

# Crown Ether Mediated Transport: A Kinetic Study of Potassium Perchlorate Transport through a Supported Liquid Membrane Containing Dibenzo-18-crown-6

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**Abstract:** The mechanism of facilitated membrane transport of salts through supported liquid membranes containing synthetic ionophores in *o*-nitrophenyl octyl ether has been studied with potassium perchlorate and dibenzo-18-crown-6. As a support the microporous polypropylene membranes Accurel and Celgard 2500 were tested. The diffusion of the crown ether and crown ether complex through the membrane phase depends only on the porosity of the membrane for Accurel and on the porosity as well as the tortuosity of the membrane for Celgard 2500. The transport rate is determined by diffusion of the crown ether complex through the membrane phase. Measurements of the flux as a function of the initial salt concentration show that the cation-crown ether complex and the anion are present in the membrane phase predominantly as free ions. The partition coefficient of dibenzo-18-crown-6 for the system *o*-nitrophenyl octyl ether/water has been determined to be  $1920 \pm 370$  but due to the large ratio of aqueous to membrane volume ( $V_w/V_m = 1200$ ), at equilibrium 40 mol % of the initial carrier concentration is present in the aqueous phases. From the effect of carrier concentration on the flux it was concluded that in the membrane an average fraction of crown ether of  $0.35 \pm 0.07$  is complexed to a cation.

Synthetic macrocyclic carriers are of interest for the selective extraction of ions and polar organic molecules from aqueous solutions. In order to mimic biological carriers the macrocycle must be selective for one type of guest or even for one configuration of the guest, e.g. (*R,S*)-amino acids.<sup>1</sup> Previously, the complexation behavior of synthetic carriers has been evaluated in our laboratory by single liquid-liquid extraction experiments<sup>2</sup> or by bulk liquid membrane transport experiments.<sup>3</sup> However, these systems required a large quantity of carrier solution in proportion to the interfacial area. This disadvantage can be redressed if supported liquid membranes are used. They consist of an organic carrier solution immobilized in a thin microporous film, separating the two aqueous phases. The organic layer is immobilized by capillary forces and surface tension. The organic solvent must be immiscible with water, nonvolatile, and inert to the support, must be able to solubilize the carrier and the complex, and must have a suitable polarity related to an optimal value of the association constant of the complex.

Our work on selective complexation and transportation is focused mainly on molecules such as urea and guanidine derivatives using synthetic macrocyclic receptor molecules.<sup>2-5</sup> The selective removal of urea from aqueous solutions by means of membranes with crown ethers as synthetic carriers would be of considerable importance in biomedical technology and in waste water treatment.

Supported liquid membranes might be useful for such technological applications.

Supported liquid membranes have been used to selectively remove copper ions from aqueous solutions.<sup>6</sup> Carriers previously tested include bathocuproine<sup>6a</sup>, 1-[2-hydroxy-5-(1,1,3,3-tetramethylbutyl)phenyl]ethanone oxime<sup>6b-f</sup>, and (2-hydroxy-5-nonylphenyl)phenylmethanone oxime.<sup>6b,g,h,i</sup> These carriers are soluble in water-immiscible solvents like toluene, xylene, *n*-dodecane, decalin, and paraffin. The copper ions are concentrated by proton-coupled transport (the oximes) or by a redox-potential difference (bathocuproine). More recently, Ohki<sup>6j</sup> used a tetradentate thioether (13,14-benzo-1,4,8,11-tetrathiacyclopentadecane) as a copper-selective carrier in a polymer-supported liquid membrane. Hitherto, the use of other synthetic macrocycles in supported liquid membranes is limited.<sup>7-10</sup> Reusch and Cussler<sup>10</sup> studied selective transport of various cations across a membrane which consisted of a solution of dibenzo-18-crown-6 in chloroform held by capillary action in a piece of filter paper. Such membranes were not very stable. However, to the best of our knowledge, kinetic studies of crown ether mediated transport through polymer-supported liquid membranes have not been reported.

In this paper we report the kinetics of the transport of potassium perchlorate by crown ethers in a polymer-supported liquid membrane. A choice of the membrane system was made based on both the effect of the support geometry on the flux and the stability of the immobilized liquid membrane. A mathematical model for crown ether mediated transport has been derived by describing the supposed transport mechanism with mathematical equations using the mass balances for the crown ether, the cation, and the anion. This model was verified by changing the membrane

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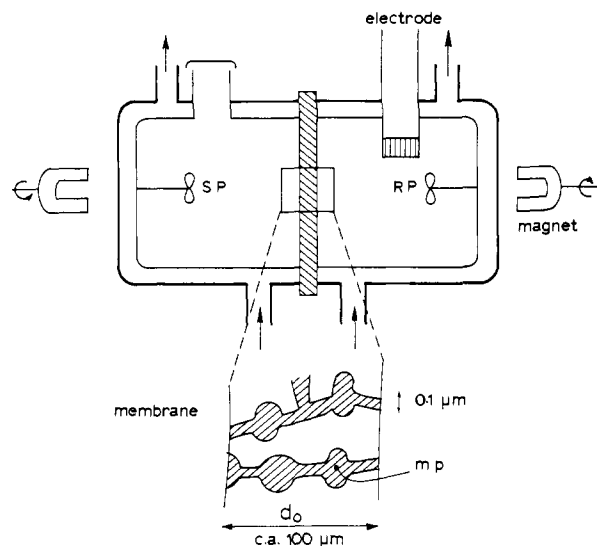
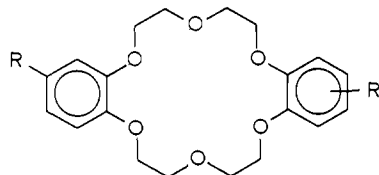


Figure 1. Measurement setup: sp = source phase, rp = receiving phase, mp = membrane phase,  $d_0$  = thickness of the support.

thickness to gain information about the rate-determining step of transport, the initial salt concentration to measure the influence of the polarity of the membrane phase on the transport rate, and the initial crown ether concentration to verify the stoichiometry of complexation and to calculate the average complexed fraction of the crown ether. The results may be of use for the development of separation processes in medical technology and waste water treatment.

### Experimental Section

**Materials.** Dibenzo-18-crown-6 (**1**) was obtained from Merck Schuchardt and was used without further purification. The functionalized crown ether **2**, 2,3:11,12-bis[4,4''(or 5'')-*n*-octadecanoylbenzo]-18-crown-6 was synthesized from **1** following literature procedures.<sup>11</sup> Crown ether **3**, 2,3:11,12-bis[4,4''(or 5'')-*n*-octadecanoylbenzo]-18-crown-6, was prepared by a Clemmensen reduction of **2**.<sup>12</sup> In both cases



1. R = H
2. R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>CO
3. R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>

the unseparated mixture of isomers was used. *o*-Nitrophenyl phenyl ether was prepared as described.<sup>13</sup> *o*-Nitrophenyl octyl ether (Fluka) was distilled before use. The other solvents, *o*-dichlorobenzene (Fluka), di-*n*-butyl phthalate (BDH), and 1-octanol (Fluka), as well as potassium perchlorate (Brocades) were used without purification. The polymeric film Accurel was obtained from Enka Membrana, and the polymeric film Celgard 2500 was from Celanese Plastics Co.

**Apparatus.** The transport experiments were carried out in a permeation cell, developed and constructed in our laboratory (Figure 1). The permeation cell consisted of two identical cylindrical compartments (half cell volume, 45 mL; effective membrane area, 9.8 cm<sup>2</sup>). 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 impellers secured a large top-to-bottom circulation, creating well-mixed solutions without signifi-

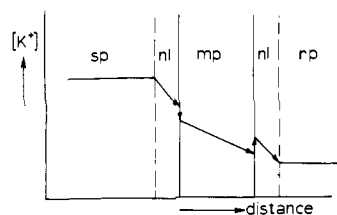


Figure 2. Idealized concentration profile of the cation as a function of the distance. Nernst layer = nl; see also Figure 1.

cant 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 two cylindrical compartments containing the two aqueous phases. The supported liquid membrane consisted of a thin microporous polypropylene film (Accurel or Celgard 2500), immobilizing the solution of crown ether in the organic solvent. A potassium perchlorate solution was used as the source phase and doubly distilled and deionized water was used as the receiving phase. The amount of potassium perchlorate transported through the membrane phase was monitored continuously 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<sup>-1</sup>).

**Immobilization of the Liquid Membrane into the Support.** The immobilized liquid consisted of a solution of crown ether in an organic solvent (*o*-dichlorobenzene, 1-octanol, di-*n*-butyl phthalate, *o*-nitrophenyl octyl ether, or *o*-nitrophenyl phenyl ether). The support (Accurel or Celgard 2500) was submerged in the crown ether solution under vacuum ( $2 \times 10^3$  Pa) in order to avoid air remaining in the pores. The pores were filled at room temperature by the action of capillary forces for all the organic solvents tested, except for *o*-nitrophenyl phenyl ether. In that case the solvent had to be warmed to 80 °C to facilitate immobilization. The superfluous organic solution at the outside of the support was removed by a jet of water from a siphon.

**Determination of the Partition Coefficient of Crown Ethers 1, 2, and 3 by Analyzing both the Receiving and Source Phases.** During the transport experiments the crown ether equilibrates inevitably between the membrane and the aqueous phase. For the determination of the crown ether concentration in the aqueous phase by UV spectroscopy (Varian Cary 17), it was necessary to concentrate the crown ether by the evaporation of water and dissolving the residue in a small volume of chloroform. Only carrier **1** could be analyzed ( $\lambda_{\max} = 278$  nm,  $\epsilon = 5.8 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) while the water solubility of the carriers **2** and **3** was too low for accurate detection ( $[2]_w$  and  $[3]_w$  were lower than  $10^{-7}$  M). The concentrations of crown ether in both the source and receiving phases were found to be almost equal. Therefore it was possible to neglect differences due to different potassium perchlorate concentrations. The partition coefficient of crown ether **1**,  $[I]/[1]_w = 1920 \pm 370$ , was calculated from the crown ether concentration in the aqueous phase. Crown ethers **2** and **3** have a partition coefficient greater than  $10^5$ .

### Theory of Supported Liquid Membrane Transport

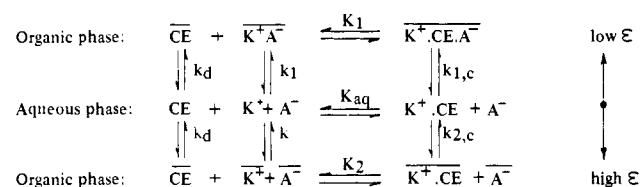
The transport of a salt through a supported liquid membrane is described with a concentration profile of the cation for both aqueous phases and the membrane phase in Figure 2. We assume that in the bulk of the source and receiving phases efficient mixing avoids concentration gradients. In a stagnant film (Nernst layer, with thickness  $d_a$ ) at both sides of the membrane phase mixing is not possible. The thickness of the stagnant film depends on the rate of stirring and will be minimal at a high stirring rate. When the transport in this layer is limited by diffusion, Fick's first law can be applied (eq 1). At the source phase/membrane phase interface the change of cation concentration is related linearly to the value of the phase-transfer coefficient (eq 2). In the membrane phase (thickness  $d_0$ ) the transport of the cation is determined by diffusion described by Fick's first law (eq 3). In this respect the transport of the cation through a supported liquid membrane differs from the transport through a bulk liquid membrane (U-tube type of experiments) where transport is affected by convection because the membrane phase is being stirred. As we have shown in our previous study,<sup>3</sup> the transport in the bulk liquid membrane is kinetically controlled by diffusion of the carrier/complex through the stagnant layer (water/chloroform) at the interface. Danesi et al.<sup>6c,f</sup> have shown that, when the partition of the permeating species at the interface between source

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## Scheme I



phase/membrane phase is much larger than at the interface between receiving phase/membrane phase, in a steady-state approximation the flux through the aqueous boundary layer, through the interfacial exchange reaction, and through the membrane phase must be equal to the overall flux (eq 4).

Diffusion through the aqueous boundary layer

$$J_a = (D_a/d_a)([\text{K}^+] - [\text{K}^+]_i) \quad (1)$$

Interfacial flux

$$J_b = k_1[\text{K}^+]_i - k_{-1}[\overline{\text{K}^+}] \quad (2)$$

Membrane diffusion

$$J_c = (D_0/d_0)[\overline{\text{K}^+}] \quad (3)$$

Steady-state flux

$$J = \frac{k_1[\text{K}^+]}{k_1d_a/D_a + k_{-1}d_0/D_0 + 1} \quad (4)$$

When the diffusion of the complex in the membrane phase is the rate-determining step the complex concentration is related to the flux by eq 3. This equation has been worked out in detail. The transport of the cation complex through the membrane phase is accompanied by an anion. Depending on the dielectric constant of the organic solvent the complexed cation and anion will form an ion pair (low  $\epsilon$ ) or will be present as free ions (high  $\epsilon$ ). Reusch and Cussler<sup>10</sup> as well as Lamb et al.<sup>14</sup> derived an equation for the flux of a salt through media of low  $\epsilon$ . In Scheme I the equilibria for complexation in both the organic phase and the aqueous phase as well as the equilibria for partition of the crown ether, the salt, and the complex between the organic and the aqueous phase are represented. From these equilibria the equation for the complex concentration in the organic phase will be derived and expressed in known or experimentally accessible data with the use of mass balances for the crown ether, the cation, and the anion. The expressions for the complex concentration in media of high and low  $\epsilon$ , respectively, are different. Hence, it will be possible to gain information about the existence of the cation-crown ether anion complex as an ion pair or as free ions. The complexation constant at low  $\epsilon$  is defined as in eq 5. In eq 6 the complexation constant in the organic phase is expressed as a function of the partition coefficients of the crown ether ( $k_d$ , eq 7), the salt ( $k_1$ , eq 8), and the complex ( $k_{1,c}$ , eq 9), respectively, and the complexation constant in the aqueous phase ( $K_{\text{aq}}$ , eq 10). In the mass balances for the crown ether (eq 11), the cation (eq 12), and the anion (eq 13) the different concentrations are multiplied by the volumes of the organic ( $V_m$ ) and of the aqueous phase ( $V_w$ ), respectively.

$$K_1 = \frac{[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}]}{[\overline{\text{K}^+\text{A}^-}][\overline{\text{CE}}]} \quad (5)$$

$$K_1 = (k_d k_1 K_{\text{aq}})/k_{1,c} \quad (6)$$

$$k_d = [\overline{\text{CE}}]/[\text{CE}] \quad (7)$$

$$k_1 = \{[\text{K}^+][\text{A}^-]\}/[\overline{\text{K}^+\text{A}^-}] \quad (8)$$

$$k_{1,c} = \{[\overline{\text{K}^+\text{CE}}][\overline{\text{A}^-}]\}/[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] \quad (9)$$

$$K_{\text{aq}} = [\text{K}^+\text{CE}]/\{[\text{K}^+][\text{CE}]\} \quad (10)$$

$$V_m[\overline{\text{CE}}] = V_m[\overline{\text{CE}}]^\circ - V_m[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] - V_w[\text{CE}] \quad (11)$$

$$V_{w,\text{sp}}[\text{K}^+]_{\text{sp}} = V_{w,\text{sp}}[\text{K}^+]^\circ_{\text{sp}} - V_m[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] - V_m[\overline{\text{K}^+\text{A}^-}] - V_{w,\text{rp}}[\text{K}^+]_{\text{rp}} - V_w[\text{K}^+\text{CE}] \quad (12)$$

$$V_{w,\text{sp}}[\text{A}^-]_{\text{sp}} = V_{w,\text{sp}}[\text{A}^-]^\circ_{\text{sp}} - V_m[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] - V_m[\overline{\text{K}^+\text{A}^-}] - V_{w,\text{rp}}[\text{A}^-]_{\text{rp}} \quad (13)$$

$$V_w = V_{w,\text{sp}} + V_{w,\text{rp}} \quad (14)$$

In eq 11  $[\overline{\text{CE}}]^\circ$  is the initial crown ether concentration in the organic phase and  $[\text{CE}]$  is the total crown ether concentration in the aqueous phase. In a bulk liquid membrane or in a single extraction experiment the transfer of crown ether from the organic to the aqueous phase is usually neglected because of a low partition coefficient of the crown ether and nearly the same volumes of the organic and aqueous phases. However, in supported liquid membranes the volume of the organic phase is much smaller than the volume of the aqueous phase. Equations 12<sup>15</sup> and 13<sup>15</sup> can be simplified to eq 15 and 16 since  $V_{w,\text{sp}}$  and  $V_{w,\text{rp}}$  are much greater

$$V_{w,\text{sp}}[\text{K}^+]_{\text{sp}} = V_{w,\text{sp}}[\text{K}^+]^\circ_{\text{sp}} \quad (15)$$

$$V_{w,\text{sp}}[\text{A}^-]_{\text{sp}} = V_{w,\text{sp}}[\text{A}^-]^\circ_{\text{sp}} \quad (16)$$

$$[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] = K_1[\overline{\text{K}^+\text{A}^-}]\{[\overline{\text{CE}}]^\circ - [\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] - [\text{CE}]V_w/V_m\} \quad (17)$$

$$[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] = (K_1/k_1)[\text{K}^+]^\circ_{\text{sp}}[\text{A}^-]^\circ_{\text{sp}}\{[\overline{\text{CE}}]^\circ - [\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] - [\text{CE}]V_w/V_m\} \quad (18)$$

$$[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}] = \frac{(K_1/k_1)[\text{K}^+]^\circ_{\text{sp}}[\text{A}^-]^\circ_{\text{sp}}}{1 + (K_1/k_1)[\text{K}^+]^\circ_{\text{sp}}[\text{A}^-]^\circ_{\text{sp}}}\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\} \quad (19)$$

than  $V_m$ ,  $[\text{K}^+]_{\text{sp}}$  and  $[\text{A}^-]_{\text{sp}}$  are much greater than  $[\text{K}^+\text{CE}]$ , and, if only a small fraction is transported,  $[\text{K}^+]_{\text{sp}}$  is much greater than  $[\text{K}^+]_{\text{rp}}$  and  $[\text{A}^-]_{\text{sp}}$  is much greater than  $[\text{A}^-]_{\text{rp}}$ . An expression for  $[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}]$  follows from eq 5, and substituting eq 11 leads to eq 17. The complex concentration is expressed in known or experimentally accessible data (eq 18) with the eq 6, 8, 15, and 16. Equation 18 is rewritten in eq 19. Equation 19 shows that the complex concentration is a function of both the cation and anion concentration. The complex concentration in an organic liquid with high  $\epsilon$  is derived analogously by using the mass balances (eq 11–14) in which  $[\overline{\text{K}^+\text{CE}\cdot\text{A}^-}]$  is replaced by  $[\overline{\text{K}^+\text{CE}}]$ . The expression for the association constant is given by eq 20 and 21,

$$K_2 = [\overline{\text{K}^+\text{CE}}]/\{[\overline{\text{K}^+}][\overline{\text{CE}}]\} \quad (20)$$

$$K_2 = (k_d k K_{\text{aq}})/k_{2,c} \quad (21)$$

$$k = \{[\text{K}^+][\text{A}^-]\}/\{[\overline{\text{K}^+}][\overline{\text{A}^-}]\} \quad (22)$$

$$k_2 = [\text{K}^+]/[\overline{\text{K}^+}] \quad (23)$$

$$k_3 = [\text{A}^-]/[\overline{\text{A}^-}] \quad (24)$$

$$[\overline{\text{K}^+\text{CE}}] = (K_2/k_2)[\text{K}^+]^\circ_{\text{sp}}\{[\overline{\text{CE}}]^\circ - [\overline{\text{K}^+\text{CE}}] - [\text{CE}]V_w/V_m\} \quad (25)$$

$$[\overline{\text{K}^+\text{CE}}] = \frac{(K_2/k_2)[\text{K}^+]^\circ_{\text{sp}}}{1 + (K_2/k_2)[\text{K}^+]^\circ_{\text{sp}}}\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\} \quad (26)$$

and the partition coefficient of the salt is given by eq 22. The latter is composed of two different independent partition coefficients,<sup>16</sup> viz., the partition coefficient of the cation ( $k_2$ , eq 23) and of the anion ( $k_3$ , eq 24). The complex concentration is expressed in known or experimentally accessible data (eq 25). Equation 25 is rewritten in eq 26. With eq 19 and 26 for the complex

(15)  $[\ ]^\circ$  means the initial concentration, and the subscripts sp and rp stand for source phase and receiving phase, respectively.

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**Table I.** Membrane Properties, Flux,<sup>a</sup> Normalized Flux, and Normalized Flux Corrected for Tortuosity

membrane	Accurel	Celgard 2500
thickness, <sup>b</sup> μm	100	25
porosity, vol %	64 <sup>c</sup>	45
pore diameter, μm	0.1	0.04
10 <sup>8</sup> J, mol cm <sup>-2</sup> h <sup>-1</sup>	24.9 ± 1.4	21.8 ± 1.1
10 <sup>8</sup> J <sub>n</sub> , mol cm <sup>-2</sup> h <sup>-1</sup> <sup>d</sup>	70.0 ± 3.9	21.8 ± 1.1
10 <sup>8</sup> J <sub>nc</sub> , mol cm <sup>-2</sup> h <sup>-1</sup> <sup>e</sup>	70.0 ± 3.9	75.0 ± 3.8

<sup>a</sup> [KClO<sub>4</sub>]<sup>o</sup><sub>sp</sub> = 10<sup>-1</sup> M; [1]<sup>o</sup> = 10<sup>-2</sup> M; T = 298 K. <sup>b</sup> The thickness of the membrane was taken equal to the thickness of the support; the thickness of the liquid film outside the filled membrane is neglected. <sup>c</sup> Measured in our laboratory. <sup>d</sup> J<sub>n</sub> is the normalized flux. <sup>e</sup> J<sub>nc</sub> is the normalized flux corrected for the tortuosity.

concentration, in media of low and high ε, respectively, it will be possible to gain information about the presence of the cation-crown ether anion complex as an intimate ion pair or as free ions. In these equations the dependence of the complex concentration as a function of the salt concentration is different; for free ions in the membrane phase the reciprocal complex concentration is proportional to the reciprocal salt concentration (1/[K<sup>+</sup>]<sup>o</sup><sub>sp</sub>) and for ion pairs in the membrane phase the reciprocal complex concentration is proportional to the square of the reciprocal salt concentration (1/[K<sup>+</sup>]<sup>o</sup><sub>sp</sub>[A<sup>-</sup>]<sup>o</sup><sub>sp</sub>). When the diffusion of the complex in the membrane phase is the rate-determining step (eq 3) the complex concentration is related to the flux by eq 27 or

$$J = \frac{D_0}{d_0} \overline{[K^+ \cdot CE \cdot A^-]} = \frac{D_0}{d_0} \frac{(K_1/k_1)[K^+]^o_{sp}[A^-]_o_{sp}}{1 + (K_1/k_1)[K^+]^o_{sp}[A^-]_o_{sp}} \{[\overline{CE}]^o - [CE]V_w/V_m\} \quad (27)$$

$$J = \frac{D_0}{d_0} \overline{[K^+ \cdot CE]} = \frac{D_0}{d_0} \frac{(K_2/k_2)[K^+]^o_{sp}}{1 + (K_2/k_2)[K^+]^o_{sp}} \{[\overline{CE}]^o - [CE]V_w/V_m\} \quad (28)$$

28. In the case of high crown ether concentrations it would be more correct to use activities. However, in our experiments crown ether concentrations are low, which justifies the use of concentrations. For the salt concentrations activity coefficients were used.

## Results and Discussion

**Effect of the Membrane System on the Flux.** The polypropylene membranes Accurel (A) and Celgard 2500 (B) were tested as the porous polymeric support of the organic phase. They differ in thickness, porosity, and pore size. The fluxes of potassium perchlorate through an immobilized phase of dibenzo-18-crown-6 (1) in *o*-nitrophenyl octyl ether (NPOE) were compared. The fluxes measured with Accurel (*J*<sub>A</sub>; membrane thickness *d*<sub>A</sub>, porosity θ<sub>A</sub>) were normalized (*J*<sub>n,A</sub>) to the thickness (*d*<sub>B</sub>) and porosity (θ<sub>B</sub>) of the Celgard 2500 membrane using eq 29.<sup>17</sup> When *J*<sub>n,A</sub> is com-

$$J_{n,A} = J_A \frac{d_A}{d_B} \frac{\theta_B}{\theta_A} \quad (29)$$

pared to *J*<sub>B</sub> (Table I), the value for Celgard 2500 is anomalously low. However, in the normalized flux the effects of the pore size and shape are not included. A factor τ is introduced to allow a correction for the fact that the diffusion path is greater than the distance perpendicular to the interface and for variation of cross sections of the pores, which cannot be considered as straight round tubes. This factor τ is called a tortuosity factor.<sup>18</sup> A value of 3.44 for τ has been suggested for a liquid membrane supported by a Celgard 2500 polymer.<sup>19</sup> In the case of Accurel τ is cal-

**Table II.** Flux of Potassium Perchlorate as a Function of Organic Liquids

solvent	10 <sup>8</sup> J, <sup>a</sup> mol cm <sup>-2</sup> h <sup>-1</sup>	η, <sup>b</sup> cP	ε <sup>b</sup>
<i>o</i> -dichlorobenzene	<i>c</i>	1.3	9.9 (25 °C)
1-octanol	<i>c</i>	7.6	10.3 (20 °C)
di- <i>n</i> -butyl phthalate	7.8 ± 0.2	15.4	6.1 (25 °C)
<i>o</i> -nitrophenyl octyl ether	24.9 ± 1.4	12.8	23.5 (25 °C)
<i>o</i> -nitrophenyl phenyl ether	38.4 ± 2.6	16.1	28.3 (25 °C)

<sup>a</sup> [KClO<sub>4</sub>]<sup>o</sup><sub>sp</sub> = 10<sup>-1</sup> M; [1]<sup>o</sup> = 10<sup>-2</sup> M; Accurel support; T = 298 K. <sup>b</sup> η = viscosity at T = 298 K and ε = dielectric constant from ref 21. <sup>c</sup> See text.

culated from {*D*<sub>0</sub>/(τ*d*<sub>0</sub>)} = (3.2 ± 0.5) × 10<sup>-5</sup>/θ cm s<sup>-1</sup> (vide infra) with *D*<sub>0</sub> = 4 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>.<sup>20</sup> The normalized fluxes have to be corrected for the tortuosity: τ(Celgard 2500) = 3.44; τ(Accurel) = 0.83 ± 0.13. However, τ must be at least 1, which means that the diffusion path length is equal to the membrane thickness. The new values of the normalized fluxes are also listed in Table I. With a correction for the tortuosity both normalized fluxes are nearly the same. For further experiments Accurel was chosen because the value of θ/τ is more favorable. The organic solvent in the membrane phase has to be water immiscible, nonvolatile, and inert to the support and has to be able to solubilize the carrier and the complex. The KClO<sub>4</sub> flux was measured for different organic solvents in the membrane phase in the presence of 1 (concentration: 10<sup>-2</sup> M) and with a 10<sup>-1</sup> M potassium perchlorate solution in the source phase. The value of the flux measured for each solvent, combined with some physical constants<sup>21</sup> (viscosity, dielectric constant), is shown in Table II. With *o*-dichlorobenzene, the equilibrium between the source phase and the receiving phase was reached within 24 h. However, the membrane without carrier also transported potassium perchlorate at a substantial rate; 10% of the initial salt concentration was transported within 24 h. After the end of an experiment the membrane was not completely transparent and this indicates dissolution of organic solvent into the aqueous phases. In 1-octanol, a well-known solvent in liquid-liquid extraction,<sup>22</sup> the required concentration of 1 could not be achieved. However, the plasticizers used in ion-selective electrodes, e.g. di-*n*-butyl phthalate,<sup>23</sup> *o*-nitrophenyl octyl ether (NPOE),<sup>24</sup> and *o*-nitrophenyl phenyl ether (NPPE),<sup>24</sup> gave membranes that remained transparent for more than 1 week. On the basis of the membrane stability and of the measured flux, NPOE was chosen as organic solvent for further kinetic studies.

**Rate-Determining Step in the Transport Mechanism.** According to eq 4 the steady-state flux should be a function of the interfacial reaction, the diffusion through the aqueous boundary layer at the interface between the source phase/membrane phase, and the membrane diffusion. For derivation of eq 27 and 28 it was assumed that the diffusion through the membrane phase was the rate-determining step. We have proven that this assumption is valid by measuring the flux as a function of membrane thickness. During this experiment the initial salt concentration in the source phase and the stirring rate in both aqueous phases were kept constant. The membrane thickness was varied by a factor *n* (*n* = 2, 3, 4, and 5). As a consequence, the membrane volume is changed by the same factor *n*. The effective crown ether concentration in the membrane phase (eq 27 and 28) depends on *n* and is described as {[CE]<sup>o</sup> - [CE]V<sub>w</sub>/*n*V<sub>m</sub>}. In Figure 3 the observed flux, corrected for the effective crown ether concentration, is displayed as a function of the reciprocal membrane thickness

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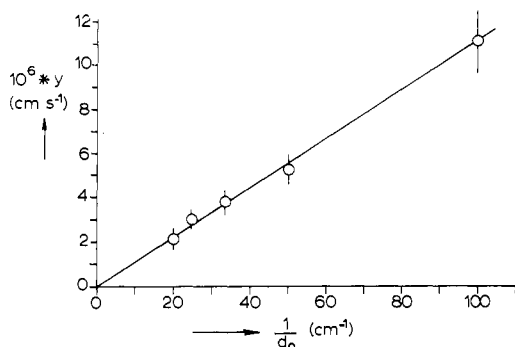


Figure 3. Plot of  $J/([\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m)/d_0J (=y)$  vs reciprocal membrane thickness.  $[\text{KClO}_4]_{\text{sp}}^\circ = 10^{-1}$  M;  $[\mathbf{1}]^\circ = 10^{-2}$  M; Accurel support;  $T = 298$  K.

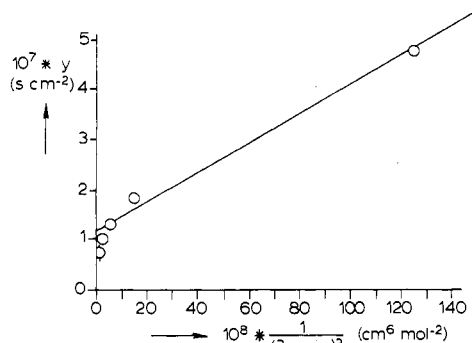


Figure 4. Plot of  $\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\}/d_0J (=y)$  vs  $1/(a_{\text{KClO}_4})^2$  corresponding to eq 30.  $[\mathbf{1}]^\circ = 5 \times 10^{-3} - 15 \times 10^{-3}$  M;  $d_0 = 100-400$   $\mu\text{m}$ ; Accurel support;  $T = 298$  K.

(compare eq 3). The observed linear relationship leads to the conclusion that the transport rate is determined by diffusion of the complex through the membrane phase. Therefore, the interfacial flux and the diffusion through the aqueous boundary layers must be fast compared to membrane diffusion. In eq 3  $[\text{K}^+]$  is determined predominantly by the complex concentration since the flux is corrected for passive transport (diffusion of potassium perchlorate in the absence of  $\mathbf{1}$ ).

**Nature of the Salt-Crown Ether Complex in the Membrane Phase.** Our interest in the mechanism of transport prompted us to measure the flux as a function of the initial salt concentration because by comparing eq 27 and 28 one can distinguish between the cation complex and the paired anion (eq 27) or the cation complex and the free anion (eq 28). When eq 27 and 28 were transformed into eq 30 and 31, respectively, the left-hand term is represented as a function of the square of the reciprocal activity of the salt (eq 30) or the reciprocal activity of the salt (eq 31).

$$\frac{\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\}}{d_0J} = \frac{1}{D_0} + \frac{1}{D_0} \frac{k_1}{K_1} \frac{1}{a_{\text{K}^+} a_{\text{ClO}_4^-}} \quad (30)$$

$$\frac{\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\}}{d_0J} = \frac{1}{D_0} + \frac{1}{D_0} \frac{k_2}{K_2} \frac{1}{a_{\text{K}^+}} \quad (31)$$

This difference in dependency discriminates between the two mechanisms. The intercept and the slope are independent values and the left-hand term can be calculated when the values of  $[\text{CE}]$  and  $V_w/V_m$  are known. Shchori et al.<sup>25</sup> reported that the solubility of  $\mathbf{1}$  in water is  $1.3 \times 10^{-5}$  M. However, the partition of the crown ether between the organic phase and the aqueous phase is important. Experiments showed that the ratio of  $[\mathbf{1}]^\circ/[\mathbf{1}]_w$  is  $1920 \pm 370$ . This means that the  $[\mathbf{1}]^\circ$  in the membrane phase is lowered by about 40 mol % when  $V_m = 0.075$  mL and  $V_w = 90.0$  mL (see Experimental Section). The  $[\mathbf{1}]_w$  at equilibrium is a factor

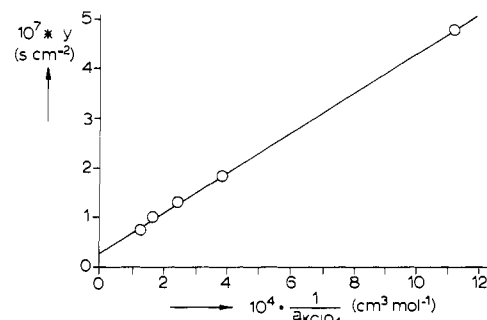


Figure 5. Plot of  $\{[\overline{\text{CE}}]^\circ - [\text{CE}]V_w/V_m\}/d_0J (=y)$  vs  $1/a_{\text{KClO}_4}$  corresponding to eq 31.  $[\mathbf{1}]^\circ = 5 \times 10^{-3} - 15 \times 10^{-3}$  M;  $d_0 = 100-400$   $\mu\text{m}$ ; Accurel support;  $T = 298$  K.

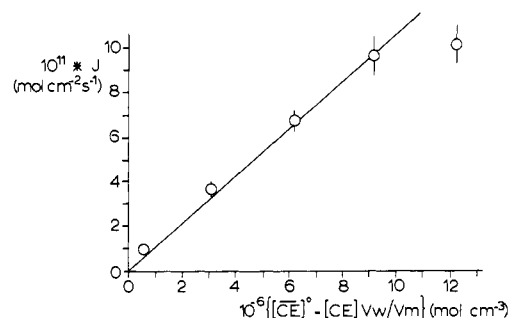


Figure 6. Flux vs crown ether concentration in the membrane phase at equilibrium.  $[\text{KClO}_4]_{\text{sp}}^\circ = 10^{-1}$  M; Accurel support;  $T = 298$  K.

4 lower than  $[\mathbf{1}]_w = 1.3 \times 10^{-5}$  M at saturation. In Figures 4 and 5 the measured fluxes are displayed according to eq 30 and 31. The flux was measured as a function of the salt activity for different crown ether concentrations and membrane thicknesses. In Figure 4 the average value of the left-hand term had a poor proportionality with  $1/(a_{\text{KClO}_4})^2$ : the value of the linear regression coefficient  $r$  is 0.977 (least-squares analysis). The correlation between the average value of the left-hand term and  $1/a_{\text{KClO}_4}$  (Figure 5) was much better:  $r = 0.999$ . From these results it is concluded that the cation complex and the anion stayed mainly as free ions in the membrane phase. The presence of free ions in the membrane phase is a consequence of the value of the dielectric constant of NPOE ( $\epsilon = 23.5$ ).<sup>21</sup>

The intercept and the slope of Figure 5 correspond to  $1/D_0$  and  $1/D_0(k_2/K_2)$ , respectively.  $D_0$ , the effective diffusion coefficient, is equal to  $(3.2 \pm 0.5) \times 10^{-7}$   $\text{cm}^2 \text{s}^{-1}$ , and  $k_2/K_2$  is equal to  $(1.3 \pm 0.2) \times 10^{-4}$   $\text{mol cm}^{-3}$ .

Variation of the initial crown ether concentration shows a linear relationship between the flux and the crown ether concentration in the membrane phase at equilibrium for low crown ether concentrations (Figure 6). This result is in agreement with the supposed 1:1 complexation (Scheme I) between the cation and the crown ether. The slope is equal to  $D_0/d_0\{(K_2/k_2)[\text{K}^+]_{\text{sp}}^\circ/(1 + (K_2/k_2)[\text{K}^+]_{\text{sp}}^\circ)\}$  and must be constant according to eq 28. However, for high crown ether concentrations some deviation is observed. Probably the diffusion coefficient decreases because the viscosity of the solution at high crown ether concentration increases. From the slope the average complexed fraction of the crown ether was calculated:

$$\frac{(K_2/k_2)a_{\text{KClO}_4}}{1 + (K_2/k_2)a_{\text{KClO}_4}} = 0.35 \pm 0.07$$

For a high value of  $K_2/k_2$  the complexed fraction will be equal to 1, which means complete complexation at the source phase/membrane phase interface. In this case no decomplexation takes place at the other interface and no transport will be measured.

**Variation of the Structure of the Crown Ether Carrier.** In order to enlarge the hydrophobicity of  $\mathbf{1}$  the more lipophilic crown ethers  $\mathbf{2}$  and  $\mathbf{3}$  were synthesized. The concentration of  $\mathbf{2}$  and  $\mathbf{3}$  in the aqueous phase was found to be below  $10^{-7}$  M, resulting in a

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**Table III.** Flux of Potassium Perchlorate for Functionalized Dibenzo-18-crown-6

carrier	$10^8 J, ^a \text{ mol cm}^{-2} \text{ h}^{-1}$
1	$24.9 \pm 1.4$
2	$20.4 \pm 0.6$
3	$8.3 \pm 0.9$

<sup>a</sup>  $[\text{KClO}_4]_{\text{sp}} = 10^{-1} \text{ M}$ ;  $[\text{carrier}] = 10^{-2} \text{ M}$ ; Accurel support;  $T = 298 \text{ K}$ .

partition coefficient of the crown ether between organic and aqueous phase greater than  $10^5$ . The flux of potassium perchlorate across the membrane was measured for each of the crown ethers and the data are listed in Table III. The introduction of two acyl substituents lowers the flux despite a higher effective crown ether concentration in the membrane phase. Because the transport is determined by diffusion through the membrane phase (vide supra) the diminution of the flux is caused substantially by a lower value of the diffusion coefficient of **2**.<sup>26</sup> The difference in flux between **2** and **3** is great, while the difference in structure is small. The acyl substituent attached to the aryl ring diminishes the partition coefficient in contrast with the alkyl substituent,<sup>28</sup> resulting in

(26) Besides the diffusion coefficient also the complexation constant will influence the flux. Ungaro<sup>27</sup> has measured substituent effects on the stability of cation complexes of 4'-substituted monobenzo crown ethers in acetone. He found that the stabilities of complexes of  $\text{Na}^+$  with benzo-15-crown-5 ( $\log K(\text{Na}^+) = 3.54$ ) and of  $\text{K}^+$  with benzo-18-crown-6 ( $\log K(\text{K}^+) = 5.10$ ), respectively, decreased with a formyl substituent (4'-formylbenzo-15-crown-5,  $\log K(\text{Na}^+) = 3.05$ ; 4'-formylbenzo-18-crown-6,  $\log K(\text{K}^+) = 4.89$ ). A lower value of the complexation constant is related to a lower flux, but the effect is too small for a complete explanation.

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a better interaction with the water molecules at the interface as well as a higher complex concentration. Therefore, we suggest that when the lipophilic character of the carrier is too pronounced, the transport is no longer limited by diffusion through the membrane phase but by complex formation at the interface between the source phase/membrane phase.

### Conclusions

For the system investigated in this study the transport of potassium perchlorate through the membrane is determined by the diffusion of the complex through the membrane phase. In the membrane phase the cation complex and the anion are present as free ions, which was ascribed to the high value of the dielectric constant. The values of the effective diffusion coefficient  $D_0$  and the complexed fraction of the crown ether are  $(3.2 \pm 0.5) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  and  $0.35 \pm 0.07$ , respectively. The diffusion of the crown ether through the membrane phase is dependent on the support and is influenced only by the porosity of the membrane for Accurel or by the porosity as well as the tortuosity of the membrane for Celgard 2500. The partition coefficient of the carrier is very important in these systems; the effective concentration of **1** in the membrane phase is reduced by 40 mol % of the initial crown ether concentration by dissolution in the aqueous phases.

**Registry No.** **1**, 14187-32-7;  $\text{KClO}_4$ , 7778-74-7; Accurel, 9002-88-4; Celgard 2500, 9003-07-0; polypropylene, 9003-07-0; *o*-nitrophenyl octyl ether, 37682-29-4.

(28) The effect of the carbonyl substituent on the partition coefficient can be demonstrated by comparison of ethylbenzene with acetophenone for the system 1-octanol/water:<sup>22</sup>  $\log P(\text{ethylbenzene}) = 3.13$  and  $\log P(\text{acetophenone}) = 1.70$ .

## Supramolecular Catalysis of Phosphoryl Transfer: Pyrophosphate Synthesis from Acetyl Phosphate Mediated by Macrocyclic Polyamines<sup>†</sup>

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**Abstract:** The macrocyclic polyamine [24]- $\text{N}_6\text{O}_2$  (**1**) catalyzes the hydrolysis of acetyl phosphate (AcP) to orthophosphate (P) and the synthesis of pyrophosphate (PP) from an intermediate 1-PN and P. The course of these reactions was monitored by <sup>31</sup>P NMR spectroscopy, which revealed the formation of PP and of an intermediate which was identified as the monophosphorylated macrocycle 1-PN by <sup>1</sup>H and <sup>31</sup>P NMR studies. The rate of 1-PN disappearance was first order and decreased with increasing pH of the solution. The first-order rate constants on AcP consumption showed a maximum at pH 7 with an acceleration factor of about 5 at 40 °C. In the presence of an excess of compound **1**, a rate saturation was observed at pH 7. With an excess of AcP, compound **1** reacted until all AcP was consumed, indicating that the process was catalytic. Addition of competitive anions such as  $\text{AMP}^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HPO}_4^{2-}$  retarded both AcP consumption and 1-PN formation and decreased the yield of PP, except for P, which increased markedly the amount of PP generated. The formation of PP probably involves precomplexation of P by the 1-PN intermediate followed by an intramolecular phosphoryl transfer from PN to P. The mechanism of PP synthesis was analyzed by <sup>18</sup>O-labeling, inhibition, and saturation experiments. The ditopic receptor molecule **1** performs a process of *cocatalysis* in which its two subunits cooperate for bringing together reagents and inducing bond formation. It provides at the molecular level conditions suitable for PP synthesis by binding AcP and mediating two phosphoryl transfers from AcP to **1**, giving 1-PN, and then from 1-PN to P. Studies of 11 related macrocyclic polyamines **2**–**12** allow analysis of structural effects on the rates and products of the AcP reaction. They indicate that both amine basicity and geometry effects operate; PN formation is more influenced by the former, whereas PP generation depends on both and is much more sensitive to structural variations.

Reactivity and catalysis represent major features of the functional properties of supramolecular systems.<sup>1-4</sup> Molecular receptors bearing appropriate functional groups may bind selectively a substrate, react with it, and release the products. Supramolecular reactivity and catalysis thus involve two main steps: *recognition* of the substrate, followed by *transformation* of the bound species

into products. The design of efficient and selective molecular catalysts may give mechanistic insight into the elementary steps

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<sup>†</sup> Dedicated to the memory of Professor Iwao Tabushi.