Stoichiometry of Uranyl Salophene Anion Complexes

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In PVC/NPOE ion-selective membranes of potentiometric sensors, the guest−host stoichiometry of the anion complex of $H_2PO_4^-$ and F^- selective uranyl salophene derivatives is 2:1. This stoichiometry is different from the stoichiometry observed in DMSO solution (^{1}H NMR) or solid state (X-ray crystal structure). However, the 2:1 stoichiometry like that in the PVC/NPOE membrane matrix is also observed by ^{1}H NMR spectroscopy in *nonpolar* solvents such as chloroform. In contrast with the relatively hard $H_2PO_4^-$ and F^- anions, the softer Cl^- is bound in a 1:1 stoichiometry by the uranyl salophenes in chloroform.

Introduction

In our hands the neutral uranyl salophene building block has been very successful for the development of anion receptors.[1−3] The uranyl (UO_2^{2+}) center immobilized in the salophene unit favors a pentagonal bipyramidal coordination, with the oxygen atoms at the apical positions and four of the equatorial positions occupied by the deprotonated salophene ligand. The fifth equatorial position can coordinate to nucleophilic neutral guest species, e.g., urea,[4] methanol, or dimethyl sulfoxide, or to anions. The relatively hard electron-accepting uranyl center preferentially binds hard anions and binds $H_2PO_4^-$ with an association constant of 5×10^2 M^{-1} in DMSO.[1] The binding strength and selectivity can be modified by the introduction of additional hydrogen bond donating or accepting substituents in close proximity to the anion coordination site. The stoichiometry of these anion complexes in DMSO solutions was deduced from a Job plot analysis of ^{1}H NMR experiments. The experiments indicated for several $H_2PO_4^-$−uranyl salophene complexes a 1:1 ratio between anion and receptor in this solvent. In the *solid state* the stoichiometry depends on the type of additional binding site.[1] X-ray crystal structures show that salophene derivatives with $OCH_2C(O)$-NHR substituents bind $H_2PO_4^-$ with a 2:1 guest−host stoichiometry. One $H_2PO_4^-$ anion is coordinated to the uranyl center and forms additional hydrogen bond interactions with the amido moieties. The second $H_2PO_4^-$ anion is bound via hydrogen bond formation to the first anion and has no direct interaction with the receptor. A different stoichiometry is found for uranyl salophene derivatives with methoxy substituents. These receptors bind $H_2PO_4^-$ in a 1:1 stoichiometry. However, a centrosymmetric (2:2) dimer is formed by two of these complexes, in which the two $H_2PO_4^-$ anions interact with each other via hydrogen bond formation.

Recently we have modified the uranyl salophenes with lipophilic dodecyl substituents to improve the solubility in ion-selective membranes of chemically modified field effect transistor (CHEMFET)[5] potentiometric anion sensors. Based on these receptors, microsensors were developed with high selectivity toward $H_2PO_4^-$ or F^-.[2] This novel generation of lipophilic uranyl salophene derivatives is soluble even in nonpolar solvents such as chloroform and toluene, whereas the first generation of uranyl salophene derivatives was only soluble in polar solvents such as DMSO and acetonitrile. In contrast to DMSO, chloroform solvent molecules do not coordinate at the free position of the uranyl center, and anions are poorly solvated in chloroform. Consequently, solvents such as chloroform are probably much more representative for the situation in the nonpolar ion-selective membranes of potentiometric sensors and should be used to study the anion complexation.

Information about the complex stoichiometry in the membrane is required to obtain optimal sensor selectivity. This stoichiometry determines the maximum complex concentration in the membrane, and consequently this defines the upper limit of the concentration lipophilic counterions which always have to be present in the membrane. This maximum complex concentration *in* the ion-selective membrane can be determined independently by variation of the concentration of counterions in the ion-selective membrane. When the counterion concentration exceeds the maximum complex concentration, a reduction in the sensor selectivity is observed.

This paper describes our investigations of the uranyl salophene anion complex stoichiometry in chloroform solution and in the ion-selective membrane of potentio-

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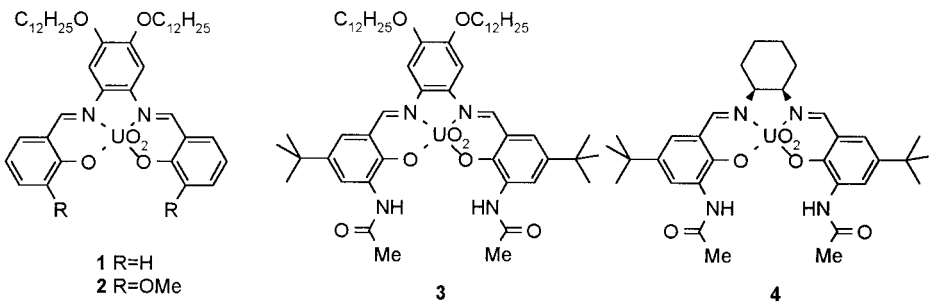
Chart 1



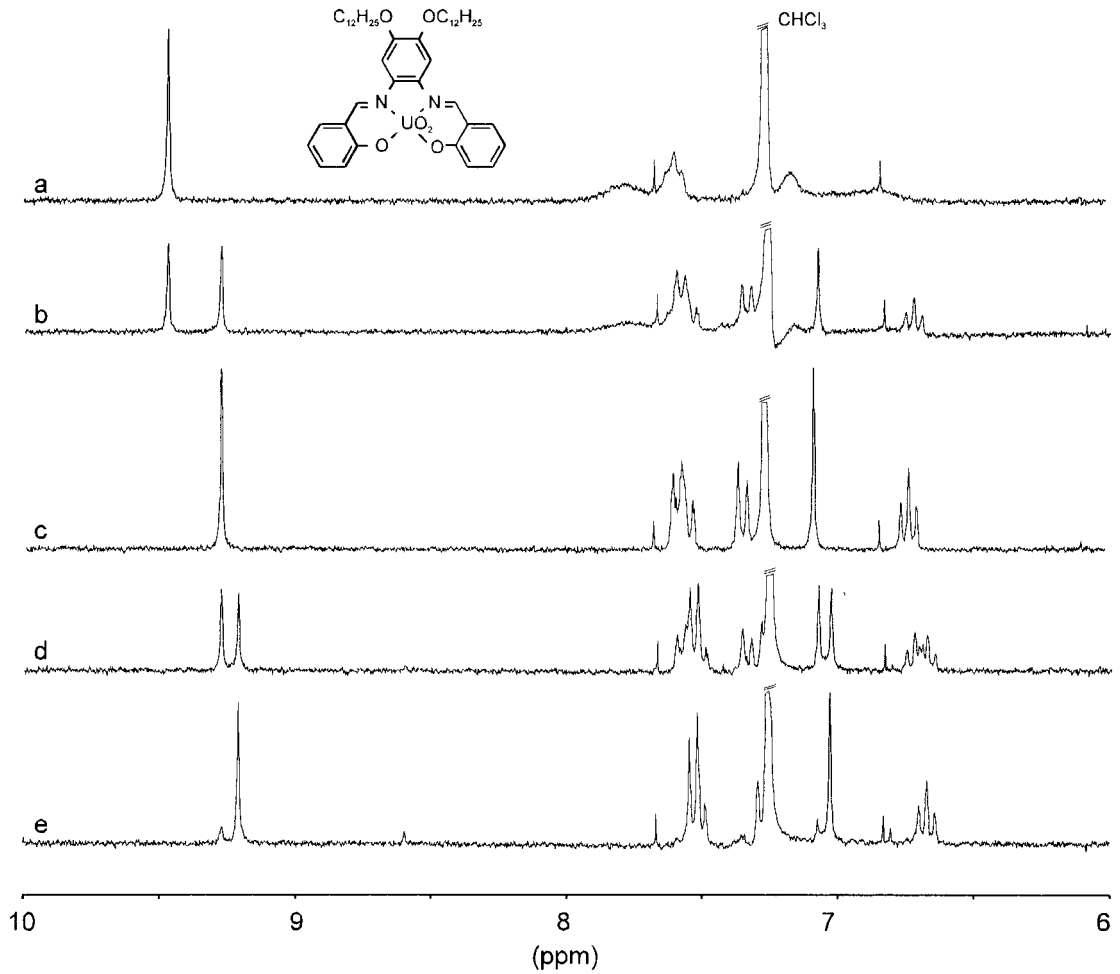


Figure 1. ^{1}H NMR spectrum of uranyl salophene **1** in $CDCl_3$ (a), and in the presence of 0.25 (b), 0.5 (c), 0.75 (d), or 1.0 (e) equiv of tetrabutylammonium dihydrogenphosphate.

metric sensors and the comparison with the complex stoichiometry in other media like the solid state or DMSO solution.

Results and Discussion

Complex Stoichiometry in $CDCl_3$ Solution (NMR experiments). Uranyl salophene derivative **1** selectively binds the $H_2PO_4^-$ anion and has previously been used in $H_2PO_4^-$ selective sensors. In Figure 1 the ^{1}H NMR spectra of the solutions are depicted that were obtained when small amounts of tetrabutylammonium salt of $H_2PO_4^-$ were added to a 1.0 mM solution of **1** in $CDCl_3$. In the absence of $H_2PO_4^-$ the signals are rather broad (spectrum a). However, a clear singlet of the imine hydrogen atoms is present at 9.47 ppm. Upon addition of $H_2PO_4^-$, the spectrum sharpens and a second signal of the imine hydrogen atoms appears at 9.28 ppm, indicating the binding of $H_2PO_4^-$ to the host. With 0.25 equiv of guest added (spectrum b), the intensities of these two imine signals are equal. When 0.5 equiv of $H_2PO_4^-$ is added, the initial imine hydrogen atom signal is absent and only the signal at 9.28 ppm is present (spectrum c). Also the other aromatic hydrogen atoms are present as distinct signals, e.g., at 7.08 ppm is the singlet of the catechol moiety. The high association constant in $CDCl_3$ results in complete complex formation, and the 1:2 guest−host ratio present in the sample indicates that the observed species is indeed the 1:2 anion−receptor complex, as was also observed in the ion-selective membrane of CHEMFETs. Upon further addition of $H_2PO_4^-$ the 1:2 anion−uranyl salophene complex is gradually converted

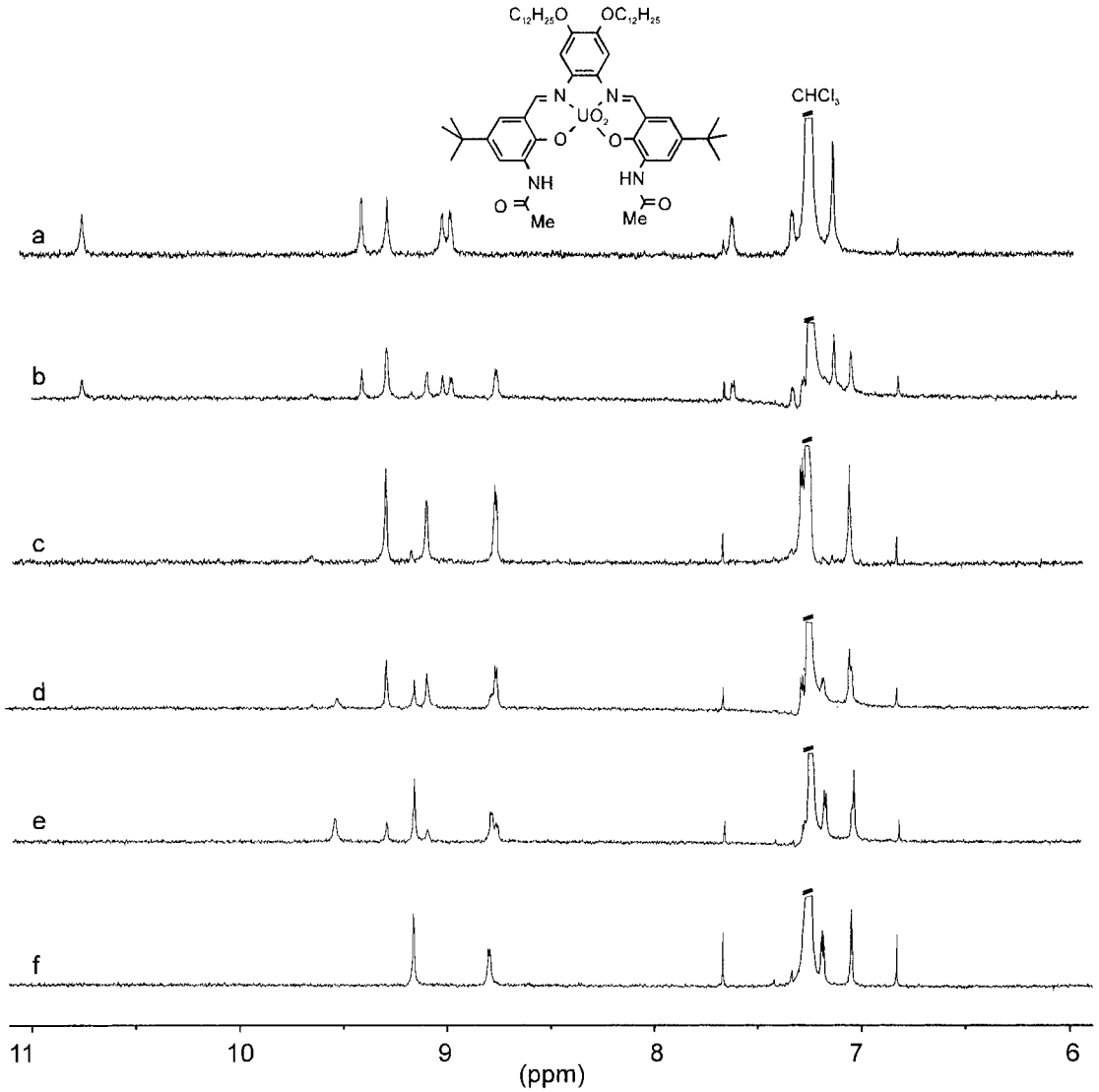


Figure 2. ^{1}H NMR spectrum of uranyl salophene **3** in $CDCl_3$ (a), and in the presence of 0.25 (b), 0.5 (c), 0.75 (d), 1.0 (e), or 5.0 (f) equiv of tetrabutylammonium fluoride.

into a 1:1 complex. In the NMR spectrum of **1** with 0.75 equiv of $H_2PO_4^-$ the presence of the 1:1 complex is reflected in the second imine hydrogen atom singlet at 9.21 ppm and the second singlet of the diamino catechol moiety at 7.03 ppm. At 1.0 equiv of guest (spectrum e) at least 90% of the uranyl salophene molecules are present as the 1:1 $H_2PO_4^-$ complex. The uranyl salophene receptor **2**, another derivative which has been used for $H_2PO_4^-$ selective CHEMFETs, also forms a 1:2 anion−receptor complex with $H_2PO_4^-$. This is apparent from the complete shift of the imine singlet from 9.36 to 9.24 ppm upon the addition of 0.5 equiv of $H_2PO_4^-$. Like in the case of **1**, a further increase of the anion concentration results in the conversion of the 1:2 complex to the 1:1 complex (imine singlet at 9.21 ppm).

Receptor **1** also complexes Cl^- in $CDCl_3$. Upon addition of tetrabutylammonium chloride, the Cl^- complexation shifts the imine hydrogen atom singlet in the ^{1}H NMR spectrum of **1** from 9.47 to 9.15 ppm. However, in contrast to the NMR experiment with $H_2PO_4^-$, with 0.5 equiv of Cl^-, still no complete complex formation is obtained and both imine singlets are present. Even with 1.0 equiv of Cl^-, only 40% of the uranyl salophene is present as complex, which illustrates the lower association constant for this complex. The complex formation is complete with 5 equiv of Cl^-, and only the imine singlet of the complex at 9.15 ppm is present. From these results it can be concluded that Cl^- forms a 1:1 complex with the parent salophene **1** which is thermodynamically less stable than the 1:1 complex of $H_2PO_4^-$. This nicely confirms the 60-fold selectivity for $H_2PO_4^-$ over Cl^- as has been observed for CHEMFETs.

The ^{1}H NMR spectrum of F^- receptor **3** in $CDCl_3$ shows double signals of equal intensity for imine and aromatic hydrogen atoms and the hydrogen atoms of the acetamido substituent (Figure 2, spectrum a). Especially the amido hydrogen atoms (at 10.76 and 9.02 ppm) and the signals of the aromatic hydrogen atom *ortho* to the amido substituent (at 8.99 and 7.26 ppm) have very different chemical shifts. According to CPK models, the distance between the uranyl center and the amido carbonyl oxygen atom is too large for intramolecular interactions. The asymmetry in the ^{1}H NMR spectrum might therefore be due to the formation of a dimer in which one amido oxygen atom is coordinated to the uranyl center of a second uranyl salophene molecule and vice versa. Similar dimeric structures have previously been reported for related amido substituted uranyl salophene derivatives

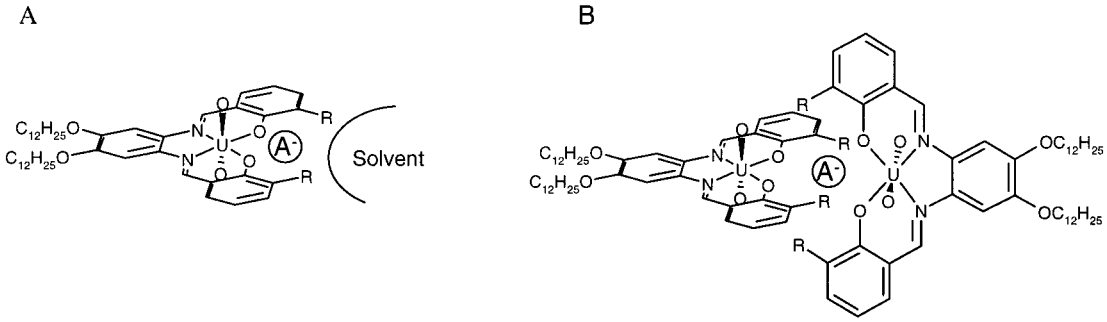


Figure 3. Possible structures for anion−uranyl salophene complexes with a 1:1 stoichiometry in a polar coordinative solvent (A), or a 1:2 stoichiometry in apolar solvents (B).

in the solid state.[1] The addition of tetrabutylammonium fluoride results in complex formation, and in the presence of 0.5 equiv of F^- unique signals are obtained for all aromatic and amide hydrogen atoms (spectrum c). The 1:2 ratio between the concentrations of F^- and uranyl salophene in the sample again indicates that this is the spectrum of a 1:2 F^-−uranyl salophene complex. At higher F^- concentration the 1:1 complex is formed. Compared to the 1:2 complex, the amide hydrogen atom singlet and one of the aromatic hydrogen atom doublets shift to lower field (from 9.10 to 9.54 ppm and from 8.77 to 8.79 ppm, respectively), whereas the other aromatic doublet and the imine singlet shift to higher field (from 7.28 to 7.19 ppm and from 9.29 to 9.16 ppm, respectively). In contrast to the $H_2PO_4^-$ selective derivative **1**, at 0.75 equiv of F^- a larger fraction of receptor **3** is present as the 1:2 complex rather than the 1:1 complex. At 1.0 equiv of F^-, 30% of the uranyl salophene receptor still is present as the 1:2 anion−receptor complex (spectrum e). This indicates that in the case of receptor **3** the 1:2 complex has a higher stability (relative to the 1:1 complex) than that observed for the $H_2PO_4^-$ complex of salophene **1**. Upon further increase of the F^- concentration to 5 equiv, complete formation of the 1:1 complex is observed (spectrum f).

Also, addition of tetrabutylammonium chloride breaks up the dimer of **3** which is initially present in $CDCl_3$ solution by the formation of the Cl^- complex of **3**. With 1.0 equiv of Cl^- added, the signals of the dimer have completely disappeared and only signals of the 1:1 complex are present. The chemical shifts of the 1:1 Cl^- complex are close to the values of the 1:1 F^- complex (Figure 2e,f). Further addition of Cl^- (up to 5 equiv) does not lead to any further changes in the spectrum. The Cl^- complexation by **3** has a higher association constant than complexation by **1**, because whereas **3** requires only 1 equiv of Cl^- for complete complex formation, derivative **1** requires an excess of anion.

The stoichiometry of the F^- complex was also investigated by mass spectrometry. For this purpose, the F^- selective uranyl salene derivative **4** was dissolved in acetonitrile with 0.5 equiv of tetrabutylammonium fluoride. After evaporation of the solvent, the FAB mass spectrum of the solid shows a strong signal of the 1:2 anion−receptor complex at $m/z = 1651.1$. Furthermore, signals for the masses of the 1:1 complex and the free receptor are present at $m/z = 836$ and $m/z = 816$, respectively.

These ^{1}H NMR experiments point out that in $CDCl_3$ the uranyl salophene derivatives can bind anions in a 2:1 anion−receptor stoichiometry. However, in previous anion complexation studies of uranyl salophene derivatives in solid state and solution, this anion binding stoichiometry was not observed. Several X-ray crystal structures of $H_2PO_4^-$ uranyl salophene complexes show that the $H_2PO_4^-$ oxygens that are not coordinated at the uranyl center form hydrogen bonds with a second $H_2PO_4^-$ anion. This already indicates the tendency toward a second interaction leading to a more stable complex. In a coordinating polar solvent (like DMSO previously used in the NMR experiments) the free side of the anion can be well solvated, and a 1:1 stoichiometry is observed.[1] In nonpolar solvents such as $CDCl_3$ such a stabilization is not available, and the "free" side of the anion might well be coordinated by a second uranyl salophene receptor (e.g., **1** and **3**, see Figure 3).

Since the complex stoichiometry is very important for optimizing the selectivity of potentiometric sensors, the stoichiometry in the ion-selective membrane was determined independently and compared with the result of the ^{1}H NMR experiments in order to decide which solvent is the best model system in this respect.

Complex Stoichiometry in Polymeric Membranes (CHEMFET experiments). The ion-selective membranes of potentiometric sensors contain both receptor molecules and lipophilic counterions. The receptor sites introduce the anion-selectivity into the sensor, whereas the positively charged counterions (tetraoctylammonium (TOAB) sites) compensate for the charge of the ion-receptor complex. Without the lipophilic counterions in the membrane, ions that are bound by the receptor molecules must coextract counterions from the sample. Such a coextraction does not contribute to the boundary potential when the sample ion concentration varies and consequently there is no sensor response. When the concentration of TOAB counterions is close to the concentration of receptor sites, more anions are attracted from the sample solution than can be bound by receptor molecules. This effect will be most pronounced for relatively lipophilic anions, e.g. NO_3^-. Several investigations of cation- and anion-selective sensors have shown that this results in a loss of the selectivity for the hydrophilic anions which are normally bound by the receptor molecules.[6−8] A good illustration is a sensor based on the neutral NO_2^- selective Co^{3+} porphyrin. The optimal selectivity of NO_2^- over NO_3^- (log $K^{Pot}_{NO_2,NO_3}$ =

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Table 1. Sensor Characteristics of $H_2PO_4^-$ Selective CHEMFETs with Receptor 1 (1 wt % in NPOE/PVC membrane) and Different Concentrations of Lipophilic Counterions (TOAB)

% TOAB	det limit[b]	log $K^{Pot}_{H_2PO_4,j}$ [slope mV/decade][a]		
		SO_4^{2-}	Br^-	NO_3^-
10	−3.1 [−56]	−2.3 [−49]	−1.4 [−48]	−1.1 [−50]
20	−3.1 [−59]	−2.5 [−55]	−1.7 [−58]	−1.1 [−52]
30	−3.1 [−58]	−2.4 [−57]	−1.5 [−57]	−1.0 [−50]
40	−3.6 [−59]	−2.4 [−57]	−1.6 [−50]	− [−37][c]
50	no $H_2PO_4^-$ response			

[a] [j] = 0.1 M in 0.01 M MES pH = 6.0. [b] log [$H_2PO_4^-$] in 0.01 M MES pH = 6.0. [c] Slope too low for determination of selectivity.

−2.1) is obtained when 50 mol % of ammonium sites are added with respect to the receptor, but the selectivity is lost when this amount is increased to 80 mol % (log $K^{Pot}_{NO_2,NO_3} = 0$).[9] Besides the concentration of the receptor [R], the maximum concentration of counterions is also determined by the charge *z* of the bound anion. For example, membranes with receptors that are selective toward bivalent ions should contain up to 150 mol % to get the optimal selectivity.[6] Moreover, the maximum concentration of counterions is determined by the *stoichiometry* of the complex. When a complex is formed by two receptor molecules and one monovalent ion, the maximum complex concentration is half the total receptor concentration in the membrane. Consequently, the concentration of counterions should not exceed a concentration of 50 mol % with respect to the receptor. For cation sensors, this has been observed for Li^+ selective sensors in which the optimal selectivity is observed below 50 mol % of ionic sites.[10] Summarizing, the maximum allowed concentration ionic sites $[N]_{max}$ is given by $[N]_{max} = z[R]/n$, with *n* the number of receptor molecules per anion in the complex.[6,11] Therefore, variation of the relative concentration of counterion vs the concentration of receptor is a method to determine the anion−receptor stoichiometry in the membrane.

We have varied the molar ratio between TOAB sites and lipophilic uranyl salophene derivative **1** in the $H_2PO_4^-$ selective membrane of CHEMFETs from 10 to 2 (10−50 mol % with respect to the receptor). The sensor characteristics of these CHEMFETs are given in Table 1. In contrast to what would be expected for complexes with a 1:1 stoichiometry, there is only a $H_2PO_4^-$ response below 50 mol % of TOAB. The optimal selectivity and response slopes are obtained for CHEMFETs with ion selective membranes containing between 20 and 30 mol % of TOAB. When the relative concentration of TOAB is higher than 30 mol %, the interference of lipophilic anions (for example NO_3^-) becomes especially predominant and the slope of CHEMFETs with membranes that contain 40 mol % of TOAB in the presence of 0.1 M $NaNO_3$ is reduced to −37 mV/decade (Figure 4).

The slope of the F^- response is even more sensitive to the relative concentration of TOAB than that of the $H_2PO_4^-$ selective CHEMFETs (Table 2). The F^- response of −50 mV/decade obtained for CHEMFETs with 20 mol % of TOAB reduces to −40 mV/decade for CHEMFETs

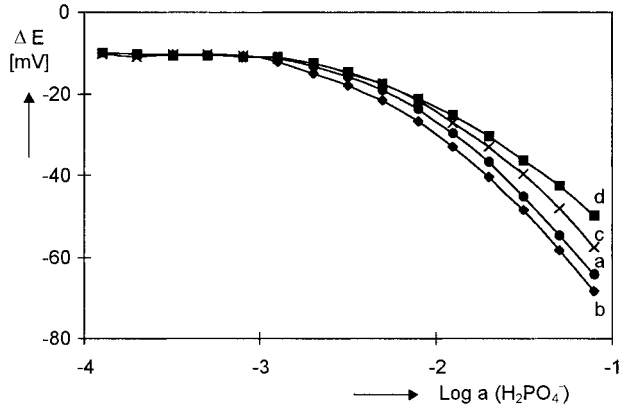

Figure 4. Phosphate response of CHEMFETs with receptor **1** and varying amount of TOAB in the presence of 0.1 M $NaNO_3$ (in 0.01 M MES, pH = 4.5). (a) 10 mol % TOAB; (b) 20 mol % TOAB; (c) 30 mol % TOAB; (d) 40 mol % TOAB.

Table 2. Sensor Characteristics of F^- Selective CHEMFETs with Receptor 3 (1 or 0.5 wt % in NPOE/PVC membrane) and Different Concentrations of Lipophilic Counterions (TOAB)

% TOAB	det limit[b]	log $K^{Pot}_{F,j}$ [slope mV/decade][a]		
		Cl^-	NO_3^-	ClO_4^-
10	−3.8 [−40]	−2.7 [−41]	−2.7 [−42]	−1.9 [−40]
20	−3.6 [−50]	−2.5 [−51]	−2.7 [−50]	−1.8 [−46]
30	−3.6 [−52]	−2.5 [−51]	−2.7 [−50]	−1.5 [−46]
40	−3.5 [−44]	−2.2 [−44]	−2.4 [−45]	> 0
50	no F^- response			
20[c]	−3.5 [−47]	−2.4 [−48]	−2.5 [−48]	−1.6 [−41]

[a] [j] = 0.1 M in 0.01 M MES pH = 6.0. [b] log [F^-] in 0.01 M MES pH = 6.0. [c] 0.5 wt % receptor.

with 10 mol % of TOAB. Also, a higher concentration TOAB above 30 mol % results in reduced response slopes (−44 mV/decade with 40 mol % of TOAB), and eventually with 50 mol % of TOAB the response is completely lost. Moreover, an increased concentration of TOAB results in higher interference of the lipophilic anions, and for example for ClO_4^- the selectivity reduces from −1.8 to −1.5, and to >0 for CHEMFET membranes with 20, 30, and 40 mol % of TOAB, respectively.

The sensor characteristics of the CHEMFETs with uranyl salophene derivatives **1** or **3** strongly change when the concentration of lipophilic counterions in the membrane exceeds 50 mol % with respect to the receptor concentration. Since both receptors are selective toward monovalent anions, this indicates that the uranyl salophene receptor must form complexes in the membrane with a 1:2 anion−receptor stoichiometry as has been observed in the ^1H NMR experiments.

The similarity between the complex stoichiometry observed in *nonpolar* solvents such as chloroform and in the NPOE plasticized membranes points out that these nonpolar solvents are a better model system for the membrane phase than solvents such as DMSO or acetonitrile. Although we and many others have used the latter polar solvents to illustrate the strong ion binding of novel receptors,[12] the complex properties (i.e., the stoichiometry and association constant) can be completely

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different under the conditions of real applications, like the ion-selective membrane of ion-selective sensors or ion separation membranes.[13]

Experimental Section

General. The tetrabutylammonium salts were purchased from Fluka. The synthesis of uranyl salophene derivatives **1**−**3** have been described previously.[2] Uranyl salophene derivative **4** was synthesized following the procedure for the synthesis of salophene **3** using 1,2-diaminocyclohexane. The composition of the ion-selective membrane of CHEMFETs and the CHEMFET measurements have been described previously.[2] The NMR spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ unless otherwise indicated. Residual solvent protons were used as internal standard and chemical shifts are given in ppm relative to TMS. Ion fast atom bombardment (FAB) mass spectra were obtained with *m*-nitrobenzyl alcohol as a matrix.

[*N*,*N*′-[1,2-cyclohexanediylbis[nitrilomethylidyne(5-*tert*-butyl-2-hydroxy-1,3-phenylene)] acetamide] (2-)-*N*,*N*′,*O*,*O*′]Dioxouranium (4). Yield 65%. Mp: >300 °C. ^{1}H NMR (DMSO-d_6) δ 9.49 (s, 2H), 9.13 (s, 2H), 8.66 (s, 2H), 7.38 (s, 2H), 4.7−4.6 (m, 2H), 2.45−2.3 (m, 8H), 1.9−1.8 (m, 2H), 1.7−1.6 (m, 2H), 1.3 (s, 18H). ^{13}C NMR (DMSO-d_6) δ 168.5 (d), 168.0 (s), 156.9 (s), 138.0 (s), 129.1 (s), 124.5 (d), 121.3 (s), 121.0 (d), 70.6 (d), 33.7 (s), 31.4 (q), 27.4 (t), 24.9 (q), 21.5 (t). MS−FAB 816.0 ([M]$^-$, calcd 816.4), 1631.1 ([2M − H]$^-$, calcd 1631.8). Anal. Calcd for $C_{32}H_{42}N_4O_6U\cdot0.25CH_2Cl_2$: C, 46.0; H, 5.1; N, 6.7. Found: C, 46.0; H, 5.1; N, 6.7.

NMR Experiments. Samples with between 0.25 and 1 equiv of anion guest with respect to the receptor were obtained by the addition of small volumes of a stock solution of the guest (7.5×10^{-3} M $H_2PO_4^-$, Cl^-, or F^- tetrabutylammonium salt in $CDCl_3$) to 0.5 mL of a 10^{-3} M solution of the receptor **1**, **2**, or **3** in $CDCl_3$.

[[4,5-Bis(dodecyloxy)-1,2-phenylenebis[nitrilomethylidyne(2-hydroxyphenyl)]] (2-)-*N*,*N*′,*O*,*O*′]Dioxouranium (1). 1:2 $H_2PO_4^-$−receptor complex: ^{1}H NMR δ 9.28 (s, 2H), 7.57 (m, 4H), 7.34 (d, 2H, J = 8.1 Hz), 7.08 (s, 2H), 6.72 (t, 2H, J = 7.3 Hz), 4.14 (t, 4H, J = 6.6 Hz), 1.95−1.85 (m, 4H), 0.88 (t, 6H, J = 6.8 Hz).

1:1 $H_2PO_4^-$−receptor complex: ^{1}H NMR δ 9.21 (s, 2H), 7.52 (m, 4H), 7.29 (d, 2H), 7.03 (s, 2H), 6.67 (t, 2H, J = 7.3 Hz), 4.11 (t, 4H, J = 6.6 Hz), 1.95−1.85 (m, 4H), 0.87 (t, 6H, J = 6.9 Hz).

1:1 Cl^-−receptor complex: ^{1}H NMR δ 9.15 (s, 2H), 7.49 (m, 4H), 7.16 (d, 2H, J = 7.5 Hz), 6.97 (s, 2H), 6.60 (t, 2H, J = 7.9 Hz), 4.09 (t, 4H, J = 6.6 Hz), 1.8−1.9 (m, 4H), 0.87 (t, 6H, J = 6.7 Hz).

[[4,5-Bis(dodecyloxy)-1,2-phenylenebis[nitrilomethylidyne(2-hydroxy-3-methoxyphenyl)]] (2-)-*N*,*N*′,*O*,*O*′]Dioxouranium (2). 1:2 $H_2PO_4^-$−receptor complex: ^{1}H NMR δ 9.24 (s, 2H), 7.22 (d, 2H), 7.09 (d, 2H, J = 7.7 Hz), 7.03 (s, 2H), 6.56 (t, 2H, J = 7.8 Hz), 4.14 (t, 4H, J = 6.3 Hz), 4.03 (s, 6H), 1.95−1.85 (m, 4H), 0.87 (t, 6H, J = 6.7 Hz).

1:1 $H_2PO_4^-$−receptor complex: ^{1}H NMR δ 9.20 (s, 2H), 7.19 (d, 2H, J = 6.6 Hz), 7.13 (d, 2H, J = 7.7 Hz), 7.00 (s, 2H), 6.56 (t, 2H, J = 7.7 Hz), 4.15 (s, 6H), 1.95−1.85 (m, 4H).

[*N*,*N*′-[4,5-Bis(dodecyloxy)-1,2-phenylenebis[nitrilomethylidyne(5-*tert*-butyl-2-hydroxy-1,3-phenylene)]acetamide] (2-)-*N*,*N*′,*O*,*O*′]Dioxouranium (3). 1:2 F^-−receptor complex: ^{1}H NMR δ 9.30 (s, 2H), 9.10 (s, 2H), 8.76 (d, 2H, J = 2.1 Hz), 7.28 (d, 2H, J = 2.5 Hz), 7.06 (s, 2H), 4.17 (t, 4H, J = 6.7 Hz), 2.46 (b, 6H), 1.95−1.85 (m, 4H), 0.88 (t, 6H, J = 6.4 Hz).

1:1 F^-−receptor complex: ^{1}H NMR δ 9.54 (s, 2H), 9.16 (s, 2H), 8.79 (d, 2H, J = 2.4 Hz), 7.19 (d, 2H, J = 2.5 Hz), 7.05 (s, 2H), 4.12 (t, 4H, J = 6.4 Hz), 2.42 (s, 6H), 1.95−1.85 (m, 4H), 0.87 (t, 6H, J = 6.4 Hz).

1:1 Cl^-−receptor complex: ^{1}H NMR δ 9.65 (s, 2H), 9.17 (s, 2H), 8.77 (d, 2H, J = 2.3 Hz), 7.18 (d, 2H, J = 2.1 Hz), 7.05 (s, 2H), 4.13 (t, 4H, J = 6.5 Hz), 2.46 (s, 6H), 1.95−1.85 (m, 4H), 0.87 (t, 6H, J = 6.8 Hz).

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(13) Also under the conditions of supported-liquid ion separation membranes the 1:2 guest−host stoichiometry has been observed. Chrisstoffels, L. A. J.; de Jong, F.; Reinhoudt, D. N. Manuscript in preparation.