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COMPLEXES OF DIALKYLTIN(IV) CATIONS WITH FLUORIDE IONS

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Summary

The formation of complexes between alkyltin(IV) cations and fluoride ligands has been studied in a constant ionic medium (1 *M* $NaClO_4$) at 25° by potentiometric and solubility methods. In the concentration range examined only mononuclear complexes have been found, and their stability constants have been determined. The influence of the organic groups on the values of the formation constants is discussed, and properties of dialkyltin(IV) and dialkyllead(IV) cations are compared.

Introduction

There have been many studies of the formation of complexes between organotin(IV) cations and inorganic ligands [1 - 9]. Cassol et al. [6 - 9], in particular, in their studies on the association of alkyltin(IV) cations with fluoride ion, have established the existence in aqueous solution of the following species: $[(CH_3)_3SnF_n]^{(1-n)+}$ $(n = 1, 2)$, $[(CH_3)_2SnF_n]^{(2-n)+}$ $(n = 1, 2, 3, 4)$, and $[CH_3SnF_n]^{(3-n)+}$ $(n = 1, 2, 3, 4, 5)$.

A more recent study of an homologous series of alkyllead(IV) cations has shown that the nature of the organic groups has a substantial influence on the magnitude of the formation constant [10,11].

Experimental

Materials

The standard solutions of sodium fluoride (equilibrated at 1 *M* Na^+ with sodium perchlorate) of sodium perchlorate and of perchloric acid were prepared as described in a previous paper [11].

$(C_2H_5)_2SnCl_2$ and $(n\text{-}C_4H_9)_2SnCl_2$ were prepared by the method of

Kozeschkow [12]. For the preparation of the alkyltin perchlorates, weighed amounts of the dichlorides were titrated against standard silver perchlorate solution. The silver chloride was filtered off and the recovered solutions were diluted to appropriate volumes. To prevent decomposition the solutions of organotin(IV) compounds were stored in dark bottles at low temperature.

A standard solution of ferrocyanide was prepared by dissolving a weighed amount of sodium ferrocyanide in water. The ferrocyanide content was confirmed by argentometric titration.

Quinhydrone, Merck (p.a.), was crystallised from water at 70°. 99.99% Nitrogen, further purified as described by Arthur [13] and equilibrated to the correct vapour pressure for a solution of 1 M $NaClO_4$, was employed for removal of oxygen.

Symbols

B = total organotin concentration;
A = total fluoride concentration;
H = total acid concentration;
b = equilibrium concentration of organotin ion;
a = equilibrium concentration of fluoride ion;
h = equilibrium concentration of hydrogen ion;
$K_1 = [HF] \cdot h^{-1} \cdot a^{-1}$;
$K_2 = [HF_2^-] \cdot [HF]^{-1} \cdot a^{-1}$;
$\bar{n}_B = A - a - K_1 \cdot h \cdot a - 2K_1 \cdot K_2 \cdot h \cdot a^2 / B$ = average number of fluoride ions bound to each organotin ion;
$K_{so} = [n\text{-}Bu_2Sn^{2+}] \cdot [F^-]^2$ = solubility product of $n\text{-}Bu_2SnF_2$.

Measurements of equilibrium potentials

The formation of complexes between Et_2Sn^{2+} and fluoride ion was studied at 25 ± 0.05° by measuring, with a quinhydrone half cell, the competition between hydrogen ions and organotin cations for fluoride.

The cell employed in the determination of the equilibrium hydrogen ion concentration was similar to that described by Forsling et al. [14]. It can be represented as: — R.E.| test solution, quinhydrone(s) | Au^+.

The reference electrode (R.E.), a silver|silver chloride electrode, prepared as recommended by Brown [15], was dipped in a 0.01 M Cl^-, 0.99 M ClO_4^-, 1 M Na^+ solution.

The test solution had the general composition: BM Et_2Sn^{2+}, HM H^+, $(1-2B-H)M$ Na^+, AM F^-, $(1-A)M$ ClO_4^-.

The indicator electrode was a bright gold foil, which was always cleaned with hot chromic acid before use.

The standard NaF solution was added from a Radiometer Auto-burette type ABU 1b equipped with a burette type B 150 unit with a total volume of 2.500 ml. The volumes were read to ± 0.001 ml.

All the parts of the cell system which could come into contact with fluoride solution were either constructed in Plexiglas or lined with paraffin.

The experiments were carried out as potentiometric titrations: known amounts of standard NaF solution were added to a solution of known organotin and acid content, and the corresponding equilibrium potentials were read. A Kietly model 630 voltmeter was employed in all measurements. The EMF's were read at ± 0.01 mV while the cell potentials were stable and reproducible within 0.05 mV.

Solubility measurements

The very low solubility of n-Bu_2SnF_2 prevented the investigation of the reaction between n-Bu_2Sn^{2+} and F^- by the potentiometric method alone. In order to obtain the total concentration of fluoride and of alkyltin cation present in the solution in this case, potentiometric measurements were associated with solubility measurements.

Known amounts of NaF, $HClO_4$, $NaClO_4$ and of n-$Bu_2Sn(ClO_4)_2$ were introduced in polyethylene bottles which were allowed to stand for some days at 25 ± 0.05° under vigorous stirring. After equilibration the solutions were recovered by gentle suction, with a standard pipette equipped with a sintered glass disk to prevent any contamination from the precipitate. Appropriate amounts of every solution were used both for the potentiometric determination of the equilibrium hydrogen ion concentration (see above) and for the determination, by the following analytical procedure, of the total concentration of the organotin cation. After addition of an excess of perchloric acid to decompose all the fluoride complexes, the solution was titrated with standard sodium ferrocyanide [16]. The end-point of the titration reaction:

$$2\ \text{n-}Bu_2Sn^{2+} + [Fe(CN)_6]^{4-} \rightarrow [\text{n-}Bu_2Sn]_2[Fe(CN)_6]$$

was detected monoamperometrically by measuring the anodic current, due to the excess of ferrocyanide ion, through a rotating platinum disk electrode. The accuracy of this analytical procedure was checked by titrating solutions of n-Bu_2Sn^{2+} previously standardised by the cation exchange method.

Results

Et_2Sn^{2+}—F^- system

The EMF (in mV) of the cell at 25° is given by the relation:

$$E = E_0' + 59.15 \log h + E_j \qquad (1)$$

where E_0' is a constant in our experimental conditions and E_j, which can be expressed in the form [17]:

$$E_j = J \cdot h$$

is the liquid junction potential between the test solution and the salt bridge.

Preliminary tests carried out in absence of organotin(IV) and fluoride ions gave the values $E_0' = 161.31$ mV and $J = -0.0584$ mV · mM^{-1} respectively. If neither hydrolysis of the alkyltin cations nor formation of mixed complexes occur under our experimental conditions then the following relations must hold:

$$H = h + [HF] + [HF_2^-] \qquad (2)$$

$$A = a + [HF] + 2[HF_2^-] + \bar{n}_B \cdot B \qquad (3)$$

TABLE 1

TYPICAL TITRATION DATA FOR Et_2Sn^{2+}—F^- COMPLEXES FOR A SOLUTION WITH H= 38.36 mM, B = 66.18 mM, V = 100 ml

Vol of NaF solution (ml)	E(mV)	A(mM)	h(mM)	a(mM)	$\bar{n}$
8.000	246.39	60.59	29.22	0.235	0.882
9.000	244.60	67.54	27.12	0.324	0.974
10.000	242.57	74.36	24.94	0.433	1.063
11.000	240.26	81.06	22.68	0.569	1.150
12.000	237.70	87.64	20.42	0.735	1.236
13.000	234.80	94.10	18.15	0.945	1.320
14.000	231.51	100.4	15.89	1.212	1.402
15.000	227.78	106.7	13.67	1.559	1.483
16.000	223.57	112.8	11.55	2.015	1.562
18.000	213.73	124.8	7.808	3.403	1.718
20.000	201.99	136.3	4.911	5.871	1.864
22.000	189.65	147.5	3.025	9.866	1.994
24.000	178.35	158.3	1.944	15.36	2.105
26.000	168.64	168.8	1.330	22.01	2.197
28.000	160.47	178.9	0.967	29.41	2.275
30.000	153.55	188.8	0.758	37.23	2.342

By inserting the values of K_1 and K_2 (K_1 = 899 ± 5 $l \cdot mol^{-1}$ and K_2 = 3.4 ± 0.2 $l \cdot mol^{-1}$) determined by potentiometric techniques, the equations (2) and (3) can be written as:

$$H = h + K_1 \cdot h \cdot a + K_1 \cdot K_2 \cdot h \cdot a^2 \qquad (4)$$

$$A = a + K_1 \cdot h \cdot a + 2K_1 \cdot K_2 \cdot h \cdot a^2 + \bar{n}_B \cdot B \qquad (5)$$

The known values of H, h, A, K_1 and K_2 allow the calculation of "a", and consequently of the function $\bar{n}_B$ (log a).

Typical titration data are reported in Table 1. The first titration data are not reported because at low fluoride concentration the hydrolysis of the acceptor could not be completely disregarded in spite of the acidity of the medium.

Figure 1 shows the formation curve for the system Et_2Sn^{2+}—F^-. The existence of a single curve within the experimental error indicates that both the assumptions made above, viz, the absence of hydrolysis and of mixed complexes, were correct, and that only mononuclear complexes were formed. Furthermore the maximum value reached by the formation curve (about 2.4) strongly suggested that only the species Et_2SnF^+, Et_2SnF_2 and $Et_2SnF_3^-$ were formed under our experimental conditions, according to the equilibria:

$$Et_2Sn^{2+} + F^- \rightleftharpoons Et_2SnF^+$$

$$[Et_2SnF^+] \cdot [Et_2Sn^{2+}]^{-1} \cdot [F^-]^{-1} = \beta_1$$

$$Et_2Sn^{2+} + 2F^- \rightleftharpoons Et_2SnF_2$$

$$[Et_2SnF_2] \cdot [Et_2Sn^{2+}]^{-1} \cdot [F^-]^{-2} = \beta_2$$

$$Et_2Sn^{2+} + 3F^- \rightleftharpoons Et_2SnF_3^-$$

$$[Et_2SnF_3^-] \cdot [Et_2Sn^{2+}]^{-1} \cdot [F^-]^{-3} = \beta_3$$

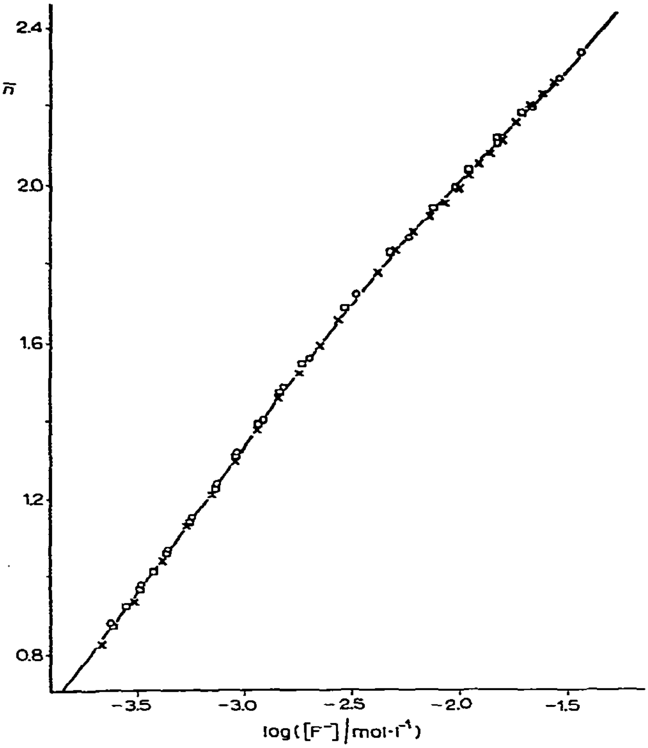

Fig. 1. Average number of bound fluoride ions for the diethyltin(IV) ion as a function of log F^- at 25° in a 1 *M* perchlorate medium: X 8.27 m*M*; □ 33.09 m*M*; ○ 66.18 m*M* stoichiometric Et_2Sn^{2+} concentration. Full line: curve calculated with $\beta_1 = 11.7 \times 10^3$ l·mol^{-1}, $\beta_2 = 7.3 \times 10^6$ l^2·mol^{-2} and $\beta_3 = 11.6 \times 10^7$ l^3·mol^{-3}.

Hence for $\bar{n}_B$ it is possible to write:

$$\bar{n}_B = \frac{\beta_1 \cdot a + 2\beta_2 \cdot a^2 + 3\beta_3 \cdot a^3}{1 + \beta_1 \cdot a + \beta_2 \cdot a^2 + \beta_3 \cdot a^3} \tag{6}$$

For $\bar{n}_B < 1.5$ the relation (6) can be approximated to the form:

$$\bar{n}_B = \frac{\beta_1 \cdot a + 2\beta_2 \cdot a^2}{1 + \beta_1 \cdot a + \beta_2 \cdot a^2} \tag{7}$$

which by simple rearrangement gives:

$$\frac{\bar{n}_B}{(1-\bar{n}_B) \cdot a} = \beta_1 + \beta_2 \frac{(2-\bar{n}_B) \cdot a}{(1-\bar{n}_B)} \tag{8}$$

The plot of this relation allowed the graphical evaluation of β_1 and of a first value of β_2. The insertion of the value of β_1 into equation (6) and rearrangement in the form:

$$\frac{\bar{n}_B/a - \beta_1(1-\bar{n}_B)}{a(2-\bar{n}_B)} = \beta_2 + \beta_3 \frac{a(3-\bar{n}_B)}{2-\bar{n}_B}$$

TABLE 2

STABILITY CONSTANTS OF ORGANOTIN(IV) FLUORIDE COMPLEXES

Species	β_1 (l·mol^{-1})	β_2 (l^2·mol^{-2})	β_3 (l^3·mol^{-3})	K_2 (l·mol^{-1})	K_3 (l·mol^{-1})	K_{so} (mol^3·l^{-3})
$(Me)_2Sn^{2+}$ [a]	(5.0 ± 0.2) × 10^3	(3.75 ± 0.25) × 10^6	(11.0 ± 1.5) × 10^7	750	29.3	
$(Et)_2Sn^{2+}$ [b]	(11.7 ± 0.4) × 10^3	(7.3 ± 0.2) × 10^6	(11.6 ± 0.2) × 10^7	620	15.9	
n-Bu_2Sn^{2+} [b]	(37.3 ± 3.3) × 10^3	(18.5 ± 2.2) × 10^6	(44.6 ± 3.8) × 10^7	500	24	(1.27 ± 0.12) × 10^{-11}

[a] Data from ref. 7. [b] The uncertainties shown are standard deviations.

in turn allowed the determination of β_2 and β_3. Both the equations for the two linear plots were obtained by the "least square method".

In Table 2 the values of β_1, β_2 and β_3 for the system Et_2Sn^{2+}—F^- are reported. Figure 2 shows the distribution curves of the species Et_2Sn^{2+}, Et_2SnF^+, Et_2SnF_2 and $Et_2SnF_3^-$ as a function of the ligand concentration.

n-Bu_2Sn^{2+}—F^- system

In this case also, the value of "a" (equilibrium ligand concentration) could be determined by potentiometric measurements through equation (4), but the value of $\bar{n}_B$ could not be calculated from the relation:

$$\bar{n}_B = \frac{A - a - K_1 \cdot h \cdot a - 2K_1 \cdot K_2 \cdot h \cdot a^2}{B} \tag{9}$$

because of the low solubility of n-Bu_2SnF_2. To determine the nature of the precipitate elemental analysis and titration tests were carried out. For the titration tests weighed amounts of the precipitate were dissolved in 1 *M* $HClO_4$; the number of equivalents of n-Bu_2Sn^{2+} found by titration with $[Fe(CN)_6]^{4-}$ agreed accurately with those theoretically predicted.

The plot in Fig. 3 indicates that n-Bu_2Sn^{2+} also undergoes subsequent complexation. The branch at the right of this curve shows a slope of less than unity, suggesting that, if hydrolytic and polynuclear complexes are not formed, the highest complex is n-$Bu_2SnF_3^-$. The following relation can thus be written:

$$B = K_{so} \cdot a^{-2} + K_{so} \cdot \beta_1 \cdot a^{-1} + K_{so} \cdot \beta_2 + K_{so} \cdot \beta_3 \cdot a \tag{10}$$

The graphical method employed for the determination of the equilibrium constants of the Et_2Sn^{2+} —F^- system was not suitable in this case, because in

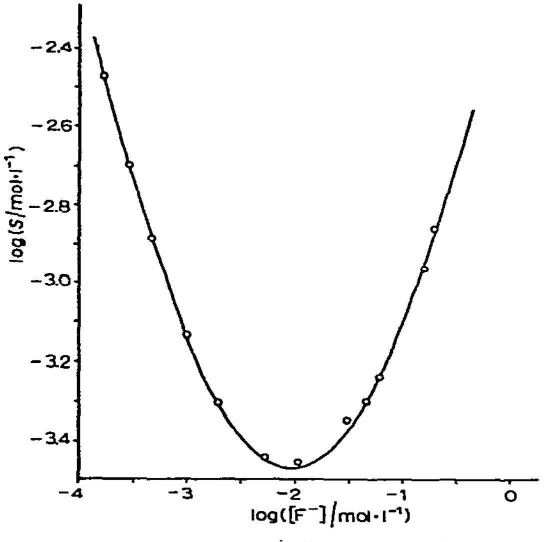

Fig. 2. Plot of log S vs. log $[F^-]$ for n-Bu_2Sn^{2+}—F^- system at 25° in 1 *M* perchlorate medium. Full line: curve calculated with β_1 37.3 × 10^3 $l \cdot mol^{-1}$; $\beta_2 = 18.5 \times 10^6$ $l^2 \cdot mol^{-2}$; $\beta_3 = 44.6 \times 10^7$ $l^3 \cdot mol^{-3}$ and $K_{so} = 24.0 \times 10^{12}$ $mol^3 \cdot l^{-3}$.

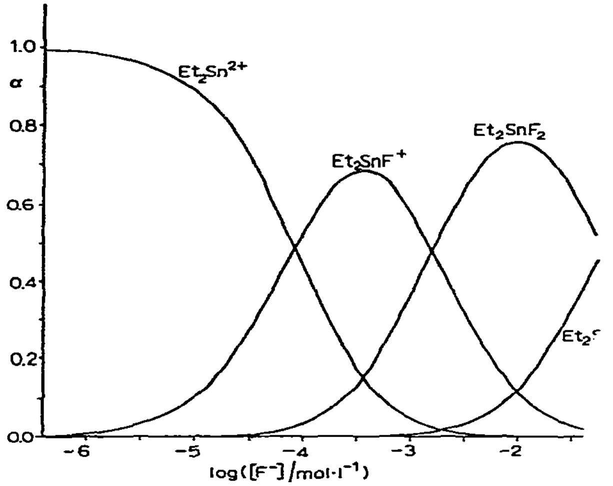

Fig. 3. Distribution curves for complexes of Et_2Sn^{2+} ions and fluoride as a function of the free ligand concentration.

the investigated fluoride concentration range two species could never be disregarded relative to the other two. Consequently a numerical method drawn from the Sillen procedure [18,19] was used. In this type of calculation, which generalizes the least squares method, an initial set of values for K_{so}, β_1, β_2 and

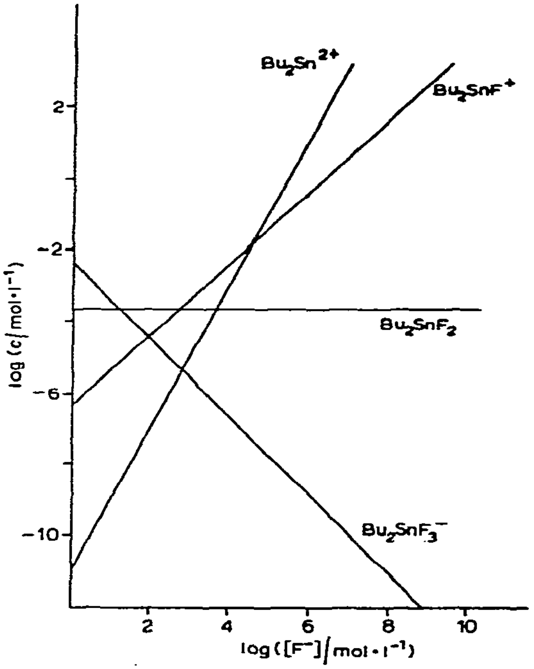

Fig. 4. Logarithmic concentration plot for solutions saturated with $(n\text{-}Bu)_2SnF_2$ as a function of—log F^-.

β_3 is employed for the calculation of equation (10). The same procedure is repeated for every "a" value, the same statistical weight being attributed to all the experimental measurements. The sum of the squares of the residuals between calculated and experimental values is minimized by changing in a suitable way the polynomial roots until a set of values for K_{so}, β_1, β_2 and β_3 was derived which furnished a minimum value for the function $U = \Sigma\Delta^2$*. In Table 2 the derived constants for the n-Bu_2Sn^{2+}—F^- system are reported. Figure 4 presents the logarithmic concentration diagram showing the concentration of every species as a function of F^- in saturated n-Bu_2SnF_2 solution.

Discussion

In Table 2 the overall and stepwise formation constants for the systems Me_2Sn^{2+}—F^-, Et_2Sn^{2+}—F^- and n-Bu_2Sn^{2+}—F^- are listed. It is evident that the chain length of the R group markedly affects the values of the constants. In order to explain this trend, three main factors must be taken into account viz, steric, inductive and solvent effects. The small size of the fluoride ligand suggests that the steric effect will be insignificant, and consequently only the last two factors will be considered. The inductive effect, acting to lower the positive charge on the tin atom, would give an order for the β values of Me > Et > n-Bu. On the other hand, since the formation of the fluoride complexes involves the replacement of bound water molecules by fluoride ions, the hydrophobic character of the alkyl groups, which increases with the number of C atoms, will give an order for the β values of Me < Et < n-Bu.

Our results indicate that for β_1 the solvent effect seems to predominate, while for K_2 the inductive effect predominates. The difference in the sequences for the β_1 and the K_2 values can be accounted for in terms of the lower hydration of the R_2SnF^+ ions towards the R_2Sn^{2+} acceptors. For the K_3 values, inductive and solvent effects seem to have comparable influences.

Comparison between the β-values for the R_2Sn^{2+}—F^- system with those for R_2Pb^{2+}—F^- systems [11] indicates that the two classes of complexes have quite different orders of stability. The much lower values of β for the alkyllead cations can be explained in terms of their lower charge density. This also accounts for the fact that for the β_1 values of the alkyltin cations only one factor (the solvent effect) is important, while for the alkyllead acceptors there is a balance between solvent and inductive effect.

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* The numerical calculations were made at the "Centro Elettronico di Calcolo Scientifico" of the University of Padua on an IBM 360/44 computer.

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