190. Multiorganyltin Compounds. Designing a Novel Phosphate-Selective Carrier

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A series of distannyl derivatives, **1**–**9**, were studied for their application as phosphate-selective carriers in polymer-based liquid membranes. A drastically different potentiometric behavior was observed depending on the distance between the tin(IV) coordinating centers and the ligands attached to them. Some of the compounds examined, *i.e.* $(PhSnBr_2)_2CH_2$ (**1**) and $(Me_3SiCH_2SnCl_2CH_2)_2CH_2$ (**3**) showed very high potentiometric selectivity towards phosphate over other lipophilic anions such as perchlorate and thiocyanate. Results indicate that *1*) the optimal number of CH_2 groups between the Sn-centers are either one or three, *2*) the electron-withdrawing power of the organic ligands attached to Sn-centers strongly influences the overall response towards phosphate, and *3*) the steric effect of the organic substituents is important in the potentiometric selectivity observed.

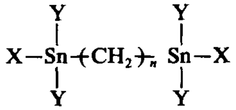
Introduction. – The search for selective anion carriers has recently focused on the coordinating organometallic complexing agents, some of which containing mercury [1], tin [2], manganese [3], and ruthenium [4] moieties. When such *Lewis* acidic species were employed as carriers in liquid membranes, they showed selectivities that clearly deviate from the classical *Hofmeister* selectivity series [5] $ClO_4^- > IO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > NO_2^- > HCO_3^- > SO_4^{2-} > H_2PO_4^-$.

The design of a carrier for selective recognition of orthophosphates is not a trivial matter, due mainly to two reasons: *a*) The free energy of hydration of orthophosphate (*ca.* −95° cal/mol) [6] is much smaller than that of other oxoanions such as perchlorate (*ca.* −50° cal/mol) [7] and *b*) the large size of this anion prohibits the use of size-exclusion principles for increased selectivity. For these reasons, and to design a phosphate carrier, the sum of the free energy of interaction or ligation with the carrier combined with the negative free energy of hydration has to be higher than that of any interfering ions. Another difficulty arises from the fact that the tetrahedral geometry of the orthophosphate ion closely resembles that of the perchlorate and sulfate while the sizes of all three are very similar. The selective phosphate carrier would thus have to have certain distinct characteristics which are: *a*) a strong ligation energy towards orthophosphate to overcome its high negative energy of hydration, and *b*) the right shape of accommodate the ion and to take advantage of the multidentate effect.

There are two characteristics of the phosphate anion that can be utilized for the design of a phosphate carrier, which are: *a*) the formation of multiple H-bonding between the four O-atoms of the phosphate and any surrounding H-atoms [8], and *b*) the ability of the phosphate O-atoms to form stronger metal complexes than those with similar structures such as perchlorate and sulfate with the order being phosphate > perchlorate > sulfate [9].

Our efforts were directed toward the development of a synthetic phosphate carrier by the utilization of the high affinity for coordination of the phosphate O-atoms toward Sn^{IV}. The effect of the number of Sn-atoms to the overall response towards many anions was already examined [2]. Here we report on the effect of the distance between the Sn-centers, a parameter that is controlled by the number of CH_2 groups employed to connect these coordinating centers, and on the effect of the organic substituents attached to them.

Results and Discussion. – The multidentate organotin compounds **1**–**9** were examined from the view of their potentiometric anion response by incorporation in PVC-plasticized membranes.



$X{-}SnY_2{-}(CH_2)_n{-}SnY_2{-}X$

	X	Y	*n*	Ref.
1	Ph	Br	1	[10]
2	Ph	Br	2	[11]
3	Me_3SiCH_2	Cl	3	[12]
4	Me_3SiCH_2	Cl	4	[13]
5	Cl	Me	1	[14]
6	Cl	Me	3	[15]
7	Bu	Cl	1	[16]
8	Cl	Ph	1	[10]
9	Cl	Ph	2	[11]

The selectivity factors ($k^{\mathrm{pot}}_{\mathrm{H_2PO_4^-,X^-}}$; see *Exper. Part*) show the preference of the membranes towards phosphate over other interfering anions. All membranes exhibit selectivities that clearly deviate from the *Hofmeister* series, a behavior that is substantiated also by the electrode-response characteristics of the carriers presented in the *Table* and *Fig. 1* [17].

Table. *Overall Potentiometric Response of Carriers*[a])

Anion	Carrier								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$H_2PO_4^-$	-284	-129	-290	-143	-92	-50	-26	-29	-16
ClO_4^-	-90	-52	-118	-99	-19	-15	-120	-34	-53
SO_4^{2-}	-61	-51	-48	-52	-23	-30	-50	-41	-19
SCN^-	-166	-88	-128	-203	-29	-20	-218	-217	-228
I^-	-89	-62	-128	-86	-19	-22	-146	-72	-76
Cl^-	-39	-34	-112	-59	-10	-15	-91	-41	-45
F^-	-70	-59	-124	-104	-51	15	-110	-229	-180

[a]) Overall potentiometric response in mV for liquid polymeric membrane electrodes based on carriers **1**–**9**, in 0.01M MES/NaOH pH 5.5 at $9.1 \cdot 10^{-3}$ M anion concentration.

Initially, the distance between the Sn-centers was examined (*Fig. 2*). The possibility for bidentate ligation is determined by two carrier characteristics: *a*) the Sn-centers should have the appropriate conformation to each other and *b*) the distance between the coordinating centers should be close to the distance of the phosphate O-atoms. *Fig. 2a* shows that, even though both carriers **1** and **2** are phosphate selective, carrier **1** exhibits an

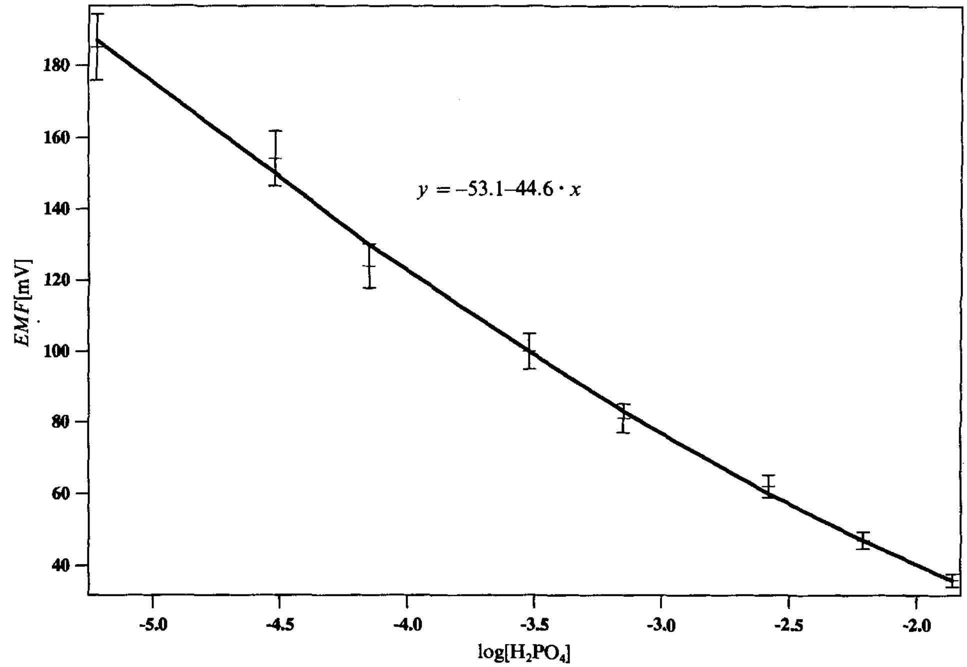


Fig. 1. *Electrode function towards phosphate of a cell assembly with a membrane based on carrier* **1** *measured in MES/NaOH* (0.01M pH 5.5)

even higher selectivity towards this anion. For carrier **2**, the Sn-centers are in antiperiplanar position, and the molecule must thus be rotated to the thermodynamically unfavorable synperiplanar conformation to act as bidentate ligand. The same conclusion is obtained, when the results for the carriers **3** and **4** are compared (*Fig. 2b*). In addition to the unfavorable conformation for bidentate coordination of carrier **4** (antiperiplanar) as compared to that of **3** (synperiplanar), the distance of the two Sn-atoms is increased by one CH_2 group in **4** allowing also monodentate interaction. These results indicate that an odd number of C-atoms (1 or 3) provides the appropriate conformation to the carrier for suitable phosphate binding. To determine the optimal number of CH_2 groups between the Sn-centers, the selectivity patterns of carriers **5** and **6** are compared (*Fig. 2c*). Even though the selectivity coefficients of these carriers are closer together in comparison with those of **1** and **3**, carrier **5** has a better potentiometric behavior, suggesting that one CH_2 group provides the preferred distance between coordinating centers for a selective phosphate response. This could originate from a balance between optimal distance of the Sn-centers and minimal steric hindrance from the H-atoms of the CH_2 groups. This is also supported by the results obtained with carriers **1** and **3** (*Fig. 2a* and *2b*), even though the ligands attached to the Sn-atoms are not identical.

Carriers with two organic substituents on the Sn-centers show worse selectivities than their counterparts with one because the former are weaker *Lewis* acids. This is in accordance with results obtained by *Wuthier et al.* [18] which indicate that distannyl compounds with trialkyltin centers are not active as anion-selective ionophores, probably

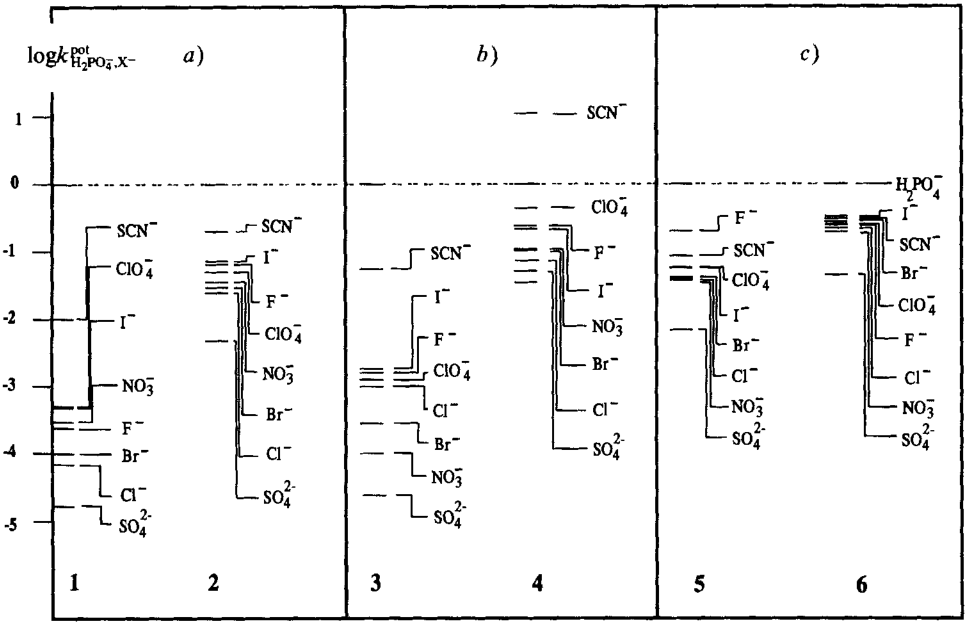


Fig. 2. *Effect of the number of* CH_2 *groups between tin coordinating centers on the membrane anion selectivity sequence expressed by experimental selectivity coefficients* ($k^{pot}_{H_2PO_4^-,X^-}$): a) *one and two* CH_2 *groups*, b) *three and four* CH_2 *groups, and* c) *one and three* CH_2 *groups*

due to the low acidity of the Sn-center. It has also been reported that the kind of the electronegative substituent (Cl, Br) attached to Sn-centers does not greatly influence the function of the organotin carriers [19], a fact that is also corroborated by our results. On the other hand, the kind of the organic substituents and especially their structures [19] as well as their electron-withdrawing power [20] determine the complexing behavior of these compounds. *Fig. 3* shows the effect of the organic groups on the anion selectivity of multidentate organotin carriers. Carrier **1** with a Ph group as organic substituent shows an extremely different selectivity pattern from carrier **7** with a Bu group attached to each Sn-center (*Fig. 3a*). Electron-withdrawing groups such as Ph favor the response towards phosphate, while electron-donating groups such as Bu do not. However, changing the Me groups of carrier **5** to Ph groups (carrier **8**), the selectivity for phosphates diminishes while an extraordinarily high preference towards F^- is observed (*Fig. 3b*). Although carrier **8** is a better *Lewis* acid than **5**, the bulky Ph groups do not allow the ligation to Sn-centers by a large anion, such as phosphate. On the other hand, F^-, a small anion and a good *Lewis* base, can form stable complexes with Sn^{IV} [21a, b] (complexes of **8**, **9**, and related compounds with F^- were isolated and characterized by X-ray analyses [21c]). The steric shielding is also supported by the fact that by increasing the distance between the Sn-atoms (see **9** in *Fig. 3b*), the response for F^- decreases, while the response towards larger and more lipophilic anions (I^-, ClO_4^-) increases.

Conclusions. – A careful design of the Sn-based carriers can bring the binding to the highly hydrophilic anion of phosphates to the top of the *Hofmeister* series. The parame-

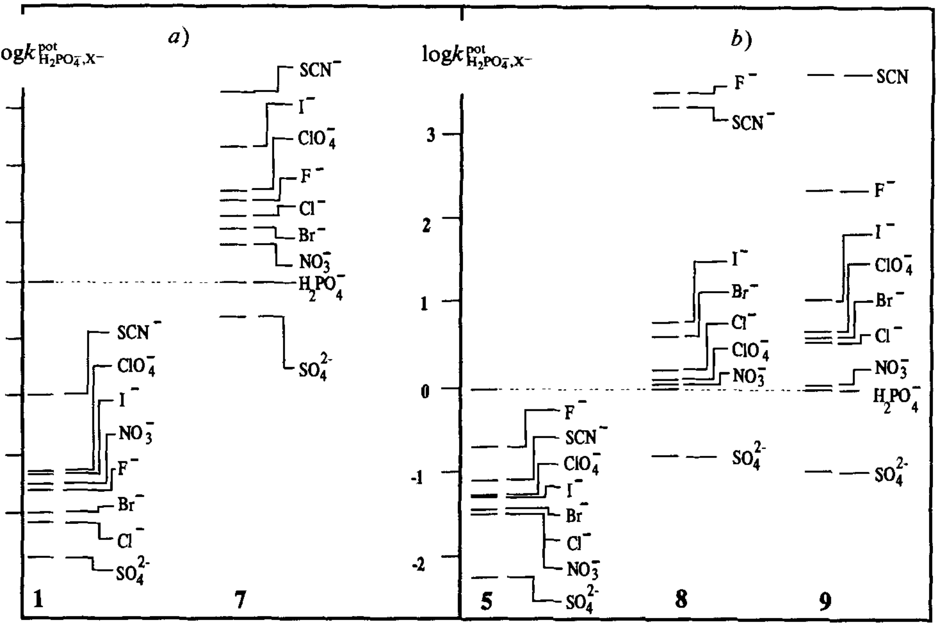


Fig. 3. *Experimental selectivity coefficients* ($k^{pot}_{H_2PO_4^-,X^-}$) *of multidentate organotin compounds with different organic substituents attached to the Sn-centres showing:* a) *the electron-withdrawing effect and* b) *the steric effect of the organic substituents*

ters that control this binding are: *i*) One electron-withdrawing organic substituent is needed on the Sn-centers to obtain great selectivity for phosphates. *ii*) An odd number of CH_2 groups between Sn-atoms is preferable for optimal phosphate response. *iii*) Carriers with two electronegative substituents (Cl, Br) on each Sn atom show better selectivity coefficients than those with one.

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Experimental Part

Apparatus. Potentiometric data were recorded using a single-channel system; the signal from an expandable ion analyzer *E940* (*ATI Orion*, Boston, USA) was recorded on a *Gow-Mac 70-150* strip-chart recorder. A potentiometric system of the following type was used:

Hg, Hg_2Cl_2; KCl (satd.) ‖ sample soln. | membrane | 0.1 M KCl; AgCl, Ag

The external half cell was a double-junction calomel reference electrode.

Membranes. All membranes examined were of the same composition (*w*/*w*): 2% of carrier, 33% of PVC, and 65% of DOS. The mixture of the components (100 mg) was dissolved in *ca.* 2 ml tetrahydrofuran, the soln. poured in a glass ring (i.d. 17 mm), the latter 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 off and mounted on *Phillips* electrode bodies type *IS 561* (*N.V. Philips' Gloeilampenfabrieken*, Eindhoven, Holland) for testing.

Reagents. The carriers were synthesized according to the published procedures [9–15]. Doubly quartz-distilled H_2O and potassium or sodium salts of high purity (*p.a. Fluka, p.a. Merck*) were used for the preparation of electrolyte solns. As pH-buffer, 2-morpholinoethanesulfonic acid (MES, *Merck*) was used. For the membranes construction were used poly(vinyl chloride) (PVC; high molecular weight, *Selectophore, Fluka*) as membrane matrix, bis(2-ethylhexyl) sebacate (DOS; *Selectophore, Fluka*) as plasticizer, and tetrahydrofuran (*p.a. Merck*; distilled before use) as membrane solvent.

Selectivity Measurements. For the determination of selectivity factors ($k^{\mathrm{pot}}_{\mathrm{H_2PO_4^-,X^-}}$), the separate-soln. method was used [22]. In 25.0 ml of 0.01 M MES buffer pH 5.50, 2.5 ml of electrolyte soln. were added to bring the final concentration to $9.09 \cdot 10^{-3}$ M while the potential changes were recorded. For the calculation of the selectivity coefficient, the assumption was made that electrodes show a theoretical slope of −59.2 mV for monovalent, and of −29.6 mV for the divalent anions.

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