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Appearance of Phosphate-Selectivity by Hydrolytic Trimerization of Simple Dialkyltin(Ⅳ) Compounds Used as Carrier

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The complexation equilibria of dimethyltin(Ⅳ) and trimethyltin(Ⅳ) ions with several anions in aqueous solutions were potentiometrically studied as a model of the interaction of lipophilic dialkyltin(Ⅳ) and trialkyltin(Ⅳ) compounds, the carriers of ion-selective electrodes, with anions in the membrane phase. Phosphate and arsenate reacted with dimethyltin(Ⅳ) ion to yield partially hydrolyzed trimeric species, $[(SnMe_2)_3(OH)_2(HPO_4)_2]$ and $[(SnMe_2)_3(OH)_2(HAsO_4)_2]$. Such oligomerization, which ensures the interaction of phosphates or arsenate with two Sn centers, is also possible for lipophilic dialkyltin(Ⅳ) compounds. Moreover, shielding these anions from the solvent by lipophilic alkyl groups projected from Sn atoms may enhance the distribution of the carrier-anion associates into the membrane phase. These cooperate to give lipophilic dialkyltin(Ⅳ) compounds with high selectivities to these ions. The presence of such electroactive species in the membrane phase was discussed with reference to the previous studies.

The potentiometric sensing of phosphate, which is of biological and environmental importance, is difficult, due to its huge dehydration energy. Although supramolecular chemists have recently been trying to design and synthesize diverse phosphate-selective ionophores,[1,2] those to be used as the carrier of ion-selective electrodes (ISE) require an especially strong interaction; e.g., some bis-thiourea ionophores showed a high selectivity to $H_2PO_4^-$ in dimethyl sulfoxide[3] but were rather selective to chloride and hydrogensulfate as the carrier of ISE.[4,5] At this moment, multi-point recognition by two or more hydrogen bonds,[6,7] by two or more Lewis acid-base reactions,[8–11] or by their combination[12,13] has succeeded in exerting a phosphate-selectivity as the carrier of ISE.

In contrast to such elaborated ionophores, Russian chemists had found that even the simple dialkyltin(Ⅳ) compounds, such as dioctyltin(Ⅳ) bis(nitrate), show high selectivities to phosphate and arsenate as the carrier of liquid membrane (20% octanol in chloroform) electrodes.[14–16] The performance was later improved as poly(vinyl chloride) (PVC)-membrane electrodes using dibenzyltin(Ⅳ) chloride ($SnBz_2Cl_2$) derivatives by Arnold et al.[17,18] Although the response mechanism was studied by ^{119}Sn-NMR titration in organic solvents,[19] the reason for such a unique selectivity has not yet been fully elucidated. It is also noteworthy that trialkyltin(Ⅳ) compounds, another group of simple organotin(Ⅳ) compounds, do not respond to phosphate, but are used as a carrier selective to chloride or salicylate ($Hsal^-$).[20,21]

In this work, dimethyltin(Ⅳ) and trimethyltin(Ⅳ) were adopted as water-soluble analogues of organotin(Ⅳ) compounds (org-Sn^{m+}), and their complexation behaviors with several anions in aqueous solutions were investigated. The potentiometric selectivities are discussed in terms of formation of the electroactive species in an aqueous phase and their partition into a membrane phase.

Experimental

Reagents. In a nitrogen atmosphere, dimethyltin(Ⅳ) oxide and trimethyltin(Ⅳ) chloride (Strem Chemicals) were dissolved in nitric acid to give 0.1 mol dm^{-3} stock solutions. The acid contents were determined by Gran plots. Other reagents were of analytical grade and used as received.

Potentiometry. The potentiometric measurements were carried out on a concentration scale at 25 °C and at an ionic strength of 1.0 mol dm^{-3} KNO_3 under anaerobic conditions. A series of solutions containing an organotin(Ⅳ) compound ($C_{Sn} = 2$–3 mmol dm^{-3}), an anion in an acid or salt form (KH_2PO_4, Na_2HAsO_4, KF, H_2sal; $C_A = 3$–4 mmol dm^{-3}) and nitric acid were titrated with a standard KOH solution, and the change in $-\log[H^+]$ was monitored. The chemical equation and the stability constant for the formation of a general species, $[(\text{org-Sn})_pH_qA_r]^{(2p+q-nr)+}$, were defined as

$$p(\text{org-Sn})^{m+} + qH^+ + rA^{n-} \rightleftharpoons [(\text{org-Sn})_pH_qA_r]^{(mp+q-nr)+},$$

$$\beta_{pqr} = [(\text{org-Sn})_pH_qA_r]^{(mp+q-nr)+}/[(\text{org-Sn})^{m+}]^p[H^+]^q[A^{n-}]^r,$$

which were evaluated using a computer program BEST.[22]

Potentiometry with anion-selective electrodes for halides including fluoride was carried out as described previously.[23] A series of solutions containing an organotin(Ⅳ) ($C_{Sn} = 3$–30 mmol dm^{-3}) at $-\log[H^+] = 1.5$–2 were titrated with a standard halide solution (KA: KCl, KF, KBr, KI), and the change in $-\log[A^-]$ was monitored. The $-\log[H^+]$ value was kept constant by addition of nitric acid during the titration. The average number of halides bound to the organotin(Ⅳ) was calculated by

$$\bar{n}_o = \{C_X - [A^-](-[HF] - 2[HF_2^-])\}/C_{Sn}, \quad (1)$$

where the term in parentheses ( ) was considered only for fluoride. The stepwise stability constants in Eq. 2 were refined to give a minimum error square sum, $U = \Sigma(\bar{n}_o - \bar{n}_c)^2$, where

Table 1. Equilibrium Constants for the Reaction of Organotin(IV) Compounds with Anions

Anion	p	q	r	$\log \beta_{pqr}$ a)	Chemical equation	$\log K_{pqr}$ b)
					$SnMe_2{}^{2+}$	
OH^-	1	−1	0	−3.84	$SnMe_2{}^{2+} + OH^- \rightleftharpoons [(SnMe_2)(OH)]^+$	−3.84
	1	−2	0	−9.21	$SnMe_2{}^{2+} + 2\ OH^- \rightleftharpoons [(SnMe_2)(OH)_2]$	−9.21
	2	−2	0	−4.76	$2\ SnMe_2{}^{2+} + 2\ OH^- \rightleftharpoons [(SnMe_2)_2(OH)_2]^{2+}$	−4.76
	3	−2	0	−1.78	$3\ SnMe_2{}^{2+} + 2\ OH^- \rightleftharpoons [(SnMe_2)_3(OH)_2]^{4+}$	−1.78
	4	−6	0	−17.10	$4\ SnMe_2{}^{2+} + 6\ OH^- \rightleftharpoons [(SnMe_2)_4(OH)_6]^{2+}$	−17.10
$PO_4{}^{3-}$	0	1	1	12.36	$H^+ + PO_4{}^{3-} \rightleftharpoons HPO_4{}^{2-}$	12.36
	0	2	1	18.77	$H^+ + HPO_4{}^{2-} \rightleftharpoons H_2PO_4{}^-$	6.41
	0	3	1	20.50	$H^+ + H_2PO_4{}^- \rightleftharpoons H_3PO_4$	1.73
	1	0	1	12.20	$SnMe_2{}^{2+} + PO_4{}^{3-} \rightleftharpoons [(SnMe_2)PO_4]^-$	12.20
	1	1	1	17.73	$SnMe_2{}^{2+} + HPO_4{}^{2-} \rightleftharpoons [(SnMe_2)HPO_4]$	5.37
	2	−1	1	12.03	$[(SnMe_2)_2(OH)_2]^{2+} + HPO_4{}^{2-} \rightleftharpoons [(SnMe_2)_2(OH)_2HPO_4]$	4.43
	3	−1	1	16.88	$[(SnMe_2)_3(OH)_2]^{4+} + HPO_4{}^{2-} \rightleftharpoons [(SnMe_2)_3(OH)_2HPO_4]^{2+}$	6.30
	3	0	2	33.52	$[(SnMe_2)_3(OH)_2HPO_4]^{2+} + HPO_4{}^{2-} \rightleftharpoons [(SnMe_2)_3(OH)_2(HPO_4)_2]$	4.28
$AsO_4{}^{3-}$	0	1	1	11.52	$H^+ + AsO_4{}^{3-} \rightleftharpoons HAsO_4{}^{2-}$	11.52
	0	2	1	17.87	$H^+ + HAsO_4{}^{2-} \rightleftharpoons H_2AsO_4{}^-$	6.35
	0	3	1	19.93	$H^+ + H_2AsO_4{}^- \rightleftharpoons H_3AsO_4$	2.06
	1	0	1	11.10	$SnMe_2{}^{2+} + AsO_4{}^{3-} \rightleftharpoons [(SnMe_2)AsO_4]^-$	11.10
	1	1	1	16.79	$SnMe_2{}^{2+} + HAsO_4{}^{2-} \rightleftharpoons [(SnMe_2)HAsO_4]$	5.27
	2	−1	1	10.90	$[(SnMe_2)_2(OH)_2]^{2+} + HAsO_4{}^{2-} \rightleftharpoons [(SnMe_2)_2(OH)_2HAsO_4]$	4.14
	3	−1	1	14.58	$[(SnMe_2)_3(OH)_2]^{4+} + HAsO_4{}^{2-} \rightleftharpoons [(SnMe_2)_3(OH)_2HAsO_4]^{2+}$	4.84
F^-	0	1	1	3.06	$H^+ + F^- \rightleftharpoons HF$	3.06
	1	0	1	3.55	$SnMe_2{}^{2+} + F^- \rightleftharpoons [(SnMe_2)F]^+$	3.55
	1	0	2	6.46	$[(SnMe_2)F]^+ + F^- \rightleftharpoons [(SnMe_2)F_2]$	2.91
	2	−2	1	−1.42	$[(SnMe_2)_2(OH)_2]^{2+} + F^- \rightleftharpoons [(SnMe_2)_2(OH)_2F]^+$	3.34
	3	−2	1	1.82	$[(SnMe_2)_3(OH)_2]^{4+} + F^- \rightleftharpoons [(SnMe_2)_3(OH)_2F]^{3+}$	3.60
sal^{2-}	0	1	1	13.40	$H^+ + sal^{2-} \rightleftharpoons Hsal^-$	13.40
	0	2	1	16.21	$H^+ + Hsal^- \rightleftharpoons H_2sal$	2.81
	1	0	1	11.6	$SnMe_2{}^{2+} + sal^{2-} \rightleftharpoons [(SnMe_2)sal]$	11.6
	2	−2	1	5.5	$[(SnMe_2)_2(OH)_2]^{2+} + sal^{2-} \rightleftharpoons [(SnMe_2)_2(OH)_2sal]$	10.3
	3	−1	1	14.4	$[(SnMe_2)_3(OH)_2]^{4+} + Hsal^- \rightleftharpoons [(SnMe_2)_3(OH)_2Hsal]^{3+}$	2.8
					$SnMe_3{}^+$	
OH^-	1	−1	0	−6.25	$SnMe_3{}^+ + OH^- \rightleftharpoons [(SnMe_3)(OH)]$	−6.25
	1	−2	0	−14.84	$SnMe_3{}^+ + 2\ OH^- \rightleftharpoons [(SnMe_3)(OH)_2]^-$	−14.84
	2	−1	0	−10.41	$2\ SnMe_3{}^+ + OH^- \rightleftharpoons [(SnMe_3)_2(OH)]^+$	−10.41
$PO_4{}^{3-}$	1	1	1	15.28	$SnMe_3{}^+ + HPO_4{}^{2-} \rightleftharpoons [(SnMe_3)HPO_4]^-$	2.92
	1	2	1	19.69	$SnMe_3{}^+ + H_2PO_4{}^- \rightleftharpoons [(SnMe_3)H_2PO_4]$	0.92
$AsO_4{}^{3-}$	1	1	1	14.47	$SnMe_3{}^+ + HAsO_4{}^{2-} \rightleftharpoons [(SnMe_3)HAsO_4]^-$	2.95
	1	2	1	19.4	$SnMe_3{}^+ + H_2AsO_4{}^- \rightleftharpoons [(SnMe_3)H_2AsO_4]$	1.5

a) $\beta_{pqr} = [(\text{org-Sn})_p H_q A_r]^{(mp+q-nr)+}/[(\text{org-Sn})^{m+}]^p[H^+]^q[A^{n-}]^r$. b) K_{pqr}: equilibrium constant for the left reaction.

$$\bar{n}_c = (K_1[F^-] + 2K_1K_2[F^-]^2)/(1 + K_1[F^-] + K_1K_2[F^-]^2). \quad (2)$$

The molar fraction of the species was calculated using a computer program SPE.[22] In this calculation, the fraction of the oligomeric species was multiplied by the number of Sn(IV) ions involved in the relevant species.

Preparation and Characterization of Complexes. The complex expected to be electroactive was prepared by adding KOH to a mixture of dimethyltin(IV) and phosphate. The yields were 22% for $C_{Sn} = 30$ mmol dm^{-3}, $C_P = 10$ mmol dm^{-3} and 82% for $C_{Sn} = 30$ mmol dm^{-3} and $C_P = 20$ mmol dm^{-3}. The Sn and P contents in the precipitates were determined by inductively coupled plasma atomic emission spectrometry (SPS 7000A, Seiko), after dissolution in nitric acid. The crystal structure was determined by a single crystal X-ray diffraction method (Enraf Nonius CAD4). A secondary ion mass spectrometry was carried out

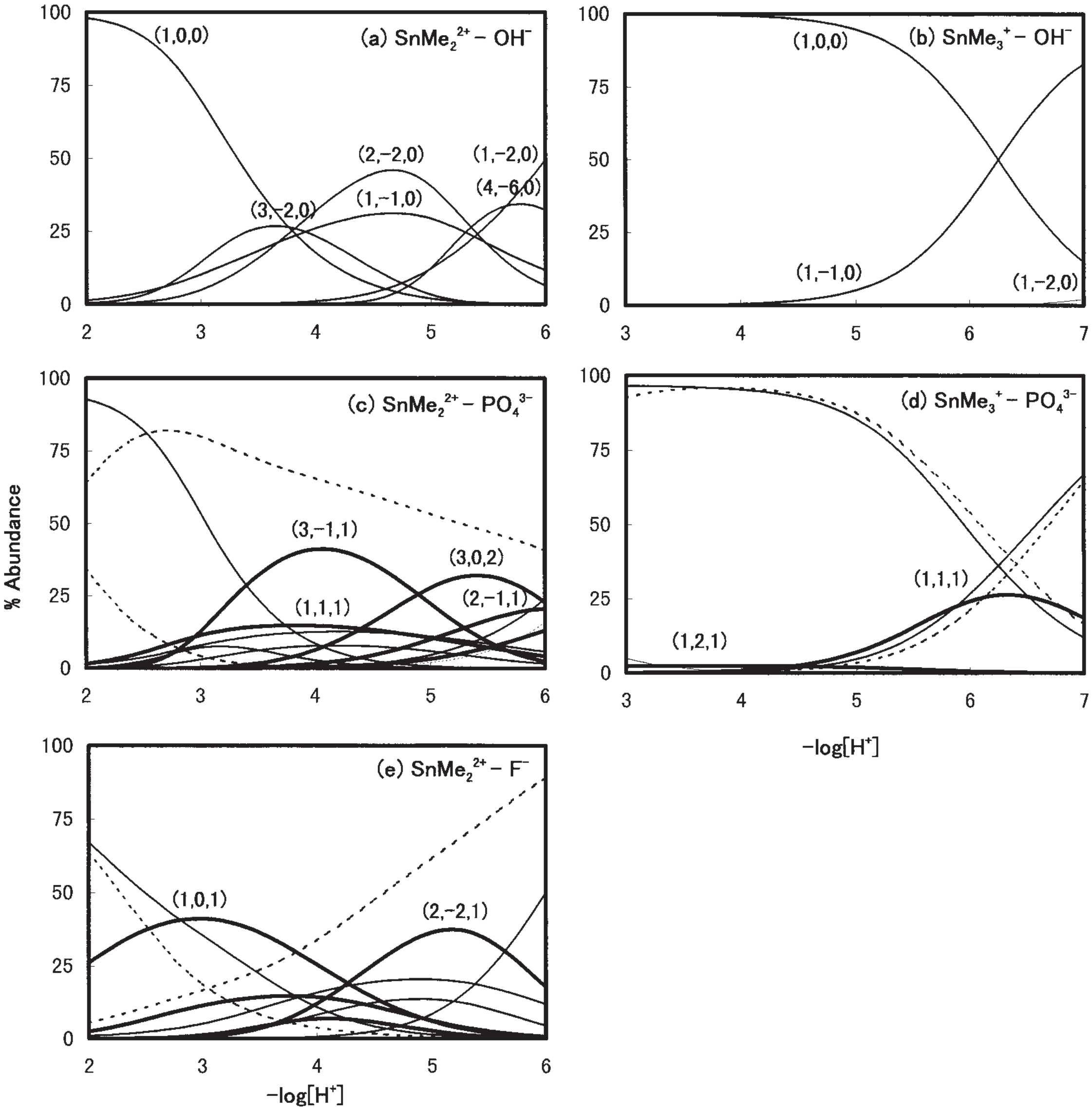

Fig. 1. Distribution of species as a function of $-\log[H^+]$ in the reaction of organotin(IV) with several anions at 25 °C and at 1.0 mol dm^{-3} KNO_3. Thick curves: organotin(IV) species complexed with anions; thin curves: species consisting of organotin(IV) and OH^-; broken curves: species consisting of anions and H^+.

using *m*-nitrobenzyl alcohol as a matrix (M-200S, Hitachi).

Semi-Empirical Calculations. The optimization of the conformation and the total energy calculation for two possible carrier-phosphate associates respectively for dimethyl and dibenzyl derivatives were carried out by PM3 in MOPAC,[24,25] with a Dell XPS H266 computer.

Results

Hydrolysis of Dimethyltin(IV) and Trimethyltin(IV) Ions. The hydrolysis equilibria of dimethyltin(IV) and trimethyltin(IV) in a $-\log[H^+]$ range of 2 to 6 were investigated for subsequent equilibrium analyses. The equilibrium constants summarized in Table 1 agreed well with the literature values obtained at 25 °C and at 0.1 mol dm^{-3} $NaNO_3$, taking into account the difference in salt concentration.[26,27] An appreciably higher value for $[(SnMe_2)_3(OH)_2]^{4+}$ may be ascribed to stabilization of its high positive charge by a concentrated supporting electrolyte. The distribution diagrams for the hydrolysis of dimethyltin(IV) and trimethyltin(IV) at $C_{Sn} = 3$ mmol dm^{-3} are shown in Figs. 1(a) and 1(b), respectively.

Dimethyltin(IV) hydrolyzed at $-\log[H^+] > 2$, and formed oligomeric species, such as $(3,-2,0)$, $(2,-2,0)$ and $(4,-6,0)$. The fractions of monomeric species, such as $(1,-1,0)$ and $(1,-2,0)$, were not so large under these conditions, although they were predominant at a lower total concentration (not shown). Trimethyltin(IV) hydrolyzed at higher pH than dimethyltin(IV) and formed only a monomeric species of $(1,-1,0)$ at $-\log[H^+] > 4$, irrespective of the total concentration.

Complexation of Organotin(IV) Ions with Phosphate and Arsenate. Dimethyltin(IV) showed high affinities to both the anions at $-\log[H^+] > 2.5$. The equilibrium constants obtained are summarized in Table 1. Although the corresponding species were found in these two reaction systems, the stability constants with phosphate were slightly larger than those with arsenate for all the species. The distribution diagrams at $C_{\mathrm{Sn}} = C_{\mathrm{P}} = 3$ mmol dm^{-3} are shown in Fig. 1(c). A series of oligomeric species, $(3, -1, 1)$, $(3, 0, 2)$ and $(2, -1, 1)$, were successively formed with an increase in $-\log[\mathrm{H}^+]$, and their cumulative abundance was around 50% over a wide $-\log[\mathrm{H}^+]$ range of 4–6. The monomeric species of $(1, 1, 1)$ was formed only as a minor species.

Under the conditions of a total dimethyltin(Ⅳ) concentration > 5 mmol dm^{-3}, there formed a precipitate at $-\log[\mathrm{H}^+]$ of around 4. The Sn:P ratio determined by ICP–AES was exactly 3:2. The X-ray crystal structure of a single crystal slowly grown in an aqueous solution was coincident with that reported earlier, i.e. $[(\mathrm{SnMe_2})_3(\mathrm{PO_4})_2]\cdot 8\mathrm{H_2O}$.[28] Two tetrahedral Sn and one octahedral Sn atoms were linearly connected by two phosphates, and the resulting units were linked to give an infinite ribbon-like structure. The SIMS spectrum of this crystal suspended in methanol showed a peak for $(\mathrm{M} + \mathrm{H})^+$ at m/z 673.4, where M denotes $[(\mathrm{SnMe_2})_3(\mathrm{OH})_2(\mathrm{HPO_4})_2]$.

Trimethyltin(Ⅳ), in contrast, reacted with these anions only at $-\log[\mathrm{H}^+] > 4$. The equilibrium constants are summarized in Table 1, and the distribution diagrams at $C_{\mathrm{Sn}} = C_{\mathrm{P}} = 3$ mmol dm^{-3} in Fig. 1(d). Only the monomeric species of $(1, 2, 1)$ and $(1, 1, 1)$ were formed, and the maximum abundance was 25% at $-\log[\mathrm{H}^+]$ of around 6.2.

Complexation of Dialkyltin(Ⅳ) with Halides. The complexation equilibria of dimethyltin(Ⅳ) with halides were studied potentiometrically with halide-selective electrodes at $-\log[\mathrm{H}^+] < 2$, where the hydrolysis of dimethyltin(Ⅳ) was negligible. The formation functions are shown in Fig. 2. None of the chloride, bromide or iodide showed any interactions with dimethyltin(Ⅳ) up to 10 mmol dm^{-3}, while fluoride showed appreciable reactivities. Since the formation curves were independent of the total dimethyltin(Ⅳ) concentration between 3–30 mmol dm^{-3} and of $-\log[\mathrm{H}^+]$ between 1.5 and 2, only monomeric species without any hydrolysis were formed at $-\log[\mathrm{H}^+] < 2$. The complexation with fluoride was also studied by pH titration. The equilibrium constants are summarized in Table 1 and the distribution curves in Fig. 1(e). Only monomeric species were found at $-\log[\mathrm{H}^+] < 2$, in agreement with the results by potentiometry using a fluoride ISE. The stability constants for the monomeric species also agreed well with the above results. At $-\log[\mathrm{H}^+] > 2$, oligomeric species, such as $[(\mathrm{SnMe_2})_2(\mathrm{OH})_2\mathrm{F}]^+$ and $[(\mathrm{SnMe_2})_3(\mathrm{OH})_2\mathrm{F}]^{3+}$, were also found. In contrast, trimethyltin(Ⅳ) is known to have much less reactivities with halides.[29]

Discussion

Formation of Trimeric Dialkyltin(Ⅳ) Species. The hydrolysis of dimethyltin(Ⅳ) mainly yields monomeric and dimeric species, $[(\mathrm{SnMe_2})(\mathrm{OH})]^+$ and $[(\mathrm{SnMe_2})_2(\mathrm{OH})_2]^{2+}$, in acidic media. In the presence of phosphate or arsenate, however, trimeric species become major. Namely, phosphate and arsenate induced the trimerization of dimethyltin(Ⅳ).

Simon and his group measured the change in ^{119}Sn-NMR shift on the reaction of a lipophilic dialkyltin(Ⅳ) compound, dioctyltin(Ⅳ) dichloride, with Kryptofix222/$\mathrm{K_2HPO_4}$ in $\mathrm{CDCl_3}$ and suggested the presence of P:Sn = 1:2 species as well as 1:1 and/or oligomeric species.[19] But, when the ^{119}Sn-NMR chemical shift from the literature was plotted against the molar ratio of P/Sn, a clear inflection point was observed rather at P/Sn = 1/3. This also indicates the trimerization induced by phosphate; a longer alkyl chain does not cause any steric hindrance to the trimerization.

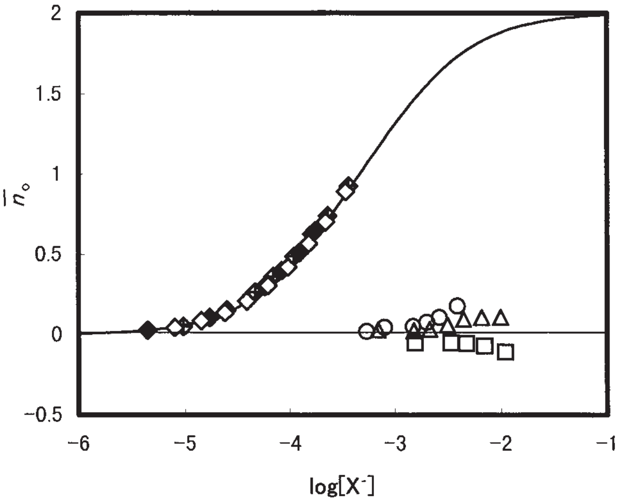

Fig. 2. Formation curves in the reaction of $\mathrm{SnMe_2}^{2+}$ with halides at 25 °C and at 1.0 mol dm^{-3} $\mathrm{KNO_3}$. Halides: F$^-$ (◇, ◆, ⟐); Cl$^-$ (□); Br$^-$ (○); I$^-$ (△). C_{Sn}/mmol dm^{-3}: 10 (◇, ◆, □, ○, △); 3 (⟐). $-\log[\mathrm{H}^+]$: 2.0 (◇, ⟐, □, ○, △); 1.5 (◆).

Arnold and his group recommended a carrier concentration much higher than usual for preparation of the phosphate-selective PVC-membrane electrode based on dibenzyltin(Ⅳ) dichloride; 18% compared with 2–3%.[17,18] This is explained by a general trend that the formation of such oligomeric species becomes favorable with an increase in total concentration of the relevant species. They also noticed that the initial exposure of the membrane to a concentrated phosphate solution or of a prolonged conditioning is essential for the proper functions of the phosphate-selective electrode. These are considered to be necessary for the formation of the trimeric species, $[(\mathrm{SnBz_2})_3(\mathrm{OH})_2(\mathrm{HPO_4})_2]$, as an electroactive species in the membrane phase.

The formation of such species, which is expected to be entropically unfavorable, may be accomplished by the following two factors. First, the residual reactivity of $[(\mathrm{SnR_2})_3(\mathrm{OH})_2]^{4+}$ is generally higher than those of $[(\mathrm{SnR_2})(\mathrm{OH})]^+$ and $[(\mathrm{SnR_2})_2(\mathrm{OH})_2]^{2+}$, because of its lower hydrolysis degree, OH/Sn = 2/3 compared with 1/1 and 2/2. Second, such self-assembly enables one phosphate to interact with two Sn atoms.

Three $\mathrm{SnMe_2}^{2+}$ and two OH$^-$ are considered to be arrayed tandem in $[(\mathrm{SnMe_2})_3(\mathrm{OH})_2]^{4+}$ core-unit,[26] and thus, there are two possible structures for $[(\mathrm{SnMe_2})_3(\mathrm{OH})_2(\mathrm{HPO_4})_2]$, which are shown in Fig. 3. In the structure (a), two $\mathrm{HPO_4}^{2-}$ ions bridge between the central Sn and one of two terminal Sn atoms to form two six-membered rings. In the structure (b), on the other hand, two $\mathrm{HPO_4}^{2-}$ ions bridge between two terminal Sn atoms to form two eight-membered rings. The PM3 calculation for structures (a) and (b) indicated the possible presence of these species; the difference in total energy was not

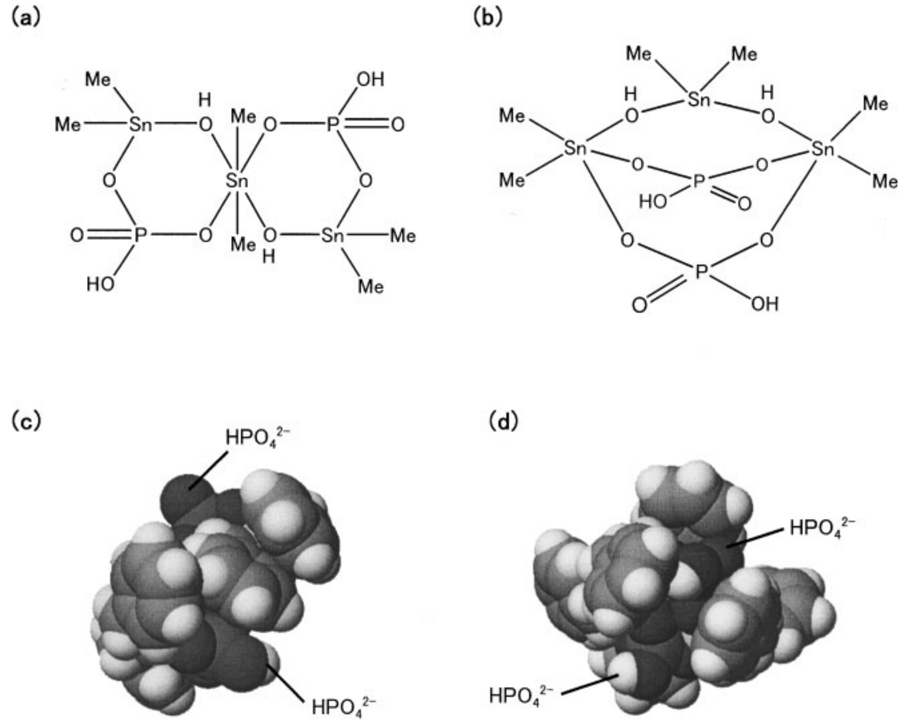

Fig. 3. Possible structures for $[(SnMe_2)_3(OH)_2(HPO_4)_2]$ in the aqueous phase (a, b) and PM3-optimized structures for $[(SnBz_2)_3(OH)_2(HPO_4)_2]$ as an electroactive species in the membrane phase (c, d).

large enough to identify the structure.

Introduction of two or more Sn(Ⅳ) ions into the carrier has been examined as the multidentate carriers.[8–11] Chaniotakis and his group found that a series of organotin(Ⅳ) compounds containing two Sn(Ⅳ) centers, $XY_2Sn–(CH_2)_n–SnXY_2$, showed phosphate-selectivity at $n = 1$ and, in some cases, at $n = 3$.[9,11] This corresponds to the replacement of –OH– by $–CH_2–$ group in the structure (a) and that of $–OH–SnMe_2–OH–$ by $–(CH_2)_3–$ group in the structure (b), respectively.

Partition of Carrier-Anion Associate. Appreciable complexation was found in the $SnMe_2^{2+}–PO_4^{3-}$, AsO_4^{3-}, F^- and $Me_3Sn^+–PO_4^{3-}$ systems so far studied. Since the compositions of the carrier-anion associates are different, their stabilities cannot be directly compared using the stability constants. The maximum abundances of the neutral species, 35% for $[(SnMe_2)_3(OH)_2(HPO_4)_2]$, 40% for $[(SnMe_2)F]^+$ and $[(SnMe_2)F_2]$, and 25% for $[SnMe_3(HPO_4)]^-$, however, suggest comparable stabilities of these species in aqueous solutions. In spite of these facts, lipophilic dialkyltin(Ⅳ) compounds as a carrier of ISEs showed selectivities to phosphate and arsenate, and trialkyltin(Ⅳ) compounds did not respond to phosphate.

The PM3 calculation for two expected structures of $[(SnBz_2)_3(OH)_2(HPO_4)_2]$ shown in Figs. 3(c) and (d), respectively corresponding to (a) and (b) for $[(SnMe_2)_3(OH)_2(HPO_4)_2]$, again indicated their possible presence. At the same time, appreciable shielding of HPO_4^{2-} from the solvent by benzyl groups projected from the Sn atoms was observed as an energy-minimum conformation, especially for (d). Thus, the carrier-phosphate associates are neutral, hydrophobic, and easily partitioned into a low dielectric medium to show phosphate-selectivity. On the other hand, electric charges remain in $[(SnR_2)F]^+$ and $[SnR_3(HPO_4)]^-$, and the anions bound to Sn atoms are exposed to water on the counter side and suffer from hydration in $[(SnR_2)F_2]$. These findings will be helpful for the further development of phosphate-selective carriers.

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References

1 P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, **40**, 486 (2001).

2 A. Bianchi, K. Bowman-James, and E. Garcia-Espana, “Supramolecular Chemistry of Anions,” Wiley-VCH, New York (1997).

3 P. Buhlmann, S. Nishizawa, K. Xiao, and Y. Umezawa, *Tetrahedron Lett.*, **53**, 1647 (1997).

4 K. P. Xiao, P. Buhlmann, S. Nishizawa, S. Amemiya, and Y. Umezawa, *Anal. Chem.*, **69**, 1038 (1997).

5 S. Nishizawa, P. Buhlmann, K. Xiao, and Y. Umezawa, *Anal. Chim. Acta*, **358**, 35 (1998).

6 C. M. Carey and W. B. Riggan, *Anal. Chem.*, **66**, 3587 (1994).

7 M. Fibbioli, M. Berger, F. P. Schmidtchen, and E. Pretsch, *Anal. Chem.*, **72**, 156 (2000).

8 N. A. Chaniotakis, K. Jurkschat, and A. Ruhlemann, *Anal. Chim. Acta*, **282**, 345 (1993).

9 J. K. Tsagatakis, N. A. Chaniotakis, and K. Jurkschat, *Helv. Chim. Acta*, **77**, 2191 (1994).

10 D. Liu, W. Chen, R. Yang, G. Shen, and R. Yu, *Anal. Chim. Acta*, **338**, 209 (1997).

11 J. K. Tsagatakis, N. A. Chaniotakis, R. Altmann, K.

Jurkschat, R. Willem, J. C. Martins, Y. Qin, and E. Bakker, *Helv. Chim. Acta*, **84**, 1952 (2001).

12 M. M. G. Antonisse, B. H. M. Snellink-Ruel, I. Yigit, J. F. J. Engersen, and D. N. Reinhoudt, *J. Org. Chem.*, **62**, 9034 (1997).

13 W. Wroblewski, K. Wojciechowski, A. Dybko, Z. Brzozka, R. J. Egberink, B. H. M. Snellink-Ruel, and D. N. Reinhoudt, *Anal. Chim. Acta*, **432**, 79 (2001).

14 V. A. Zarinskii, L. K. Shpigun, V. M. Shkinev, B. Ya. Spivakov, V. M. Trepalina, and Yu. A. Zolotov, *Russ. J. Anal. Chem.*, **35**, 1376 (1980).

15 V. A. Zarinskii, L. K. Shpigun, V. M. Shkinev, B. Ya. Spivakov, and Yu. A. Zolotov, *Russ. J. Anal. Chem.*, **35**, 1381 (1980).

16 V. M. Shkinev, B. Ya. Spivakov, G. A. Vorobeva, and Yu. A. Zolotov, *Anal. Chim. Acta*, **167**, 145 (1985).

17 S. A. Glazier and M. A. Arnold, *Anal. Chem.*, **60**, 2540 (1988).

18 S. A. Glazier and M. A. Arnold, *Anal. Chem.*, **63**, 754 (1991).

19 K. Fluri, J. Koudelka, and W. Simon, *Helv. Chim. Acta*, **75**, 1012 (1992).

20 U. Wuthier, H. V. Pham, R. Zund, D. Welti, R. J. J. Funck, A. Bezegh, D. Ammann, E. Pretsch, and W. Simon, *Anal. Chem.*, **56**, 535 (1984).

21 D. Liu, W.-C. Chen, G.-L. Shen, and R.-Q. Yu, *Analyst*, **121**, 1495 (1996).

22 A. E. Martell and R. J. Motekaitis, ''Determination and Use of Stability Constants,'' VCH Publishers, New York (1992).

23 A. Yuchi, J. Sakurai, A. Tatebe, H. Hattori, and H. Wada, *Anal. Chim. Acta*, **387**, 189 (1999).

24 J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).

25 J. J. P. Stewart, *MOPAC, QCPR Bull.*, **3**, 43 (1983).

26 T. Natsume, S. Aizawa, K. Hatano, and S. Funahashi, *J. Chem. Soc., Dalton Trans.*, **1994**, 2749.

27 A. Takahashi, T. Natsume, N. Koshino, S. Funahashi, Y. Inada, and H. D. Takagi, *Can. J. Chem.*, **75**, 1084 (1997).

28 J. P. Ashmore, T. Chivers, K. A. Kerr, and J. H. G. Van Roode, *Inorg. Chem.*, **16**, 191 (1977).

29 A. Cassol, L. Magon, and R. Barbieri, *Inorg. Nucl. Chem. Letters*, **3**, 25 (1967).