Recl. Trav. Chim. Pays-Bas **114**, 285–294 (1995)
SSDI 0165-0513(95)00032-1

0165–0513/95/06285–10$9.50

Alkali-cation transport through supported liquid membranes mediated by solvent-linked carriers

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(Received November 28, 1994)

Abstract. Neutral macrocyclic alkali-cation receptors have been covalently linked to one or more molecules of the membrane solvent 2-nitrophenyl *n*-octyl ether (NPOE). These compounds are all highly lipophilic and soluble in NPOE. The flux of alkali-perchlorate salts through supported liquid membranes (SLMs) has been optimized by variation of the carrier content in the membrane and the temperature. With all carriers, the optimum flux is reached at carrier contents of about 20% (w/w) in NPOE. Above this carrier content the flux decreases because of an increase in the viscosity of the membrane solutions. Relatively low activation energies for transport indicate that the transport is diffusion-limited. The excellent compatibility between the carriers and the membrane solvent leads to very stable membranes (NPOE/Accurel®). The mechanism of alkali perchlorate transport has been investigated by variation of the source-phase salt activity and the carrier concentration. Indications about ion pair formation and 2/1 carrier/cation complexation have been obtained from variation of the carrier concentration and transport selectivity measurements.

Introduction

Since the first report by *Reusch* and *Cussler*[1], numerous papers have appeared on carrier-mediated transport through supported liquid membranes (SLMs). However, the relatively short life-time of SLMs has limited their large-scale application. The stability of SLMs has been studied widely and different degradation mechanisms have been proposed, *viz.* (*i*) chemical degradation[2], (*ii*) partition of the carrier and/or membrane solvent to the adjacent aqueous phases[3,4], (*iii*) depletion of the membrane phase under the influence of an osmotic[5] or hydrostatic pressure gradient[6,7,8], (*iv*) formation of emulsions[9], or (*v*) inverted micelles[10,11]. The stability of SLMs has been improved by *e.g.* using a gelled membrane phase[9,12] or stacking the SLM in between dialysis membranes[13]. In our laboratory, attention has mainly been focussed on increasing the lipophilicity of macrocyclic carriers. This has been achieved by attachment of long-alkyl chains[14] or binding the carriers to a polymer[15]. However, long-alkyl- and polymer-modified carriers are generally only moderately soluble in membrane solvents such as 2-nitrophenyl *n*-octyl ether (NPOE). This solvent is frequently used because of its relatively low viscosity, and high lipophilicity and polarity[16]. In order to improve their solubility and, not simultaneously, detergency (which may lead to a different transport mechanism[17]), we have covalently linked the lipophilic membrane solvent (NPOE) to macrocyclic carriers. Such a carrier is more compatible with the membrane solvent and consequently its solubility in the membrane phase is greatly enhanced[18]. Hence, their concentrations in the membrane can be varied over a wide range. Effects of the carrier concentration (L_0) on the flux (J) have been extensively described and the overall picture is rather complex. The way in which L_0 affects J depends on whether ion–pairs[1] or free ions[19] are present in the membrane, and whether the carrier is saturated at the source phase interface[1]. Furthermore, at high L_0 the carrier may influence the viscosity of the medium[20] and tend to form aggregates[21]. For transport mediated by fixed-site carriers, *Cussler* et al.[22] reported a percolation threshold. This is the carrier concentration above which the distances between the carriers are small enough for a cation to 'jump' from site to site. This phenomenon was also described by *Kalachev* et al.[23] who used 'free' tridodecylamine as a carrier.

In this paper we describe the covalent attachment of one or more NPOE moieties to carriers that are well-known for their complexing ability with Na^+ or K^+. The carrier concentrations in NPOE/Accurel® were varied over a wide range in order to optimize the flux. In order to increase the flux even more, transport experiments have also been carried out at elevated temperatures. The membrane stability was monitored over a period of weeks. The transport mechanism is discussed in terms of the diffusion constants (D_m) and extraction constants (K_{ex}) and finally, initial transport selectivity (K^+ *vs.* Na^+) is described.

Results and discussion

Synthesis

The structures of carriers that have been used are given in Chart 1. The starting material **9a** for the synthesis of the

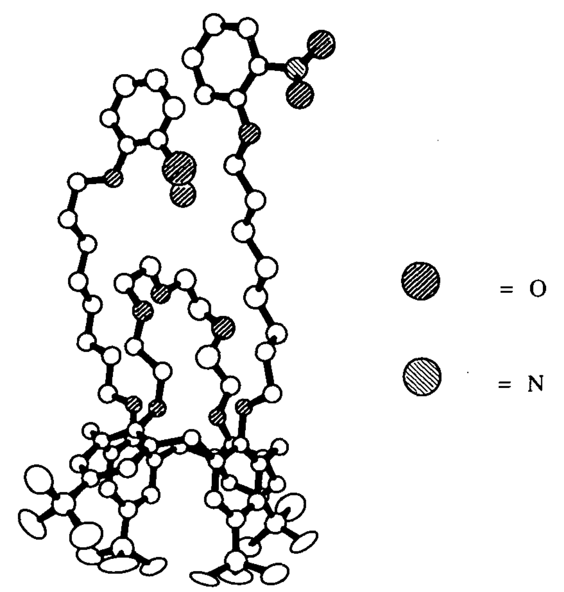


Figure 1. Crystal structure of **4**.

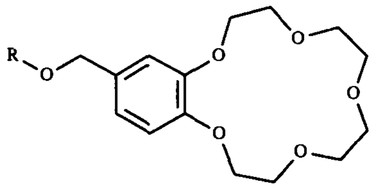
NPOE derivatives, was obtained in 75% by alkylation of 2-nitrophenol using a 4–5 fold excess of 1,8-dibromooctane. The acetate **9b** was obtained (91%) from reaction of **9a** with KOAc in the presence of 18-crown-6 in acetonitrile. The acetate was successively hydrolysed to yield **9c** (94%).

The benzo crown **2** and the dicarboxamide **6**, both having one covalently linked NPOE moiety, were synthesized in 48 and 29%, respectively, from the 4′-(hydroxymethyl) derivatives **1**^{24} and **5**^{25} by alkylation with **9a** using NaH as a base. The calix[4]arene crown-5 **4** was analogously obtained in 77% yield from **3**^{26} and **9a** in DMF/THF. The reaction of **7**^{27} with **9c** in CH_2Cl_2/Et_3N afforded the calix[4]arene tetraester **8** in 61%.

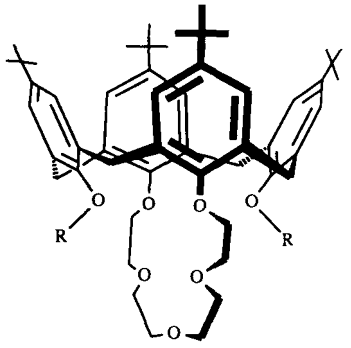
Carriers **2**, **6**, and **8** were obtained as viscous oils. The calix crown **4** was obtained as a solid after chromatographic purification and recrystallization from $CHCl_3$/MeOH. Slow crystallization from a mixture of hexane/dichloromethane gave crystals suitable for structure elucidation by single crystal X-ray analysis. According to the X-ray structure (Figure 1) the calix crown **4** has a 'flattened' cone conformation, i.e. the aryl rings substituted with the NPOE moieties are positioned parallel, whereas the crown-linked phenyl rings point inwards. Furthermore, Figure 1 shows that the terminal C atoms of the *tert*-butyl groups exhibit rather large anisotropy because of the thermal motion.

Optimization of the flux

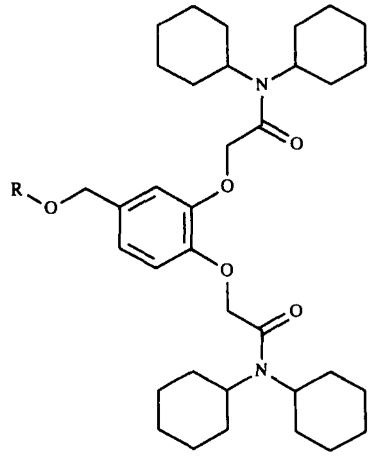
Because of their increased compatibility with the membrane solvent, the solubility of all carriers in NPOE is



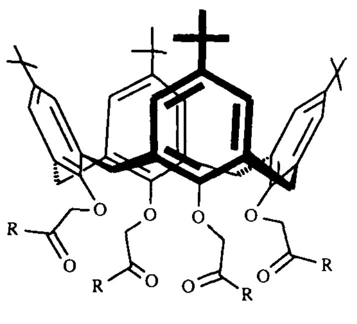
1 R = H
2 R = -*n*-$C_8H_{16}O$-*o*-$C_6H_4NO_2$



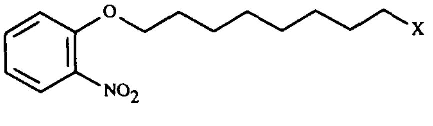
3 R = H
4 R = -*n*-$C_8H_{16}O$-*o*-$C_6H_4NO_2$



5 R = H
6 R = -*n*-$C_8H_{16}O$-*o*-$C_6H_4NO_2$



7 R = Cl
8 R = -*n*-$C_8H_{16}O$-*o*-$C_6H_4NO_2$



9a X = Br
9b X = OC(O)CH_3
9c X = OH

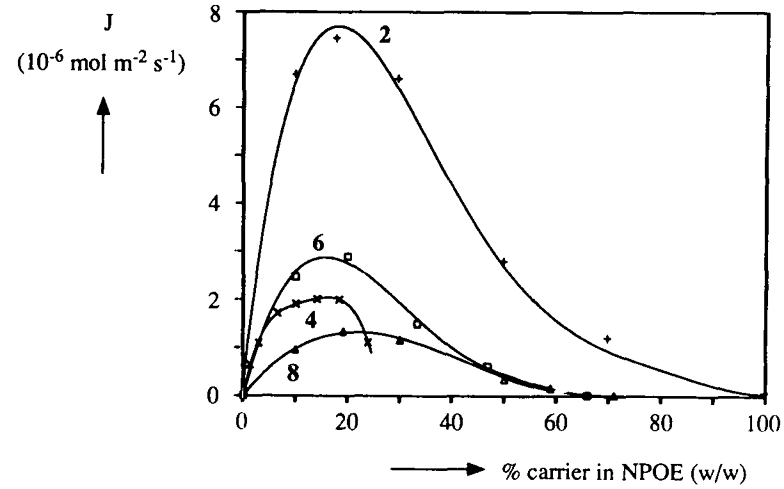


Figure 2. Alkali-perchlorate flux as a function of carrier content; **2** *$K^+(+)$,* **4** *$K^+(\times)$,* **6** *$Na^+(\square)$,* **8** *$Na^+(\triangle)$; both $[KClO_4]_s$ and $[NaClO_4]_s = 0.1$ M.*

high. Hence, the effect of the carrier concentration on the flux could be studied over a wide concentration range. Carrier **2** could be mixed with NPOE in any ratio up to 100%. Above 30% (w/w) carrier **4** did not completely dissolve in NPOE. Solutions of carriers **6** and **8** were not used above 70% (w/w) because of their extremely high viscosity. The initial alkali perchlorate flux was measured using 0.1M source-phase salt concentrations (Figure 2).

All curves first show an increase of flux with the carrier content in the membrane, whereas above a carrier percentage of about 20% (w/w) the flux decreases. Strikingly, the flux of $KClO_4$ through a membrane containing 100% **2** is of the same magnitude as the flux obtained in the absence of a carrier ($\approx 2 \cdot 10^{-8}$ mol $\cdot$ m^{-2} $\cdot$ s^{-1}). The fact that all curves have an optimum, suggests that the transport is strongly affected by the viscosity of the membrane solution. In order to confirm this, rheological measurements were performed on NPOE and its mixtures with carriers **2** and **6** using a thermostated cone-on-plate viscosity meter. The viscosity obtained for NPOE (11 mPa · s) is in good agreement with the value from capillary viscosity measurements reported elsewhere (11.5 mPa · s)[16]. The viscosities of mixtures of NPOE and carriers **2** and **6** are shown in Figure 3. Up to about 20% (w/w) of carrier in NPOE the viscosities of the mixtures are almost the same. Above this point the exponential increase of the viscosity becomes evident.

Variation of temperature

In order to increase the flux even more and obtain information about the transport regime (diffusion and/or kinetic control), transport experiments have been carried out at elevated temperatures. Furthermore, the kinematic viscosity (υ) of NPOE and its density have been determined as a function of temperature. When the carrier is saturated at the source-phase interface, the flux is only affected by the diffusion constant D_m. In turn, the diffusion constant in the membrane is linearly related to that in bulk (D_b) after corrections for the porosity and tortuosity of the support[16]. According to the Stokes–Einstein equation (Eqn. 1), D_b is a function of the viscosity of the medium (η), which in turn is an exponential function of the temperature (Eqn. 2). E_a represents the activation energy for self-diffusion or viscous flow of the solvent. Combination of Eqns. 1 and 2 yields a simple relation between temperature and flux (Eqn. 3).

$$D_b = \frac{R \cdot T}{6 \cdot \pi \cdot N_A \cdot \eta \cdot r} \qquad (1)$$

$$\eta = A \cdot e^{E_a/(R \cdot T)} \qquad (2)$$

$$\ln(J) \approx C - \frac{E_a}{R \cdot T} \qquad (3)$$

The kinematic viscosity of NPOE has been determined at temperatures between 20–60°C and from the logarithmic function fitted to the data points an activation energy of about 24 kJ/mol has been obtained[28]. Since the density of NPOE is only slightly temperature dependent (the expansion coefficient is $8 \cdot 10^{-4}$/°C)[28], activation energies for diffusion-limited transport were also expected to be about 24 kJ/mol.

Transport experiments have been carried out with all four carriers using 0.1M source-phase salt concentrations. The fluxes were calculated from the conductivity of the receiving aqueous phase. The temperature dependence of the conductivity was corrected for (see Experimental). The temperature was increased in steps of a few degrees centigrade and in between the measurements, the source and/or receiving phases were renewed. After the experiment the flux at 25°C was determined again for all carriers and found to be equal to the original flux. This indicates that the carriers do not markedly partition to the aqueous phases.

The $KClO_4$ flux mediated by 0.4M carrier **2** could be increased to $2.15 \cdot 10^{-5}$ mol $\cdot$ m^{-2} $\cdot$ s^{-1} at 61°C, which is about 3 times as high as the flux at 25°C.

The activation energies for transport were calculated from plots of ln(J) versus $1/T$ (Figure 4): 34 ± 2 (**2**), 29 ± 3 (**6**) and 27 ± 1 (**8**) kJ/mol. At 10% (w/w) of the calix crown carrier 4 in NPOE, the $KClO_4$ flux did not increase with

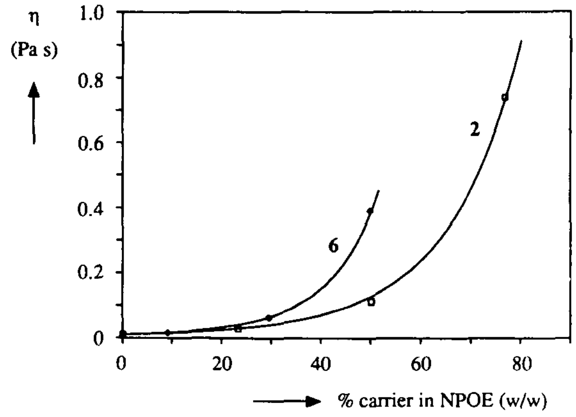


Figure 3. Viscosity of solutions of **2** *(□) and* **6** *(◇) in NPOE.*

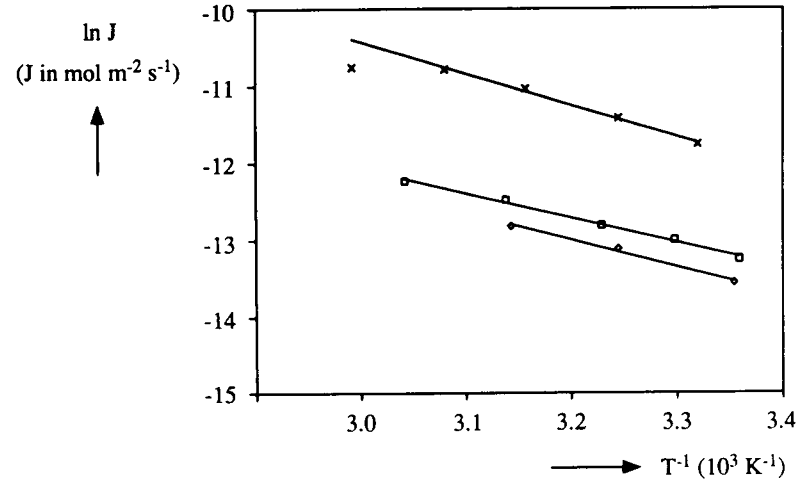


Figure 4. Arrhenius plot of alkali-perchlorate transport with carriers **2** *(20% (w/w), $[KClO_4]_s = 0.1$ M, (×)),* **6** *(4% (w/w), $[NaClO_4]_s = 0.1$ M, (□)), and* **8** *(15% (w/w), $[NaClO_4]_s = 0.1$ M, (◇)).*

temperature, probably because this carrier has a very low extraction constant[29].

Since the activation energies for transport of $KClO_4$ with carrier **2** and of $NaClO_4$ with **6** and **8** closely resemble the activation energy for self-diffusion of NPOE, it can be concluded that the transport is indeed diffusion-limited.

Membrane stability

The stability of the membranes was very high: even after several replacements of the receiving and/or source phase at elevated temperatures the flux at 25°C remained constant within experimental error (15%). In order to test the long-term stability of the membranes a more rigorous method had to be used. Therefore, a set-up was developed in which the membranes were clamped between dismantled slide windows, contained in a special slide holder. This holder containing five slides was placed in a reservoir through which tap water was run from bottom to top at an average speed of about 1000 l/week. The stability of membranes containing a 0.01M solution of the calix crown carrier **4** in NPOE was tested in the set-up for five weeks (Figure 5).

Every week another slide was taken out of the set-up and $KClO_4$ transport from a 0.1M source phase was measured in a small cell (membrane area 2 cm^2) described elsewhere[30]. The cell as a whole was rotated as the method of stirring. The flux after 3 weeks of about $3.5 \cdot 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1}$ is the lowest measured in this series and the average flux is about $5 \cdot 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1}$. Although the methods used are rather inaccurate, it is obvious that the carrier is still present in the membrane and that no water channels, short-circuiting the aqueous phases, have been formed.

Transport mechanism

Previously, a model for carrier-mediated transport of monovalent salts has been derived, in which it is assumed that free ions are present in the membrane, that the cation associates with the carrier to form a 1/1 complex, and that diffusion of this complex through the membrane is the rate-limiting step[19]. In the flux equation (Eqn. 4), the diffusion constant of the complex (D_m) and the extraction constant (K_{ex}) are the characteristic transport parameters ($A = K_{ex} \cdot a_s^2$).

$$J = \frac{D_m}{2 \cdot d_m} \cdot \left\{ -A + \sqrt{\left(A^2 + 4 \cdot A \cdot L_0\right)} \right\} \tag{4}$$

L_0 denotes the carrier concentration, a_s represents the source-phase salt activity, and d_m is the membrane thickness. K_{ex} and D_m can be determined from Eqn. 4 by performing a series of transport experiments at different

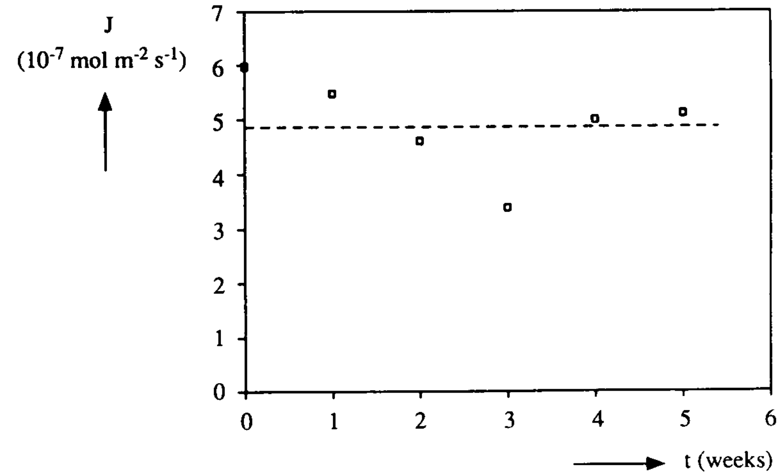


Figure 5. Long-term membrane stability of Accurel® membranes containing 0.01M of **4** *in NPOE; the dotted line represents the average flux value over the time of the experiment.*

source-phase-salt concentrations[19]. The basic feature of carrier-mediated transport is that the initial flux (J) increases with a_s until, at the source phase interface, the carrier is saturated.

Variation of the source-phase salt activity has been carried out for transport of $KClO_4$ with the benzo crown **2** and the calix crown **4** and for transport of $NaClO_4$ with the dicarboxamide **6** and calix tetraester **8** (Figures 6 and 7, respectively). Carriers **2**, **6**, and **8** could be saturated at the source-phase interface, whereas the solubility of $KClO_4$ in water (≈ 0.1 M) is too low to obtain data points up to saturation of **4**. Consequently, K_{ex} and D_m values for this carrier salt combination from the plot of J versus a_s (Figure 6) are less accurate. Alternatively, D_m was determined from the lag time (t_{lag}), defined as the time it takes for the complex to move across the membrane. The diffusion constant obtained directly from pre-steady-state-flux measurements, D_{lag}, is related to D_m according to Eqn. 5, in which Θ represents the porosity of the support[31].

$$D_{lag} = \frac{\langle d_m{}^2 \rangle}{6 \cdot t_{lag}} = \frac{D_m}{\Theta} \qquad (5)$$

From these lag-time measurements a D_m value of $1.0 \cdot 10^{-11}$ m^2/s was calculated for calix crown **4** (Table I), which is almost the same as the diffusion constant of its dimethoxy analog ($9.9 \cdot 10^{-12}$ m^2/s)[32]. D_m of the calix tetraester **8** closely resembles the value of $1.2 \cdot 10^{-11}$ m^2/s reported for the calix[4]arene tetraethyl ester[32]. Thus, for carriers **4** and **8**, their size does not markedly influence the diffusion constant. However, the K_{ex} of **8** for $NaClO_4$ is lower than that of the tetraethyl ester by a factor of about 13[32]. This could imply that modification of the carrier close to the region of complexation significantly alters the extraction efficiency of the carrier.

Table I K_{ex} *and* D_m *values at low carrier concentration.*

Carrier	Salt	Carrier conc. (mM)	D_m (10^{-12}m^2/s)	K_{ex} (M^{-1})	R^2
2	$KClO_4$	10	5.5	35	0.98
4	$KClO_4$	10	(19.7)10 [a]	0.3	0.998
6	$NaClO_4$	50	5.2	5.1	0.995
8	$NaClO_4$	10	11.7	0.8	0.96

[a] This D_m value was determined from lag-time measurements.

The diffusion constants obtained from transport of $KClO_4$ with **2** and of $NaClO_4$ with **6** are relatively low ($5.5 \cdot 10^{-12}$ and $5.2 \cdot 10^{-12}$ m^2/s, respectively). At these low carrier concentrations aggregation of the carriers is not likely to occur, but probably benzo crown **2** does not form a 1/1 carrier/K^+ complex. It is known[33,34] that benzo-15-crown-5 can form a 2/1 complex with K^+. According to *Simon* et al., Na^+ is probably complexed by **5** in a 1/1 stoichiometry[25]. More information about the stoichiometry of the complexes has been obtained from flux measurements at various carrier concentrations.

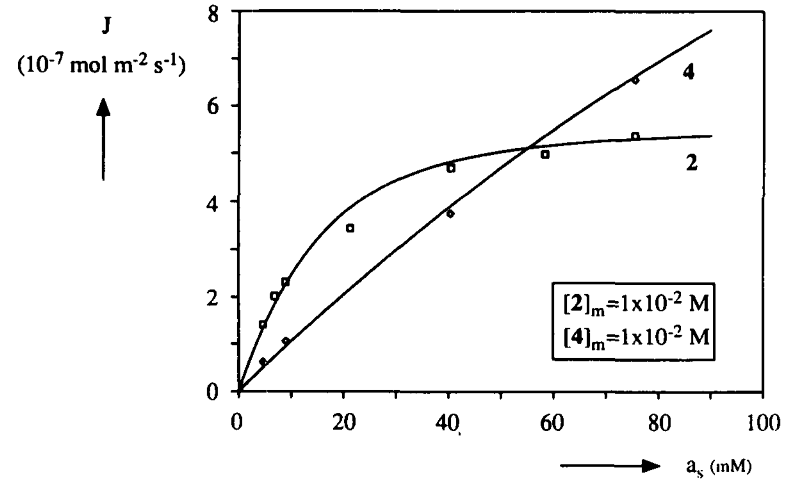


Figure 6. $KClO_4$ flux as a function of source-phase salt concentration with carriers **2** *(□) and* **4** *(◇).*

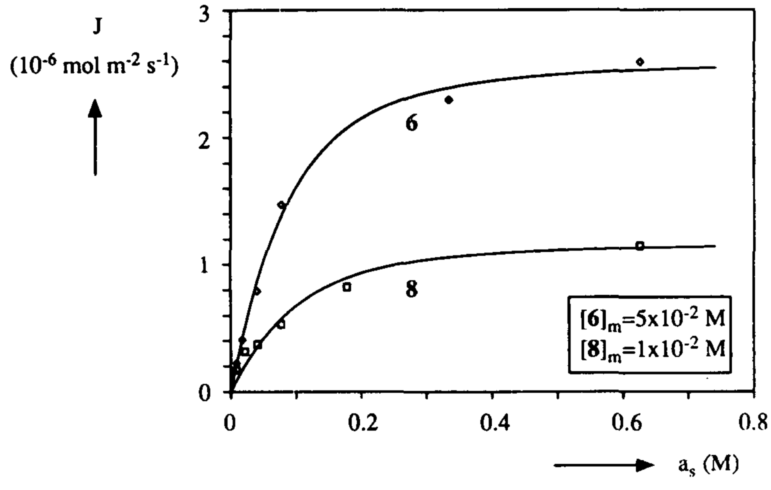


Figure 7. $NaClO_4$ flux as a function of source-phase salt concentration with carriers **6** *(◇) and* **8** *(□).*

Although the initial $KClO_4$ flux obtained with benzo crown carrier **2** at about 20% (w/w) in NPOE is the highest we ever obtained, at high carrier **2** concentration the flux rapidly decreased in time, a phenomenon that is usually only observed for thermodynamically very stable complexes. Therefore, the K_{ex} value was probably much higher than reported in Table I[28]. This was checked by determination of K_{ex} and D_m values at $[\mathbf{2}]_m = 0.4$ M and 1.0 M from variation of the source-phase salt activity (Figure 8).

In line with the increase of the viscosity, D_m decreases with the carrier concentration. The K_{ex} values calculated according to the 1/1 free ion model are: K_{ex} (0.4 M l) $= 5.5 \cdot 10^3$ and K_{ex} (1.0 M l) $= 4.9 \cdot 10^4$. Hence, it must be concluded that the complexing ability of carrier **2** strongly increases with the carrier concentration. This apparent increase in K_{ex}, calculated to the 1/1 free-ion model, may arise from several factors. Firstly, on increasing the carrier concentration, the polarity of the solvent mixture increases, which has previously[16] been found to increase K_{ex}. Secondly, in addition to the 1/1 stoichiometry, 2/1 carrier/K^+ complexes may also be formed. And thirdly, at high carrier concentrations, ion-pair formation may take place. The flux equations for the latter modes of transport are given in Appendix 1. Since the remarkable low diffusion constant (Table I), and the concentration-

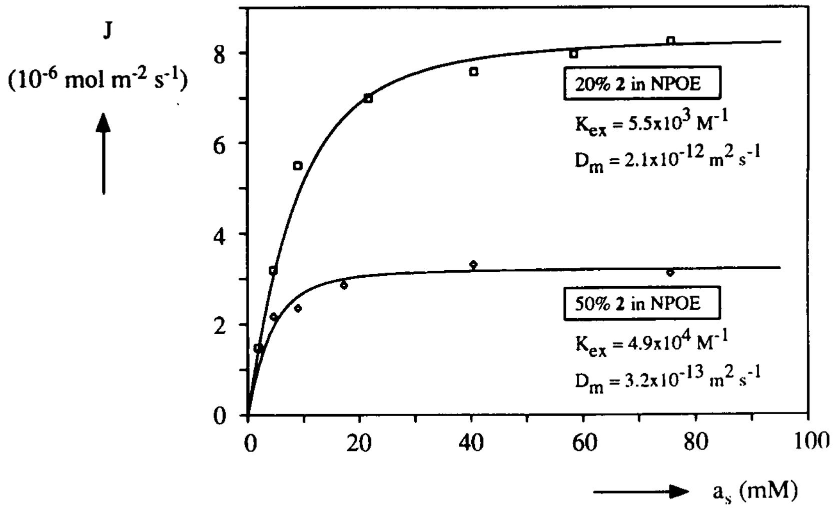


*Figure 8. Determination of K_{ex} and D_m at high carrier **2** concentration; $[\mathbf{2}] = 0.4$ M (□), $[\mathbf{2}] = 1$ M (◇).*

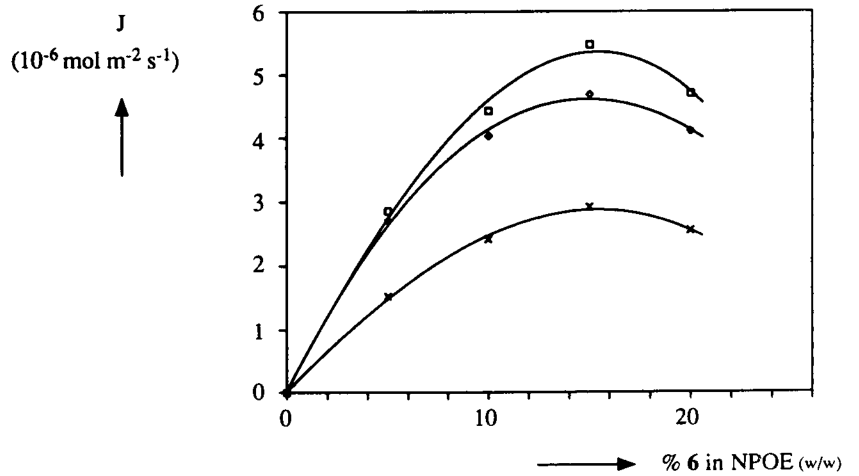


*Figure 9. Flux as a function of carrier **6** and source-phase $NaClO_4$ concentration; $[NaClO_4]_s = 1.10^{-1}$ M (×), $[NaClO_4]_s = 1$ M (◇), 1 M < $[NaClO_4]_s$ < 5 M (□).*

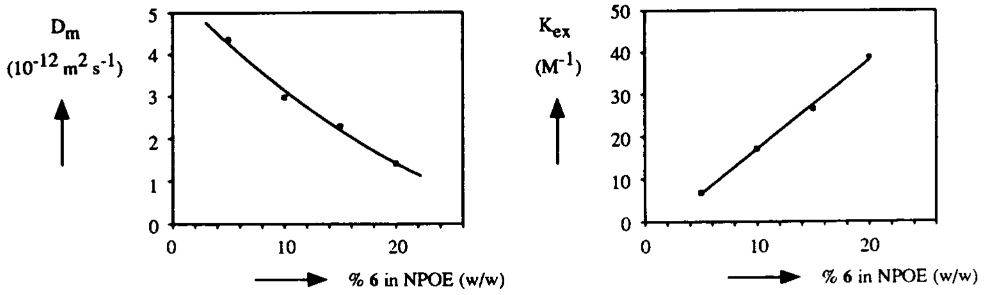


*Figure 10. Apparent K_{ex} and D_m as a function of carrier **6** concentration in NPOE.*

dependent K/Na selectivity (next paragraph) cannot be explained by involving ion-pair formation, we conclude that carrier **2** also forms 2/1 complexes with K^+.

The flux of $NaClO_4$ has also been measured at different source-phase salt concentrations and high dicarboxamide carrier **6** concentrations (Figure 9). Independent of the source-phase salt concentration the optimum flux of $NaClO_4$ is obtained at about 15% (w/w) **6** in NPOE. The flux values obtained have also been used to calculate K_{ex} and D_m values according to the free-ion model for a 1/1 complex (Figure 10). Again the diffusion constant decreases and the complexing ability of **6** improves with increasing carrier content in the membrane.

In this case more information would be required to distinguish between 1/1 ion-pair formation and 2/1 free-ion complexes.

Transport selectivity

The initial transport selectivities of benzo crown **2** and calix crown **4** for K^+ over Na^+ and of dicarboxamide **6** for Na^+ over K^+ were determined from competitive transport experiments (Table II).

The selectivity, S, is defined by Eqn. 6, in which P_1 denotes the permeability of the primary and P_2 that of the competing cation.

$$S = \frac{J_{M1} \cdot [M_2]_s}{J_{M2} \cdot [M_1]_s} = \frac{P_1}{P_2} \qquad (6)$$

The transport selectivity of **4** for K^+ over Na^+ only slightly increases with decreasing $[K^+]_s/[Na^+]_s$, whereas the Na^+/K^+ selectivity of **6** is independent of the source-phase salt concentrations. This constant selectivity is to be expected in case the transport of both cations is diffusion limited and if both cations are complexed by the carrier in a 1/1 stoichiometry[35].

Indications about (partial) $\mathbf{2}/K^+ = 2/1$ complexation were obtained from initial and time-dependent flux measurements as a function of carrier and source-phase salt concentrations (*vide supra*). The fact that the Na^+ and K^+ complexes may have different stoichiometries, complicates the prediction of initial transport selectivity. Apparently, the transport selectivity of **2** for K^+ over Na^+ strongly increases with decreasing $[K^+]_s/[Na^+]_s$. This can be explained by the more favorable formation of $(\mathbf{1}_2 \cdot KClO_4)$, at low carrier loading, which occurs at low source-phase $KClO_4$ concentrations.

Conclusions

Neutral macrocyclic alkali-cation receptors that are covalently linked to one or more NPOE moieties show very high solubility in this membrane solvent and because of their enhanced compatibility, the membranes are stable for a long period of time and at elevated temperatures. Activation energies for transport of about the same magnitude as that for viscous flow of NPOE indicated that the transport is diffusion-limited. With all carriers the optimum flux was reached at a carrier content of about 20% (w/w) in NPOE. Above this carrier content the flux decreased because of an increase of the viscosity of the membrane solutions, as confirmed by rheological measurements. At high carrier concentrations $KClO_4$ predominantly associates with carrier **2** in a 2/1 carrier/salt stoichiometry. This explains the increase of the extracting ability of **2** for $KClO_4$ at high carrier concentrations and the fact that its transport selectivity for $KClO_4$ over $NaClO_4$ increases when $[KClO_4]_s$ is lowered. At high carrier **6** concentrations either a 1/1 carrier/$NaClO_4$ ion pair or a 2/1 complex is formed inside the membrane.

Experimental

Synthesis

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. N,N-Dimethylformamide (DMF) and acetonitrile were dried over molecular sieves (3 Å). Petroleum ether was used with a bp of 40–60°C. Column separations were carried out on silica gel (SiO_2, E. Merck, particle size 0.040–0.063 mm, 230–240 mesh) or alumina (Activity II/III).

Melting and boiling points are uncorrected. FAB (Fast Atomic Bombardment) mass spectra were recorded with 3-nitrobenzyl alcohol as a matrix. IR spectra were recorded of samples in KBr pellets. ^1H- and ^{13}C-NMR spectra were recorded in $CDCl_3$.

*4-[[8-(2-Nitrophenoxy)octyloxy]methyl]benzo-15-crown-5 (**2**).* NaH (0.45 g, 15 mmol) was washed twice with petroleum ether under nitrogen. Then THF (100 ml) was added followed by **1** (4.5 g, 15 mmol)[24,25]. After deprotonation, **9a** (6.6 g, 20 mmol) was added and the mixture was stirred under reflux for 24 h. Then water (100 ml) was added carefully followed by CH_2Cl_2 (200 ml), after which the organic layer was washed with water (2×100 ml) and dried over $MgSO_4$. The residue was purified by column chromatography (Al_2O_3, EtOAc/petroleum-ether 1/1) to yield **2** as a yellow viscous oil; yield 3.92 g (7.2 mmol, 48%); n_D^{20} 1.5435. ^1H-NMR δ: 7.73 (dd, 1 H, J_o 8.1 Hz, J_m 1.7 Hz, Ar H), 7.50–7.35 (m, 1 H, Ar H), 7.0–6.9 (m, 2 H, Ar H), 6.9–6.8 (m, 3 H, Ar H), 4.33 (s, 2 H, $ArCH_2O$), 4.1–3.95 (m, 6 H, $ArOCH_2$), 3.85–3.75 (m, 4 H, $ArOCH_2CH_2O$), 3.7–3.6 (s, 8 H, $OCH_2CH_2OCH_2CH_2O$), 3.35 (t, 2 H, J 6.6 Hz, $ArCH_2OCH_2$), 1.8–1.6 (m, 2 H, $ArOCH_2CH_2$), 1.6–1.45 (m, 2 H, $ArCH_2OCH_2CH_2$), 1.5–1.2 (m, 8 H, CH_2). ^{13}C-NMR δ: 152.5 (s, Ar $CO(CH_2)_3$), 149.2 and 148.6 (s, Ar $COCH_2CH_2O$), 140.0 (s, Ar CNO_2), 133.9 (d, Ar CH), 131.9 (s, Ar CCH_2O), 125.5, 120.7, 120.0, 114.4, 113.9 and 113.7 (d, Ar CH), 72.6, 71.0, 70.5, 70.2, 69.6, 69.2 and 68.9 (t, CH_2O), 29.7, 29.3, 29.2, 28.9, 26.1 and 25.8 (t, CH_2). MS (EI) m/z: 547.269 (M^+, calcd. 547.278).

*25,27-Bis[8-(2-nitrophenoxy)octyloxy]-p-tert-butylcalix[4]arene-26,28-crown-5 (**4**).* NaH (155 mg, 5 mmol) was washed twice with petroleum ether under nitrogen. Then DMF (50 ml) was added followed by **3** (1 g, 1.24 mmol)[27]. After deprotonation **9a** was added and the mixture was stirred under reflux for 16 h. Water and EtOAc were added carefully. The organic layer was washed successively with dilute HCl,

Table II Initial transport selectivities (S) *of carriers* **2**, **4**, *and* **6**.

Carrier	[Carrier]	$[K^+]_s$–$[Na^+]_s$	K^+ flux	Na^+ flux	S	
	(M)	(M)–(M)	(10^{-8} mol·m^{-2}·s^{-1})		K/Na	Na/K
2	0.4	0.08–0.08	621	7.2	87	
		0.01–0.1	621	20	307	
		0.001–0.1	339	64	530	
4	0.01	0.08–0.08	56	1.2	48	
		0.01–0.1	24	3.6	68	
		0.001–0.1	6	6.9	87	
6	0.05	0.08–0.08	4.8	90		19
		0.1–0.01	14	32		24
		0.1–0.001	21	4.4		21

saturated NH_4Cl and water, and dried over $MgSO_4$. The residue was purified by column chromatography (SiO_2, EtOAc/petroleum-ether 1/1) to afford **4** as a light-yellow solid; yield 1.24 g (77%); mp 146–148°C ($CHCl_3$/MeOH). ^{1}H NMR δ:7.79 (dd, 2 H, J_o 8.1 Hz, J_m 1.7 Hz, Ar H), 7.6–7.4 (m, 2 H, Ar H), 7.12 (s, 4 H, Ar H), 7.1–6.9 (m, 4 H, Ar H), 6.43 (s, 4 H, Ar H), 4.35 (d, 4 H, $J_{ax,eq}$ 12.6 Hz, $ArCH_2Ar$, H_{eq}), 4.3–4.1 (m, 8 H, CH_2OAr), 4.10 (t, 4 H, J 6.4 Hz, $ArOCH_2$), 3.9–3.6 (m, 12 H, CH_2OCH_2), 3.13 (d, 4 H, $J_{ax,eq}$ 12.6 Hz, $ArCH_2Ar$, H_{ax}), 2.0–1.7 (m, 8 H, $CH_2CH_2CH_2O$), 1.6–1.35 (m, 16 H, CH_2), 1.34 (s, 18 H, CH_3), 0.80 (s, 18H, CH_3). ^{13}C NMR δ: 155.0, 152.5, 152.4, 144.9, and 143.9 (s, Ar CO), 140.0 (s, Ar CNO_2), 135.4 and 133.9 (d, Ar CH), 131.7 (s, Ar CCH_2O), 125.5(3), 125.4(9), 124.4, 120.0 and 114.4 (d, Ar CH), 72.6, 72.2, 71.2, 70.2, 69.6 (t, CH_2O), 34.1 and 33.6 (s, CCH_3), 31.8 and 31.1 (q, CH_3), 31.0, 30.4, 29.5, 29.2, 29.0, 26.2 and 25.9 (t, CH_2). MS (FAB) m/z: 1328 ($M+Na^+$), 1344 ($M+K^+$). IR (cm^{-1}): 1527 (NO_2). Anal. calcd. for $C_{80}H_{108}N_2O_{13}\cdot 0.38H_2O$: C 73.21, H 8.35, N 2.13; found: C 72.92, H 8.35, N 2.06%, Karl-Fisher 0.52% H_2O.

2,2′-[4-[[8-(2-Nitrophenoxy)octyloxy]methyl]-1,2-phenylenedioxy] bis(N,N-dicyclohexylacetamide) (**6**). NaH (0.22 g 80% in oil, 7.3 mmol) was washed twice with petroleum ether under nitrogen. Then THF (50 ml) and DMF (20 ml) were added, followed by **5** (4.25 g, 7.3 mmol)[26]. After deprotonation, **9a** was added and the mixture was stirred under reflux for 16 h. Water and CH_2Cl_2 were added carefully. The organic layer was washed with dilute HCl and water, dried with $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (Al_2O_3, EtOAc/petroleum-ether 1/1) to afford **6** as a viscous yellow oil; yield 1.73 g (2.1 mmol, 29%); n_D^{20} 1.5340. ^{1}H-NMR δ: 7.75 (dd, 1 H, J_o 8.1 Hz, J_m 1.7 Hz, Ar H), 7.5–7.4 (m, 1 H, Ar H), 7.05–6.9 (m, 2 H, Ar H), 6.9–6.75 (m, 3 H, Ar H), 4.59 (s, 4 H, $CH_2C{=}O$), 4.35 (s, 2 H, $ArCH_2O$), 4.04 (t, 2 H, J 6.4 Hz, $ArOCH_2$), 3.6–3.35 (br m, 2H, CHN), 3.39 (t, 2 H, J 6.6 Hz, $ArCH_2OCH_2$), 3.0–2.8 (br m, 2 H, CHN), 2.55–2.3 (broad m, 4 H, CH_2), 1.8–0.9 (br m, 48 H, CH_2). ^{13}C-NMR δ: 166.9 and 166.7 (s, C=O), 152.4 (s, Ar CO), 147.8 and 147.3 (s, Ar $COCH_2C{=}O$), 140.0 (s, Ar CNO_2), 133.9 (d, Ar CH), 132.1 (s, Ar CCH_2O), 125.4, 120.9, 120.0, 114.4, 113.5 and 113.3 (d, Ar CH), 72.6, 70.4, 70.0, 69.6 and 69.5 (t, CH_2O), 57.8 and 56.2 (d, CHNC=O), 31.4, 29.7, 29.3, 29.1, 28.9, 26.5, 26.1, 25.7 and 25.2 (t, CH_2). MS (FAB) m/z: 583.5 [($M+H^+$), calcd]. IR (cm^{-1}): 1645 (C=O), 1524 and 1354 (NO_2).

25,26,27,28-Tetrakis [[(8-(2-nitrophenoxy)octyloxy]carbonylmethoxy]-p-tert-butylcalix[4]arene (**8**). **9c** (6.78 g, 25.38 mmol) in CH_2Cl_2 was added slowly to a solution of **7**[34] (2.43 g, 2.54 mmol) and 1.5 ml triethylamine in CH_2Cl_2 and the mixture was refluxed for 48 h. After cooling to room temperature, the mixture was washed with 5% aqueous $KHCO_3$ and water, and dried over $MgSO_4$. After washing three times with MeOH (stirring, centrifuging and decanting), **8** was obtained as a viscous yellow oil; yield 2.98 g (1.56 mmol, 61%); n_D^{20} 1.5430. ^{1}H-NMR δ: 7.85–7.75 (m, 4 H, Ar H), 7.55–7.4 (m, 4 H, Ar H), 7.1–6.9 (m, 8 H, Ar H), 6.78 (s, 8 H, Ar H), 4.87 (d, 4 H, $J_{ax,eq}$ 12.9 Hz, $ArCH_2Ar$, H_{eq}), 4.82 (s, 8 H, $CH_2C{=}O$), 4.15–4.0 (m, 16 H, CH_2O), 3.20 (d, 4 H, $J_{ax,eq}$ 13.0 Hz, $ArCH_2Ar$, H_{ax}), 1.9–1.75 (m, 8 H, $ArOCH_2CH_2$), 1.75–1.55 (m, 8 H, $CH_2CH_2OC{=}O$), 1.5–1.25 (m, 48 H, CH_2), 1.08 (s, 36 H, CH_3). ^{13}C-NMR δ: 170.6 (s, C=O), 153.1, 152.4, and 145.1 (s), 140.0 (s, Ar CNO_2), 134.0 (d), 133.5 (s), 125.4, 125.3, 120.0 and 114.5 (d, Ar CH), 71.3, 69.5 and 64.5 (t, CH_2O), 33.8 (s, CCH_3), 32.0 (t, CH_2), 31.4 (q, CH_3), 29.5, 29.2, 28.9, 28.6, 25.8 (2x) (t, CH_2). MS-FAB m/z: 1901 ($M+Na^+$, calcd. 1901.4). IR (cm^{-1}): 1757 (C=O), 1526 and 1354 (NO_2).

8-Bromooctyl 2-nitrophenyl ether (**9a**). 2-Nitrophenol (7.0 g, 50.4 mmol), 1,8-dibromooctane (54.4 g, 200 mmol), and K_2CO_3 (10.4 g, 75.3 mmol) were added successively to CH_3CN (400 ml). The mixture was refluxed for 16 h after which the solvent was removed under reduced pressure and CH_2Cl_2 (300 ml) and water (300 ml) were added. The organic layer was washed with 2M aqueous KOH (2×200 ml) and water (2×200 ml). Column chromatography (SiO_2, EtOAc/petroleum-ether 1/5) afforded **9a** as a yellow liquid; yield 12.4 g (75%); b.p. 183–184°C (0.09 mbar); n_D^{20} 1.5400. ^{1}H-NMR δ: 7.78 (dd, 1 H, J_o 8.1 Hz, J_m 1.6 Hz, Ar H), 7.53–7.43 (m, 1 H, Ar H), 7.05–6.95 (m, 2 H, Ar H), 4.07 (t, 2 H, J 6.4 Hz, $ArOCH_2$), 3.39 (t, 2 H, J 6.9 Hz, CH_2Br), 1.95–1.75 (m, 4 H, $BrCH_2CH_2$ and $ArOCH_2CH_2$), 1.55–1.25 (m, 8 H, CH_2). ^{13}C-NMR δ: 152.4 (s, Ar $COCH_2$), 140.0 (s, Ar CNO_2), 134.0, 125.5, 120.0 and 114.4 (d, Ar CH), 69.5 (t, $ArOCH_2$) 34.0, 32.8, 29.0, 28.9, 28.6, 28.0 and 25.7 (t, CH_2). MS (EI) m/z: 329.054 (M^+, calcd. 329.063).

8-Acetoxyoctyl 2-nitrophenyl ether (**9b**). 18-Crown-6 (0.81 g, 3.08 mmol) and KOAc (5.75 g, 58 mmol) were added to MeCN (250 ml). After 15 min stirring at room temperature, **1a** (8.25 g, 25 mmol) was added to the mixture, which was then refluxed for 16 h. After evaporation of the CH_3CN, CH_2Cl_2 (200 ml) was added and the organic layer was washed with water (2×200 ml). Column chromatography (SiO_2, EtOAc/petroleum ether 1/4) afforded **9b** as a yellow liquid; yield 7.04 g (91%); n_D^{20} 1.5094. ^{1}H-NMR δ: 7.74 (d, 1 H, J_o 8.0 Hz, Ar H), 7.55–7.35 (m, 1 H, Ar H), 7.1–6.9 (m, 2 H, Ar H), 4.1–3.95 (m, 4 H, CH_2O), 1.97 (s, 3 H, CH_3), 1.85–1.2 (m, 12 H, CH_2). ^{13}C-NMR δ: 171.2 (s, C=O), 152.4 (s, Ar CO), 140.0 (s, Ar CNO_2), 133.9, 125.5, 120.0 and 114.4 (d, Ar CH), 69.5 (t, $ArOCH_2$), 64.6 (t, $CH_2OC{=}O$), 29.1, 28.9, 28.6, 25.8 and 25.7 (t, CH_2), 21.0 (q, CH_3). MS (EI) m/z 309.162 (M^+; calcd. 309.158). IR (cm^{-1}): 1735 (C=O).

Table III Crystallographic data

Crystal data $C_{80}H_{108}N_2O_{13}$ $M_r = 1305.8$ triclinic $P-1$ $a = 11.681(5)$ Å $b = 12.267(5)$ Å $c = 28.694(6)$ Å $\alpha = 95.44(3)^0$ $\beta = 90.50(3)^0$ $\gamma = 112.44(3)^0$ $V = 3779(5)$ Å^3 $Z = 2$	$D_x = 1.148$ Mg/m^3 Mo-Kα radiation $\lambda = 0.7107$ Å Cell parameters from 25 reflections $\vartheta = 7.0–15^0$ $\mu = 0.717$ cm^{-1} $T = 293(1)$ K
Data Collection Enraf-Nonius CAD4 single-crystal diffractometer $\omega/2\vartheta$ scans 13540 measured reflections 6284 observed reflections $[I > 3.0\delta(I)]$	$\vartheta_{max} = 25.0^0$ $h = -13- > 13$ $k = -14- > 14$ $l = 0- > 34$ 3 standard reflections, frequency 60 min intensity decrease less than 1%
Refinement Refinement on F_0 Final $R = 0.094$ $w\cdot R = 0.095$ $S = 2.84$ 6284 reflections 856 parameters	H atoms treated as riding atoms Calculated weights $w = 1/[\delta^2(F)]$ $(\Delta/\sigma)_{max} = 0.19$ $\Delta\rho_{max} = 0.41$ e Å^3 $\Delta\rho_{min} = -0.24$ e Å^3

8-Hydroxyoctyl 2-nitrophenyl ether (**9c**). To a mixture of THF, MeOH, and water (50 ml each) **9b** (6.8 g, 22 mmol) was added. After 18 h stirring at room temperature the organic solvents were evaporated, CH_2Cl_2 (200 ml) was added and the organic layer washed with water (2×100 ml). Column chromatography (SiO_2, EtOAc/petroleum ether 2/3) afforded **9c** as a yellow liquid; yield 5.53 g (94%); n_D^{20} 1.5256. ^{1}H-NMR δ: 7.73 (dd, 1 H, J_o 8.1 Hz, J_m 1.7 Hz, Ar H), 7.5–7.4 (m, 1 H, Ar H), 7.0–6.85 (m, 2 H, Ar H), 4.02 (t, 2 H, J 6.4 Hz, $ArOCH_2$), 3.56 (t, 2 H, J 6.5 Hz, CH_2OH), 1.85–1.15 (m, 13 H, CH_2 and OH). ^{13}C-NMR δ: 152.5 (s, Ar CO), 140.0 (s, Ar CNO_2), 134.0, 125.5, 120.0 and 114.4 (d, Ar CH), 69.6 (t, $ArOCH_2$), 62.9 (t, CH_2OH), 32.7, 29.2, 29.1, 28.9, 25.7 and 25.6 (t, CH_2). MS (EI) m/z: 267.144 (M^+, calcd. 267.147). IR (cm^{-1}): 3370 (br, OH) (cm^{-1}).

X-ray crystallography

The most important crystallographic data are collected in Table III. Data were collected in the $\omega/2\vartheta$ scan mode [scan width (ω): $1.10+0.34\tan(\vartheta)$], using graphite monochromated Mo-Kα radiation. The intensity data were corrected for Lorentz and polarization effects and for long-time-scale variation. No absorption correction was applied. The structure was solved with MULTAN[36] and refined by full-matrix least-squares. Weights for each reflection in the refinement (on F) were $w = 4\cdot F_0^2/\sigma(F_0^2)$, $\sigma(F_0^2) = \sigma^2(I)+(p\cdot F_0^2)^2$; the value of the instability factor p was determined as 0.04. All calculations were done with SDP[37]. Atomic-scattering factors were taken from *International Tables for X-Ray Crystallography*[38]. Positions and anisotropic thermal parameters of the non-hydrogens were refined. In order to keep the number of variables in the refinement small, the hydrogen atoms were put in calculated positions and were not refined. As can be seen from the figure the terminal C atoms of the *tert*-butyl groups show rather large anisotropy in the thermal motion[39].

Materials

Support: the porous polymeric support Accurel® 1E-PP was obtained from Enka Membrana (thickness $d_m = 100\ \mu m$, porosity $\Theta = 64\%$, tortuosity $\tau = 2.1$)[40].
Membrane solvent: 2-nitrophenyl n-octyl ether (NPOE, $99^+\%$) was obtained from Fluka.
Salts: potassium perchlorate (puriss., Janssen Chimica) and sodium perchlorate (anhydrous, p.a., Janssen Chimica) were used as received.

Rheological measurements

The viscosity of carrier solutions was measured on a thermostated cone-on-plate viscosity meter (Bohlin) with different torque elements. The kinematic viscosity of NPOE was measured as a function of temperature with an Ubbelhode viscosity meter. Temperature-dependent density measurements were performed with a Paar DMA58 density meter.

Transport measurements

Transport experiments were carried out in a permeation cell consisting of two identical cylindrical compartments (half-cell volume: 50 ml; effective membrane area: 13.8 cm^2). Details of this cell are described elsewhere[3]. The support consisted of a thin porous polypropylene film (Accurel®) immobilizing the solution of carrier in NPOE. Aqueous potassium and/or sodium perchlorate solutions were used as the source phase and doubly distilled and de-ionized water as the receiving phase. The measurements were usually performed at a constant temperature of 25°C and at least in duplicate. The transported perchlorate salts were determined by monitoring the conductivity of the receiving phase as a function of time (Philips PW 9527 conductivity meter and a Philips PW9512/61 electrode with a cell constant of 0.76 cm^{-1}) in case of single cation transport and by atomic absorption measurements of samples taken from the receiving phase in competitive transport. In case of single cation transport at elevated temperature, the source phase temperature indicated by a thermometer was entered into the conductivity meter of which the temperature coefficient was set at 0.021K^{-1}[28]. The standard deviation in the transport measurements is about 15%. Salt activities were calculated according to a two-parameter approximation of the Debije–Hückel theory[41].

Appendix 1

According to the model in which it is assumed that only free ions are present in the membrane and the cation associates with the carrier in a 1/1 complex, the anion (X^-) concentration in the membrane is equal to the complex concentration $[LM^+]_{ms}$. Furthermore, the concentration of free carrier can be expressed as $[L]_{ms} = L_0 - [LM^+]_{ms}$. Insertion of K_{ex} in the flux equation for diffusion-limited initial transport $[J = (D_m/d_m)\cdot[LM^+]_{ms}]$ yields Eqn. A1 ($K_{ex}\cdot a_s{}^2 \equiv A$).

$$M_s^+ + X_s^- + L_{ms} \leftrightarrows LM_{ms}^+ + X_{ms}^-$$

$$K_{ex} = \frac{[LM^+]_{ms}^2}{[L]_{ms}\cdot a_s^2} \quad 1/1 \text{ complex free ions}$$

$$J = \frac{D_m}{2\cdot d_m}\cdot\left\{-A + \sqrt{\left(A^2 + 4\cdot A\cdot L_0\right)}\right\} \qquad (A1)$$

If only ion pairs are present in the membrane, the flux is described by Eqn. A2, in which $[L]_{ms}$ has been replaced by $L_0 - [LM^+]_{ms}$.

$$M_s^+ + X_s^- + L_{ms} \leftrightarrows LMX_{ms}$$

$$K_{ex} = \frac{[LMX]_{ms}}{[L]_{ms}\cdot a_s^2} \quad 1/1 \text{ complex ion pairs}$$

$$J = \frac{D_m}{d_m}\cdot\frac{A}{1+A}\cdot L_0 \qquad (A2)$$

When according to the free ion model, a 2/1 carrier/cation complex is formed inside the membrane, the flux is described by Eqn. A3. In this case the anion and complex concentration in the membrane are equal again and $[L]_{ms} = L_0 - 2\cdot[L_2M^+]_{ms}$.

$$M_s^+ + X_s^- + 2\ L_{ms} \leftrightarrows L_2M_{ms}^+ + X_{ms}^-$$

$$K_{ex} = \frac{[L_2M^+]_m^2}{[L]_{ms}{}^2\cdot a_s^2} \quad 2/1 \text{ complex free ions}$$

$$J = \frac{D_m}{d_m}\cdot\frac{\sqrt{A}}{1+2\cdot\sqrt{A}}\cdot L_0 \qquad (A3)$$

Acknowledgement

The financial support from the Dutch Technology Foundation (STW), Technical Science Branch of the Dutch Organization for Advanced and Pure Research (NWO) is gratefully acknowledged. We thank Dr. *D. van der Ende* for assistance with rheological measurements.

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