Facilitated Transport of Salts by Neutral Anion Carriers

Lysander A. J. Chrisstoffels, Feike de Jong,* and David N. Reinhoudt*[a]

Abstract: Partitioning of ions from water to the membrane solvent (NPOE) can be quantified by Gibbs free energies of transfer, $\Delta G_{tr,NPOE}$(ion). These were derived from transport studies of lipophilic salts through supported liquid membranes (SLMs) in the absence of the carrier. Partition coefficients K_p for various salts can now be calculated. The neutral anion receptors uranyl sal(oph)enes **1**–**5** transport Cl^- and $H_2PO_4^-$ as tetrapropylammonium salts. The transport is diffusion-limited and can be described by two transport parameters D_m and K_{ex}. From the extraction constants K_{ex} and the partition coefficients K_p of the transported salts, the association constants K_a of the anion receptors for Cl^- and $H_2PO_4^-$ in NPOE were determined. Competitive transport with carriers **3** and **4** of $NPr_4H_2PO_4$ and NPr_4Cl demonstrated highly selective transport of $H_2PO_4^-$ even in the presence of excess of Cl^-.

Keywords: anion recognition · artificial receptors · host–guest chemistry · molecular recognition · supramolecular chemistry

Introduction

Anion recognition by artificial receptors is an important objective in supramolecular chemistry.[1] Although mainly positively charged ammonium receptors have been investigated as anion receptors,[2] there are now a variety of receptors that contain combinations of Lewis acid,[3] amido and urea,[4] sulfoxide and phosphine oxide,[5] pyrrole,[6] or guanidinum[7] moieties. Most anion binding studies have used ^{1}H-NMR, IR, or UV spectroscopic methods and were performed in non-hydrogen bonding and nonpolar organic media in which anions are poorly solvated. Consequently, the resulting binding affinities are reasonably high.

Carrier-facilitated transport of salts through liquid membranes by anion receptors either positively charged, protonizable, or neutral has only incidentally been reported. Tetraalkylammonium cations[8] or metal porphyrins[9] have a permanent charge and the anions are transported by means of a counter-anion gradient (e.g. OH^-). The transport selectivities are mostly governed by the anion hydrophobicity. Anion-facilitated transport by protonizable carriers, such as (expanded) porphyrins[10] trialkylamines,[11] or cryptates[12] requires the cotransport of protons.

There are only few examples of anion-facilitated transport by *neutral* anion carriers. Selective transport of Cl^- over other halides through bulk liquid membranes (BLM) has been achieved by Lewis acidic organometallic receptors, 12-silacrown-3,[3c] organogermanium macrocycles,[3g] or praseodymium complexes.[13] In these cases a cation is cotransported with the anion complex through the membrane phase.

In this paper, anion-facilitated transport by neutral anion carriers through supported liquid membranes (SLMs) is described. As transport rates and selectivities are greatly affected by anion partitioning we will first discuss the transfer of anions from water to the membrane solvent *o*-nitrophenyl *n*-octyl ether (NPOE) in the absence of carrier. We will demonstrate that the salts used are present in the membrane phase as free ions and present a scale for Gibbs free energies of transfer from water to (water-saturated) NPOE ($\Delta G_{tr,NPOE}$) for both anions and cations.

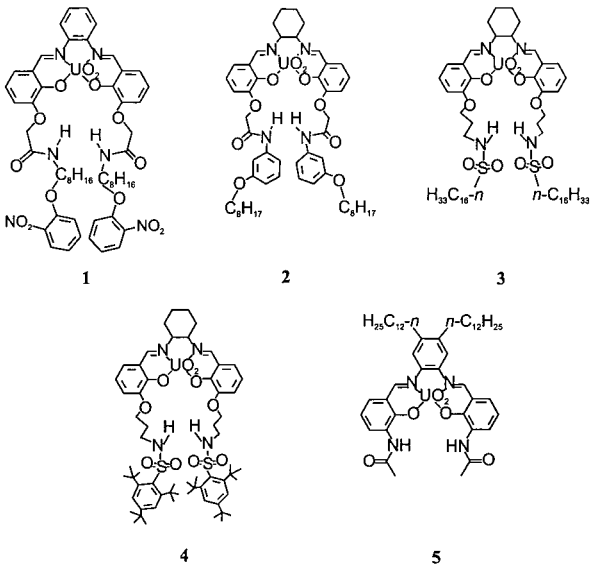
For the facilitated transport a number of novel uranyl sal(oph)ene receptors (**2**–**4**) were synthesized because we have recently demonstrated that in DMSO this class of receptors form strong complexes with $H_2PO_4^-$ ($K_a > 10^3\,M^{-1}$).[3h] The presence of two hydrogen-bond donor sites in close proximity of the uranyl cleft increases the binding and $H_2PO_4^-$ is selectively complexed over Cl^- with a selectivity factor > 100.

Anion-facilitated transport of $NPr_4H_2PO_4^-$ and NPr_4Cl with uranyl sal(oph)ene carriers **1**–**5** will be studied as a function of the membrane thickness, carrier, and salt concentrations.[14] The diffusion-limited transport will be characterised in terms of a diffusion coefficient D_m and an extraction constant K_{ex} ($K_{ex} = K_a K_p$). This model has previously been used to describe cation-facilitated transport by neutral cation carriers.[15]

Association constants K_a of host–guest complexes in NPOE were determined from the extraction constants K_{ex} and partition coefficients K_p. To the best of our knowledge this is the first time that *stability constants* of complexes were determined directly from membrane transport experiments,

[a] Prof. F. de Jong, Prof. D. N. Reinhoudt, Dr. L. A. J. Chrisstoffels
Department of Supramolecular Chemistry and Technology
MESA$^+$ Research Institute, University of Twente
P.O. Box 217, 7500 AE Enschede (The Netherlands)
Fax: (+31) 53-4894645
E-mail: d.n.reinhoudt@ct.utwente.nl

  0947-6539/00/0608-1376 $ 17.50+.50/0



1 2 3 4 5

and underlines the potential of SLM transport as a mechanistic tool for the determination of thermodynamic parameters.

Results and Discussion[16]

Synthesis of lipophilic anion carriers: The syntheses of uranyl salenes **2**–**4** is depicted in Scheme 1. Lipophilic chloroacetamide **9** was synthesized from the corresponding amine and chloroacetyl chloride under Schotten–Baumann conditions. Sulfonamides **12a** and **12b** were prepared by reaction of the commercially available sulfonyl chlorides with 2-chloroethylamine or 3-chloropropylamine (as HCl salts) in the presence of two equivalents of Et_3N in CH_2Cl_2. Subsequently, 2-(2-allyloxy)-3-hydroxybenzaldehyde was reacted with amide **9** or with sulfonamide **12a**–**b** in the presence of K_2CO_3 in MeCN. Deallylation of the resulting compounds **10** and **13a**–**b** was achieved by a Pd-catalyzed reaction with Et_3N/HCOOH in EtOH/H_2O and this afforded the corresponding aldehydes **11**, **14a**, and **14b** in 80–90% yield. Reaction these aldehydes with *cis*-1,2-cyclohexyldiamine in the presence of uranyl acetate in methanol gave uranyl salene carriers **2**–**4** in a yield of 50–90%. The molecular peak in the FAB-MS spectra indicated the formation of the uranyl salenes.

Gibbs free energies of ion transfer from water to NPOE: In the absence of carrier the rate of salt transport through SLMs is proportional to the partition coefficient K_p which is related to the Gibbs free energy of transfer $\Delta G_{tr,NPOE}(MX)$ of the salt MX from water to NPOE [(Equation (1)].

$$RT\ln(K_p) = -\Delta G_{tr,NPOE}(MX) = -[\Delta G_{tr,NPOE}(M^+)+\Delta G_{tr,NPOE}(X^-)] \quad (1)$$

Equation (1) is only valid for solvent-separated ions. The presence of ion pairs will to a large extent be determined by the polarity of the membrane solvent.[17] Previously, Cussler and co-workers concluded that ion pairing occurs in the apolar solvent *n*-heptyl nitrile ($\varepsilon_r = 13.9$) from transport experiments of NBu_4NO_3.[18] Lamb et al. also described facilitated transport through a liquid membrane of cyclohexyl phenyl ether as ion pairs.[19] In our previous studies, we assumed that cation-facilitated transport of salts through NPOE occurs as solvent-separated ions[15] as the polarity of the solvent is relatively high ($\varepsilon_r = 24$) and the concentrations of salt in the membrane phase are relatively low.

It is possible, however, to verify experimentally if salts in NPOE are transported as ion pairs or as free ions. Applying Fick's law to the diffusion-limited transport of solvent-separated ions [Eq. (2)] or ion pairs [Eq. (5)] leads to different relations between the initial flux J_0 and the aqueous salt activity a_s [Eqs. (4) and (7)].

$$[M^+]_{aq}+[X^-]_{aq} \rightleftharpoons [M^+]_{ms}+[X^-]_{ms} \quad (2)$$

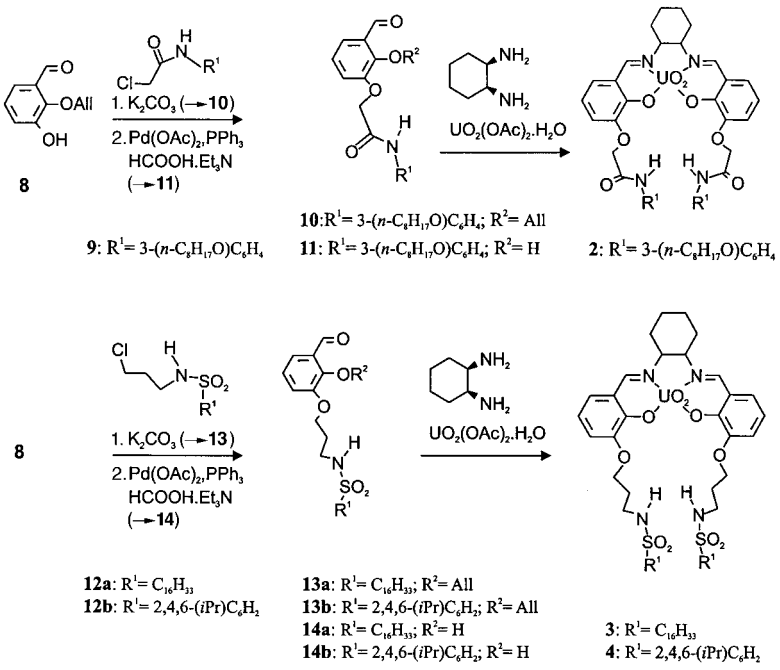
$$J_0 = \frac{D_m}{d_m}[M^+]_{ms};\ [M^+]_{ms} = a_{s,0}\sqrt{K_p} \quad (3)$$

$$\ln\left(\frac{d_m J_0}{D_m}\right) = \ln(a_{s,0}) + \frac{1}{2}\ln(K_p) \quad (4)$$

$$[M^+]_{aq}+[X^-]_{aq} \rightleftharpoons [M^+X^-]_{ms} \quad (5)$$

$$J_0 = \frac{D_m}{d_m}[M^+\cdot A^-]_{ms} = a_{s,0}^2 K_p \quad (6)$$

$$\ln\left(\frac{d_m J_0}{D_m}\right) = 2\ln(a_{s,0}) + \ln(K_p) \quad (7)$$



Scheme 1. Reaction scheme for the preparation of uranyl salenes **2**, **3**, and **4**.

For the calculation of $\ln(d_m J_0/D_m)$, the diffusion coefficient D_m needs to be known. We determined D_m independently for NBu_4NO_3 by lag-time experiments ($D_m = 14 \times 10^{-12}\ m^2 s^{-1}$).[20, 21] We assumed that D_m has the same value for all salts used.[22] The initial flux J_0 was measured as a function of the salt activity in the source phase for a range of lipophilic salts, and it was found that $\ln(d_m J_0/D_m)$ and $\ln(a_{s,0})$ are linearly related (Figure 1).

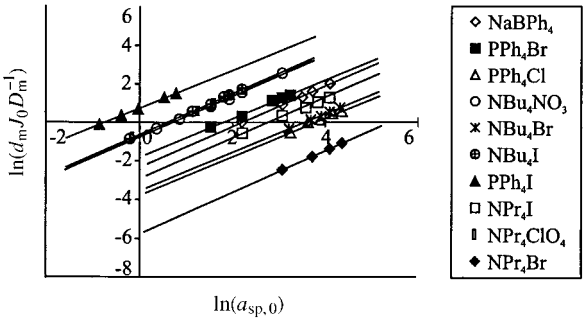


Figure 1. Transport of lipophilic salts: $\ln(d_m J_0 D_m^{-1})$ as a function of salt activity in the source phase $\ln(a_{s,0})$, $D_m = 14 \times 10^{-12}\ m^2 s^{-1}$, $d_m = 1 \times 10^{-4}$ m.

As all slopes are about 1 (Table 1), these salts are present in NPOE as solvent-separated ions. Subsequently, the partition coefficients K_p were calculated from the intercepts [Eq. (4)]; the corresponding values for $\Delta G_{tr,NPOE}(MX)$ were then obtained from Equation (1).

Table 1. Determination of the Gibbs free energies of transfer $\Delta G_{tr,NPOE}(MX)$ from the transport of lipophilic salts, $T = 298$ K.

MX	Slope	Intercept	$\Delta G_{tr,NPOE}$ (MX)[a] [kJ mol^{-1}]	$\Delta G_{tr,MeCN}$(MX)[b] [kJ mol^{-1}]
PPh_4Cl	0.99	−3.70	18.3	9.3
PPh_4Br	1.00	−1.81	9.0	−1.5
PPh_4I	0.98	+0.74	−3.7	−16
$NaBPh_4$	1.05	−2.33	11.5	−17.7
NBu_4NO_3	1.06	−0.76	3.8	−10
NBu_4Br	1.00	−3.55	17.6	0.3
NBu_4I	1.06	−0.63	3.1	−14.2
NPr_4Br	1.06	−5.75	28.5	18.3
NPr_4I	0.97	−2.68	13.3	3.8
NPr_4ClO_4	1.01	−0.57	2.8	−11
NEt_4ClO_4	1.02	−3.09	15.3	−5.0
NMe_4ClO_4	0.95	−4.33	21.4	5.0

[a] Values determined according to Equations (1) and (4). [b] Values taken from refs. [22] and [24].

In order to obtain the individual contributions of $\Delta G_{tr,NPOE}(X^-)$ and $\Delta G_{tr,NPOE}(M^+)$ to $\Delta G_{tr,NPOE}(MX)$ we first make the extrathermodynamic assumption that the individual contributions of $\Delta G_{tr,NPOE}(PPh_4^+)$ and $\Delta G_{tr,NPOE}(BPh_4^-)$ to $\Delta G_{tr,NPOE}(PPh_4BPh_4)$ are equal [Eq. (8)].[23] Together with $\Delta G_{tr,NPOE}(NaBPh_4)$, $\Delta G_{tr,NPOE}(PPh_4I)$, and $\Delta G_{tr,NPOE}(NaI)$ we get a set of four Equations (8–11) and four unknowns.

$$\Delta G_{tr,NPOE}(BPh_4^-) = \Delta G_{tr,NPOE}(PPh_4^+) \quad (8)$$

$$\Delta G_{tr,NPOE}(NaBPh_4) = \Delta G_{tr,NPOE}(BPh_4^-) + \Delta G_{tr,NPOE}(Na^+) \quad (9)$$

$$\Delta G_{tr,NPOE}(PPh_4I) = \Delta G_{tr,NPOE}(PPh_4^+) + \Delta G_{tr,NPOE}(I^-) \quad (10)$$

$$\Delta G_{tr,NPOE}(NaI) = \Delta G_{tr,NPOE}(I^-) + \Delta G_{tr,NPOE}(Na^+) \quad (11)$$

We obtained the values for $\Delta G_{tr,NPOE}(NaBPh_4)$ and $\Delta G_{tr,NPOE}(PPh_4I)$ from transport experiments (Table 1). Unfortunately, $\Delta G_{tr,NPOE}(NaI)$ could not be determined from membrane transport because NaI is too hydrophilic and there is no blank transport. Therefore, we searched for an alternative to determine $\Delta G_{tr,NPOE}(NaI)$ and used an empirically established linear free energy relationship between transfer free energies from water to NPOE and from water to acetonitrile.[24] When the transport of lipophilic tetrabutylammonium salts (0.05 M) through NPOE was measured as a function of the anion (Table 2), we found that the initial flux J_0 is inversely related to the Gibbs free energy of anion transfer from water to acetonitrile $\Delta G_{tr,MeCN}(X^-)$ (Figure 2). The correlation between $\ln(J_0)$ and $\Delta G_{tr,MeCN}(X^-)$ is good ($r^2 = 0.97$).

Table 2. Initial transport J_0 of butylammonium salts ($[Salt]_s = 0.05$ M) through NPOE.[a]

Salt	J_0 [10^{-8} mol m^{-2} s^{-1}]	$\Delta G_{tr,MeCN}(X^-)$ [kJ mol^{-1}]	$\Delta G_{tr,MeCN}(NBu_4X)$ [kJ mol^{-1}]
$NBu_4H_2PO_4$	< 0.5	–	–
NBu_4Cl	6.3	42	10
NBu_4Br	19	31	−1
NBu_4NO_3	324	21	−11
NBu_4I	447	17	−15
NBu_4SCN	1120	14	−18

[a] The transport of NBu_4ClO_4 was not measured, due to the limited solubility in water. [b] $\Delta G_{tr,MeCN}(NBu_4^+) = -32$ kJ mol^{-1}.

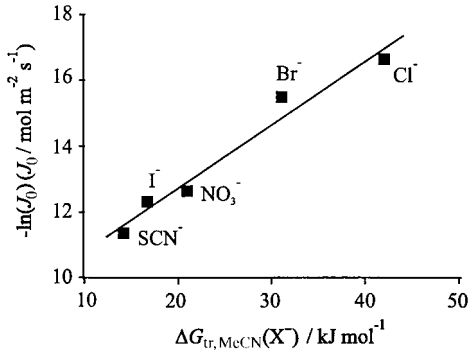


Figure 2. Transport of NBu_4^+ salts through NPOE; $\ln(J_0)$ (J_0 in mol m^{-2} s^{-1}) as a function of the Gibbs free energy of anion transfer from water to acetonitrile $\Delta G_{tr,MeCN}(X^-)$.

For all cations (NPr_4^+, NBu_4^+, PPh_4^+) shown in Table 1, the correlation between $\Delta G_{tr,NPOE}(MX)$ and $\Delta G_{tr,MeCN}(MX)$ is also good (Figure 3). The same slope for all cations of about 1.1 indicates that the relative anion-solvating properties of MeCN and NPOE are comparable.

When we now assume that Na-salts show the same slope, we can derive Equation (12) (dotted line in Figure 3).

$$\Delta G_{tr,MeCN}(NaX) = 1.1 \times \Delta G_{tr,NPOE}(NaX) - 31 \quad (12)$$

With $\Delta G_{tr,MeCN}(NaI) = 32$ kJ mol^{-1} as reported by Marcus,[25] we obtain $\Delta G_{tr,NPOE}(NaI)$ as 57.3 (±4.3) kJ mol^{-1}.

The values for $\Delta G_{tr,NPOE}$ can now be calculated from Eqs. (8–11) (Table 3). The lipophilicity of the alkylammonium

0947-6539/00/0608-1378 $ 17.50+.50/0 Chem. Eur. J. 2000, 6, No. 8

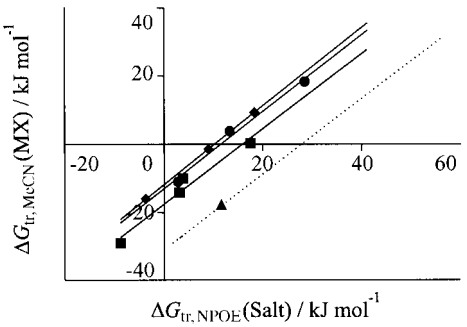


Figure 3. Free energy correlation between $\Delta G_{tr,NPOE}(MX)$ and $\Delta G_{tr,MeCN}(MX)$ for NBu_4^+ (●), NPr_4^+ (■), PPh_4^+ (◆), and Na^+ (▲) salts.

salts increases with the length of the alkyl chain as expected. The difference in lipophilicity among the anions is quite large and the order is in agreement with the Hofmeister series.[26] The correlation between $\Delta G_{tr,MeCN}(X^-)$ as reported by Marcus[25] and $\Delta G_{tr,NPOE}(X^-)$ as obtained from Table 3 is very good (Eq. (13), $r^2 = 0.99$). The good correlation confirms the comparable solvation of anions in NPOE and MeCN.

$$\Delta G_{tr,NPOE}(X^-) = 0.91 \times \Delta G_{tr,MeCN}(X^-) + 5.64 \quad (13)$$

As a result of this work partition coefficients from water to NPOE of salts can now be calculated [Eq. (1)] as the sum of the $\Delta G_{tr,NPOE}$ values of the appropriate anion and cation.[27]

Table 3. Absolute Gibbs free energies $\Delta G_{tr,NPOE}$ of single ion transfer from water to NPOE, $T = 298$ K.

M^+	$\Delta G_{tr,NPOE}(M^+)$ [kJ mol^{-1}]	X^-	$\Delta G_{tr,NPOE}(X^-)$ [kJ mol^{-1}]
PPh_4^+	−24.8	BPh_4^-	−24.8
NBu_4^+	−18	ClO_4^-	10.6
NPr_4^+	−7.8	SCN^-	19.2
NEt_4^+	4.7	I^-	21.1
NMe_4^+	10.8	NO_3^-	21.8
Na^+	36.3	Br^-	33.8
		Cl^-	43.1
		$H_2PO_4^-$	>60

Anion-facilitated salt transport: Previously, we have described facilitated transport by neutral cation carriers through SLMs with a model for diffusion-limited transport.[15, 28] The model was verified experimentally for the transport of guanidinium, alkali metal, and earth-alkaline metal cations.[15, 29] It was shown that when the carrier forms a 1:1 complex with the cation, the initial flux J_0 is related to the apparent diffusion coefficient D_m of the complex,[21] the extraction constant K_{ex}, the salt activity a_s in the source phase, the carrier concentration L_0 in the membrane phase, and the thickness d_m of the membrane [Eq. (14)].

$$J_0 = \frac{D_m}{2 d_m}\left[-A + \sqrt{(A)^2 + 4 L_0 A}\right] \text{ with } A = K_{ex} a_s^2 \quad (14)$$

By variation of the experimental parameters d_m, a_s, and L_0, the two parameters that describe the transport of cations (D_m and K_{ex}) could be obtained. We have now used the same model to describe carrier-facilitated transport by a neutral anion carrier (Figure 4).

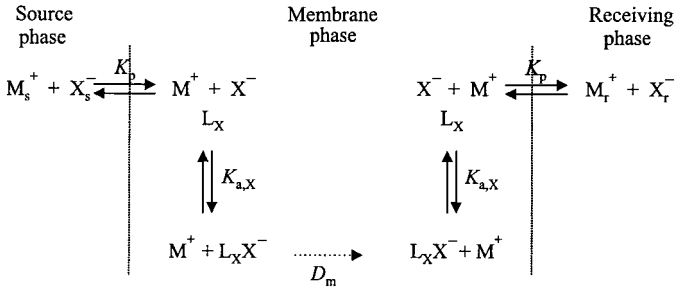


Figure 4. Mechanism of anion-facilitated transport through SLMs.

In all transport experiments the rate-limiting step is diffusion through the membrane because for the transport of NPr_4Cl (0.3 M) by uranyl salenes **2**–**5** and $NPr_4H_2PO_4$ (0.3 M) by uranyl salenes **2**–**4** the relation between $L_0 J_0^{-1}$ and d_m is linear (Figures 5 and 6) and the intercept is close to zero. For the case of transport from $NPr_4H_2PO_4$ solutions, it is assumed that the transported anion is $H_2PO_4^-$ and not HPO_4^{2-} in analogy with the findings for transport from KH_2PO_4 solution.[30]

The transport of Cl^- and $H_2PO_4^-$ salts by carriers **2**–**4** measured as a function of the carrier concentration from a

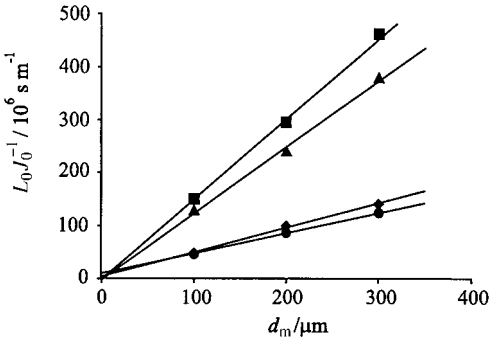


Figure 5. Influence of the membrane thickness d_m on $[L]_0 J_0^{-1}$ for the transport of NPr_4Cl by carriers **2** (◆), **3** (▲), **4** (■), and **5** (●); $[carrier]_m = 10$ mM.

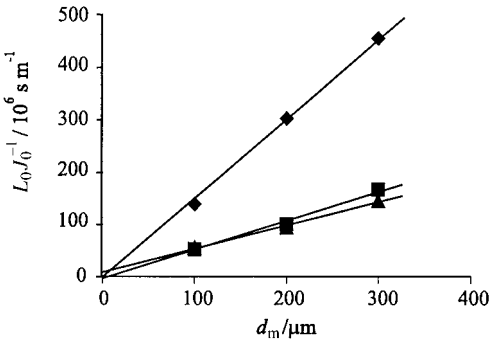


Figure 6. Influence of the membrane thickness d_m on $[L]_0 J_0^{-1}$ for the transport of $NPr_4H_2PO_4$ by carriers **2** (◆), **3** (▲), and **4** (■); $[carrier]_m = 10$ mM.

source phase containing 0.3 M NPr_4Cl or 0.3 M $NPr_4H_2PO_4$ (Figures 7 and 8) showed an almost linear relation. Carrier **2** is much more efficient in transporting NPr_4Cl than **3** and **4** whereas carriers **3** and **4** transport $NPr_4H_2PO_4$ much more efficiently than **2**.

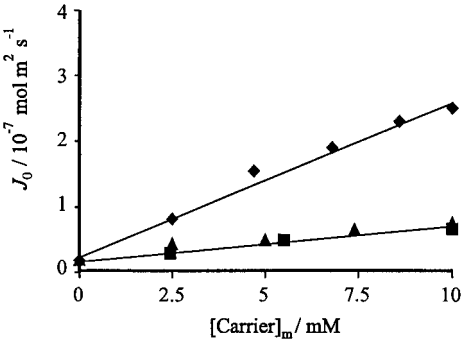


Figure 7. Transport of NPr_4Cl by carriers **2** (◆), **3** (■), and **4** (▲) as a function of the carrier concentration; $[NPr_4Cl]_s = 0.3$ M.

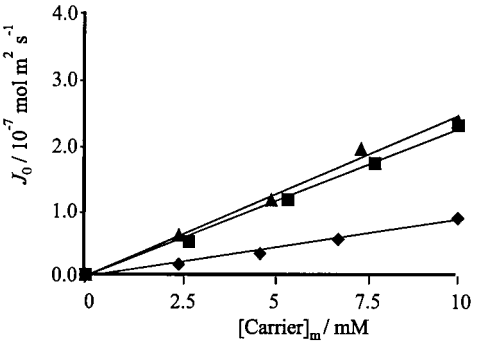


Figure 8. Transport of $NPr_4H_2PO_4$ by carriers **2** (◆), **3** (■), and **4** (▲) as a function of the carrier concentration; $[NPr_4H_2PO_4{+}NPr_4H_2PO_4]_s = 0.3$ M and pH_s 6.7.

Figures 9 and 10 show the dependency of the flux on the salt concentration in the source phase for anion-facilitated transport of NPr_4Cl and $NPr_4H_2PO_4$. Uranyl salenes **1**, **2** and salophene **5** having additional amido groups transport NPr_4Cl much faster than $NPr_4H_2PO_4$. Even at higher salt concentrations, carriers **1** and **5** hardly transport $NPr_4H_2PO_4$. Salenes **3** and **4** bearing two sulfonamido groups transport $NPr_4H_2PO_4$ much more efficiently than NPr_4Cl.

When K_{ex} is high, transport reaches a maximum at high salt concentration as all carriers are complexed at the source phase interface. From the maximum flux $J_{0,max}$ and the complex concentration in the membrane phase D_m can be calculated according to Eq. (15).[15]

$$J_{0,max} = \frac{D_m}{d_m}[\text{complex}]_m \qquad (15)$$

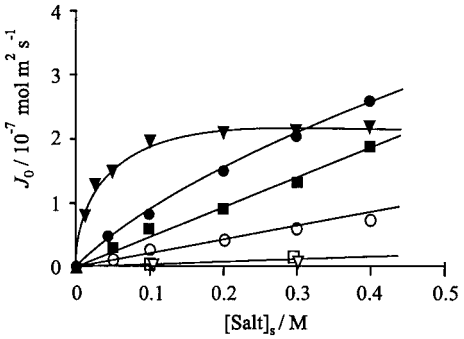


Figure 9. Transport of NPr_4Cl (■) and $NPr_4H_2PO_4$ (□) by carrier **1**, NPr_4Cl (●) and $NPr_4H_2PO_4$ (○) by carrier **2**, and NPr_4Cl (▼) and $NPr_4H_2PO_4$ (▽) by carrier **5** as a function of the source phase salt concentration; $[\text{carrier}]_m = 10$ mM.

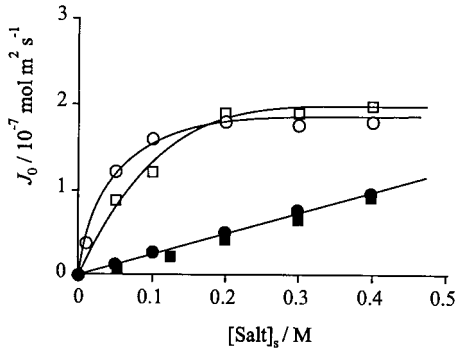


Figure 10. Transport of NPr_4Cl (●) and $NPr_4H_2PO_4$ (○) by carrier **3** and NPr_4Cl (■) and $NPr_4H_2PO_4$ (□) by carrier **4** as a function of the source phase salt concentration; $[\text{carrier}]_m = 10$ mM.

The complex concentration depends on the stoichiometry. Generally, uranyl salenes bind Cl^- as a 1:1 carrier:anion complex; only salophene **5** forms a 2:1 carrier:chloride complex.[30] All dihydrogen phosphate complexes have a stoichiometry of 2:1 (carrier:anion), in line with previous findings[31] for the stoichiometry of dihydrogen phosphate complexes in PVC/NPOE and $CDCl_3$. Figures 9 and 10 show that the initial flux J_0 reaches its maximum $J_{0,max}$ at salt concentrations higher than 0.2 M for $\mathbf{5}_2 \cdot Cl^-$, $\mathbf{3}_2 \cdot H_2PO_4^-$, and $\mathbf{4}_2 \cdot H_2PO_4^-$ and hence D_m of carrier **5** (NPr_4Cl) and of carriers **3** and **4** ($NPr_4H_2PO_4$) can be calculated (Table 4). The same diffusion coefficients were also determined independently from the relation between $L_0J_0^{-1}$ versus d_m under conditions when all carriers at the source phase interface of the membrane are complexed. The results (Table 4) show that the two methods lead to almost identical values. The observed diffusion coefficients ($D_m \approx 4 \times 10^{-12}$ m^{2}s^{-1}) are about two to

Table 4. Anion-facilitated transport of propylammonium salts; $J_{0,max}$, D_m, K'_{ex}, and $K'_{a,X}$ of uranyl sal(oph)ene carriers **3**–**5**.

Carrier	Anion	$J_{0,max}$ [10^{-7} mol m^{-2} s^{-1}]	D_m[b, c] [10^{-12} m^2 s^{-1}]	D_m[d] [10^{-12} m^2 s^{-1}]	D_m[e] [10^{-12} m^2 s^{-1}]	K'_{ex}[e] [M^{-2}]	$K'_{a,X}$[f] [10^8 M^{-2}]
3[a]	$H_2PO_4^-$	1.8	3.6	3.6	3.6	3200	$> 4 \times 10^{12}$
4[a]	$H_2PO_4^-$	1.9	3.8	4.5	3.9	1400	$> 1.7 \times 10^{12}$
5[a]	Cl^-	2.1	4.2	5.2	4.7	610	9.5×10^8

[a] $[\text{Carrier}]_m = 0.01$ M. [b] For 2:1 carrier:anion. [c] D_m values from the maximum fluxes $J_{0,max}$. [d] D_m values from transport experiments through membranes of different thickness. [e] Transport parameters obtained by fitting the fluxes in Figures 9 and 10 by Eq. (17). [f] Calculated with $K_p < 0.8 \times 10^{-9}$ for $NPr_4H_2PO_4$ and $K_p = 645 \times 10^{-9}$ for NPr_4Cl.

0947-6539/00/0608-1380 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

three times lower than previously found for the calix[4]arene based cation carriers.[15, 28]

Carriers **1** and **2** transport Cl^- as a 1:1 anion:carrier complex.[30] Since the maximum transport rate $J_{0,max}$ was not reached at high NPr_4Cl concentration the diffusion coefficient D_m was determined independently from lag-time experiments through a stack of two membranes.[20, 29]

From the measured diffusion constants the extraction constants can now be calculated. The K_{ex} values of 1:1 complexes can be obtained from Equation (14). The results (Table 5) show that the extraction constant of NPr_4Cl by uranyl salene **2** ($K_{ex} = 6.5 \times 10^{-2}\,M^{-1}$) is slightly higher than that of carrier **1** ($K_{ex} = 1.7 \times 10^{-2}\,M^{-1}$). However, when compared with the K_{ex} values of macrocyclic cation carriers, ($K_{ex} \leq 3 \times 10^4\,M^{-1}$)[28] these extraction constants are very low.

Table 5. Anion-facilitated transport of NPr_4Cl; D_{lag}, D_m, K_{ex}, and $K_{a,X}$ of uranyl salenes **1** and **2**.

Carrier	t_{lag} [s]	D_{lag} [$10^{-12}\,m^2\,s^{-1}$]	D_m [$10^{-12}\,m^2\,s^{-1}$]	K_{ex} [M^{-1}]	$K_{a,X}$ [$10^4\,M^{-1}$]
1	714	9.3	6.0	0.017	2.6×10^4
2	790	8.4	5.4	0.065	10.1×10^4

[a] Calculated with $K_p = 645 \times 10^{-9}$.

The extraction constant K for the 2:1 carrier:anion stoichiometry (as observed for $\mathbf{3}_2 \cdot H_2PO_4^-$, $\mathbf{4}_2 \cdot H_2PO_4^-$, and $\mathbf{5}_2 \cdot Cl^-$) is defined by Equation (16).

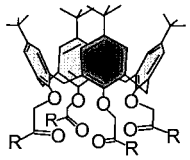
$$2\,L_{ms} + X_s^- + M_s^+ \rightleftharpoons L_2X_{ms}^- + M_{ms}^+ \quad (16)$$

The initial flux J_0 as a function of the diffusion coefficient D_m, the extraction constant K_{ex}^{ex}, the salt activity a_s, and the carrier concentration L_0 is given by Equation (17).

$$J_0 = \frac{D_m}{2\,d_m}\left[\frac{4\,A\,L_0 - \sqrt{(4\,AL_0)^2 - 4A(4A-1)\,L_0^2}}{2(4A-1)}\right] \text{ with } A = (K'_{ex}a_s^2) \quad (17)$$

The calculated extraction constants (Table 4) decrease in the order $K'_{ex}(\mathbf{3}) > K'_{ex}(\mathbf{4}) > K'_{ex}(\mathbf{5})$. Despite the fact that Cl^- is much less hydrophilic than $H_2PO_4^-$, K'_{ex} of carrier **5** for NPr_4Cl is lower than of uranyl salenes **3** and **4** for $NPr_4H_2PO_4$, indicating the high stability of dihydrogen phosphate complexes.

From the extraction constants as determined above and the partition coefficients calculated from the Gibbs free energy of transfer the association constants K_a for these complexes can be calculated. The association constants $K_{a,X}$ of uranyl salenes **1** and **2** for Cl^- in NPOE (Table 5) were 2.6×10^4 and $10.1 \times 10^4\,M^{-1}$, respectively. The stability in NPOE is higher (by a factor of about 10) than found for similar compounds in MeCN/DMSO (99:1).[3h] To put these values in perspective, a comparison is made with the association constants of the sodium selective calix[4]arene tetraester **6** and calix[4]arene tetramethylketone **7**. K_{ex} values of carriers **6** and **7** transporting $NaClO_4$ have been reported previously[32] (14 and $68\,M^{-1}$, respectively) and the partition coefficient K_p of $NaClO_4$ follows from Table 3 ($6.0 \times 10^{-9}\,M^{-1}$).



6: R= OCH_2CH_3
7: R= CH_3

The association constants $K_{a,M}$ of carriers **6** ($K_{a,M} = 2.4 \times 10^9\,M^{-1}$) and **7** ($K_{a,M} = 11.4 \times 10^9\,M^{-1}$) for Na^+ are about five orders of magnitude larger than the $K_{a,X}$ values of uranyl salenes **1** and **2** for Cl^-. It is therefore clear that the low anion transport efficiency of carriers **1** and **2** in this study is due to the low binding constant K_a.

From the extraction constants of 2:1 carrier:anion complexes, only the association constants $K'_{a,X}$ for the $\mathbf{5}_2 \cdot \mathbf{Cl}^-$ complex [as defined in Eq. (18)] could be calculated accurately ($9.5 \times 10^8\,M^{-2}$, Table 4).

$$2\,L_{x,m} + X_m^- \rightleftharpoons (L_x)_2X_m^-$$

$$K'_{a,X} = \frac{[(L_X)_2\,X^-]_m}{[L_X]_m^2[X^-]_m} \quad (18)$$

From the minimum value for the Gibbs free energy of transfer for $NPr_4H_2PO_4$ ($\Delta G_{tr,NPOE}(NPr_4H_2PO_4) > 52\,kJ\,mol^{-1}$) we estimated that the association constants of complexes $\mathbf{3}_2 \cdot H_2PO_4^-$ and $\mathbf{4}_2 \cdot H_2PO_4^-$ in NPOE are more than two orders of magnitude higher than of $\mathbf{5}_2 \cdot Cl^-$. Apparently, the two sulfonamido hydrogen bond donating groups in close proximity of the uranyl salene cleft make them excellent phosphate receptors.[3f]

Competition experiments: The selectivity S for the transport of $H_2PO_4^-$ in the presence of Cl^- is defined by Equation (19).

$$S = \frac{J_{H_2PO_4^-}}{J_{Cl^-}} \times \frac{[Cl^-]_s}{[H_2PO_4^-]_s} \quad (19)$$

The intrinsic anion selectivity in NPOE was measured by the competitive transport of the lipophilic tetrabutylammonium salts NBu_4Cl and $NBu_4H_2PO_4$ without carrier in the membrane phase. The transport of $NBu_4H_2PO_4$ was too slow to be determined accurately and the phosphate concentration was taken equal to or smaller than the detection limit $S < 0.035$ (Table 6). The selectivity S gives a lower limit for the

Table 6. Transport selectivities S from time-averaged fluxes (24 h) of Cl^- and $H_2PO_4^-$ for uranyl sal(oph)enes **1**–**5** in competitive transport experiments.

Carrier	$[H_2PO_4^-]_s$ [$10^{-3}\,M$]	$[Cl^-]_s$ [$10^{-3}\,M$]	$J_{24h}(H_2PO_4^-)$[a] [$10^{-8}\,mol\,m^{-2}\,s^{-1}$]	$J_{24h}(Cl^-)$[a] [$10^{-8}\,mol\,m^{-2}\,s^{-1}$]	S[b]
–[c]	150	150	< 0.5[e]	14.5	< 0.035
2[d]	150	150	5.6	8.5	0.66
3[d]	150	150	19	< 0.5[e]	> 38
1[d]	24	150	< 0.5[e]	7.1	–
2[d]	24	150	1.7	7.6	1.4
3[d]	24	150	17	< 0.5[e]	> 212
4[d]	24	150	10.7	1.0	67
5[d]	24	150	< 0.5[e]	22	–
3[d]	10	150	12	< 0.5[e]	> 360
4[d]	10	150	6.0	1.3	69

[a] J_{24h} determined after 24 h of transport. [b] S is defined according to Equation (19). [c] Inherent selectivity S to NPOE from the difference in the transport of NBu_4^+ salts. [d] Selectivity determined from the competitive transport of NPr_4^+ salts. [e] Estimated maximum flux from the detection limit of the UV experiment.

difference in Gibbs free energy of transfer between Cl^- and $H_2PO_4^-$ of $\Delta(\Delta G_{tr,NPOE}) > 16.6$ kJ mol^{-1}.[31] This intrinsic difference needs to be compensated by a favorable anion complexation by the carrier in order to transport $H_2PO_4^-$ over Cl^-.

The selectivities of receptors **1**–**5** were measured in competition experiments with mixtures of NPr_4Cl and $NPr_4H_2PO_4$ (Table 6), at a constant concentration of Cl^- (150 mM) and varying concentrations of $H_2PO_4^-$ (10 to 150 mM). The fluxes were determined from the concentrations of Cl^- and $H_2PO_4^-$ in the receiving phase after 24 h. Carriers **1** and **5** do not transport $H_2PO_4^-$ selectively. The selectivity S for **2** is in the range $0.7 < S < 1.4$ and is significantly different from the inherent selectivity in NPOE ($S < 0.035$).

Carriers **3** and **4** transport very selectively $H_2PO_4^-$ in the presence of Cl^-. The selectivity increases with decreasing ratio of $[H_2PO_4^-]/[Cl^-]$ in the aqueous source phase reaching a value of 350 for a concentration ratio of 0.067.

Conclusion

Gibbs free energies of transfer of individual ions from water to NPOE were determined from partition coefficients. NPOE and MeCN have comparable anion solvation properties and an empirical free energy relationship holds between $\Delta G_{tr,NPOE}(X^-)$ and $\Delta G_{tr,MeCN}(X^-)$.

Tetrapropylammonium salts of Cl^- and $H_2PO_4^-$ were transported by neutral uranyl sal(oph)ene anion receptors **1**–**5**. The rates of salt transport by anion carriers are much lower than of salt transport by cation carriers, due to the low values for both D_m and K_{ex}. The diffusion coefficients D_m of the uranyl sal(oph)enes are about two to three times lower, whereas the extraction constants are more than four orders of magnitude lower than of the cation carriers.

The competition experiments illustrate the importance of anion receptors in selective extraction processes. In order to achieve selective phase transfer to organic solutions, large differences in Gibbs free energies of transfer for different anions have to be compensated by highly selective anion complexation.[22, 25] Generally, the differences of Gibbs free energies of transfer between anions (ClO_4^-, NO_3^-, Cl^-, and $H_2PO_4^-$) are much larger than between cations (Na^+, K^+, Rb^+, and Cs^+). It is therefore much more difficult to reverse the inherent and solvent-imposed selectivity in anion transport than in cation transport.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker AC 250 spectrometer in $CDCl_3$, unless stated otherwise. The presence of solvent in the analytical samples was confirmed by ^{1}H-NMR spectroscopy. Fast atom bombardment (FAB) mass spectra were obtained with a Finnigan MAT 90 spectrometer. The spectra were obtained with use of *m*-nitrobenzyl alcohol as a matrix.

CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves (4 Å) prior to use. CH_3CN and DMSO were dried over molecular sieves (4 Å) prior to use. Petroleum ether refers to the fraction with b.p. 40–60 °C. Other chemicals were of reagent grade and were used without purification. Column chromatography was performed with silica gel (Merck, 0.015–0.040 mm) unless stated otherwise. All reactions were carried out under an argon atmosphere. Uranyl salene **1**[32] and uranyl salophene **5**[3k] were prepared according to a literature procedure.

***N*-[3-(*n*-Octyloxyphenyl)]chloroacetamide (9)**: Chloroacetyl chloride (1.47 g, 13 mmol) was added dropwise to a vigorously stirred solution of *m*-octyloxyaniline (2.21 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) in EtOAc/H_2O (1:1, 100 mL). The reaction was stirred for 3 h at room temperature. The organic layer was separated from the aqueous layer, dried with $MgSO_4$ and evaporated. The residual solid was purified by column chromatography (CH_2Cl_2) (82 %). M.p.: 92–94 °C; ^{1}H NMR: δ = 8.12 (br s, 1H, NH), 7.2–7.1 (m, 2H, ArH), 6.95 (d, 1H, J = 7.9 Hz, ArH), 6.7–6.6 (m, J = 8.3 Hz, 1H, ArH), 4.11 (s, 2H, ClCH_2CO), 3.91 (t, 2H, J = 6.5 Hz, OCH_2), 1.8–1.6 (m, 2H, OCH$_2$CH_2), 1.4–1.2 (m, 10H, CH_2), 0.84 (t, 3H, J = 4.5 Hz, CH_3); ^{13}C NMR: δ = 129.8 (s, NCO), 68.1 (t, OCH_2), 42.9 (t, ClCH_2CO), 31.9–22.7 (t, CH_2), 14.1 (q, CH_3); FAB-MS: *m*/*z*: 298.2 $[M+H]^+$, calcd 298.2; anal. calcd for $C_{16}H_{24}ClNO_2$: C 64.53, H 8.12, N 4.70; found: C 64.48, H 7.77, N 4.89.

General procedure for the preparation of compounds 12a–b: A mixture of the appropriate sulfonyl chloride (15 mmol), chloroalkylamine · HCl (19 mmol), and Et_3N (3.11 g, 31 mmol) was stirred in CH_2Cl_2 (100 mL) at 0 °C for 1 h. Subsequently, the solution was stirred at room temperature for 10 h. The organic layer was washed with saturated NH_4Cl (2 × 50 mL), 1N HCl (2 × 50 mL), H_2O (2 × 50 mL), and dried with $MgSO_4$. After filtration, the solvent was evaporated and the residual solid was purified by trituration or column chromatography.

***N*-(3-Chloropropyl)-*n*-hexadecanesulfonamide (12a)**: The crude product was triturated from acetone. Yield 37 %; m.p.: 86–87 °C; ^{1}H NMR: δ = 4.32 (t, 1H, J = 6.4 Hz, NH), 3.67 (t, 2H, J = 6.0 Hz, ClCH_2), 3.34 (q, 2H, J = 6.5 Hz, CH_2N), 3.1–2.9 (m, 2H, SO_2CH_2), 2.1–1.95 (m, 2H, ClCH$_2$CH_2), 1.85–1.7 (m, 2H, $SO_2CH_2CH_2$), 1.4–1.15 (m, 26H, CH_2), 0.89 (t, 3H, J = 6.3 Hz, CH_3); ^{13}C NMR: δ = 53.6 (t, SO_2CH_2), 44.9 (t, ClCH_2), 44.4 (t, CH_2N), 32.8 (t, $SO_2CH_2CH_2$), 31.9–22.7 (t, CH_2), 14.1 (q, CH_3); FAB-MS: *m*/*z*: 382.2 $[M]^+$, calcd 382.2; anal. calcd for $C_{19}H_{40}ClNO_2S$: C 59.73, H 10.55, N 3.67; found: C 59.77, H 10.60, N 3.80.

***N*-(3-Chloropropyl)-[(2,4,6-triisopropyl)benzene]sulfonamide (12b)**: The crude product was purified by column chromatography (SiO_2, CH_2Cl_2). Yield 91 %; m.p.: 81–82 °C; ^{1}H NMR: δ = 7.18 (s, 2H, ArH), 5.45 (br s, 1H, NH), 4.3–4.0 [m, 2H, *o*-ArCH(CH$_3$)$_2$], 3.60 (t, 2H, J = 6.2 Hz, ClCH_2), 3.17 (t, 2H, J = 6.6 Hz, CH_2N), 3.0–2.8 [m, 1H, *p*-ArCH(CH$_3$)$_2$], 2.1–1.9 (m, 2H, ClCH$_2$CH_2), 1.4–1.2 [m, 18H, ArCH(CH_3)$_2$]; ^{13}C NMR: δ = 42.0 (t, ClCH_2), 40.1 (t, CH_2N), 34.1, 29.6 [d, ArCH(CH$_3$)$_2$], 32.4 (t, ClCH$_2$CH_2), 24.9 and 23.6 [q, ArCH(CH_3)$_2$]; FAB-MS: *m*/*z*: 360.3 $[M+H]^+$, calcd 360.2; anal. calcd for $C_{18}H_{30}ClNO_2S$: C 60.06, H 8.40, N 3.89; found: C 60.30, H 8.57, N 3.98.

General procedure for the preparation of compounds 10, 13a–b: A mixture of **9**, **12a**, or **12b** (10 mmol), 2-(2-allyloxy)-3-hydroxybenzaldehyde (1.78 g, 10 mmol), and K_2CO_3 (2.76 g, 20 mmol) was refluxed in MeCN (200 mL) for 48 h. The solution was filtered and the solvent evaporated. The crude product was taken up in CH_2Cl_2 (50 mL) and washed with a saturated solution of Na_2CO_3 (2 × 50 mL), water (2 × 50 mL), and brine (50 mL). The organic layer was dried with $MgSO_4$ and the solvent evaporated.

2-[3-Formyl-2-(2-propenyloxy)]-*N*-[3-(*n*-octyloxyphenyl)phenoxy]acetamide (10): The crude product was triturated from *i*PrOH. Yield 63 %; m.p.: 92–94 °C; ^{1}H NMR: δ = 10.43 (s, 1H, CHO), 8.61 (s, 1H, NH), 7.6–7.5 (m, 1H, ArH), 7.15–7.1 (m, 1H, ArH), 7.32 (s, 1H, ArH), 7.25–7.15 (m, 2H, ArH), 7.07 (d, 1H, J = 7.9 Hz, ArH), 6.75–6.65 (m, 1H, ArH), 6.25–6.0 (m, 1H, CH=CH$_2$), 5.55–5.25 (m, 2H, CH=CH_2), 4.71 (d, 2H, J = 4.7 Hz, OCH_2CH=CH$_2$), 4.69 (s, 2H, OCH_2CO), 3.99 (t, 2H, J = 6.5 Hz, OCH_2CH$_2$), 1.85–1.7 (m, 2H, OCH$_2$CH_2), 1.5–1.15 (m, 10H, CH_2), 0.84 (t, 3H, J = 6.5 Hz, CH_3); ^{13}C NMR: δ = 189.4 (d, CHO), 132.6 (d, OCH$_2$CH=CH$_2$), 130.9 (s, NCO), 119.7 (t, OCH$_2$CH=CH_2), 76.6 (t, OCH_2CH=CH$_2$), 69.4 (t, OCH_2CO), 68.1 (t, OCH_2CH$_2$), 31.9–22.6 (t, CH_2), 14.1 (q, CH_3); FAB-MS: *m*/*z*: 440.5 $[M+H]^+$, calcd 440.2; anal. calcd for $C_{26}H_{33}NO_5 \cdot 0.5\,H_2O$: C 69.62, H 7.42, N 3.12; found: C 69.54, H 7.28, N 3.37.

***N*-[3-[3-Formyl-2-(2-propenyloxy)phenoxy]propyl]-*n*-hexadecanesulfonamide (13a)**: The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give a light yellow solid. Yield: 45 %; m.p.: 64–66 °C; ^{1}H NMR: δ = 10.40 (s, 1H, CHO), 7.43 (dd, 1H, J = 6.3 Hz, 3.1 Hz, ArH),

  0947-6539/00/0608-1382 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

7.15–7.1 (m, 2H, ArH), 6.15–6.0 (m, 1H, C*H*=CH$_2$), 5.4–5.25 (m, 2H, CH=C*H*$_2$), 4.77 (t, 1H, J = 6.2 Hz, NH), 4.65 (d, 2H, J = 6.1 Hz, OC*H*$_2$CH=CH$_2$), 4.15 (t, 2H, J = 5.8 Hz, OC*H*$_2$CH$_2$), 3.37(q, 2H, J = 6.3 Hz, C*H*$_2$N), 3.0–2.9 (m, 2H, SO$_2$C*H*$_2$), 2.15–2.0 (m, 2H, OCH$_2$C*H*$_2$), 1.8–1.7 (m, 2H, SO$_2$CH$_2$C*H*$_2$), 1.3–1.1 (m, 26H, CH$_2$), 0.86 (t, 3H, J = 6.8 Hz, CH$_3$); ^{13}C NMR: δ = 190.1 (d, CHO), 133.0 (d, *C*H=CH$_2$), 118.9 (t, CH=*C*H$_2$), 75.7 (t, O*C*H$_2$CH=CH$_2$), 67.0 (t, O*C*H$_2$CH$_2$), 53.2 (t, SO$_2$*C*H$_2$), 42.6 (t, *C*H$_2$N), 31.9–22.7 (t, CH$_2$), 14.1 (q, CH$_3$); FAB-MS: m/z: 524.3 [M+H]$^+$, calcd 524.4; anal. calcd for $C_{29}H_{49}NO_5S$: C 66.50, H 9.43, N 2.67; found: C 66.62, H 9.35, N 2.68.

***N*-[3-[3-Formyl-2-(2-propenyloxy)phenoxy]propyl]-[(2,4,6-triisopropyl)-benzene] sulfonamide (13b)**: The crude product was purified by column chromatography (CH$_2$Cl$_2$) to give a yellow solid. Yield 38%; m.p.: 81–82 °C; ^{1}H NMR: δ = 10.32 (s, 1H, CHO), 7.38 (t, 1H, J = 4.6 Hz, ArH), 7.09 (s, 2H, ArH), 7.05–6.95 (m, 2H, ArH), 6.1–5.8 (m, 1H, C*H*=CH$_2$), 5.3–5.1 (m, 2H, CH=C*H*$_2$), 4.95 (t, 1H, J = 6.3 Hz, NH), 4.54 (d, 2H, J = 6.1 Hz, OC*H*$_2$CH=CH$_2$), 4.2–4.0 [m, 4H, OC*H*$_2$CH$_2$, *o*-ArC*H*(CH$_3$)$_2$], 3.20 (q, 2H, J = 6.3 Hz, C*H*$_2$N), 2.90–2.70 [m, 2H, *p*-ArC*H*(CH$_3$)$_2$], 2.1–1.9 (m, 2H, OCH$_2$C*H*$_2$), 1.25–1.1 [m, 18H, ArCH(C*H*$_3$)$_2$]; ^{13}C NMR: δ = 190.4 (d, CHO), 132.8 (d, *C*H=CH$_2$), 119.3 (t, CH=*C*H$_2$), 75.5 (t, O*C*H$_2$CH=CH$_2$), 67.1 (t, O*C*H$_2$CH$_2$), 40.6 (t, *C*H$_2$N), 34.1 and 29.6 [d, Ar*C*H(CH$_3$)$_2$], 29.4 (t, ArOCH$_2$*C*H$_2$), 24.9, 23.6 [q, ArCH(*C*H$_3$)$_2$]; EI-MS: m/z: 501.1 [M]$^+$, calcd 501.3; anal. calcd for $C_{28}H_{39}NO_5S$: C 67.04, H 7.84, N 2.79; found: C 67.18, H 8.24, N 2.68.

General procedure for deallylation of the protected aldehydes 10, 13a–b: A mixture of **10**, **13a–b** (3 mmol), Pd(OAc)$_2$ (20 mg, 0.1 mmol), PPh$_3$ (125 mg, 0.5 mmol), Et$_3$N (3.7 g, 37 mmol), and HCOOH (1.65 g, 37 mmol) was refluxed in 80% aqueous EtOH (60 mL) for 2 h. The solvent was evaporated and water (100 mL) was added. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 100 mL). Subsequently, the organic layer was dried with MgSO$_4$ and the solvent evaporated. A yellow solid was obtained after column chromatography of the crude mixture.

2-[3-Formyl-2-hydroxyphenoxy]-*N*-[3-(*n*-octyloxyphenyl)]acetamide (11): The crude product was purified by column chromatography (CH$_2$Cl$_2$/EtOAc 95:5). Yield 88%; m.p.: 73–74 °C; ^{1}H NMR: δ = 11.29 (s, 1H, OH), 9.87 (s, 1H, CHO), 8.81 (s, 1H, NH), 7.3–7.2 (m, 2H, ArH), 7.2–7.1 (m, 2H, ArH), 7.1–6.8 (m, 2H, ArH), 6.7–6.5 (m, 1H, ArH), 4.64 (s, 2H, OC*H*$_2$CO), 3.92 (t, 2H, J = 6.5 Hz, OC*H*$_2$CH$_2$), 1.8–1.6 (m, 2H, OCH$_2$C*H*$_2$), 1.6–1.2 (m, 10H, CH$_2$), 0.91 (t, 3H, J = 6.4 Hz, CH$_3$); ^{13}C NMR: δ = 196.7 (d, CHO), 129.7 (s, NCO), 70.5 (t, O*C*H$_2$CO), 68.1 (t, O*C*H$_2$CH$_2$), 31.9–22.6 (t, CH$_2$), 14.1 (q, CH$_3$); EI-MS: m/z: 399.1 [M]$^+$, calcd 399.2; anal. calcd for $C_{23}H_{29}NO_5 \cdot 0.25\,H_2O$: C 68.38, H 7.36, N 3.47; found: C 68.25, H 7.13, N 3.64.

***N*-[3-(3-Formyl-2-hydroxyphenoxy)propyl]-*n*-hexadecanesulfonamide (14a)**: The crude product was purified by column chromatography (CH$_2$Cl$_2$). Yield 80%; m.p.: 83–85 °C; ^{1}H NMR: δ = 11.10 (s, 1H, OH), 9.90 (s, 1H, CHO), 7.23 (d, 1H, J = 7.7 Hz, ArH), 7.20 (d, 1H, J = 7.8 Hz, ArH), 6.95 (t, 1H, J = 7.8 Hz, ArH), 5.21 (t, 1H, J = 6.1 Hz, NH), 4.15 (t, 2H, J = 5.5 Hz, OC*H*$_2$), 3.38(q, 2H, J = 6.0 Hz, C*H*$_2$N), 3.1–2.9 (m, 2H, SO$_2$C*H*$_2$), 2.2–2.0 (m, 2H, ArOCH$_2$C*H*$_2$), 1.85–1.75 (m, 2H, SO$_2$CH$_2$C*H*$_2$), 1.4–1.2 (m, 26H, CH$_2$), 0.86 (t, 3H, J = 6.8 Hz, CH$_3$); ^{13}C NMR: δ = 196.5 (d, CHO), 68.4 (t, O*C*H$_2$CH$_2$), 52.5 (t, SO$_2$CH$_2$), 41.4 (t, NHCH$_2$), 31.9–22.6 (t, CH$_2$) 14.1 (q, CH$_3$); FAB-MS: m/z: 483.1 [M]$^+$, calcd 483.3; anal. calcd for $C_{26}H_{45}NO_5S$: C 64.56, H 9.38, N 2.90; found: C 64.55, H 9.18, N 2.89.

***N*-[3-(3-Formyl-2-hydroxyphenoxy)propyl]-[(2,4,6-triisopropyl)benzene]-sulfonamide (14b)**: The crude product was purified by column chromatography (CH$_2$Cl$_2$). Yield 79%; m.p.: 119–120 °C; ^{1}H NMR: δ = 11.08 (s, 1H, OH), 9.89 (s, 1H, CHO), 7.19 (d, 1H, J = 7.8 Hz, ArH), 7.14 (s, 2H, ArH), 7.10 (d, 1H, J = 7.9 Hz, ArH), 6.96 (t, 1H, J = 7.9 Hz, ArH), 5.43 (t, 1H, J = 6.2 Hz, NH), 4.3–4.1 [m, 4H, OC*H*$_2$, *o*-ArC*H*(CH$_3$)$_2$], 3.20 (q, 2H, J = 6.2 Hz, C*H*$_2$N), 3.0–2.8 [m, 1H, *p*-ArC*H*(CH$_3$)$_2$], 2.1–2.0 (m, 2H, OCH$_2$C*H*$_2$), 1.3–1.2 [m, 18H, ArCH(C*H*$_3$)$_2$]; ^{13}C NMR: δ = 196.6 (d, CHO), 68.4 (t, O*C*H$_2$), 40.9 (t, CH$_2$N), 34.1, 29.6 [d, Ar*C*H(CH$_3$)$_2$], 29.1 (t, OCH$_2$*C*H$_2$), 24.9 and 23.6 [q, ArCH(*C*H$_3$)$_2$]; EI-MS: m/z: 461.0 [M]$^+$, calcd 461.2; anal. calcd for $C_{25}H_{35}NO_5S$: C 65.05, H 7.64, N 3.03; found: C 65.35, H 7.77, N 3.04.

General procedure for the synthesis of UO$_2$-salens 2–4: A solution of aldehyde **11**, **14a**, or **14b** (1.03 mmol) and *cis*-1,2-dicyclohexane diamine (0.062 mL, 0.52 mmol) was refluxed in MeOH (25 mL) for 1 h. A solution of UO$_2$(OAc)$_2 \cdot$ H$_2$O (0.219 g, 0.52 mmol) in MeOH (10 mL) was added and refluxing was continued for 1 h. The solution was evaporated to give the crude product.

[[2,2′-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]-bis-[*N*-(3-*n*-octyloxyphenyl)acetamidato]](2-)]dioxouranium (2): The crude product was triturated from MeOH. Yield 89%; m.p.: 149–151 °C; ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO 9:1): δ = 10.45 (s, 2H, HC=N), 9.27 (s, 2H, NH), 7.4–7.2 (m, 6H, ArH), 7.12 (d, 2H, J = 7.8 Hz, ArH), 6.79 (t, 2H, J = 8.2 Hz, ArH), 6.70 (t, 2H, J = 7.8 Hz, ArH), 6.5–6.3 (m, 2H, ArH), 4.84 (s, 4H, OC*H*$_2$CO), 4.66 (br s, 2H, C=NCH), 3.59 (t, 4H, J = 6.4 Hz, OC*H*$_2$CH$_2$), 2.6–2.3, 2.1–1.9 (m, 2 × 2H, C=NCHC*H*$_2$CH$_2$), 1.8–1.4 (m, 2 × 4H, C=NCHCH$_2$C*H*$_2$, OCH$_2$C*H*$_2$), 1.3–1.1 (m, 20H, CH$_2$), 0.83 (t, 6H, J = 6.4 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO 9:1): δ = 167.9 (d, C=N), 129.1 (s, NCO), 72.2 (t, O*C*H$_2$CO), 71.5 (d, C=N*C*H), 67.7 (t, O*C*H$_2$CH$_2$), 31.9–22.6 (t, CH$_2$), 14.1 (q, CH$_3$); FAB-MS: m/z: 1145.5 [M]$^+$, calcd 1145.8; anal. calcd for $C_{54}H_{66}N_4O_{10}U$: C 54.21, H 5.93, N 4.85; found: C 54.54, H 5.81, N 4.89.

[[2,2′-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)-oxy]] bis-[*N*-(3-propyl)-*n*-hexadecanesulfonamidato]](2-)]dioxouranium (3): The crude product was purified by column chromatography (Al$_2$O$_3$, CH$_2$Cl$_2$/MeOH 95:5) and recrystallized from MeOH/diisopropyl ether. Yield: 67%; m.p.: 82–84 °C; ^{1}H NMR: δ = 9.21 (s, 2H, HC=N), 7.14 and 7.10 (d, 4H, J = 7.8 Hz ArH), 6.56 (t, 2H, J = 7.8 Hz, ArH), 6.44 (t, 2H, J = 5.5 Hz, NH), 4.56 (br s, 2H, C=NCH), 4.29 (t, 4H, J = 5.9 Hz, OC*H*$_2$), 3.34 (q, 4H, J = 6.0 Hz, C*H*$_2$N), 2.9–2.8 (m, 4H, SO$_2$C*H*$_2$), 2.6–2.5, 2.1–1.9 (m, 2 × 2H, C=NCHC*H*$_2$CH$_2$), 2.2–2.0 (m, 2H, OCH$_2$C*H*$_2$), 1.7–1.5 (m 8H, C=NCHCH$_2$C*H*$_2$, SO$_2$CH$_2$C*H*$_2$), 1.4–1.1 (m, 52H, CH$_2$), 0.86 (t, 6H, J = 6.8 Hz, CH$_3$); ^{13}C NMR: δ = 167.4 (d, HC=N), 71.3 (d, C=N*C*H), 67.2 (t, O*C*H$_2$CH$_2$), 51.8 (t, SO$_2$CH$_2$), 40.5–39.1 (t, CH$_2$N), 31.7–21.6 (t, CH$_2$) 14.0 (q, CH$_3$); FAB-MS: m/z: 1336.0 [M+Na]$^+$, calcd 1335.9; anal. calcd for: $C_{58}H_{98}N_4O_{10}S_2U \cdot 0.5\,(C_6H_{14}O)$: C 53.69, H 7.75, N 4.11; found: C 53.69, H 7.90, N 4.24.

[[2,2′-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)-oxy]]-bis-[*N*-(3-propyl)-[(2,4,6-triisopropyl)benzene]sulfonamidato]](2-)]-dioxouranium (4): The crude product was purified by column chromatography (Al$_2$O$_3$, CH$_2$Cl$_2$). Yield 56%; m.p.: 83–86 °C; ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO 9:1): δ = 9.21 (s, 2H, HC=N), 7.2–7.0 (m, 6H, ArH), 6.44 (br s, 2H, NH), 6.54 (t, 2H, J = 7.8 Hz, ArH), 4.54 (br s, 2H, C=NCH), 4.3–4.0 [m, 8H, OC*H*$_2$, *o*-ArC*H*(CH$_3$)$_2$], 3.22 (q, 4H, J = 6.4 Hz, C*H*$_2$N), 3.0–2.7 [m, 2H, *p*-ArC*H*(CH$_3$)$_2$], 2.5–2.2, 1.8–1.6 (m, 2 × 2H, C=NCHC*H*$_2$CH$_2$), 2.1–2.0 (m, 4H, OCH$_2$C*H*$_2$), 1.8–1.6 (m, 4H, C=NCHCH$_2$C*H*$_2$), 1.2–1.1 [m, 18H, ArCH(C*H*$_3$)$_2$]; ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO 9:1): δ = 167.1 (d, HC=N), 71.0 (d, C=N*C*H), 66.9 (t, O*C*H$_2$CH$_2$), 40.6 (t, CH$_2$N), 33.5 and 29.3 [d, Ar*C*H(CH$_3$)$_2$], 28.8 (t, OCH$_2$*C*H$_2$), 27.4 (t, NCH*C*H$_2$CH$_2$), 24.5, 23.1 [q, ArCH(*C*H$_3$)$_2$], 21.2 (t, NCHCH$_2$*C*H$_2$); FAB-MS: m/z: 1369.7 [M+H]$^+$, calcd 1369.5]; anal. calcd for $C_{56}H_{78}N_4O_{10}S_2U \cdot 2\,H_2O$: C 51.52, H 6.33, N 4.29; found: C 51.54, H 6.18, N 4.59.

Transport measurements: The polymeric film Accurel 1E-PP was obtained from Enka Membrana (thickness d_m = 100 mm, porosity Q = 64%). *o*-Nitrophenyl *n*-octyl ether (NPOE) was purchased from Fluka and used without further purification. All salts (Phosphoric acid, tetrapropylammonium hydroxide, tetrapropyl-ammonium chloride, tetrabutylammonium hydroxide and tetrabutylammonium chloride) were of analytical grade and were obtained from Acros. The transport experiments were performed at 298 K in an apparatus that consists of two identical cylindrical compartments made of glass (half-cell volume ca. 50 mL, effective membrane area ca. 13.5 cm^2). Details of the cell have been described elsewhere.[32] The membrane was positioned in between the cylindrical compartments containing the two aqueous phases. The carrier was dissolved in *o*-nitrophenyl *n*-octyl ether (NPOE). The carrier was dissolved in *o*-nitrophenyl *n*-octyl ether (NPOE) and immobilized in the solid support according to a standard procedure previously described by our group.[33] Solutions of NPr$_4$H$_2$PO$_4$ were obtained by titration of a known amount of H$_3$PO$_4$ with NPr$_4$OH to the required pH value. Dilution of the sample with distilled water gave the desired concentration of NPr$_4$H$_2$PO$_4$/(NPr$_4$)$_2$HPO$_4$, pH 6.7. The transport of salts was monitored by measuring the conductivity (Radiometer CDM 83) as a function of time. The concentration was calculated using a salt constant that correlates the conductivity to the concentration. The activity was determined by calculation of the activity coefficient using the Debye–Hückel equation[34] The transport rates of NPr$_4$H$_2$PO$_4$ and NBu$_4$H$_2$PO$_4$ were determined by phosphate analysis of the

receiving phase after 14 h of transport. From the receiving phase several aliquots of 100 mL were taken. To each sample, 1 mL of commercial phosphorus reagent (Sigma chemicals) was added. The reaction of the inorganic phosphorus with ammonium molybdate in the presence of sulfuric acid, produces an unreduced phosphomolybdate complex, of which the absorbance at 320 nm is directly proportional to the phosphorus concentration. All transport experiments were performed at least in duplicate.

Caution: Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.[35]

[1] For reviews on anion recognition see: a) J. L. Atwood, K. T. Holman, J. W. Steed, *J. Chem. Soc. Chem. Commun.* **1996**, 1401; b) F. Schmidtchen, M. Berger, *Chem. Rev.* **1997**, *97*, 1609; c) *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. García-España), Wiley-VCH, New York, **1997**; d) B. D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71; e) M. M. G. Antonisse, D. N. Reinhoudt, *Chem. Commun.* **1998**, 443.

[2] a) C. H. Park, H. E. Simmons, *J. Am. Chem. Soc.* **1968**, *90*, 2431; b) E. Graf, J.-M. Lehn, *J. Am. Chem. Soc.* **1976**, *98*, 6403; c) F. P. Schmidtchen, *Angew. Chem.* **1977**, *89*, 751; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 720; d) F. P. Schmidtchen, *J. Chem. Soc. Chem. Commun.* **1984**, 1115; e) D. Heyer, J.-M. Lehn, *Tetrahedron Lett.* **1986**, *27*, 5869; f) M. W. Hosseini, J.-M. Lehn, *Helv. Chim. Acta* **1988**, *71*, 749; g) J.-M. Lehn, R. Meric, J.-P. Vigneron, B. Waksman, C. Pascard, *J. Chem. Soc. Chem. Commun.* **1991**, *79*, 942; h) F. Diederich, P. Seiler, B. Hinzen, *Helv. Chim. Acta* **1996**, *79*, 942.

[3] a) H. E. Katz, *J. Org. Chem.* **1985**, *50*, 5027; b) H. E. Katz, *J. Am. Chem. Soc.* **1986**, 108, 73; c) M. E. Jung, H. Xia, *Tetrahedron Lett.* **1988**, *29*, 297; d) M. T. Blanda, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626; e) M. T. Reetz, C. M. Niemeyer, K. Harms, *Angew. Chem.* **1991**, *103*, 1515; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1472; f) D. M. Rudkevich, W. P. R. V. Stauthamer, W. Verboom, J. F. J. Engbersen, S. Harkema, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1992**, *114*, 9671; g) S. Aoyagi, K. Tanaka, Y. Takeachi, *J. Chem. Soc. Perkin Trans. 2* **1994**, 1549; h) D. M. Rudkevich, W. Verboom, Z. Brzozka, M. J. Palys, W. P. R. V. Stauthamer, G. J. van Hummel, S. M. Franken, S. Harkema, J. F. J. Engbersen, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1994**, *116*, 4341; i) K. T. Holman, M. M. Halihan, S. S. Jurisson, J. L. Atwood, R. S. Burkhalter, A. R. Mitchell, J. W. Steed, *J. Am. Chem. Soc.* **1996**, *118*, 9567; j) M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.* **1997**, *30*, 267; k) M. M. G. Antonisse, B. H. M. Snellink-Ruël, I. Yigit, J. F. J. Engbersen, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 9034; l) M. M. G. Antonisse, B. H. M. Snellink-Ruël, J. F. J. Engbersen, D. N. Reinhoudt, *J. Org. Chem.* **1998**, *63*, 9776.

[4] a) Y. Morzherin, D. M. Rudkevich, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1993**, *58*, 7602; b) E. Fan, S. A. V. Arman, S. Kincaid, A. D. Hamilton, *J. Am. Chem. Soc.* **1993**, *115*, 369; c) S. Valiyaveetil, J. F. J. Engbersen, W. Verboom, D. N. Reinhoudt, *Angew. Chem.* **1993**, *105*, 942; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 900; d) T. R. Kelly, M. H. Kim, *J. Am. Chem. Soc.* **1994**, *116*, 7072; e) J. Scheerder, M. Fochi, J. F. J. Engbersen, D. N. Reinhoudt, *J. Org. Chem.* **1994**, *59*, 7815; f) P. D. Beer, P. A. Gale, D. Hesek, *Tetrahedron Lett.* **1995**, *36*, 767; g) C. Raposo, M. Almariz, M. Martin, V. Weinrich, L. Mussons, V. Alcazar, C. Caballero, J. R. Mosan, *Chem. Lett.* **1995**, 759; h) J. Scheerder, J. F. J. Engbersen, A. Casnati, R. Ungaro, D. N. Reinhoudt, *J. Org. Chem.* **1995**, *60*, 6448; i) A. P. Davis, J. F. Gilmer, J. J. Perry, *Angew. Chem.* **1996**, *108*, 1410; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1312; j) P. D. Beer, *J. Chem. Soc. Chem. Commun.* **1996**, 689; k) M. P. Hughes, M. Shang, B. D. Smith, *J. Org. Chem.* **1996**, *61*, 4510; l) P. Bühlmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron* **1997**, *53*, 1647; m) A. P. Davis, J. J. Perry, R. P. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 1793; l) A. P. Bisson, V. M. Lynch, M.-K. C. Monahan, E. C. Anslyn, *Angew. Chem.* **1997**, *109*, 2435; *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 2340; m) H. Boerrichter, L. Grave, J. W. M. Nissink, L. A. J. Chrisstoffels, J. H. van der Maas, W. Verboom, F. de Jong, D. N. Reinhoudt, *J. Org. Chem.* **1998**, *63*, 4174; n) T. Shioya, S. Nishizawa, N. Teramae, *J. Am. Chem. Soc.* **1998**, *120*, 11534.

[5] a) P. B. Savage, S. K. Holmgren, S. H. Gellman, *J. Am. Chem. Soc.* **1993**, *115*, 7900; b) P. B. Savage, S. K. Holmgren, S. H. Gellman, *J. Am. Chem. Soc.* **1994**, *116*, 4069.

[6] a) V. Král, H. Furuta, K. Shreder, V. Lynch, J. L. Sessler, *J. Am. Chem. Soc.* **1996**, *118*, 1595; b) P. A. Gale, J. L. Sessler, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140; c) J. L. Sessler, A. Andrievsky, P. A. Gale, V. Lynch, *Angew. Chem.* **1996**, *108*, 2954; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2782; d) P. A. Gale, J. L. Sessler, W. E. Allen, N. A. Tvermoes, V. Lynch, *Chem. Commun.* **1997**, 665; e) M. Scherer, J. L. Sessler, A. Gebauer, V. Lynch, *Chem. Commun.* **1998**, 85.

[7] a) A. Echavarren, A. Galan, J.-M. Lehn, J. de Mendoza, *J. Am. Chem. Soc.* **1989**, *111*, 4994; b) A. Gleich, F. P. Schmidtchen, P. Mikulcik, G. Müller, *J. Chem. Soc. Chem. Commun.* **1990**, 55; c) E. Fan, S. A. van Arman, S. Kincaid, A. D. Hamilton, *J. Am. Chem. Soc.* **1993**, *115*, 369; d) D. M. Kneeland, K. Ariga, V. M. Lynch, C.-Y. Huang, J. Anslyn, *J. Am. Chem. Soc.* **1993**, *115*, 11042; e) M. Berger, F. P. Schmidtchen, *J. Am. Chem. Soc.* **1996**, *118*, 8947.

[8] a) J.-P. Behr, J.-M. Lehn, *J. Am. Chem. Soc.* **1973**, *95*, 6108; b) W. J. Molnar, C. P. Wang, D. Fennel-Evans, E. L. Cussler, *J. Membr. Sci.* **1978**, *4*, 129; c) T. Li, S. J. Krasne, B. Person, R. H. Kaback, F. Diederich, *J. Org. Chem.* **1993**, *58*, 380; d) I. M. Coelhoso, T. F. Moura, J. P. S. G. Crespo, M. J. T. Carrondo, *J. Membr. Sci.* **1995**, *108*, 71; e) I. M. Coelhoso, T. F. Moura, J. P. S. G. Crespo, M. J. T. Carrondo, *J. Membr. Sci.* **1995**, *108*, 231.

[9] a) E. Kokufuta, M. Nobusawa, *Chem. Lett.* **1988**, 425; b) E. Kokufuta, K. Sumi, W.-C. Wu, *Chem. Lett.* **1989**, 637; c) E. Kokufuta, M. Nobusawa, *J. Membr. Sci.* **1990**, *48*, 141; d) M. Huser, W. E. Morf, K. Fluri, K. Seiler, P. Schulthess, W. Simon, *Helv. Chim. Acta* **1990**, *73*, 1481; e) K. Sumi, M. Kimura, E. Kokufuta, I. Nakamura, *J. Membr. Sci.* **1994**, *86*, 155.

[10] a) J. L. Sessler, D. A. Ford, M. J. Cyr, H. Furuta, *J. Chem. Soc. Chem. Commun.* **1991**, 1788; b) K. Araki, S. K. Lee, J. Otsuki, M. Seno, *Chem. Lett.* **1993**, 493; c) J. L. Sessler, T. D. Mody, D. A. Ford, V. Lynch, *Angew. Chem.* **1992**, *104*, 461; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 452.

[11] M. A. Chaundry, B. Ahmed, *Sep. Sci. Technol.* **1992**, *27*, 1125.

[12] B. Dietrich, T. M. Fyles, M. W. Hosseini, J.-M. Lehn, K. C. Kaye, *J. Chem. Soc. Chem. Commun.* **1988**, 691.

[13] H. Tsukube, J.-I. Uenishi, H. Shiba, O. Yonemitsu, *J. Membr. Sci.* **1996**, *114*, 187.

[14] H. C. Visser, F. de Jong, D. N. Reinhoudt, *J. Membr. Sci*. **1995**, *107*, 267.

[15] W. F. Nijenhuis, E. G. Buitenhuis, F. de Jong, E. J. R. Sudholter, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1991**, *113*, 7963.

[16] Preliminary results have been reported: H. C. Visser, D. M. Rudkevich, W. Verboom, F. de Jong, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1994**, *116*, 11554.

[17] R. M. Fuoss, *J. Am. Chem. Soc.* **1958**, *58*, 5059.

[18] M. E. Duffey, D. Fennell Evens, E. L. Cussler, *J. Membr. Sci.* **1978**, *3*, 1.

[19] J. D. Lamb, R. L. Bruening, R. M. Izatt, Y. Hirashima, P.-K. Tse, J. J. Christensen, *J. Membr. Sci.* **1988**, *37*, 13.

[20] a) R. M. Barrer, D. M. Grove, *Trans. Faraday Soc.* **1951**, *47*, 837; b) L. Bromberg, G. Levin, O. Kedem, *J. Membr. Sci.* **1992**, *71*, 41.

[21] D_b in the bulk solvent is calculated from D_m as $D_b = (\tau/\Theta)D_m$. D_m is related to the diffusion coefficient from lag-times through $D_m = \Theta \cdot D_{lag}$.

[22] This assumption is supported by the calculated mean diffusion coefficients for tetrabutylammonium salts in the reference solvent nitrobenzene; $D(NBu_4Cl) = 4.09 \times 10^{-10}\,m^2\,s^{-1}$, $D(NBu_4Br) = 4.06 \times 10^{-10}\,m^2\,s^{-1}$, $D(NBu_4I) = 4.02 \times 10^{-10}\,m^2\,s^{-1}$, and $D(NBu_4Cl) = 4.11 \times 10^{-10}\,m^2\,s^{-1}$. The diffusion coefficient D_{MX} was calculated from the individual diffusion coefficients of D_M and D_X according to: $D_{MX} = (2D_MD_X)/(D_M+D_X)$. The diffusion coefficients D_m^∞ and D_X^∞ of the ions were determined from the limiting molar conductivities λ^∞ in nitrobenzene as reported by Marcus: $D^\infty = RT/z^2F^2\lambda/z^2$. $D_M^\infty(NBu_4^+) = 3.1 \times 10^{-10}\,m^2\,s^{-1}$, $D_X^\infty(Cl^-) = 6.0 \times 10^{-10}\,m^2\,s^{-1}$, $D_X^\infty(Br^-) = 5.9 \times 10^{-10}\,m^2\,s^{-1}$, $D_X^\infty(I^-) = 5.7 \times 10^{-10}\,m^2\,s^{-1}$, $D_X^\infty(NO_3^-) = 6.1 \times 10^{-10}\,m^2\,s^{-1}$ (A. Marcus, *Ion Properties*, Marcel Dekker, New York, **1997**).

[23] Y. Marcus, *Ion Solvation*, Wiley, New York, **1985**.

[24] For a comparison of the anion solvating properties of the solvents $E_T(30)$ and AN of NPOE were determined. From the observed $\lambda_{max} = 680$ nm of the longest wavelength absorption of the pyrimidinium *N*-phenoxide dye in NPOE, $E_T(30)$ was calculated; $E_T(30)_{NPOE} = 41.3\,kcal\,mol^{-1}$. The acceptor number (AN) was determined from the ^{31}P-NMR spectrum of triethylphosphine oxide extrapolated to

  0947-6539/00/0608-1384 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

infinite dilution ($AN_{NPOE} = 13.5$). For MeCN $E_T(30)_{MeCN} = 37.5$ kcal mol^{-1} and $AN_{MeCN} = 18.9$.
[25] Y. Marcus, *Pure Appl. Chem.* **1983**, *55*, 977.
[26] F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1898**, *24*, 247.
[27] $\Delta G_{tr,NPOE}(SCN^-)$ was obtained from Eq. (12), whereas $\Delta G_{tr,NPOE}(H_2PO_4^-)$ was determined from competition experiments (Table 3).
[28] a) *Chemical Separations with Liquid Membranes* (Eds.: R. A. Bartsch, J. D. Way), ACS Symposium Series Number 642, ACS, Washington DC, **1996**; b) F. de Jong, H. C. Visser in *Comprehensive Supramolecular Chemistry*, *Vol. 10* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn, D. N. Reinhoudt), Elsevier, Oxford, **1996**, Ch. 2.
[29] a) A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 2767; b) A. Casnati, A. Pochini, R. Ungaro, C. Bocchi, F. Ugozzoli, R. J. M. Egberink, W. Struijk, R. J. M. Lugtenberg, F. de Jong, D. N. Reinhoudt, *Chem. Eur. J.* **1996**, *2*, 436; c) O. Struck, L. A. J. Chrisstoffels, R. J. W. Lugtenberg, W. Verboom, G. J. van Hummel, S. Harkema, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 2487.
[30] L. A. J. Chrisstoffels, F. de Jong, D. N. Reinhoudt, S. Sivelli, L. Gazzola, A. Casnati, R. Ungaro, *J. Am. Chem. Soc.* **1999**, *121*, 10142.
[31] Assuming that the diffusion coefficients are the same S is related to the partition coefficients $S \cong \sqrt{K_p(H_2PO_4^-)}/\sqrt{K_p(Cl^-)}$. It is subsequently rearranged to give: $2RT\ln(S) = RT\ln[K_p(H_2PO_4^-)] - RT\ln[K_p(Cl^-)]$, from which $\Delta(\Delta G_{tr})$ is determined: $\Delta(\Delta G_{tr}) = -2RT\ln(S)$.
[32] H. C. Visser, *PhD Dissertation*, University of Twente, Enschede, The Netherlands, **1994**.
[33] T. B. Stolwijk, E. J. R. Sudholter, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1987**, *109*, 7042.
[34] P. C. Meier, *Anal. Chim.* Acta **1982**, *136*, 363.
[35] *Dangerous Properties of Industrial Materials* (Ed.: N. I. Sax), 5th ed., van Nostrand Reinhold, New York, **1979**, p. 1078.

Received: July 19, 1999 [F1925]