where x_q is the liquid-phase mole fraction, D is a characteristic multicomponent parameter, and g_{ij} is an energy parameter which characterizes the interaction between molecules i and j. In this study, the value of C in eq 1 was empirically determined as 1.5, and the v_j/v_i (ratio of liquid molar volumes) in eq 5 was set to unity. In the correlation of quaternary data sets, 12 binary parameters R_{ij} and a multicomponent parameter D are needed. In type I quaternary systems, one binary is partialy miscible and the other binaries are completely miscible. In type II quaternary systems, two binaries are partially miscible. The parameters R_{ij} representing the partially miscible binary system were obtained on the basis of the condition $(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}}$ from the mutual solubilities. The values were evaluated using the Newton–Raphson iterative method. The binary parameters R_{ij} for the completely miscible binary system were obtained from binary vapor–liquid equilibrium (VLE) data. A computer program described by Fredenslund et al. (*8*) was used to calculate the activity coefficients from VLE data. By using the Marquardt method to give the best fit for the experimental activity coefficients, the optimum R_{ij} values were obtained. To give a good representation for LLE of a quaternary system, the optimum value of the parameter D is needed. As the R_{ij} for binary mixtures was determined using the mutual solubility data and VLE data, only the parameter D was evaluated to give the best fit for LLE data for quaternary systems. The values of parameters and correlation performance (average deviation) are shown in Table X. The parameters R_{34} and R_{43} for type I quaternary systems in Table X were obtained from VLE data (*9*) for the benzene + toluene system. The parameters R_{14} and R_{41} for type II quaternary systems were obtained from VLE data (*10*) for the heptane + octane system. The other binary parameters were established in earlier papers (*2*, *3*). The mean deviation between experimental and calculated mole fractions are similar to that of ternary systems containing alkane, methanol, and aromatic compounds. A fairly good agreement for LLE of type I and type II quaternary systems is obtained.

Glossary

D	characteristic multicomponent parameter
g_{ij}	interaction energy between components i and j
R_{ij}	$g_{ij} - g_{ii}$
x	mole fraction
γ	activity coefficient

Subscripts

i,j	components i and j

Registry No. Methanol, 67-56-1; heptane, 142-82-5; octane, 111-65-9; benzene, 71-43-2; *p*-xylene, 106-42-3; toluene, 108-88-3.

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Extraction and Transport of Na^+ and K^+ in a Liquid Membrane Containing Crown Ethers: Effect of the Mixed Solvent

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Transport rates for K^+ and Na^+ have been measured in a bulk liquid membrane containing dibenzo-18-crown-6 as the carrier and employing chloroform, 1,2-dichloroethane, nitrobenzene, and their binary solutions as the solvent. Also distribution ratios for liquid–liquid extraction of K^+ and Na^+ from aqueous solutions into organic solvents containing the crown ether are reported. In both membrane transport experiments and solvent extraction determinations, a maximum value of the transport rate v and of the distribution ratio m, respectively, is obtained when an equimolar solution of chloroform and nitrobenzene is used as the solvent.

Introduction

Macrocyclic ligands such as certain crown ethers complex selectively with cations and have been used as cation transport carriers in liquid membranes. Many factors such as crown ether structure, complex stability, counteranion type, salt or macrocyclic concentration, and membrane solvent type play an important role in selective alkali-metal solvent extraction from aqueous solutions (*1*–*9*).

In this work we are most concerned with the effect of the solvent which is one of the key factors which governs extractions. In particular we performed some experiments employing mixed solvents at different binary composition. We used di-

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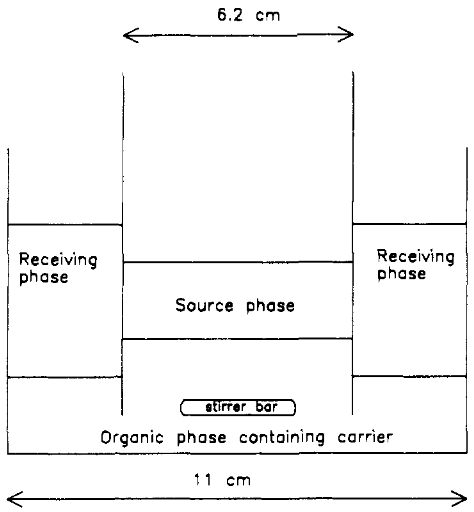

Figure 1. Schematic view of the liquid membrane cell.

Table I. Distribution Ratios and Conditional Constant Values for the Different Examined Systems

		10^3m		$10^2K'$	
system	x_1	Na^+	K^+	Na^+	K^+
chloroform	1	0.25	1.54	0.562	4.06
dichloroethane	1	0.16	1.06	0.359	2.78
nitrobenzene	1	0.53	2.74	1.190	7.31
chloroform (1) + nitrobenzene (2)	0.5	0.66	4.13	1.490	11.20
chloroform (1) + dichloroethane (2)	0.5	0.24	1.41	0.539	3.72
dichloroethane (1) + nitrobenzene (2)	0.5	0.47	2.16	1.060	5.73

benzo-18-crown-6 as carrier, since for this crown ether numerous experimental data are readily available for both membrane transport and extraction equilibria determinations employing different pure organic solvents (*2*, *10–12*). These references could be helpful to make a comparison.

Experimental Section

Dibenzo-18-crown-6 (Janssen Chemicals) was recrystallized from benzene and dried under vacuum; NaCl, KCl, chloroform, 1,2-dichloroethane, and nitrobenzene were commercially available (analytical reagent grade) and were not further purified. Before the experiments the organic solvents and water were preequilibrated with each other.

Liquid membrane experiments were performed using a cell previously described by Lamb et al. (*2*) and shown schematically in Figure 1.

Either 1 M NaCl or 1 M KCl solution was used as the source phase and distilled water as the receiving phase. Chloroform, 1,2-dichloroethane, nitrobenzene, and their binary solutions were used as the solvent in the liquid membrane, and dibenzo-18-crown-6 was used as the carrier. The phases were stirred by a magnetic stirrer driven at 300 rpm, and the temperature was 25 ± 1 °C.

Samples of the receiving-phase solution were withdrawn at regular time intervals and analyzed for cation concentration on an atomic absorption spectrophotometer (IL VIDEO 12). Blank experiments were performed with the solvents containing no crown ether, and in no case was there detectable movement of the cation across the solvent membrane.

In solvent extraction experiments, equal volumes of organic solvent (0.1 M dibenzo-18-crown-6) and aqueous solution (1 M NaCl or KCl) were shaken in a thermostatic bath at 25.0 ± 0.5 °C for 15 min. The phases were allowed to settle overnight in the bath. The organic solution was withdrawn and analyzed for alkali-metal cation M^+ (K^+ or Na^+). The results are expressed as the distribution ratio $m = (C_{M^+})_o/(C_{M^+})_a$ of M^+ between the two phases, being the concentrations C (mol dm^{-3}). The results are shown in Table I.

Results

When the equilibrium between an aqueous phase containing an alkali-metal cation M^+ and a counteranion A^- and an organic phase containing a neutral ligand L is achieved, a crown ether complex is considered to be formed and the overall equilibrium

$$M_a^+ + A_a^- + L_o = MLA_o$$

can be expressed by means of the overall equilibrium constant K:

$$K = \frac{(a_{MLA})_o}{(a_{M^+})_a(a_{A^-})_a(a_L)_o} \quad (1)$$

where MLA denotes an ion pair between ML^+ and A^-.

The conditional constant K' can be defined by

$$K' = \frac{(C_{MLA})_o}{(a_{M^+})_a(a_{A^-})_a(C_L)_o} = \frac{K\gamma_L}{\gamma_{MLA}} \quad (2)$$

where γ_L and γ_{MLA} are the activity coefficients of the neutral ligand and crown ether complex in the organic solvent, respectively.

Due to the relatively low dielectric constant of the solvents and the low solubility of the electrolyte in the membrane solvents, the concentration of the free ions and uncomplexed ion pairs in the organic phase can be considered negligible, and if the crown ether and its complex are slightly soluble in water, then

$$(C_{MLA})_o = (C_{M^+})_o \quad (3)$$

$$(C_L)_o = (C_L^0)_o - (C_{MLA})_o = (C_L^0)_o - (C_{M^+})_o$$

and

$$K' = \frac{(C_{M^+})_o}{a^2(C_L)_o} \quad (4)$$

where $a = (a_{M^+})_a = (a_{A^-})_a$ and $(C_L^0)_o$ is the initial concentration of L in the organic phase.

Then

$$(C_{M^+})_o = K'a^2(C_L)_o = \frac{K'a^2(C_L^0)_o}{1 + K'a^2} \quad (5)$$

K' values are concentration independent providing that the ratio γ_L/γ_{ML} is similarly independent. The K' values, also reported in Table I, calculated from experimental determinations of the distribution ratio m, are in good agreement with those of Marcus (*12*).

The total amounts of solute transported into the receiving phase have been plotted vs time for each carrier-containing system. The data were fitted to a straight line, the slope of which gave the values of transport rates v (mol/h) reported in Table II. The agreement of v values between three runs of the same system was within 10% in all cases. Figure 2 shows some examples.

The ion transport consists of four major steps: uptake of a cation and an anion into a membrane phase, diffusion of a metal–carrier complex associated with the anion within the membrane phase, release of the ions into an aqueous phase, and back-diffusion of a free carrier.

Since the concentration of the source phase is much greater than that of the receiving phase and the ordinary diffusion of

Table II. Effect of Carrier Concentration and Solvent Composition on the Mass Transport Rate *v* of Alkali-Metal Cations through the Organic Phase

system	x_1	C_o/(mol L^{-1})	$10^6 v$/(mol h^{-1}) K$^+$	$10^6 v$/(mol h^{-1}) Na$^+$
chloroform	1	7×10^{-4}	0.54	
		7×10^{-3}	3.5	0.18
		2×10^{-2}	7.4	0.36
		5×10^{-2}		1.2
		7×10^{-2}		1.6
dichloroethane	1	2×10^{-4}	0.14	
		2×10^{-3}	0.60	0.05
		2×10^{-2}	4.2	0.35
		5×10^{-2}		0.60
		7×10^{-2}		1.0
nitrobenzene	1	2×10^{-4}	1.5	
		7×10^{-4}		0.5
		2×10^{-3}	6.1	0.7
		2×10^{-2}	18	2.1
		5×10^{-2}		6.0
		7×10^{-2}		8.2
chloroform (1) + nitrobenzene (2)	0.50	2×10^{-3}	12	1.1
		7×10^{-3}	20	2.0
		2×10^{-2}	54	5.0
		5×10^{-2}		15
		7×10^{-2}		21
chloroform (1) + nitrobenzene (2)	0.15	2×10^{-2}	33	3.2
	0.30		42	3.7
	0.50		54	5.0
	0.70		31	3.0
	0.85		20	1.5
dichloroethene (1) + nitrobenzene (2)	0.15	2×10^{-2}	17	1.8
	0.30		16	1.5
	0.50		19	1.2
	0.70		11	0.97
	0.85		6.5	0.57
chloroform (1) + dichloroethane (2)	0.15	2×10^{-2}	5.8	0.29
	0.30		7.0	0.28
	0.50		9.3	0.27
	0.70		9.1	0.26
	0.85		8.5	0.30

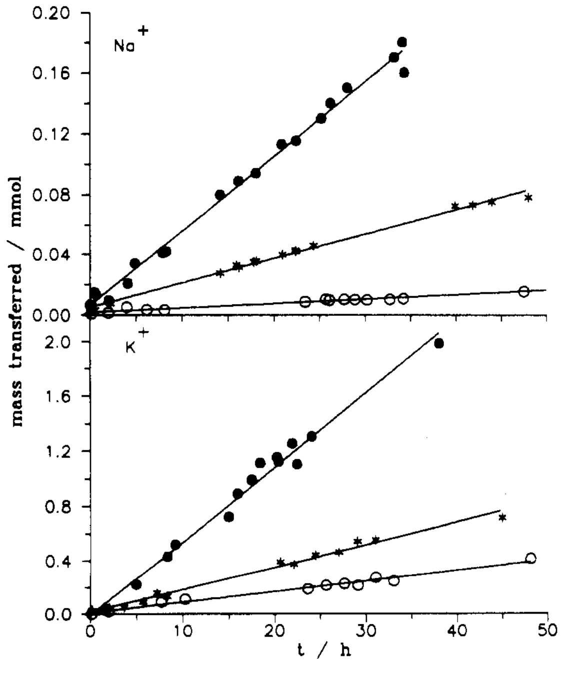

Figure 2. Amount of metal chloride in the receiving phase as a function of transport time in a membrane containing 2×10^{-2} M of dibenzo-18-crown-6, and employing chloroform (o), nitrobenzene (*), and an equimolar solution of chloroform nitrobenzene (●).

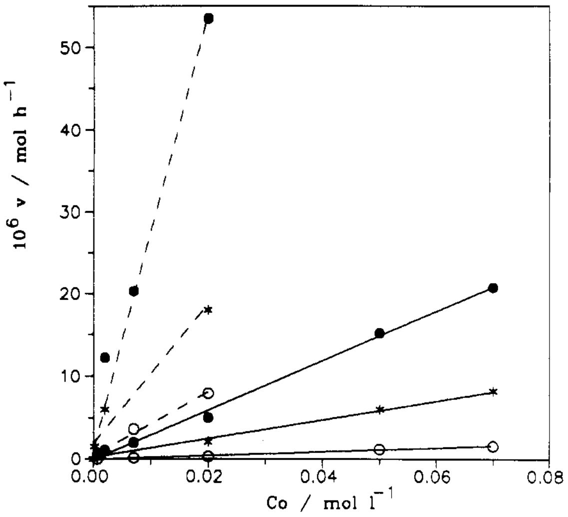

Figure 3. Effect of the dibenzo-18-crown-6 concentration on the transport rate of alkali-metal cations in a membrane containing chloroform (O), nitrobenzene (*), and an equimolar solution of chloroform + nitrobenzene (●) ((---) K$^+$; (—) Na$^+$).

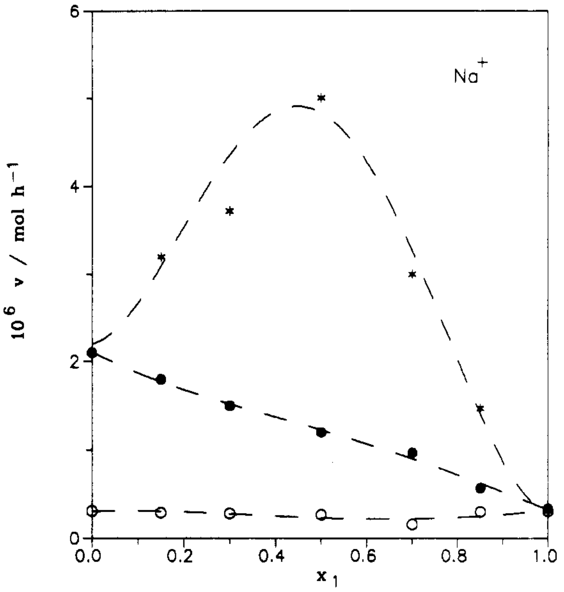

Figure 4. Dependence of the transport rate of Na$^+$ ion on the mixed solvent composition for the systems (*) chloroform (1)–nitrobenzene (2); (●) dichloroethane (1)–nitrobenzene (2); (O) chloroform (1)–dichloroethane (2).

the ion pair can be considered negligible, the salt flux J can be expressed by

$$J = \frac{D_s K' (C_L^{\,0})_0}{l} \frac{a^2}{(1 + K'a^2)} \qquad (6)$$

as described by several researchers (*1*, *2*, *10*); in eq 6 K' rather than K is used because the activity coefficients γ_L and γ_{MLA} in the organic solvents are yet unknown.

The transport rate v is expressed by $v = JA$, where A is the interface area and in all performed experiments its value can be assumed as a constant.

In accordance with eq 6 if all other terms are constant, the flux J varies linearly with the concentration of the carrier and the transport rate v behaves in the same way as illustrated in Figure 3, where the transport rates v are reported for different concentrations of crown ether in the case of K$^+$ and Na$^+$ ions in different membrane solvents.

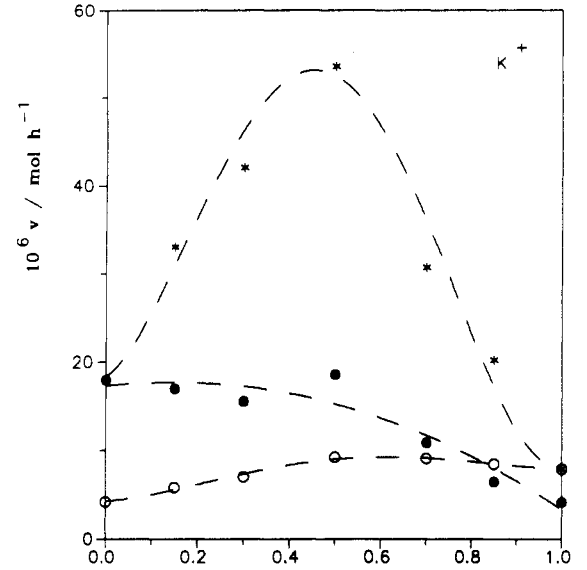

Figure 5. Dependence of the transport rate of K^+ ion on the mixed solvent composition for the systems (*) chloroform (1)–nitrobenzene (2); (●) dichloroethane (1)–nitrobenzene (2); (○) chloroform (1)–dichloroethane (2).

The results indicate that the transport rate of K^+ is much greater than that of Na^+, but the two cations behave in the same way for the mixed solvent chloroform and nitrobenzene. In both cases the trend of the transport rate as a function of the solvent composition has a maximum at about $x_{\text{nitrobenzene}} = 0.5$. Similar experiments were made with 1,2-dichloroethane + nitrobenzene and chloroform + 1,2-dichloroethane at different compositions, but for these systems the plot of v as a function of the solvent composition did not show a marked maximum as can be seen in Figures 4 and 5. The transport rate values determined for the examined pure solvents are found in the sequence

1,2-dichloroethane < chloroform < nitrobenzene

The distribution ratio shows the same sequence, and also a maximum value is found for an equimolar solution of chloroform and nitrobenzene. Therefore, it can be hypothesized that the variations in the ion fluxes are, at least in part, due to different values of the distribution ratio and in particular of the equilibrium constants for the solute–crown complexation in the different solvents. Such behavior may arise from different solvent–crown interactions in the pure and mixed solvents.

List of Symbols

A	interface area
a	activity
C	concentration
D_s	diffusion coefficient
K	overall equilibrium constant
K'	conditional constant
J	flux
l	membrane thickness
v	transport rate
γ	activity coefficient

Subscripts

a	aqueous phase
o	organic phase
M^+	alkali-metal cation
A^-	counteranion
MLA	ion pair
L	neutral ligand

Registry No. Na^+, 17341-25-2; K^+, 24203-36-9; $CHCl_3$, 67-66-3; dibenzo-18-crown-6, 14187-32-7; 1,2-dichloroethane, 107-06-2; nitrobenzene, 98-95-3.

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Correction

Ternary Liquid–Liquid Equilibria of Water, Ethanol, and Oleic Acid. Zisheng Zhang and Gordon A. Hill, *J. Chem. Eng. Data* **1991**, *36*, 453–456.

The caption to Figure 3 should read as follows:

Figure 3. Effect of temperature on interaction energy difference for water (1) + ethanol (2) + oleic acid (3): (●) A_{23}; (✱) A_{21}; (▲) A_{31}; (■) A_{13}; (—) mean values.