173. Anion Selectivity of Tetravalent Tin Compounds in Membranes Studied by ^{119}Sn-, ^{13}C- and ^{1}H-NMR

by **Hung-Viet Pham, Ernö Pretsch, Karl Fluri, Andras Bezegh,** and **Wilhelm Simon***

Department of Organic Chemistry, Swiss Federal Institute of Technology, CH-8092 Zürich

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The fundamental molecular aspects of trialkyltin compounds of the type R_3SnY have been investigated in view of their applicability as ion-selective components in solvent polymeric membranes. The interaction between these compounds and anions has been studied using ^{119}Sn- and ^{13}C-NMR. Neutral tetracoordinated trialkyltin compounds form a negatively charged pentacoordinated complex upon interaction with Cl-ions in homogeneous organic phases as well as in membranes in contact with aqueous solutions. Although in a homogeneous phase, the electronegative substituent Y determines the complex-formation constant, it has no influence on the potentiometric anion selectivity in liquid membranes containing trialkyltin carriers R_3SnY with different Y. The observed selectivity pattern is not given by the magnitude of the stability constants in a homogeneous phase but is dictated by the prevailing association-dissociation process leading to tetracoordinated compounds which change in constitution due to varying sample composition. The results obtained from equilibrium studies of tetravalent monotin compounds with anions in both homogeneous phase and in two-phase systems confirm the earlier hypothesis that trialkyltin compounds incorporated in solvent polymeric membranes act as electrically neutral carriers for anions.

Introduction. – Some trialkyl compounds of tetravalent tin of the type R_3SnY, $R^1R^2R^3SnY$, or $R^1_2R^2SnY$ (Y: electronegative substituent; R: substituent forming a Sn–C bond) induce anion selectivity in membranes [1–8]. Their mode of action may either be due to a dissociation into the anion Y and the corresponding trialkyltin cation [7] [9] or to an association with a further anion. The two modes of action correspond to electrically charged and electrically neutral carrier mechanisms, respectively [4] [6] [8] [9]. All these trialkyltin compounds, when studied in membranes, induce a selectivity sequence deviating from that observed with classical anion-exchanger membranes [5] [6] [8] (*Hofmeister* lyotropic anion-selectivity sequence: $ClO_4^- > SCN^- > I^- > NO_3^- \sim Br^- > Cl^- > F^-$ [10] [11]). This behavior supports the assumption of a selective interaction of anions with the trialkyltin compounds in the membrane phase and is, therefore, consistent with a neutral-carrier anion-transport mechanism [4].

NMR spectroscopy is well suited for the study of the mechanism of action of ion carriers. Interactions of ionophores with ions in both homogeneous solutions as well as in two-phase experiments including solvent polymeric membranes as an organic phase have been carried out [12]. For the study of the mechanism of action of tin-organic compounds, ^{119}Sn-NMR is especially attractive because of the sensitivity of the ^{119}Sn-chemical shifts to the surroundings of the Sn-atom. A significant high-field shift is caused by increasing the coordination number from 4 (tetrahedral) to 5 (trigonal bipyramidal) [13–15]. Furthermore, ^{119}Sn,^{13}C-coupling constants, which are easily observed in ^{13}C-NMR spectra, are a good indicator of the hybridization of the Sn-atom [14] [16] [17]. Finally, ^{13}C-chemical shifts of C-atoms near to the Sn-center also change substantially, if

the coordination sphere of the Sn-atom changes [4] [5] [14] [16]. In the present contribution, we report on equilibrium studies of several tetravalent monotin compounds with different anions in both homogeneous phases which include membrane phases, as well as in two-phase systems mimicking membranes.

Results and Discussion. – *Equilibrium Studies in $CDCl_3$.* A fast exchange between trialkyltin derivatives and their adducts with anions has been observed, when corresponding salts were successively added to the organotin compounds in organic solvents such as $CHCl_3$ [4] [5] [19–21], MeCN [18], or CH_2Cl_2 [20] [21].

The parameters most sensitive to an interaction of trialkyltin compounds with salts are the ^{119}Sn-chemical shift (change of 180 ppm to higher field), the ^{119}Sn,^{13}C-coupling constant (change from 330 to 475 Hz), and the ^{13}C-chemical shift of the C-atom bonded directly to the Sn-center (change from 17.5 to 25 ppm) as it is shown in *Fig. 1* for trioctyltin chloride (Oc_3SnCl). A simultaneous least squares fitting to 3 × 15 measured points of these three parameters leads to an equilibrium constant of 18 ± 1 l·mol^{-1} (average ± s.d.) for the interaction of Oc_3SnCl with Bu_4NCl. This is in accordance with the value found ($K = 151 \pm 30$ kg·mol^{-1}) by vapour-pressure osmometry (VPO) in CH_2Cl_2 as solvent. This K value has been estimated from fitting a non-linear one-parameter model to 11 points, each representing 3 parallel determinations [4]. If the cation is changed from Bu_4N^+ to the K^+ complex of the [2.2.2]cryptand (*Kryptofix® 222*), the equilibrium constants increase by a factor of 2.3 (41 ± 2 l·mol^{-1} in $CDCl_3$ from NMR studies and 345 ± 28 kg·mol^{-1} [4] [22] in CH_2Cl_2 by VPO). This correlation between the values of the stability constant as obtained from the NMR method and those obtained from the VPO method might be better if the differences in the density as well as in the polarity of the solvents ($CDCl_3$ and CH_2Cl_2) are considered. No interaction between these salts with tetraalkyltin compounds has been observed under the same experimental conditions [6] [22].

Curves analogous to that shown in *Fig. 1* were obtained in the titration of Bu_3SnCl [5], Bu_3SnCN, and Bu_3SnOAc with Bu_4NCl [22]. No significant change in the stability constant can be observed, if the alkyl substituents bonded to the Sn-atom are changed from octyl to butyl (20 ± 1 l·mol^{-1} in $CDCl_3$), or if the titration agent is changed from Bu_4NCl to tetrahexylammonium chloride (171·mol^{-1} in $CDCl_3$ [21]). No exact values can be evaluated from these curves for Bu_3SnCN and Bu_3SnOAc because of the exchange of CN^- and OAc^- with Cl^- of Bu_4NCl (see below). The estimated stability constants are, however, decreasing in the order $Bu_3SnCl > Bu_3SnCN$ (*ca.* 3.9 l·mol^{-1}) > Bu_3SnOAc (*ca.* 1.0 l·mol^{-1}).

Both the strong shielding of the Sn-center and the marked increase of the ^{119}Sn, ^{13}C-coupling constant clearly indicate that a pentacoordinated adduct is formed under these experimental conditions [14] [16]. This is in line with a neutral-carrier transport mechanism (uncharged free ligands, charged products [4]), if the same mechanism holds for a membrane phase in contact with an aqueous solution and a homogeneous phase.

Ligand-Exchange Studies. The potentiometric selectivity factors of membrane electrodes based on Bu_3SnCl, Bu_3SnOAc, and Bu_3SnCN are almost identical (see *Columns 1–3* in *Fig. 2*). This fact apparently contradicts the trend in the stability constants when changing the electronegative substituent Y. An explanation can be offered by assuming that all Bu_3Sn compounds incorporated into the membrane phase lead to the same species

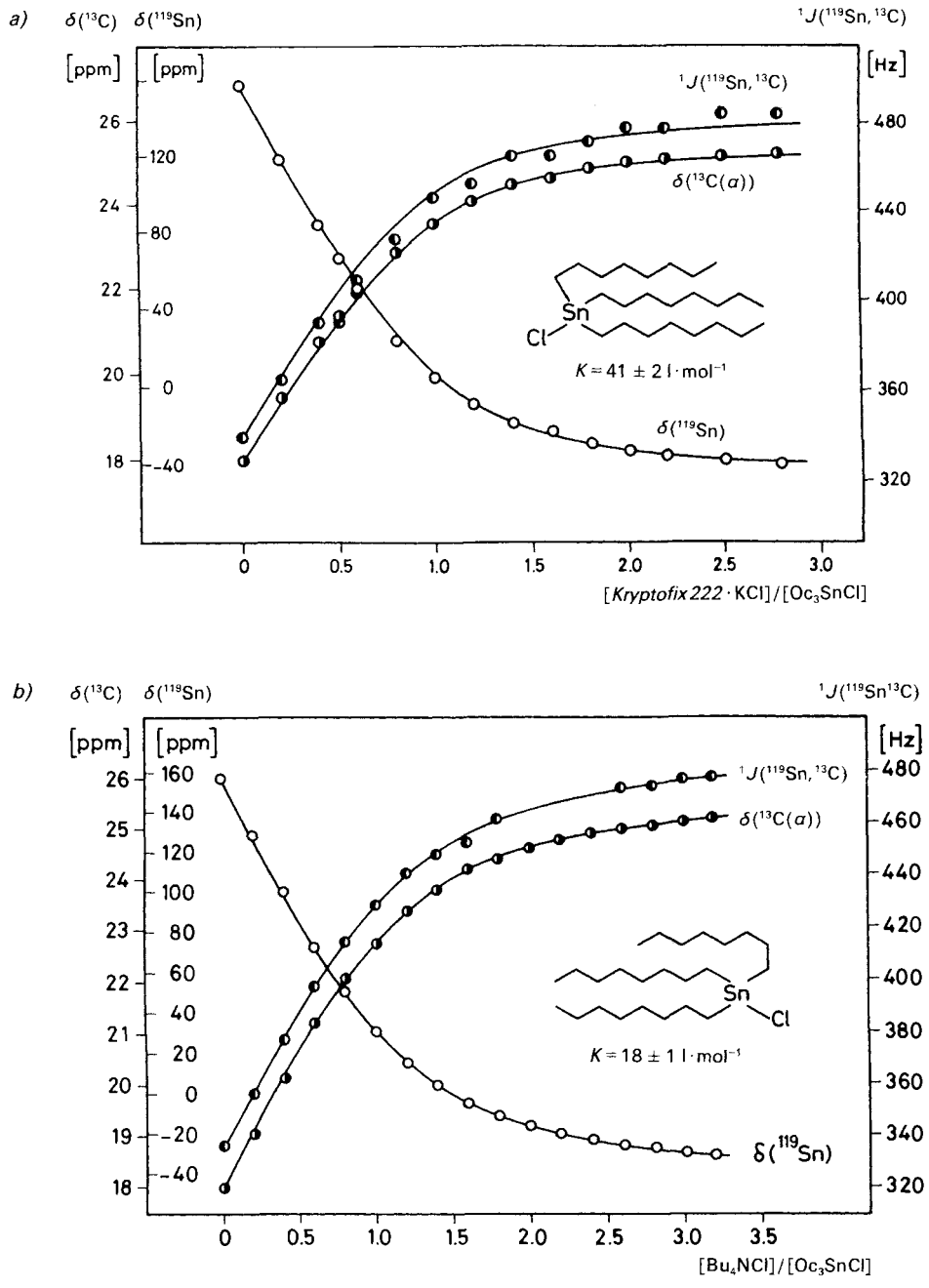


Fig. 1. *Titration curves of Oc_3SnCl in $CDCl_3$ with* a) Kryptofix® 222·KCl *and* b) *Bu_4NCl, showing the changes of the ^{119}Sn-NMR signal and the ^{13}C-NMR signal of the* C(α) *atom relative to the Sn-center as well as the coupling constant $^1J(^{119}Sn,^{13}C)$ as a function of the salt/ligand ratios*

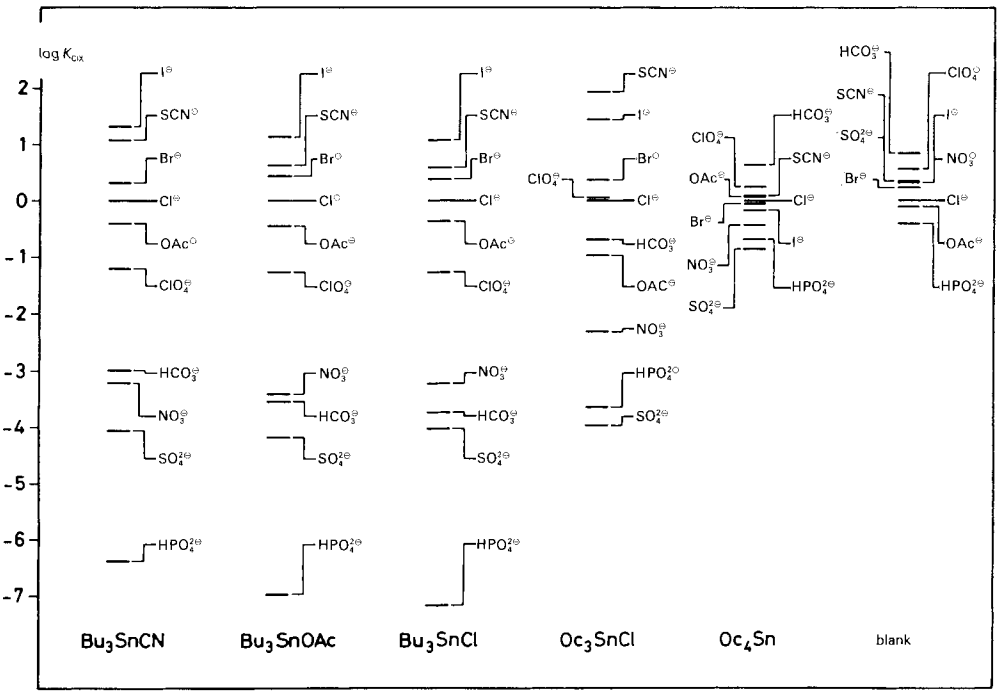


Fig. 2. *Selectivity sequences of membranes containing trialkyltin carriers of the type R_3SnY with different electronegative substituents* Y (*Columns 1–4*). The selectivity patterns of Oc_4Sn as reference compound (*Column 5*) and a blank membrane are also given (*Column 6*). The selectivity factors were determined with the separate-solution method (see also [5] [6] [8]).

via hydrolysis and/or a sufficiently fast exchange of the electronegative substituents. This hypothesis was tested in the following series of experiments.

When a $CDCl_3$ solution of Oc_3SnCl is shaken with H_2O, two small signals are observed in the ^{119}Sn-NMR at 107 and 96 ppm in addition to the signal of Oc_2SnCl (157 ppm). These signals are more intense, if the solution is shaken with 0.1M NaOH during 24 h (see *Fig. 3a*), but they disappear within *ca.* 5 min, if the solution is contacted with 0.1M HCl. Analogous reactions take place in the membrane phase, as corroborated by an investigation of the intensity of the Sn–Cl stretching vibration absorption at 326 cm^{-1} [22] in the IR spectra of membranes. The signal at 96 ppm can unequivocally be assigned to bis(trioctyltin) oxide ($Oc_3Sn–O–SnO_3$) on the basis of the chemical shift and of the satellites caused by the Sn, Sn two-bond coupling (^2J(Sn, Sn) = 369 Hz) [23]. The signal at 107 ppm is most probably due to Oc_3SnOH. Trialkyltin hydroxides with alkyl groups larger than propyl usually cannot be isolated, because they spontaneously eliminate H_2O and lead to the corresponding bis(trialkyltin) oxides [24]. The results of this study indicate, however, that, under certain conditions, trialkyltin hydroxides with rather large alkyl groups are stable.

A further support of this assignment is given in *Fig. 3b–e* where the influence of a successive addition of Bu_4NCl to the $CDCl_3$ solution containing a mixture of

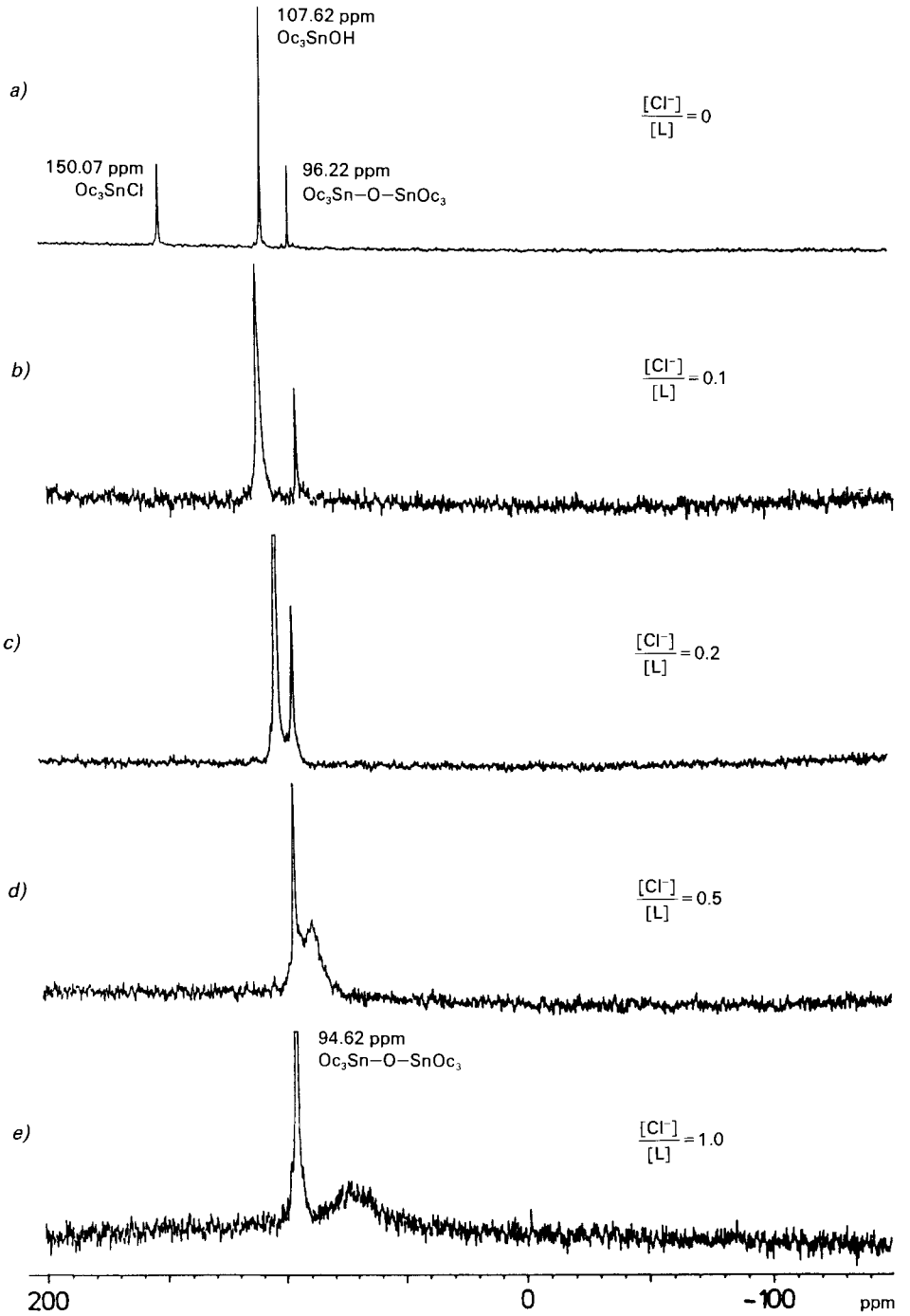


Fig. 3. *Changes of the chemical shifts δ(^{119}Sn) of Oc_3SnCl, Oc_3SnOH, and $Oc_3Sn-O-SnOc_3$ induced by addition of Bu_4NCl in a $CDCl_3$ phase.* [L]: concentration of the initially used ligand, Oc_3SnCl.

$Oc_3Sn–O–SnOc_3$, Oc_3SnCl, and Oc_3SnOH is shown. Whereas the signal of $Oc_3Sn–O–SnOc_3$ remains unchanged, a fast exchange between Oc_3SnCl, Oc_3SnOH, and the corresponding adducts can be observed. The corresponding signal shows a high-field shift with increasing amounts of added Bu_4NCl reflecting the increasing concentration of the pentavalent adducts.

In an analogous experiment, Bu_4NCl is successively added to a 1:1 mixture of Bu_3SnCl and Bu_3SnOAc. Whereas separate (but exchange-broadened) signals can be observed for the two compounds in absence of a further salt (*Fig. 4c*), the addition of a small amount of Bu_4NCl catalyzes the exchange (*Fig. 4d–f*). These observations account

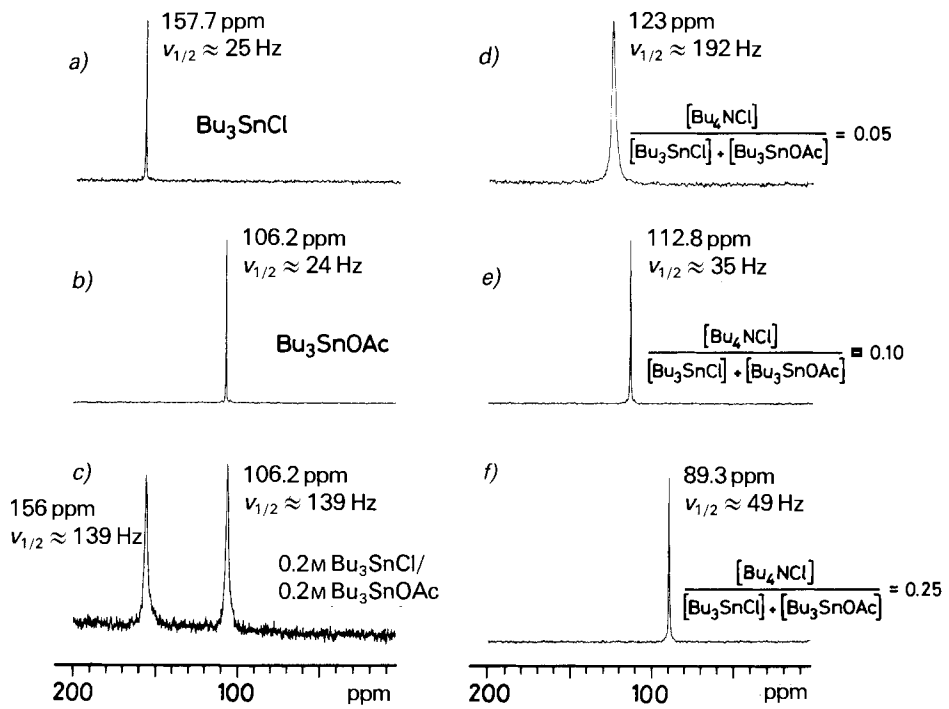
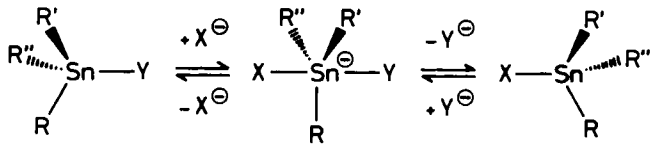


Fig. 4. *Ligand exchange between Bu_3SnCl and Bu_3SnOAc in homogeneous solution catalyzed by addition of chloride.* Solvent: $CDCl_3$.

for the absence of any marked influence of the electronegative substituent on the observed ion selectivities of trialkyltin derivatives in membranes (*Fig. 2*). Furthermore, this experiment indicates that an exchange of the electronegative substituents (Y) on the Sn-center must occur *via* the formation of a penta-coordinated Sn-atom, because the averaged signal of both species, Bu_3SnCl and Bu_3SnOAc, steadily moves upfield (from 123 ppm to 89 ppm), when the ratio of Bu_4NCl to the Sn-species increases (from 0.05 to 0.25; see *Fig. 4d–f*). This coupling of ligand exchange with the formation of a penta-coordinated Sn-atom is represented in the *Scheme*. This association-dissociation mechanism is also consistent with the optical instability of some optically active triorganyltin compounds in the presence of anions or other nucleophilic reagents [25].

Scheme. *Postulated Mechanism of the Interaction of Anion X^- with Trialkyltin Carriers of the Type RR'R''SnY*



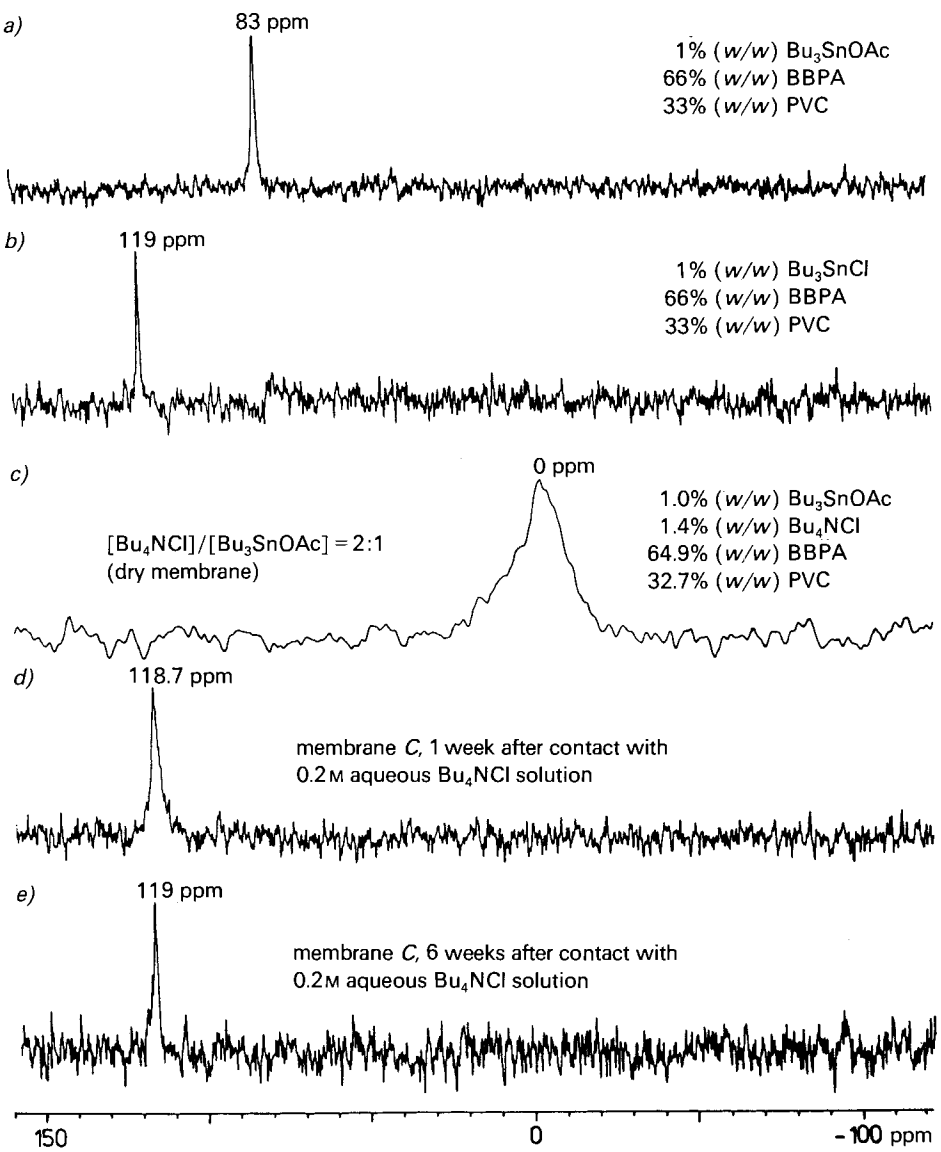


Fig. 5. *Formation of a pentacoordinated complex $[Bu_3SnOAc \cdot Cl]^-$ in a two-phase-system membrane/aqueous measuring solution, as detected by the ^{119}Sn-NMR method.* The chloride salt incorporated into the membrane is Bu_4NCl.

Contrary to the above results, no interaction could be observed between Bu_3SnOAc and Bu_4NCl in a two-phase study when increasing amounts of the ammonium salt were added to the aqueous phase. The only effect observed was a successive decrease of the signal of Bu_3SnOAc at 83 ppm, and an increase in that of Bu_3SnCl at 119 ppm. In contrast to the homogeneous-phase study, the exchange between these compounds was slow in this case. The explanation for this difference is given by the small partition coefficient of Bu_4NCl in favor of the organic phase. On the basis of ^{1}H-NMR spectra, a value of $3 \cdot 10^{-2}$ was estimated. This small partition coefficient is responsible for the fact that no penta-coordinated Sn-species could be detected in this experiment.

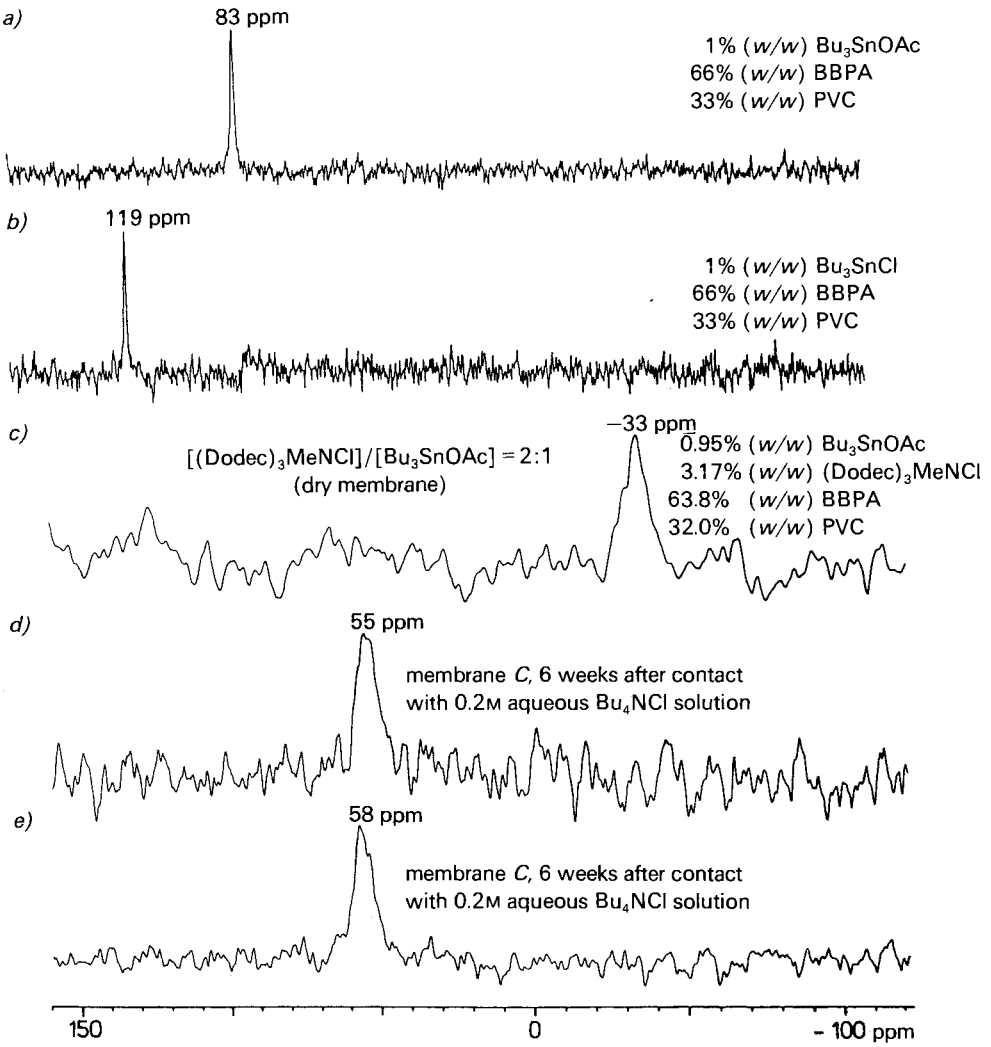


Fig. 6. *Formation of a pentacoordinated complex* $[Bu_3SnOAc \cdot Cl]^-$ *in a two-phase-system membrane/aqueous measuring solution, as detected by the* ^{119}*Sn-NMR method.* The lipophilic salt incorporated into the membrane is tridodecyl(methyl)ammonium chloride $(Dodec)_3MeNCl$.

The presence of pentacoordinated tinorganic species in the membrane phase was, however, demonstrated by the following experiments. Solvent polymeric membranes were prepared in an NMR tube as described earlier [12]. In the presence of Bu_4NCl (*Fig. 5*) and tridodecyl-methylammonium chloride ($(Dodec)_3MeNCl$; *Fig. 6*), broad signals were observed at 0 and −33 ppm, respectively, which clearly correspond to the pentavalent trialkyltin derivatives (*Fig. 5c* and *6c*). In both cases, equilibration with aqueous Bu_4NCl chloride caused a downfield shift. As expected on the basis of the above results, a shift of 119 ppm (Bu_3SnCl) at equilibrium was observed for the membrane with the less lipophilic ammonium salt Bu_4NCl (*Fig. 5e*). In contrast, a shift of 58 ppm at equilibrium for the membrane with $(Dodec)_3MeNCl$ (*Fig. 6e*) demonstrates that partially pentacoordinated tin species remain present in this membrane.

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Experimental Part

1. *Reagents.* All electrolyte solns. for the potentiometric measurements were prepared with doubly quartz distilled H_2O. For all sodium salts, except sodium thiocyanate (*Fischer Scientific Co.*, Fair Lawn, NJ), products of high purity (*pro analys. E. Merck*, Darmstadt, FRG) were used. Bu_4NCl (*purum*), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (*Kryptofix® 222*; *puriss.*), Me_4Sn (*purum*), MeOH (*puriss.*), 2-amino-2-(hydroxymethyl) propan-1,3-diol (*puriss.*), bis(1-butylpentyl)adipate (BBPA), and THF (*puriss.*) were obtained from *Fluka AG*, CH–9470 Buchs, Switzerland. Poly(vinyl chloride) (PVC *S704* high molecular weight) originated from *Lonza AG*, CH–3930 Visp, Switzerland. Naphthalene (*puriss.*) was provided by *E. Merck*, Darmstadt, FRG. Tridodecyl-(methyl)ammonium chloride was obtained from *Polyscience Inc.*, Warrington, PA. Me_4Si and $CDCl_3$ (99.8 atom-% D) were obtained from *Ciba-Geigy AG*, Basle, Switzerland. Oc_3SnCl and Bu_3SnCl were synthesized according to [28] and Bu_3SnOAc according to [8]. Bu_3SnCN and OC_4Sn were provided from *Aldrich GmbH*, D–Steinheim (*purum*); they were recrystallized or distilled in a 'Kugelrohr' apparatus, until only 1 signal was observed in the ^{119}Sn-NMR spectrum. The purity was also checked by size-exclusion chromatography and elemental analysis.

2. *NMR Measurements for Titration Curves.* ^{13}C- and ^{119}Sn-FT-NMR spectra were recorded at 50.32 and 74.63 MHz, resp., on a *4.70-T-Bruker-WP-200-SY* spectrometer. A 10-mm-o.d. tube containing 2.5 ml of 0.2M trialkyltin compound in $CDCl_3$ was prepared, and small amounts of dried Bu_4NCl or *Kryptofix® 222* KCl (obtained by separately dissolving equimolar amounts of KCl and *Kryptofix® 222* in abs. MeOH, mixing the 2 solns. and evaporating the solvent; m.p. 189–190°) were added in a dry-box consisting of a *Dri Lab DL-001-S-G*, a *Dri Train HE 493*, and a *Pedatrol HE 63 P (Vacuum/Atmospheres Co.*, Hawthorne, CA). ^{13}C- and ^{119}Sn-NMR chemical shifts were measured before and after each addition of chloride. The coupling constant $^1J(^{119}Sn,^{13}C)$ was determined from the ^{13}C-NMR spectra.

^{13}C-NMR Measurements: spectral width, 6024.10 Hz; acquisition time, 2.7197 s; data table size, 32 K of 24 bit words; pulse duration, 40 μs (*ca.* 86°); number of transients generally 500 to 1000. Broad-band ^{1}H-decoupling of *ca.* 2 W with 250 l/h r.t.-air cooling was applied during the acquisition period. In order to have similar temp. for ^{13}C and ^{119}Sn measurements, the decoupler power was reduced to the minimum of 0.5 W required to maintain the NOE for 3.0 s after each acquisition period. Me_4Si was used as an internal standard.

^{119}Sn-NMR Measurements: spectral width, 25000 Hz; acquisition time, 0.3277 s; data table size, 16 K; pulse duration, 25 μs (*ca.* 80°); number of transients, 400 to 1600 depending on the line width of the ^{119}Sn signal. In order to reduce potentially unfavorable NOE, the broad-band ^{1}H-decoupling of 2 W was switched off for 4.0 s between the end of the acquisition period and the beginning of the next pulse. The temp. for the ^{119}Sn-NMR was, therefore, slightly lower than for the ^{13}C-NMR. A coaxial 1.2-mm-o.d. capillary containing Me_4Sn was used as an external standard at the beginning of the measurements, and all subsequent spectra were referred to the same absolute frequency. At the end of the series of measurements, the capillary was again mounted, and a shift of −0.46 ppm relative to the initial value of Me_4Sn was observed. This progressive difference of $< 0.23\%$ of the total shift could safely be neglected.

3. *Quantitative NMR Determination of Stability Constants* K. For the mathematical evaluation of titration curves being registered by the NMR method, one can compare the measured values of chemical shifts as well as the coupling constants by each anion/ligand ratio [X]/[L] with the corresponding values calculated for different K values. By using the least-squares method, good agreement can be obtained.

With the assumption that trialkyltin ligand L forms a 1:1 complex with an anion X, $L + X \leftrightarrows LX$ $K = [LX]/([L] \cdot [X])$, and that the species L and LX undergo fast exchange in $CDCl_3$ (which means that the observed chemical shifts and coupling constant are a weighted average of the corresponding ones of free ligand L and complex LX), an iterative computer program based on a known model for generalized curve fitting [26] was written. It is, in principle, similar to the double-reciprocal *Hildebrand-Benesi* method [27] where an estimated K value is used to recalculate the concentration of added titration agent at each point and is iterated to give a new value for K. The only difference between our method and the previous one is that a simultaneous least-squares fitting of all three NMR parameters $\delta(^{119}Sn)$, $\delta(^{13}C)$, and $^1J(^{119}Sn,^{13}C)$ is done. Due to the weak interaction between trialkyltin ligands and chloride, it is not possible to get exact values for the chemical shifts $\delta(^{119}Sn)_{LX}$ and $\delta(^{13}C)_{LX}$ as well as for the coupling constant $^1J(^{119}Sn,^{13}C)_{LX}$ of the 1:1 complex LX, even in the presence of a large excess of chloride (see *Fig. 1*). Therefore, it is necessary to estimate values at the beginning, not only for K, but also for these three parameters. The program calculates for each chloride/ligand ratio the actual values of $\delta(^{119}Sn)_{calc}$, $\delta(^{13}C)_{calc}$ and $^1J(^{119}Sn,^{13}C)_{calc}$ and compares them with the corresponding measured values. The sum of the squares of the three deviations between calculated and measured $\delta(^{119}Sn)$, $\delta(^{13}C)$, and $^1J(^{119}Sn,^{13}C)$ for all chloride/ligand ratios is minimized. One can, therefore, get new values for the 4 variables K, $\delta(^{119}Sn)_{LX}$, $\delta(^{13}C)_{LX}$, and $^1J(^{119}Sn,^{13}C)_{LX}$, which can be used for the next iteration step of the fitting procedure. The criterion for stopping this procedure is the reduction of deviations of the three parameters ($\Delta\delta(^{119}Sn)_{LX}$, $\Delta\delta(^{13}C)_{LX}$, and $\Delta^1J(^{119}Sn,^{13}C)_{LX}$) to less than 1% of the corresponding values being used in the last iteration.

4. *NMR Measurements for Determination of the Partition Coefficient of Bu_4NCl between an Organic and an Aqueous Phase.* An aq. soln. of Bu_4NCl ($2.5 \cdot 10^{-2}$ M in H_2O) was placed in contact with the same volume of an org. phase containing Oc_3SnCl ($2.5 \cdot 10^{-2}$ M in $CDCl_3$). The extraction of Bu_4NCl from the aq. into the org. phase (K_{ex}) is characterized by the value of the stability constant of Oc_3SnCl with Bu_4NCl in the org. phase (K) and by the value of the partition coefficient of Bu_4NCl between the two phases ($k = [Bu_4NCl]_{org}/[Bu_4NCl]_{aq}$). After equilibration of the above mentioned phases (volume ratio 1:1), the amount of Bu_4NCl in the $CDCl_3$ phase was determined by ^1H-NMR. The quantitative evaluation of this extraction was based on a comparison of the integral of the ^1H-NMR signal of CH_2N of Bu_4NCl with those of a standard compound added to the org. phase with the assumption that its concentration remained unchanged during the experiment. Naphthalene was chosen as a standard ($2.23 \cdot 10^{-3}$ M in $CDCl_3$) because of its good chemical stability and lipophilicity. In this way, a concentration of extracted Bu_4NCl in the org. phase of $8.13 \cdot 10^{-4}$ M was found. The corresponding concentration of Bu_4NCl in the aq. phase was, therefore: $[Bu_4NCl]_{aq} = 2.5 \cdot 10^{-2}$ M $- 8.13 \cdot 10^{-4}$ M $= 2.42 \cdot 10^{-2}$ M, so that $k = 3.36 \cdot 10^{-2}$.

^1H-NMR Measurements: at 200.13 MHz; *4.70 T-Bruker-WP-200-SY* spectrometer with a suitable probe head. The $CDCl_3$ phase containing the extracted amount of Bu_4NCl was measured in a 5-mm-o.d. NMR tube. Spectral width, 2500 Hz; acquisition time, 3.2768 s; data table size, 16 K; pulse duration, 2 μs (*ca.* 10°); number of transients, 100 to 400. Me_4Si was used as an internal standard.

5. *NMR Measurements of Two-Phase Systems (Liquid Membrane/Aqueous Solution).* Solvent polymeric membranes having the same composition as the membranes used in EMF measurements were prepared with a spin-on method in 10-mm-o.d. NMR tubes [12]. These membranes were equilibrated with an aq. soln. of 0.2M Bu_4NCl during several weeks. They were then directly used in ^{119}Sn-NMR experiments with a 2-mm-o.d. coaxial capillary containing (D_{12})cyclohexane as D-lock and Me_4Sn as external standard. The chosen ^{119}Sn-NMR parameters remain the same as described above.

6. *EMF and VPO Measurements.* For EMF measurements, see [5] [6] [8]; for VPO measurements, see [4].

REFERENCES

[1] V. A. Zarinskii, L. K. Shpigun, V. M. Shkinev, B. Y. Spivakov, Y. A. Zolotov, *Russ. J. Anal. Chem.* **1980**, *35*, 1381.

[2] V. M. Shkinev, B. Y. Spivakov, G. A. Vorobeva, Y. A. Zolotov, *Anal. Chim. Acta* **1985**, *167*, 145.

[3] M. S. Frant, J. W. Ross, Jr., U. S. Patent No. 3406 102, 1968.

[4] U. Wuthier, H. V. Pham, R. Zünd, D. Welti, R. J. J. Funk, A. Bezegh, D. Ammann, E. Pretsch, W. Simon, *Anal. Chem.* **1984**, *56*, 535.

[5] U. Wuthier, H. V. Pham, E. Pretsch, A. K. Beck, D. Seebach, W. Simon, *Helv. Chim. Acta* **1985**, *68*, 1822.

[6] U. Oesch, D. Ammann, H. V. Pham, U. Wuthier, R. Zünd, W. Simon, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1179.

[7] M. J. Selwyn, in 'Organotin Compounds: New Chemistry and Application, Advances in Chemistry', Serie 157, Ed. J. J. Zuckerman, American Chemical Society, Washington, D. C., 1976, p. 204.

[8] U. Wuthier, H. V. Pham, B. Rusterholz, W. Simon, *Helv. Chim. Acta* **1986**, *69*, 1435.

[9] S. Koizumi, Y. Maegawa, Y. Sasaki, T. Imato, N. Ishibashi, 52nd National Meeting of the Chemical Society of Japan, April, 1986.

[10] F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1988**, *24*, 247.

[11] D. Wegmann, H.-G. Weiss, D. Ammann, W. E. Morf, E. Pretsch, K. Sugahara, W. Simon, *Mikrochim. Acta* **1984**, *III*, 1.

[12] R. Büchi, E. Pretsch, W. Simon, *Helv. Chim. Acta* **1976**, *59*, 2327.

[13] B. Wrackmeyer, '^{119}Sn-NMR Parameters, in Annual Reports on NMR Spectroscopy', Ed. G. A. Webb, Academic Press, London, 1985, Vol. 16, p. 73.

[14] V. S. Petrosyan, *Progr. NMR Spectrosc.* **1977**, *11*, 115.

[15] P. J. Smith, L. Smith, *Inorg. Chim. Acta Rev.* **1973**, *7*, 11.

[16] T. E. Mitchell, *J. Organomet. Chem.* **1973**, *59*, 189.

[17] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

[18] M. Newcomb, A. M. Madonik, M. T. Blanda, J. K. Judice, *Organometallics* **1987**, *6*, 145.

[19] M. Newcomb, J. H. Horner, M. T. Blanda, *J. Am. Chem. Soc.* **1987**, *109*, 7878.

[20] M. Newcomb, J. H. Horner, M. T. Blanda, P. J. Squattrito, *J. Am. Chem. Soc.* **1989**, *111*, 6294.

[21] M. T. Blanda, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626.

[22] H. V. Pham, Doctoral Thesis No. 8315, ETH Zürich, ADAG Administration und Druck AG, Zürich, 1987.

[23] T. P. Lockhart, W. F. Manders, F. E. Brinckman, *J. Organomet. Chem.* **1985**, *286*, 153.

[24] W. P. Neumann, 'Die Organische Chemie des Zinns', F. Enke Verlag, Stuttgart, 1967.

[25] M. Gielen, *Topics Curr. Chem.* **1982**, *104*, 57.

[26] D. S. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

[27] K. A. Connors, 'Binding Constants, The Measurement of Molecular Complex Stability', Wiley, New York, 1987, p. 189–200.

[28] K. A. Kozeschkov, *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 1348.