Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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E. G. Reichwein-buitenhuis[a]; D. N. Reinhoudt[a]; F. De Jong[a]
[a] Laboratory of Organic Chemistry, University of Twente, The Netherlands

To cite this Article Reichwein-buitenhuis, E. G. , Reinhoudt, D. N. and De Jong, F.(1995) 'Polysiloxane coupled crown ethers as carrier in supported liquid membranes', Supramolecular Chemistry, 5: 1, 71 — 82
To link to this Article: DOI: 10.1080/10610279508029889
URL: http://dx.doi.org/10.1080/10610279508029889

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 71–82
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Polysiloxane coupled crown ethers as carrier in supported liquid membranes

E. G. REICHWEIN-BUITENHUIS, D. N. REINHOUDT and F. DE JONG*

Laboratory of Organic Chemistry, University of Twente, 7500 AE Enschede, The Netherlands

(Received August 5, 1994)

Polysiloxanes bearing benzocrown-5 moieties have been synthesized and used as carriers for K^+ and Na^+ in supported liquid membranes. Although their lipophilicity is so high that leaching from the membrane is completely suppressed, their transport efficiency and selectivity can no longer be explained by a simple 1:1 crown:cation model. A more extensive multi-site model was developed that also takes into account cooperative and repulsive effects between adjacent binding sites. The transport properties were markedly influenced by the formation of 2:1 crown:K^+ complexes. No evidence was found for repulsive interactions.

INTRODUCTION

Liquid membranes are often used to study the complexation and transport properties of carrier molecules. In a supported liquid membrane a carrier solution is immobilized in a thin porous support separating two aqueous phases. It has the practical advantage over a bulk liquid membrane that it requires smaller quantities of carrier and has a relatively large exchanging area where uptake and release of compounds can take place. But because the volume of the membrane phase is so much smaller than that of the aqueous phases, the carrier has to be very lipophilic in order to prevent partitioning to the aqueous phases.

Although crown ethers are very efficient carriers for cations, especially alkali metal ions, they are usually not sufficiently lipophilic. Lipophilicity can be improved by modification with alkyl or aryl groups[1,2]. Even more lipophilic carriers are obtained by attaching a crown ether to a polysiloxane backbone[3]. Polysiloxanes are attractive because they are extremely hydrophobic, can be simply functionalized and do not transport salts when not attached to a receptor.

Several groups have synthesized polysiloxanes functionalized with crown ethers. Bradshaw et al.[4] used these polymers as stationary phase in columns for gas chromatography. Wen et al.[5] prepared a number of benzo-15-crown-5 containing thermotropic liquid crystalline side-chain polysiloxanes, as did Percec *et al*[6-8]. England *et al.* attached crown ethers bearing terminal alkene groups to polysiloxanes and used them to separate norcodeine from codeine in an extraction process[9-11]. The same polymers were used to transport primary and secondary amines through a supported liquid membrane[12,13]. In all of these studies the hydrophobic nature of the polysiloxanes was favorably exploited, but the basic question whether or not the binding sites of these receptors can still be regarded as independent has not been addressed.

The purpose of our investigations was to prepare very lipophilic carriers that do not leach from a supported liquid membrane and which allow a study of the cooperative effects of a multi-site carrier on the rate and selectivity of cation transport. To this end polysiloxanes were modified with benzo-15-crown-5 ethers and the influence of site density (the number of SiO monomeric units with a pendant benzo-15-crown-5 moiety per total number of SiO monomers) on the transport of $KClO_4$ through a supported liquid membrane was investigated. Also the K^+/Na^+ transport selectivity of the various carriers was determined. A transport model for multi-receptor site carriers was developed and used to evaluate the experimental results.

RESULTS AND DISCUSSION

Synthesis

The starting polymers for the synthesis of polysiloxanes functionalized along the backbone were commercially available random copolymers of dimethylmethylhydrosiloxane and methylhydrosiloxane. Their molecular weights varied from 900-1000 (50% SiH) to 2000-2500 (17% SiH) g mol^{-1}. These compounds will be referred to as $PS_{12}SiH_6$ (a polysiloxane consisting of twelve SiO monomers, of which six are $CH_3Si(H)O$, six are $Si(CH_3)_2O$ and terminated with a trimethylsilyl group), etc. Their purity was determined by gel permeation chro-

*To whom correspondence should be addressed.

matography (Figure 1). In all starting polysiloxanes, there was also some low molecular weight material present (< 300 g mol^{-1}), most probably the cyclic trimer hexamethyltrisiloxane (D_3) since it has the same retention time as authentic D_3.

4′-Allyloxymethylbenzo-15-crown-5 (**2**) was synthesized by allylation of 4′-hydroxymethylbenzo-15-crown-5[14,15]. Polysiloxanes functionalized with crown ethers along the polymer backbone have been synthesized by hydrosilylation[16,17]. This reaction is catalyzed by a platinum catalyst, of which Speier's catalyst (H_2PtCl_6)[4] is often used. Sometimes however, the reaction does not go to completion[18]. Therefore, we used the more active platinum divinyltetramethyldisiloxane[19,6] as catalyst and found no residual SiH signal in the IR or ^1H NMR spectra of the products. The starting polysiloxane was dissolved in dry toluene and the allylated crown ether **2** was added together with the platinum catalyst (Scheme 1). After 24 hours of reflux the product was isolated by evaporation of the solvent. The products of this synthesis will be referred to as $PS_{12}C_6$ (**3a**), $PS_{28}C_9$ (**3b**) and $PS_{30}C_5$ (**3c**) in which the first number denotes the total number of SiO monomer groups (not including end groups) and the second number is the number of crown ether moieties per polysiloxane chain.

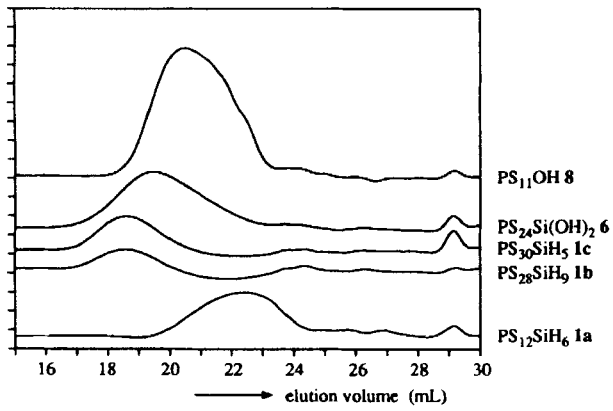
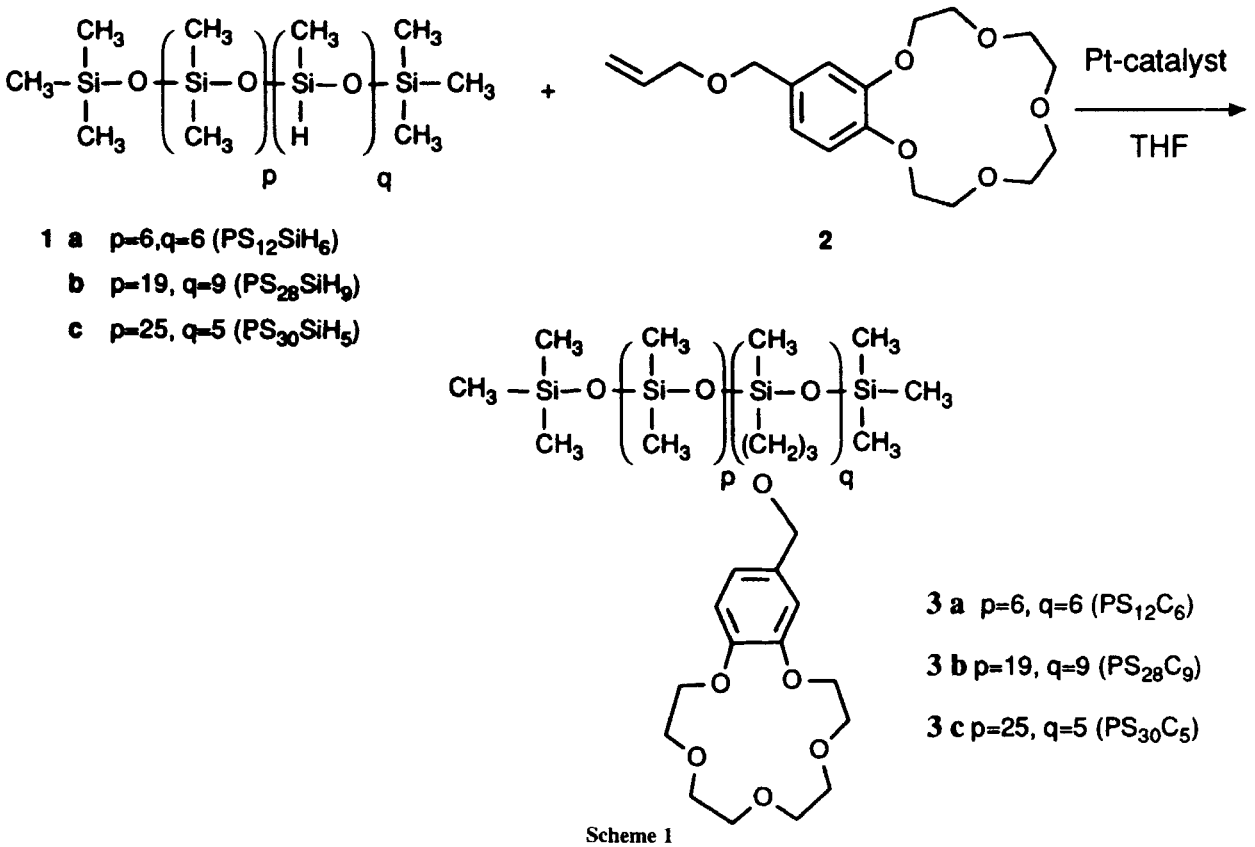


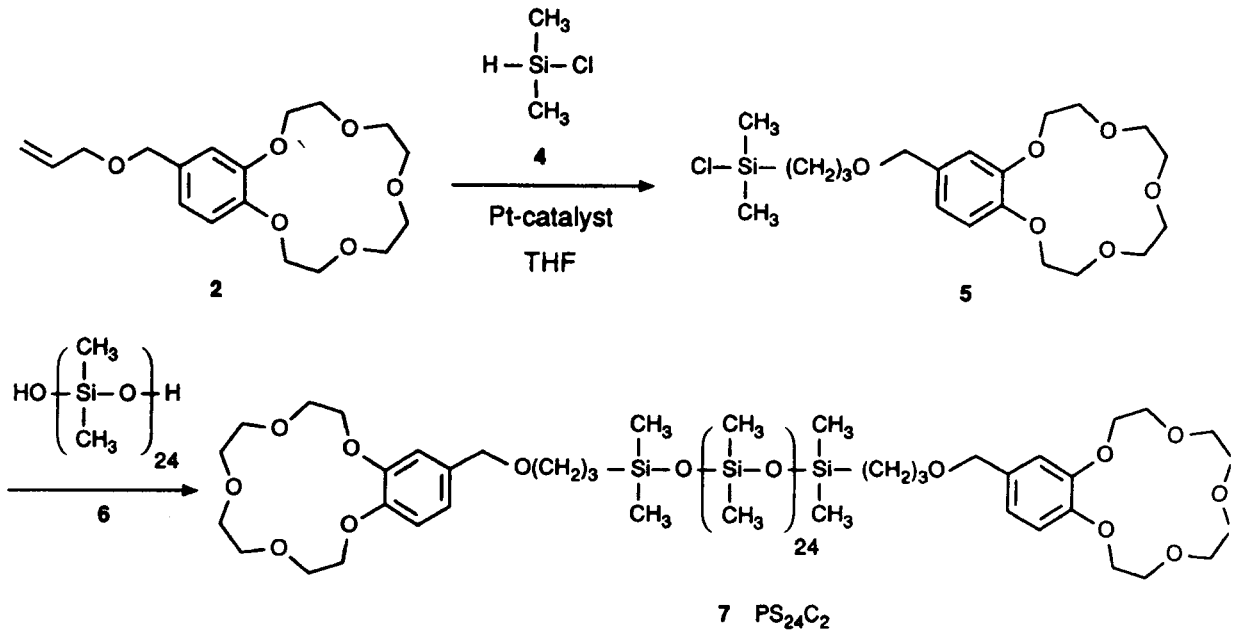
Figure 1 GPC chromatograms of the starting polysiloxanes.

The synthesis of the polysiloxane with crown ether moieties at both termini, $PS_{24}C_2$ (**7**), was performed according to Scheme 2. 4′-Allyloxymethylbenzo-15-crown-5 was dissolved in dry THF, chlorodimethylsilane and platinum catalyst were added, and the mixture refluxed. The product of this reaction was dissolved in dry petroleum ether 60-80 and added at 0 °C to a solution of polysiloxane terminated with hydroxyl groups and Hünigs base in petroleum ether 60-80. Polysiloxane terminated with one crown moiety, $PS_{11}C_1$ (**9**), was synthesized in a similar way (Scheme 3).

The crown ether substituted polysiloxanes (Table 1) were characterized with gel permeation chromatography (Figure 2). They all contained some low molecular



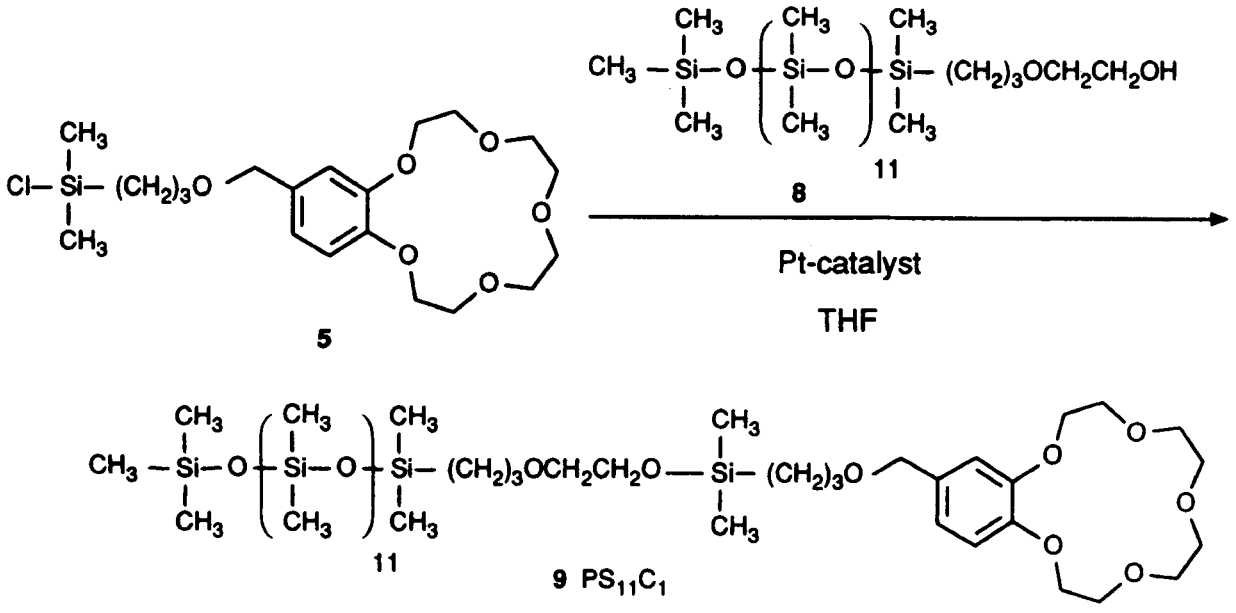
Scheme 1



Scheme 2

weight material (< 300 g mol^{-1}) also present in the chromatograms of the starting materials.

In the ^1H NMR spectra the allyl group of the starting crown ether and the SiH group of the starting polysiloxane were no longer present. In Table 2 the percentage of SiH of the starting materials according to the supplier is compared to the percentage determined by ^1H NMR spectroscopy. The values according to NMR were somewhat lower than the values from the supplier. From the intensity of the signals of the crown ether ring protons and the signal of the $SiCH_3$ protons the percentage of crown ether can be calculated. These values are in good agreement with the percentage of SiH in the starting material calculated from ^1H NMR data. In the IR spectra of the functionalized polysiloxanes the Si-H peak at 2160 cm^{-1} in the starting material was absent.



Scheme 3

Table 1 Crown ether substituted polysiloxanes

Polysiloxane	M_n[1]	*Number of Si-O units*[1]	*Crown ether/ polysiloxane chain*	*Crown density*
$PS_{12}C_6$ (**3a**)	3000	12	6	50%
$PS_{28}C_9$ (**3b**)	5100	28	9	30%
$PS_{30}C_5$ (**3c**)	4000	30	5	17%
$PS_{24}C_2$ (**7**)	2500	24	2	8%
$PS_{11}C_1$ (**9**)	1400	11	1	9%

[1]Based on information from the supplier.

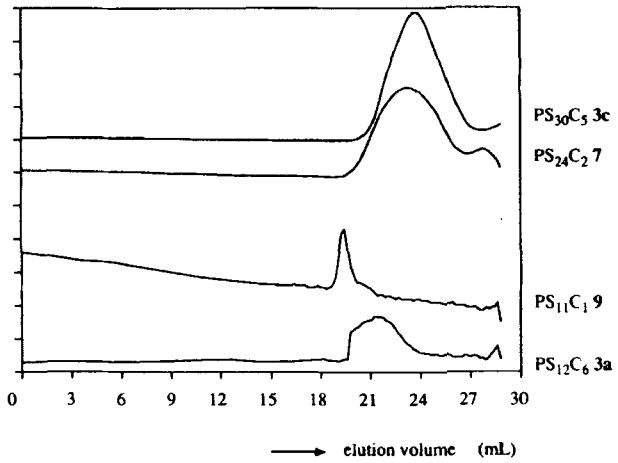


Figure 2 GPC chromatograms of PS_nC_m.

Lipophilicity requirements in supported liquid membranes

In order to quantify requirements as to the lipophilic character of the carrier, let us consider the co-transport of a salt MX from an aqueous source phase (volume V_s) through a lipophilic membrane (volume V_m) to an aqueous receiving phase (volume V_r). The fraction of the carrier lost (f_{lost}) from the organic phase can be calculated from the mass balance of the carrier assuming that: (i) the partition process of the carrier is fast compared with transport (ii) there is thermodynamic equilibrium at all interfaces (iii) the concentrations of the complexed cation in the aqueous phases are very small compared to the concentrations of free cation (iv) the concentration of free cation in the membrane is very small compared to complexed cation.

$$f_{lost} = \frac{P(1-[CM]_{ms}/[C]^0_m)+Q(1-[CM]_{mr}/[C]^0_m)}{1+P+Q} \quad (1)$$

Table 2 Percentage of SiH or crown ether of polysiloxanes

Polysiloxane	*% SiH (supplier)*	*% SiH (^{1}H NMR)*	*% carrier (^{1}H NMR)*
$PS_{12}SiH_6$ **1a**	50-55	45.4	-
$PS_{12}C_6$ **3a**	-	-	44.2
$PS_{28}SiH_9$ **1b**	30-35	26.3	-
$PS_{28}C_9$ **3b**	-	-	22.3
$PS_{30}SiH_5$ **1c**	15-18	10.4	-
$PS_{30}C_5$ **3c**	-	-	9.8

with:

$[CM]_{ms}$: complex concentration at the source phase interface

$[CM]_{mr}$: idem, at the receiving phase interface

$[C]^0_m$: initial carrier concentration

$P=(1+K_w[X]^0_s)/R_sK_c$

$Q=(1+K_w[X]^0_r)/R_rK_c$

K_w: association constant of the carrier with the cation in the aqueous phase

$[X]^0_s$: initial anion concentration in the source phase

$[X]^0_r$: idem, in the receiving phase

K_c: partition constant of the carrier ($K_c=[C]_m/[C]_w$)

$R_r=V_m/V_r$

$R_s=V_m/V_s$

It follows from eq. 1 that carrier loss is due to the following factors: (1) the geometry of the transport cell (R_s, R_r), (2) the lipophilicity of the carrier (K_c), (3) the complex stability in the aqueous phase (K_w), and (4) the association constant in the membrane phase, K_A, which determines the value of $[CM]_{ms}$ and $[CM]_{mr}$.

For our transport cell, $R_s=R_r=0.0016$. K_c can be estimated using the fragmental constants for different functional groups according to Rekker[20,21]. The partition of a compound between *n*-octanol and water is given by eq. 2 in which a_n is the number of times fragment n occurs in the structure of the compound and f_n the fragmental constant of fragment n.

$$\log K_c(\text{octanol}) = \sum_1^n a_n f_n \quad (2)$$

For partition between *o*-nitrophenyl *n*-octyl ether (NPOE, which is used as solvent in the SLM) and water a relation between log K_c in octanol and in NPOE[2] has been established (eq. 3).

$$\log K_c(\text{NPOE}) = 0.84 \log K_c(\text{octanol}) + 0.66 \quad (3)$$

The contribution of an $Si(CH_3)_2O$ group is 0.54 ($f_{Si}=0.65$, $f_{CH_3}=1.4$, $f_O=-1.54$), the contribution of the pendent crown ether fragment ($(CH_2)_3OCH_2$benzo-15-crown-5) is 1.17 ($f_{CH_2CH_2O}=-0.17$, $f_{Ar}=1.44$, $f_{CH_2}=0.53$). For a polysiloxane consisting of twelve R_1R_2SiO monomers, of which six are functionalized with a crown ether unit, a value for log K_c (NPOE/H_2O) of 12 is calculated.

For a given set of parameters the influence of K_c and K_A on the percentage of carrier leached from the membrane phase is shown in Figure 3. When K_c is small the percentage of carrier leached from the membrane is almost 100%, independent of K_A and K_w. When K_c is between 10^2 and 10^5 carrier loss decreases with increasing K_A. The carrier loss is $< 0.1\%$ when $K_c > 10^6$ and $K_A > 10^8$.

The carriers described are polysiloxanes modified with benzo-15-crown-5 units. The value of log K_w of benzo-15-crown-5 in water is 0.38, determined by both calorimetry[22] and electrophoresis[23]. With a log K_c value

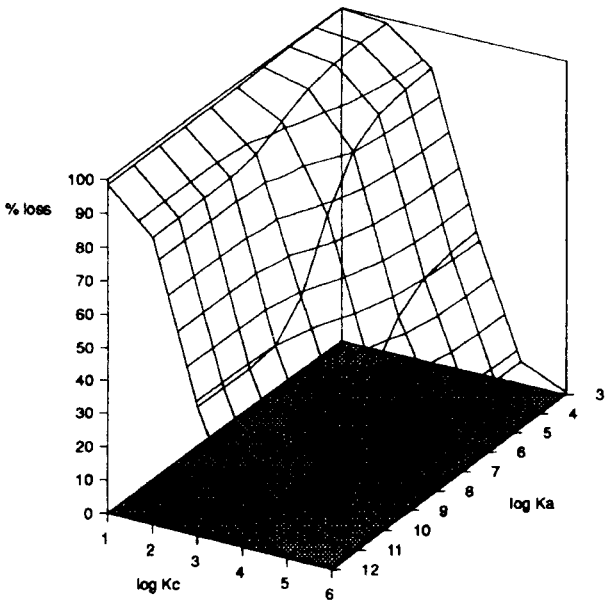


Figure 3 Effect of K_c and K_A on the percentage of carrier leached from the membrane phase[a].
[a]$V_s=V_r=50$ mL; $V_m=0.08$ mL; $K_p=1\times10^{-7}$; $K_W=1\times10^2$ M^{-1}; $[salt]_w=0.1$ M; $[C]^0_m=0.01$ M.

of 12 this means there is no partitioning at all to the aqueous phase, not even at high salt concentration or low K_A. These calculations were verified experimentally (*vide infra*).

Transport experiments

The polysiloxanes substituted with crown ethers were used as carriers in transport experiments through a supported liquid membrane, using the experimental setup depicted in Figure 4[24]. The porous polymer support material (Accurel®, d=100 μm) was impregnated with a hydrophobic organic solvent, *o*-nitrophenyl *n*-octyl ether (NPOE) in which the carrier was dissolved[24]. The cell compartments were double-walled so that all the measurements could be performed at the same temperature (25±0.1 °C). When a single salt was transported the concentration in the receiving phase was monitored by measuring the conductivity. When competition experiments were performed the concentration of the metal ions in the receiving phase was determined by atomic absorption.

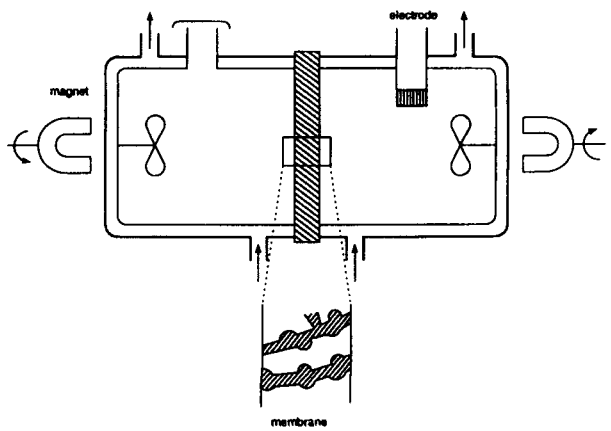


Figure 4 Measurement setup.

Leaching of the carrier to the aqueous phase was determined by replacement of the aqueous receiving phase after 24 hours of transport. The polysiloxanes functionalized with benzo-15-crown-5 were compared with 4′-allyloxymethylbenzo-15-crown-5. Within experimental error the $KClO_4$ flux mediated by all polysiloxanes as carriers was the same after each replacement whereas the flux with the allylated crown ether decreased after each replacement (Table 3).

The relation between the initial flux and the $KClO_4$ activity in the source phase was investigated for the different polysiloxanes (Figures 5 and 6). The "crown ether" concentration (*not* the polysiloxane concentration) was the same for all carriers *viz.* 0.01 M. At salt concentrations higher than 0.02 M the fluxes no longer increase noticeably with increasing salt activity. This means that at these concentrations the crown ether is fully complexed at the source phase. At or above these salt con-

Table 3 Effect of the replacement of the aqueous phase on the flux[a]

Carrier	*N*[b]	*J* (10^{-8} *mol* m^{-2} s^{-1})	*crown conc. (M)*
$PS_{12}C_6$	0	8.61	9.76×10^{-3}
	1	8.47	
$PS_{28}C_9$	0	58.1	9.40×10^{-2}
	1	58.1	
	2	59.4	
	3	63.1	
$PS_{11}C_1$	0	18.0	3.73×10^{-2}
	1	16.7	
	2	18.1	
	3	18.5	
4′-allyloxy-methylbenzo-15-c-5	0	14.4	4.15×10^{-2}
	1	5.56	
	2	3.31	

[a]Source phase 0.1 M $KClO_4$.
[b]N denotes the number of replacements of the receiving phase.

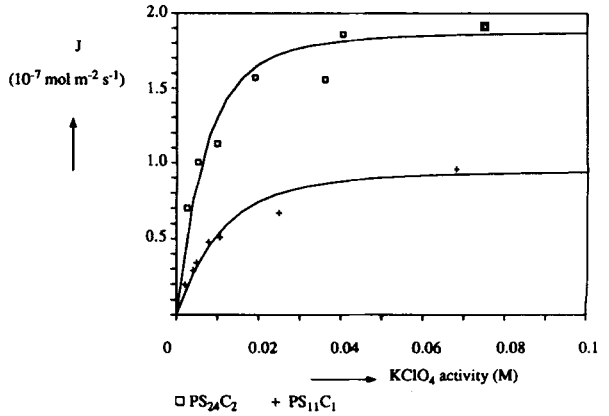


Figure 5 Relation between the flux and the $KClO_4$ activity for functionalized polysiloxanes (crown ether concentration 0.01 M); the lines drawn are calculated according to the model, the symbols are measured values.

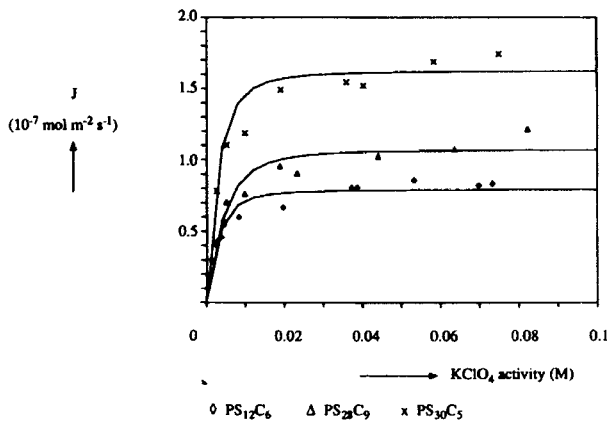


Figure 6 Relation between the flux and the $KClO_4$ activity for functionalized polysiloxanes (crown ether concentration 0.01 M); the lines drawn are calculated according to the model, the symbols are measured values.

centrations the differences in flux values for the different polysiloxanes reflect differences in the diffusion constants. The slopes of the curves before the plateau is reached differs for the polysiloxanes with different degrees of crown ether functionalization.

First, these results were interpreted with the transport model that was developed in our group[25] and which assumes 1:1 crown:cation complexation. This model relates the flux (**J**) to the extraction constant (K_{ex}) and the diffusion constant ($\mathbb{D}$) according to Fick's first law (eq. 4) in which $A=K_{ex}([X]^0_s)^2$.

$$J = \frac{\mathbb{D}}{2d}\left\{-A + \sqrt{(A^2+4A[C]^0_m)}\right\} \qquad (4)$$

The extraction constant K_{ex} is the product of the partition of the salt (K_p) and the association constant (K_A) according to eq. 5.

$$[M]_s + [X]_s \overset{K_p}{\rightleftharpoons} [M]_m + [X]_m$$
$$[M]_m + [C]_m \overset{K_A}{\rightleftharpoons} [CM]_m \qquad (5)$$

For this series of transport experiments $\mathbb{D}$ and K_{ex} were determined by optimizing eq. 4 (Table 4).

In another series of experiments the salt concentration in the source phase was kept constant (0.1 M $KClO_4$) and the initial crown ether concentration in the membrane phase was varied (Table 5, Figures 7 and 8). Up to 0.08 M "crown ether" could be reached for $PS_{11}C_1$ and $PS_{24}C_2$ whereas for the other polysiloxanes concentrations of even 0.6 M could be reached. This means that e.g. for $PS_{30}C_5$ a 0.6 M crown ether solution in NPOE contains 50 weight% functionalized polysiloxane. The high concentrations (> 0.25 M) were not taken into account in the calculation of $\mathbb{D}$ and K_{ex} because deviations from the model are to be expected due to changes in the

Table 4 K_{ex} and $\mathbb{D}$ values determined by variation of the $KClO_4$ concentration

Polysiloxane	K_{ex} $(M^{-1})^a$	$\mathbb{D}(m^2\ s^{-1})$	r^2
$PS_{12}C_6$ (**3a**)	818	0.89×10^{-12}	0.899
$PS_{28}C_9$ (**3b**)	553	1.1×10^{-12}	0.937
$PS_{30}C_5$ (**3c**)	545	1.7×10^{-12}	0.906
$PS_{24}C_2$ (**7**)	177	2.0×10^{-12}	0.884
$PS_{11}C_1$ (**9**)	79	0.94×10^{-12}	0.945

$^aK_{ex}$ is defined per crown ether unit.

Table 5 K_{ex} and $\mathbb{D}$ values determined by variation of the initial crown ether concentration

Polysiloxane	K_{ex} $(M^{-1})^a$	$\mathbb{D}(m^2\ s^{-1})$	r^2
$PS_{12}C_6$ (**3a**)	657	1.5×10^{-12}	0.987
$PS_{28}C_9$ (**3b**)	2.74	1.6×10^{-12}	0.976
$PS_{30}C_5$ (**3c**)	3.74	3.3×10^{-12}	0.945
$PS_{24}C_2$ (**7**)	16.0	2.1×10^{-12}	0.993
$PS_{11}C_1$ (**9**)	81	0.83×10^{-12}	0.946

$^aK_{ex}$ is defined per crown ether unit.

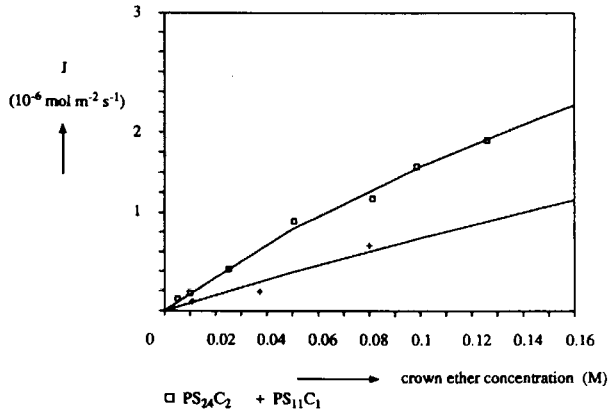


Figure 7 Relation between the flux and the crown ether concentration for functionalized polysiloxanes (source phase 0.1 M $KClO_4$); the lines drawn are calculated according to the model, the symbols are measured values.

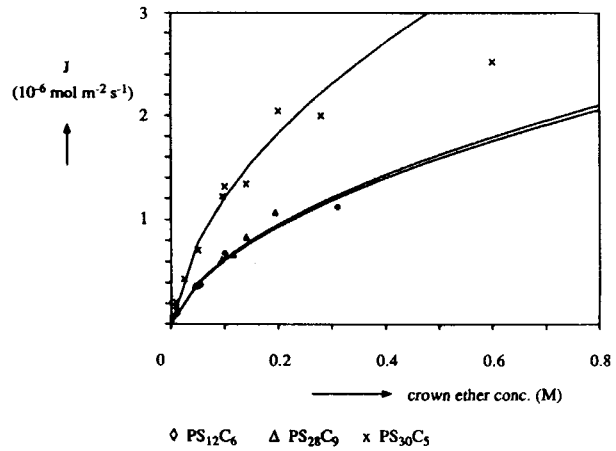


Figure 8 Relation between the flux and the crown ether concentration for functionalized polysiloxanes (source phase 0.1 M $KClO_4$); the lines drawn are calculated according to the model, the symbols are measured values.

viscosity. Ideally, the outcome of the values for $\mathbb{D}$ and K_{ex} in Table 5 should be the same as the values listed in Table 4 if the transport can be described by the 1:1 model. The diffusion constant of these polysiloxanes is in the order of 10^{-12} m^2 s^{-1} which is an order of magnitude lower than for dibenzo-18-crown-6[26] ($\mathbb{D}$ =1.9 × 10^{-11} m^2 s^{-1}). Except for $PS_{11}C_1$ which contains only one crown ether moiety there is a large discrepancy between the values of K_{ex} calculated from the variation of the salt concentration and those calculated from the variation of the crown ether concentration. Furthermore, it is obvious that K_{ex} increases with increasing crown density of the polymer chain.

This leads to the conclusion that in these cases the 1:1 model is no longer valid because the crown ether moieties can no longer be considered as independent binding sites.

Selectivity in K^+/Na^+ transport

Assuming independent 1:1 crown:cation complexes the following expression can be derived for the transport selectivity[25]:

$$\frac{J_1}{J_2} = \frac{\mathbb{D}_1}{\mathbb{D}_2} \times \frac{K_{ex1}}{K_{ex2}} \times \frac{[M_1]_w}{[M_2]_w} \qquad (6)$$

When the diffusion constants of both complexes are the same, the ratio of the fluxes corrected for the concentration difference of M_1 and M_2 is a constant which is equal to the ratio of the two extraction constants. The expression has been used by Nijenhuis *et al.* to successfully predict the selectivity of transport from a source phase that contains both K^+ and Na^+ through an SLM with NPOE as the membrane solvent using different macrocyclic carriers.

We have performed competition experiments with the functionalized polysiloxanes as carrier. The source phase consisted of a mixture of 10^{-1} M $NaClO_4$ and 10^{-3} M $KClO_4$ (Table 6). With carriers **3a**, **3b**, **3c** and **7** the K^+ flux is higher than the Na^+ flux, whereas for carrier **9**, the Na^+ flux is highest. The carriers **3a**, **3b**, **3c** and **7** have approximately the same K^+/Na^+ selectivity, which is an order of magnitude higher than the selectivity of $PS_{11}C_1$ (**9**).

$PS_{11}C_1$ (**9**) and $PS_{30}C_5$ (**3c**) were used in another series of experiments in which the source phase was a mixture of 0.1 M $NaClO_4$ and varying concentrations of $KClO_4$. The results are summarized in Table 7. For $PS_{11}C_1$ (**9**) the ratio of the normalized fluxes is independent of the K^+ concentration in the source phase. For $PS_{30}C_5$ (**3c**), the K^+/Na^+ selectivity increases with decreasing $KClO_4$ concentration.

Table 6 Potassium and sodium fluxes for different carriers in competition experiments[a]

Carrier	$J\,K^+$ (10^{-8} *mol* m^{-2} s^{-1})	$J\,Na^+$ (10^{-8} *mol* m^{-2} s^{-1})	$\frac{J\,K^+}{J\,Na^+} \times \frac{[Na^+]_w}{[K^+]_w}$
$PS_{12}C_6$(**3a**)	5.58	1.55	361
$PS_{28}C_9$(**3b**)	7.03	2.38	296
$PS_{30}C_5$(**3c**)	8.06	2.61	309
$PS_{24}C_2$(**7**)	10.2	3.06	335
$PS_{11}C_1$(**9**)	2.36	6.55	36

[a]Source phase: 10^{-3} M $KClO_4$/10^{-1} M $NaClO_4$; crown ether concentration 0.01 M.

Hence, the results from these selectivity experiments also point to a cooperative effect of the binding sites. Therefore we have developed a transport model for carriers that contain several interacting receptor sites.

Transport model for a multi-site carrier

In this section a general model is described for transport by a carrier which has *n* identical receptor sites. The cations that are transported are M_1 and M_2 and they share a common anion X. Cooperative effects between two adjacent sites are accounted for by a 2:1 complexation constant (K_{S1} and K_{S2} for M_1 and M_2, respectively), whereas repulsive interactions between two occupied sites can be accounted for by the repulsion factor R_{ij}, defined as the ratio K_{Ai} (site next to site occupied by j)/K_{Ai} (site next to unoccupied site). When R_{ij}=1 there is no repulsion and when R_{ij}=0 there is maximum repulsion which means adjacent complexes cannot be formed.

Assuming the transport is diffusion limited and $\mathbb{D}$ is the same for all complexes the flux of M_1 is given by eq. 7 (Appendix B).

$$J_1 = \frac{\mathbb{D}}{d}[M_1]_{m,total} = \frac{\mathbb{D}}{d} \times$$

$$\times \frac{C_0 \sum_{p=0}^{n} \sum_{q=0}^{n} p\, W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{-p-q}}{\sum_{p=0}^{n} \sum_{q=0}^{n} W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{-p-q}} \qquad (7)$$

For the flux of M_2 a similar expression can be derived. C_0 is the total receptor site concentration, p is the number of sites that form a complex with M_1 and q is the number of M_2 complexes. $W_{n,p,q}$ is a probability factor that includes the effects of 2:1 complexation and repulsion. The value of $W_{n,p,q}$ can be determined by counting all the possibilities of forming 1:1 or 2:1 complexes with M_1 or M_2 for a certain *n* and including the number of repulsions. In Appendix A, $W_{n,p,q}$ is given for *n*=3 as an example.

With these equations the influence of 2:1 complexation and repulsion on the flux of M_1 and M_2 and on the transport selectivity can be determined for carriers with different numbers of receptor sites. In the following simulations the receptor site concentration (*not* the carrier concentration) is always kept constant (0.01 M).

Influence of cooperative and repulsive effects for a multi-site carrier

To illustrate the effect of 2:1 complexation, we assume that there is no repulsion (R=1, Figure 9). At low salt

Table 7 Potassium and sodium fluxes for carriers **3c** and **9** in competition experiments[a]

Carrier	*Source phase*		JK^+	$J\,Na^+$	$\frac{J\,K^+}{J\,Na^+} \times \frac{[Na^+]_w}{[K^+]_w}$
	$[K^+]_w$	$[Na^+]_w(M)$	$(10^{-8}\ mol\ m^{-2}\ s^{-1})$	$(10^{-8}\ mol\ m^{-2}\ s^{-1})$	
$PS_{11}C_1$ (**9**)	0.08	0.08	7.95	0.78	10
	1×10^{-2}	1×10^{-1}	5.42	2.07	26
	5×10^{-3}	1×10^{-1}	3.95	4.09	19
	1×10^{-3}	1×10^{-1}	2.36	6.55	36
$PS_{30}C_5$ (**3c**)	0.08	0.08	15.4	1.81	9
	1×10^{-2}	1×10^{-1}	14.9	6.94	22
	5×10^{-3}	1×10^{-1}	14.5	4.86	60
	1×10^{-3}	1×10^{-1}	8.06	2.61	309

[a]Crown ether concentration 0.01 M.

concentrations (such that the loading of a carrier with one site only is below 50%) all multi-site carriers are more efficient than single-site carriers. This is because the "empty" binding sites contribute to the binding of the cation through formation of 2:1 complexes. In case the single-site carrier is occupied by more than 50%, 2:1 complexes can only be formed by release of cations, and hence the efficiency of multi-site carriers is now lower than that of single-site carriers. Under conditions where a single-site carrier is occupied by 50%, 2:1 complexation has no effect on cation binding. The observed odd-even effect is a result of the end groups. For carriers with an uneven number of sites, after formation of the maximum amount of 2:1 complexes there is always one site left that can form a 1:1 complex with a cation. When a large number of receptor sites is attached to the carrier the difference in transport efficiency between carriers with different values of n becomes negligible.

The effect of repulsion between two adjacent complexes on the site occupancy is shown in Figure 10. When the repulsion is very high (when R is close to 0) formation of neighboring complexes will be prevented. It is obvious from Figure 10 that in all cases repulsion lowers the efficiency of multi-site carriers compared to single-site carriers. The reduction is largest for even numbered carriers, again because of the end-group effect. The more sites attached to the carrier the smaller the odd/even effect on the complexation efficiency will be.

In Figure 11 the effects of 2:1 complexation and repulsion on the relation between site occupancy and salt activity in the source phase are illustrated for a carrier with two receptor sites. When there is 2:1 complexation possible the plateau value is lower and is reached at lower salt activities. When the 1:1 transport model would be applied to determine K_{ex}, a higher value would be found compared to the value of K_{ex} for a carrier that is unable to form 2:1 complexes. Repulsion shifts the plateau value to higher salt activities and this would be equivalent with a lower K_{ex} value in the 1:1 model. Experimentally, we observed an increase in the apparent K_{ex} values, and hence we conclude that 2:1 complex formation is more important than repulsion.

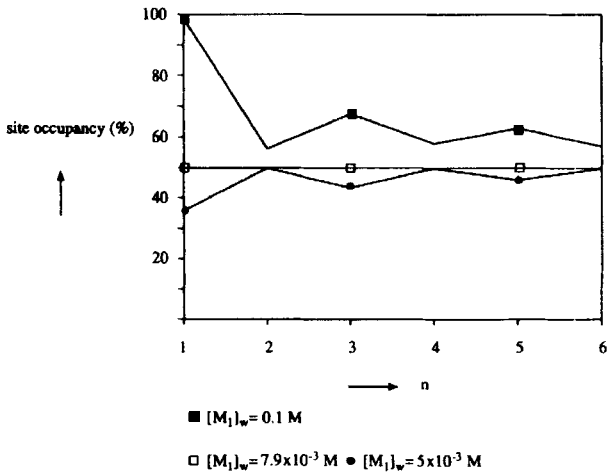


Figure 9 Influence of 2:1 complexation on the relation between site occupancy and $[M_1]_w$ for different values of n[a].
[a]Parameters used: site conc.=0.01 M; $[M_2]_w$=0; K_{ex1}=80 M^{-1}; R_{11}=1; K_{S1}=1000.

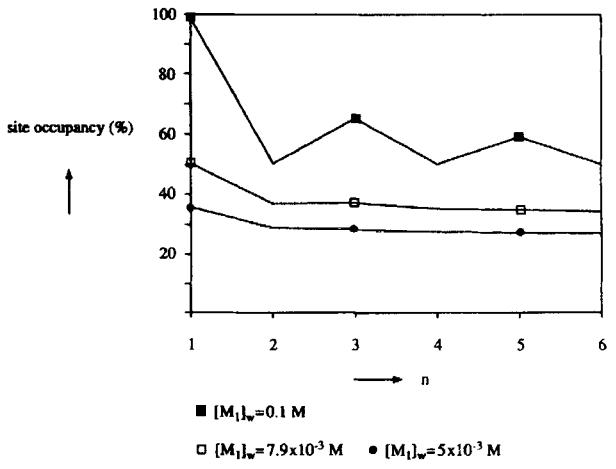


Figure 10 Influence of repulsion on the relation between site occupancy and $[M_1]_w$ for different values of n[a].
[a]Parameters used: site conc.=0.01 M; $[M_2]_w$=0; K_{ex1}=80 M^{-1}; R_{11}=0.01; K_{S1}=0.

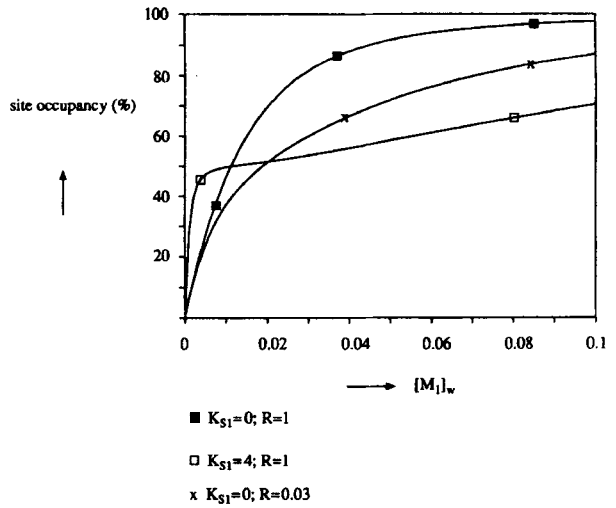


Figure 11 Influence of 2:1 complexation or repulsion on the relation between site occupancy and $[M_1]_w$[a].
[a]Parameters used: site conc.=0.01 M; $[M_2]_w$=0; K_{ex1}=80 M^{-1}; n=2.

Influence of cooperative effects and repulsion on selectivity for a multi-site carrier

In the following simulation experiments we assume the concentration of M_2 in the source phase is kept at 0.1 M, while the concentration of M_1 is varied. The carriers are slightly selective for M_1 (K_{ex1}=80 M^{-1}, K_{ex2}=60 M^{-1}).

In Figure 12 the effect of 2:1 complexation of cation M_1 on the selectivity is shown. There is a strong dependence of the selectivity on $[M_1]_w$, especially at low concentrations. Carriers with more than one site are more selective towards M_1 than a carrier with one site and the higher K_{S1}, the more pronounced this effect is. At very high $[M_1]_w$ concentrations the selectivity becomes independent of the number of binding sites.

In Figure 13 the influence of repulsion is shown. If all repulsion factors are equal (R_{11}=R_{12}=R_{22}) there is no difference in transport selectivity for the different carriers. Only when we assume that the repulsion factors between M_1-M_1, M_2-M_2 and M_1-M_2 complexes are different there is a distinct difference in selectivity between the carriers with a different number of sites attached but the selectivity changes little with increasing $[M_1]_w$. Since the K^+/Na^+ selectivity was found to increase drastically at low K^+ concentrations, we again conclude that 2:1 complex formation is the overriding effect.

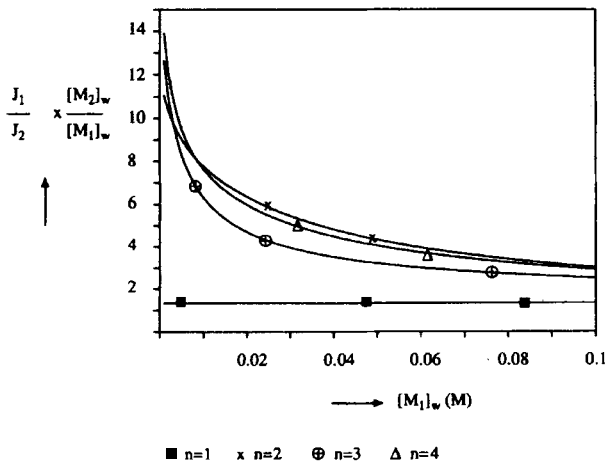


Figure 12 Influence of 2:1 complexation on the relation between selectivity and $[M_1]_w$[a].
[a]Parameters used: site conc.=0.01 M; $[M_2]_w$=0.1 M; K_{ex1}=80 M^{-1}; K_{ex2}=60 M^{-1}; R_{11}=R_{22}=R_{12}=1; K_{S1}=1000; K_{S2}=0.

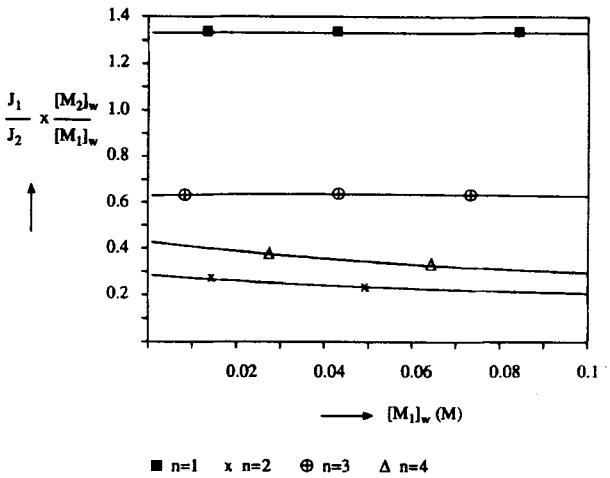


Figure 13 Influence of repulsion on the relation between selectivity and $[M_1]_w$[a].
[a]Parameters used: site conc.=0.01 M; $[M_2]_w$=0.1 M; K_{ex1}=80 M^{-1}; K_{ex2}=60 M^{-1}; R_{11}=0.001; R_{22}=0.1; R_{12}=0.01; K_{S1}=K_{S2}=0.

CONCLUSIONS

Binding of crown ether molecules to a polysiloxane backbone results in a carrier that is extremely suitable for use in an SLM because there is no partitioning to the aqueous phases as was observed for an unfunctionalized crown ether. It also results in a carrier that is much better soluble in the membrane phase than simple crown ethers and this allows very high carrier concentrations in the membrane.

According to a 1:1 transport model the value for K_{ex} should be the same for all polysiloxanes functionalized with benzo-15-crown-5, independent of the method used (either variation of the salt concentration in the source phase or crown ether concentration in the membrane phase). Furthermore the K^+/Na^+ selectivity should be independent of the salt concentrations in the source phase. Only for $PS_{11}C_1$ this is indeed the case. The value of K_{ex} of the other carriers depends on the method used and is different for each carrier, while their selectivity is dependent of the K^+ concentration in the source phase. This means that in polysiloxanes substituted with several crown ethers the receptor sites can no longer be regarded as independent. A new transport model has been devel-

oped which takes into account the interactions of receptor sites attached to the same polymer chain. This model correctly predicts that 2:1 complexation increases the apparent extraction constant K_{ex}, and also increases the K^+/Na^+ selectivity at low K^+ concentrations. No evidence was found for the occurrence of repulsive interactions.

MATERIALS AND METHODS

Transport measurements

The apparatus used for the transport experiments consists of two identical cylindrical compartments (half-cell volume 45 mL; effective membrane area 9.8 cm^2) made of glass. Stirring is accomplished by a flat-bladed turbine positioned at the center of the half-cells and driven by a magnet outside the compartment at a stirring rate of 1000 rpm. The compartment is double-walled for thermostating using a thermostated water bath (Tamson, TC). All measurements were performed at 25 °C.

The membrane is positioned between the cylindrical compartments containing the two aqueous phases. The supported liquid membrane consists of a thin porous polypropylene film (Accurel®, obtained from Enka Membrana; thickness d=100 μm, porosity Θ= 64%).

The carriers were dissolved in *o*-nitrophenyl *n*-octyl ether (NPOE). The membrane was submerged in this solution under vacuum (2×10^{-3} Pa) for 15 minutes. The membrane was wiped carefully with a tissue to remove excess fluid at the outside of the support.

For the aqueous source phase solutions and for the receiving phases, doubly distilled and deionized water was used.

All measurements were performed at least in duplicate (with a deviation that was normally 10-15%).

In case of single cation transport, the concentration of salt in the receiving phase as a function of time was determined by monitoring the conductivity (Philips PW 9527 conductivity meter and a Philips PW 9512/61 electrode with a cell constant of 0.76 cm^{-1}). In case of competitive ion transport, samples were taken after 24 hours of transport and analyzed by atomic absorption.

Synthesis

The polysiloxane starting materials were obtained from Petrarch (now ABCR). The NPOE (Fluka) and the $KClO_4$ and $NaClO_4$ (Janssen Chimica) were used without further purification. All other chemicals were reagent grade and used without further purification.

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC250F spectrophotometer in $CDCl_3$. No internal standard was used when the sample was a polysiloxane, otherwise $(CH_3)_4Si$ was used as an internal standard.

Infrared spectra were recorded on a Nicolet 5SXC FT-IR spectrometer.

For the GPC measurements a Waters 510 HPLC pump was used. Detection was performed by a Waters 410 differential refractometer. THF p.a. was used as eluent.

2,3-[4-(Hydroxymethylbenzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-(hydroxymethyl)benzo-15-crown-5. This compound was synthesized according to literature procedures[14,15].

4′-(Allyloxymethyl)benzo-15-crown-5 (2). This reaction was carried out under N_2 atmosphere. 0.42 g NaH (80% in oil, 0.010 mol) were treated with dry petroleum ether to remove the oil and suspended in THF (destilled from Na). 2.08 g (0.0070 mol) 4′-(hydroxymethyl)benzo-15-crown-5 were dissolved in 10 mL of THF and added dropwise to the well-stirred suspension. After the addition stirring was continued for another 15 min. before a solution of 1.21 g (0.010 mol) allyl bromide in 4 mL of THF was added dropwise. The mixture was heated to reflux and stirred for 3 h. After cooling, some water was added and the mixture was extracted with diethyl ether and dried on $MgSO_4$. After filtration, the solvent was removed by evaporation under vacuum.

The product was purified by column chromatography on alumina (activity II-III) with petroleum ether 60-80/ethyl acetate in a 1:1 ratio.

The yield was 1.87 g (79%) of a yellow oil.

Polysiloxanes substituted with benzo-15-crown-5 (3a-c). The starting copolymer of dimethylmethylhydrosiloxane was dissolved in toluene (1 g in 40 mL) and together with 1.2 eq. of 4′-(allyloxymethyl)benzo-15-crown-5 and 10 μL of platinum divinyltetramethyldisiloxane (3-5% in xylene) refluxed for 24 h. After this period, an extra amount of 10 μL catalyst was added and the solution was refluxed for another 24 h. The solvent was removed by evaporation under vacuum. The product was dissolved in petroleum ether 60-80 and extracted with water until all of the excess crown ether was removed. The product was obtained quantitatively as a thick yellow oil; ^1H NMR: (δ) 6.84 (m, ArH), 4.40 (s, OCH_2Ar), 4.00 (m, OCH_2CH_2O), 3.38 (t, $\underline{CH_2}OCH_2Ar$, J=8.48 Hz), 0.00 (s, $SiCH_3$); ^{13}C NMR (δ): 149.1 (C, Ar), 148.5 (C, Ar), 131.9 (CH, Ar), 120.6 (CH, Ar), 114.0 (CH, Ar), 76.5-68.9 (CH_2, OCH_2CH_2O, CH_2OCH_2Ar), 29.7 (CH_2, $SiCH_2\underline{CH_2}$), 23.2 (CH_2, $SiCH_2$), 0.00 (CH_3, $SiCH_3$); IR (KBr) 2962-2870 (CH), 1261 ($SiCH_3$), 1094, 1025 (SiOSi), 844 cm^{-1} ($SiCH_3$).

$PS_{24}C_2$ (7). 0.54 g (0.0016 mol) 4′-(Allyloxymethyl)benzo-15-crown-5 and 0.24 g (0.0025 mol) chlorodimethylsilane were dissolved in 10 mL of THF and 5 μL of Pt catalyst was added. The mixture was refluxed for 24 h., during which period three times an additional amount of 0.3 g chlorodimethylsilane was added. The mixture was cooled and the solvent, together with the excess chlorodimethylsilane, was evaporated

under reduced pressure. The product was used without further purification.

This product (0.45 g; 0.0010 mol) was dissolved in 15 mL of dry petroleum ether and added dropwise to a cooled and stirred solution of 0.79 g (0.00045 mol) silanol terminated polysiloxane and 0.12 g (0.0009 mol) N,N-diisopropylethylamine in 10 mL of petroleum ether.

After stirring for 2 h the salts were removed by filtration and the solvent was removed under reduced pressure. The product was obtained quantitatively as a thick yellow oil; ^{1}H NMR (δ): 6.76 (m, ArH), 4.34 (s, OCH_2Ar), 4.00 (m, OCH_2CH_2O), 3.33 (t, $\underline{CH_2}OCH_2Ar$, J=6.91 Hz), 1.60 (m, $SiCH_2\underline{CH_2}$), 0.50 (m, $SiCH_2$), 0.00 (s, $SiCH_3$); ^{13}C NMR (δ): 149.1 (C, Ar), 148.6 (C, Ar), 131.9 (CH, Ar), 125.5 (C, Ar), 120.7 (CH, Ar), 113.7 (CH, Ar), 76.5-68.9 (CH_2, OCH_2CH_2O, CH_2OCH_2Ar), 29.7 ($SiCH_2\underline{CH_2}$), 23.5 (CH_2, $SiCH_2$), 0.00 (CH_3, $SiCH_3$); IR (KBr) 2962-2870 (CH), 1261 ($SiCH_3$), 1094, 1025 (SiOSi), 844 cm^{-1} ($SiCH_3$).

$PS_{11}C_1$ (9). This reaction was carried out like the previous one, except that the polymer was now mono silanol terminated polysiloxane (M=1000); ^{1}H NMR δ 6.81 (m, ArH), 4.34 (s, OCH_2Ar), 3.70 (m, OCH_2CH_2O, $\underline{CH_2}OCH_2Ar$), 1.55 (m, $SiCH_2\underline{CH_2}$), 0.46 (m, $SiCH_2$), 0.00 ($SiCH_3$); IR (KBr) 2962-2870 (CH), 1261 ($SiCH_3$), 1094, 1025 (SiOSi), 844 cm^{-1} ($SiCH_3$).

APPENDIX A

Calculation of the probability factor $W_{n,p,q}$ for n=3

$W_{3,0,0} = 1$
$W_{3,1,0} = 3 + 2K_{s1}$
$W_{3,0,1} = 3 + 2K_{s2}$
$W_{3,2,0} = 1 + 2R_{11} + 2K_{s1}$
$W_{3,1,1} = 2 + 4R_{12} + 2K_{s1} + 2K_{s2}$
$W_{3,0,2} = 1 + 2R_{22} + 2K_{s2}$
$W_{3,3,0} = (R_{11})^2$
$W_{3,2,1} = 2R_{11}R_{12} + (R_{12})^2$
$W_{3,1,2} = 2R_{12}R_{22} + (R_{12})^2$
$W_{3,0,3} = (R_{22})^2$

APPENDIX B

A_1 and A_2 are defined according to eq. 8 and 9 in which K_{p1} is the partition constant of M_1X and K_{p2} is the partition constant of M_2X, and $[M]_{w,tot}=[M_1]_w+[M_2]_w$.

$$A_1 = K_1K_{p1}[M_1]_w[M]_{w,tot} \quad (8)$$

$$A_2 = K_2K_{p2}[M_2]_w[M]_{w,tot} \quad (9)$$

$S_{n,p,q}$ is defined as a species with n identical binding sites of which p sites form a complex with M_1 and q sites form a complex with M_2. The complexation equilibria can be described in the usual way.

$$S_{n,p,q} + [M_1]_m \overset{K_1}{\rightleftharpoons} S_{n,p+1,q}$$

$$S_{n,p,q} + [M_2]_m \overset{K_2}{\rightleftharpoons} S_{n,p,q+1}$$

Eq. 10 relates $S_{n,p,q}$ to $W_{n,p,q}$.

$$S_{n,p,q} = W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{-p-q} S_{n,0,0} \quad (10)$$

The mass balance of the carrier is given by eq. 11 in which C_0 represents the total carrier concentration.

$$C_0 = \sum_{p=0}^{n} \sum_{q=0}^{n} S_{n,p,q} \quad (11)$$

For convenience let the empty carrier $S_{n,0,0}$=C, then form eq. 10 and 11 a relation between the total carrier concentration and $[X]_m$ can be derived (eq. 12).

$$C_0 = C \left\{ \sum_{p=0}^{n} \sum_{q=0}^{n} W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{-p-q} \right\} \quad (12)$$

In order to maintain electroneutrality, the anion concentration $[X]_m$ is given by eq. 13.

$$[X]_m = \sum_{p=0}^{n} \sum_{q=0}^{n} (p+q)\, S_{n,p,q} \quad (13)$$

Together with eq. 10 this leads to eq. 14.

$$[X]_m = C \left\{ \sum_{p=0}^{n} \sum_{q=0}^{n} (p+q)\, W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{-p-q} \right\} \quad (14)$$

From eq. 12 an expression for C is obtained which together with eq. 14 results in eq. 15.

$$\sum_{p=0}^{n} \sum_{q=0}^{n} \left\{ W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{n+1-p-q} - (p+q)\, C_0\, W_{n,p,q}\, A_1{}^p A_2{}^q [X]_m{}^{n-p-q} \right\} = 0 \quad (15)$$

This polynome in $[X]_m$ can be solved iteratively according to the Newton method[27,28]. Once the solution of $[X]_m$ is obtained the concentrations of the other species can be calculated, for example the flux of cation M_1 can be obtained from eq. 7.

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