yH^+ \qquad (1)$$

For the dimethyltin ion the following species list was considered: $[SnR_2(OH)]^+$, $[SnR_2(OH)_2]$, $[SnR_2(OH)_3]^-$, $[\{SnR_2(OH)\}_2]^{2+}$, $[(SnR_2)_2(OH)_3]^+$, $[(SnR_2)_3(OH)_4]^{2+}$, and $[(SnR_2)_4(OH)_6]^{2+}$, with $[SnR_2(OH)]^+$, $[SnR_2(OH)_2]$, and $[SnR_2(OH)_3]^-$ as the base model and the other species added in different combinations. Stability constants are reported in Table 3 together with some literature values. The data show that our model resembles that obtained in a chloride medium,[17] rather than that previously obtained in the same medium, $[NO_3]^-$,[18] with the only significant exception being the $[SnR_2(OH)_3]^-$ species. It has to be said though, that this species, not detected by Tobias and Yasuda,[17] was later reported by Tobias and Friedline,[19] who also found some Raman and n.m.r. evidence supporting its existence. Without the $[SnMe_2(OH)]^+$, $[SnMe_2(OH)_2]$, and $[SnMe_2(OH)_3]^-$ species it was impossible to begin to reproduce the experimental data. In fact, high R values (MINIQUAD) and dramatic χ^2 increase (SUPERQUAD), or even model failure, were observed when trying to fit the data with the set of species found by Yasuda and Tobias [20] in NO_3^- medium (*e.g.* $\chi^2 = 602$ and $\sigma = 93$ when refining the data by using SUPERQUAD). Thus, there is no doubt about the existence of the main species. Questions do arise about the existence of the larger polymeric complexes formed. In fact, as shown in Table 3, the data are equally well reproduced with two sets of constants. The reason for this is to be found in the small fraction of dimethyltin distributed in these species. Some authors [17] point out that there may even be several additional complexes present in low concentrations just before the precipitation pH is reached. Thus, the only difference between our model and that of Tobias concerns the $[(SnMe_2)_3(OH)_4]^{2+}$ species. The value of log β for this species became negative when processing the data with both MINIQUAD and SUPERQUAD. However, the statistical parameters obtained with the set of constants reported in Table 3, column 1, were slightly better than those obtained when including the $[(SnMe_2)_4(OH)_6]^{2+}$ species. Consequently, we used this set of constants to fit the calorimetric data.

Table 3 also shows that our constants are slightly larger than those obtained in chloride medium. This is reasonable since, with a chloride medium, a measurable degree of complexing by chloride ions is to be expected.

Table 4 shows the data obtained for $[SnEt_2]^{2+}$ hydrolysis. We investigated the concentration range 2—8 mmol dm^{-3}. Precipitation prevented investigation above pH 5.5. For comparison some literature data are also reported. The differences observed can be attributed to different conditions and to 'incomplete' speciation.[21,22] Both MINIQUAD and SUPERQUAD give essentially the same set of constants. The hydroxo species $[(SnEt_2)_2(OH)_3]^+$ never exceeds 5% of the

Table 3. Stability constants of dimethyltin(IV)–hydroxo complexes at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Reaction	log β[a]				log β[b]		log β[c]
$M^{2+} + H_2O \rightleftharpoons [M(OH)]^+ + H^+$	−3.124(3)[d]	−3.116(2)[e]	−3.129(3)[d]	−3.121(2)[e]	−3.251	−3.245	−3.2
$2M^{2+} + 2H_2O \rightleftharpoons [\{M(OH)\}_2]^{2+} + 2H^+$	−5.05(3)	−5.11(2)	−4.95(3)	−5.02(2)	−5.05	−5.00	−4.6
$2M^{2+} + 3H_2O \rightleftharpoons [M_2(OH)_3]^+ + 3H^+$	−9.74(1)	−9.77(1)			−9.81		
$3M^{2+} + 4H_2O \rightleftharpoons [M_3(OH)_4]^{2+} + 4H^+$	Neg.	Neg.			−11.52		
$4M^{2+} + 6H_2O \rightleftharpoons [M_4(OH)_6]^{2+} + 6H^+$			−16.30(2)	−16.31(2)		−16.85	
$M^{2+} + 2H_2O \rightleftharpoons M(OH)_2 + 2H^+$	−8.428(2)	−8.425(2)	−8.423(2)	−8.420(2)	−8.535	−8.516	
$M^{2+} + 3H_2O \rightleftharpoons [M(OH)_3]^- + 3H^+$	−19.450(4)	−19.437(7)	−19.445(5)	−19.432(7)			

[a] This work. [b] Values from ref. 17 [$I = 0.1$ mol dm^{-3} (NaCl)]. [c] Values from ref. 20 [$I = 0.1$ mol dm^{-3} (KNO_3)]. [d] SUPERQUAD. [e] MINIQUAD. Standard deviations are given in parentheses. $M^{2+} = [SnMe_2]^{2+}$.

Table 4. Stability constants of diethyltin(IV)–hydroxo complexes at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Reaction	log β[a]		log β[b]		log β[c]
$M'^{2+} + H_2O \rightleftharpoons [M'(OH)]^+ + H^+$	−3.102(2)	−3 104(2)	−2.65	−2.40	−3.40
$2M'^{2+} + 2H_2O \rightleftharpoons [\{M'(OH)\}_2]^{2+} + 2H^+$	−5.07(3)	−5.05(3)	−4.00	−3.40	−4.37
$2M'^{2+} + 3H_2O \rightleftharpoons [M'_2(OH)_3]^+ + 3H^+$	−10.26(4)	−10.25(5)	−7.60	−6.70	
$M'^{2+} + 2H_2O \rightleftharpoons M'(OH)_2 + 2H^+$	−8.563(2)	−8.563(4)	−7.49	−6.98	

[a] This work (column 1: SUPERQUAD, column 2: MINIQUAD). [b] From ref. 21 [column 3, $I = 1$ mol dm^{-3} (KCl), column 4, $I = 0$]. [c] From ref. 22 [$I = 0.1$ mol dm^{-3} (KNO_3)]. Standard deviations are given in parentheses. $M'^{2+} = [SnEt_2]^{2+}$.

Table 5. Thermodynamic parameters for dimethyltin(IV)–(M) and diethyltin(IV)–(M′) hydroxo complexes at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Reaction	$-\Delta G^\circ$ (kcal mol^{-1})	$-\Delta H^\circ$ (kcal mol^{-1})	ΔS° (cal mol deg^{-1})
$M^{2+} + OH^- \rightleftharpoons [M(OH)]^+$	14.482(4)	6.57(7)	26.5(2)
$MOH^+ + OH^- \rightleftharpoons M(OH)_2$	11.510(3)	6.10(3)	18.2(1)
$M(OH)_2 + OH^- \rightleftharpoons [M(OH)_3]^-$	3.714(5)	4.5(1)	−2.9(5)
$2M^{2+} + 2OH^- \rightleftharpoons [\{M(OH)\}_2]^{2+}$	30.59(4)	12.1(5)	61(2)
$2M^{2+} + 3OH^- \rightleftharpoons [M_2(OH)_3]^+$	42.94(1)	20.8(1)	74.4(5)
$M'^{2+} + OH^- \rightleftharpoons [M'(OH)]^+$	14.510(3)	6.09(8)	28.2(2)
$M'OH^+ + OH^- \rightleftharpoons M'(OH)_2$	11.352(3)	7.2(1)	13.7(4)
$2M'^{2+} + 2OH^- \rightleftharpoons [\{M'(OH)\}_2]^{2+}$	30.57(5)	16.8(6)	46(2)

Standard deviations are given in parentheses.

total organotin. However, fitting the data without taking this species into consideration caused a large increase in the statistical parameters of both programs (*e.g.*, $\chi^2 = 6.8$ and 20 with and without this species, respectively). Moreover, even if present in low percentage this species is formed in our experimental conditions. Changes in ΔH° and ΔS° values for $[(SnEt_2)_2(OH)_3]^+$ are not reliable owing to its low degree of formation. Thus, in order to avoid attribution, perhaps erroneous, of its thermal effect to other species present in the same pH range, we decided to perform the calorimetric experiments in conditions where $[(SnEt_2)_2(OH)_3]^+$ does not exist.

We chose to work at 0.1 mol dm^{-3} in KNO_3 to avoid the formation of chloro complexes and for the following reasons. (*i*) Higher concentration of dialkyltin, achieved by using higher ionic strengths, rarely serve any useful purpose and do not facilitate detections of higher polymeric species as shown by several authors.[23] (*ii*) High ionic strengths militate against attainment of high pH values because of the increased ease of precipitation under such conditions.

Table 5 shows the thermodynamic parameters for the hydroxy complexes of organotin ions. No comparison is possible with other, previously determined, data, since, to the best of our knowledge, ΔH° and ΔS° values are reported here for the first time. The larger deviation in the enthalpy changes obtained for the diethyltin system is attributed to the lower solubility of this ion, compared to dimethyltin.

Discussion

In the concentration ranges studied in the present work the $[SnR_2(OH)]^+$ species is important over all concentration ranges investigated, whereas the dimer is relevant at pH ≈ 4 and high metal-ion concentration. The distribution diagrams for the dimethyltin and diethyltin system are shown in Figures 1 and 2, respectively.

There is no significant difference in the acidity of the two organometallic cations (Tables 3 and 4). This result is in contrast with previous findings,[22] showing an acidity increase in the series $[SnMe_2]^{2+}$, $[SnEt_2]^{2+}$, and $[SnPr_2]^{2+}$, with log K values of −3.54, −3.40, and −2.92, respectively. The latter trend,[23] opposite to that observed for trimethyl- and triethyltin ions, and to that expected simply on the basis of inductive effects, was explained by invoking decreasing solvation of the acid with increase in size of the alkyl groups. It is likely that the difference between the present and the literature data is attributable to an incomplete model that considers the $[SnR_2(OH)]^+$ and $[(SnR_2)_2(OH)_2]^{2+}$ species only.[23]

The formation of hydroxo species is both enthalpy and entropy favoured (Table 5). At first sight, the negative ΔH° value seems opposite to that expected for hard donors such as the hydroxide ion. Literature data[24] show not only that the enthalpy and entropy values are not significantly dependent upon the nature of the metal ion, but also that the ΔH° changes range from −6 to −8 kcal mol^{-1}. Our data support Ahrland's

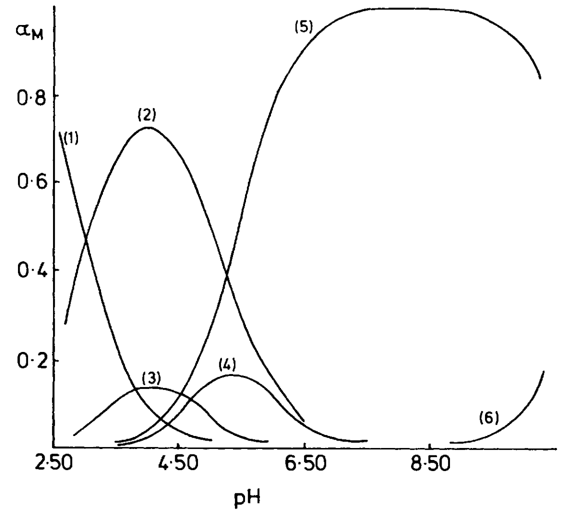

Figure 1. Species distribution diagram for the hydrolysis of $[SnMe_2]^{2+}$ (8×10^{-3} mol dm^{-3}): (1), free central ion; (2), $[SnMe_2(OH)]^+$; (3), $[(SnMe_2)_2(OH)_2]^{2+}$; (4), $[(SnMe_2)_2(OH)_3]^+$; (5), $[SnMe_2(OH)_2]$; (6), $[SnMe_2(OH)_3]^-$

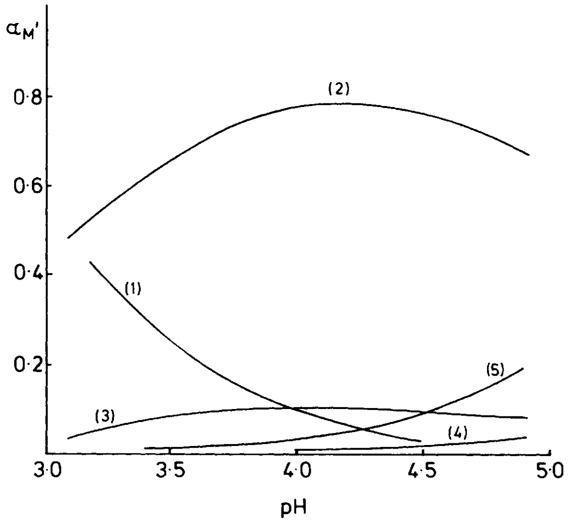

Figure 2. Species distribution diagram for the hydrolysis of $[SnEt_2]^{2+}$ (6×10^{-3} mol dm^{-3}): (1), free central ion; (2), $[SnEt_2(OH)]^+$; (3), $[(SnEt_2)_2(OH)_2]^{2+}$; (4), $[(SnEt_2)_2(OH)_3]^+$; (5), $[SnEt_2(OH)_2]$

hypothesis[25] on the peculiarity of the thermodynamics of hydroxo complex formation. At least as far as inner sphere complexes are concerned, formation of a complex ordinarily implies the substitution of water of hydration with a ligand. This means breaking of bonds between the metal ion and the oxygen of the water molecule and formation of bonds between the metal ion and the ligand. The formation of hydroxo complexes in acid solution is best described as a transfer of protons from water molecules within the hydration shell to water molecules outside this shell. In such a process, metal to oxygen bonds are neither broken nor formed. Consequently, the formation of hydroxo species represents the detachment of a proton rather than the substitution of water molecules by OH^- ions. This explains the exothermic contribution that would otherwise be in contrast to the 'hard' character of the hydroxide ion.

Although the above considerations allow correct interpretation of the trend of thermodynamic data concerning the hydroxo complex formation of dialkyltin(IV) ions, there are still some aspects which need further clarification. In particular, we shall discuss the ΔH° and ΔS° differences observed for dimethyl- and diethyl-tin–hydroxo species. The discussion that follows is based on the assumption that the aqua–dialkyltin(IV) ions have linear C–Sn–C skeletons and the cations contain four water molecules in the first co-ordination sphere that are essentially bound by ion–dipole forces.[26]

The formation of $[SnR_2(OH)]^+$ shows ΔH° and ΔS° values that are slightly less negative and more positive, respectively, for the diethyl than for the dimethyl derivative. The desolvation process seems to be more effective for $[SnEt_2(H_2O)]^{2+}$ than for $[SnMe_2(H_2O)]^{2+}$ species, probably owing to the slightly different inductive effect of the two alkyl groups. The entropy values associated with the formation of the monohydroxo species are larger than those concerning formation of the dihydroxo complexes. This is attributed to the larger desolvation process accompanying the formation of the monohydroxo species, which is, in turn, due to a structural rearrangement of the alkyl groups from a *trans* to a *cis* configuration. This is in line with previous findings suggesting that the C–Sn–C angle in the monohydroxo complex is significantly less than 180°, owing to the different donor capability between hydroxo and aqua groups.[26]

The formation of $[SnMe_2(OH)_3]^-$ is enthalpically favoured and entropically unfavoured. The negative ΔS° value is mainly due to the formation of a charged species and to the desolvation occurring in the previous hydrolysis steps. The enthalpy value of the third step is less exothermic if compared to the other two steps. This cannot be unambiguously explained on the basis of the thermodynamic data alone. One may hypothesize that we are dealing with the co-ordination of an hydroxo ion to $[SnMe_2(OH)_2]$ rather than with a proton transfer. In such a case the OH^- co-ordination is enthalpically favoured because the desolvation process having been completed with the formation of $[SnMe_2(OH)_2]$, the reaction is only due to the exothermic formation of the organometallic–hydroxo ion bond, without the endothermic contribution due to the breaking of the organometallic–water bond.

The differences (in ΔH° and ΔS°) observed for $[SnMe_2(OH)_2]$ and $[SnEt_2(OH)_2]$ are atrributable both to different neutralization of the formal charge of the cation and to structural reasons. In fact, by analogy with the dimethylgermanium–dihydroxo species, which has been shown to be tetrahedral by Raman spectroscopy in aqueous solution,[19] a tetrahedral structure has also been proposed for the neutral dialkyltin(IV)–dihydroxo complex in solution.[19] In our case, the hydrophobic interaction between the diethyl groups would be responsible for the larger enthalpic and smaller entropic contributions observed for the diethyl derivative. In fact, we have already shown that the hydrophobic 'bond' is enthalpically favoured and entropically unfavoured.[27]

The dimer formation shows similar ΔG° values but significantly different ΔH° and ΔS° values (Table 5). Namely, the enthalpy contribution increases with the increasing length of the alkyl chain, whereas the entropy value is larger for the dimethyl than for the diethyl derivatives. Dreiding models show that, in the latter case, the alkyl chains can interact with one another, which is not possible for the methyl chains. Thus, once again, a hydrophobic interaction would account for the differences observed.

In conclusion, an investigation which is not limited to the determination of the sole ΔG° value shows that: (*i*) similar stability constants may 'hide' different enthalpic and entropic contributions, and (*ii*) useful information on the structural features of organometallic species may be obtained through the determination of ΔH° and ΔS° values.

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References

1 C. A. Kraus and C. C. Callis, *J. Am. Chem. Soc.*, 1923, **45**, 2624.
2 R. S. Tobias, *Organomet. Chem. Rev.*, 1966, **1**, 93.
3 J. A. Zubieta and J. J. Zuckerman, in 'Progress in Inorganic Chemistry,' ed. S. J. Lippard, John Wiley and Sons, New York, 1978, vol. 24, p. 251.
4 R. F. Bennet, *Ind. Chem. Bull.*, 1983, **2**, 171.
5 J. J. Zuckerman, R. P. Reisdorf, H. V. Ellis III, and R. R. Wilkinson, in 'Organometals and organometalloids, occurrence and fate in the environment,' eds. F. E. Brinckman and J. M. Bellama, *Am. Chem. Soc. Symp. Ser.*, 1978, **82**, 388.
6 A. J. Crowe, P. J. Smith, and G. Atassi, *Chem. Biol. Interact.*, 1980, **32**, 171.
7 F. Huber and R. Barbieri, in 'Tin as a vital nutrient,' ed. N. F. Cardarelli, CRC Press, Boca Raton, 1986, p. 175.
8 M. Gielen, in 'Tin as a vital nutrient,' ed. N. F. Cardarelli, CRC Press, Boca Raton, 1986, p. 169.
9 J. S. Thayer, 'Organometallic Compounds and Living Organism,' Academic Press, Orlando, 1984.
10 G. Arena and V. Cucinotta, *Inorg. Chim. Acta*, 1981, **52**, 275.
11 G. Arena, C. Rigano, E. Rizzarelli, and S. Sammartano, *Talanta*, 1979, **26**, 1.
12 P. Gans, A. Vacca, and A. Sabatini, *Inorg. Chim. Acta*, 1978, **18**, 237.
13 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
14 A. Vacca, A. Sabatini, and M. A. Christina, *Coord. Chem. Rev.*, 1972, **8**, 45.
15 C. Rigano, E. Rizzarelli, and S. Sammartano, *Thermochim. Acta*, 1979, **33**, 211.
16 R. Maggiore, S. Musumeci, and S. Sammartano, *Talanta*, 1976, **23**, 43.
17 R. S. Tobias and M. Yasuda, *Can. J. Chem.*, 1964, **42**, 981.
18 C. F. Baes, jun., and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley, New York, 1976, p. 354.
19 R. S. Tobias and C. E. Friedline, *Inorg. Chem.*, 1965, **4**, 215 and refs. therein.
20 M. Yasuda and R. S. Tobias, *Inorg. Chem.*, 1963, **2**, 207.
21 M. Asso and G. Carpeni, *Can. J. Chem.*, 1968, **46**, 1795.
22 R. S. Tobias, H. N. Farrer, M. B. Hughes, and B. A. Nevett, *Inorg. Chem.*, 1966, **5**, 2052.
23 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 31.
24 R. E. Mesmer and C. F. Baes, jun., *Inorg. Chem.*, 1967, **6**, 1951.
25 S. Ahrland, 'Struct. and Bonding,' Springer, Berlin Heidelberg, New York, 1968, vol. 5, pp. 118—149.
26 M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, 1964, **3**, 1157.
27 G. Arena and E. Rizzarelli, in 'Metal Complexes in Solution,' eds. E. A. Jenne, E. Rizzarelli, V. Romano, and S. Sammartano, Piccin (Padua), 1986, pp. 105—117, and refs. therein.

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