Carrier-mediated Transport through Liquid Membranes

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1 Introduction

The separation of molecules by membranes is not only a very important event in biological systems, it has also important large-scale industrial applications, and therefore, it is of a broad scientific interest.[1] An efficient separation process combines a high transport rate with a high selectivity. In a steady-state permeation experiment, the flux of a species S through a membrane of thickness l, is related to the concentration gradient (Δc_s) through Fick's first law:

$$J_s = (D_s/l)\Delta c_s \qquad (1)$$

High fluxes can only be obtained when a large chemical potential is maintained over a thin membrane in which the diffusivity D_s of the species is high. In this review we describe our systematic approach to such systems, which has led us from bulk liquid membranes to very thin supported monolayers.

Four different types of liquid membranes can be distinguished: bulk, supported, emulsion, and polymer composite membranes. Bulk liquid membranes (BLM) consist of a source and receiving phase separated by an immiscible membrane phase. In most cases, the source and receiving phase are aqueous and the membrane organic, but the reverse configuration can also be used.[2] The thickness of the diffusion layer l is of the order of the Nernst layer,[3] which is dependent on the experimental conditions, but is typically in the order of 50—500 μm.

Supported liquid membranes (SLM) have essentially the same configuration as BLMs, but now the organic phase is contained in the pores of a macroporous (pore size 0.1—1.0 μm) polymer sheet, of which the thickness is in the range of 10—100 μm. For practical applications, the SLM-concept has been developed into practical hollow fibre modules.[4] Polymer composite membranes are another SLM-variant: thin (10—50 μm) films of a polymer-supported liquid phase can be obtained by solvent casting of mixtures of polymer and organic phase.[5]

A further reduction in membrane thickness can be accomplished in emulsion liquid membranes (ELM). With the aid of a surfactant, relatively stable water-(receiving phase)-in-oil(membrane phase)-in-water(source phase) emulsions can be created.[6] On average, ELMs have a thinner membrane separating source and receiving phase, although membrane thickness changes with the amount of the material transported.[7] Still thinner (5—10 nm) are membranes composed of bilayers (vesicles, liposomes).[8] In many cases, however, the thickness of the separating layer has become so small that diffusion is no longer rate-limiting.

In the approach pictured above, transport rates are increased by going to ever thinner membranes. The transport selectivity, however, generally does not change. In order to achieve high selectivity, a substrate-specific receptor must be present in the membrane phase, in which it can act as a carrier between source and receiving phase. Whereas in biological membranes this task is fulfilled by ionophores such as valinomycin (1), in artificial membranes we rely on the realm of synthetic macrocyclic receptors developed during the past two decades.[9]

## 2 Bulk Liquid Membranes

### 2.1 Transport Model in Bulk Liquid Membranes

Ever since the first transport experiments, theory and practice have developed side-by-side. A theoretical model for transport in a simple BLM system was formulated by Reusch and Cussler[10] as early as 1973, and still serves as the basis of more

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(1)
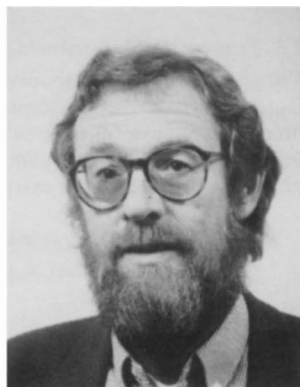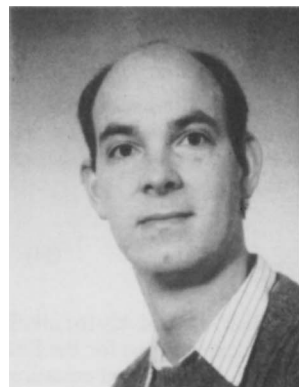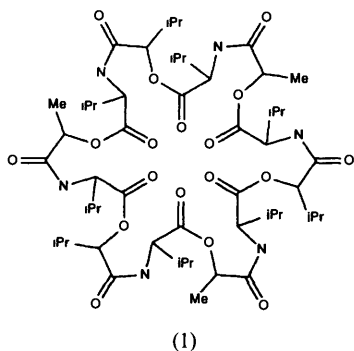
complicated systems. The concentration profile in a BLM consisting of an organic phase containing a carrier L, separating two aqueous phases containing the substrate S, is schematically shown in Figure 1.
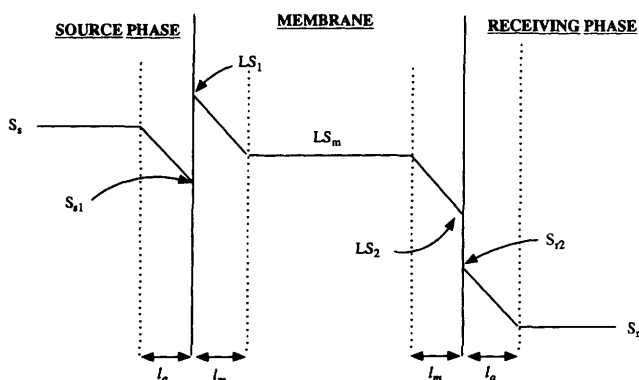

Figure 1 Concentration profile in a BLM.

The transport from the aqueous source phase through the organic membrane into the aqueous receiving phase can be dissected into the following discrete steps:
(i) diffusion through the aqueous boundary layer of the source phase:

$$J_A = D_A([S_S] - [S_{S1}])/l_a \qquad (2)$$

(ii) uptake at the source/organic interface (3)
(iii) diffusion through the stagnant membrane layer at the source-side of the membrane:

$$J_B = D_B([L_{S1}] - [L_{Sm}])/l_m \qquad (4)$$

(iv) transport by convection through the stirred region of the membrane phase (5)
(v) diffusion through the stagnant membrane layer at the receiving side of the membrane:

$$J_{B'} = D_B([L_{Sm}] - [L_{S2}])/l_m \qquad (6)$$

(vi) release at the organic/receiving phase interface (7)
(vii) diffusion through the aqueous boundary layer of the receiving phase:

$$J_{A'} = D_A([S_{R2}] - [S_R])/l_a \qquad (8)$$

Once the extraction reactions 3 and 7 have been defined, the system can be solved assuming: (i) steady-state conditions (then all fluxes are necessarily the same), and (ii) thermodynamic equilibrium at the uptake and release interfaces.

2.2 Basic Features of Carrier-mediated Transport
In the most simple case, there is no ligand present in the organic

membrane, and the species to be transported is simply distributed over the phases. The partition coefficient K_p is defined as:

$$S_a \rightleftarrows S_m$$
$$K_p = [S_m]/[S_a] \qquad (9)$$

This leads to the following relation for the flux J, expressed in the form chemical-potential/flux = resistance:

$$([S_s] - [S_r])/J = 2l_a/D_a + 2l_m/D_m K_p \qquad (10)$$

For particles of the same size, transport rates depend on the partition coefficient K_p only, and consequently, the transport selectivity arises from differences in solubility (ratios of K_p's), and hence, transport selectivity only depends on the solvents used.

When the membrane contains a carrier that is able to form a complex with the substrate in the organic phase:

$$S_m + L_m \rightleftarrows SL_m$$
$$K_a = [SL_m]/[S_m][L_m] \qquad (11)$$

the extraction steps 3 and 7 discussed above become:

$$S_a + L_m \rightleftarrows SL_m$$
$$K_p K_a = K_{ex} = [SL_m]/[S_a][L_m] \qquad (12)$$

In combination with the diffusive processes, this leads to the following equation for the flux:

$$([S_s] - [S_r])/J = 2l_a/D_a + 2l_m/D_B(K_p + F) \qquad (13)$$

in which

$$F = K_{ex}L_0/\{(1 + K_{ex}[S_s])(1 + K_{ex}[S_r])\}$$

The effect of carrier addition is contained in the term F, and since $F > 0$, the presence of the carrier lowers the resistance of the membrane. Behr et al.[11] used an equation similar to 13 to illustrate the most important basic features of carrier-mediated transport:
(i) the flux is proportional to the carrier concentration
(ii) the initial (when $S_r = 0$) flux shows typical saturation behaviour, J being proportional to S_s for low substrate concentrations, and J being independent of S_s for high substrate concentration
(iii) the flux J versus $\log(K_{ex})$ shows a maximum, the position depending on S_S and S_R. A too strongly complexing carrier becomes fully loaded with substrate even for very low substrate concentrations, and therefore does not produce a gradient over the membrane. This leads to the conclusion, that the best carrier is not necessarily the one with the strongest complexing behaviour. Apart from this thermodynamic reason, by which strong complexing agents retain the metal ion in the membrane, there may also be a kinetic reason: strong complexing agents frequently show a slow rate of decomplexation.

2.3 Transport of Ion-pairs in Bulk Liquid Membranes
The choice of membrane solvent in BLMs is often governed by factors such as low viscosity and low water solubility. In practice, chloroform and dichloromethane are used most frequently, and as a consequence of their low dielectric constant, univalent cations will be extracted as ion-pairs:

$$M_a^+ + X_a^- + L_m \rightleftarrows MLX_m$$
$$K_a K_p = K_{ex} = [MLX_m]/[M_a^+][X_a^-][L_m] \qquad (14)$$
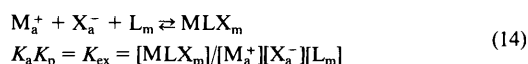
Izatt et al. have studied this type of BLM extensively for alkali metal ions,[12] and have derived lengthy expressions for the flux for single and multiple-cation transport. A simplified equation has been used by us[3] and others,[11] by taking the experimental

finding that the concentration drop over the aqueous boundary layers is small compared to the drop over the organic boundary layers. This leads to a simple expression for the flux J:

$$J = (D_B/2l_m)K_{ex}L_0\{[S_s]^2/(1 + K_{ex}[S_s]^2\} - \{[S_r]^2/(1 + K_{ex}[S_r]^2\}$$
(15)

The features of ion-pair transport are essentially the same as for neutral compounds: the flux J is proportional to the carrier concentration, it shows saturation behaviour with respect to aqueous substrate concentration, and an optimum in the relation of J and K_{ex} when $S_r > 0$. All these relations have been experimentally verified.[13]

The effect of carrier structure on the flux, is contained in the complexation constant K_a. Although this parameter is known for many receptor/substrate combinations in solvents such as methanol, they are frequently unknown in the solvent system used for transport. This problem can be circumvented by assuming that $(K_a)_{solvent}$ and $(K_a)_{MeOH}$ are linearly related, in which case equation 15 can be rewritten as (initial transport, $S_r = 0$):

$$L_0/J = 2l_m/D + 2l_m/DK_aK_p[S_s]^2$$
(16)

Although the thermodynamic basis for this assumption is not always valid,[14] the relationship holds in many cases. For example, Figure 2 shows the relation for the flux of guanidinium thiocyanate as a function of $(K_a)_{MeOH}$ through a chloroform BLM containing various benzo-(2) and dibenzo-(3) crown ethers as carriers.[3]
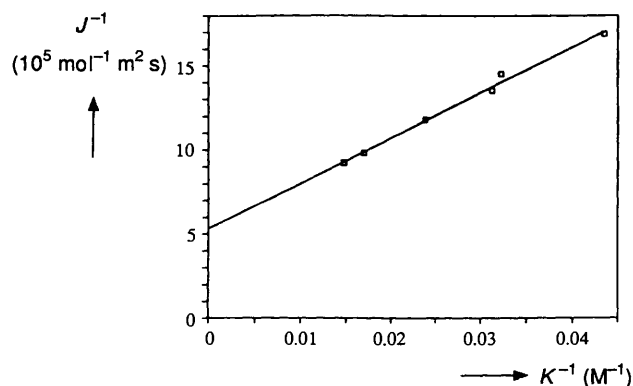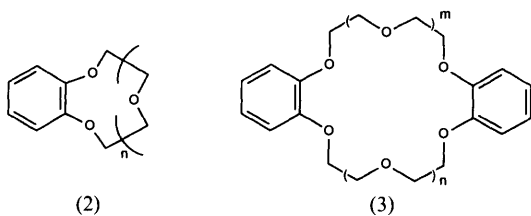

Figure 2 Relation between the flux J through a chloroform liquid membrane and the association constants K in methanol for guanidinium complexes of carriers (2) ($n = 7,8,9$) and (3) ($n = 10,11,12$).

(2)   (3)

The agreement is excellent in this case; from the intercept (l_m/D) and a literature value for D a thickness of 38 μm for the stagnant chloroform layer can be obtained.

When the source phase contains a mixture of two cations M_1^+ and M_2^+, the individual initial ($S_r = 0$) fluxes J_1 and J_2 can also be related to the fundamental parameters:

$$J_1/J_2 = (D_1/D_2)(K_{ex,1}/K_{ex,2})([M_1]/[M_2])$$
(17)

Since the diffusion coefficients D_1 and D_2 are very similar, the selectivity is determined by the ratio of the extraction constants. Indeed, there is abundant proof for this statement in the litera-

ture.[15] We also found a good correlation for the selectivity of valinomycin (1) and crown ethers (7) and (8) in the competitive transport of guanidinium and imidazolidinium thiocyanate[16] through a chloroform bulk liquid membrane.

3 Supported Liquid Membranes

3.1 Stability of Supported Liquid Membranes

Supported liquid membranes consist of an organic carrier solution immobilized in a porous polymer sheet, separating the aqueous source and receiving phases (Figure 3). The support is often a hydrophobic polymer such as polyethylene, polypropylene, polytetrafluoroethylene, or polysulfone. For fast transport, the exchanging surface between source and membrane should be large, and therefore, a thin film with high porosity is attractive.[17]
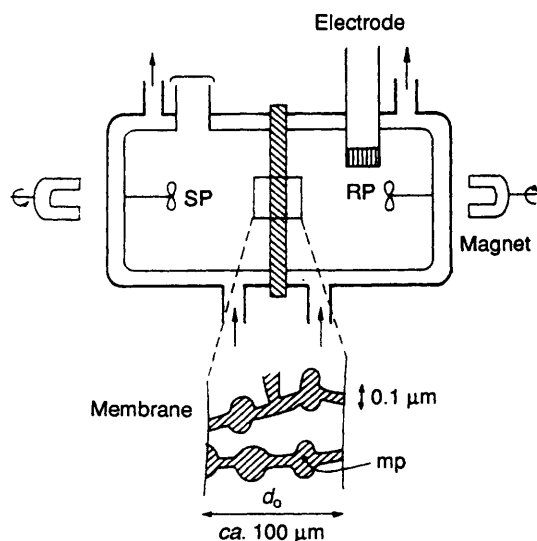

Figure 3 Supported liquid membrane.
(Reproduced by permission from *Recl. Trav. Chim. Pas-Bas*, 1993, **6**, 317.)

The small membrane volume compared to the large exchanging interface is an important advantage of SLMs over BLMs, since much less of the more expensive carrier component is needed. However, at the same time precautions have to be taken to ensure that both the solvent and the carrier are retained in the polymer sheet.

Several factors come into play in the loss of solvent: solubility in water, solubility of water in the solvent, volatility, interfacial tension, ability to form emulsions in the aqueous phase, and the pore size of the support.[18] Polypropylene membranes Celgard® and Accurel®, in combination with solvents such as o-dichlorobenzene, phenylcyclohexane, or o-nitrophenyl octyl ether (NPOE), give SLMs that are stable under most laboratory conditions. For practical purposes however, the stability is still unsatisfactory.

The loss of carrier is related to the partition coefficient (P) of the carrier itself:

$$L_a \rightleftarrows L_m$$

The partition coefficients can either be determined experimentally, or be calculated using an empirical relationship based on the group additivity approach introduced by Rekker:[19]

$$\log(P) = \sum N.f + p$$
(18)

in which f is the 'hydrophobic fragmental constant', N the number of fragments, and p the 'proximity effect', which accounts for neighbouring group interactions. For various fragments, f-values are known for the water/1-octanol system.

In the same solvent system, we have determined the partition coefficients for the crown ethers (2) and (3) According to equation 18, the fragmental constant for the oxyethylene fragment is obtained from a plot of $\log(P)_{oct}$ against N The slopes of the relation for benzo and dibenzo-crown ethers are equal (Figure 4), and give a f-value of $-0\ 17$ for the $-OCH_2CH_2O-$ unit Using this value, partition coefficients for a large number of carriers can be calculated [20] These values can be converted into the NPOE/water system frequently used in SLMs by the empirical relation [20][21]

$$\log(P)_{NPOE} = 0\ 84\ \log(P)_{oct} + 0\ 66 \tag{19}$$

It can be calculated that in order to retain the carrier in the NPOE layer, $\log(P)_{NPOE}$ values should exceed 5, and hence $\log(P)_{oct} > 5\ 2$ It is clear from Figure 4 that the hydrophobicity of all common crown ethers is too low Transport studies with these carriers that do not explicitly take into account the differences in hydrophobicity are unlikely to yield reliable values for the extraction constant and diffusion coefficient For example, transport of guanidinium thiocyanate through a NPOE/ Accurel[k]-supported liquid membrane with benzo and dibenzo-crown ethers, (2) and (3), was more affected by differences in lipophilicity than by differences in complexing ability [21]
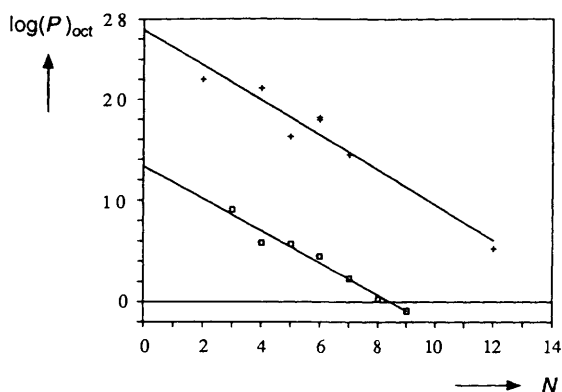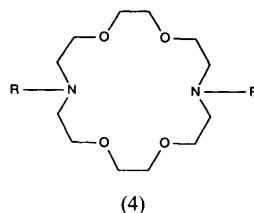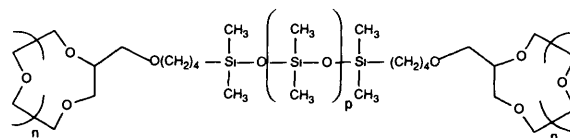

Figure 4 Experimental partition coefficient, $\log(P)_{NPOE}$ vs the number of oxyethylene units for the benzo [(2), $N = n$, □] and dibenzo [(3), $N = m + n$, +] crown ethers

Obviously, in order to create a stable SLM system, the lipophilicity of the carriers needs to be improved We have used the following three approaches (i) attachment of long alkyl chains, (ii) attaching the carrier onto a polymer, (iii) attachment of one or more NPOE-moieties The first approach is illustrated by a series of diaza-18-crown-6 carriers, (4) The unsubstituted carrier has $\log(P)_{NPOE} = -0\ 15$, and hence leaks from the membrane extensively Providing the carrier with long alkyl chains improves the lipophilicity into the desired range, and consequently, the membranes are stable[22] (Table 1)

In the second approach, a hydrophilic crown ether such as benzo-18-crown-6 [(2),$n = 4$] was coupled to the terminal positions of a polysiloxane backbone to give carriers such as (5)

Table 1 Partition coefficients of some selected carriers for the system NPOE/water

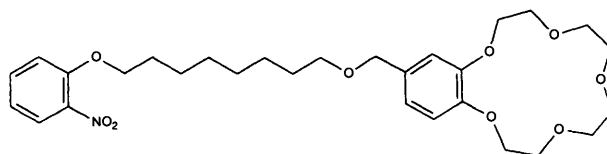| Carrier	$\log(P)_{NPOE}$	Carrier	$\log(P)_{NPOE}$
(2) $n = 3$	0 91	(5) $p = 6, n = 4$	4 7
$n = 4$	0 58	$p = 46, n = 2$	27
(3) $n = 1, m = 1$	3 3	(7)	7 9
(4) R = H	$-0\ 15$	(8)	13
R = C_5H_{11}	4 05		
R = $C_{10}H_{21}$	8 25		
R = $C_{14}H_{29}$	11 6		

(4)

(5)

In agreement with the very large calculated $\log(P)$ values (Table 1), membranes with these carriers retain their properties even after contact with large volumes of water [23]

Although the two approaches discussed above lead to carriers with the desired hydrophobicity, they still are not perfect Long-alkyl and polymer-modified carriers generally do not show high solubility in NPOE (the solubility of didecyl-diaza-18-crown-6 is 0 35 M at 25 °C) Furthermore, polymer-bound carriers show reduced rates of diffusion These drawbacks can be avoided by providing the carrier with one or more 'solvent-like' substituents For example, NPOE-modified carriers such as (6) are completely miscible with NPOE, and allow very stable membranes with high permeability to be constructed [24]

(6)

3.2 Transport Model for Supported Liquid Membranes

The mechanism of ion transport through a liquid contained in the pores of a polymer sheet is not fundamentally different from transport through a bulk liquid as depicted in Figure 1 the stirred part of the membrane phase is now lacking, and the stagnant layers form the whole polymer sheet Therefore, as a first approximation, the flux equations for SLMs can be obtained by replacing the term $2l_m$ in BLMs by d, the thickness of the polymer sheet

However, corrections have to be made for the morphological characteristics of the sheet The apparent diffusion, D_{app}, coefficient is related to the true coefficient of diffusion, D_m, through

$$D_{app} = D_m(\epsilon/\tau) \tag{20}$$

ϵ is the membrane porosity, and τ the tortuosity (which is related to β, the tortuosity factor defined as the average pore length/ sheet thickness) Values of ϵ and τ are available for commonly used macroporous membranes such as Celgard[R] and Accurel[R]

It is customary in literature to assume that $D_m = D_0$, D_0 being the diffusion coefficient of the species in bulk solution By doing so, we are in the comfortable position to estimate D_m by empirical methods such as the Stokes–Einstein relation

$$D_0 = D_m = kT/(6\pi\eta r) \tag{21}$$

η being the viscosity of the solvent, and r the radius of the solute Alerted by the fact that diffusion in confined geometries can be much slower than in bulk solution,[25] we have compared diffusion rates in bulk NPOE and in NPOE confined in the pores of

Accurel® (pore diameter 0 1 μm) and in Celgard® (pore diameter 0 04 μm) using pulsed-field-gradient NMR [26] It turned out that the diffusion constant in Accurel® was reduced by a factor of 2, and in Celgard® even more, compared to bulk NPOE Therefore, diffusion constants obtained from transport experiments, even when corrected for porosity and tortuosity, remain dependent on the morphology of the membrane

3.3 Transport of Free Ions through Supported Liquid Membranes

The volatile solvents mostly used in BLMs (chlorinated hydrocarbons) cannot be used in SLMs since they are washed out of the support [27] Therefore, non-volatile solvents of low dielectric constant such as hexylbenzene have frequently been used In this type of solvent, salts are transported as ion-pairs,[27] and fluxes are given by an expression similar to equation 15 However, polar lipophilic solvents such as NPOE (ϵ_r = 24) can also be retained in polypropylene membranes A mechanistic study of potassium perchlorate transport through NPOE contained in an Accurel® membrane, mediated by dibenzo-18-crown-6 [(3),$m = n$ = 1], showed that the flux could not be described by equation 15 for the transport of ion-pairs [28] Instead, a model assuming fully separated ions in the membrane phase was found to predict the observed fluxes quantitatively

$$(K^+)_{aq} + (ClO_4^-)_{aq} + L_m \rightleftarrows (KL^+)_m + (ClO_4^-)_m$$
$$J = D_{app}/2d \; [-1 + \sqrt{(1 + 4L_o/K_{ex}S^2)}] \qquad (22)$$

This model was experimentally verified for the transport of alkali cations[29 30] and guanidinium cation[30] using a wide variety of carriers the natural potassium ionophore valinomycin (1), crown ethers (3), calixcrowns (7), and calix[6]arenes (8)

(7)   (8)
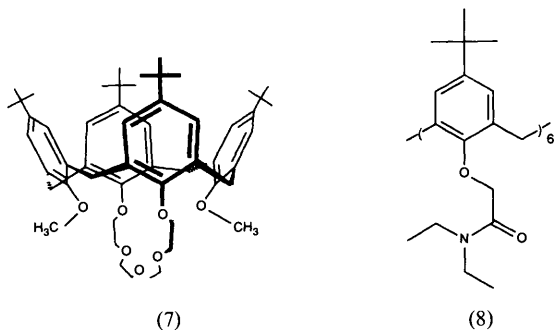
The basic features of free-ion transport through SLMs are illustrated in Figures 5 and 6 The transport of KClO₄ and NaClO₄ by the calix[4]crown-5 (7) is shown in Figure 5 as a function of the cation concentration in the aqueous phase The transport rate is first order in cation only at very low concentrations, at high concentration, typical saturation behaviour is observed The dependence of the flux on the carrier concentration is linear under conditions of full saturation at the source interface (high aqueous salt concentration and/or strong complexing behaviour), but the order in carrier is less than unity for weakly complexing carriers (Figure 6) By simple curve-fitting procedures applied to the relations as shown in Figures 5 and 6, K_{ex} and D_{app} can be obtained (Table 2) The values obtained for K_{ex} in single-ion transport experiments can subsequently be used to predict the selectivity in competitive transport experiments The agreement between theory (with equation 17) and experiment is excellent, both for potassium/sodium as well as for combinations with guanidinium cations As for BLMs, we found that transport selectivity in SLMs is determined by extraction

3.4 Uphill Transport of Cations

From Fick's law (equation 1) it follows that cation transport will cease when the concentration of the ion in source and receiving
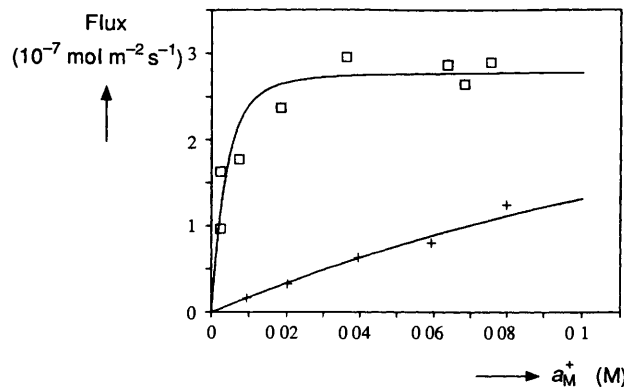
Figure 5 KClO₄ (□) and NaClO₄ (+) flux as a function of the salt activity in the source phase for calixcrown (7), [carrier]$_m^o$ = 10^{-2}M, T = 298 K Solid lines are calculated according to equation 22
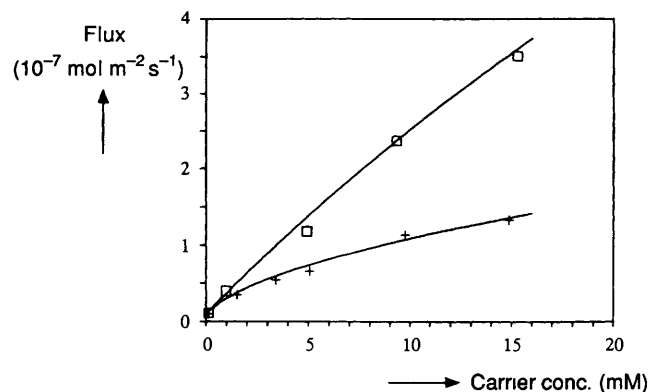
Figure 6 KClO₄ (□) and NaClO₄ (+) flux as a function of the calix crown (7) concentration in NPOE, [alkali perchlorate] = 0 1 M, T = 298 K

phase is the same Obviously, in practice one would like to (re)move one component completely from the source phase In order to do so, we need an extra driving force to transport the cation against its concentration gradient According to Figure 1, the gradient over the membrane, Δc_S, is given by [LS₁] − [LS₂], and the problem becomes how to keep this term positive, even in situations where the concentration in the receiving phase, S_r is higher than in the source phase, S_s

The complex concentration at the source interface, LS_1, can be manipulated by the addition to the source phase of a salt having a common anion and a cation which is not extracted (e g Li⁺) The common-anion effect is accounted for through equation 22, and it can be shown that at equilibrium, the concentrations in source, S_s, and receiving, S_r, phase are related to the lithium concentration, A_0

Table 2 Calculated diffusion coefficient, D_m, and extraction constant, K_{ex}, for carriers in NPOE/Accurel® at 298 K

Carrier		D_m (10^{-11} m² s⁻¹)	K_{ex} (M⁻¹)	K⁺/Na⁺ selectivity
(3) $m = n$ = 1	K⁺	2	1 3	
	Na⁺	2	1 9 × 10⁻²	66
(7)	K⁺	0 67	2 3 × 10³	
	Na⁺	0 67	4 5 × 10⁻¹	5100
(8)	K⁺	0 28	5 6 × 10²	
	Na⁺	0 28	4 2 × 10⁻¹	1300
(9)	Na⁺	1 6	2 1 × 10⁻¹	
	K⁺	1 3	3 2 × 10⁻¹	
	Gu⁺	1 0	2 9	
(10)	urea	0 97	2 0 × 10¹	
(11)	urea	0 61	2 2 × 10¹	

$$S_r/S_s = 1 + A_o/S_o \qquad (23)$$

In full agreement with these predictions, we were able to extract virtually all potassium from a mixture of potassium and sodium perchlorate to which an excess of lithium perchlorate was added.[29]

The complex concentration at the receiving interface can be kept very low by applying a favourable exchange reaction with a different cation, for example a proton:

$$[LS_1]_m + H^+ \rightleftharpoons [LH^+]_m + [S]_r$$
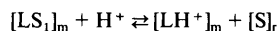
The counter-transport of protons, from the acidic receiving phase to the basic source phase, is now the driving force for cation transport. Using this mechanism, potassium perchlorate can be transported uphill by using diaza-crown-6 (4) derivatives.[22]

3.5 Transport of Urea through SLMs

Selective removal of urea from blood is of great importance in medicine. Very recently, lipophilic macrocyclic receptors for urea have become available in our group. Metallo-macrocycles (9) and (10) complex urea by coordination of the urea carbonyl to UO_2. Dissolved in NPOE, these carriers transport urea through an Accurel® membrane.[31] Transport rates can be described by the SLM equivalent of equation 13 (neglecting the aqueous boundary layers, and putting $2l_m = d$). Figure 7 shows the predicted first order dependence on the carrier concentration for binaphthyl carrier (9). Curve-fitting of experiments with varying urea concentration in the aqueous phase[32] yields the diffusion coefficient D_m and the extraction constant K_{ex} (Table 2). The transport selectivity for a mixture of urea/N-methylurea was 8.2, close to the selectivity observed in extraction experiments ($viz.$, 8.7). In competition with K^+, urea was extracted exclusively. Several polyazareceptors were found to transport urea as well, albeit slightly less efficiently.[33]
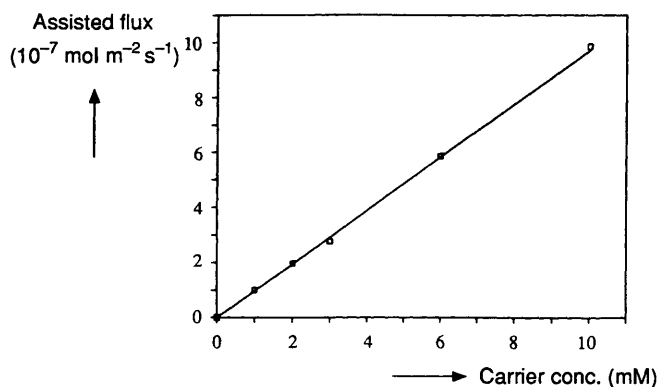
Figure 7 Dependence of urea flux on the concentration of carrier (9) through a NPOE/Accurel® SLM.

4 Supported Monolayers

With the possible exception of certain calixarenes,[24] the membrane transport discussed above is limited by diffusion. According to Fick's law, the flux is inversely proportional to the thickness of the membrane. The desire to make membranes as thin as possible has guided us to the use of monolayers. As such, these layers are mechanically too weak to be used as stable membranes, hence they are supported by a cation-transparent Nafion® film. Nafion® (11) is a perfluorinated polymer containing sulfonic acid groups, many of which occupy the surface when a Nafion film is in contact with water. We envisaged the use of these surface sulfonate groups to bind alkyltriphenylphosphonium amphiphiles (12) via an ion-exchange process.

The conductivity over the Nafion® membrane decreased
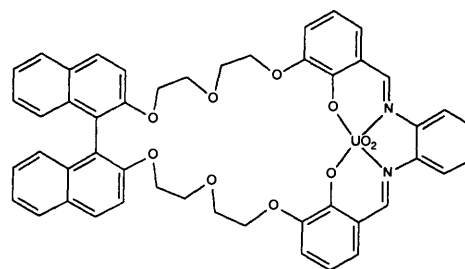
(9)
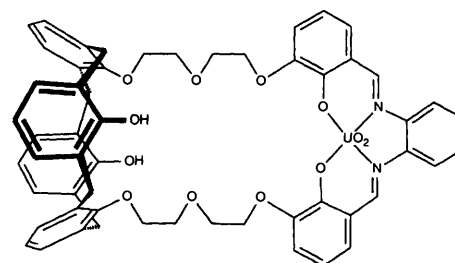
(10)

dramatically by the presence of 25 mM of amphiphiles (Figure 8).[34] Subsequent analysis of the adsorbed layer by UV-spectroscopy, attenuated total reflection IR, XPS, and SIMS, has led us to conclude that the amphiphile is indeed ionically linked to the membrane, to form an incomplete monolayer, most of which is located at or very near to the surface of the membrane. The next step will be to equip these amphiphiles with macrocyclic carriers to obtain a stable and thin membrane.
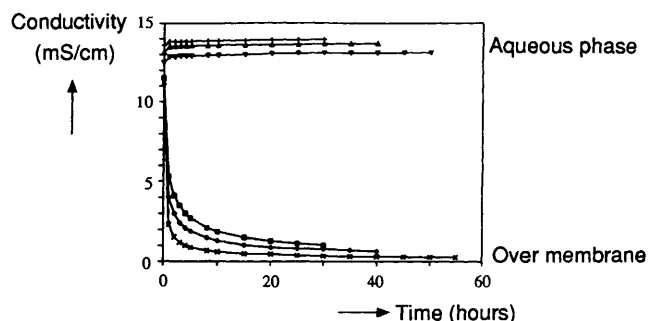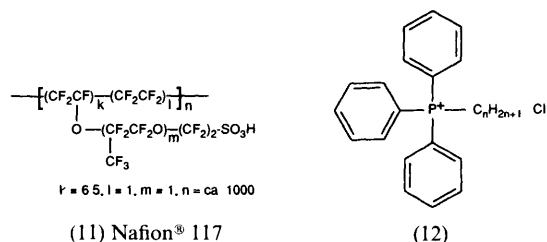
Figure 8 Conductivity experiments of the adsorption of n-alkyltriphenylphosphonium amphiphiles (12) (aqueous solution of 25 mM of amphiphile and 0.1 M KCl as electrolyte) on a Nafion® 117 (11) membrane at 298 K. (12) $n = 8 + $, □; $n = 10$ △, ◇; $n = 16$ ▽, ×.

$l = 6 5. l = 1. m = 1. n = ca\ 1000$

(11) Nafion® 117

(12)

5 Conclusions

The (neutral) carrier-mediated transport of alkali cations and neutral species through bulk liquid membranes is well-understood on the basis of a model in which exchange processes at the interfaces are fast, and diffusion through stagnant solvent layers is rate-limiting. This model predicts that transport selectivity is based on differences in extraction. Supported liquid membranes have a better chance of being applied, but the concurrent

requirements for fast and selective transport as well as a good membrane stability, necessitate a careful choice of carrier/solvent/support combination Studies on these systems have revealed that transport through porous polymer membranes is still often diffusion-controlled, but the specific morphology of the membrane affects the properties of the supported liquid as well In order to increase transport rates still further, very thin membranes are needed This will take us into the area of kinetic rather than diffusion control

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