Potentiometric studies of complexation properties of tetrafunctionalized resorcinarene-based cavitands

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Resorcinarene-based cavitands functionalized with [–NH–C(O)–CH_2–$(Ph)_2PO$] (**I**), [–NH–C(O)–CH_2–$(EtO)_2PO$] (**II**), [–NH–C(S)–NHC(O)Ph] (**III**) and [–NH–C(O)–NHC(O)Ph] (**IV**) moieties have been characterized potentiometrically. Both P-containing cavitands (**I** and **II**) form very stable complexes (log $\beta_{IL} > 18$) for most of the examined cations as determined with the segmented sandwich membrane method. The order of the stability constants was found to be: $Eu^{3+} > UO_2^{2+} > Pb^{2+}$, Cd^{2+}, Sr^{2+} and Cu^{2+}. Much weaker complexation occurs in the case of compounds **III** and **IV** (log $\beta_{IL} < 10.6$) and the order of the stability constants was: $Eu^{3+} > Pb^{2+} > Cu^{2+} > Ag^+ > UO_2^{2+} > Na^+ > K^+$ for **III** and $UO_2^{2+} > Cd^{2+} > Pb^{2+} > Eu^{3+}Cu^{2+} > Na^+ > Ag^+ > K^+$ for **IV**. The response to representatives of various cation groups and the selectivity of polymeric membrane electrodes based on these compounds are presented. While cavitands functionalized with phosphine oxide or phosphonate moieties (**I** or **II**) exhibited the highest selectivity for UO_2^{2+} and Pb^{2+} and a pronounced discrimination of Ag^+ ions, thioamide- (**III**) and amide-functionalized (**IV**) cavitands showed preferences for Ag^+ and Pb^{2+} and reduced selectivity toward UO_2^{2+} ions. The correlation between the potentiometric selectivity and the ability of examined cavitands to form metal–ligand complexes is discussed.

Introduction

It is known that by proper selection of a donor atom and its distribution in a molecular structure, the complexing properties of a potential receptor can be influenced.[1] Pearson's hard–soft acid–base principle is very useful for the design as well as for a good understanding of the complexation behavior of ligands.[2] Calixarenes and resorcinarene-based cavitands have proven to be very fruitful platforms for the attachment of different ligating sites giving rise to ionophores for anions, cations, and neutral molecules.[3]

The studies of chemical recognition of ionic guests by neutral receptors started with Pedersen's publication on crown ethers and their complexes with alkali and alkaline earth cations.[4] Since shortly after that, synthetic receptors have been successfully used as ion-carriers (ionophores) in the membranes of potentiometric ion-selective electrodes (ISEs). Although thousands of various ionophores have already been designed and synthesized,[5] still there is a need for more selective ionophores, especially now that the feasibility of a decrease of a low detection limit has recently been shown.[6]

The response of ISEs to ions can be described by the empirical Nicolsky–Eisenman equation:

$$\mathrm{EMF} = E_{\mathrm{I}}^{0} + (RT/z_{\mathrm{i}}F)\ln\left(a_{\mathrm{I}} + \sum K_{\mathrm{I,J}}^{\mathrm{pot}} a_{\mathrm{J}}^{z_{\mathrm{i}}/z_{\mathrm{j}}}\right) \qquad (1)$$

where a_I is the analyte ion activity, a_J is the interfering ion activity, z_i and z_j are the charges of analyte and interfering ions, respectively and the symbols R,T and F have their usual meaning. The selectivity coefficient, $K_{I,J}^{pot}$, describes the ability of an electrode to recognize analyte ion (I) in the presence of interfering ions (J). When the value of log $K_{I,J}^{pot}$ is smaller than 0, it means that the electrode is more selective to the primary ion than to interfering ions.[7] It is well established that selectivity coefficients for neutral carrier-based membranes are typically related to the differences in the free energies of solvation of the ions in the sample and membrane phase, the stability constants of ion-ionophore complexes in the membrane and the membrane concentrations of the ionophore and ionic sites.[8,9] However, the main factor that is primarily responsible for the selectivity of polymeric membrane electrodes is the selectivity of ion–ionophore interactions that can be expressed by relative stability constants of complexes formed by an ionophore with primary and interfering ions within the membrane phase. Various techniques have been employed in order to evaluate the complexation abilities of ionophores, including measurements in water–ethanol mixtures,[10–12] extraction into an apolar organic solvent[13] or measurements at the interface of two immiscible electrolyte solutions.[14] However, the correlation between measured complex formation constants and ion selectivity of sensors has only been observed in very limited cases.

Several methods allowing the measurement of formal ion–ionophore complex formation constants in solvent polymeric membrane phases have been proposed.[15–24] Stability constants of complexes have been determined by means of optical[17,19] and potentiometric[15,16,18–24] methods. The sandwich membrane methods[15,16,21–24] seem to be the most appropriate for the characterization of the chemical properties of lipophilic ligands, since other methods suffer from drawbacks related

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to requirements for an additional reference (*e.g.*, chromoionophore,[17] pH ionophore[18,19] or a lipophilic cation (TMA^+)[20]).

The sandwich membrane consists of two membranes attached one to another. One of these membranes contains ionophore and ion-exchanger and the second membrane is ionophore free, with the other constituents the same. The electrode with sandwich membrane, assembled just prior to the measurement, is immersed into the sample solution of composition identical to that of the internal electrolyte of the electrode. The resulting initial membrane potential reflects the ion activity ratio at both aqueous phase-membrane interfaces:[21]

$$E_{\text{mem}} = \frac{RT}{z_{\text{I}}F}\ln\frac{a_{\text{I}}(\text{org})''}{a_{\text{I}}(\text{org})'} \qquad (2)$$

where $a_{\text{I}}(\text{org})'$ is the ion activity at the sample–membrane interface and $a_{\text{I}}(\text{org})''$ is the ion activity at the interfilling electrolyte–membrane interface. Due to specific interaction of tested ion with the ionophore, the activity of uncomplexed ion is decreased at the ionophore-containing side of sandwich membrane, compared to the ionophore-free side. This decrease, related to the strength of ion–ionophore interaction, is responsible for the measured potential of the electrode and used to calculate the ion–ionophore complex stability constant.

In this paper, tetrafunctionalized resorcinarene-based cavitands are studied as cation-selective ionophores in plasticized poly(vinyl chloride) membranes. The potentiometric response to selected cations and the selectivity of membranes containing examined compounds as well as the determination of the stability constants of ion–ionophore complexes are reported.

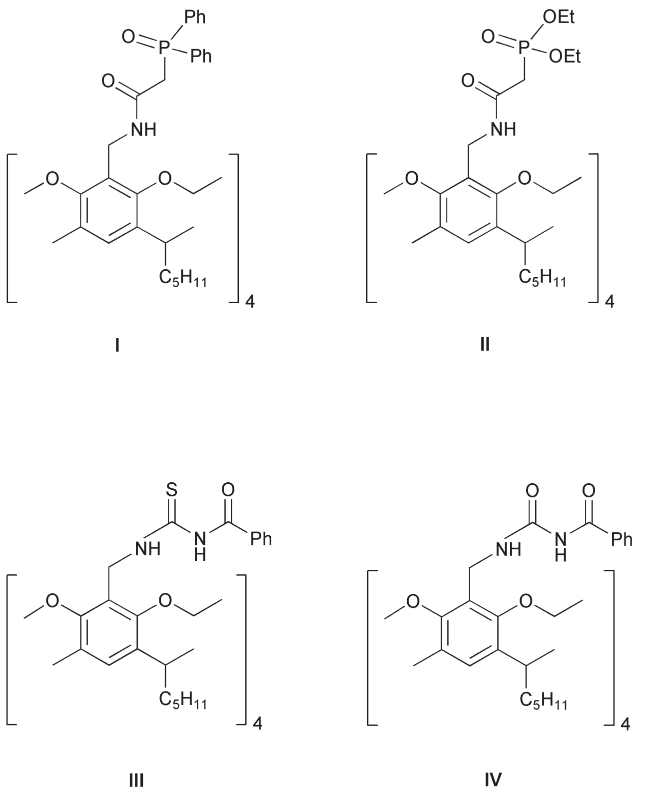

Fig. 1 Chemical structures of the resorcinarene-based cavitands.

Results and discussion

Synthesis of ionophores

The structures of the examined tetrafunctionalized cavitand-based cation ligands are shown in Fig. 1.

Ionophores **I** and **II** were prepared according to the procedure described in ref. 25 Reaction of tetrakis(aminomethyl)cavitand[25] with benzoyl isothiocyanate and benzoyl isocyanate gave the ionophores **III** and **IV** in 63% and 55% yield, respectively.

The series **I**–**IV** allows the quantitative investigation of the influence of the donor atoms basicity on the complexation capability of the functionalized cavitands. According to Pearson's theory, the P=O group is a hard Lewis base and can preferably interact with hard Lewis acids. The replacement of phosphine oxide/phosphonate by amide/thioamide groups might lead to receptors, the complexation properties of which will shift toward soft metal cations. Ionophores **III** and **IV** possess soft ligating groups: C=O and C=S, and therefore they are expected to form preferentially complexes with soft metal cations. Indeed, the results presented in Table 1 confirm these expectations.

Measurements of complex stability constants

The experiments on the determination of complex formation constants were carried out for membranes containing tetrakis[3,4-bis(trifluoromethyl)phenyl]borate (KTFPB) as lipophilic anionic sites and 2-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer in order to minimize the effects of ion-pairing and the cation–plasticizer interaction competitive to the ionophore, respectively, that might affect the binding constants.[21,22,24] The stoichiometry of the ion–ionophore complexes formed by ionophores **I**–**IV** was assumed to be 1 : 1.

The values of the complex formation constants for ionophores **I**–**IV** are collected in Table 1. Cavitands with [$-NH-C(O)-CH_2-(Ph)_2PO$] (**I**) and [$-NH-C(O)-CH_2-(EtO)_2PO$] (**II**) groups form much stronger complexes than the ones with [–NH–C(S)–NHC(O)Ph] (**III**) or [–NH–C(O)–NHC(O)Ph] (**IV**) moieties with most of the examined cations. This can be explained by the fact that the phosphoryl oxygens are known to be stronger donating than the amide carbonyls[26,27] (and very likely thioamide thiocarbonyls as well).

As shown in Table 1, the logarithmic values of the complex formation constants for P-containing ionophores (**I** and **II**) essentially follow the order: $Eu^{3+} \gg UO_2^{2+} > Pb^{2+}$, Cu^{2+}, Cd^{2+}, $Sr^{2+} > Ca^{2+}$, $Mg^{2+} \gg Ag^+$, K^+, Na^+. The high values of the complex stability constants for Eu^{3+}, UO_2^{2+} and Sr^{2+} confirm that cavitands **I** and **II** are strong receptors for the extraction of these cations.[25]

The values of log $\beta_{\text{ML}}$for **II** are significantly larger than those for **I**. This indicates that the phosphonate-functionalized cavitand (**II**) exhibits stronger complexation properties than the phosphine oxide-functionalized one (**I**). These results are quite surprising, since it has been reported that the complexation properties of P-containing compounds follow the order: phosphonate < phosphate < phosphine oxide, when alkyl chains are present at those groups.[28,29] However, it has also been shown that phenyl substituents decrease the basicity of a P=O group.[30] This is very likely the explanation for the lower β_{IL} values measured for phenyl phosphine oxide-functionalized cavitand (**I**) compared to the ethylphosphate-functionalized one (**II**). Moreover, the geometry of the substituents (C_6H_5- *vs.* EtO-) might also affect the architecture of the cavity of the resorcinarene-based cavitands and, as a consequence, the complexing properties of **I** and **II**.

For thioamide- and amide-functionalized cavitands (**III** and **IV**), lower complex stability constants were measured, compared to the P-containing ones **I** and **II** (see Table 1). The β_{ML} values follow the order: $Pb^{2+} > UO_2^{2+}$, Cu^{2+}, $Cd^{2+} > Ag^+ > K^+$, Na^+. The complex formation constants are generally lower for cavitand **IV** than for cavitand **III**. Comparison of the log β_{IL}values for **III** and **IV** revealed that **III** exhibits a higher affinity toward softer cations than **IV** (see log β_{ML} for Pb^{2+} *vs.* UO_2^{2+}).

Table 1 Formal complex formation constants, log β_{IL_n} [a] obtained with ionophores **I**–**IV** in PVC/*o*-NPOE (1 : 2) membranes, using the segmented sandwich method

Cation Ionophore	Eu^{3+}	UO_2^{2+}	Pb^{2+}	Cd^{2+}	Sr^{2+}	Cu^{2+}	Ag^+	Ca^{2+}	Mg^{2+}	K^+	Na^+
I	27.6	22.4	18.8	18.1	18.5	17.4	6.4	14.0	14.4	6.7	7.2
II	31.0	25.5	22.5	22.7	21.4	21.7	8.9	16.9	16.5	10.2	12.0
III	10.6	5.4	8.9			8.1	7.2			< 2	4.9
IV	5.2	6.1	5.6	5.9		4.5	3.2			< 3	4.2

[a] Standard deviations < 0.3 (from at least three replicate measurements).

Potentiometric response to cations and membrane selectivity

Compounds **I**–**IV** were studied as ionophores in *o*-NPOE/PVC membranes. Their potentiometric selectivity toward representatives of various cation groups (*e.g.*, K^+, Na^+, Ca^{2+}, Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}) has been investigated. To obtain unbiased $K_{I,J}^{pot}$ values, the calibrations for cations were collected starting from the most discriminated ones.[9,31,32] The order in which cations were examined for each ionophore was established after the preliminary screening of the electrodes' selectivities. Electrodes with examined membranes exhibited a Nernstian or near-Nernstian cationic response in pure solutions of the moderate and highly discriminated ions, at least within the range 10^{-3}–10^{-1} M. When a flattening (or a reversing) of the calibration curves was observed, the selectivity coefficients were obtained from the Nernstian portion of the response curve at lower activities.

A diagram of the logarithmic values of the selectivity coefficients calculated for lead as the primary cation (log $K_{Pb,J}^{pot}$) is presented in Fig. 2. As seen from Fig. 2, all examined compounds induce a selectivity that differs from the Hofmeister selectivity pattern, observed for membranes based on a typical ion-exchanger (see last column in Fig 2) and related to the free energy of hydration of the cations.[9] Comparison of the results reveals significant differences in the selectivity of electrodes based on the examined cavitands. The type of functional group present in the ionophore structures (**I**–**II** *vs.* **III**–**IV**) is responsible for these differences.

CMPO and CMP derivatives. CMPO (carbamoylmethylphosphine oxide) **I** and CMP (carbamoylmethylphosphonate) **II** cavitands, used as ionophores within the polymeric membrane, exhibit a high selectivity towards UO_2^{2+} and Pb^{2+} ions. The values of the selectivity coefficients, log K_{Pb,UO_2}^{pot}, were found to be +2.1 and +1.6 for **I** and **II**, respectively. This indicates a better selectivity towards UO_2^{2+} than to Pb^{2+} ions. Pronounced interferences (log$K_{Pb,M}^{pot}$ ranging from −1 to −2.5) were observed for Ca^{2+}, Cd^{2+}, Cu^{2+} and Ag^+. Essentially, the selectivity pattern shown in Fig. 2 reflects the complexation capability of P-containing cavitands described by their complex stability constants (see Table 1). It should be pointed out that the selectivity for Pb^{2+} over Ag^+ ions for membranes based on **I** and **II** was found to be much better than reported for tri-*n*-octylphosphine oxide[33] and calixarene phosphine oxides[34] investigated in *o*-NPOE/PVC membranes. The values of the selectivity coefficients (log$K_{Pb,Ag}^{pot}$) for membranes with those phosphine oxides were by at least three logarithmic units lower than obtained for membranes doped with **I** and **II**.

In the case of **I** and **II**, the strongest discrimination was observed for alkali metal ions (Na^+, K^+). At this point it should be noted that the values of the selectivity coefficients for sodium and potassium cations should be treated as an approximate (overestimated) due to a sub-Nernstian response (40–45 mV dec^{-1} slopes) of the electrodes to these ions.

Cavitands functionalized with ligands containing N and O (or S) donating atoms. The amide carbonyls (and very likely thioamide thiocarbonyls as well) are known to be weaker donating than the phosphoryl oxygens.[26,27] The values of the complex stability constants for **III** and **IV**, significantly lower than those observed for **I** and **II**, confirm this fact (see Table 1). Moreover, soft cations are preferentially bound by ligands with a donor atom of lower electronegativity than oxygen,

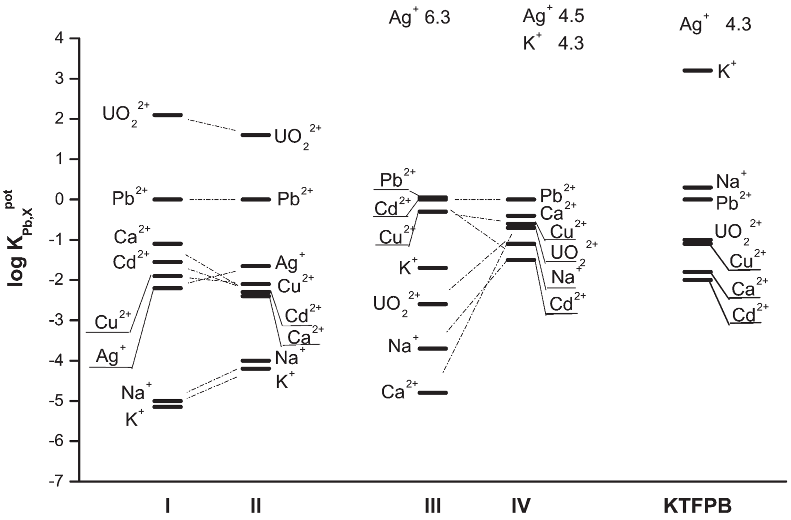

Fig. 2 Selectivity coefficients for electrodes prepared with PVC/*o*-NPOE (1 : 2) membranes containing compounds **I**–**IV** and lipophilic sites (KTFPB) as well as membranes with ion-exchanger only.

such as nitrogen or sulfur (electronegativity of 3.5, 3.0 and 2.5, respectively).[2] The selectivity observed for membranes doped with **III** or **IV** correlates well with these predictions and measured complex stability constants.

Ionophore **III**, containing thioamide groups, exhibits a much better selectivity towards the softer Ag^+ than Pb^{2+} ion, compared to **I** and **II**. Also, a pronounced increase of the interference from Cu^{2+} and Cd^{2+} can be seen. In contrast, the discrimination of hard UO_2^{2+} and Ca^{2+} ions is much stronger than observed for CMP- or CMPO-functionalized cavitands. In the case of cavitand **III** the value of log $\beta_{IL}$is greater for Pb^{2+} than for UO_2^{2+}, while cavitands **I** and **II** form stronger complexes with UO_2^{2+} than with Pb^{2+} (see Table 1).

Among the compounds studied, the smallest complex stability constants were determined for **IV**. Moreover, the values of log β_{IL} are almost equal. This is reflected in the selectivity of the membranes containing this cavitand as ionophore. The selectivity pattern is dominated by the lipophilicity of the cations; Ag^+ and K^+ are most preferred. For other cations the log$K^{pot}_{Pb,M}$ values do not exceed -2.

The potentiometric responses to the selected cations are shown in Figs. 3 and 4. The electrodes exhibited a fast and reversible response with near-Nernstian slopes at the linear domain of the calibration curves. The lower detection limits of the electrodes with membranes doped with the studied cavitands, after the equilibration with Pb^{2+} or UO_2^{2+}, was within the range $5{\cdot}10^{-6}$–$5{\cdot}10^{-7}$ M. As seen from Fig. 3, a reversing of the calibration curves at higher UO_2^{2+} ion concentrations was observed for electrodes with membranes doped with ionophore **I** or **II**. In the case of Pb^{2+} ion and ionophore **II**, only a flattening of the calibration curve was observed. This can be explained by the co-extraction of counter-anions (Donnan failure), that is related to a very strong ion–ionophore complexation.[35]

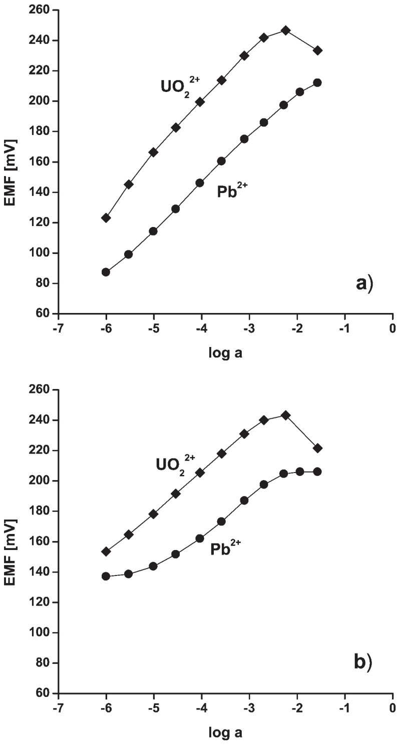

Fig. 3 Calibration curves toward Pb^{2+} and UO_2^{2+} cations for electrodes with membranes doped with a) ionophore **I** and b) ionophore **II**. Measurements carried out at pH 4 and pH 3 for Pb^{2+} and UO_2^{2+} cations, respectively.

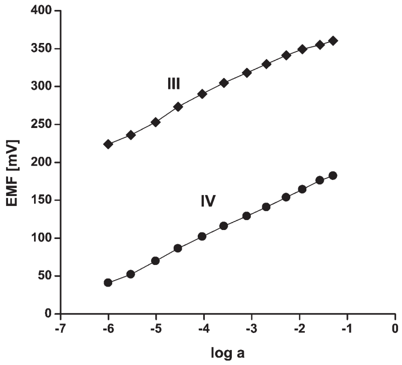

Fig. 4 Calibration curves toward Pb^{2+} for electrodes with membranes doped with ionophores **III** and **IV**. Measurements carried out at pH 4.

Conclusions

It has been demonstrated, *via* potentiometric sandwich membrane measurements, that cavitands tetrafunctionalized with [–NH–C(O)–CH$_2$–(Ph)$_2$PO] (**I**) and [–NH–C(O)–CH$_2$–(EtO)$_2$-PO] (**II**) moieties form very strong complexes with hard cations, such as Eu^{3+} and UO_2^{2+}. The complex formation constants obtained for other cations tested are significantly lower.

The replacement of the [–NH–C(O)–CH$_2$–(Ph)$_2$PO] (**I**) and [–NH–C(O)–CH$_2$–(EtO)$_2$PO] (**II**) groups with [–NH–C(S)–NHC(O)Ph] (**III**) or [–NH–C(O)–NHC(O)Ph] (**IV**) decreases the complexation properties of the resorcinarene-based cavitands. This can be explained by the fact that the phosphoryl oxygens are stronger donating than the amide and thioamide (thio)carbonyls.

Cavitands **I**–**IV** have also been used as ionophores in the membranes of ion-selective electrodes. The selectivity coefficients obtained with these measurements correlate well with the complex stability constants. It can be concluded that CMP- and CMPO-modified cavitands (**I**, **II**) can be considered as ionophores in membranes of UO_2^{2+}- and Pb^{2+}-selective electrodes, especially, since the discrimination of Ag^+ ions is larger than for already reported ionophores. The selectivity of electrodes with membranes based on thioamide- (**III**) and amide- (**IV**) derivatives are less interesting in terms of preparing analytically useful ion-selective electrodes. It seems, however, that strong discrimination of Ca^{2+} and Na^+ by thioamide derivative (**III**) makes this ionophore potentially useful as a lead selective ionophore in the absence of significant amounts of Cd^{2+} and Cu^{2+} ions in a test solution.

Experimental section

Synthesis

P-containing cavitands (**I** and **II**) were prepared as previously described.[25]

***N*-Acylthiourea-functionalized cavitand III.** A solution of tetrakis(aminomethylcavitand) (100 mg, 0.107 mmol) and benzoyl isothiocyanate (121 mg, 0.744 mmol) in chloroform (10 ml) was stirred overnight at room temperature. The solution was washed with H_2O (2 × 20 ml) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by flash chromotagraphy (SiO_2, CH_2Cl_2/hexanes 3:2) to yield III as a yellowish solid. Yield 107 mg (63%); mp 157–159 °C; FAB-MS: m/z 1585.3 ($[M+H]^+$, calcd 1585.6); ^1H NMR ($CDCl_3$) δ 8.91 (s, 4H, NH), 7.70 (d, 8H, J = 7.2 Hz, ArH), 7.51 (t, 4H, J = 7.2 Hz, ArH), 7.42–7.35 (m, 8H, ArH), 7.09 (s, 4H, ArH), 6.05 (d, 4H, J = 7.5 Hz,

OCH_2O), 4.74 (t, 4H, $J = 8.2$ Hz, ArCHAr), 4.10 (d, 4H, $J = 7.5$ Hz, OCH_2O), 2.01–2.10 (m, 8H, CH_2), 1.34–1.21 (m, 24H, CH_2), 0.85 (t, 12H, $J = 6.6$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) 178.9, 166.1, 133.0, 153.3, 137.8, 131.2, 128.6, 128.1, 126.9, 119.9, 99.8, 39.9, 36.4, 31.6, 29.7, 29.2, 27.1, 22.1, 13.6.

***N*-Acylurea-functionalized cavitand IV.** A solution of tetrakis(aminomethyl) cavitand (200 mg, 0.858 mmol) and benzoyl isocyanate in THF (20 ml) was refluxed overnight. The reaction mixture was evaporated to dryness and redissolved in CH_2Cl_2 (20 ml). Subsequently, the solution was washed with H_2O (2×100 ml) and dried over $MgSO_4$. Evaporation of the solvent gave a yellowish solid, which was recrystallized two times from diethyl ether giving a white solid. Yield 180 mg (55%); mp 137–139 °C; MALDI-MS: m/z 1544.6 ($[M + Na]^+$, calcd 1544.8); ^{1}H NMR ($CDCl_3$) δ 8.93 (s, 4H, NH), 7.78 (d, 8H, $J = 6.9$ Hz, ArH), 7.51–7.64 (m, 4H, ArH), 7.39–7.48 (m, 8H, ArH), 6.01(d, 4H, $J = 7.8$ Hz, OCH_2O), 4.82 (t, 4H, $J = 8.1$ Hz, ArCHAr), 4.42 (d, 4H, $J = 7.8$ Hz, OCH_2O), 2.3–2.18 (m, 8H, CH_2), 1.31–1.49 (m, 24H, CH_2), 0.93 (t, 12H, $J = 6.6$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) 207.2, 154.9, 153.5, 138.2, 133.7, 131.4, 129.2, 128.9, 128.2, 127.7, 65.8, 36.8, 32.1, 30.1, 27.6, 22.7, 15.3, 14.1.

Potentiometric measurements

Reagents. The membrane components potassium tetrakis[3,4-bis(trifluoromethyl)phenyl]borate (KTFPB), 2-nitrophenyl octyl ether (*o*-NPOE), high molecular weight poly(vinyl chloride) (PVC), and tetrahydrofuran (THF, distilled prior to use) and all salts were purchased from Fluka (Ronkonkoma, NY). Aqueous solutions were obtained by dissolving the appropriate salts in Nanopure purified water.

Membrane preparation. The polymeric membranes used for determination of stability constants contained ionophore (20 mmol kg^{-1}) and KTFPB (2 mmol kg^{-1}) in PVC/*o*-NPOE (1:2 by weight) polymeric matrix (total 140 mg), unless otherwise indicated in the text. The membrane components were dissolved in freshly distilled THF (1.4 ml). The solution was placed in a glass ring (22 mm i.d.) mounted over a glass plate and then covered with another glass plate to slow down the solvent evaporation. After 24 hours, the resulting membrane (of the approximate thickness 130–140 μm) was peeled from the glass plate and discs of 7 mm diameter were cut out.

The procedure of the preparation of polymeric membranes evaluated for the potentiometric ion response was similar to that described above. The total amount of membrane components was 200 mg and membranes consisted of 1 wt% of ionophore, 30–40 mol% of KTFPB and PVC/*o*-NPOE (1 : 2 by weight).

Potentiometric response to cations and selectivity measurements. Membrane discs were mounted in conventional ISE electrode bodies (Type IS 561; Philips, Eindhoven, The Netherlands) for electromotive force (EMF) measurements. All measurements were performed at ambient temperature (22 ± 1 °C) using a galvanic cell of the following type: Ag/$AgCl_{(s)}$/3 M KCl/bridge electrolyte/sample/ion-selective membrane/inner filling solution/$AgCl_{(s)}$/Ag. The bridge electrolyte consisted of 1 M lithium acetate. The inner filling solution of the ISEs was a 0.01 M solution of NaCl. The EMF values were measured using a custom made 16-channel electrode monitor. Details of this equipment were described previously.[36]

The performance of the electrodes was examined by measuring the EMF for aqueous solutions of examined cations over the concentration range of 10^{-7} 10^{-1} M.

Potentiometric selectivity coefficients were determined by the separate solution method (SSM) according to the procedure described in ref. 8. Selectivity coefficient $K^{\mathrm{pot}}_{\mathrm{I,J}}$ values were obtained from adequate, unbiased E^0 measurements for each ion, based on the equation:

$$K^{\mathrm{pot}}_{\mathrm{I,J}} = \exp\left\{\frac{z_{\mathrm{I}}F}{RT}\left(E^0_{\mathrm{J}} - E^0_{\mathrm{I}}\right)\right\} \tag{3}$$

where R, T and F are the gas constant, absolute temperature and the Faraday constant, respectively. The charge of primary ion, I, is indicated as z_{I} and potentials obtained by an extrapolation of the linear part of calibration curve to $\log a = 0$ for primary and interfering ions are E^0_{I} and E^0_{J}, respectively.

Activity coefficients were calculated according to the Debye–Hückel approximation.[37]

Potentiometric determination of stability constants. The measurement setup was the same as described above. Experiments were carried out according to the procedure described in refs. 21,22 Two sets of membranes were prepared: membranes with and without ionophore. A series of 7 mm i.d. membrane discs were cut from the parent membranes, and these disks were conditioned over 2–3 days in appropriate salt solutions (10^{-1} M NaCl, 10^{-1} M KCl, 10^{-2} M $CuCl_2$, 10^{-2} M $SrCl_2$, 10^{-1} M $MgCl_2$, 10^{-1} M $CaCl_2$, 10^{-2} M $CdCl_2$, $5{\cdot}10^{-3}$ M $PbCl_2$, 10^{-3} M $AgNO_3$, 10^{-3} M $UO_2(NO_3)_2$/10^{-3} M NaCl (pH = 3) or 10^{-2} M $EuCl_3$ (pH = 3)).

To determine the stability constants for a given ionophore and a given cation, two measurements, for a membrane without ionophores and then for a sandwich membrane, have been carried out. The sandwich membrane was made, after the drying of individual membranes, by attaching the membrane with ionophore to the membrane without ionophore. The segmented membrane was then mounted into a Philips electrode body (membrane with ionophore facing the sample solution) and immediately immersed into an appropriate salt solution (identical with that used for conditioning the membrane). The potential was recorded as the mean of the last minute of a 10 min measurement period in the test solution. The potential of the electrodes with sandwich membranes remained free of diffusion-induced drifts for 20–50 min, depending on the ionophore incorporated within the membrane and the ion measured. The membrane potential values ΔEMF were calculated by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane. The formation constant, β_{IL_n}, was calculated from the equation:[21,22]

$$\beta_{\mathrm{IL}_n} = \left(L_{\mathrm{T}} - \frac{n}{z_{\mathrm{I}}}R_{\mathrm{T}}^{-}\right)^{n-} \exp\left(\frac{z_{\mathrm{I}}F}{RT}\Delta\mathrm{EMF}\right) \tag{4}$$

where: n is the complex stoichiometry, L_{T} and R_{T} are the concentrations of ionophore and ionic site additives in the membrane, respectively.

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