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Kinetics of carrier-mediated alkali cation transport through supported liquid membranes: Effect of membrane solvent, co-transported anion, and support

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Abstract

The rate-limiting step in the transport of alkali cations through supported liquid membranes mediated by calix[4]arene carriers can be the diffusion of the carrier cation complex through the membrane and/or the kinetics of cation release from the complex. The effects of membrane solvent, co-transported anion, and support on the diffusion constant D_m , the extraction constant K_{ex} and the rate constant k have been studied. These were determined from flux measurements as a function of source phase salt activity (D_m and K_{ex}) and membrane thickness (D_m and k). Additional information about the transport resistances was obtained from variation of the operating temperature and from lag time measurements. The diffusion constants (D_m) for 1/ NaClO_4 and 2/ KClO_4 linearly increased with reciprocal solvent viscosity. On increasing the solvent polarity, the extraction constant increased, while the rate of cation release decreased. Both $\log K_{ex}$ and $\log k$ correlate linearly with the Kirkwood function, $(\epsilon_r - 1)/(2\epsilon_r + 1)$. The co-transported anion (ClO_4^- vs. SCN^-) affects the kinetics of release but not the diffusion constant. The normalized k and D_m values for 2/ KClO_4 in NPOE/Accurel[®] 1E-PP and NPOE/Celgard[®] 2500 are nearly the same. This means that the transport regime (diffusion or kinetic control) depends only on the tortuosity (τ) and thickness of the support, irrespective of its morphology.

Keywords: Supported liquid membranes; Carrier-mediated transport; Alkali cation transport; Neutral carriers; Membrane solvents

1. Introduction

The carrier mediated co-transport of alkali cations through a Supported Liquid Membrane (SLM) is usually determined by diffusion of the carrier cation complex through the membrane [1]. However, we recently showed that when crowned calix[4]arenes or calixspherands with a shielded cavity are used as the carrier, the low rate of decomplexation of the carrier/cation complex can drastically lower the flux. As a conse-

quence for these carriers the transport rate is determined by both diffusion and the rate of release of the cation [2]. We have previously reported a model which describes the exclusive diffusion limited transport in terms of the extraction constant (K_{ex}) and the diffusion constant of the carrier cation complex (D_m) [3]. This model has to be modified in order to account for slow rates of release by introduction of a decomplexation rate constant (k). The effects of *operating conditions* (stirring rate, membrane thickness, and temperature) on the parameters D_m , K_{ex} and k were found to be as follows: the stirring rate does not influence any of these

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parameters, the membrane thickness affects only the diffusional resistance (d_m/D_m), and at higher temperature both diffusion and decomplexation processes are accelerated, while the extraction constant decreases. Overall, the contribution of the kinetic resistance to the total membrane resistance decreases. Consequently, membrane thickness and operating temperature are powerful tools to adjust the transport regime (diffusion vs. kinetic control). In this paper the effects of the *materials* (membrane solvent, co-transported anion, and support) on the transport parameters are discussed.

The effects of the membrane solvent on carrier mediated salt transport have previously been studied qualitatively in our laboratory for diffusion limited transport. At a constant source phase salt activity the fluxes mediated by dibenzo-18-crown-6 are higher in the more polar solvents such as 2-nitrophenyl octyl ether (2-NPOE) and 2-nitrodiphenyl ether (2-NDPE). Sugiura et al. [4] reported only fluxes through solvent polymeric membranes in different solvents or their mixtures and although Brown et al. [5] attempted to correlate physical parameters of the solvents (η , ϵ_r) with alkali cation fluxes, they found no linear relation. Deblay et al. [6] and Dozol et al. [7] correlated diffusion constants from the Wilke–Chang equation [8] and solute distribution coefficients with membrane permeabilities. To the best of our knowledge the solvent effects on extraction efficiency have never been studied directly in membrane transport experiments [9–11].

The effect of the counter-ion on diffusion limited flux has not been studied in SLMs. In a bulk liquid membrane (BLM) Izatt and co-workers [12] found that $\log J$ linearly decreased with the dehydration energy of the anion. Anions can also influence the flux and transport selectivity by ion-pair formation in the source aqueous phase [13,14]. Yoshida and Hayano showed that kinetics of release from the membrane (BLM, chloroform/polynactin, K^+ co-transport) were influenced by the co-transported anion (ClO_4^- vs. SCN^-) [15].

Several authors have compared the transport rates in different supports. Fluxes can be normalized by correcting for the porosity and the tortuosity of the support [16].

The activation energy for transport is often considered to be indicative for the rate limiting step of transport and values ranging from 9.5 [17] to 186 [18] kJ mol^{-1} have been found. High activation energies have

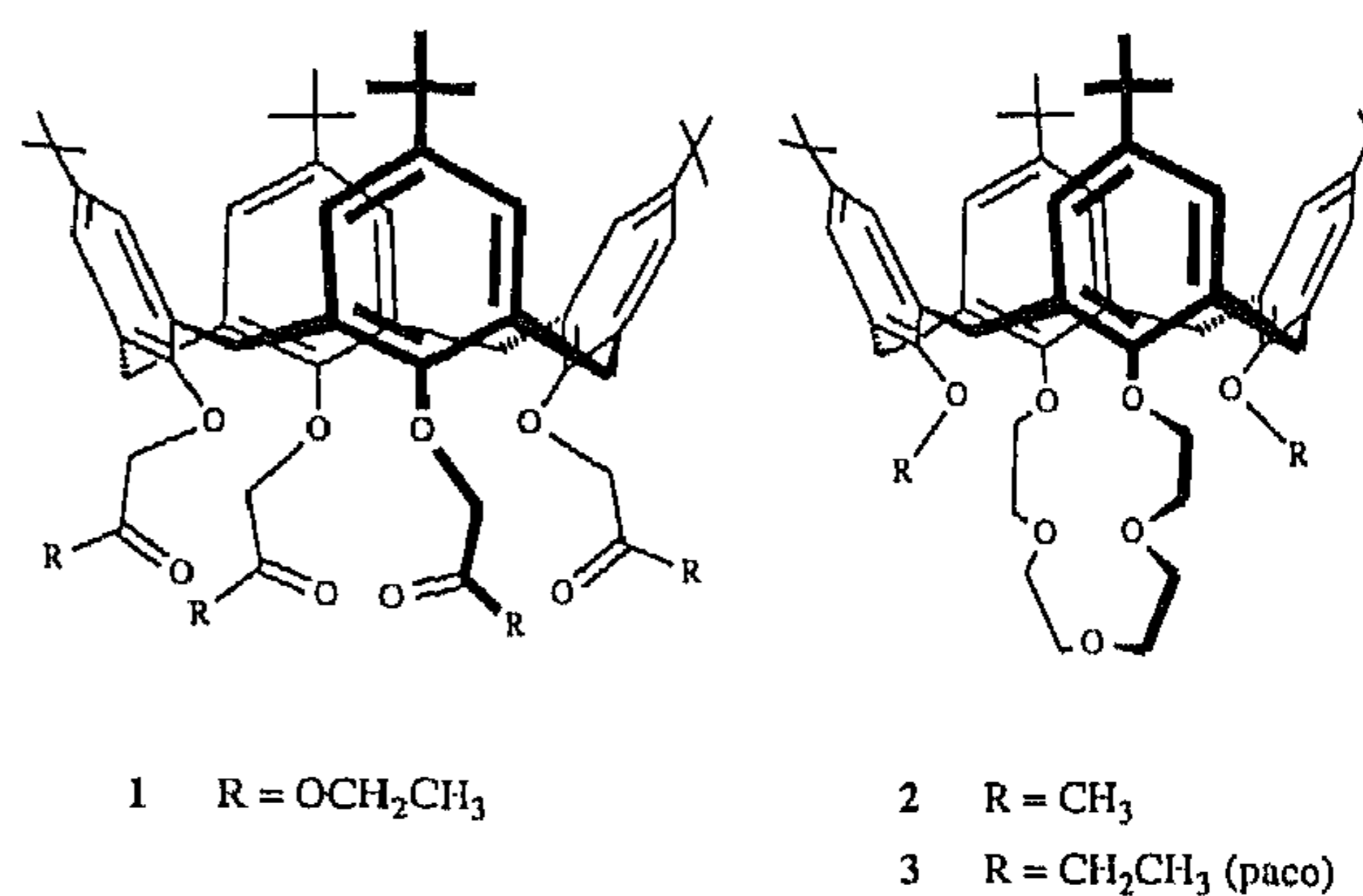
been attributed to mechanisms of site-to-site jumping [18] and slow kinetics of decomplexation [18]. An increase of the operating temperature apparently enhances the flux.

For our study three calix[4]arene carriers were selected, the structures of which are depicted in Scheme 1. The transport of $NaClO_4$ mediated by carrier 1 is only limited by diffusion of the complex through the membrane, whereas $KClO_4$ transport with carriers 2 and 3 is limited by the kinetics of release (2-NPOE/Accurel) [2]. Eight membrane solvents were used in combination with carriers 1 and 2, all phenyl octyl or diphenyl ethers substituted with polar groups (Scheme 2). They were chosen because of their high lipophilicity, mutual similarity, and relatively high polarity.

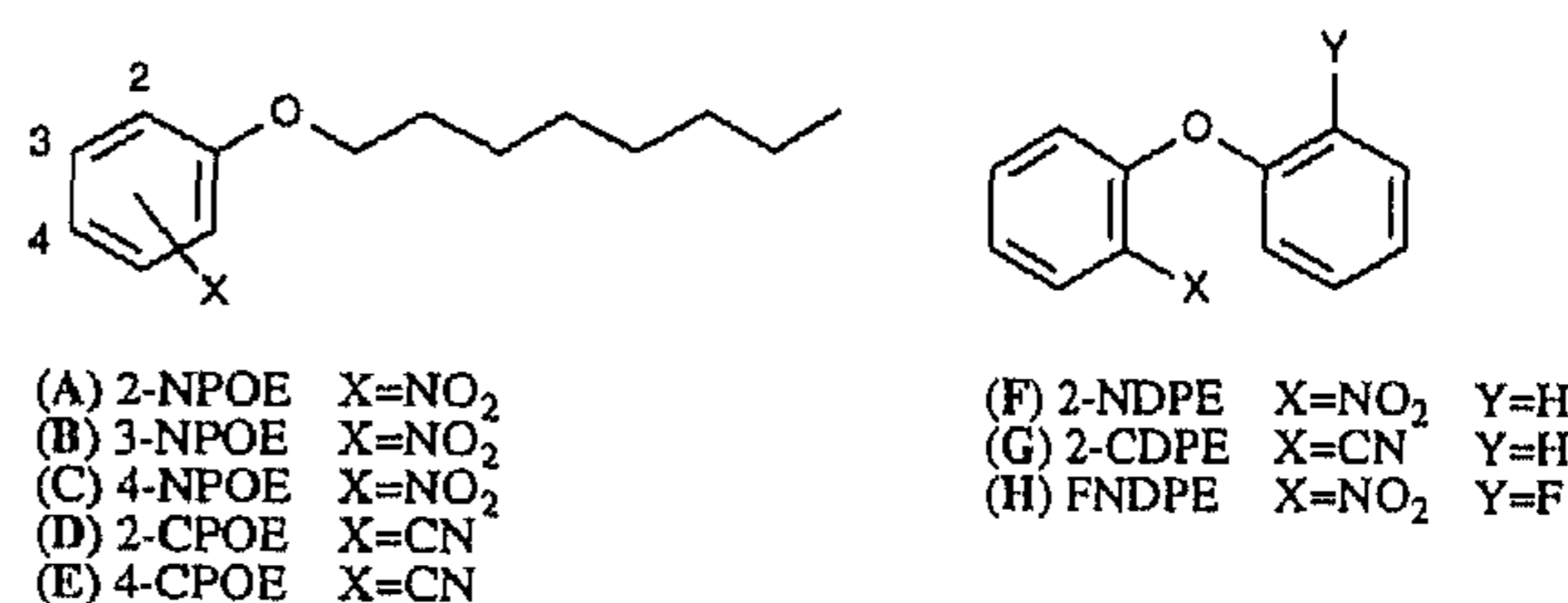
2. Transport equations

We have published a model which describes diffusion limited co-transport of monovalent ions mediated by a carrier that forms a 1:1 cation:carrier complex [3].

In a more general description slow kinetics of release should be taken into account, with the assumption that the rate of release is first order in complex concentration [Eq. (1)] [2]. In Eq. (1) A represents the product of



Scheme 1.



Scheme 2.

the extraction constant and the square of the source phase salt activity ($K_{ex}a_s^2$), L_o the overall carrier concentration, and d_m the membrane thickness. The dimensionless number ϵ represents the ratio between the diffusional and kinetic resistances, expressed as D_m/kd_m . As a consequence, k has the dimensions of $m\ s^{-1}$ and therefore should be regarded as a phase transfer coefficient. When $\epsilon \rightarrow 0$, i.e. $k \gg D_m/d_m$, Eq. (1) becomes identical with the transport equation previously derived for diffusion limited transport [3]. When $\epsilon < 1$ ($k > D_m/d_m$), the transport is mainly diffusion limited, whereas an ϵ value larger than 1 indicates that the transport is mainly kinetically controlled.

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

A special case arises when the carrier at the source phase interface becomes completely loaded by cations. This will occur under conditions when A is very large, and Eq. (1) transforms into Eq. (2). In Eq. (2) the first term ($D_m L_o/d_m$) describes pure diffusion limited transport, while the second ($1/(1+\epsilon)$) accounts for slow rates of cation release.

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

In order to disentangle the contributions of the diffusion and the kinetic term in Eq. (2), the flux should be expressed in the form (driving force/flux) = Σ resistances [Eq. (3)].

$$\frac{L_o}{J_{max}} = \frac{d_m}{D_m} + \frac{1}{k} \quad (3)$$

Consequently, a plot of L_o/J_{max} vs. d_m should give a straight line with a slope of $1/D_m$ and an intercept of $1/k$.

The description in terms of ϵ is beneficial when D_m can be determined independently, e.g. from measurement of the lag time. This is the time it takes for a compound to move across the membrane, which is directly related to the diffusion constant from steady state transport according to Eq. (4).

$$D_{lag} = \frac{\langle d_m^2 \rangle}{6t_{lag}} = \frac{D_m}{\Theta} \quad (4)$$

By combination of Eqs. (2) and (4), ϵ can be expressed in terms of D_{lag} and J_{max} as denoted in Eq. (5). The two methods described above (lag time and J_{max} vs. d_m) should yield equal ϵ values when compared at the same membrane thickness.

$$\epsilon = \frac{D_{lag} \Theta L_o}{d_m J_{max}} - 1 \quad (5)$$

The diffusion constant of a spherical species in a bulk liquid (D_b) depends on the viscosity of the solvent according to the theoretically derived Stokes–Einstein equation [Eq. (6)]. Although in our case the complexes are probably not exactly spherical, we assume that their diffusion constants in the membrane (D_m) linearly increase with T/η .

$$D_b = \frac{RT}{6\pi N_A \eta r} \quad (6)$$

In order to compare the diffusion and phase transfer coefficients obtained from flux measurements with different supports, corrections have to be carried out for membrane porosity (Θ) and tortuosity (τ) as denoted in Eqs. (7) and (8), respectively. Since the normalized diffusion constant ($D_{m,n}$) and the normalized phase transfer coefficient (k_n) both contain the factor Θ , the transport regime (ϵ) only depends on membrane thickness and tortuosity.

$$D_{m,n} = D_m \frac{\tau}{\Theta} \quad (7)$$

$$k_n = k \frac{1}{\Theta} \quad (8)$$

3. Experimental

3.1. Materials

Supports

The porous polymeric support Accurel 1E-PP was obtained from Enka Membrana ($d_m = 100\ \mu m$, $\Theta = 0.64$, $\tau = 2.1$) [19] and Celgard 2500 ($d_m = 25\ \mu m$, $\Theta = 0.45$, $\tau = 2.35$) [19] from Hoechst Celanese.

Carriers

p-*tert*-Butylcalix[4]arene tetraethyl ester (**1**) [20] and 1,3-dimethoxy-*p*-*tert*-butylcalix[4]arene crown-5 (**2**) [21] were synthesized according to literature procedures.

Solvents

o-Nitrophenyl *n*-octyl ether [22], *m*-nitrophenyl *n*-octyl ether [23], *p*-nitrophenyl *n*-octyl ether [23], *o*-cyanophenyl *n*-octyl ether [24], *p*-cyanophenyl *n*-octyl ether [25], 2-nitrodiphenyl ether [26], 2-cyanodiphenyl ether [27], and 2-fluorophenyl-2'-nitrophenyl ether [26] were synthesized according to literature procedures, purified by flame distillation under reduced pressure (<0.1 mmHg) and checked for purity by GLC (>99%).

Salts

Potassium perchlorate, sodium perchlorate, and sodium thiocyanate (Janssen), and potassium thiocyanate (Fluka) were used as received.

3.2. Physical constants of the membrane solvents

The dielectric constants of the membrane solvents were determined on a WTW Dekameter DK300 (measuring cell M II), calibrated at 25°C with acetone ($\epsilon_r = 20.7$) and methanol ($\epsilon_r = 32.63$). The kinematic viscosity measurements were performed with a Ubbelohde viscosity meter ($K_{25} = 9.744 \times 10^{-3}$). The densities of the solvents were measured at 25°C with a Paar DMA58 density meter.

3.3. Transport measurements

The transport experiments were carried out in a permeation cell consisting of two identical cylindrical compartments (half-cell volume 50 ml; effective membrane area 13.8 cm²). Details of this cell are described elsewhere [28]. The supported liquid membrane consisted of a thin porous polypropylene film immobilizing the solution of carrier (1×10^{-2} M). In order to promote the dissolution of the carrier in the membrane solvent dichloromethane was added, which was subsequently evaporated under reduced pressure (<0.1 mmHg). The support was submerged in the carrier solution and kept until the membrane was uniformly filled, i.e. transparent in the cases of phenyl octyl

ether solvents. In order to fill the pores of the support with diphenyl ether solutions a volatile cosolvent was added which was subsequently slowly evaporated under reduced pressure. The superfluous organic solution at the outside of the support was removed by carefully wiping the membrane surface with a tissue. Aqueous salt solutions were used as the source phase and doubly distilled and deionized water was used as the receiving phase. The measurements were performed at least in duplicate in a single Accurel sheet at 25°C. The concentrations of the transported 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). Initial steady state transport was measured up to receiving phase salt concentrations of at most 10⁻⁴ M. Salt activities were calculated according to a two-parameter approximation of the Debye–Hückel theory [29]. The standard deviation in the transport measurements is about 15%.

Lag time measurements, variation of the membrane thickness, and variable temperature measurements were carried out as reported [2]. The stirring speed in both aqueous phases was as high as 750 rpm, which validates neglect of diffusional resistances outside the membrane.

4. Results and discussion

4.1. Effects of membrane solvent

The solvent that is most commonly used as the medium for membrane transport in our laboratory, 2-nitrophenyl-*n*-octyl ether (2-NPOE) [3,30], has the lowest viscosity of the series (11.5 mPa s) and a dielectric constant (23.1) comparable to that of ethanol. The dielectric constants and (dynamic) viscosities of all membrane solvents are listed in Table 1. In the series of octylphenyl ethers the electron withdrawing group (NO₂ or CN) and its position on the phenyl ring (2, 3 or 4) have been varied. The diphenyl ethers were selected for transport studies because of their high polarity.

Although the membrane solvents all have similar structures, their physical properties are remarkably different. Apparently, small structural changes induce relatively large effects on their dielectric constants and

Table 1
Physical constants of the membrane solvents

Membrane solvent ^a	ϵ_r^b	ν^b (cS)	Density ^b (g cm ⁻³)	η^c (mPa s)
(A) 2-NPOE	23.1	11.0	1.048	11.5
(B) 3-NPOE	16.3	13.1	1.036	13.6
(C) 4-NPOE	16.7	18.3	1.040	19.0
(D) 2-CPOE	23.4	15.5	0.958	14.9
(E) 4-CPOE	14.6	16.5	0.955	15.8
(F) 2-NDPE	28.1	14.8	1.236	18.3
(G) 2-CDPE	29.1	20.3	1.129	22.9
(H) FNDPE	50	19.8	1.210	25.9

^aCodes are illustrated in Scheme 2.

^bThe dielectric constants (ϵ_r), kinematic viscosities (ν), and densities were determined at 298 K.

^cThe dynamic viscosities (η) at 298 K were calculated from ν and density values.

Table 2
Diffusion and extraction constants for transport of NaClO₄ with carrier 1: variation of membrane solvent

Membrane solvent ^a	J (10 ⁻⁸ mol m ⁻² s ⁻¹)		D_m^c (10 ⁻¹² m ² s ⁻¹)	K_{ex}^c (M ⁻¹)
	2 × 10 ⁻² M ^b	1 × 10 ⁻¹ M ^b		
(A) 2-NPOE	47.8	118	121	10.6
(B) 3-NPOE	7.63	42.0	88.6	0.35
(C) 4-NPOE	10.9	41.4	64.2	1.68
(D) 2-CPOE	38.1	84.6	99.6	8.38
(E) 4-CPOE	8.17	34.4	80.3	0.46
(F) 2-NDPE	46.9	75.0	72.5	40.0
(G) 2-CDPE	36.4	65.3	63.1	24.4
(H) FNDPE	49.2	56.4	55.8	220

^aThe structures of the membrane solvents are illustrated in Scheme 2.

^bActivities of salts in the source phase were calculated 1.74 × 10⁻² M (2 × 10⁻² M); 7.76 × 10⁻² M (1 × 10⁻¹ M); 6.26 × 10⁻¹ M (1 M).

^cCalculated according to Eq. (1).

dynamic viscosities. Since there is no simple relationship between the ϵ_r and η values, they will be considered as independent variables.

Since the transport of NaClO₄ mediated by carrier 1 is determined by diffusion of the carrier cation complex through the membrane [2], Eq. (1) ($\epsilon=0$) can be used to describe the initial steady state flux. Diffusion constants (D_m) and extraction constants (K_{ex}) were determined from the flux as a function of source phase salt concentration in all eight membrane solvents

(Table 2). [3] The diffusion constants are plotted against reciprocal solvent viscosity in Fig. 1.

Least square analysis shows a good correlation ($r^2=0.94$) thus validating the use of Eq. (6). The calculated extraction constants in Table 2 vary over a range of almost three orders of magnitude as a function of the solvent dielectric constant. In the more polar membrane solvents the extraction constants are relatively high compared to those in the less polar solvents. An empirical relation ($r^2=0.96$) has been tested, viz. $\log K_{ex}$ vs. $(\epsilon_r - 1)/(2\epsilon_r + 1)$, the Kirkwood function (Fig. 2).

The solvent effect on K_{ex} is the combination of the influence on salt partition (K_p) and complex formation (K_a). In general polar solvents favor salt partition, but show diminished tendency for complex formation [10]. Since the overall effect of solvent polarity on partition and complexation is positive, the polarity

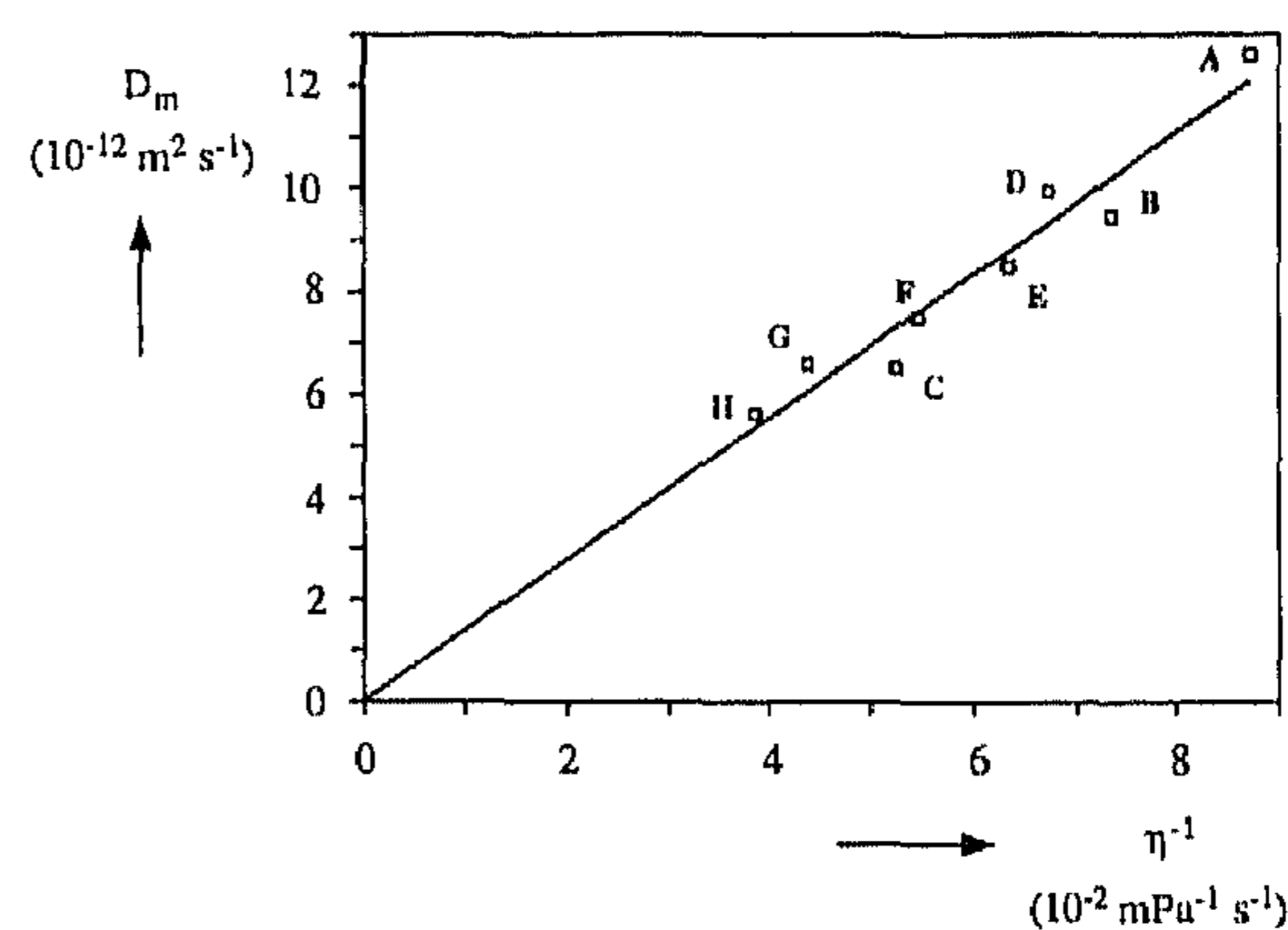


Fig. 1. Relationship between diffusion constant and solvent viscosity for transport of NaClO₄ with carrier 1.

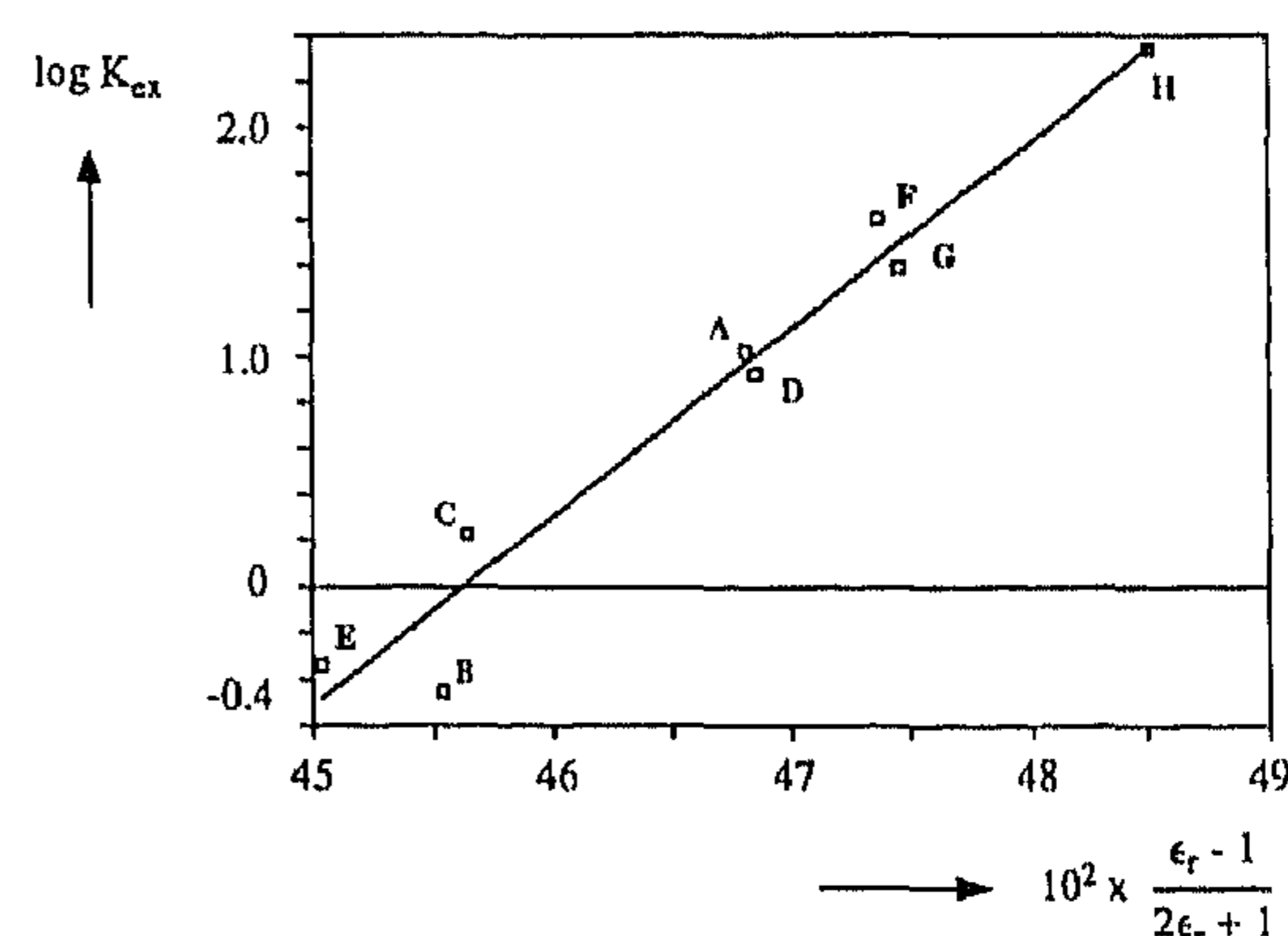


Fig. 2. Relationship between extraction constant and solvent polarity for transport of NaClO₄ with carrier 1.

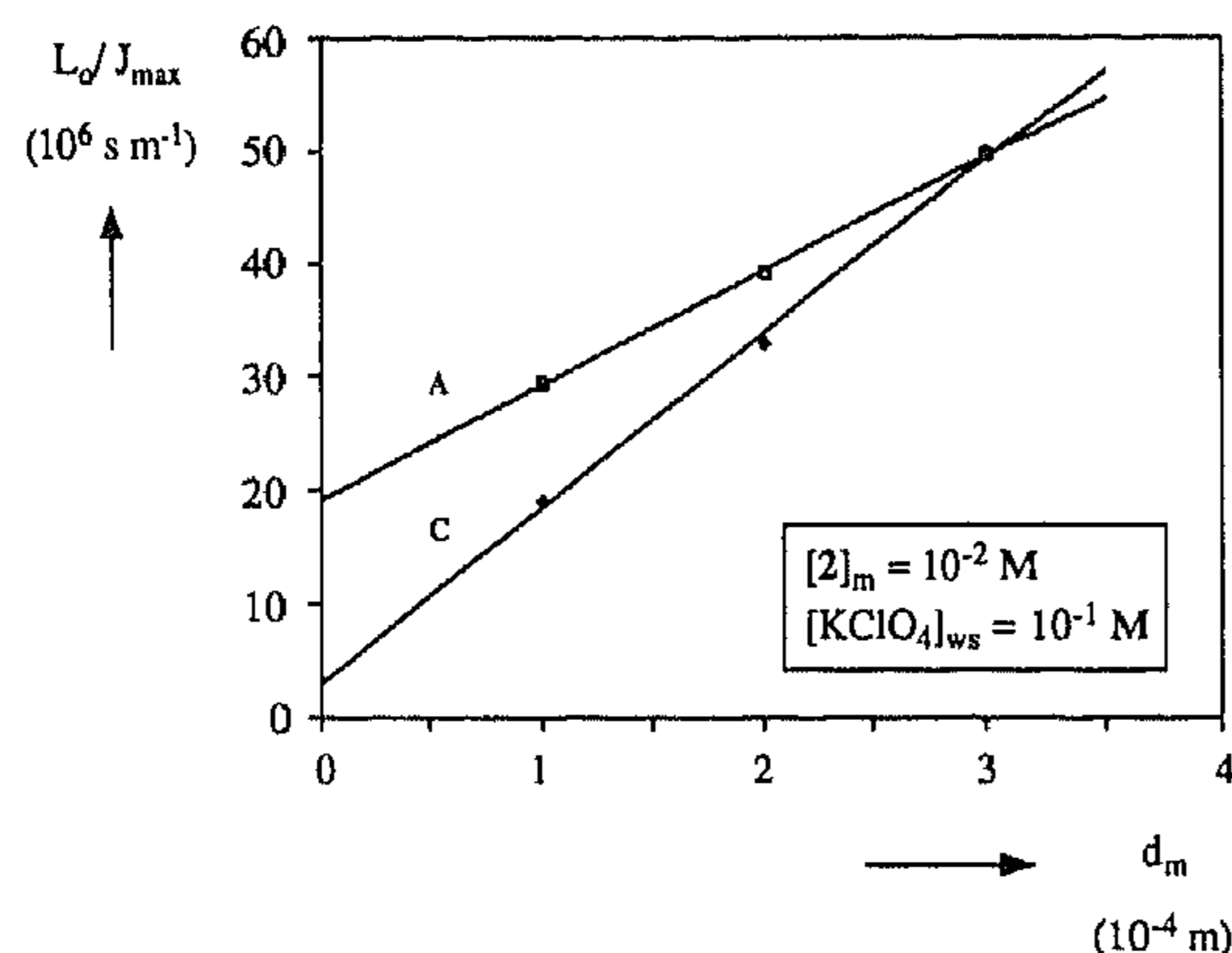


Fig. 3. KClO_4 transport mediated by carrier 2 as a function of membrane thickness for 2-NPOE (A) and 4-NPOE (C) as the membrane solvent.

appears to affect the partition process to a higher degree.

In order to verify whether the solvent effects described so far may be generalized, the parameters for transport of KClO_4 with carrier 2 were determined. In 2-NPOE/Accurel the transport is affected by the slow rate of cation release [2]. When the carrier is saturated, D_m and k determine the flux according to Eq. (3). The saturation of carrier 2 was verified by flux measurement as a function of the source phase KClO_4 activity using 4-CPOE as the membrane solvent. Since the ϵ_r value of 4-CPOE and hence the K_{ex} is the lowest for the series of solvents used, Eq. (3) is valid for all solvents.

The effects of the membrane solvent on D_m and k are nicely illustrated for transport through 2-NPOE and 4-NPOE (Fig. 3). The slopes of the lines ($1/D_m$) indi-

cate that the diffusion constant in 2-NPOE is almost twice as high as that in 4-NPOE. Since the viscosity of 4-NPOE is about twice as high as that of 2-NPOE, this is in accordance with the Stokes–Einstein equation [Eq. (6)]. Moreover, by comparing the data of Table 2 and Table 3 it appears that the diffusion constants of $1 \cdot (\text{NaClO}_4)$ and $2 \cdot (\text{KClO}_4)$ in 2-NPOE are almost equal. The large intercept ($1/k$) for transport through 2-NPOE indicates that the kinetic resistance is substantial, while this is relatively small for transport through 4-NPOE. Apparently, the cation release is slower when the solvent polarity is higher.

The same measurements have been carried out in the other six solvents and the D_m and k values are listed in Table 3. The transport regime strongly depends on the solvent. Transport of KClO_4 with 2 through 4-CPOE is mainly diffusion limited ($\epsilon = 0.2$), whereas transport through FNDPE is mainly kinetically controlled ($\epsilon = 3.8$).

Fig. 4 shows that the D_m values (Table 3) increase with the reciprocal viscosity of the membrane solvents (Fig. 4). The least square fit is reasonably good ($r^2 = 0.94$) and the line virtually goes through the origin, in accordance with the Stokes–Einstein equation [Eq. (6)].

The k values of Table 3 vary by at most a factor of about 30, decreasing in the direction of increasing polarity. In order to quantify the effect of the dielectric constants of the solvent on k , $\log k$ is again plotted versus the Kirkwood function (Fig. 5).

Table 3

Diffusion and decomplexation rate constants for transport of KClO_4 with carrier 2: variation of membrane solvent

Membrane solvent ^a	J_{\max} ($10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$)				D_m^c ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)	k^c (10^{-8} m s^{-1})	ϵ
	1 ^b	2 ^b	3 ^b	4 ^b			
(A) 2-NPOE	34.1	25.5	20.1		9.85	5.24	1.9
(B) 3-NPOE	52.7	31.6	23.7	18.1	8.40	13.8	0.6
(C) 4-NPOE	52.8	30.4	20.1		6.48	33.1	0.2
(D) 2-CPOE	35.3	25.0	19.5	15.2	8.12	6.44	1.3
(E) 4-CPOE	48.9	29.3	20.0	16.8	7.54	12.8	0.6
(F) 2-NDPE	13.4	11.1	9.0		5.38	1.82	3.0
(G) 2-CDPE	17.0	12.0			4.04	2.94	1.4
(H) FNDPE	9.1	7.5			4.31	1.14	3.8

^aSolvent structures are depicted in Scheme 2.

^bThe thickness of one membrane is 10^{-4} m .

^c D_m and k were obtained from Eq. (3).

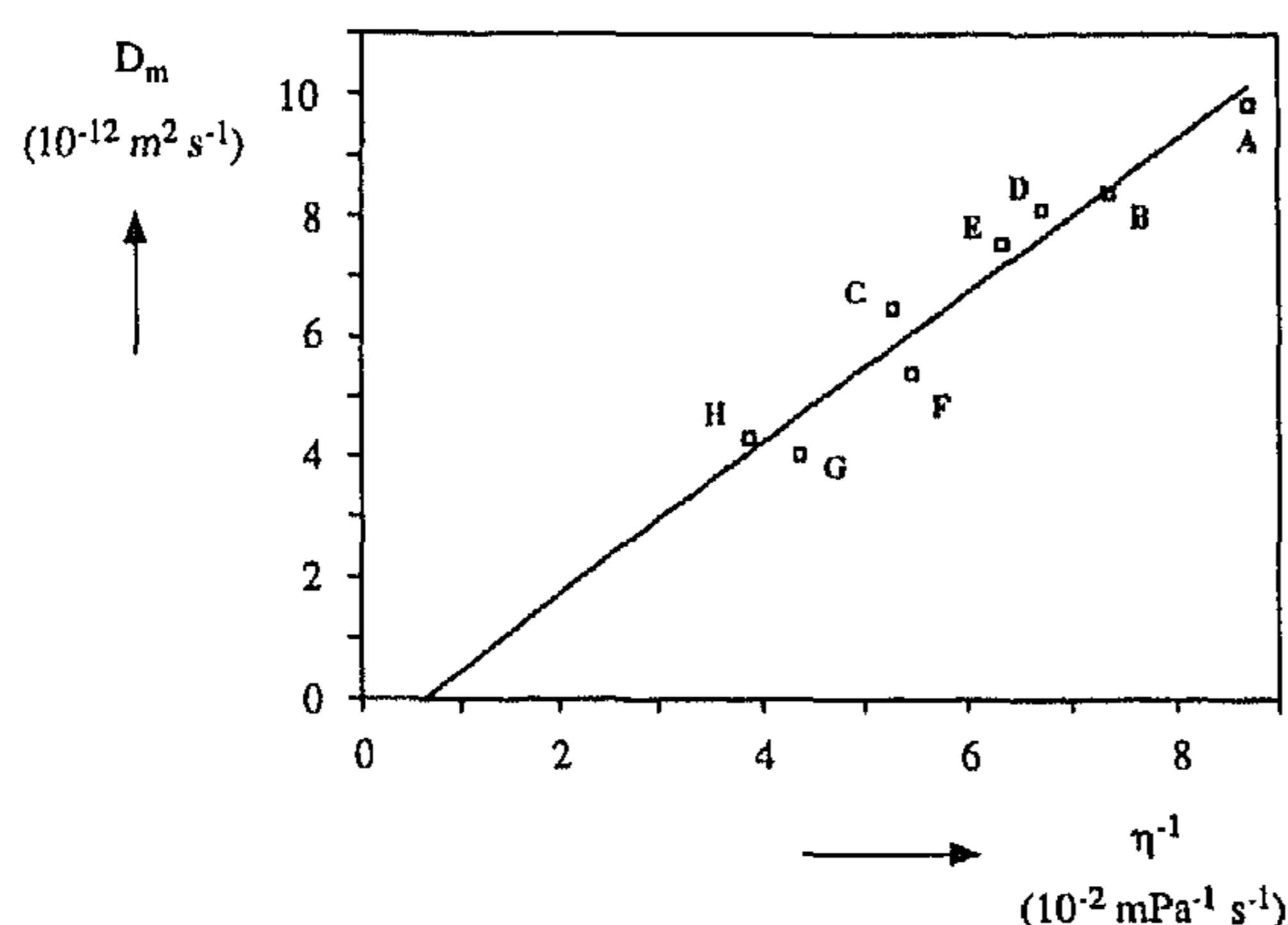


Fig. 4. Relationship between diffusion constant and solvent viscosity for transport of KClO_4 with carrier 2.

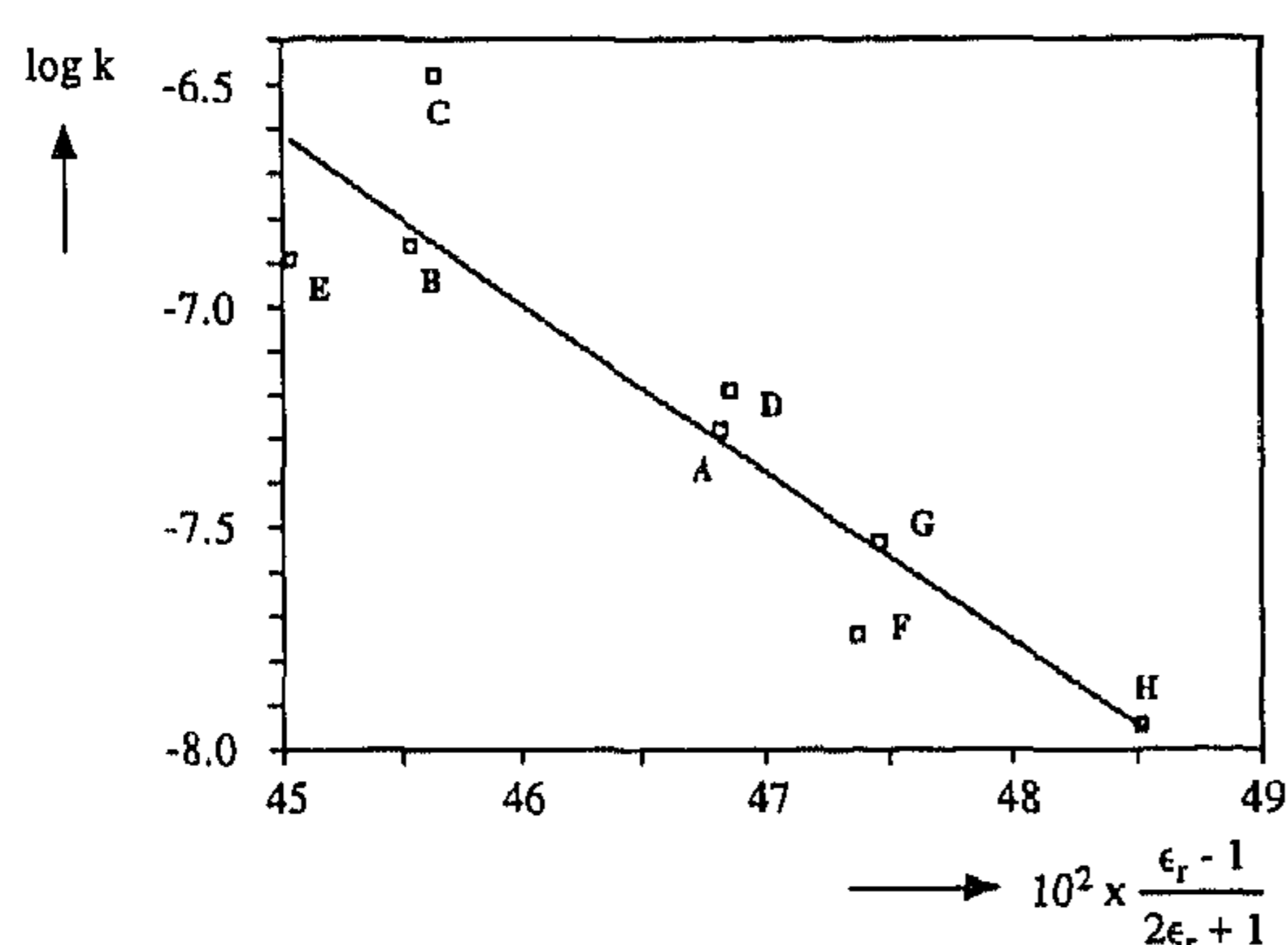


Fig. 5. Relationship between decomplexation rate constant and solvent polarity for transport of KClO_4 with carrier 2.

This empirical relationship fits reasonably well, except in the low ϵ_r region (solvents B, C, and E) where the data points are somewhat more scattered because the intercepts are relatively small. However, from all the evidence presented above it can be concluded that an increase of the solvent polarity promotes extraction and slows down the rate of cation release.

4.2. Effect of co-transported anion

According to the transport model in which it is assumed that only free ions are present in the membrane, the maximum flux is not affected by the nature of the anion. However, in a study of the effect of the anion on the transport properties of carrier 2, the maximum K^+ flux with ClO_4^- markedly differed from that with SCN^- as the counter-ion. In order to find the reason for this, maximum fluxes were measured with carriers 1–3, while independently diffusion constants were determined from lag times [Eq. (4)]. Eq. (5) was used to calculate ϵ values from J_{max} and D_{lag} . The results are shown in Table 4.

From Table 4 it is clear that the maximum attainable fluxes differ markedly, although the lag times are all about equal, independent of the carrier or the anion. The ϵ value for transport of NaClO_4 with carrier 1 is very small and indicative for diffusion limited transport. The transport of KSCN with 2 is mainly limited by diffusion of the complex ($\epsilon=0.6$), while that of KClO_4 is primarily kinetically controlled ($\epsilon=2.3$). The highest ϵ value was obtained for transport of KClO_4 with 3, indicating that in this case transport has the strongest kinetic limitation.

Additional information about the effect of the anion was obtained from variation of the operating temperature and the membrane thickness. Both affect the rate-limiting step of transport, as is evident from Eq. (3). In order to eliminate the effect of temperature on the extraction constant, transport experiments were carried out at source phase salt concentrations sufficient to saturate the carrier completely. The activation energies calculated from Arrhenius plots, $\ln J_{\text{max}}$ vs. T^{-1} , are listed in Table 5.

Table 4

Diffusion constants from lag times, maximum fluxes and calculated ϵ values: variation of co-transported anion

Carrier ^a	Salt	Lag-time ^b (s)	D_{lag} ($10^{-11} \text{ m}^2 \text{ s}^{-1}$)	J_{max} ($10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$)	ϵ
1	NaClO_4	370	1.8	12.6 ^c	(-0.1)
	NaSCN	370	1.8		
2	KClO_4	395	1.7	3.3 ^c	2.3
	KSCN	415	1.6	6.3	0.6
3	KClO_4	350	1.9	2.6	3.6

^a $L_0 = 1 \times 10^{-2} \text{ M}$.

^b $d_m = 2 \times 10^{-4} \text{ m}$.

^cValues taken from Tables 2 and 3.

Table 5
Activation energies for alkali cation transport: variation of anion and membrane thickness

Carrier	Salt	d_m (μm)	E_a (kJ/mol)
1	NaClO ₄	100	32 ± 2
2	KClO ₄	100	63 ± 2
	KSCN	100	41 ± 2
3	KClO ₄	100	61 ± 3
	KClO ₄	400	60 ± 3
	KSCN	100	66 ± 1
	KSCN	200	42 ± 1

NaClO₄ transport with carrier **1** has an activation energy of 32 ± 2 kJ/mol. This is close to the E_a value for viscous flow of bulk 2-NPOE (24 kJ/mol) [2], confirming the diffusion limited transport. On increasing the relative contribution of the kinetic resistance, the activation energy is expected to increase proportionally, as is illustrated by the E_a values for transport of K⁺ salts with carriers **2** and **3**. The transport of KClO₄ with **2** is limited more by slow kinetics (63 ± 3 kJ/mol) than that of KSCN (41 ± 2 kJ/mol). The transport of KSCN with **3** through two membranes is already close to diffusion limitation (42.4 ± 0.7 kJ/mol), whereas the transport of KClO₄ is still kinetically limited (60 ± 3 kJ/mol) when four membranes are used. Thus the kinetic limitation is more important with carrier **3** and KClO₄ instead of KSCN. These findings are in line with the ϵ values (Table 4).

Since the anion has hardly any influence on diffusion constants, but it does affect the maximum flux and activation energies for transport, we conclude that the anion has to be involved in the kinetics of release. Apparently, KClO₄ is released more slowly than KSCN. From a plot of L_o/J_{max} vs. d_m , k and D_m values were determined (Table 6). Again the effect of the anion on D_m is minimal, while the value of k for trans-

port of KSCN is 2.7 times higher than that of KClO₄.

Both from lag times and from fluxes as a function of membrane thickness, the values of ϵ ($d_m = 1 \times 10^{-4}$ m) were calculated for the transport of KClO₄ and KSCN with carrier **2**. The values listed in Table 4 are in good agreement with those from Table 6: $\epsilon(\text{KClO}_4) = 2.3$ and 1.9; $\epsilon(\text{KSCN}) = 0.6$ and 0.8.

In order to explain the fact that the co-transported counter-ion affects the kinetics of release, several phenomena may be considered: ion-pair formation, influence of the size and shape of the anion, or independent partition of the anion. Previously, ion pairs in the membrane (2-NPOE/Accurel $L_o = 1 \times 10^{-2}$ M) were ruled out in transport of perchlorates [7]. However, ion-pair formation in the membrane may play a role in the transport of KSCN.

4.3. Effects of support

Two different macroporous polypropylene supports (Accurel and Celgard) with a different thickness, porosity, and tortuosity have been used. Accurel membranes have a random three-dimensional pore structure while in Celgard the pores are more or less perpendicular to the membrane surface. According to Eqs. (7) and (8) the diffusion constants and decomplexation rate constants can be corrected for tortuosity and porosity. In the absence of pore size effects, the normalized parameters (D_m , k) should be comparable with the corresponding parameters in bulk [16].

From flux measurements as a function of membrane thickness, D_m and k values have been obtained for transport of KClO₄ with carrier **2** (Table 6). The normalized diffusion and phase transfer coefficients through the two different supports are about equal. This means that the effects of the support morphology are accounted for by Θ and τ . However, the support may

Table 6
Diffusion and phase transfer coefficients for K⁺ transport mediated by carrier **2**: variation of anion and support^a

Salt	Support	D_m (10^{-12} m ² s ⁻¹)	$D_{m,n}$ (10^{-12} m ² s ⁻¹)	k (10^{-8} m s ⁻¹)	k_n (10^{-8} m s ⁻¹)	ϵ^c
KClO ₄	Accurel	9.9 ^b	32	5.2 ^b	8.2	1.9
KSCN	Accurel	11.2		13.9		
KClO ₄	Celgard	5.6	29	4.6	10	4.9

^a[**2**]_m = 1 × 10⁻² M.

^bValues from Table 3.

^cCalculated for one membrane.

influence the transport regime, indicated by the ϵ values, as the result from the different thicknesses of Accurel and Celgard 2500.

5. Conclusions

The transport of salt by calix[4]arene carriers in SLMs depends on the polarity and viscosity of the membrane solvent. The diffusion constants of the carrier complexes linearly increase with reciprocal solvent viscosity as predicted by the Stokes–Einstein equation. $\log K_{\text{ex}}$ linearly increases with the Kirkwood function, whereas $\log k$ linearly decreases. Consequently, the flux always increases in a solvent of lower viscosity, while the effect of solvent polarity on the flux depends on the rate-limiting step as well as on the source phase salt concentration.

The co-transported anion has hardly an effect on the diffusion constant of the complex but it influences the kinetics of cation release and consequently the transport regime.

Since the normalized k and D_m values obtained for 2/KClO₄ in 2-NPOE/Accurel 1E-PP and 2-NPOE/Celgard 2500 are about equal, the support affects the transport regime (ϵ) by its tortuosity and thickness, but not by its morphology.

6. List of symbols

Roman

a_s	salt activity
A	$K_{\text{ex}} a_s^2$ (M or mol m ⁻³)
d_m	membrane thickness (m)
D_m	diffusion constant of the complex in the membrane (m ² s ⁻¹)
D_b	diffusion constant of the complex in the bulk (m ² s ⁻¹)
$D_{m,n}$	normalized diffusion constant as defined in Eq. (7) (m ² s ⁻¹)
E_a	activation energy (kJ mol ⁻¹)
J	flux (mol m ⁻² s ⁻¹)
J_{max}	flux under conditions that [complex] _{ms} = L_o (mol m ⁻² s ⁻¹)
k	decomplexation rate constant (m s ⁻¹)

k_n	normalized decomplexation rate constant as defined in Eq. (8) (m s ⁻¹)
K_{ex}	extraction constant (M ⁻¹ or mol ⁻¹ m ³)
L_o	carrier concentration (M or mol m ⁻³)
N_A	Avogadro's constant (6.022×10^{23} mol ⁻¹)
r	radius of the solute (m)
R	gas constant (8.314 J K ⁻¹ mol ⁻¹)
T	temperature (°C or K)
Greek	
ϵ	dimensionless number defined as D_m/kd_m
ϵ_r	dielectric constant
η	dynamic viscosity (mPa s)
Θ	porosity of support
ν	kinematic viscosity (cS)
τ	tortuosity of support
Subscripts	
ws	denotes in the aqueous source phase
ms	denotes in the membrane at the source phase interface

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