77. Trialkyltin Compounds as Neutral Carriers for Anions in PVC Liquid Membranes and Complex Formation with Oxoanions

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Under the influence of an electric field, trialkyltin compounds of the type R_3SnX behave as electrically neutral carriers for anions in poly(vinyl chloride) liquid membranes. The interaction of tinorganic compounds with oxoanions was studied in organic phase by means of ^{119}Sn-NMR-monitored titrations. In the case of tributyltin chloride, no appreciable amount of complex was formed with hydrogensulfate, whereas dihydrogenphosphate gave rise to a new species. Dioctyltin dichloride and dioctyltin diacetate formed a 1:2 (salt/ligand) complex with hydrogenphosphate.

Introduction. – Some di- and trialkyltin compounds of the type R_2SnX_2 and R_3SnX (X, electronegative substituent; R, alkyl and/or aryl substituent) induce anion selectivities in liquid membranes which significantly deviate from those observed with classical anion-exchanger membranes [1–8] (*Hofmeister* lyotropic anion selectivity sequence: $ClO_4^- > SCN^- > I^- > NO_3^- \approx Br^- > Cl^- > F^-$ [9] [10]). Their mechanistic behaviour in membranes which are in contact with an aqueous electrolyte solution is, however, unclear. Indeed, experiments indicate that trialkyltin compounds can either act as electrically neutral or charged carriers [11]. Most of the arguments are in support of the hypothesis that they do not significantly dissociate in nonpolar organic solvents [12] [13]. Their interaction with chloride was studied using ^{119}Sn- and ^{13}C-NMR spectroscopy [14]. Upon interaction with anions Y^- in a homogeneous organic phase, neutral tetracoordinate trialkyltin compounds form negatively charged, pentacoordinate complexes [15] (*Eqn. 1*).

$$R_3SnX\ (mem) + Y^-\ (aq) \rightleftharpoons [R_3SnXY]^-\ (mem) \qquad (1)$$

It must be taken into account that these NMR experiments do not necessarily represent the situation found in the corresponding electrode system. The fact that the deviation from the above *Hofmeister* selectivity sequence is most pronounced for membrane electrodes without any lipophilic cationic sites supports the hypothesis that trialkyltin compounds act as electrically charged ligands similar to the metalloporphyrins [16] (*Eqn. 2*).

$$[R_3Sn^+]\ (mem) + Y^-\ (aq) \rightleftharpoons R_3SnY\ (mem) \qquad (2)$$

Neutral-carrier-based membranes selective for cations such as Li^+, Na^+, K^+, and Ca^{2+} were studied previously [17] [18]. The main problem consisted in explaining the permse-

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lectivity of these carrier membranes for cations, which can be corroborated both with potentiometric and electrodialysis experiments. Such neutral carrier membranes indeed are permeable for cations only, the cation transference number being nearly 1 for the primary ion involved, in agreement with the Nernstian slope of the potentiometric electrode response for this ion [19]. Accordingly, the electric properties are predominantly influenced by lipophilic sample anions, such as perchlorate or thiocyanate, which cause the electrode response to suffer from anionic interference.

The previous theoretical treatment of the electrodialytic ion transport across solvent polymeric membranes containing electrically neutral or charged carriers is based on models assuming that the transport processes of cations and anions mediated by these carriers are similar [19]. Under the influence of an electric potential difference, the resulting current is, therefore, primarily transferred either by anionic species ($[R_3SnXY]^-$, *Eqn. 1*) or by positively charged, uncomplexed ligands (R_3Sn^+, *Eqn. 2*). Due to the closed-circuit flux of the carrier in the membrane phase, this migration of charged species is coupled with that of electrically neutral carriers or complexes in the opposite direction. The current-voltage characteristics of such liquid membranes show a saturation of the current at high voltages because of the limited back-diffusion of the electrically neutral species. The current saturation phenomenon in the case of neutral-carrier-based anion-selective membranes is caused by the accumulation of carrier species at the anodic and by its depletion at the cathodic side. The reverse would be expected in the case of membranes containing positively charged carriers for the anion transport.

In order to investigate the mechanism of anion permselectivity of PVC liquid membranes based on trialkyltin compounds, a series of electrodialytic experiments was carried out. The distribution of trialkyl compounds in stacks of PVC liquid membranes under the influence of an electric field was determined.

Liquid-membrane electrodes based on di- and triorganotin compounds show different selectivity patterns. With dialkyl- or diaryltin compounds (*e.g.* bis(4-chlorobenzyl)tin dichloride), hydrogenphosphate is preferred [3–6], whereas with trialkyltin compounds, analytically relevant selectivity for chloride is found [7] [8]. Here, we report on the interaction of tinorganic compounds with oxoanions, such as hydrogensulfate, hydrogenphosphate, and dihydrogenphosphate, studied with ^{119}Sn-NMR in organic phase.

Results and Discussion. – *Current-Voltage Characteristics.* At high voltages, the current-voltage curve of an anion-selective PVC liquid membrane based on tributyltin chloride (Bu_3SnCl) does not clearly exhibit saturation (*Fig. 1*). The saturation flux, and thus the shape of the current-voltage curve, is largely determined by the charge concentration within the membrane phase which, according to the theoretical description by *Morf et al.* [18], must be very low. Kinetic limitations at the phase boundary between electrolyte and membrane as well as the weak complex formation of Cl^- by triorganotin compounds [14] probably render the extraction of chloride from the sample solution into the membrane phase rather difficult.

Carrier-Concentration Profiles. In order to elucidate the carrier mechanism of anion-sensitive PVC liquid membranes, the distribution of the tinorganic carrier within a membrane stack was determined. To this end, a stack of five identical membranes (each *ca.* 100 μm thick; see *Exper. Part*) with dibutyl(octadecyl)tin acetate ($Bu_2(Od)SnOAc$) or equimolar amounts of trioctyltin chloride (Oc_3SnCl) was mounted in a transport cell with

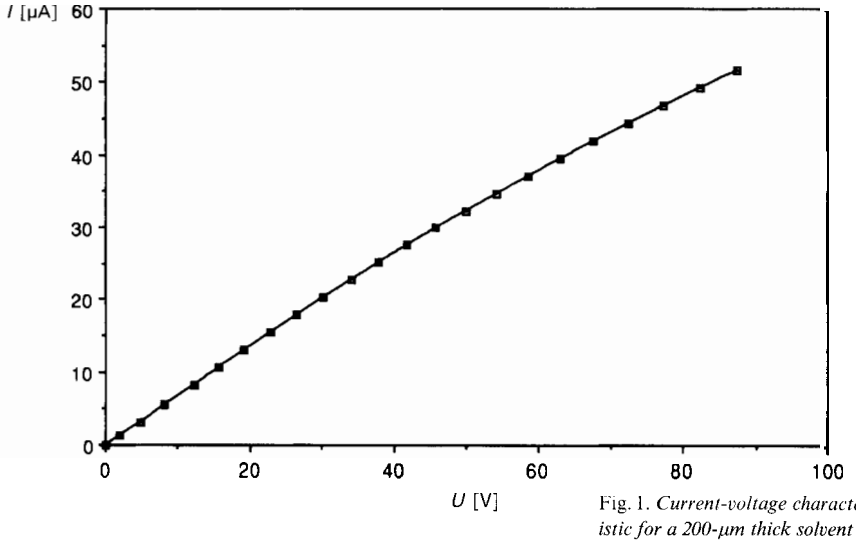

Fig. 1. *Current-voltage characteristic for a 200-μm thick solvent polymeric membrane containing trioctyltin chloride.* Membrane composition (wt.-%): Oc_3SnCl (5.0), *ETH 469* (65.0), PVC (30.0); electrolyte solution, 0.01M NaCl; active membrane surface, 12.6 cm^2.

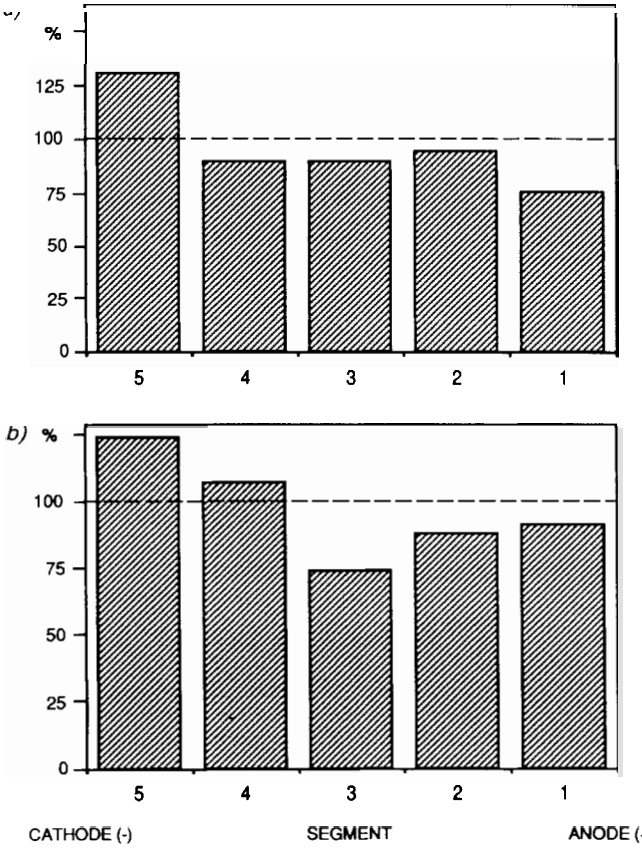

Fig. 2. *Electrodialytic anion-transport experiment.* Distribution of triorganotin carriers in a five-segmented membrane stack after interrupting the current. A current of 15 μA was applied during 120 min. Membrane composition (wt.-%): *a*) $Bu_2(Od)SnOAc$ (3.5), *ETH 469* (66.5), PVC (30.0); *b*) Oc_3SnCl (3.2), *ETH 469* (66.8), PVC (30.0). Electrolyte solution, 0.01M NaCl; active membrane surface, 3.1 cm^2. Dotted lines: initial distribution of the carrier.

0.01M NaCl solution on either side, and a current of 15 μA was passed during 120 min. Immediately after interrupting the current, the five membranes were separated and the tin concentration analysed by inductively coupled Ar plasma atomic emission spectroscopy (ICP-AES). The resulting carrier profiles (*Figs. 2a* and *2b*) do not correspond to the typical behaviour of an electrically neutral or charged carrier (see [20]). Although the two concentration profiles are slightly different, there is a greater accumulation of carrier at the cathode than at the anode for both cases. In previous investigations with membranes containing the electrically neutral (octaethylporphyrinato)ruthenium(II) complex ([Ru(oep)]CO) [20] and the lipophilic ammonium salt tri(dodecyl)methylammonium chloride ([$(Dd)_3$MeN]Cl), a similar behaviour was observed (*Fig. 3*). The fact that electrically neutral or negatively charged porphyrinatoruthenium(II) complexes are accumulated more rapidly at the cathodic side of the membrane confirms the earlier proposition that the current-induced carrier transport is influenced by additional factors.

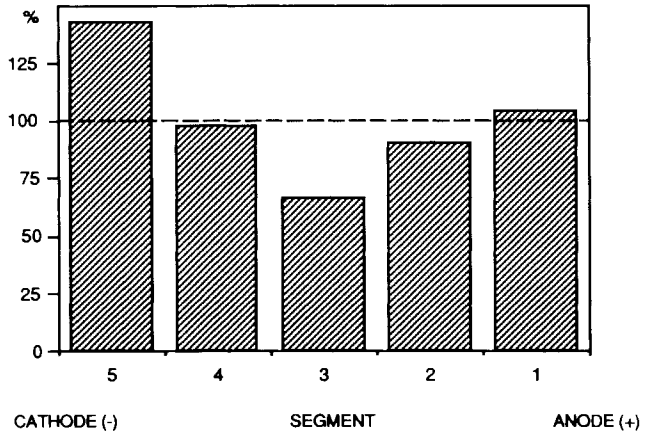

Fig. 3. *Electrodialytic anion-transport experiment.* Distribution of the electrically neutral (octaethylporphyrinato)-ruthenium(II) complex in a five-segmented membrane stack after interrupting the current. A current of 10 μA was applied during 120 min. Membrane composition (wt.-%): [Ru(oep)]CO (1.0), [$(Dd)_3$MeN]Cl (0.8), *ETH 469* (65.2), PVC (33.0); electrolyte solution, 0.01M NaSCN; active membrane surface, 3.1 cm^2. Dotted line: initial distribution of [Ru(oep)]CO [20].

Generally, PVC liquid membranes are considered as nonporous organic phases so that the convective flow of solvents through the membrane may be neglected [20] [21]. It seems, however, that under the influence of a strong electric field, the transport behaviour in liquid membranes does not only depend on migration and diffusion. Electrokinetic phenomena, such as electroosmosis, are quite generally observed in porous membranes, diaphragms, and capillary systems [22–24]. The direction and velocity of the electroosmotic flow of a liquid depends on the membrane composition and the strength of the electric field. With higher potentials, the flow of negatively charged species is influenced by electroosmosis and electrical migration [25–27]. This might explain the concentration profiles presented in *Figs. 2* and *3*. Although the properties of porous systems [21] [24] [28] [29] differ from those of nonporous liquid membranes, whose structure is not yet clear, it

is convenient, in a first approximation, to adopt the well-known models of porous systems to compare and interpret the phenomenologies observed with liquid membranes.

In order to investigate the electroosmotic behaviour of liquid membranes, a current-induced transport experiment with an optically labelled trialkyltin compound was carried out. Again, a stack consisting of five membranes was placed in the transport cell. The labelled centre membrane was equilibrated in an aqueous eosin or erythrosin solution, the other four in 0.01M NaCl. Eosin and erythrosin are extracted from the aqueous solution into the membrane phase only when the latter contains an ion exchanger ($[(Dd)_3MeN]Cl$) or a trialkyltin compound. Unfortunately, the low solubility of the trialkyltin-eosin complex prevented its structure to be elucidated by ^{119}Sn-NMR spectroscopy. It can, however, be assumed that either negatively charged pentacoordinate tin complexes of the type $[R_3SnXY^-]$ or tetrahedral trialkyltin compounds (R_3SnY) (Y = anion of eosin) are favourably formed by coordination or ion exchange, respectively. The concentration profiles (*Figs. 2* and *3*) indicate that the electroosmotic flow is directed towards the cathode. It is irrelevant whether the transported species are negatively charged or electrically neutral. *Fig. 4a* illustrates the distribution of eosin after interrupting the current flow

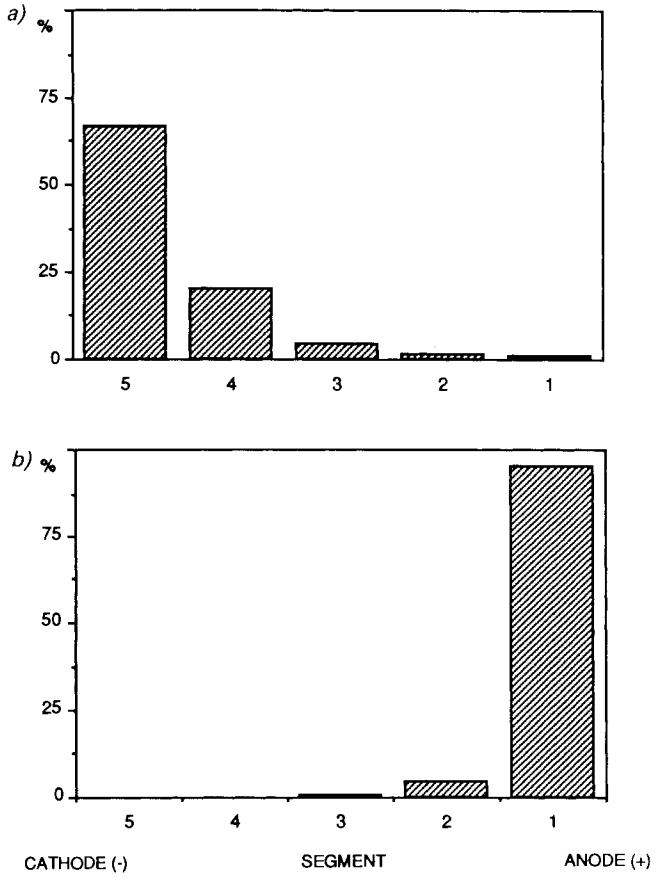

Fig. 4. *Electrodialytic transport experiment.* Distribution of eosin in a five-segmented membrane stack after interrupting the current. *a*) Membrane composition (wt.-%): Oc_3SnCl (3.3), *ETH 469* (66.7), PVC (30.0); electrolyte solution, 0.01M NaCl; active membrane surface, 3.1 cm^2; current of 10 μA applied during 100 min. *b*) Membrane composition (wt.-%): Oc_3SnCl (3.2), *o*-NPOE (65.8), PVC (31.0); electrolyte solution, 0.01M $[(Hd)Me_3N]Br$; active membrane surface, 3.1 cm^2; current of 400 μA applied during 120 min.

at 78 V. Obviously, more than 90% of the eosin available were accumulated in the membrane segments No. 4 and 5 near the cathode. The same result was obtained with erythrosin as dye indicator.

For porous membranes, the direction of the electroosmotic flow is determined by the membrane matrix and the composition of the liquid phase. Generally, the phase with the higher dielectric constant is positively charged [30]. Therefore, H_2O having a high dielectric constant, migrates towards the cathode. The electroosmotic flow may also be influenced by the specific adsorption of ionic surfactants onto the wall of the membrane pores or by the presence of charged groups in the membrane itself. For a negatively charged membrane, as *e.g.* a microporous *Nafion*® perfluorosulfonic acid membrane, an electroosmotic flow towards the cathode is observed. On the other hand, if the membrane contains positively charged immobile sites, the flow of solvent is in the opposite direction [23] [25] [31]. In order to reverse the electroosmotic flow, the influence of the composition of the membrane phase and of the electrolyte solution was investigated. Firstly, the cationic surfactant (hexadecyl)trimethylammonium bromide ([(Hd)Me_3N]Br) was used instead of NaCl as electrolyte (0.01M). After an electrodialysis of 150 min at 60 μA, eosin had again accumulated near the cathodic membrane boundary (see *Fig. 4a*). Secondly, the plasticizer bis(1-butylpentyl)decane-1,10-diyl diglutarate (*ETH 469*; $\varepsilon = 4.91$ [32]) was replaced by the more polar 2-nitrophenyl octyl ether (*o*-NPOE; $\varepsilon = 23.9$ [32]), the electrolyte again being 0.01M [(Hd)Me_3N]Br. From *Fig. 4b*, it is evident, that the electroosmotic flow was reversed, eosin having accumulated within the anodic segments. The same behaviour was observed with 2-nitrophenyl dodecyl ether (*ETH 217*) as plasticizer. Thus, the assumption is confirmed that by applying high electric currents or voltages, the electroosmotic flow strongly influences the carrier-mediated anion transport. Different investigations showed that carrier-based liquid membranes have the capability of absorbing considerable amounts of H_2O in condensed form as clusters within the membrane [33] [34]. It is assumed that at high voltages, under the influence of electroosmotic pressure, the H_2O clusters or isolated pores are united to H_2O arteries. Under these conditions, PVC liquid membranes, therefore, behave as porous membranes.

The interference of electroosmosis with the migration of anionic species within a liquid membrane makes it even more difficult to investigate the mechanism of anion permselectivity, especially to determine transference numbers of anions. Nevertheless, the unusual concentration profile of the neutral porphyrinatoruthenium(II) anion carrier [Ru(oep)]CO [20], as a result of the electroosmotic flow, confirms the assumption that trialkyltin compounds indeed act as electrically neutral carriers for anions. The absence of a plateau in the current-voltage curve may also be attributed to the reversed flow of solvent and anionic solutes.

The permselectivity of PVC liquid membranes based on neutral carriers for cations is mainly induced by fixed or nearly immobile anionic and corresponding ionogenic sites [33] [35–37]. The presence of anionic sites as impurities in anionselective PVC membrane electrodes may, however, have a detrimental effect and cause serious interference from cations. The anion permselectivity can be achieved by outbalancing the anionic sites with a sufficient amount of lipophilic cations. Quaternary ammonium compounds were, therefore, added to the membrane [20] [38]. However, as the complex formation constants of the pentacoordinate trialkyltin complexes are low [14], the potentiometric selectivities of the corresponding electrodes with 5 and 10 mol-% of [$(Dd)_3$MeN]Cl (relative to the

neutral carrier) showed a significant tendency towards the *Hofmeister* selectivity sequence [39]. Nevertheless, the influence of cationic sites, capable to generate anion permselectivity, is not fully understood. Because the dissociation of trialkyltin compounds cannot be measured in media of low polarity (*e.g.* CH_2Cl_2 [12]), it is assumed that only the hydrophilic counterions (*e.g.* H^+, Na^+, Ca^{2+} [40]) of the anionic sites generate the anion permselectivity of liquid membranes containing trialkyltin compounds.

^{119}Sn-NMR Measurements. A fast exchange between organotin derivatives and their adducts with anions was usually observed when the corresponding salts were successively added to the ligands in organic solvents [14]. The ^{119}Sn-NMR chemical shift, as a rule, is a sensitive parameter for investigating an interaction of organotin compounds with salts [14]. Unfortunately, the interaction of eosin with R_3SnX could not be corroborated by ^{119}Sn-NMR studies because of solubility reasons (see above). Instead, the interaction of tri- and dialkyltin compounds were investigated in $CDCl_3$ by means of ^{119}Sn-NMR titrations (*Tables 1* and *2*).

The difference $\Delta\delta$ in chemical shift indicates that the complex formation of Bu_3SnCl with hydrogensulfate is very weak, whereas with dihydrogenphosphate a considerable upfield shift is observed ($\Delta\delta$ = 73 ppm; *Table 1*). In comparison with ^{119}Sn-NMR data

Table 1. *Changes in ^{119}Sn-Chemical Shifts, $\delta(^{119}Sn)$* [ppm], *of Bu_3SnCl, Induced by Adding $(Bu_4N)HSO_4$, $(Bu_4N)H_2PO_4$, or $[(Dd)_3MeN]Cl$ in $CDCl_3$*

Molar ratio anion/Bu_3SnCl	$\delta(^{119}Sn)$ [ppm]		
	HSO_4^-	$H_2PO_4^-$	Cl^-
0.0	157.8	157.7	157.8
0.5	157.2	140.5[a])	143.8
1.0	156.5	115.7[a])	125.5
1.5			109.4
2.0	154.9	79.5[a])	92.0
3.0		84.5[b])	61.5

[a]) Opaque. [b]) Homogeneous solution.

Table 2. *Changes in ^{119}Sn-Chemical Shifts, $\delta(^{119}Sn)$* [ppm], *of Dioctyltin Dichloride and Dioctyltin Diacetate Induced by Adding* Kryptofix® 222/*K_2HPO_4 Salt in $CDCl_3$*

Oc_2SnCl_2		$Oc_2Sn(OAc)_2$	
Molar ratio salt/ligand (ligand concentration 0.064M)	$\delta(^{119}Sn)$ [ppm]	Molar ratio salt/ligand (ligand concentration 0.077M)	$\delta(^{119}Sn)$ [ppm]
0.0	122.4	0.0	–152.2
0.22	–33.2	0.28	–190.5
0.35	–102.1	0.40	–205.9
0.44	–116.1	0.65	–277.5[a])
0.62	–118.2, –270.2[a])	1.17	–276.6[a])
0.75	–118.5, –269.0[a])		
0.83	–118.3, –270.7[a])		
0.98	–118.8, –273.5[a])		
1.51	–276.3[a])		

[a]) Turbid solution.

for trialkyl oxo complexes [41] [42], the formation of a tetracoordinate trialkyltin phosphate complex is more probable than a change in the coordination number from 4 to 5 ($\Delta\delta = 200$ ppm).

A different behaviour is observed for dioctyltin dichloride with hydrogenphosphate. The ^{119}Sn-NMR spectra (see *Table 2*) show one signal for molar ratios salt/ligand of up to *ca.* 0.5, reflecting the formation of a strong 1:2 complex ($\Delta\delta \approx -240$ ppm). For molar ratios in the range 0.5–1.0, a second signal appears at δ *ca.* −270 ppm, whose intensity increases with increasing amount of salt added, while the first signal gradually disappears. This indicates a slow exchange between the 1:2 complex and a newly formed species (either a 1:1 complex and/or an oligomer), the total $\Delta\delta$ amounting to *ca.* −400 ppm. Taking into account the change in the chemical shift and the stoichiometry, the coordination number of the Sn-atom in the 1:2 complex is assumed to be 5 [43]. For the 1:1 compound, the coupling constants $J(^{119}Sn,^{13}C)$ could not be determined because of solubility problems. The possible oligomer and/or polymer may contain pentacoordinate Sn-centres. The change in chemical shift ($\Delta\delta \approx -155$ ppm) from the 1:2 to the 1:1 complex could be caused by the exchange of one or two Cl-atoms for O-atoms of hydrogenphosphate groups [43].

Similar results were obtained with dioctyltin diacetate. The reason for the considerably smaller change in chemical shift ($\Delta\delta \approx -60$ ppm) observed for the salt/ligand 1:2 complex probably lies in the different coordination behaviour of AcO^- group [44] as compared with Cl^-. Regarding the 1:1 complex, the chemical shift $\delta = -278$ ppm again indicates a pentacoordinate Sn-centre in an oligo- or polymeric structure. A hexacoordinate tin complex is less probable as such compounds usually exhibit lower chemical shifts [45].

The existence of a complex formed between dioctylin dichloride and chloride, of unclear stoichiometry, was already observed by ^{119}Sn-NMR spectroscopy [12]. Furthermore, potentiometric experiments showed a stronger complexation with hydrogenphosphate than with chloride [12]. When titrating dioctyltin diacetate with $[(Dd)_3MeN]Cl$, only slight changes in chemical shift were obtained ($\Delta\delta \approx -2$ ppm for a salt/ligand molar ratio of 1.3).

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Experimental Part

Reagents and Solvents. Aq. solns. were prepared with anal.-grade reagents from *Fluka* or *Merck* using doubly quartz distilled H_2O. The following compounds were obtained from *Fluka*: Trioctyltin chloride (Oc_3SnCl), *purum* > 98%; 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (*Kryptofix® 222*), *puriss.* > 99%; tetramethyltin (Me_4Sn), *purum* > 98%; bis(1-butylpentyl)decane-1,10-diyl diglutarate (*ETH 469*); 2-nitrophenyl octyl ether (*o*-NPOE), > 99%; poly(vinyl chloride) (PVC), high molecular weight; tri(dodecyl)methylammonium chloride ($[(Dd)_3MeN]Cl$), *ca.* 97%; tetrabutylammonium hydrogensulfate ($(Bu_4N)HSO_4$), *puriss.* > 99%; tetrabutylammonium dihydrogenphosphate ($(Bu_4N)H_2PO_4$), *purum* > 99%; dipotassium hydrogenphosphate, *puriss.* > 99%; (hexadecyl)trimethylammonium bromide ($[(Hd)Me_3N]Br$), *purum ca.* 98%; erythrosin extra bluish (iodoeosin; 2′,4′,5′,7′-tetraiodofluorescein, sodium salt), *standard Fluka*; eosin, alcohol soluble (ethyl eosin; 2′,4′,5′,7′-tetrabromoeosin ethyl ester, sodium salt), *standard Fluka*; tetrahydrofuran (THF), *puriss. p.a.* > 99.5% (freshly distilled before use); dimethylformamide (DMF), *puriss. p.a.* > 99.5%. $CDCl_3$ was obtained from *Dr. Glaser AG*, Basel, tributyltin chloride (Bu_3SnCl) from *ICN Pharmaceuticals, K&K Labs. Division*, Plainview, NY 11803, tris(hydroxymethyl)aminomethane (= 2-amino-2-(hydroxymethyl)propane-1,3-diol; *Tris*) from *Sigma Chemical Company*, St. Louis, MO. Dioctyltin dichloride from *Riedel-de-Haën*, and dioctyltin diacetate from

Merck-Schuchardt. Bu_3SnCl and Oc_3SnCl were distilled by bulb-to-bulb distillation until one signal only was observed in the ^{119}Sn-NMR spectrum. The purity was also controlled by size-exclusion chromatography and elemental analysis. The 2-nitrophenyl dodecyl ether (*ETH 217*) and dibutyloctadecyltin acetate (Bu_2(Od)SnOAc) were synthesized in our laboratory [8].

Membrane Preparation. The solvent polymeric membranes used for the electrodialytically induced carrier transport consisted of 1.5–5 wt.-% of carrier, 30 wt.-% of PVC, and the rest as plasticizer. The compounds were dissolved in THF and poured into a glass ring (i.d. 58 mm) resting on a glass plate covered with a fluoroethylene-propylene foil. Membrane stacks were prepared by dissolving the components totalling 600 mg in 25 ml of THF and pouring 5 ml each into glass rings (i.d. 28 mm). The rings were covered with a second glass plate leaving a small space in between. Thus, it took two days to slowly evaporate the THF. Membrane pieces of 25 mm in diameter were then cut out, and five identical segments, each 100 μm thick, were put together to a stack.

Cell Assembly. For the electrodialysis experiments, the transport cell, made of *Teflon®*, consisted of two electrolyte compartments (each 30 ml) separated by the membrane and equipped with two Pt wires. The active surface had a diameter of 40 mm for a single membrane and 20 mm for membrane stacks. The membranes were held in place by two *Kel-F®* rings. During the transport experiments, the chloride or the bromide solns. were continuously stirred.

Electrodialytic Transport. Depending on the number of gauge points of the current range chosen, the current applied was increased stepwise. The corresponding time-constant voltage was reached after 3–5 min for the ohmic and after 120 min for the non-ohmic range of the current/voltage curve.

Determination of the Carrier Distribution. Immediately after interrupting the electrodialytic experiment, the five membrane segments were separated, and membrane pieces of 18 mm in diameter cut out, dissolved in DMF, and filtered (*Millex®-HV, Millipore*, 0.45 μm pore size). The concentration of the tinorganic carrier was determined by ICP-AES at 284.0 nm, the most sensitive wavelength for Sn. A detailed description of the ICP-AES type is given in [46].

Experiments with Dye Indicators. The migration behaviour of anions in a polymeric liquid membrane under the influence of an electric field was investigated with the help of dye indicators. During several h, one of the five identical membrane segments (see above) was conditioned in 10 ml of aq. 0.001M eosin or erythrosin soln. This labelled segment was then kept overnight in 10 ml of distilled H_2O and the other four in 0.01M NaCl. The five segments were wiped dry and put together to a stack, with the labelled segment in the centre. The electrodialytic experiment was carried out as described above. The membrane segments were weighed and dissolved in THF and the distribution of the dye indicator determined on a *Uvikon 816*, UV/VIS spectrophotometer (*Kontron Instruments AG*, Zürich).

Apparatus. The equipment for controlling the current during the electrodialytic transport experiments consisted of an *Apple IIe* computer (*Cupertino*, CA); a current source (*Keithley 222*; *Keithley Instruments S.A.*, Dübendorf), and a digital multimeter (*Solartron/Schlumberger 7150 plus*; *Solartron Instruments*, Farnborough, England).

NMR Measurements for Titration Curves. ^{119}Sn-FT-NMR spectra were recorded at 74.63 MHz on a *4.70-T-Bruker-WP-200-SY* spectrometer. To a 10-mm tube (o.d.) containing 2.5 ml of 0.02–0.08M di- or trialkyltin compound in $CDCl_3$, small amounts of a quaternary ammonium salt or *Kryptofix® 222*/K_2HPO_4 (obtained by dissolving equimolar amounts of K_2HPO_4 and *Kryptofix® 222* in abs. MeOH, stirring the soln. for several h at r.t., and evaporating the solvent) were added in a drybox 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).

^{119}Sn-NMR Measurements. Spectral width, 45500 Hz; acquisition time, 0.36 s; data table size, 32 K; pulse duration, 15 μs; number of transients, 400 to 10000 depending on the line width of the ^{119}Sn-NMR signal. In order to reduce potentially unfavourable NOE, the broad-band ^{1}H-decoupling of 2 W was switched off for 5.0 s between the end of the acquisition period and the beginning of the next pulse. A coaxial 1.2 mm (o.d.) capillary containing Me_4Sn was used as external standard.

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