wiped with Kimwipe between scans. A Ag/AgI reference electrode was made by dipping a silver wire coated with AgI by anodic deposition into a saturated solution of $\mathrm{Et_4N^+I^-}$ in DMSO and sealed by a VYCOR membrane.

An amount of the neutral compound sufficient to make 5 mL of 3.0 mM solution was weighed into the electrochemical cell and placed on the cell holder. Tetraethylammonium tetrafluoroborate (electrometric grade from Southwestern Analytical Chemicals Inc., dried under vacuum at 70 °C for 48 h, 0.108 mg) was placed in the cell and 5 mL of purified DMSO was added. Pure argon was bubbled through the solution constantly except while recording the scan, at which time the solution was blanketed with argon. About 0.3 equiv of $\mathrm{CH_3SOCH_2K}$ (150–200 mM solution) was added in aliquots and the cyclic voltammogram recorded after each addition. In the case of thiazolium salts, the neutral solution was scanned under argon to ensure that the oxidation of the counterion would not cause interference. Cyclic voltammograms were recorded at a scan rate of 100 mV/s on a Houston 100 X-Y recorder. The ferrocenium/ferrocene redox couple (0.875 mV vs Ag/AgI) was used as a standard. The redox couple of ferrocenium/ferrocene was checked against the reference electrode before and after the measurements.

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Stabilization of Crown Ether Containing Supported Liquid Membranes

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Abstract: Lipophilic ionophores, synthesized by coupling crown ethers 18-crown-6 and 12-crown-4 at the termini of polysiloxane backbones, have been tested as carriers in the transport of potassium perchlorate through a supported (Accurel) liquid membrane that contains *o*-nitrophenyl *n*-octyl ether (NPOE) as the membrane phase. The polysiloxane-coupled crown ethers are able to facilitate the ion transport. The stability of the membrane is enhanced in comparison with that of simple crown ethers like dibenzo-18-crown-6 by at least a factor of 25, because of the high partition coefficient (log P_{CE} = 4.7–27) of the carrier for which the contribution of one siloxane moiety to the value of log P_{CE} is 0.6. Experiments with polysiloxane-coupled crown ethers in poly(dimethylsiloxane) as the membrane phase showed a large decrease of the flux, probably due to the unfavorable partition of the salt between water and poly(dimethylsiloxane). The transport through these membranes can be described by a model, assuming thermodynamic equilibrium at the interfaces and linear concentration gradients of both complex and free crown ether. The experimental relation between the flux and the initial carrier concentration can only be explained when the transport takes place via 2:1 (crown ether:cation) complexes for both polysiloxane-coupled 12-crown-4 and polysiloxane-coupled 18-crown-6.

Conventional mass separation techniques are currently supplemented by processes that utilize semipermeable membranes. Disadvantages of solid (micro)porous polymer membranes are the often insufficient transmembrane flux or an insufficient selectivity. Liquid membranes with carrier molecules offer a possible solution for both problems.

So far most of the work in this area has been carried out with bulk liquid membranes composed of a hydrophobic organic solvent which separates two aqueous phases.[1-5] The disadvantage of bulk liquid membranes is the large quantity of carrier relative to the effective area where phase transfer can take place. Consequently, supported liquid membranes have been developed. These are composed of solutions of a carrier in hydrophobic organic solvents, immobilized in thin porous microfiltration films, that separate two aqueous phases. These systems resemble biological membranes in which carrier molecules such as valinomycin facilitate selective transport of potassium ions. Previously, we have reported the mechanism of transport of potassium and guanidinium salts through supported liquid membranes.[6,7]

In order to create a stable supported liquid membrane, the carriers in the membrane phase must possess a high lipophilicity. In a previous paper, we reported the influence of the lipophilicity of the crown ether on the flux of guanidinium thiocyanate through a supported liquid membrane.[7] The experimental results were described in terms of a general model. This model includes as parameters the partition of both the crown ether and the salt, electroneutrality, the complexation constants in both the membrane and the aqueous phases, and the concentration gradients of the crown ether, complex, and salt in the membrane phase. We concluded that with increasing lipophilicity of the crown ether the membrane stability is enhanced while the diffusion coefficient of the carrier molecule hardly decreases. The increased lipophilicity was accomplished by introduction of alkyl or aryl functional groups, but the lifetime of these membrane systems is still limited. An alternative approach would be to bind the carrier molecules to a polymeric support such as liquid polysiloxanes that possess better diffusion properties than solid polymeric materials. Bradshaw et al. have used such polysiloxane-coupled crown ethers as a stationary phase in capillary

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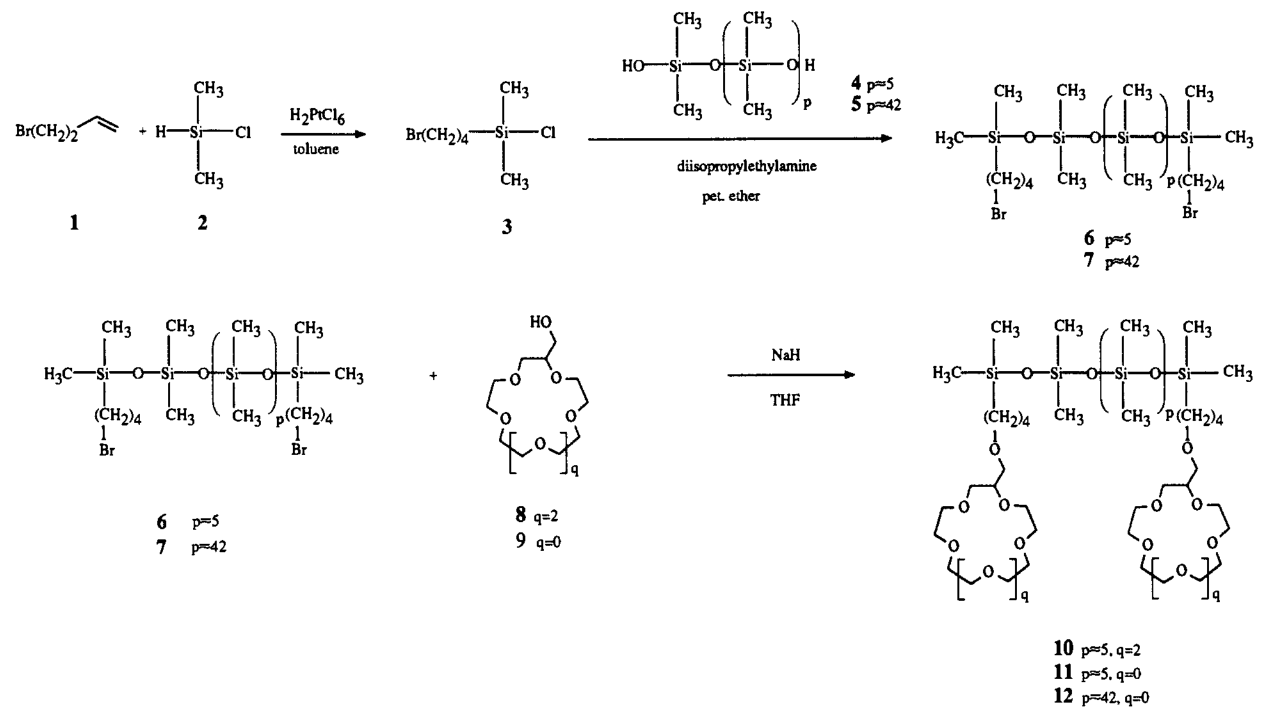
Scheme I



chromatography with specific selectivities toward polar solutes.[8-11]

In our work we have used the polysiloxane backbone as the lipophilic moiety of the carrier molecule because of its very low water solubility. We have synthesized polysiloxanes terminated with crown ethers of different ring size. Solutions in *o*-nitrophenyl *n*-octyl ether (NPOE) were immobilized in a polymeric support (Accurel), and these systems have been tested for the transport of potassium perchlorate. The stability of the membrane system has been determined, and the fluxes have been interpreted in terms of a general model that differs from the model previously described for the transport of guanidinium thiocyanate in the stoichiometry of the complex.

Results and Discussion

Synthesis of Polysiloxane-Bound Crown Ethers. The crown ethers (**8** and **9**) were covalently linked to bromobutyl-functionalized polysiloxanes (**6** and **7**) via a Williamson ether synthesis in THF with NaH as a base (Scheme I). Bromine groups were introduced in the polysiloxanes by reaction of (4-bromobutyl)chlorodimethylsilane (**3**) with silanol-terminated poly(dimethylsiloxanes) of different molecular weights [PS1 (**4**), $M_w \approx 460$ and PS2 (**5**), $M_w \approx 3200$]. (4-Bromobutyl)chlorodimethylsilane was synthesized by a hydrosilylation reaction between chlorodimethylsilane and 4-bromo-1-butene, chloroplatinic acid (H_2PtCl_6) being used as a catalyst.

Three carriers were synthesized, viz., PS1(18C6) (**10**), consisting of a low molecular weight siloxane terminated with 18-crown-6 groups, PS1(12C4) (**11**), also a low molecular weight siloxane but terminated with 12-crown-4 groups, and PS2(12C4) (**12**), a high molecular weight siloxane terminated with 12-crown-4 groups. According to ^{1}H NMR spectroscopy these products have a degree of crown ether functionalization of 60–75%. In order to determine the influence of the polysiloxane moiety on the membrane transport, a polymer with hexyl groups instead of crown ethers [PS1(hexyl)] was also synthesized and investigated.

Table I. Flux of Potassium Perchlorate for Different Carriers

carrier	J (10^{-8} mol cm^{-2} h^{-1})[a]
DB18C6[b]	24.9 ± 1.4
PS1(18C6) (**10**)	19.9 ± 1.6
PS1(12C4) (**11**)	2.3 ± 0.3
PS2(12C4) (**12**)	1.9 ± 0.2
PS(hexyl)$_2$	0.6 ± 0.1
none[c]	0.7 ± 0.1

[a] $[KClO_4]_{wl}$ = 0.1 M, $[carrier]_m$ = 0.01 M, and T = 298 K. [b] Dibenzo-18-crown-6, ref 6. [c] Only NPOE in membrane phase.

Transport of Potassium Perchlorate. PS1(18C6) (**10**), PS1(12C4) (**11**), PS2(12C4) (**12**), and dibenzo-18-crown-6 (DB18C6) were used as carriers for the transport of potassium perchlorate through a supported liquid membrane. The membrane consisted of a solution of the carrier in *o*-nitrophenyl *n*-octyl ether (NPOE), immobilized in a porous polymeric support (Accurel). This membrane separates the source phase (s.p.), an 0.1 M aqueous solution of $KClO_4$, and the receiving aqueous phase (r.p.), which initially contains no salt. We have previously shown that in this system the transport is determined by the diffusion through the membrane and can be described by Fick's first law.[6] Because transport occurs via the complex and not via the free salt, the flux is proportional to the complex concentration in the membrane source interface [eq 1; J = flux, D_m = diffusion coefficient, d = membrane thickness, $[K^+CE]_{ml}$ = complex concentration in membrane source interface].[12]

$$J = (D_m/d)[K^+CE]_{ml} \qquad (1)$$

The flux of potassium perchlorate across the membrane was measured for each carrier, and the results are listed in Table I. With PS1(18C6) the flux is of the same order of magnitude as the flux for DB18C6. The observed lower flux with PS1(12C4) can be expected because of a much lower association between a potassium cation and a 12-crown-4 molecule. The flux with PS2(12C4), the carrier with the longer siloxane moiety, is not much lower than that with PS1(12C4). The increase of the molecular weight of the carrier causes only a minor decrease of

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(12) It has been shown that D_m hardly changes with increasing lipophilicity.[5] Therefore, we assume that D_m is equal for all complexes. The absolute value is trivial; we chose the value of the most lipophilic carrier determined previously. $D_m = 8.3 \times 10^{-4}$ cm^2 h^{-1}.

Table II. Flux[a] as a Function of the Number of Replacements of the Receiving Phase

carrier	no. of replacements 0	1	2	6
18C6	1.7	0.9	0.8	
PS1(18C6)	79	80	78	79
PS2(12C4)	4.3	4.5	4.6	4.7

[a] 10^{-8} mol cm^{-2} h^{-1}; $[KClO_4]_{w1} = 0.1$ M; $[carrier]_m = 0.04$ M; $T = 298$ K.

Table III. log P_{CE} of Some Selected Silicon Compounds and Corresponding Carbon Compounds

	log P_{CE}(octanol)[a]	Δ log P_{CE}(octanol)
$(C_6H_5)Si(CH_3)_3$	4.72	0.61
$(C_6H_5)C(CH_3)_3$	4.11	
$HO(C_6H_4)Si(CH_3)_3$	3.84	0.53
$HO(C_6H_4)C(CH_3)_3$	3.31	

[a] Reference 14.

the flux. In order to determine the effect of the polysiloxane itself on the transport, the transport through a membrane containing PS1(hexyl) was also measured. The flux was not significantly higher than the flux through a membrane which contains only NPOE as the membrane phase, indicating that the polysiloxane moiety of the carriers has no influence on the flux.

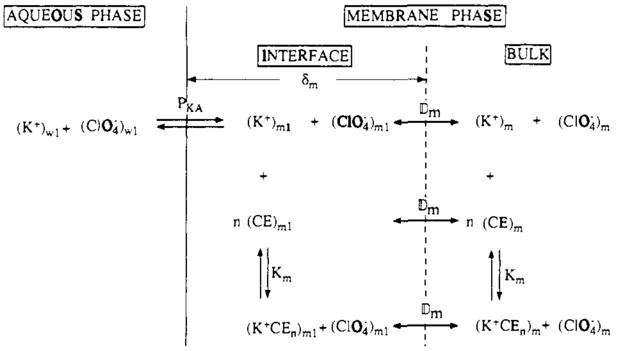
Stability of the Membrane System. In order to estimate the stability of the membranes that contain polysiloxane-coupled carriers, experiments were carried out in which, after 24-h measurement (total transport ≤4%), the receiving phase was replaced with fresh water. Replacement of the aqueous phase causes a new equilibration, and again, a part of the carrier may therefore be transferred from the membrane into the new aqueous phase. Then the flux was monitored again, in order to determine how much of the carrier had been transferred. These experiments were carried out with 18-crown-6 (18C6), PS1(18C6), and PS2(12C4) as a carrier in the membrane. The observed results are shown in Table II. In case of 18C6, the flux already dropped to the value of the blank experiment after the first time the r.p. had been replaced. When PS1(18C6) was present in the membrane phase, the flux did not decrease. The procedure was repeated six times subsequently, and no decrease of the flux was observed. This indicates that this carrier does not leak out of the membrane phase. For PS2(12C4) as carrier, we observed an increase of flux upon replacement of the r.p. This surprising observation can only be rationalized by assuming a decrease of the membrane thickness by flushing away of the NPOE present at the outside of the supporting membrane. This interpretation is supported by the observation that the increased flux reaches a plateau value of 1.1 times the initial value.

Estimation of the Partition Coefficients. According to Rekker[13] the log of the partition coefficient (log *P*) of a compound can be considered as the sum of the contributions of all fragments of this compound (eq 2). In this expression, a_n is a numerical factor

$$\log P_{CE} = \sum_{1}^{n} a_n f_n \qquad (2)$$

for a given fragment in the structure, and f_n, the hydrophobic fragmental constant, is the contribution of that fragment to the lipophilicity of the structure. It can be calculated that the crown ether and aliphatic fragments of the carrier molecules together have no significant influence on log P_{CE}. Therefore, the lipophilicity is determined by the siloxane moiety of the carriers. The contribution of the siloxane part can be split up into the contributions of the methyl groups, the oxygen, and the quaternary silicon atoms. The f_n value for a silicon atom is estimated by comparing the values of log *P* of silicon-containing compounds with the f_n values of corresponding compounds with a carbon atom instead of the silicon (Table III).[14] From this table the f_n value

Scheme II



of a quaternary silicon atom was calculated to be ca. 0.57 higher than that for a carbon atom, which is 0.15 in octanol. Therefore, $f(Si) = 0.57 + 0.15 = 0.72$. Finally, $f(Si(CH_3)_2O) = 0.72 + (2 \times 0.70) - 1.54 = 0.6$. For PS1(18C6) which has an average of eight siloxane units, log P_{CE}(octanol) comes to 4.8. This partition coefficient can be converted into a log P_{CE} value of 4.7 for the system NPOE/water with the empirical relation log P_{CE}(NPOE) = 0.84 log P_{CE}(octanol) + 0.66.[7] This value for log P_{CE} would result in a loss of ca. 9% of the carrier molecules from the membrane phase after six replacements. This may explain the observation that the flux remained constant, even after six replacements of the r.p., because the relative loss of carrier is of the same order of magnitude as the relative decrease of the membrane thickness. For PS2(12C4) with an average of 45 siloxane units a P_{CE} of 10^{27} can be calculated. It is evident that no significant part of this carrier will be lost from the membrane phase.

Model for Membrane Transport. The steady-state flux through the membrane can be decreased by a diffusion process of the complex. Complexation takes place in a thin reaction zone within a thickness of δ_m (Scheme II). It is further assumed that the potassium crown ether complex and the perchlorate anion are present in the membrane phase predominantly as free ions.[6] According to Stolwijk et al.,[7] equations for the crown ether and complex concentrations in the interface between membrane and source phase can be derived (eq 3 and 4). In these equations

$$[CE]_{m1} = \frac{[CE]_m^0 - [K^+CE]_{m1}\left\{1 + \frac{V_w}{V_m}\frac{1}{P_{CE}}\right\}}{1 + 2\frac{V_w}{V_m}\frac{1}{P_{CE}} + \frac{V_w}{V_m}\gamma_{\pm}K_w[K^+]_{w1}^0\frac{1}{P_{CE}}} \qquad (3)$$

$$[K^+CE]_{m1} = K_m P_{KA}\frac{\gamma_{\pm}[K^+]_{w1}^0[ClO_4^-]_{w1}^0}{[K^+]_{m1} + [K^+CE]_{m1}}[CE]_{m1} \qquad (4)$$

the subscripts m, m1, w, and w1, refer to the membrane phase, membrane source interface, aqueous phase, and aqueous source phase, respectively; [ ] and $[\ ]^0$ represent equilibrium concentrations and initial concentrations, respectively. *V* represents a volume, *K* an association constant, $\gamma_{\pm}$ the activity coefficient of potassium perchlorate, and P_{KA} the partition coefficient of the salt. The assumption has been made that the concentration gradient of the crown ether is equal and opposite to the concentration gradient

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(15) The values for $[K^+CE]_{m1}$, $[K^+]_{m1}$, and $[CE]_{m1}$ can be calculated directly from the flux:

$$[K^+]_{m1} = \frac{P_{KA}[K^+]_{w1}^{0\ 2}\,D_m}{2J^d{}_m}$$

$$[K^+CE]_{m1} = \frac{d_m J}{D_m} - [K^+]_{m1}$$

$$[CE]_{m1} = [CE]_m^0 - [K^+CE]_{m1}$$

The partition coefficient for the potassium perchlorate (P_{KA}) can be calculated from the flux of the blank experiment: P_{KA}(NPOE/water) = 6.7×10^{-7}.

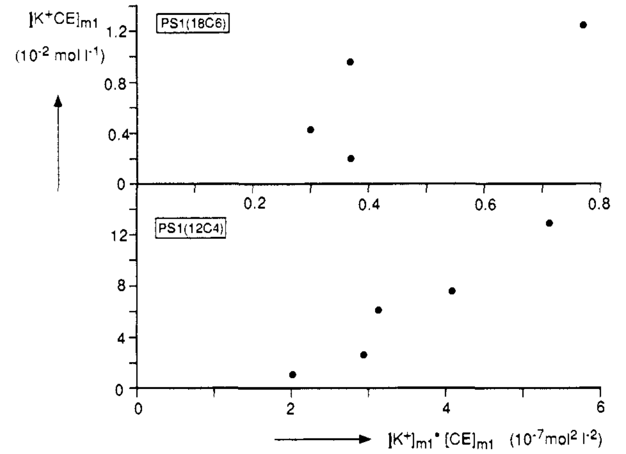

Figure 1. $[K^+CE]_{m1}$ vs $[K^+]_{m1}[CE]_{m1}$ for PS1(18C6) (**10**) and PS1(12C4) (**11**).

of the complex.[7] This means that at every position in the membrane the sum of complex and crown ether concentrations is constant. If we furthermore assume that the complex concentration in the membrane phase is considerably higher than the free salt concentration (vide infra) and that no carrier leaks out when the polysiloxane-coupled crown ethers are used, we can derive an expression for the complex concentration in the source interface $[K^+CE]_{m1}$ as a function of the initial crown ether concentration $[CE]^0_m$ (eq 5). According to eq 5 the relation between the complex

$$[K^+CE]_{m1} = \{-K_mP_{CE}[K^+]^0_{w1}{}^2 \pm [(K_mP_{CE}[K^+]^0_{w1}{}^2)^2 + 4K_mP_{CE}[K^+]^0_{w1}{}^2[CE]^0_m]^{1/2}\}/2 \quad (5)$$

$$K_m = \frac{[K^+CE]_m}{[K^+]_m[CE]_m} = \frac{[K^+CE]_{m1}}{[K^+]_{m1}[CE]_{m1}} \quad (6)$$

concentration (or the flux) and the initial carrier concentration should not be linear. According to the expression for the complexation constant K_m (eq 6), the relation between $[K^+CE]_{m1}$ and $[K^+]_{m1}[CE]_{m1}$ should go through the origin and be linear with a slope = K_m. These plots for PS1(18C6) and PS1(12C4) are shown in Figure 1. Since in both cases the results do not fit the predicted linear relation, this indicates that the transport does not take place via a 1:1 complex.

Assuming a 2:1 complex of carrier and salt results in other expressions for the complexation constant and for the complex concentration (eq 7 and 8). In case of 2:1 complexation there

$$[K^+CE_2]_{m1} = [CE]^0_m\left\{\frac{2b \pm \sqrt{b}}{4b - 1}\right\},\ b = K_{m2}P_{KA}[K^+]^0_{w1}{}^2 \quad (7)$$

$$K_{m2} = \frac{[K^+CE_2]_m}{[K^+]_m[CE]_m{}^2} = \frac{[K^+CE_2]_{m1}}{[K^+]_{m1}[CE]_{m1}{}^2} \quad (8)$$

should be a linear relation between the complex concentration (or the flux) and the initial carrier concentration. Figure 2, in which the flux is plotted versus the initial crown ether concentration, exhibits such a linear relationship for both carriers. The deviation at higher concentrations is probably due to a limited solubility of the carrier in the membrane phase. According to eq 8 a plot of $[K^+CE_2]_{m1}$ vs $[K^+]_{m1}[CE]_{m1}{}^2$ should give a linear relationship through the origin, and Figure 3 shows that the results reasonably fit this model for low carrier concentration.

It is surprising that our results strongly indicate a 2:1 complexation and not a 1:1 complexation because 18-crown-6 usually forms 1:1 complexes with potassium cations.[16] This might be due to the very low free salt concentration in the membrane and the relative large excess of crown ether present.[17] From Figure 3 the association constants of the complexes can be estimated from the slopes of the plots; the values are approximately 10^7 L^2 mol^{-2} (log K_{m2} = 7) for PS1(18C6) and 10^5 L^2 mol^{-2} (log K_{m2} = 5) for PS1(12C4).

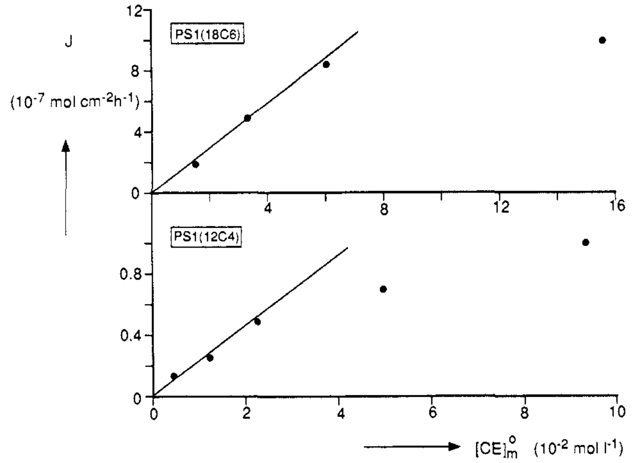

Figure 2. Flux of $KClO_4$ as function of the crown ether concentration in the membrane phase for PS1(18C6) (**10**) and PS1(12C4) (**11**). T = 25 °C.

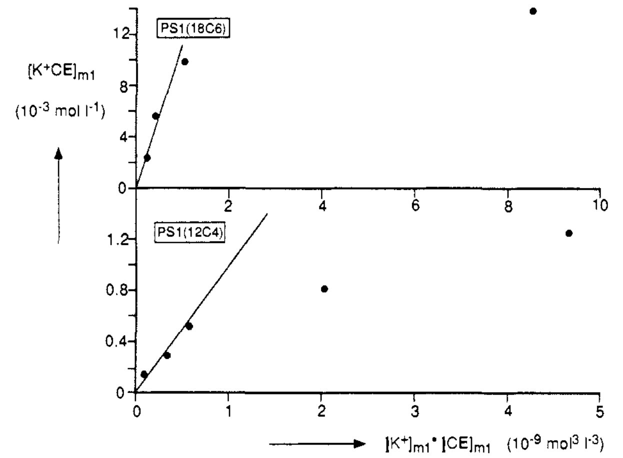

Figure 3. $[K^+CE_2]_{m1}$ vs $[K^+]_{m1}[CE]_{m1}{}^2$ for PS1(18C6) (**10**) and PS1(12C4) (**11**).

Influence of the Membrane Phase. Due to the limited solubility of the carriers in NPOE, it was not possible to increase the effective carrier concentration above 0.1 M. Assuming that the solubility of the polysiloxane-coupled carrier would be higher in a polysiloxane medium, experiments have been carried out with low molecular weight polysiloxane as the organic solvent and PS1(18C6) as the carrier. We observed a flux that was 10 times lower than the flux of a comparable membrane with NPOE as the membrane phase. Apparently the membrane phase has a great influence on the ion transport. This is in accordance with the model proposed previously which assumes thermodynamic equilibrium at the interfaces. Therefore, partition of the salt to the membrane phase plays a significant role in the transport process. If the partition coefficient of the salt is much lower in the case of the more apolar polysiloxane, this will result in a lower complex concentration and therefore a reduced flux.

Conclusions

Loss of carriers from the membrane phase of supported liquid membranes can successfully be reduced by the covalent attachment of the carriers to polysiloxanes. This improves the stability of the membrane system considerably. The contribution of one polysiloxane unit to log P_{CE} for the system NPOE/water is 0.6. This

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(16) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271-339.

(17) In a typical transport experiment the concentrations at the source phase interface are, for instance, $[K^+]_{m1} = 2.8 \times 10^{-6}$, $[CE]_{m1} = 1.0 \times 10^{-2}$, and $[K^+CE_2]_{m1} = 2.4 \times 10^{-3}$.

corresponds to log P_{CE} = 4.7 and 27 for PS1(18C6) and PS2(12C4), respectively.

The experimental data can be interpreted nicely by a model developed in our group recently. From this interpretation a 2:1 stoichiometry of the complexes in the membrane phase was deduced, for both 12-crown-4- and 18-crown-6-containing carriers.

Experimental Section

The ^{1}H NMR spectra were recorded with a Bruker WP-80 spectrometer with $(CH_3)_4Si$ or $CHCl_3$ as an internal standard.

Materials. The synthesis of (hydroxymethyl)-18-crown-6 (**8**) has been carried out according to known procedures.[18-20] (Hydroxymethyl)-12-crown-4 (**9**) was obtained from Janssen, dibenzo-18-crown-6 was from Merck Schuchardt, and both were used without further purification. *o*-Nitrophenyl *n*-octyl ether (Fluka) was distilled before use. Potassium perchlorate (Brocades) was used without purification. The polymeric film Accurel was obtained from Enka Membrana.

(4-Bromobutyl)chlorodimethylsilane (3). 4-Bromo-1-butene (6.0 g, 0.05 mol), chlorodimethylsilane (7.1 g, 0.075 mol), and the catalyst (10 μL of 0.1 M $H_2PtCl_6{\cdot}6H_2O$ in 2-propanol) were dissolved in 20 mL of toluene and stirred under nitrogen at 85 °C for 18 h. Toluene was evaporated under reduced pressure, and the residue was distilled at reduced pressure (34–36 °C at 2.3 mmHg). Yield 7.2 g (63%); ^{1}H NMR ($CDCl_3$) δ 3.4 (t, *J* = 6.5 Hz, 2 H, CH_2Br), 1.9 (quintet, *J* = 6.5 Hz, 2 H, CH_2CH_2Br), 1.8–1.3 (m, 2 H, $CH_2CH_2CH_2Br$), 1.0–0.7 (m, 2 H, SiH_2C), 0.4 (s, 6 H, SiH_3C).

4-Bromobutyl-Terminated Poly(dimethylsiloxanes) (6 and 7). (4-Bromobutyl)chlorodimethylsilane (**3**) (4.45 g, 19.4 mmol) was dissolved in 25 mL of petroleum ether (bp 60–80 °C) and added slowly to a stirred solution of the silanol-terminated siloxane (8.8 mmol) and *N*,*N*-diisopropylethylamine (1.14 g, 8.8 mmol) in 25 mL of petroleum ether under nitrogen atmosphere at 0 °C. Stirring was continued for 1 h. The solid salts were removed by filtration, and subsequently, the solvent was evaporated. The excess of chlorodimethylsilane was removed by distillation at reduced pressure (80–90 °C at 2.4 mmHg) to yield **6** and **7** (70–90%). ^{1}H NMR ($CDCl_3$) δ 3.4 (t, *J* = 6.5 Hz, 4 H, CH_2Br), 1.9 (quintet, *J* = 6.5 Hz, 4 H, CH_2CH_2Br), 1.8–1.3 (m, 4 H, $CH_2CH_2CH_2Br$), 0.7–0.4 (m, 4 H, $SiCH_2$), 0.1 (s, $SiCH_3$).

Crown Ether Terminated Poly(dimethylsiloxanes) (10–12). The hydroxymethyl crown ether (**8** or **9**) (4 mmol) was dissolved in 10 mL of dry THF, and 1.5 equiv of NaH, previously washed with petroleum ether (bp 60–80 °C), was added. While this solution was refluxed, a solution of 0.9 equiv of **6** or **7** in 15 mL of dry THF was added slowly. The reaction mixture was refluxed overnight. After quenching with ethanol, the solvent was evaporated. The residue was dissolved in $CHCl_3$, and the salts were removed by filtration. The filtrate was washed with H_2O and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 50–70%; ^{1}H NMR ($CDCl_3$) δ 3.8–3.2 (m, OCH_2), 1.8–1.0 (m, $CH_2CH_2CH_2$), 0.8–0.4 (m, $SiCH_2$), 0.1 (s, $SiCH_3$).

Apparatus. The permeation cell consisted of two identical cylindrical compartments (half-cell volume, 45 mL; effective membrane area, 9.8 cm^2). Each compartment contained four baffles, which are flat strips set radially along the wall of the compartments. The baffle width was one-tenth of the diameter of the cell. A flat-bladed turbine positioned at the center was driven by a magnet outside the compartment at a stirring rate of 1000 rpm. The use of baffles with turbine impellors secured a large top-to-bottom circulation, creating well-mixed solutions without significant concentration gradients. The diameter of the turbine was one-third of the diameter of the compartment. The compartment was double-walled for thermostating using a thermostated water bath (Tamson, TC). The membrane was positioned between the cylindrical compartments containing the two aqueous phases. The supported liquid membrane consisted of a solution of carrier in *o*-nitrophenyl *n*-octyl ether immobilized in a porous polypropylene film (Accurel; thickness, d_m = 100 μm; porosity, θ = 64%). A 0.1 M potassium perchlorate solution was used as the source phase, and doubly distilled and deionized water was used as the receiving phase. The amount of transported potassium perchlorate was determined by measuring the conductivity of the receiving phase (Philips PW 9527 conductivity meter and a Philips PW 9512/61 electrode with a cell constant of 0.74 cm^{-1}).

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Structure–Energy Relations for the Aldol Reaction in Nonpolar Media

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Abstract: A complete thermochemical analysis is presented for the aldol reaction of lithiopinacolonate with pivalaldehyde in hexane at 25 °C and in cyclohexane at 25 and 6 °C. Reactions were performed in the presence and absence of tetrahydrofuran, tetramethylethylenediamine, and dimethoxyethane. Solution structures of the reactants and products were determined by using colligative property techniques (vapor pressure osmometry and freezing point depression) to measure the degrees of aggregation and by using ^{6}Li and 2D ^{6}Li–^{1}H heteronuclear Overhauser enhancement (HOESY) NMR. Titration calorimetry was used to determine the heats of reaction of pivalaldehyde with the hexameric lithiopinacolonate, the tetrameric and dimeric enolate·ligand complexes, and heats of interaction of the hexameric enolate with the ligands. It is shown that the tetrameric lithium aldolate product does not complex with any of the three ligands in hydrocarbon solution. A complete description of experimental techniques is given, and most of the data have been confirmed by two complete and independent repetitions. However, attention is drawn to an erroneous, and presently unexplained value (ΔH_{rxn} = −30.19 kcal/mol) reported in our previous communication for the aldol reaction of the uncomplexed hexameric lithiopinacolonate with pivalaldehyde in hexane at 25 °C. To our knowledge, the present article is the first complete structure–energy analysis of an aldol reaction under conditions approaching those used in modern synthesis. The results emphasize the importance of caution in proposing detailed mechanisms for this important reaction.

Base-promoted reactions of carbonyl compounds and their nitrogen equivalents are by any accounting the most important class of modern synthetic reactions. Within this family, the aldol reaction has become one of the most powerful means for forming carbon–carbon bonds.[2] Although now over 150 years old,[3] it has only been since the early 1970s[4] that the aldol reaction has as-

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