

Kinetic versus Diffusion Control in Carrier-Mediated Cotransport of Alkali Cations through Supported Liquid Membranes

E. G. Reichwein-Buitenhuis, H. C. Visser, F. de Jong, and D. N. Reinhoudt*

Contribution from the Department of Organic Chemistry, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract: Usually, the rate-limiting step of alkali cation transport through supported liquid membranes (SLM) mediated by neutral carriers is the diffusion of the carrier cation complex through the membrane. However, in this study, it is demonstrated that some macrocyclic carriers like calix[4]arene crown ethers and calixspherands show such slow kinetics of decomplexation that the release of salt from the membrane strongly affects the transport rates. The influence of rates of decomplexation on alkali cation transport can be described by a simple mathematical model. Data for the rate-limiting steps in the transport process have been obtained from maximum fluxes, lag-time measurements, temperature variation, and membrane permeation experiments with dyes. The relative contributions of diffusive and kinetic resistances inside the SLM were determined by variation of the membrane thickness. When kinetics of release are relatively slow, the transport selectivity (K^+/Na^+) is lower than in the transport regime of diffusion limitation.

Introduction

The transport of alkali cations through supported liquid membranes (SLM) mediated by neutral carriers can be regarded as a sequential process including phase transfer of salt, complexation/decomplexation, and diffusion steps as schematically depicted in Figure 1. In the case that phase transfer and complexation/decomplexation processes are fast, the transport through the SLM is limited by diffusion of the carrier cation complex through the membrane. A model describing diffusion-limited transport has been reported by us before.¹ This model, in which the extraction constant K_{ex} , being the product of the salt partition constant K_p and the cation/carrier association constant K_a , and the diffusion coefficient of the complex (D_m) are the basic parameters, has been successfully applied to predict alkali cation initial fluxes in single cations and the selectivities in competition transport experiments.²

In 1985, Lehn *et al.*³ and Fyles⁴ addressed theoretically the influence of slow rates of alkali cation release on transport through chloroform *bulk liquid membranes* (BLM). However, in practice, this phenomenon has only been observed by Yoshida and Hayano,⁵ who showed that the transport of $KClO_4$ mediated by polynactin through a BLM was indeed limited by the rate of cation release from the membrane. In a recent article⁶ Echegoyen *et al.* clearly stated that the rate of (alkali) cation release from the complex could never be rate-limiting because of the relatively large membrane thicknesses of SLMs and BLMs.

Several kinetic studies have been carried out on carrier-mediated counter-transport through SLMs. However, in these cases, uptake and release occur according to an *ion-exchange*

mechanism. Anionic carriers such as oximes^{7–9} have been used in the transport of Cu^{2+} , and phosphoric acid derivatives, in the transport of bivalent cations of Cu,¹⁰ Co,¹¹ Mn,¹² and Zn.¹³ In these systems, the transport regimes have been investigated by variation of, for example, stirring speed and membrane thickness in order to elucidate the contributions of diffusional resistance of the membrane to the overall transport resistance.¹⁴ The residual resistance often is attributed entirely to the diffusion through the stagnant aqueous layers outside the support.^{15,16} In some cases, the temperature has been varied in order to determine activation energies (E_a) of transport from Arrhenius plots. E_a values below ca. 20 $kJ \cdot mol^{-1}$ are generally accepted as indicative of pure diffusion-limited transport¹⁷ while higher values, up to about 80 $kJ \cdot mol^{-1}$, are characteristic for kinetic control.¹⁸

From ¹H NMR studies, we have found that the decomplexation rates of the 1,3-diethoxycalix[4]arene crown-5 fixed in the partial cone conformation (2) and calixspherand 7 (Chart 1) with potassium ions are extremely low,^{19,20} and this prompted us to investigate their transport kinetics in SLMs. Because of

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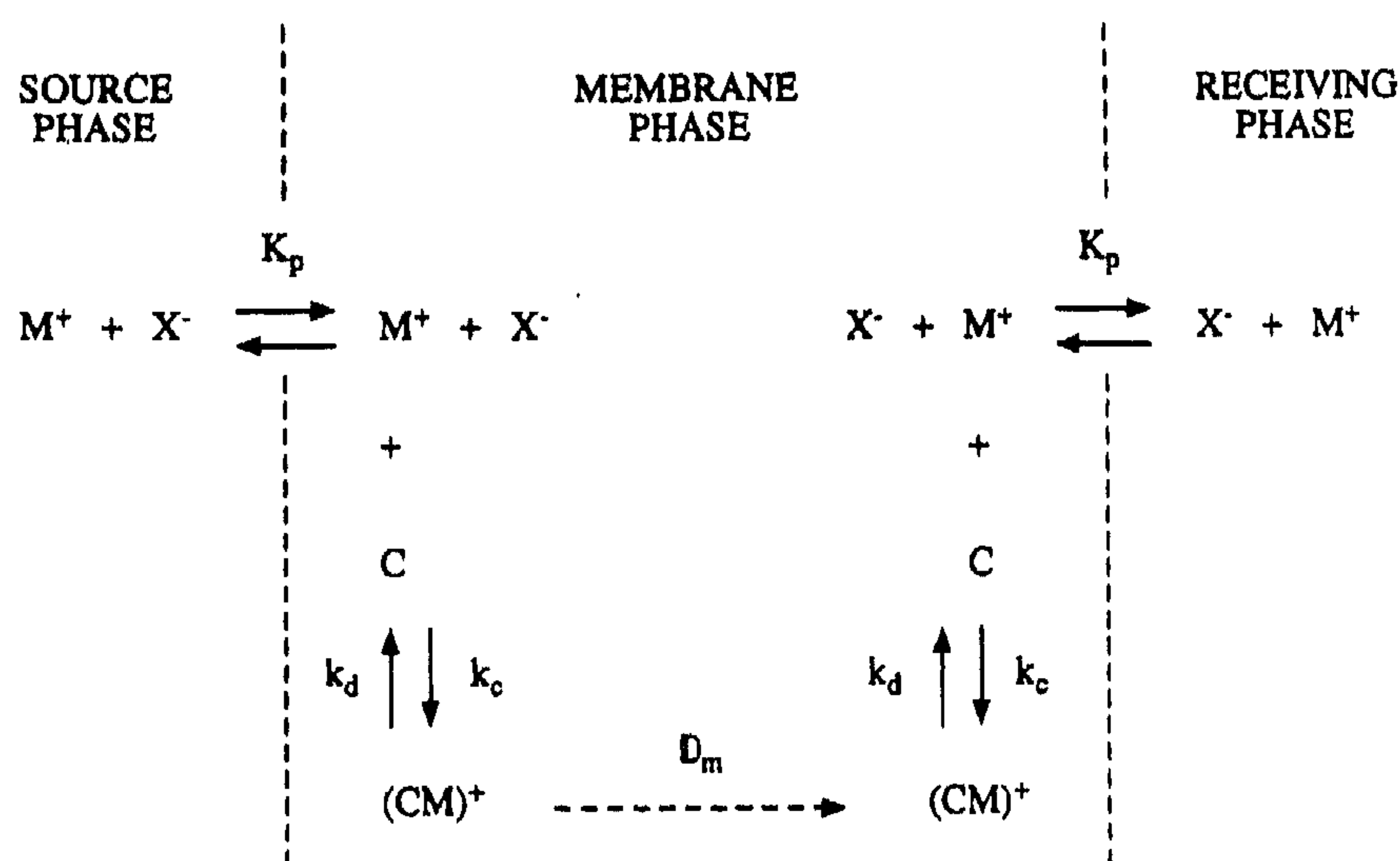


Figure 1. Successive steps in cation carrier-mediated salt transport through a SLM.

the unexpected low diffusion constant that we found previously² for the K^+ transport by 1,3-dimethoxycalix[4]arene crown-5 (1), compared to the corresponding 1,3-diethoxycalix[4]arene crown-5 fixed in the cone conformation (3), the transport kinetics of these carrier cation combinations were investigated as well. The calix[4]arene tetraester (4) was used as reference compound, since we have previously demonstrated that the transport of Na^+ with 4 is diffusion limited.²¹ In order to reveal the transport resistances, our previous transport model had to be adjusted to describe diffusion as well as decomplexation rate-limited transport (*vide infra*). In our study the effects of stirring speed and membrane thickness and/or operating temperature on salt transport were investigated. Furthermore, lag-time measurements and permeation experiments with dyes (5 and 6) were carried out to illustrate the role of diffusion in the overall transport process. Finally, the effect of slow decomplexation on transport selectivity is discussed.

In this paper, we will show from transport experiments with neutral macrocyclic carriers that *slow kinetics of alkali cation decomplexation can be the rate-limiting step, also in SLMs*. To the best of our knowledge and according to the recent paper by Echegoyen *et al.*,⁶ this is the first report in which slow kinetics of release are indeed experimentally found in transport through SLMs using *neutral carriers*.

Initial Rates of Transport

Previously we have published a model describing monovalent salt transport mediated by a carrier that complexes cations in a 1:1 carrier:cation stoichiometry.¹ In this model, it was assumed that diffusion of the carrier cation complex is the rate-limiting step of transport and only free ions are present in the membrane phase. A more general transport model, also including the rate of cation release, is derived in Appendix 1. According to this model, the flux is described by eq 1, in which D_m is the apparent

$$J = \frac{D_m}{2d_m} \left\{ \frac{-A + \sqrt{A^2 + 4AL_0 \frac{(1+2\alpha)}{(1+\alpha)}}}{1+2\alpha} \right\} \quad (1)$$

diffusion constant of the complex, d_m represents the membrane

thickness, L_0 denotes the total carrier concentration in the membrane, and α is defined as $D_m/kd_m\theta$, a dimensionless number, in which k is the rate of release at the membrane-water interface and θ is the porosity of the membrane. The extraction constant (K_{ex}) and the source phase salt activity (a_s) are incorporated in A , defined as $A = K_{ex}a_s^2$.

The basic transport parameters in this model are D_m , K_{ex} , and α . When the transport is purely diffusion limited ($\alpha \rightarrow 0$), D_m and K_{ex} can be obtained from measurements of the flux as a function of a_s .¹ In principle, all three parameters can be determined by variation of a_s and d_m , although from eq 1 the experimental procedure for this is not evident. However, a special case arises when the carriers at the source phase interface become completely loaded by cations, i.e. at high source phase salt concentration and consequently a large value of A . In this case, the maximum flux (J_{max}) is obtained and eq 1 can be simplified to eq 2. The first term describes the diffusion-limited flux, while the second is a correction for slow kinetics of release.

$$J_{max} = \left(\frac{D_m}{d_m} L_0 \right) \left(\frac{1}{1+\alpha} \right) \quad (2)$$

In order to find the value of α , independent methods are required to determine D_m and/or k . Two methods will be described, *viz.* (i) determination of diffusion constants from lag-time measurements and (ii) direct determination of k and D_m from flux measurements as a function of membrane thickness.

The lag time (t_{lag}) is defined as the time required for the complex to diffuse through the membrane²²⁻²⁴ (eq 3). The

$$D_{lag} = \frac{d_m^2}{6t_{lag}} \quad (3)$$

diffusion constant (D_{lag}) obtained from the lag-time experiments can be compared to the diffusion constant from steady state transport after correction for the porosity (θ) of the support ($D_m = \theta D_{lag}$). By combining this with eq 2, an expression for α is obtained in terms of J_{max} and D_{lag} (eq 4).

Furthermore, the diffusional and kinetic terms can be separated by rewriting them in the form of transport resistances, as in eq 5. A plot of L_0/J_{max} versus d can be used to obtain D_m

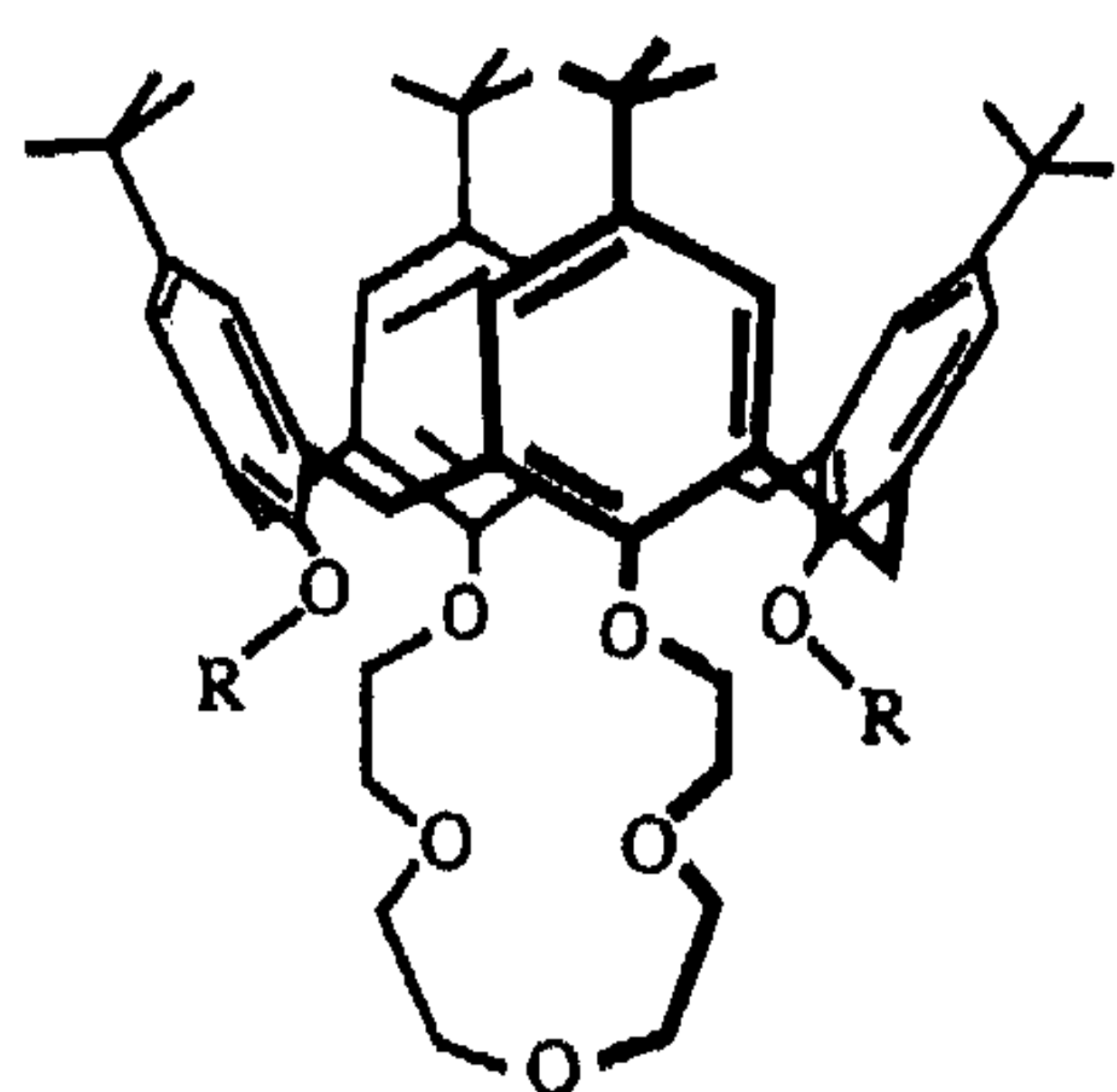
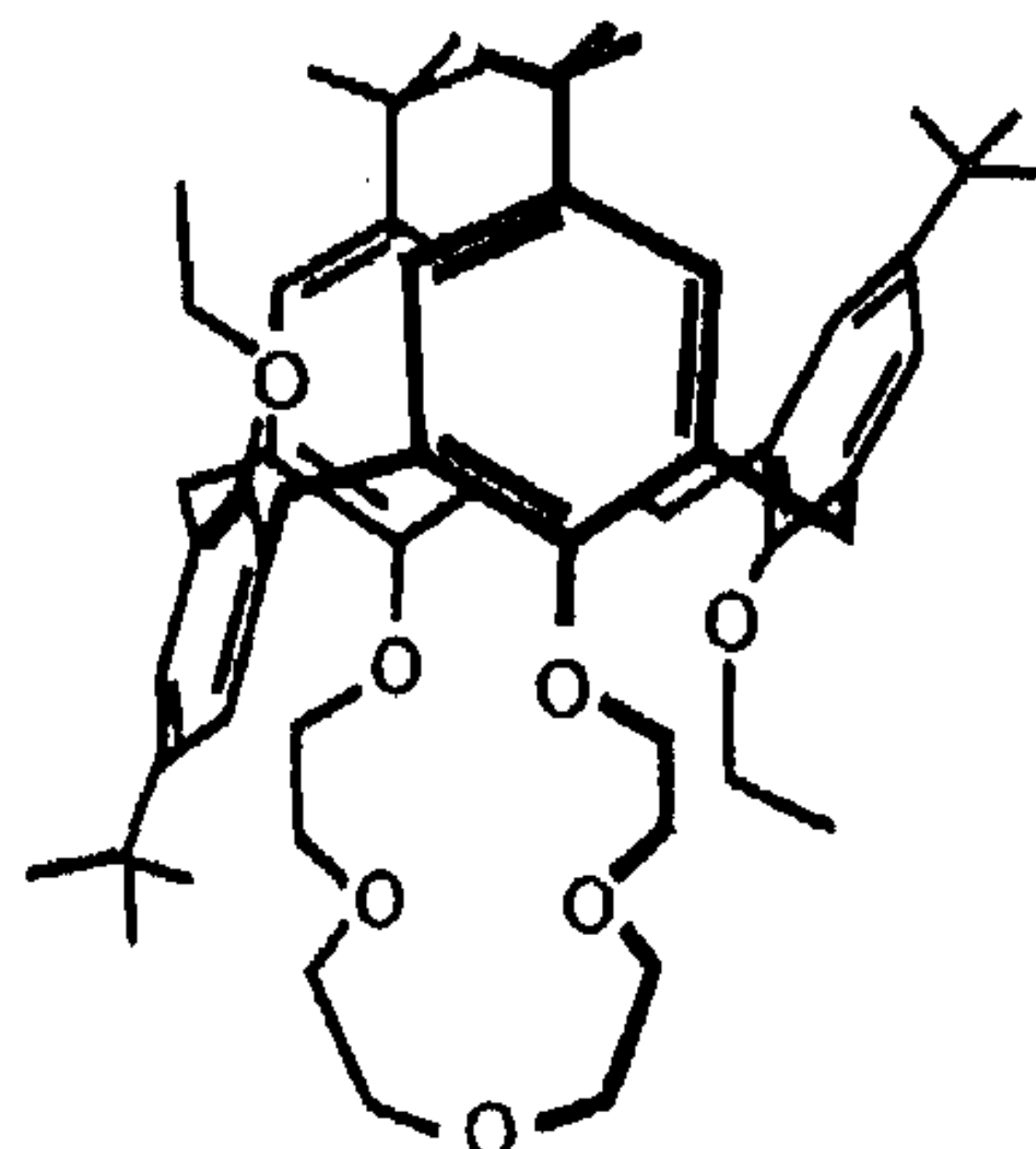
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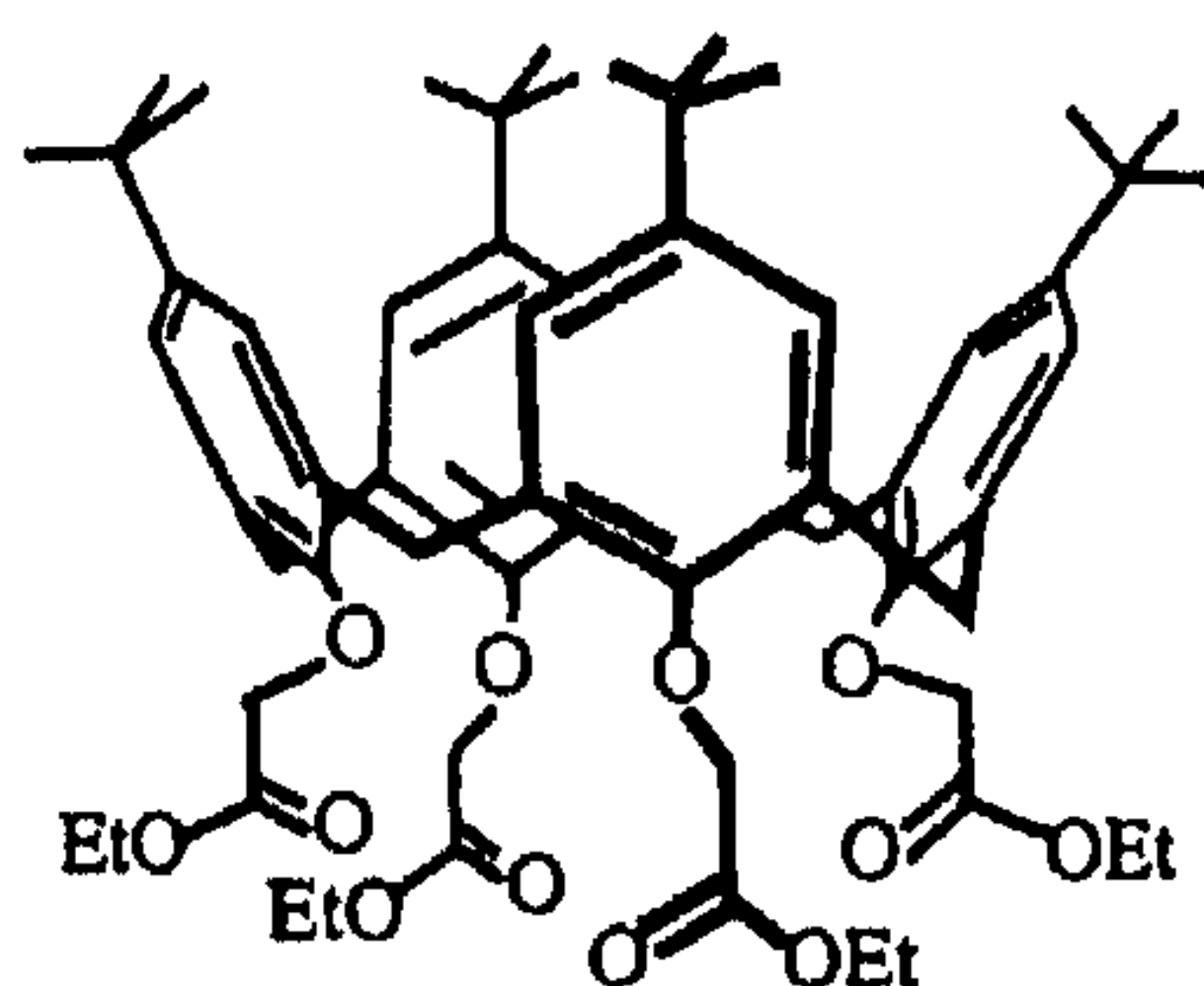
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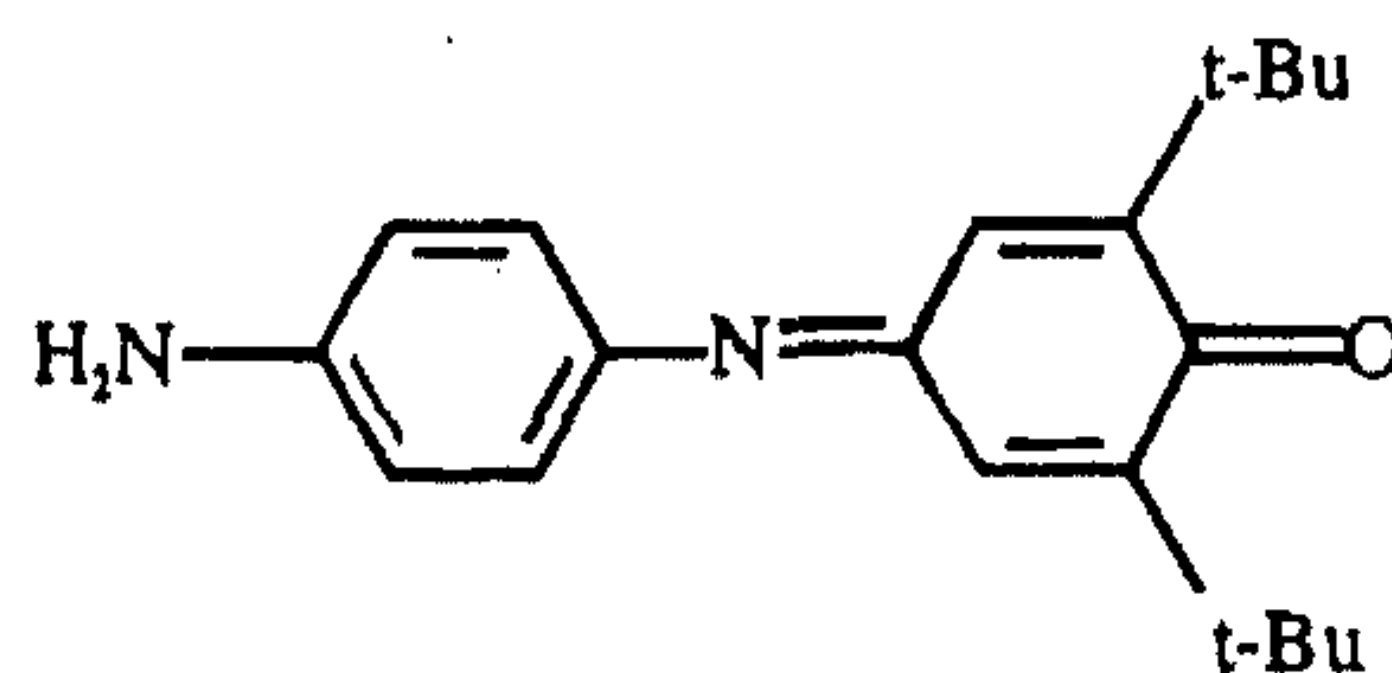
Chart 1

1: R=CH₃3: R=CH₂CH₃

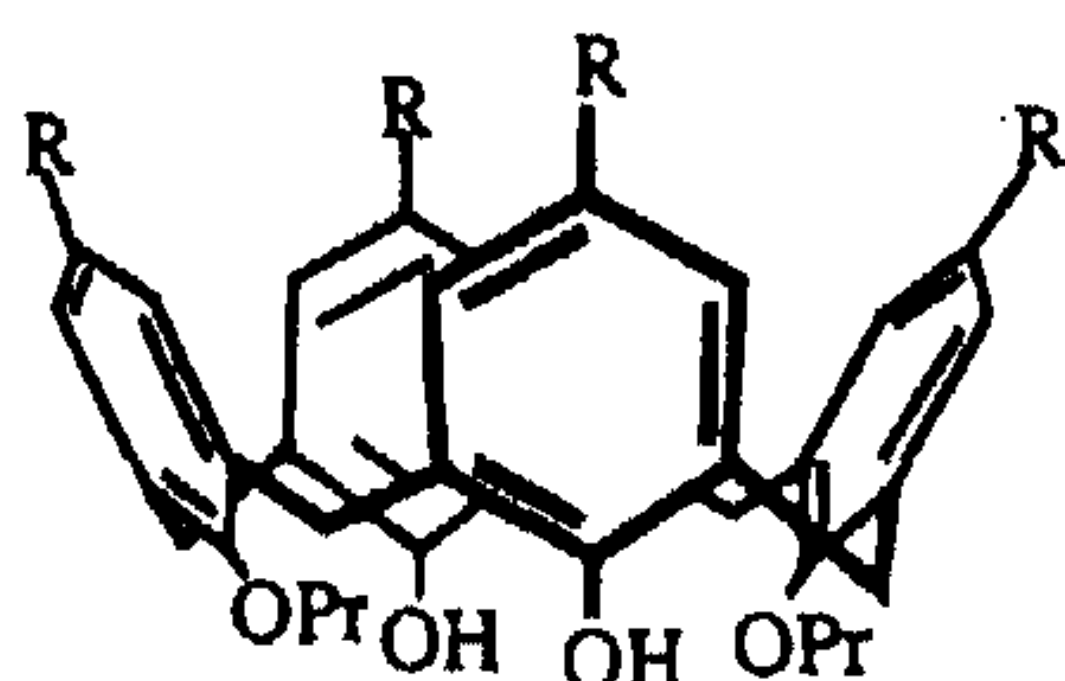
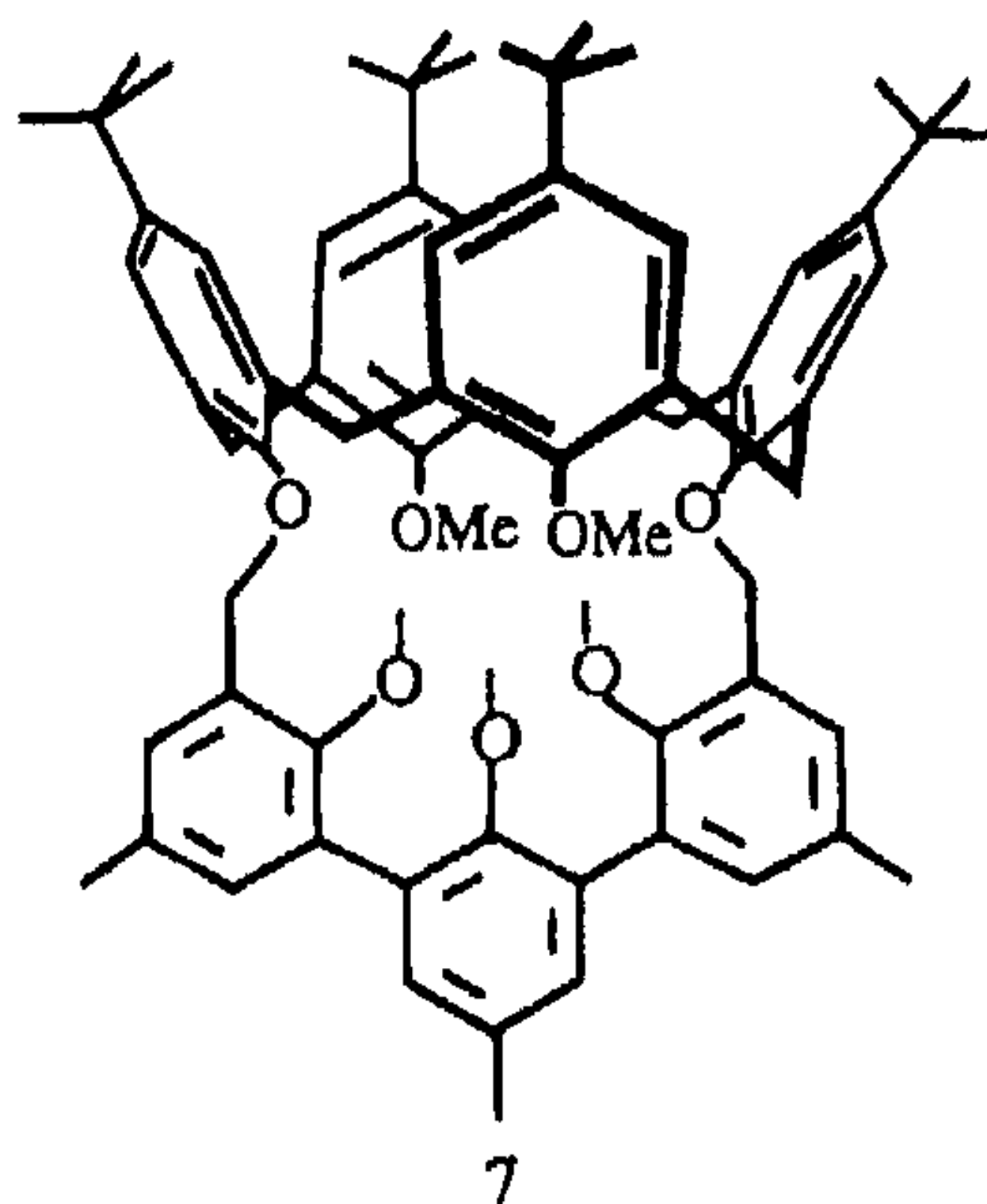
2



4



5

6 R = N=N-C₆H₄-NO₂

7

$$\alpha = \frac{D_{\text{lag}} \theta L_0}{d_m J_{\text{max}}} - 1 \quad (4)$$

$$\frac{L_0}{J_{\text{max}}} = \frac{d_m}{D_m} + \frac{1}{\theta k} \quad (5)$$

and k from its slope ($1/D_m$) and the intercept ($1/\theta k$). Consequently, α can be calculated at any membrane thickness.

The transport regime is determined by the value of α . A value lower than 1 indicates that the transport is mainly limited by diffusion of the complex, while the transport is primarily controlled by cation release from the membrane when $\alpha > 1$.

Experimental Section

Materials. The syntheses of 1–3,^{19,25} 4,²⁶ 5,²⁷ 6,²⁸ and 7²⁰ were carried out according to literature procedures. The membrane solvent *o*-nitrophenyl *n*-octyl ether (NPOE) was obtained from Fluka (>99%).

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The porous polymeric support Accurel 1E-PP ($d_m = 100 \mu\text{m}$, $\theta = 64\%$)^{29,30} was obtained from Enka Membrana. Sodium and potassium perchlorate were obtained from Janssen Chimica and were used without further purification.

Transport Measurements. The carrier-mediated transport experiments were carried out in a permeation cell consisting of two identical compartments (half-cell volume, 50 mL; effective membrane area, 12.5 cm²) described previously.²⁹ The supported liquid membrane consisted of a thin, porous propylene film (Accurel 1E-PP) immobilizing the

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solution of the carrier in NPOE. Aqueous potassium and/or sodium perchlorate solutions were used as the source phase, and doubly distilled and deionized water was used as the receiving phase. As a reference temperature for the experiments, 25 °C was chosen. The transported perchlorate salts were determined by monitoring the conductivity of the receiving phase as a function of time (Philips PW 9527 conductivity meter and a Philips PW 9512/61 electrode with a cell constant of 0.76 cm⁻¹) in the case of single cation transport or by atomic absorption measurements of samples taken from the receiving phase in the case of competitive transport. The temperature coefficient of the conductivity meter was set on 0.021 K⁻¹. Initial transport was measured up to receiving phase salt concentrations of at most 10⁻⁴ M. The standard deviation in the transport measurements is about 15% or less. In all experiments in which membrane thickness, temperature, or stirring speed were varied, the carrier was saturated with salt at the source phase interface.

Variation of Membrane Thickness. Supports were immersed in the membrane solution, wiped dry with a tissue, and successively stacked with a droplet of membrane solution in between the sheets; the liquid film between the membrane layers does not increase the total thickness within experimental error.^{1,2}

Variation of Operating Temperature. The operating temperature was increased in steps of a few degrees centigrade. In between, the receiving aqueous phase was replaced by prethermostated bidistilled water.

Variation of Stirring Speed. Stirring speed was measured by manually counting the rpm of a slower bar connected through gears to the actual stirring rod, using the obtained ratio of 6/51 to calculate the relative speeds.

Lag-Time Measurements. Lag times were measured by filling the half-cell compartments with prethermostated aqueous phases and monitoring the receiving phase conductivity at time intervals of at most 60 s until steady state conditions were reached. The presence of salt in the membrane prior to these experiments was excluded by contacting the membranes with bidistilled and deionized water until the conductivity of the water phases was constant.

Equilibrium Experiments. The membrane was presaturated with salt by contacting with a concentrated source phase for at least one-half hour. The membrane was successively wiped dry and contacted with a receiving aqueous phase ($V_{rp} = 50$ mL, $T = 25$ °C), of which the conductivity was monitored in time.

Permeation of Dyes. Permeation experiments were carried out in a small cell described elsewhere ($A = 2.01$ cm², $V_{sp} = V_{rp} = 1.4$ mL),³¹ which was stirred by rotating the complete setup. The permeation of dyes was monitored in time with UV/vis by regularly sampling the receiving organic phase, which was diluted with ethanol (5: $\lambda = 546$ nm, $\epsilon_{546} = (1.21 \pm 0.06) \times 10^4$ dm³ mol⁻¹ cm⁻¹) or ethanol saturated with NaOH (6: $\lambda = 550$ nm, $\epsilon_{550} = (3.1 \pm 0.3) \times 10^4$ dm³ mol⁻¹ cm⁻¹).³¹

Results and Discussion

For the transport model (vide supra), it is assumed that no ion pairs are formed in the membrane, which is justified when relatively low carrier concentrations are used in polar membrane solvents. Carrier concentrations in this study are typically 10⁻² M, dissolved in the polar 2-nitrophenyl *n*-octyl ether (NPOE, $\epsilon_r = 24$) as the membrane solvent throughout. Furthermore, it is assumed that the resistance of the stagnant aqueous layers adjacent to the membrane is negligible compared to all other resistances. In order to verify this assumption, the effect of stirring speed in the aqueous phases on the flux was determined during salt transport mediated by carriers 1 ([KClO₄]_{ws} = 0.1 M) and 4 ([NaClO₄]_{ws} = 1 M). In both cases, the flux appeared constant within experimental error at stirring rates between 300–900 rpm.

Variation of Membrane Thickness. In order to determine whether NaClO₄ transport mediated by 4 is diffusion limited,

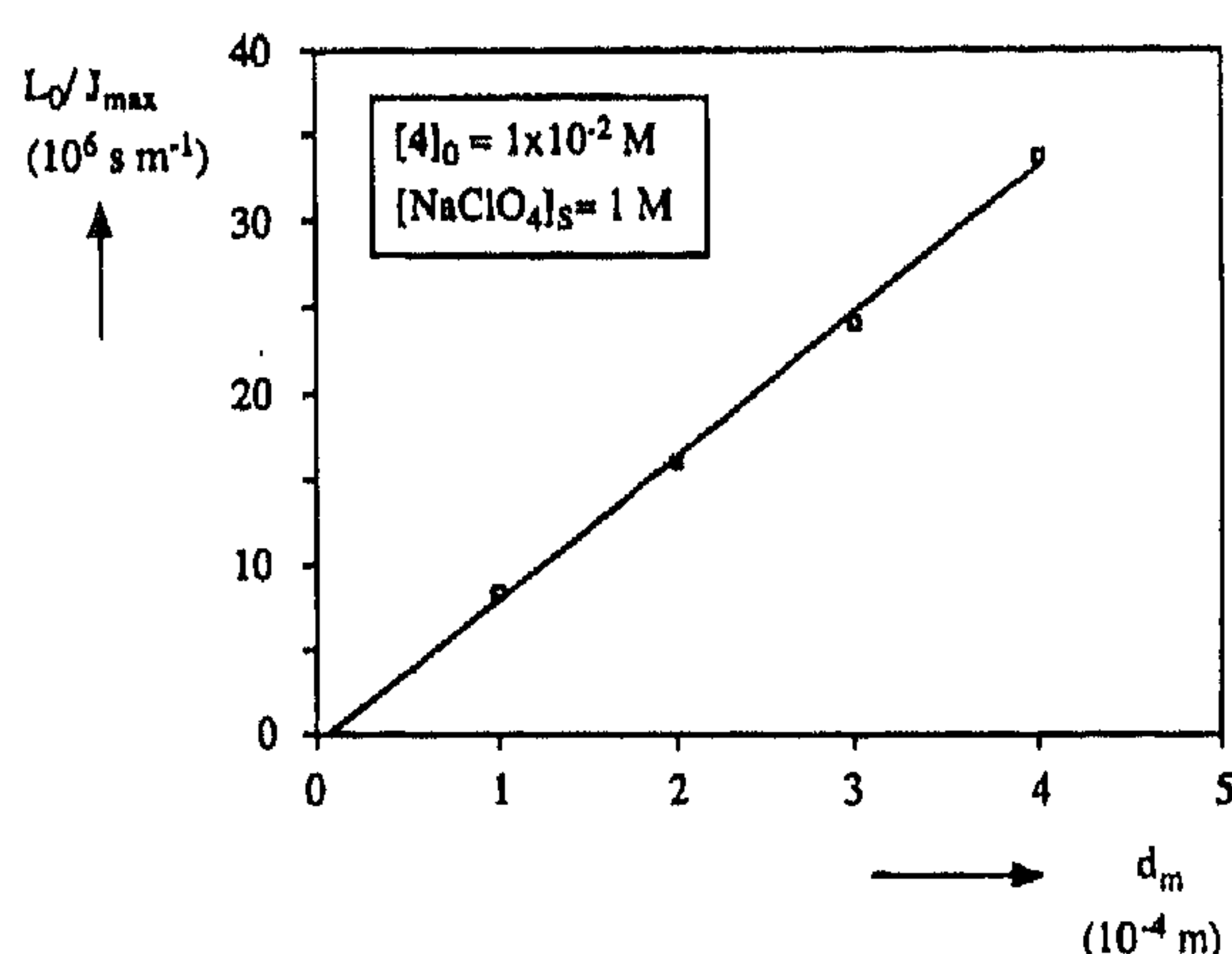


Figure 2. Maximum flux as a function of membrane thickness for NaClO₄ transport with the calix[4]arene tetraethyl ester 4.

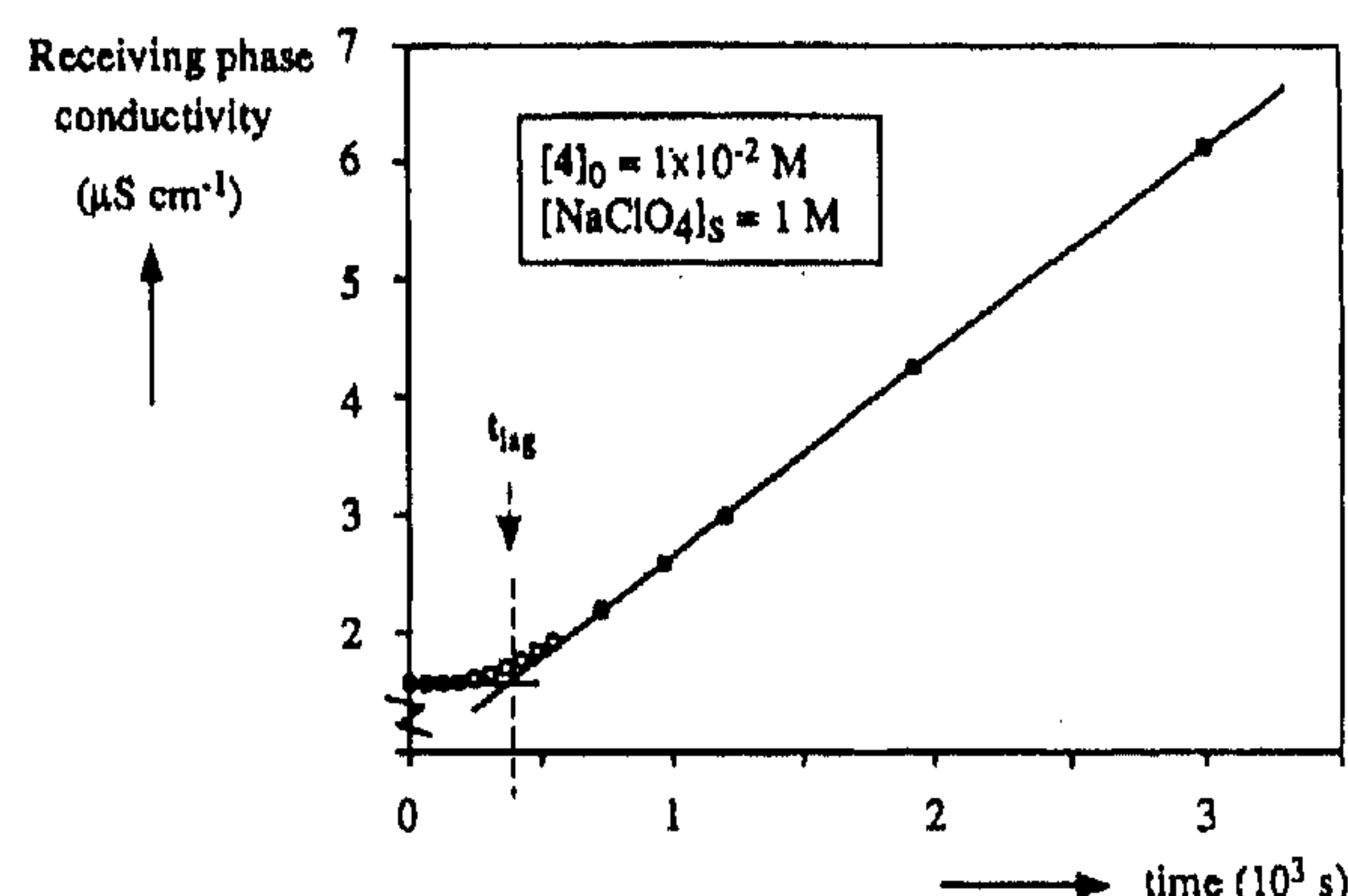


Figure 3. Lag-time measurement for the transport of NaClO₄ with carrier calix[4]arene tetraethyl ester 4.

the flux was measured as a function of membrane thickness. In this experiment, a 1 M NaClO₄ aqueous source phase was used since at this salt concentration carrier 4 is saturated at the interface, so that eq 5 is valid. From the plot of L_0/J versus d_m (Figure 2), a diffusion constant D_m of 1.2×10^{-11} m² s⁻¹ is evaluated.

Furthermore, since the line fitted through the data points virtually goes through (0,0), it can be concluded that the transport is solely limited by diffusion of the carrier cation complex through the membrane ($\alpha < 0.1$).

Lag-Time Measurements. Lag times were measured for transport of KClO₄ with carriers 1–3 and NaClO₄ with 4. A representative example of a lag-time measurement (transport of NaClO₄ with carrier 4) is shown in Figure 3. A stack of two membranes was used for reasons of accuracy. From Figure 3, a diffusion constant of $D_m = 1.1 \times 10^{-11}$ m² s⁻¹ has been determined. This value is equal to that obtained from steady state flux measurements (vide supra).

The diffusion constants (D_{lag}) were calculated according to eq 3. These values together with those of the maximum fluxes (J_{max}) were entered into eq 4 to yield α values (Table 1).

For 1,3-diethoxycalix[4]arene crown-5 in the cone conformation (3) and for calix[4]arene tetraethyl ester (4), the calculated α values are too low to be determined accurately. This indicates that the transport is purely diffusion limited. However, the α values for transport of KClO₄ with 1,3-diethoxycalix[4]arene crown-5 in the partial cone conformation (2) and 1,3-dimethoxycalix[4]arene crown-5 (1) are higher than 1. Hence, the transport is primarily limited by the rate of decomplexation.

(31) Reichwein-Buitenhuis, E. G. Thesis, University of Twente, Enschede, The Netherlands, 1994.

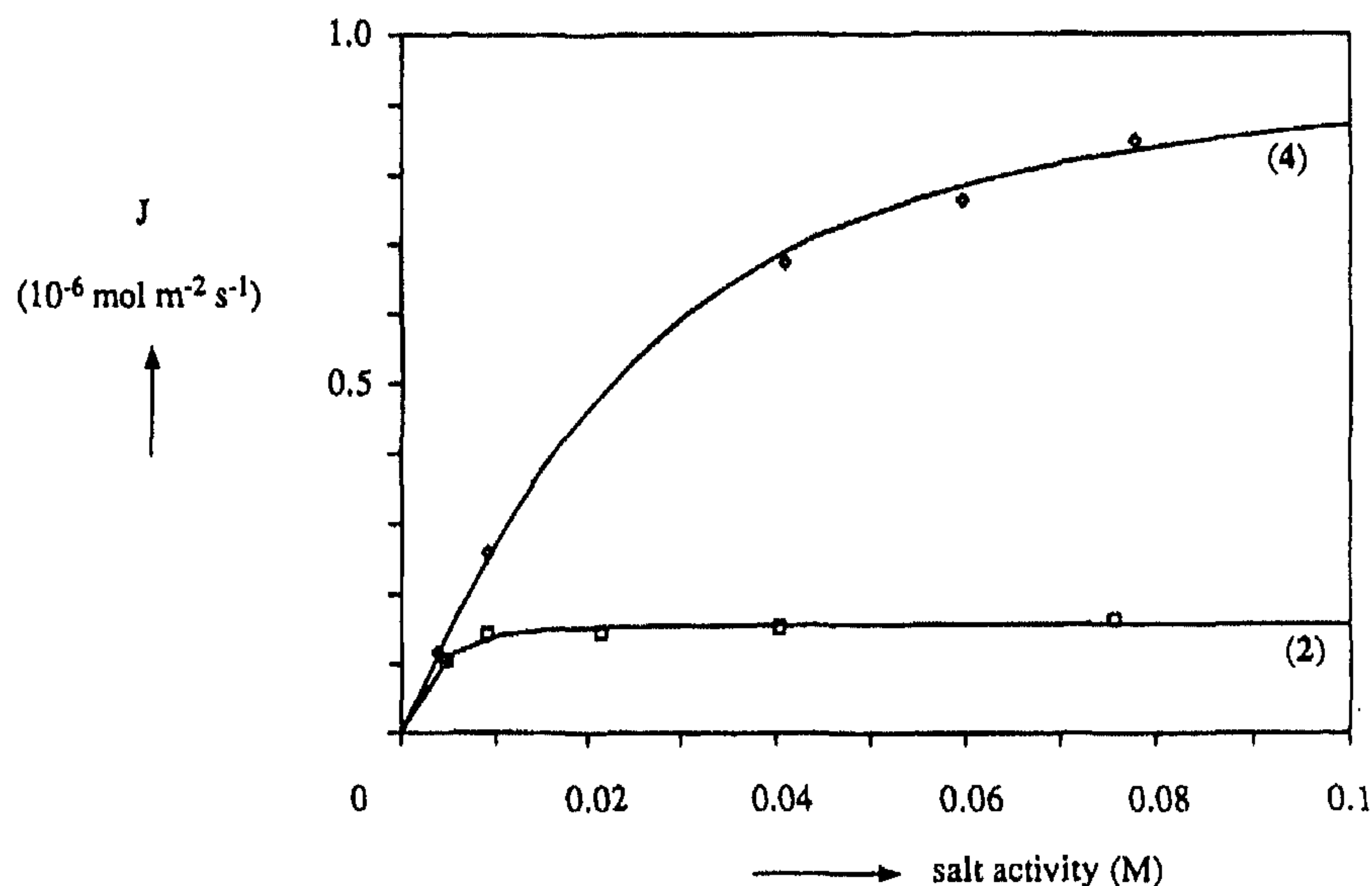


Figure 4. Relation between flux and salt activity for 1,3-diethoxycalix[4]arene crown-5 (partial cone) 2 (KClO_4) (\square) and calix[4]arene tetraethyl ester 4 (NaClO_4) (\diamond) at 25 °C.

Table 1. Calculated α Values from Lag Times and Maximum Fluxes^a

carrier ^b	salt	D_{lag} ($10^{-11} \text{ m}^2 \text{ s}^{-1}$)	J_{max} ($10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$)	α
1	KClO_4	1.7	3.3	2.3 ^c
2	KClO_4	1.9	2.6	3.6 ^c
3	KClO_4	1.8	12.5	-0.1 ^d
4	NaClO_4	1.8	12.6	-0.1 ^d

^a Temperature = 25 °C. ^b Carrier concentration $1 \times 10^{-2} \text{ M}$. ^c Estimated accuracy of $\pm 30\%$. ^d Too small to be determined accurately.

Figure 4 illustrates the fact that although carriers 2 and 4 have the same D_m , the maximum flux using 4 as carrier is much higher than the flux using 2 as the carrier. These results indicate that apart from the diffusional resistance an additional kinetic resistance has to be taken into account in describing the transport mediated by carriers 1 and 2.

Slow Rate of Cation Release at the Membrane–Water Interface. In order to verify the assumption that the decomplexation reaction is slow, the release of cations from a presaturated set of membranes was followed as a function of time (Figure 5). The set of membranes contained 10^{-2} M of carrier that had been saturated with salt and was brought into contact with the receiving phase containing bidistilled water. From Figure 5, it is clear that decomplexation of the 1,3-dimethoxycalix[4]arene crown-5 $1\cdot\text{K}^+$ complex is much slower than the decomplexation of the calix[4]arene tetraethyl ester $4\cdot\text{Na}^+$ complex. Hence, it is indeed the decomplexation of $1\cdot\text{K}^+$ which affects the flux.

Variation of Operating Temperature. Apart from calculating the maximum flux and comparing this value with the measured flux value, determination of the activation energy gives information about the rate-limiting step in the transport process as was discussed in the Introduction. The diffusion constant of a solute in dilute solution is related to the viscosity of the solvent, e.g. by the theoretically derived Stokes–Einstein equation ($D_m = kT/6\pi\eta r$) or the empirical Wilke–Chang equation,³² both predicting a linear increase of D_m with T/η . The effect of temperature on the viscosity of a medium strongly depends on the state and the constitution of the medium, viz.

the viscosity of gases increases while that of liquids decreases with temperature; the viscosity of liquid metals is almost constant, while the viscosity of organic solvents may depend strongly on temperature. The viscosity of organic solvents often shows Arrhenius-type behavior, and consequently, an activation energy for self-diffusion or viscous flow can be calculated according to $\eta(T) = \eta_0 \exp(E_a/RT)$. Furthermore, the activation energy for self-diffusion of a solvent often correlates well with that of the diffusion of a solute species, since on the molecular level diffusion of a solute can be considered as a process in which either solute or solvent molecules jump from solvent cavity to cavity. The activation energy for self-diffusion may vary from about $6 \text{ kJ}\cdot\text{mol}^{-1}$ for pentane or acetone to $68 \text{ kJ}\cdot\text{mol}^{-1}$ for glycerin.³³ This illustrates the importance of determining the temperature–viscosity relationship for the membrane solvent used. The kinematic viscosity of NPOE was measured as a function of temperature between 20 and 60 °C, and the activation energy for self-diffusion was calculated to be about $24 \text{ kJ}\cdot\text{mol}^{-1}$.³⁴ Since flux depends on both the diffusion constant of the complex and its concentration gradient inside the membrane, the effect of temperature on transport is preferentially determined under such conditions that the carrier is saturated with salt at the source phase interface (eq 2).³⁵ For several carriers the value of the activation energy of the salt transport has been determined. A typical example of an Arrhenius plot from which E_a has been obtained is shown in Figure 6.

In Table 2, the values of E_a are summarized. These results indicate that K^+ transport mediated by 1,3-dimethoxycalix[4]arene crown-5 (1) or 1,3-diethoxycalix[4]arene crown-5 (2) is limited by the rate of release. Increasing the membrane thickness results in a change from rate-limited to diffusion-limited transport for 1, but K^+ transport by 2 is still rate-limited when the membrane thickness is $400 \times 10^{-6} \text{ m}$.

(33) Values calculated from the following: *Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983–84; Table F39.

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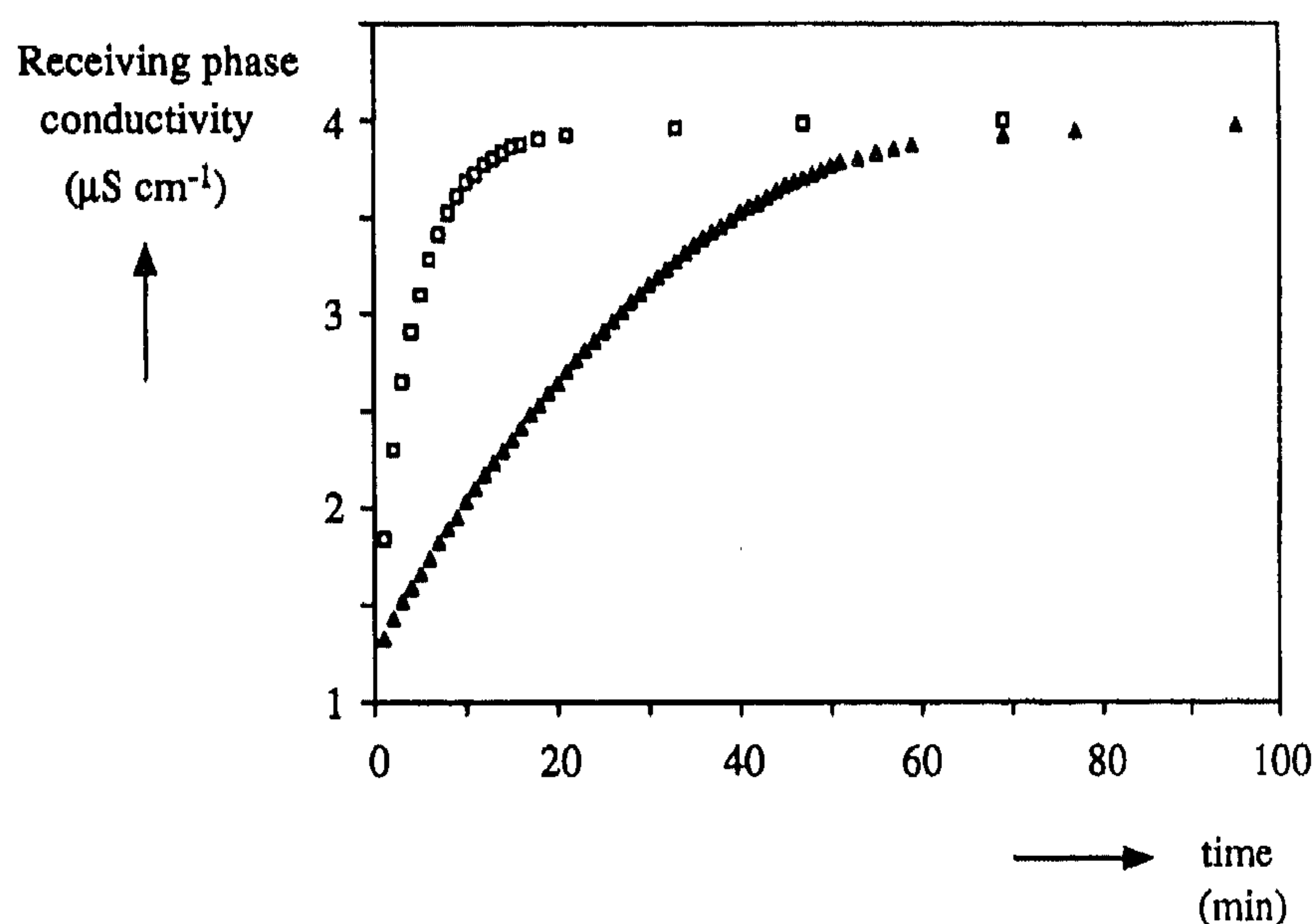


Figure 5. Receiving phase conductivity as a function of time for release of KClO_4 from 1,3-dimethoxycalix[4]arene crown-5 **1** (Δ) and NaClO_4 from calix[4]arene tetraethyl ester **4** (\square).

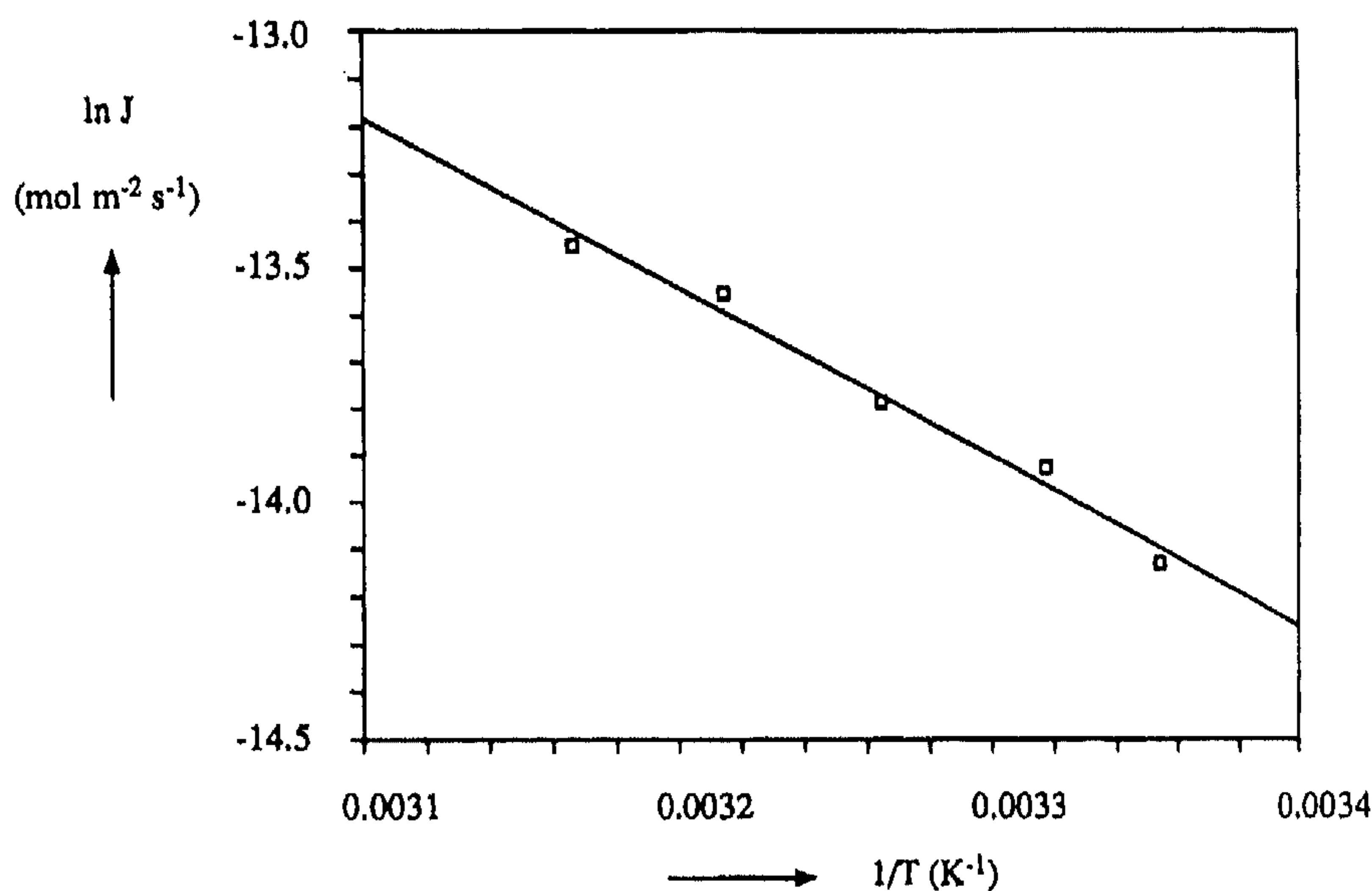


Figure 6. Relation between $\ln J(\text{NaClO}_4)$ and $1/T$ for 1,3-diethoxycalix[4]arene crown-5 (partial cone) **2**: source phase, 1 M NaClO_4 ; carrier concentration, 10^{-2} M. The symbols are measured values, the line drawn from linear least squares analysis.

Table 2. Activation Energies of Transport across SLM for Different Calix[4]arene Complexes and Dyes **5** and **6**

carrier	salt	d_m (μm)	E_a (kJ mol^{-1})
1	KClO_4	100	63 ± 2
1	KClO_4	200	37 ± 0.5^a
2	KClO_4	100	61 ± 3
2	KClO_4	400	60 ± 3
2	NaClO_4	100	30 ± 2
4	NaClO_4	100	32 ± 2
5		100	24 ± 6
6		100	27 ± 5

^a Obtained from data points above $T = 35^\circ\text{C}$.

In crown-immobilized polymeric membranes, E_a values have been obtained of around 50 kJ mol^{-1} , while those for carrier-mediated ion transport across liposomal membranes can be as high as 130 kJ mol^{-1} .³⁶

To obtain the activation energy of transport limited by diffusion through the membrane, permeability experiments with dyes have been performed. Dye **5** and calix[4]arene **6** were the compounds of choice for permeation experiments because their absorption maxima are in the UV/vis region, far from the absorption bands of the solvent NPOE. The transport velocity was measured from a source phase consisting of a solution of the dye in NPOE through a membrane soaked with NPOE to a receiving phase of neat NPOE. Both compartments were stirred so that diffusion through the membrane is rate-limiting. The diffusion constant is obtained from eq 6, in which $c_s(0)$ is the initial dye concentration in the source phase, $c_r(t)$ the concentration in the receiving phase, A the membrane area, V the volume of the receiving phase, and d_m the membrane thickness.

(36) Shinkai, S.; Torigoe, K.; Manabe, O.; Kajiyama, T. *J. Am. Chem. Soc.* 1987, 109, 4458.

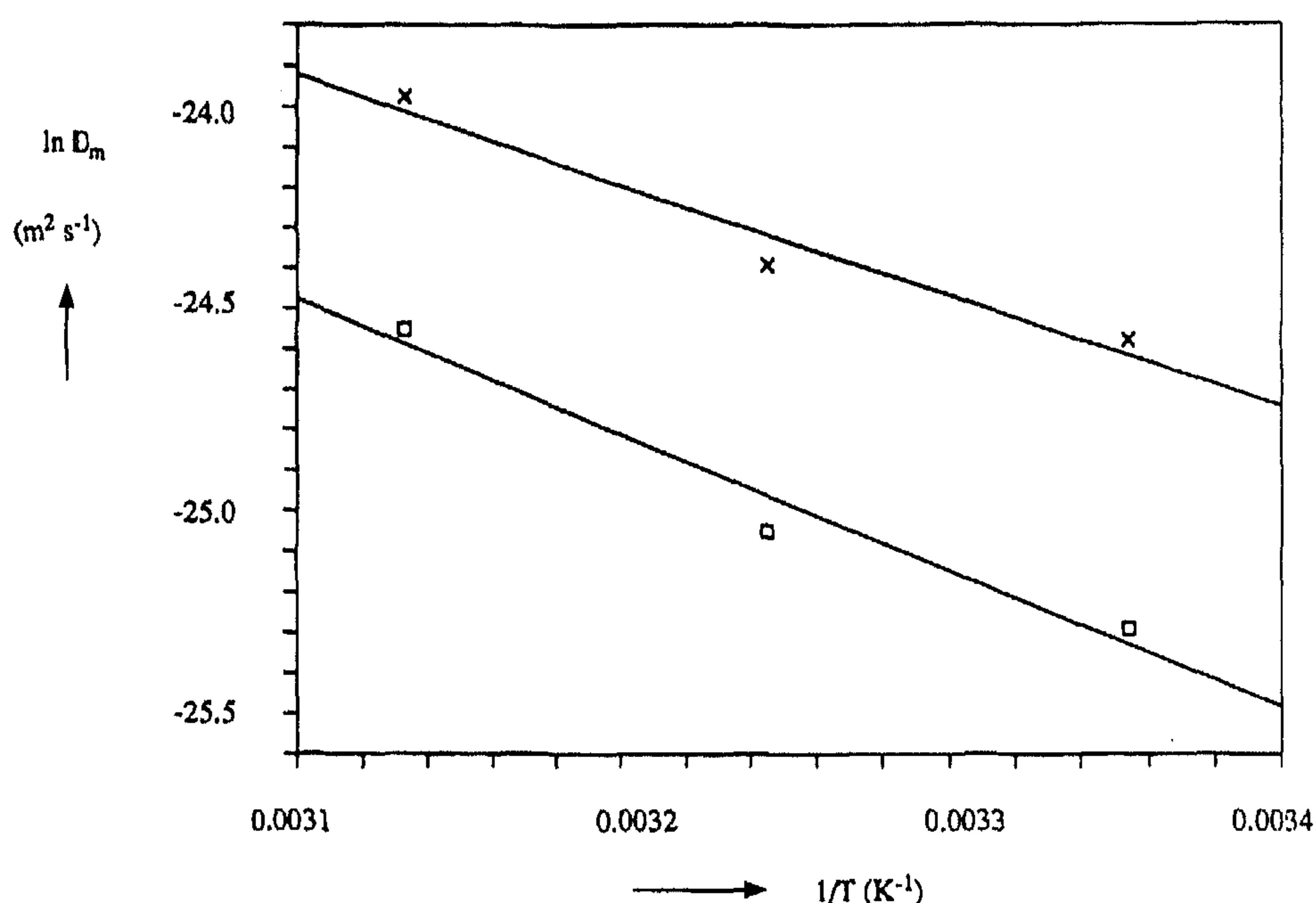


Figure 7. Relation between $\ln D_m$ and $1/T$ for dyes 5 (x) and 6 (□).

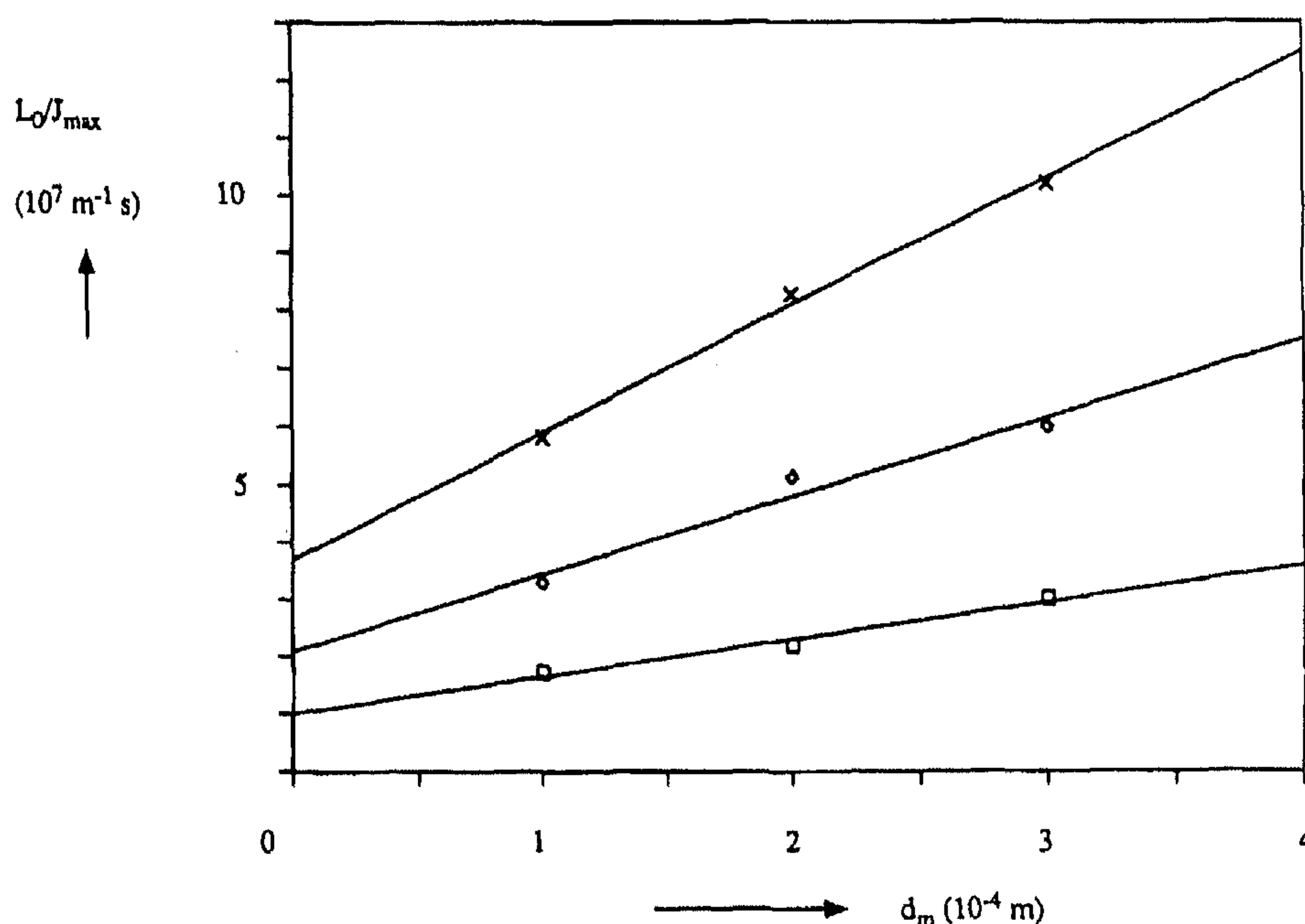


Figure 8. Relation between the flux (J) and the membrane thickness (d_m) for 1,3-diethoxycalix[4]arene crown-5 (partial cone) 2 for temperatures 25 °C (x), 34 °C (◇), and 43 °C (□): carrier concentration, 10^{-2} M; source phase, 10^{-1} M KClO_4 . The symbols are measured values, the line drawn from linear least squares analysis.

By performing these experiments at different temperatures, a plot of $\ln D_m$ against T^{-1} can be obtained and E_a can be calculated from the slope (Figure 7). The values of E_a obtained from these experiments (Table 2) are compared to the values obtained from the salt transport experiments, and they agree very well. This means that for diffusion-limited transport the phase-transfer process (the crossing of the membrane-water interface) hardly contributes to the activation energy of the transport process.

Variation of Temperature and Membrane Thickness. The value for the rate of cation release (k) can be determined by

Table 3. D_m , k , and α Values for Transport of KClO_4 by Different Carriers

carrier	Θk (10^{-8} m s ⁻¹)	D_m^a (10^{-12} m ² s ⁻¹)	α	temp (°C)
1	5.24	9.85	1.9	25
2	2.70	4.6	1.7	25
2	4.79	7.4	1.5	34
2	9.92	15.6	1.6	43
7	0.24	0.48	2.0	25

^a Estimated accuracy of $\pm 20\%$.

measuring the flux as a function of the membrane thickness and by applying eq 5. In Figure 8, the relation of the flux vs

Table 4. K⁺/Na⁺ Selectivity for 1,3-Diethoxycalix[4]arene Crown-5 (Partial Cone) 2^a

source phase (M)		no. of membranes	temp (°C)	<i>J</i> (K ⁺) (10 ⁻⁸ mol m ⁻² s ⁻¹)	<i>J</i> (Na ⁺) (10 ⁻⁸ mol m ⁻² s ⁻¹)	$\frac{J(K^+)}{J(Na^+)} \times \frac{[Na^+]_s}{[K^+]_s}$	
[KClO ₄]	[NaClO ₄]						
10 ⁻¹	10 ⁻¹	1	25	6.73	≤0.20 ^b		≥34
10 ⁻²	10 ⁻¹	1	25	7.28	0.48		150
10 ⁻³	10 ⁻¹	1	25	6.33	3.99		160
10 ⁻³	10 ⁻¹	3	25	4.47	1.48		300
10 ⁻¹	10 ⁻¹	1	43	46.0	≤0.47 ^b		≥97
10 ⁻²	10 ⁻¹	1	43	52.4	1.34		390
10 ⁻³	10 ⁻¹	1	43	28.7	6.83		420

^a Carrier concentration of [2] = 10⁻² M. ^b Too low to measure accurately.

$$\ln \frac{c_s(0) - 2c_r(t)}{c_s(0)} = -2 \frac{AD_m}{Vd_m} t \quad (6)$$

membrane thickness is given at different temperatures. As the temperature increases, the intercept becomes smaller, which means that the rate of cation release increases. The transport mechanism changes from rate-limited to more diffusion-limited transport.

In Table 3, the values of *k* and *D_m* for carriers 1, 2, and 7 are summarized. Pentamethoxycalixspherand (7) exhibits the lowest rate of release compared to the flexible 1,3-dimethoxycalix[4]arene crown-5 (1) and preorganized 1,3-diethoxycalix[4]arene crown-5 (partial cone) (2), as was also found by Dijkstra *et al.*³⁷ and Iwema Bakker²⁵ in CDCl₃.

Transport Selectivity. In the case that the transport is limited by diffusion of the carrier cation complex, the transport selectivity only depends on the ratio of the extraction constants of the carrier for the different cations. However, when kinetic resistances play a role, the transport selectivity is also expected to be influenced by temperature as well as the membrane thickness.

The K⁺/Na⁺ selectivity of 1,3-diethoxycalix[4]arene crown-5 (partial cone) (2) has been investigated in competition experiments with various K⁺/Na⁺ concentration ratios in the source phase. The results are shown in Table 4. The obtained selectivities are lower than if the transport was diffusion limited for both K⁺ and Na⁺.

Increasing the membrane thickness from 100 to 300 × 10⁻⁶ m or the temperature from 25 to 43 °C increases the selectivity because, in both cases, the transport of K⁺ is more determined by the diffusional resistance in the membrane and to a lower extent by the kinetics of cation release.

Conclusions

Assuming uptake of the cation is relatively fast, there are two transport resistances, viz. (i) diffusional resistance and (ii) kinetic resistance at the receiving phase interface. Indications about the relative contributions of those resistances to the overall transport resistance have been obtained by (i) comparison of the maximum flux values of cation transport with carriers that have about the same values of *D_m* (determined from lag-time experiments), (ii) determination of *E_a*, and (iii) measuring of the flux as a function of the membrane thickness. From the latter method the value of *k* is determined. For carriers 1, 2, and 7 transporting K⁺, the rate of cation release is slow compared to the diffusion through the membrane. Increasing the temperature or the membrane thickness results in a change from decomplexation rate-limited transport to diffusion-limited transport.

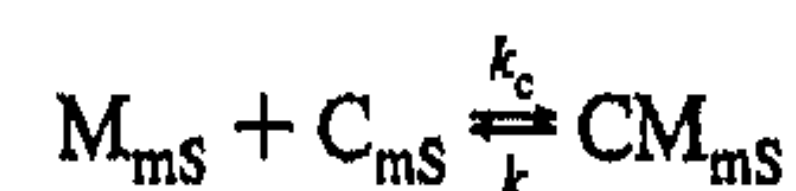
(37) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K. E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc.* 1989, 111, 7567.

Appendix 1. Model for Carrier-Assisted Cation Cotransport

Equation 1 describes carrier-assisted cation cotransport in such a way that diffusion as well as kinetics of release can be rate-limiting. The partition constant of the salt is given by eq A.1.

$$K_p = \frac{[M]_m[X]_m}{a_s^2} \quad (A.1)$$

M denotes the cation, *X* denotes the anion, *a_s* is the activity of the cation in the aqueous (source) phase, and subscript *m* denotes the membrane phase. The complex formation at the source interface is given by the following reaction in which *k_c* is the complexation rate constant, *k* is the decomplexation rate constant, *C* is the carrier, *CM* is the complex, and the subscript *S* denotes the source phase interface.



Under steady state conditions (*d*[*CM*]_{*m*1}/*dt* = 0), the corresponding flux is related to the concentrations at the interface by eq A.2, in which *k_c'* and *k'* are the rates of ion uptake and release at the interface, respectively. Assuming [*X*]_{*ms*} = [*CM*]_{*ms*} and neglecting resistances of aqueous boundary layers outside the membrane, eqs A.1 and A.2 lead to eq A.3. *K_{ex}* and *B_s* are

$$J = k'_c[M]_{ms}[C]_{ms} - k'[CM]_{ms} \quad (A.2)$$

$$J = \frac{k'_c[C]_{ms}K_p a_s^2}{[CM]_{ms}} - k'[CM]_{ms} \quad (A.3)$$

defined according to eqs A.4 and A.5, respectively, in which *L₀* is the initial carrier concentration. Assuming *L₀* = [*CM*]_{*ms*} + [*C*]_{*ms*} and putting *f_s* = [*CM*]_{*ms*}/*L₀*, eq A.6 is obtained.

$$K_{ex} = K_p \frac{k'_c}{k'} \quad (A.4)$$

$$B_s = \frac{K_{ex} a_s^2}{L_0} \quad (A.5)$$

$$P \equiv \frac{J}{k'L_0} = \left\{ \frac{1 - f_s}{f_s} \right\} B_s - f_s \quad (A.6)$$

The diffusion across the membrane is described by eq A.7, in which the subscript *R* denotes the receiving phase interface, *D₀* denotes the diffusion of the complex in the membrane phase, and *d₀* is the effective membrane thickness. Rearrangement of eq A.7 leads to eq A.8, in which *f_R* = [*CM*]_{*mR*}/*L₀*.

The situation at the receiving phase interface is the mirror situation of the situation at the source phase interface, and the

$$J_0 = \frac{D_0}{d_0} \{ [\text{CM}]_{\text{ms}} - [\text{CM}]_{\text{mR}} \} \quad (\text{A.7})$$

$$Q \equiv \frac{J_0 d_0}{D_0 L_0} = f_s - f_R \quad (\text{A.8})$$

flux is given by eq A.9, in which a_R denotes the cation activity in the aqueous receiving phase, in analogue with eq A.3.

$$J = - \frac{k_c' [\text{C}]_{\text{mR}} K_p a_R^2}{[\text{CM}]_{\text{mR}}} + k' [\text{CM}]_{\text{mR}} \quad (\text{A.9})$$

B_R is defined according to eq A.10, similar to eq A.5, which together with eq A.9 leads to eq A.11. In eq A.12, α , the parameter relating the diffusion constant D_0 and k' , is defined. Solving eqs A.6 and A.11 and substitution into eq A.8 leads to eq A.13. The general solution for Q can be obtained by iteration or rearranging eq A.13 into a fourth-order polynome. In the case that B_R equals 0 (initial transport), eq A.13 converts into eq A.14 with $P = \alpha Q$. From eqs A.8 and A.14, the expression for the flux, eq A.15 can be obtained with $A = K_{\text{ex}} a_s^2$.

$$B_R = \frac{K_{\text{ex}} a_R^2}{L_0} \quad (\text{A.10})$$

$$P = - \left\{ \frac{1 - f_R}{f_R} \right\} B_r + f_R \quad (\text{A.11})$$

$$\alpha = \frac{D_0}{d_0 k'} \quad (\text{A.12})$$

$$2(1 + \alpha)Q = -(B_s - B_R) + \sqrt{\{(P + B_s)^2 + 4B_s\}} - \sqrt{\{(P - B_R)^2 + 4B_R\}} \quad (\text{A.13})$$

$$(1 + 2\alpha)Q^2 + B_s Q - \frac{B_s}{(1 + \alpha)} = 0 \quad (\text{A.14})$$

$$J_0 = \frac{D_0}{2d_0} \frac{-A + \sqrt{A^2 + 4L_0 A \left(\frac{1 + 2\alpha}{1 + \alpha} \right)}}{1 + 2\alpha} \quad (\text{A.15})$$

In practice, the above parameters need to be adjusted for the porosity (θ) and tortuosity (τ) of the membrane: $J = \theta J_0$, $d_0 = \tau d_m$, and $D_m = \theta D_0 / \tau$, where J is the measured flux, d_m the wall-to-wall thickness of the membrane, and D_m the apparent diffusion constant.

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