Phosphate-Binding Characteristics and Selectivity Studies of Bifunctional Organotin Carriers

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The selective recognition of the orthophosphate anion by a series of bifunctional *Lewis* acidic organotin compounds is investigated. The binding affinity of these carriers to anions, as measured by NMR titrations in CH_2Cl_2 obeyed the potentiometric selectivity order phosphate > sulfate > perchlorate, and provided the corresponding complex-formation constants. More accurate calculations of these values were obtained by the segmented-sandwich-membrane method performed directly inside the liquid polymeric membrane. These carriers were also studied potentiometrically in polymeric liquid membranes. The results indicate that $(PhBr_2Sn)_2CH_2$ is 2 to 5 orders of magnitude more selective towards phosphate over other oxoanions. These results set the ground for the development of a new series of highly selective anions carriers with a wide range of possible applications.

Introduction. – The design of a phosphate-selective carrier for applications in ion-selective electrodes (ISEs) [1–3] is not an easy task for various reasons. Phosphate, in contrast to other oxoanions such as perchlorate, nitrate, carbonate, or even sulfate, is very hydrophilic [4–5]. Additionally, it is large (PO_4^{3-}: 238 pm [6]), with a charge and chemical structure highly dependent on the pH. Its tetrahedral structure requires the use of a large, multifunctional substrate able to achieve a significant but reversible coordination. It is clear that, for a successful chemical recognition, the carrier used must have the following characteristics: appropriate topography, at least 2 ligation sites, and a labile interaction with the phosphate active sites (O- or H-atoms). Only under these conditions can complexation capable of overcoming the high-energy barrier of the phosphate transfer from the aqueous to organic phase be developed. Additionally, if these carriers are to be used in chemical sensors, the overall partitioning of the phosphate anion into the sensor-membrane phase should be larger than that of the other anions.

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Up until now, mainly two phosphate-recognition approaches have been utilized for the development of phosphate-selective carriers. The first is based on the multiple H-bonding of the phosphate O-atoms with the amine [7] or amide groups [8–10] of the carrier and the second on the complexation with the Sn^{IV} *Lewis* acidic centers of organotin compounds [11–17]. In the first case, H-bond-based phosphate electrodes show poor selectivity but relatively high stability and lifetime [10], while organotin-based phosphate electrodes show excellent selectivity but limited electrode stability and lifetime. Additionally, carriers based on *Lewis* acidic UO_2^+ centers with promising characteristics have also been recently reported [18].

Recently [15][16][19], we have reported on a range of multifunctional organotin compounds containing one to four Sn^{IV} centers with different halide ligands and different distances between the active Sn-sites undergoing anion coordination. These compounds have been evaluated as carriers in potentiometric ion-selective electrodes. It is interesting to note that the monodentate organotin compounds have been previously used as anion carriers for salicylate [20][21] and chloride [19][22]. Increasing the number of coordinating sites enabled one to obtain a remarkable selectivity towards phosphate. Attempts to correlate this behavior with carrier structural characteristics was unsuccessful, since the potentiometric data obtained were not very consistent, and thus did not allow easy carrier optimization [15].

Organoditin compounds have previously shown high potentiometric responses and excellent selectivity towards phosphate [16]. The structural characteristics that determine the selectivity are the distance, *i.e.* the number of CH_2 groups, separating the two Sn^{IV} centers and the substituent patterns, either organic or electronegative (halide), on the Sn-atoms. The highest selectivity was obtained when compounds containing two electronegative substituents (Cl or Br) and one organic group (Ph) on each Sn-center were used. This was explained by the fact that such compounds show considerable *Lewis* acidity that favors coordination to phosphate, while, at the same time, they have low steric hindrance for the effective interaction of the *Lewis* basic, bulky phosphate anion. *Liu et al.* later reported a similar group of phosphate carriers with promising results based on binuclear tin oxides [17].

In this work, a closer evaluation of a series of bifunctional organotin compounds is attempted. Anion-selectivity patterns, as studied by potentiometric measurements in ion-selective membranes, are shown to be dependent on the structural characteristics of the organotin compounds. The selectivities obtained from the potentiometric results are compared with the complex-formation constants obtained from organic-phase ^{117}Sn-NMR titrations [19][23] and those obtained from the segmented-sandwich-membrane method [24][25] in aqueous-organic solutions, used for the first time for anion-selective carriers.

Experimental. – *Instrumentation.* Potentiometric measurements were performed with a *Xenon CI-317* 8-channel electrometer (*Halandri*, Athens, Greece) *vs.* an *Orion Res.* (Beverly, MA, USA) *900200* double-junction reference electrode. The data were collected with a personal computer program written in BASIC for storage and further analysis. The potentiometric measurements for the segmented-sandwich-membrane method were obtained by a *Macintosh* computer equipped with a *LAB-MIO 16XL-42* 16 bit A/D I/O board (*National Instruments*, Austin, TX) and up to four battery-powered 4-channel high Z interface modules with built-in low pass filters (*World Precision Instruments*, Sarasota, FL) controlled by *LabView* software (*National Instruments*). ^{117}Sn-NMR Spectra: *Bruker AC-250* spectrometer; at 89.15 MHz for ^{117}Sn nuclei.

Reagents. Nanopure water (18.3 MΩ/cm) and potassium salts of high purity (*p.a.*, *Fluka*) were used for the preparation of the electrolyte solns. 2-Morpholinoethanesulfonic acid (= MES; *Merck*) was used to prepare the pH buffer. For the membrane cocktails, polyvinylchloride (= PVC; high molecular weight, *Selectophore*®; *Fluka*) was used as a membrane matrix, bis(2-ethylhexyl) sebacate (= DOS; *Selectophore*®; *Fluka*) as a plasticizer, and THF (*p.a.*, *Merck*), distilled before use, as a membrane solvent.

The synthesis of the organoditin compounds tested here as carriers has been described previously [26–31].

For the NMR titrations, CD_2Cl_2 (*Cambridge Isotopic Laboratories Inc*; isotopic purity grade > 99.9%) was used as a solvent, while the tetrabutylammonium salts (dihydrogen phosphate (97%; *Aldrich 26,809-7*), hydrogen sulfate (99%; *Sigma T-7158*), and perchlorate (*Sigma T-7283*)) were used for the titrations.

Membrane Preparation and Testing. All the membranes examined had the following composition: 2% of carrier, 33% of PVC, and 65% of DOS or TEHP (= tris(2-ethylhexyl) phosphate). When anionic additives were used, the wt.-% of the carrier and the plasticizer remained the same, lowering the amount of PVC accordingly. The mixture of the components (100 mg) was dissolved in *ca.* 1.5 ml of THF, the soln. poured into a glass ring (i.d. 2.2 mm), the latter being placed on a glass plate. The membranes were formed after solvent evaporation. Circular pieces (diameter 7 mm) of the membranes were cut off and mounted on *Phillips* electrode bodies of the type *IS 561* (*Glasbläserei Willi Möller AG*, Zürich, Switzerland) for testing. The internal soln. of the electrodes for all membranes was 0.01M KCl.

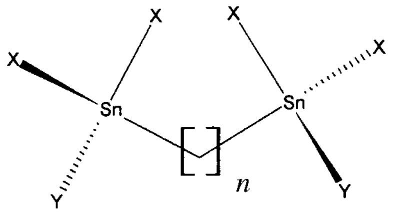
For the segmented-sandwich-membrane method, two membranes were prepared, one with 5% of carrier **1** and 20 mol-% of tridodecylmethylammonium chloride ($[(C_{12}H_{25})_3MeN]Cl$) in a molar ratio 1:5 relative to the carrier, and the other only with the same amount of $[(C_{12}H_{25})_3MeN]Cl$ (without the carrier **1**). PVC and DOS in the ratio 1:2 (*w*/*w*) were also used. The membrane components, in total 140 mg, were dissolved in 1.5 ml of THF and poured into a glass ring (2.2 cm i.d.) affixed with rubber bands onto a microscope slide. The solvent was allowed to evaporate overnight. 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 beaker containing 50.0 ml of 10 mM MES buffer (pH 5.50) and 0.01M anion-salt soln. in the same buffer. The potential difference between the buffer without and the buffer with 0.01M anion-salt soln. was used for the calculation of the potentiometric selectivity coefficients according to the separate-solution method (SSM) [32], assuming that the electrodes show *Nernst*ian responses either to phosphate or all other interfering anions.

^{117}Sn-NMR Titrations. ^{117}Sn-NMR Spectra were acquired from 0.5-ml CD_2Cl_2 solns. containing 0.11M carrier **1** to which increasing aliquots of $(Bu_4N)X$ (X = dihydrogen phosphate, hydrogen sulfate, or perchlorate) were added in molar ratios up to 5. The chemical shifts were referenced to $\Xi = 35.632295$ MHz [33]. ^{117}Sn rather than the more common ^{119}Sn spectra were recorded to overcome local radio interferences around 93.2 MHz [34]. Comparing ^{117}Sn and ^{119}Sn data generates no misinterpretation, since ^{117}Sn/^{119}Sn isotopic effects are negligible [35].

The formation constants *K* were obtained by nonlinear least-squares fitting (ORIGIN 4.0 for Windows 3.1) with the experimental values applied on nonlinear models of 1:1 and 1:2 complexations [23].

Segmented-Sandwich-Membrane Method. Membrane circular pieces were conditioned in each of the 0.01M $H_2PO_4^-$, 0.01M HPO_4^{2-}, 0.01M SO_4^{2-}, and 0.01M ClO_4^- solns. for 1/2. The same solns. were used as inner-filling soln. and samples. Measurements were first taken for single membranes (with or without carrier) incorporated into the same electrode body separately, giving potential values that deviated less than 2 mV. Afterwards, the two single membranes were dried with tissue paper and fused together with pressure onto the internal module of the same *Phillips* electrode body, in order to prepare the sandwich membrane. The carrier-containing segment of the sandwich membrane was facing the sample soln. The potential was recorded for a 5-min period in each sample, and the mean of the measurements during the last minute was used for the calculation of the formation constants.

Results and Discussion. – The organoditin compounds shown in *Fig. 1* were used as the dopands in liquid polymeric membranes and tested potentiometrically for their selectivity towards a series of anions. These compounds were chosen to elucidate which main structural characteristics, such as the tin substituents and the length of the alkanediyl linker between the Sn-atoms, determine the selectivity towards phosphate, and how these are related to the binding constants.



	X	Y	*n*
1	Br	Ph	1
2	Cl	Bu	1
3	Cl	Octyl	1
4	Cl	Ph	2
5	Cl	Ph	3

Fig. 1. *Organoditin carriers investigated for phosphate anionic response as a function of substituents and number of* CH_2 *groups between the two Sn-centers*

The initial covalently bound substituents X and Y at the reactive Sn-sites can influence the ligation capabilities of the compound in two ways. First, the substituents determine the *Lewis* acidity of the Sn-centers, and consequently, the energy of complexation with anions. Second, the size of the substituents controls the steric environment into which the basic ligand will have to penetrate for coordinating the Sn-atoms. Both effects influence the observed potentiometric selectivity, as well as the measured binding constants. For carriers **1**–**3**, structural factors, such as the electronegativity of the inorganic substituent as well as the electron-withdrawing power and the lipophilicity of the organic substituents (Ph, Bu, octyl), were tested. In *Table 1*, the overall potentiometric response of the ISEs based on the carriers **1**–**5** are shown for comparison purposes.

Table 1. *Total Potentiometric Response in mV of Carriers* **1**–**5**

	$H_2PO_4^-$	ClO_4^-	SO_4^-	SCN^-	I^-	NO_3^-	Cl^-
Carrier **1**	330	50	75	130	105	45	25
2	25	120	10	190	160	85	105
3	260	100	35	205	125	50	75
4	148	50	25	200	145	55	90
5	100	70	0	100	80	15	40

The differences observed in selectivity patterns towards phosphate of carriers **1**–**3** are attributed to the differences in electron-withdrawing power and lipophilicity of the organic substituents. Carrier **1** shows much higher potentiometric responses than either carrier **2** or **3** since the Ph group is a better electron-withdrawing group than Bu or octyl, a fact that makes the active sites better *Lewis* acids. The dramatic decrease in the potentiometric response, and consequently the decrease in selectivity, of carrier **2** to phosphate can be explained by the fact that the Bu group has a lower lipophilicity than the octyl group (carrier **3**). This property drastically affects the partitioning of the carrier in the membrane and results in the quick leaching of the carrier into the aqueous solution.

The number of CH_2 groups between the Sn-centers should be a main factor that influences the selectivity of the carriers. The Sn-centers should receive the appropriate conformation for the effective bidentate complexation of the Sn-atoms by the phosphate ligand. In a previous work, it was shown that the optimum distance between the Sn-centers for phosphate coordination is either 1 or 3 CH_2 groups [16]. In this study, the carriers **1**, **4**, and **5** with 1, 2 and 3 CH_2 groups between the Sn-centers and the electronegative substituent being either a Cl- or Br-atom were also evaluated and compared. A dramatic reduction in the potentiometric responses to phosphate is observed in the order carrier **1** > carrier **4** > carrier **5**.

It is clear that, as the number of CH_2 groups between the Sn-centers increases from 1 to 3, the selectivity towards phosphate diminishes. The comparison of carriers **1** and **4** also verifies the influence of the Sn-center distance in potentiometric responses and selectivities towards phosphate. Based on these results, it is concluded that the electronegativity of the inorganic substituents, the electron-withdrawing power of the organic substituents, as well as their bulkiness and lipophilicity, all contribute simultaneously to the effective potentiometric selectivity observed, and are vital in the optimization process of the sensors.

From the carrier-optimization stage, it was shown that carrier **1** shows the best selectivity towards phosphate over all other anions tested. It is well-known that phosphate forms stronger metal complexes than other oxoanions [6] following the order phosphate > sulfate > perchlorate.

To investigate further the thermodynamics of this high selectivity towards phosphate of the organoditin carriers, ^{117}Sn-NMR titrations (*Fig. 2*) of the carrier **1** were performed by Bu_4N^+ salts of dihydrogen phosphate, hydrogen sulfate, and perchlorate in CH_2Cl_2 solutions. The ^{117}Sn chemical shift of the average resonance of all complexes generated is plotted as a function of the molar ratio $(Bu_4N)X$/carrier **1**. The titration of carrier **1** with dihydrogen phosphate gave much larger ^{117}Sn chemical-shift variations to lower frequency than the other two oxoanions, in agreement with the potentiometric measurements. In the titration with the perchlorate, a small change in the chemical shift is observed (*ca.* 40 ppm) up to the molar ratio 5:1. In the titrations with hydrogen sulfate and dihydrogen phosphate, larger chemical-shift drops are observed (*ca.* 130 and *ca.* 200 ppm up to a 1:1 molar ratio, resp.), while a further shift is observed up to the ratio 2:1, indicating a possible 2:1 complex stoichiometry.

In all titrations, a single averaged resonance line is observed, indicating that the anion complexation/decomplexation exchange rate is very fast on the ^{117}Sn-NMR time scale. This makes the two Sn-centers of carrier **1** chemically undistinguishable in both complexed and uncomplexed forms. In the case of the complex 2:1, most possibly each Sn-center is complexed with one phosphate molecule. The possibility of the simultaneous complexation of two phosphate molecules with both Sn-centers is rather unlikely because in such a case, much larger chemical-shift decreases would be expected [36]. It is also interesting to mention that, during the titration with dihydrogen phosphate and hydrogen sulfate, a white deposit precipitates from the solution. Concurrently, and above the molar ratios of 2:1, there is a drastic increase of the signal noise and a gradual decrease of the resonance line.

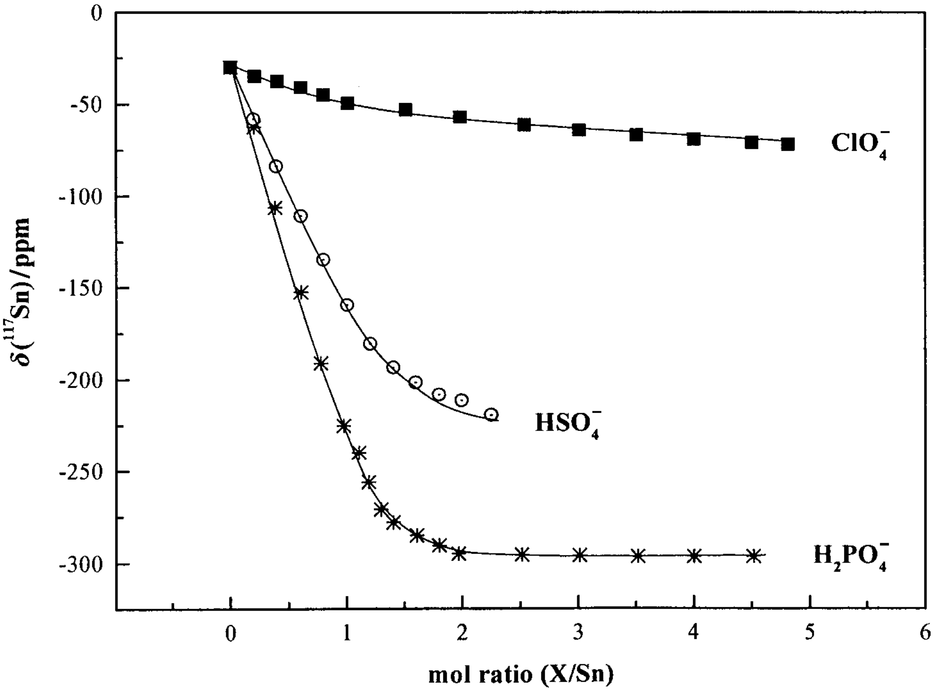


Fig. 2. *^{117}Sn-NMR Titrations of CD_2Cl_2 solutions of carrier* **1** *with tetrabutylammonium salts of dihydrogen phosphate, hydrogen sulfate, and perchlorate* (^{117}Sn-NMR chemical shifts *vs.* the molar ratio tetrabutylammonium salt/carrier **1**). Solid lines from the two-parameter nonlinear regression analysis based on a 1:1 complexation model for perchlorate and a 1:2 model for phosphate and sulfate.

From the titration curves, the complex-formation constants of the carrier **1** with the oxoanions could be extracted by a nonlinear regression analysis and with the complexation models 1:1 and 2:1. The 1:1 model was successfully applied to the perchlorate titration giving a $K_{1:1} = 4.8$. This model could not be applied with good results to the titrations with phosphate and sulfate, indicating that higher-order complexes were formed with these two anions. The complexation model 2:1 was applied in these cases, and formation constants could be obtained, assuming that the plateau values of the chemical shift observed in the titration curves tend asymptotically to be the one of the 2:1 complex. The results are summarized in *Table 2*. It can be seen that there are large errors obtained for the calculated values in the cases of phosphate and hydrogen-sulfate titrations. This is probably due to the problem of the formation of a precipitate, or even the possibility of higher degrees of complexation. Despite this, the observed formation-constant values reflect the high selectivity of carrier **1** towards phosphate over sulfate and perchlorate. The validity of these results is enhanced, since they agree, at least qualitatively, with the obtained potentiometric data.

Even though the ^{117}Sn-NMR titrations gave useful information about the stoichiometry and the structure of the complexes of the organotin carriers with different oxoanions, the specific carriers could behave differently when incorporated into a liquid polymeric membrane. Additionally the formation constants measured in

Table 2. *Complex-Formation Constants* [M^{-1}] *of Carrier* **1** *with Oxoanions in* CH_2Cl_2 *Solutions, as Calculated from Nonlinear Regression of* ^{117}*Sn-NMR Titration Data*

	HPO_4^-	HSO_4^-	ClO_4^-
$K_{1:1}$	3 ± 5	8 ± 1	4.8 ± 0.3
$K_{1:2}$	193 ± 70	28 ± 6	–

organic solvents may differ significantly from the values directly obtained within the solvent polymeric membrane.

Recently, different methods have been proposed for the determination of formation constants *in situ* for solvent polymer membranes [37–41]. These methods require an additional ionophore in the membrane, careful pH control, or they are not applicable for anion-selective ionophores. The most convenient method for our purposes appeared to be the recently proposed segmented-sandwich-membrane method [24][25]. Two membranes containing the same number of cationic sites, with only the one containing ionophore, are fused together in an electrode body, forming a sandwich membrane. Since the inner filling solution is the same as the sample solution, the uncomplexed anion concentration in the membrane segment with the ionophore is many orders of magnitude smaller than in the membrane segment without ionophore. The measured potential difference between the sandwich membrane and the single membrane can be related with the formation constant according to *Eqn. 1*, where β is the overall formation constant, ΔEMF the potential difference between the sandwich and the single membranes, z_I the charge of the anion, L_T the total ionophore concentration, R_T the ionic additive concentration, and n the complex stoichiometry. R, T, and F are the gas constant, the absolute temperature, and the *Faraday* constant, respectively. It should be noted that it is difficult to completely displace chloride in the ionophore-free membrane with phosphate. The listed experimental ΔEMF data, therefore, reflect conservative limits, and the true values (and stability constants) will be equal or larger than the ones shown.

$$\log \beta = \frac{\Delta EMF \cdot z_I \cdot F}{2.303RT} - n \log\left(L_T - \frac{nR_T}{z_I}\right) \quad (1)$$

The experimental results obtained with this technique for dihydrogen phosphate, hydrogen phosphate, and sulfate are summarized in *Table 3*. The plasticizer was DOS, and $[(C_{12}H_{25})_3MeN]Cl$ was used for the cationic sites. No stable measurements could be taken for perchlorate because the complex precipitated out of the membrane with the ionophore after soaking in the perchlorate solution. The high apparent formation-constant values to both phosphate forms explain the high potentiometric responses to dihydrogen phosphate obtained with the ISEs, and supports the formation-constant values obtained from the NMR titration experiments. It is the first time that the segmented-sandwich-membrane method was applied with success to anion-selective ionophores.

In *Fig. 3*, a typical calibration curve obtained of ISEs based on carrier **1** and TEHP as the plasticizer with 5 mol-% anionic sites to carrier, PVC-OH, measured in MES 10 mM buffered solutions (pH 5.5) is shown. The response time of the sensor is short, and usually less than 1 min, depending on the test solution. The detection limit based on

Table 3. *Complex-Formation Constants of Carrier* **2** *with Oxoanions in PVC/DOS Membranes Determined with the Segmented-Sandwich-Membrane Technique*

	pH	*ΔEMF*	log *β*	z_I	n^{a})
Sample (0.01M) NaH_2PO_4	4.73	−479	8.6	−1	1/2
Na_2HPO_4	8.85	−530	18.5	−2	1/2
Na_2SO_4	5.89	−353	12.5	−2	1/2

[a]) Assumed according to the NMR titration results.

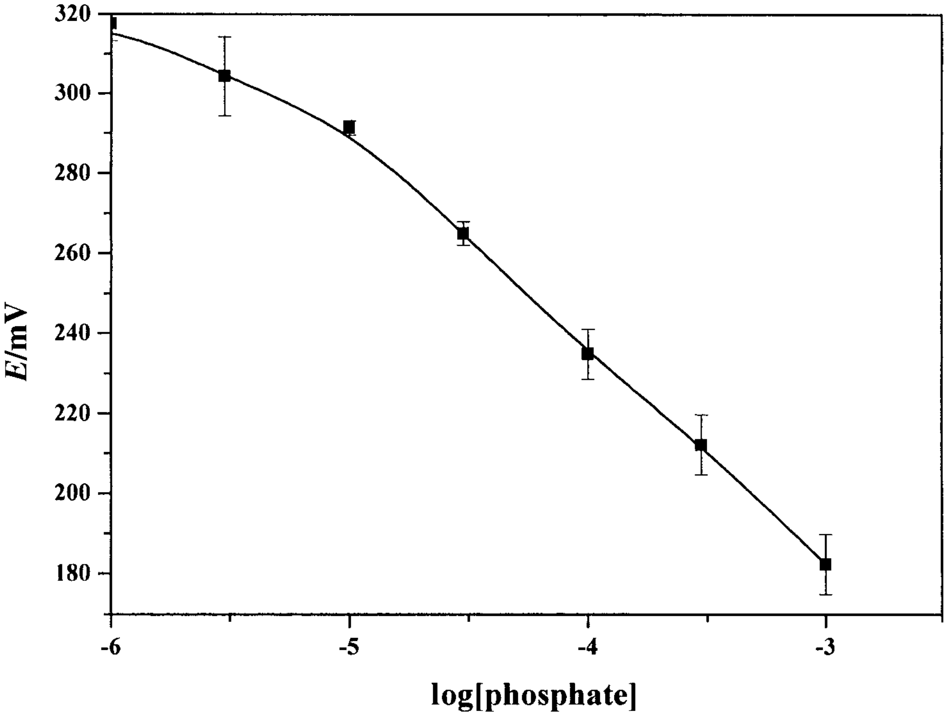


Fig. 3. *Typical calibration curve for phosphate of an ISE with carrier* **2** *obtained in MES 0.01M buffered solutions of* pH 5.5. The calculated slope is −54.6 (±0.6) with $R = -0.9998$, as calculated from 5 separate experiments

this curve was calculated to be $3 \cdot 10^{-6}$, while the slope was close to the theoretical one for the monobasic phosphate anion. It should be mentioned here that the use of different platicizers or polymers decreases the sensitivity of the ISE. Even though the selectivity, the detection limit, the response time, and the sensitivity of the sensor developed is excellent, the life time of the system is still unsatisfactory, being in the order of 3 to 20 days of continuous operation, depending on experimental parameters. The instability of the system is attributed to either hydrolysis of the carrier, or is more probably due to the intermolecular polymerization brought about by either a hydroxy or a phosphate as a bringing group. The precipitate observed whenever the carrier is in contact with phosphate, such as in the case of the NMR titration or the measurement of high concentrations of phosphate at the outside of the ISE membrane, corroborates this.

The good stability of the system over a short period of time could lend itself to the development of a disposable, one-analysis system, a possibility that is currently under investigation.

Conclusions. – A highly selective phosphate-recognition system was developed based on bidentate organotin compounds. It was shown that the structural characteristics of the carrier play a major role for the optimization of the selectivity. Careful adjustment of these parameters led to the development of the carrier methylenebis[dibromophenylstannane] (**1**), which exhibits superb selectivity towards phosphate over many other anions, as it is shown by three independent experimental methods. This carrier is now investigated for the development of a disposable, highly selective phosphate sensor.

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REFERENCES

[1] P. Bühlmann, E. Pretsch, E. Bakker, *Chem. Rev.* **1998**, *98*, 1593.
[2] S. O. Engblom, *Biosens. Bioelectron.* **1998**, *13*, 981.
[3] E. Bakker, P. Bühlmann, E. Pretsch, *Electroanalysis* **1999**, *11*, 915.
[4] Y. Marcus, 'Ion Solvation', John Wiley & Sons, New York, 1985.
[5] F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247.
[6] B. E. Douglas, D. H. MacDaniel, J. J. Alexander, 'Concepts and Models of Inorganic Chemistry', 2nd edn., J. Wiley & Sons, New York, 1983.
[7] C. M. Carey, W. B. Riggan, *Anal. Chem.* **1994**, *66*, 3587.
[8] P. Bühlmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron* **1997**, *53*, 1647.
[9] S. Nishizawa, P. Bühlmann, K. P. Xiao, Y. Umezawa, *Anal. Chim. Acta* **1998**, *358*, 35.
[10] M. Fibbioli, M. Berger, F. P. Schmidtchen, E. Pretsch, *Anal. Chem.* **2000**, *72*, 156.
[11] V. M. Shkinev, B. Y. Spinakov, G. A. Vorob'eva, Y. A. Zolotov, *Anal. Chim. Acta* **1985**, *167*, 145.
[12] S. A. Glazier, M. A. Arnold, *Anal. Chem.* **1988**, *60*, 2540.
[13] S. A. Glazier, M. A. Arnold, *Anal. Chem.* **1991**, *63*, 754.
[14] R. L. DeMeulenaere, P. Onsrud, M. A. Arnold, *Electroanalysis* **1993**, *5*, 833.
[15] N. A. Chaniotakis, K. Jurkschat, A. Rühlmann, *Anal. Chim. Acta* **1993**, *282*, 345.
[16] J. K. Tsagatakis, N. A. Chaniotakis, K. Jurkschat, *Helv. Chim. Acta* **1994**, *77*, 2191.
[17] D. Liu, W.-C. Chen, R.-H. Yang, R.-Q. Yu, *Anal. Chim. Acta* **1997**, *338*, 209.
[18] M. M. G. Antonisse, B. H. M. Snellink-Ruel, J. F. J. Engbersen, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* **1998**, 773.
[19] J. K. Tsagatakis, N. A. Chaniotakis, K. Jurkschat, S. Damoun, P. Geerlings, A. Boundid, M. Gielen, I. Verbruggen, M. Biesemans, J. C. Martins, R. Willem, *Helv. Chim. Acta* **1999**, *82*, 531.
[20] N. A. Chaniotakis, S. B. Park, M. E. Meyerhoff, *Anal. Chem.* **1989**, *61*, 566.
[21] D. Liu, W. C. Chen, G. L. Shen, R. Q. Yu, *Analyst* **1996**, *121*, 1495.
[22] U. Wuthier, H. V. Pham, R. Zund, D. Welti, R. J. F. Funck, A. Bezegh, D. Ammann, E. Pretsch, W. Simon, *Anal. Chem.* **1984**, *56*, 535.
[23] K. A. Connors, 'Binding Constants, the Measurement of Molecular Complex Stability', John Wiley & Sons, Chichester, 1987.
[24] Y. Mi, E. Bakker, *Anal. Chem.* **1999**, *71*, 5279.
[25] Y. Qin, Y. Mi, E. Bakker, *Anal. Chim. Acta* **2000**, in press.
[26] M. Gielen, K. Jurkschat, *J. Organomet. Chem.* **1984**, *273*, 303.
[27] D. Dakternieks, K. Jurkschat, H. Wu, E. R. T. Tiekink, *Organometallics* **1993**, *12*, 2788.

[28] H. Wu, Masters Thesis, Deakin University, Geelong, Victoria, Australia, 1993.
[29] R. Hummeltenberg, K. Jurkschat, unpublished results.
[30] E. Kleinpeter, A. Tzschach, *J. Organomet. Chem*. **1990**, *388*, 259.
[31] D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, *J. Organomet. Chem*. **1995**, *492*, 145.
[32] G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, J. D. R. Thomas, *Pure Appl. Chem*. **1976**, *48*, 127.
[33] J. Mason, 'Multinuclear NMR', Plenum Press, New York, 1987.
[34] B. R. Koch, G. V. Fazakerley, E. Dijkstra, *Inorg. Chim. Acta* **1980**, *45*, L51.
[35] H. C. E. McFarlane, W. McFarlane, C. J. Turner, *Mol. Phys.* **1979**, *37*, 1639.
[36] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc*. **1985**, *16*, 73.
[37] E. Bakker, M. Lerchi, K. Seiler, E. Pretsch, *Anal. Chem*. **1994**, *66*, 516.
[38] E. Bakker, E. Pretsch, *J. Electrochem. Soc.* **1997**, *144*, L125.
[49] E. Bakker, E. Pretsch, *Anal. Chem.* **1998**, *70*, 295.
[40] A. Ceresa, E. Pretsch, *Anal. Chim. Acta* **1999**, *395*, 41.
[41] H. J. Lee, C. Beriet, H. H. Girault, *J. Electroanal. Chem*. **1998**, *453*, 211.

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