

Tributyl- and Triphenyltin Benzoates, Phenylacetates, and Cinnamates as Anion Carriers: an Electrochemical Assessment Coupled to Structural NMR Studies and AM1 Calculations

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A series of tributyl and triphenyltin benzoates, phenylacetates, and cinnamates, with different electron-withdrawing substituents, were evaluated for their selectivity as anion carriers and for their application in liquid-membrane potentiometric ion-selective electrodes. The tributyltin carboxylates exhibited good sensitivity and significant chloride selectivities, while the corresponding triphenyltin benzoates were much less active. The observed potentiometric response differences were related to Sn-atom *Lewis* acidity, as assessed by binding constants of chloride to the tin carriers determined from ¹¹⁷Sn-NMR titration experiments and theoretical simulations of the resulting titration curves. The thermodynamic characteristics as well as the expected chloride-carrier adducts in relation to starting substrates were analyzed theoretically by AM1 calculations.

1. Introduction. – Selective anion recognition is an important topic in a wide range of disciplines [1][2]. The development of chemical compounds for the selective anion recognition has been of primary importance in many organic, organometallic, and analytical laboratories in the last twenty years. Organometallic compounds, with one or more *Lewis*-acidic metal centers, have been used as carriers for selective anion recognition [3]. One of the most successful such centers, so far, has been the *Lewis* acidic tin(IV) [4–13]. Many of these organotin carriers, when introduced into a polymeric membrane phase, have shown potentiometric anion selectivity depending on their concentration, as well as on the type, size, and shape of the organic substituents bound to the Sn-atom. Organotin compounds of the type R₃SnX have been found to selectively bind and transport anions in biological [14] as well as in plasticized polymeric membranes [7][15]. In particular, triorganotin acetates and halides (*i.e.*, (acetyloxy)- and halogenotrialkylstannanes) have shown increased potentiometric response towards chloride [16], depending on the concentration of the carrier in the membrane

and on the bulkiness of the organic substituents at the Sn-atom. By contrast, the selectivity is not strongly influenced by the nature of the electronegative substituent X.

Even though considerable efforts in anion-sensor development and optimization have been achieved for biologically important anions such as chloride [4], salicylate [13][17], and phosphate [9][18], little is known about the dependence of the observed carrier properties, such as selectivity, detection limit, and stability, on the chemical ligation capabilities of the coordinating Sn^{IV} center. In particular, the effect of the binding strength on the potentiometric behavior is to be outlined.

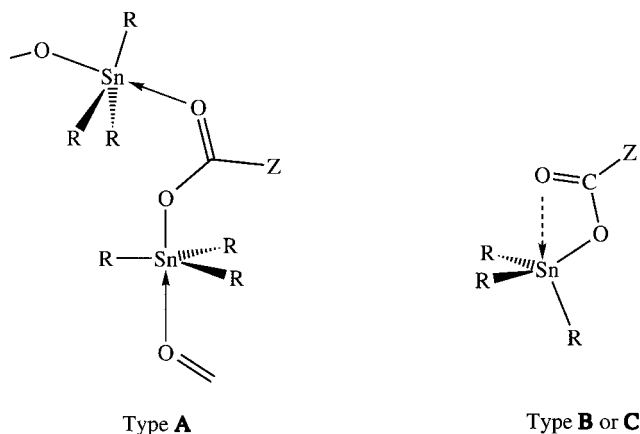
In this report, a series of tributyl- and triphenyltin benzoates, phenylacetates, and cinnamates [19][20], with or without the perfluorophenyl group in the carboxylate moiety, has been investigated to correlate the potentiometric chloride response with the *Lewis* acidity of the organotin carrier. It is shown that this potentiometric response is inversely related with the *Lewis* acidity of the organotin carrier. The binding constants of these carriers with chloride are determined in organic media from ¹¹⁷Sn-NMR titration curves. In addition, theoretical calculations based on AM1 quantum-mechanical methods complete the experimental data and support the presented correlation. This approach opens a novel way to selective anion-sensor development and optimization.

Results and Discussion. – *Structural Considerations.* The triorganotin carboxylates **1**–**12** of which the potentiometric response to chloride was investigated after incorporation into PVC-plasticized ion-selective membranes, have the general formula Z–CO₂–SnR₃ (see *Table 1*). The structures in the solid state and in solution of all these compounds, except those of **7**, are not identical, as shown by X-ray diffraction, *Mössbauer*, and NMR studies [19][20]. In the solid state, they exhibit a polymeric structure in which the Sn-atom has a five-coordinated *trans*-R₃SnO₂ type configuration **A** with trigonal bipyramidal geometry in which the three organic groups (R = Ph or Bu) occupy the equatorial positions and two O-atoms occupy the axial positions [21][22]. One of the Sn–O bonds is rather short (*ca.* 2.2 Å), the longer Sn–O bond (*ca.* 2.4 Å) arising from a donor-acceptor contact between the Sn-atom and the carbonyl O-atom of a neighboring triorganotin carboxylate [19][20]. On the other hand, the structure in solution is monomeric of type **B** or **C**, the latter being a limiting case of the former with non-existent O(carbonyl)-Sn contact. This is due to the fact that the weak second Sn–O bond found in the solid state breaks easily upon dissolution. Type **A** can be discriminated from the types **B** and **C** on the basis of ¹J(¹³C, ¹¹⁹Sn) coupling constant values [19][20][23–27], ^{119/117}Sn chemical shifts [19][20], and quadrupole-splitting data from *Mössbauer* spectroscopy [19][20]. Compound **7** is exceptional in that it is

Table 1. *Compounds of the Type Z–CO₂–SnR₃ Investigated upon Potentiometric Chloride Response.*

Z–CO ₂ –SnR ₃	R	Z	Z–CO ₂ –SnR ₃	R	Z
1	Bu	Ph	7	Ph	Ph
2	Bu	PhCH ₂	8	Ph	PhCH ₂
3	Bu	PhCH=CH	9	Ph	PhCH=CH
4	Bu	C ₆ F ₅	10	Ph	C ₆ F ₅
5	Bu	C ₆ F ₅ CH ₂	11	Ph	C ₆ F ₅ CH ₂
6	Bu	C ₆ F ₅ CH=CH	12	Ph	C ₆ F ₅ CH=CH

monomeric in both the solid and solution states, indicating that the *Lewis* acidity of the Sn-atom must be lower in **7** than in the other triphenyltin carboxylates and even the tributyltin carboxylates.



Electrode Characteristics and Measurements: Anion Selectivity and Calibration Curve. – Even though the systems presented here were not optimized as chloride sensors, a calibration curve using a membrane doped with carrier **1** is presented in *Fig. 1*, and the selectivities of carriers **1–3** are given in *Table 2* as representative examples. Values for the calibration curve were taken in unbuffered aqueous solutions by addition of successive aliquots of 0.1M KCl. At low chloride concentrations, potential drift was observed, while quite stable values were obtained in the concentration range 10^{-4} – 10^{-2} M giving a linear change with a slope of *ca.* 60 mV. Electrodes gave responses to higher chloride concentrations within 2 min. Similar results were obtained when 0.01M morpholine-2-ethanesulfonic acid (MES) based buffer, adjusted to pH 5.5 with NaOH, was used. This buffer was thus used for all subsequent potentiometric experiments.

Electrochemical Chloride-Anion Response and Relationship to the Structure. – To elucidate the structure/potentiometric-response relationship, the chloride anion was chosen as the primary ion. *Fig. 2* shows the measured overall potential differences obtained with electrodes based on the tin carriers **1–12** for MES-buffered solutions containing 0.01M KCl. It is clear that the tributyltin carboxylates **1–6** show a significantly greater anionic response to chloride than the triphenyltin analogs **8–12**.

While low chloride response of triphenyltin chloride has been previously attributed [16] to the steric bulkiness of the Ph groups, the results obtained from the compounds presented here indicate that the observed behavior is rather strongly dependent on the *Lewis*-acidity characteristics of the carrier. The Sn-atom in the Bu_3Sn moiety is a weaker *Lewis* acid than it is in the Ph_3Sn [26][28]. This is because the Bu group is an inductively electron-releasing group, while the Ph group is an inductively withdrawing one. Hence, the Bu_3Sn series of carriers will show weaker chloride binding than the Ph_3Sn series. This leads to the conclusion that chloride elimination is easier in the

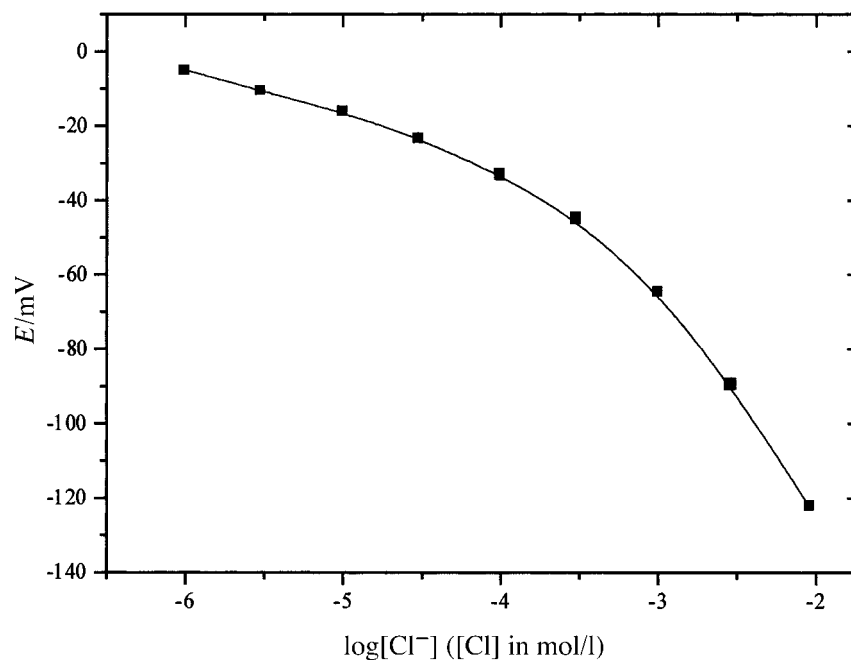


Fig. 1. Typical calibration curve of chloride anion for the electrode with tin carrier **1**. For conditions, see text.

Table 2. Potentiometric Potential Responses to 10 mM Anion Solutions of Electrodes with Tin Carriers **1–3**. Measured in 0.01M MES buffer (pH = 5.5).

	E/mV		
	1	2	3
Cl ⁻	-134	-118	-159
SO ₄ ²⁻	5.4	3.8	-1.0
ClO ₄ ⁻	-153	-153	-127
NO ₃ ⁻	-59.2	-57	-25
SCN ⁻	-264	-274	-227
I ⁻	-162	-156	-203

former case (Bu₃Sn containing compounds). The higher potential response to chloride of the Bu₃Sn based compounds can thus be justified based on the reversibility of the system. In the case of carrier **7**, the unusually low four-coordination of the Sn-atom indicates an abnormally low *Lewis* acidity, being closer in this respect to tributyltin than to triphenyltin compounds. That the nucleophilic attack at a four-coordinate species is slower than at a five-coordinate one (higher LUMO energy) corroborates this idea [29]. With the apparent lower potential difference, the triorganotin perfluorobenzoates **4** (R = Bu) and **10** (R = Ph) within their Bu and Ph series, respectively, are expected to have the highest *Lewis* acidity as a result of the proximity of the strongly electron-withdrawing pentafluorophenyl group.

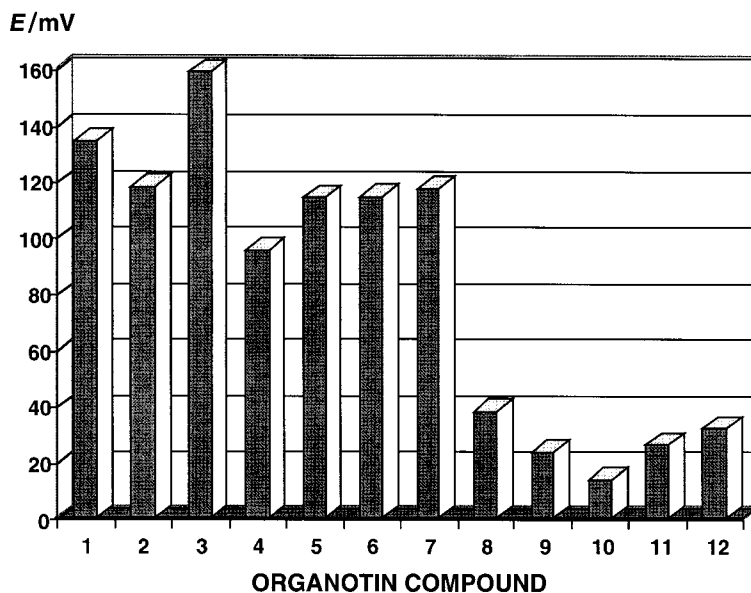
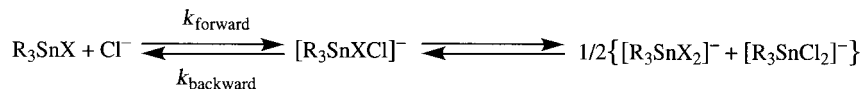


Fig. 2. Electrochemical activity of the triorganotin compounds 1–12 against an aqueous solution of chloride anions. The potential response represents the positive difference between the potential measured in the absence and in the presence of 0.01M KCl with the same aqueous buffer.

The higher sensitivity to chloride shown by the tributyltin over that of the triphenyltin compounds can be rationalized based on the fact that a reversible potentiometric sensor requires not only that a donor-acceptor interaction between the Sn-atom and the Cl-anion exists, but also that the resulting addition-elimination equilibrium between the carrier and the anion is fast. More specifically, elimination of the Cl-anion from the $[R_3SnXCl]^-$ complex should be as fast as possible so that there is a reversible potential development. This requires an optimal balance between, on one hand, the existence of an interaction between the Sn-center and the anion (effective association) and, on the other hand, a fast elimination kinetics (high k_{backward}) for chloride from $[R_3SnXCl]^-$, in the reaction pattern as shown in the *Scheme*.

Scheme



In the *Scheme*, the possibility that the adduct $[R_3SnXCl]^-$ itself equilibrates fast with $[R_3SnX_2]^-$ and $[R_3SnCl_2]^-$ is left open, since the ^{117}Sn -NMR titration data do not rule this out. However, *Noyori* and co-workers have shown that the stability of $[R_3SnXCl]^-$ is higher than that of $[R_3SnX_2]^-$ and $[R_3SnCl_2]^-$ [30].

^{117}Sn -NMR Titrations and Association Constants. To experimentally support the above proposal, ^{117}Sn -NMR titrations were performed on the selected compounds 3 and 6–11. This choice was based on the following: first, compound 3 exhibits the

highest potentiometric chloride response, while **9**–**11** show the lowest ones (see *Fig. 2*). Examining these compounds, the question of whether this duality is associated with a strong contrast between their association constants towards chloride can be elucidated. Second, compounds **3** and **6** differ only in a Ph group of the former being replaced by a pentafluorophenyl group. The influence of the pentafluorophenyl group on the binding constants can be investigated for derivatives where the C_6F_5 group is not directly bound to the carboxyl function. Similarly, compounds **7** and **10**, with pentafluorophenyl and phenyl groups, respectively, now directly bound to the carboxyl C-atoms, are investigated. Finally, a comparison between **3**, **6**, and **7** can determine whether the ‘abnormal’ behavior of compound **7** is associated with similarly low association constants of the tributyltin carboxylates **3** and **6**.

As an example, the experimental titration curve of compound **6** by $(Bu_4N)Cl$ is shown in *Fig. 3*. Such a graph provides the ^{117}Sn chemical shift of the averaged ^{117}Sn resonance of the mixture as a function of increasing analytical Cl^-/R_3SnX molar ratio. The single ^{117}Sn resonance observed indicates a fast chloride exchange on the ^{117}Sn NMR time scale. The shift of the ^{117}Sn resonance to lower frequency upon increase of the chloride-ion concentration indicates the expected increasing molar fraction of the Cl^- adduct $[R_3SnXCl]^-$ in the fast-equilibrium mixture. Assuming that the asymptotic ^{117}Sn chemical shift observed at high Cl^- concentration (-60 ppm) can be ascribed entirely to the presence of the adduct, and taking into account the chemical shift of the pure free species ($+120$ ppm), *Fig. 3* indicates that the equilibrium mixture consists of equal amounts of free species R_3SnX and Cl^- adduct $[R_3SnXCl]^-$ for an observed chemical shift of $+30$ ppm, achieved with an analytical molar ratio Cl^-/R_3SnX of *ca.* 0.8. Under these conditions, $k_{forward}[Cl^-]_e = k_{backwards}$.

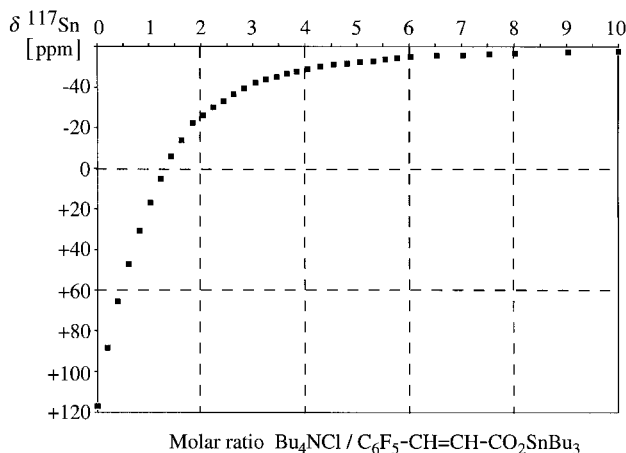


Fig. 3. ^{117}Sn -NMR Titration curve of a CD_2Cl_2 solution of **6** to which increasing aliquots of Bu_4NCl are added. The chemical shifts on the ordinate represent the resonance frequency of the averaged ^{117}Sn signal observed, indicating a fast-exchange regime between the starting compound **6** and its Cl^- adduct.

The intrinsic difference of 180 ppm in resonance frequencies between the free species R_3SnX and the Cl^- adduct $[R_3SnXCl]^-$ corresponds to *ca.* 16000 Hz at 89.15 MHz ^{117}Sn resonance frequency. Because a single, exchange-averaged, relatively

narrow ^{117}Sn resonance is observed in the titration spectra, meaning that the chemical exchange is relatively fast on the ^{117}Sn -NMR time scale, and, far beyond the resonance coalescence area, the value of 16000 s^{-1} can be considered as the lowest limit of the value of $k_{\text{forward}}[\text{Cl}^-] = k_{\text{backwards}}$ ($\gg 16000\text{ s}^{-1}$).

Table 3 shows the association constants obtained from a nonlinear fit of the titration curves obtained from CD_2Cl_2 solutions of compounds **3**, **6**, **8**, **9**, and **11** to which increasing amounts of tetrabutylammonium chloride have been added in molar ratios $\text{Cl}^-/\text{R}_3\text{SnX}$ of up to 10:1. Compound **11** exhibits a very high association constant towards chloride and a low potentiometric response. It is thus concluded that lower potentiometric chloride responses are indeed associated with higher association constants and *vice versa*, as most appropriately confirmed by the lowest K value of compound **3**, with the highest potentiometric response. This corroborates the proposal that low rate constants for the elimination of chloride from the Cl^- adduct ($k_{\text{backwards}}$) (reflected by the very high association equilibrium constant), hinder large potentiometric response to chloride.

Table 3. Association Constants of Carboxylates **3**, **6**, **8**, **9**, and **11** towards Chloride in CD_2Cl_2 . The values are given together with the standard error of the fit.

	3	6	8	9	11
$K [\text{M}^{-1}]$	4.8 ± 0.1	14.2 ± 0.3	111 ± 34	103 ± 14	475 ± 61

Comparison of the association constants of compounds **3** and **6** confirm that the pentafluorophenyl group induces (to a limited extent) a higher association between the carboxylate and the chloride anion than the corresponding non-fluorinated phenyl group. Compounds **8** and **9**, on the other hand, exhibit medium to high association constants, with low overall potentiometric responses. It is thus clear that the correlation between the potentiometric responses and the association constants should be considered with care, and at a semiquantitative level only. Additionally, the slight decrease in the potentiometric response associated with the increase in the association constant when the Ph group of **3** is replaced by the C_6F_5 group in **6** should not be overstated. Based on these considerations, the presented data indicates that a chemical system with high reversibility, *i.e.*, an association constant which is not too different from 1, is ideally suited as the basis for the development of potentiometric sensors.

The appearance of very fine precipitates observed when carriers **7** and **10** are used in the NMR titrations suggests that the complexation of these compounds with the chloride ion lead to more complicated systems. This justifies the large errors accompanying the association constant for **7** ($K = 144 \pm 48$), and the inability to measure the association constant for **10**. The titration curve for compound **10** exhibits a very steep drop in chemical shift with a subsequent asymptotic leveling-off upon the addition of Cl^- close to a ratio of 1:1. This suggests a high association constant (> 1000), much larger than observed with the other compounds.

It is thus concluded that small association constants (highly reversible systems) lead to better potentiometric behavior, as illustrated by compounds **3** and **6**. On the other hand, large association constants are not desirable (compounds **8**, **9**, and **11**) since they may lead to electrode surface overload [31] and possible precipitation.

Structure and Association Constants for $[ZCO_2ClSnR_3]^-$ Adducts by AM1 Calculations. To get a more precise insight into the structure of the adducts of such compounds, structure calculations *in vacuo* were performed on the starting free triorganotin carboxylates, **3**, **6**, **7**, and **10** as well as on their chloride complexes. The results are shown in Table 4, together with $^1J(^{13}C, ^{119/117}Sn)$ coupling constants obtained from ^{13}C -NMR data. Fig. 4 shows the structures towards which the AM1 calculations converge, both for the carboxylate and the corresponding Cl^- adducts.

Table 4. *Structural and Energetic Data Obtained by AM1 Calculations and $^1J(^{13}C, ^{119/117}Sn)$ Coupling Constants [Hz] Obtained from ^{13}C -NMR Spectra for the Compounds **3**, **6**, **7**, and **10***

$^1J(^{13}C, ^{119/117}Sn)$	Distances		Mulliken populations				Total energies [eV]		$\Delta E (E_{SnCl^-} - E_{Sn} - E_{Cl^-})^a$	
	Sn–O(1)	Sn–O(2)	Sn–Cl	O(1)	O(2)	Cl	Sn			
3	357/340	2.268	2.347	–	–0.486	–0.467	–	1.151	–3882.782	
3 / Cl^-	501/479	2.394	2.412	2.398	–0.488	–0.490	–0.565	1.268	–4259.601	–1.731
6	356/340	2.268	2.371	–	–0.472	–0.467	–	1.149	–6239.106	
6 / Cl^-	499/475	2.416	2.433	2.393	–0.481	–0.486	–0.555	1.261	–6616.106	–1.911
7	650/620	2.243	2.371	–	–0.478	–0.467	–	1.341	–4198.302	
7 / Cl^-	850/813	2.373	2.386	2.375	–0.484	–0.490	–0.524	1.400	–4575.377	–1.987
10	644/614	2.243	2.371	–	–0.443	–0.467	–	1.344	–6554.448	
10 / Cl^-	838/804	2.383	2.472	2.368	–0.469	–0.472	–0.507	1.392	–6931.764	–2.228

^a) $E_{Cl^-} = -375.088$ eV.

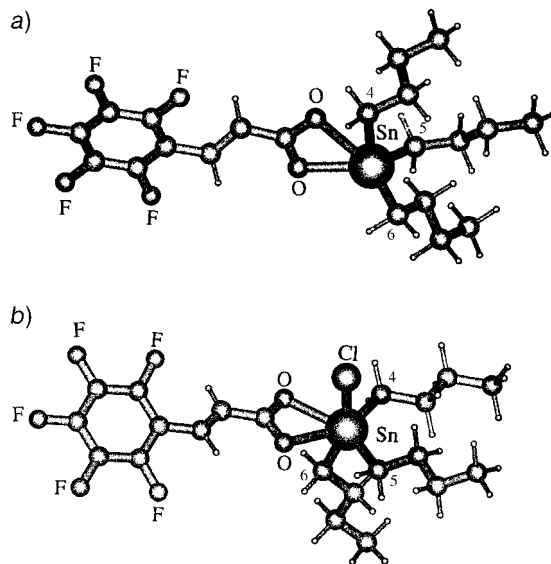


Fig. 4. *Structures obtained from in vacuo AM1 calculations a) for the ZCO_2SnR_3 derivative **6** and b) for its corresponding Cl^- adduct. Structural characteristics of the similar derivatives **3**, **7**, and **10** are given in Table 4.*

The $^1J(^{13}C, ^{119/117}Sn)$ coupling constants for the Cl^- adducts observed in the ^{13}C -NMR spectra of the mixture R_3SnX/Cl^- 1:10 are characteristic for mono-adducts of triorganotin carboxylates [23–27]. The AM1 structures obtained for the free

triorganotin carboxylates are best described as distorted tetrahedral molecules, in which the distortion is due to the additional coordination by the carboxylate atom O(2). The difference between the Sn–O(1) and Sn–O(2) bond lengths is 0.079, 0.104, 0.127, and 0.188 Å for **3**, **6**, **7**, and **10**, respectively, in agreement with the increasing *Lewis* acidity qualitatively predicted by the association constants from the NMR-titration data. Indeed, because the bond length between Sn and the ‘second’ O-atom becomes increasingly larger with respect to that of the ‘first’ Sn–O bond, the binding ability of chloride to Sn should increase, from both the points of view of Sn *Lewis* acidity and steric access of the anion. The increasing stabilization energy of the chloride complexation reaction in the order **3** < **6** < **7** < **10** (Table 3) is in agreement with this proposal, while it follows the trend of the increasing association constants. On the other hand, it should be noted that the difference between the Sn–O(1) and Sn–O(2) bonds found by AM1 calculations for **7** (2.243 and 2.371 Å, resp.) is not in agreement with that found for **7** in the crystalline state (2.073(3) and 2.674(3) Å, resp.) [20]. It should be remembered, however, that AM1 structures are obtained *in vacuo*. Moreover, it is well known [32] that, in solution, only a single ¹⁷O resonance is found for triorganotin carboxylates, reflecting a fast oxygen-tin exchange on the ¹⁷O-NMR time scale, which points to a carboxylate–tin bonding scheme similar to that obtained from the AM1 calculations in the non-crystalline environment, and not to that in the crystalline state. Similar values were, however, obtained when averaging the Sn–O bond lengths found by AM1 calculations and X-ray diffraction, 2.307 and 2.373 Å, respectively, revealing globally comparable *Lewis* acidities both *in vacuo* and in the crystalline state.

The C(4)–Sn–C(5) and C(5)–Sn–C(6) angles of the free triorganotin carboxylates are close to the ideal tetrahedral angles, being between 112 and 113° for the Bu₃Sn compounds **3** and **6**, and between 108.4 and 109.5° for the Ph₃Sn compounds **7** and **10** (C(4), C(5), and C(6) denote the C-atoms of the three R groups Bu or Ph directly bound to the Sn-atom). The distortion from the ideal tetrahedral geometry is best reflected by the larger C(4)–Sn–C(6) angles, 118° for the Bu₃Sn compounds and 115–116° for the Ph₃Sn ones.

The AM1 structures of the Cl[–] adducts are best described as distorted octahedra with *fac*-configuration, the three electronegative substituents constituting one triangular face, the three organic R groups being located on the opposite triangular face of the pseudo-octahedron. The difference between the Sn–O(1) and Sn–O(2) bond lengths of 0.018, 0.017, 0.013, and 0.089 Å for the Cl[–] adducts of **3**, **6**, **7**, and **10**, respectively, are significantly smaller than in the parent compounds. Compound **10**, however, displays obviously a higher Sn–O bond length difference, maybe in relation to its dramatically larger association constant. The strong distortion from the ideal octahedron is illustrated by the fact that the C(4)–Sn–C(5) and C(5)–Sn–C(6) angles of the adducts are close to one another for all four compounds (96–99°), while the C(4)–Sn–C(6) angle lies between 117 and 118° for the Bu₃Sn compounds, and between 113 and 114° for the Ph₃Sn compounds. The Cl-atom is in the *cis* position with respect to the atoms C(4) and C(5) (C(4)–Sn–Cl and C(5)–Sn–Cl angles between 91 and 93°), in contrast with the C(6) atom which is in the *trans* position (C(6)–Sn–Cl angle between 158 and 160° for the Bu₃Sn compounds, and between 161 and 164° for the Ph₃Sn compounds), although the angle distortion with respect to the ideal angle of 180° is rather large.

Finally, structural data are assessed in view of the electronic distribution in the complexes. Upon formation of an electron donor-acceptor complex between the organotin compound and chloride, the amount of charge transferred from Cl^- (Table 4) increases with increasing stability of the complex (decreasing Sn–Cl distance). In all cases, the positive charge on Sn increases upon complexation, reflecting the well-known spill-over effect [33]. Most remarkably, the increase in positive charge in compounds **3** and **6** is much larger than in **7** and **10**, indicating that the Bu groups show a stronger charge stabilization effect as compared to the Ph group. Taking into account the *in vacuo* nature of AM1 calculations, this sequence can be traced back to the softness of the alkyl group enabling it to adopt an electron-accepting role when located next to a highly charged atom [34][35]. Finally, O(1) and O(2) show a tendency to get closer to each other upon complexation due to the geometrical rearrangement of the complex from trigonal bipyramidal to octahedral coordination, making their overall charge more negative.

Conclusion. – In this work, a series of *Lewis*-acidic tributyl- and triphenyltin benzoates, phenylacetates, and cinnamates, with or without the perfluorophenyl group in the carboxylate moiety, are examined to assess possible correlations between their observed potentiometric chloride sensitivity and their binding constant to this anion. The potentiometric data combined with ^{117}Sn -NMR titration plots and theoretical AM1 calculations show that the observed potentiometric response is related to the binding constant, at least in a semiquantitative manner. Carriers with very high binding constants show lower potentiometric response, stressing the fact that finding the optimum binding constant values between the organometallic carrier and the anion of interest is very important in sensor design. The information obtained provides the basis for a process to allow accurate tuning of binding constants of similar anion carriers to desired value ranges, for increased detection limit and improved selectivity, whenever potentiometric, optical, or other chemical sensors are to be developed and optimized.

Experimental Part

1. *Electrochemical Measurements. Apparatus.* Potentiometric measurements were performed with a CI-317 8-channel electrometer from Xenon (Halandri, Athens, Greece) vs. a 900200 double-junction reference electrode from Orion Research (Beverly, MA, USA). The data were collected with a personal computer, with a program written in BASIC, for storage and further analysis.

Reagents. Nanopure water (18.3 M Ω) and potassium chloride of high purity (*Fluka, p.a.*) were used for the preparation of the electrolyte solutions. Morpholine-2-ethanesulfonic acid (MES) (*Merck*) was used to prepare the pH buffer. For the membrane setup, polyvinylchloride (PVC) (high molecular weight, *Selectophore*[®]; *Fluka*) was used as a membrane matrix, bis(2-ethylhexyl) sebacate (= bis(2-ethylhexyl) decanedioate; DOS) (*Selectophore*[®]; *Fluka*) as a plasticizer, and tetrahydrofuran (THF; *p.a., Merck*), distilled before use, as a membrane solvent.

Membranes. All the membranes examined had the following composition: 5% of carrier, 31.5% of PVC, and 63.5% of DOS. The mixture of the components (100 mg) was dissolved in THF (*ca.* 1.5 ml), the soln. poured into a glass ring (i.d. 17 mm), the latter being placed on a glass plate, and the THF allowed to evaporate slowly. The membranes were formed after evaporation of the solvent. Circular pieces (diameter 7 mm) of the membranes were cut out and mounted on *Phillips* electrode bodies of the type IS 561 (*Glasbläserei Willi Möller AG, Zürich, Switzerland*) for testing. The internal solution of the electrodes for all membranes was 0.1M KCl.

Potentiometric Measurements. All electrodes were tested without any prior pretreatment, except when specifically mentioned. The potential changes reported represent the anionic response obtained by dipping the electrode system (working and reference electrodes) successively into a double-wall thermostatic beaker

containing 10 mM MES buffer pH 5.50 (50.0 ml) and 0.01M KCl (50.0 ml) in the same buffer. The potentiometric response recorded is the difference between the potential in the buffer and that of the buffer with 0.01M KCl, giving rise to positive numerical values. Each measurement was taken three times, and the mean value is reported with a standard deviation of max. 5 mV. The potentiometric responses to a series of other anions reported in *Table 2* were obtained in the same manner.

2. *Triorganotin Compounds*. The synthesis and structural characterization of the tributyl- and triphenyltin benzoates, phenylacetates, and cinnamates containing [19] or not containing [20] the perfluorophenyl group in the carboxylate moiety, have been described previously [19][20].

3. *NMR Measurements*. The ^{117}Sn -NMR data were recorded on a *Bruker-AC-250* spectrometer operating at 89.15 MHz for ^{117}Sn -nuclei, with 0.5 ml of CD_2Cl_2 solutions containing 40 mg (91 μmol) of **3**, 40 mg (76 μmol) of **6**, 28 mg (60 μmol) of **7**, 49 mg (100 μmol) of compound **8**, 40 mg (81 μmol) of **9** and 58 mg (100 μmol) of **11**, to which increasing aliquots of $(\text{Bu}_4\text{N})\text{Cl}$ were added in molar ratios up to 1:10. The chemical shifts were referenced to $\bar{\nu} = 35.632295$ MHz [36]. ^{117}Sn rather than the more common ^{119}Sn spectra were recorded to overcome local radio interferences around 93.2 MHz [37][38]. Comparing ^{117}Sn and ^{119}Sn data generates no misinterpretation, since $^{117}\text{Sn}/^{119}\text{Sn}$ isotopic effects are negligible [39].

The stability constants K were obtained by nonlinear least-square fitting (in ORIGIN 4.0 for Windows 3.1) with the experimental values of a two-parameter nonlinear model of a 1:1 complexation [40].

4. *Quantum-Chemical Calculations*. In view of both the relatively large size of the structures and the presence of an Sn-atom, a semi-empirical method was chosen for the energy and charge-distribution calculations. The AM1 method [41], for which the parameters for Sn have only recently been published [42], was selected, for its efficient applicability to a very wide range of chemical problems [43] and its successful application in structure-reactivity studies of tin compounds [44][45].

Both geometry optimizations and single-point calculations were performed using the GAUSSIAN92 program [46] coupled to the UNICHEM [47] software package. The charge distributions were analyzed in terms of the Mulliken atomic populations [48]. All calculations were performed on the *Cray-Y-MP/116* computer of the Free Universities of Brussels Computer Center.

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REFERENCES

- [1] J. M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 89.
- [2] B. Dietrich, *Pure Appl. Chem.* **1993**, 65, 1457.
- [3] P. Bühlmann, E. Pretsch, E. Bakker, *Chem. Rev.* **1998**, 98, 1593.
- [4] U. Wuthier, H. V. Pham, R. Zünd, D. Welti, R. Funck, A. Bezegh, D. Ammann, E. Pretsch, W. Simon, *Anal. Chem.* **1984**, 56, 535.
- [5] M. Nanjo, T. J. Rohm, G. C. Guilbault, *Anal. Chim. Acta* **1975**, 77, 19.
- [6] V. M. Shkinev, B. Y. Spivakov, G. A. Varobeva, Y. A. Zolotov, *Anal. Chim. Acta* **1985**, 167, 145.
- [7] K. Fluri, J. Koudelka, W. Simon, *Helv. Chim. Acta* **1992**, 75, 1012.
- [8] S. A. Glazier, M. A. Arnold, *Anal. Chem.* **1988**, 60, 2542.
- [9] S. A. Glazier, M. A. Arnold, *Anal. Chem.* **1991**, 63, 754.
- [10] R. L. DeMeulenaere, P. Onsrud, M. A. Arnold, *Electroanalysis* **1993**, 5, 833.
- [11] N. A. Chaniotakis, K. Jurkschat, A. Rühlemann, *Anal. Chim. Acta* **1993**, 282, 345.
- [12] J. K. Tsagatakis, J. A. Chaniotakis, K. Jurkschat, *Helv. Chim. Acta* **1994**, 77, 2191.
- [13] D. Liu, W. C. Chen, G. L. Shen, R. Q. Yu, *Analyst* **1996**, 121, 1495.
- [14] M. J. Selwyn, in 'Organotin Compounds: New Chemistry and Applications', Ed. J. J. Zuckermann, ACS Washington, DC, 1976, pp. 204–225.
- [15] H. V. Pham, E. Pretsch, K. Fluri, A. Bezegh, W. Simon, *Helv. Chim. Acta* **1990**, 73, 1894.
- [16] U. Wuthier, H. V. Pham, B. Rusterholz, W. Simon, *Helv. Chim. Acta* **1986**, 69, 1435.
- [17] N. A. Chaniotakis, S. B. Park, M. E. Meyerhoff, *Anal. Chem.* **1989**, 61, 566.
- [18] N. A. Chaniotakis, K. Jurkschat, A. Rühlemann, *Anal. Chim. Acta* **1993**, 282, 345.

- [19] R. Willem, A. Bouhdid, M. Biesemans, J. C. Martins, D. de Vos, E. R. T. Tiekink, M. Gielen, *J. Organomet. Chem.* **1996**, *514*, 203.
- [20] R. Willem, A. Bouhdid, M. Biesemans, B. Mahieu, D. de Vos, E. R. T. Tiekink, M. Gielen, *J. Organomet. Chem.* **1997**, *531*, 151.
- [21] E. R. T. Tiekink, *Appl. Organomet. Chem.* **1991**, *5*, 1.
- [22] E. R. T. Tiekink, *Trends Organomet. Chem.* **1994**, *1*, 71.
- [23] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, *J. Organomet. Chem.* **1983**, *241*, 177.
- [24] M. Nadvornik, J. Holecek, K. Handlir, A. Lycka, *J. Organomet. Chem.* **1984**, *275*, 43.
- [25] A. Lycka, J. Holecek, M. Nadvornik, K. Handlir, *J. Organomet. Chem.* **1985**, *280*, 323.
- [26] J. Holecek, K. Handlir, M. Nadvornik, A. Lycka, *J. Organomet. Chem.* **1983**, *258*, 147.
- [27] A. Lycka, M. Nadvornik, K. Handlir, J. Holecek, *Czech. Chem. Commun.* **1984**, *49*, 1497.
- [28] J. T. B. H. Jastrzebski, G. Van Koten, *Adv. Organometal. Chem.* **1993**, *35*, 241.
- [29] M. Beuter, U. Kolb, A. Zickgraf, E. Bräu, M. Bletz, M. Dräger, *Polyhedron* **1997**, *16*, 4005.
- [30] M. Suzuki, J.-H. Son, R. Noyori, H. Masuda, *Organometallics* **1990**, *9*, 3043.
- [31] W. E. Morf, in 'The Principles of Ion-Selective Electrodes and of Membrane Transport', Akademiai Kiado, Budapest, and Elsevier, Amsterdam, 1981, p. 269.
- [32] A. Lycka, J. Holecek, *J. Organomet. Chem.* **1985**, *294*, 179.
- [33] V. Gutmann, 'The Donor-Acceptor Approach to Molecular Interactions', Plenum Press, New York, 1978.
- [34] G. Vanermen, S. Toppet, M. Van Beylen, P. Geerlings, *J. Chem. Soc., Perkin Trans. 2* **1986**, 699.
- [35] F. De Proft, W. Langenaeker, P. Geerlings, *Tetrahedron* **1995**, *51*, 4021.
- [36] J. Mason, in 'Multinuclear NMR', Plenum Press, New York, 1987, p. 627.
- [37] B. R. Koch, G. V. Fazakerley, E. Dijkstra, *Inorg. Chim. Acta* **1980**, *45*, L51.
- [38] P. G. Harrison, in 'Chemistry of Tin', Ed. P. G. Harrison, Blackie & Son Limited; Glasgow, 1989; Chapt. 3, p. 113.
- [39] H. C. E. McFarlane, W. McFarlane, C. J. Turner, *Mol. Phys.* **1979**, *37*, 1639.
- [40] K. A. Connors, in 'Binding Constants, the Measurement of Molecular Complex Stability', John Wiley & Sons, Chichester, 1987, p. 189.
- [41] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- [42] M. J. S. Dewar, E. F. Healy, D. R. Khun, A. J. Holder, *Organometallics* **1991**, *10*, 431.
- [43] M. J. S. Dewar, C. Jic, J. Yu, *Tetrahedron* **1993**, *49*, 5003.
- [44] M. Biesemans, R. Willem, S. Damoun, P. Geerlings, M. Lahcini, P. Jaumier, B. Jousseau, *Organometallics* **1996**, *15*, 2237.
- [45] M. Biesemans, R. Willem, S. Damoun, P. Geerlings, E. R. T. Tiekink, P. Jaumier, M. Lahcini, B. Jousseau, *Organometallics* **1998**, *17*, 90.
- [46] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Repogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, 'GAUSSIAN 92, Revision C4', Gaussian Inc., Pittsburgh PA, 1992.
- [47] UNICHEM, Cray Research Inc., Eagon MN, **1994**.
- [48] R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833.

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