Multifunctional Calix[4]arenes Containing Pendant Amide and Phosphoryl Groups: Their Use as Extracting Agents and Carriers for Alkali Cations

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Abstract. The complexing, extracting and mobile carrier properties of the tetra(phosphine oxide)-calix[4]arene **1** and the hybrid diamide-di(phosphine oxide)-calix[4]arene **2** were studied. Both ligands give 1 : 1 complexes with alkali cations in THF as shown by the *picrate method.* ^{1}H NMR experiments were run to follow encapsulation of sodium and potassium cations. The corresponding spectra indicate C_2-symmetrical structure. The observed extraction orders of the alkali picrates were as follows $K^+ > Rb^+ > Li^+ > Cs^+ > Na^+$ for **1** and $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ for **2**. Transport kinetics was analysed by means of a model which assumes pure diffusion and which allows the evaluation of mass transfer coefficients in all systems. These coefficients and their influences on the transport rate are discussed in terms of size of the transporting species in the liquid membrane.

Key words: Alkali cations, calixarene, amide, phosphine oxide, complexation, extraction, transport.

1. Introduction

Calix[4]arenes [1] bearing substituents attached at the phenolic oxygen atoms (i.e., functionalized at the lower rim) have been shown to exhibit interesting complexing, extraction and transport properties towards a great variety of metal ions [2]. In recent years, many neutral calix[4]arene-derived extractants containing functional groups such as amides, esters, ketones and ethers have been synthesized and their ion binding properties investigated by solvent extraction, UV-Vis. and NMR spectroscopy [3–10]. Most of these calixarenes are homo tetra–functionalized ligands. Encapsulation of alkali metal cations involving the four pendant groups has been proved in several instances by NMR studies and/or X-ray analysis [3, 5, 9, 11–13].

In this paper we describe the complexing, extracting and carrier properties of the recently reported calix[4]arenes [14, 15] **1** and **2** containing amide and/or phosphine oxide functional groups (Figure 1). These ligands were shown to adopt a cone-shaped conformation. The extraction efficiency of these ligands will be discussed considering their ligating functions and compared with that of the tetra-amide **3**, previously reported in the literature [16].

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Figure 1. Structures of the calixarenes mentioned in the text.

2. Experimental

2.1. MATERIAL

Ligands **1** and **2** were synthesized according to the procedures described previously [14, 15]. DC18C6 was used as purchased (Fluka).

The alkali picrates were obtained by neutralization of picric acid with a solution of the corresponding hydroxide. The resulting yellow precipitates were recrystallized from water and washed with ethanol and ether, dried under vacuum and stored in the dark.

Cesium and rubidium thiocyanate were prepared by addition of cesium carbonate and rubidium hydroxide to a solution of ammonium thiocyanate and recrystallized from water [17].

Tetrahydrofuran was used without further purification. 1,2-Dichloroethane was purified by washing it several times with distilled water.

2.2. COMPLEXATION IN THF

For each ligand, variable quantities of a 10^{-3} M THF solution of the ligand were added to a 10^{-3} M solution (1 mL) of the alkali picrate in THF. Tetrahydrofuran

was then added and made up to a volume of 10 mL. The absorbance of the solutions were measured in the range 300–500 nm (Perkin-Elmer model 550S).

2.3. EXTRACTION PROCEDURE

A 2.5×10^{-4} M aqueous alkali picrate solution (10 mL) and 10 mL of a 2.5×10^{-4} M solution of the ligands in 1,2-dichloroethane were transferred into a stoppered cylindrical glass tube immersed in a thermostatted water bath (20°C). The extraction equilibrium was reached after 20 min magnetic stirring and the mixture was subsequently allowed to stand for 10 min to complete the separation. The concentrations of the picrates in the aqueous phase were determined spectrophotometrically at the wavelength of maximum absorption of the picrate ion (355 nm, 14400 L mol^{-1} cm^{-1}). The extractability was determined from the difference of picrate ion absorbances in the aqueous phase.

2.4. TRANSPORT EXPERIMENTS

Membrane transport experiments were carried out in a U-shaped glass tube (diameter 41 mm, arm heights 150 mm) immersed in a thermostatted water bath at 25°C. This cell was filled with 160 mL of a 7×10^{-4} M ligand solution in 1,2-dichloroethane interfaced to 80 mL of a 0.1 M aqueous solution of alkali thiocyanate in one of the arms and 80 mL distilled water in the other one. One uniform mixer was inserted in each arm and two synchronous motors (Heidolph RZR 2000) provided a constant rotation of the mixers (100 cycles/min) which ensured stirring of the phases. The appearence of the cation in the receiving phase was monitored by titration of thiocyanate ion simultaneously appearing as the co-anion. At a regular time interval, 2 mL of the receiving phase was sampled and diluted to 4 mL by a 0.02 M solution of $Fe(NO_3)_3$ in a 0.2 M solution of HNO_3 for spectrophotometric measurements (480 nm, 4400 L mol^{-1} cm^{-1}) [18]. In order to maintain the position of the interfaces, 2 mL of the feed phase was also removed. The variation of the volume of the receiving phase was taken into account in the calculations. Alkali thiocyanate concentration in the organic phase was determined by withdrawal of 2 mL of the organic phase and stripping with 5 mL of distilled water and measured according to the method described above.

Additionally, in order to determine the equilibrium extraction concentration (C_1), 10 mL of 10^{-1} M aqueous alkali thiocyanate solution and the same volume of a solution of the ligand in 1,2-dichloroethane were placed in a tube immersed in the thermostatted bath at 25°C and stirred magnetically for 20 min. The phases were allowed to settle and 5 mL of the organic phase was taken up. This solution was stripped with distilled water for spectrophotometric titration as described above.
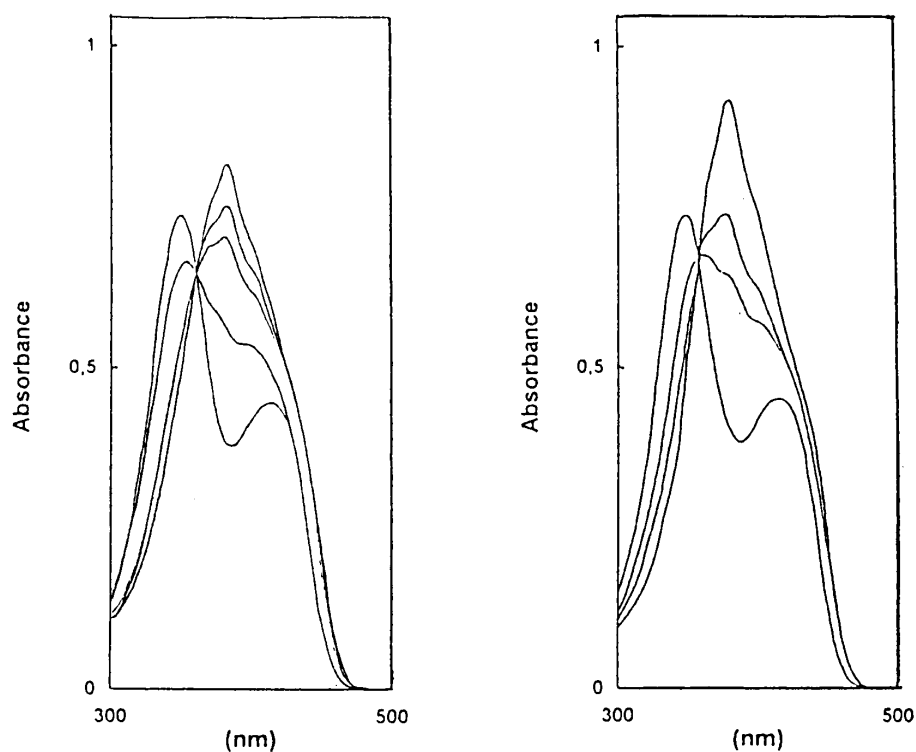
Figure 2. Change of the absorption spectrum of sodium picrate upon addition of various amounts of **1** (left) and **2** (right). The ligand : sodium ratios vary between 0 and 2 for **1** (left) and 0 and 1 for **2** (right).

2.5. COMPLEXATION STUDIES BY NMR

Variable amounts of NaSCN and KSCN solutions (1.2 M) in CD_3OD were transferred to a $CDCl_3$ solution of **2** (3×10^{-2} M) in the NMR tubes. The ^1H spectra were recorded by using a FT Bruker WP-200 SY instrument. The ^1H NMR data were referenced to residual protiated solvents.

3. Results and Discussion

To demonstrate the suitability of **1** and **2** for alkali ion complexation in THF, the ability of these ligands to transform tight alkali picrate ion pairs, M^+Pic^-, into separated ones were studied. To this end, UV-Vis spectra of alkali picrate ion pairs in THF were measured in the presence of different ligand/metal ratios. This study revealed for both ligands the presence of an isosbestic point (as illustrated in Figure 2 for sodium) which indicates the following equilibrium:
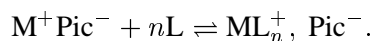
$$M^+Pic^- + nL \rightleftharpoons ML_n^+, \ Pic^-.$$

Table I. Bathochromic shifts ($\Delta\lambda$, nm), at 20 °C.

Ligand	M^+Pic^-				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	38	31	22	21	20
2	37	31	24	21	2
3[a]	c	29	24	c	c
4[b]	1	31	2	c	0
Cryptand222[b]	c	31	29	c	25

[a] Ref. 4; [b] Ref. 19; [c] No reported data.

The λ_{max} values of Li, Na, K, Rb, and Cs picrates (M^+Pic^-) are 344, 351, 357, 360 and 362 nm respectively. For all ML^+, Pic^- systems (L = **1** or **2**, M = alkali cations), except for Cs-**2**, a common λ_{max} was observed (382 nm), indicating that upon complexation full separation between cation and picrate takes place. A similar behaviour was observed by Ungaro *et al.* [5] for sodium and potassium complexation with tetra-amide **3**. The bathochromic shifts for M^+Pic^- complexes of **1** and **2** (M = Li, Na, K, Rb, Cs) as well as that of some alkali complexes obtained from **3**, **4** and cryptand 222 are given in Table I. Taking the bathochromic shifts of the corresponding cryptand-complexes as reference, one can conclude that at least for sodium and potassium ions, the bathochromic shift is to be related to the encapsulation of the cation in the ionophoric cavity of **1**, **2** and **3**. The data obtained for Cs complexation do not provide a clear picture of the nature of the Cs-**2** complex-ion pair.

The absorbance at λ_{max} of the metal picrates before and after complexation was studied as a function of the ligand/M^+Pic^- concentration ratios. This method is exemplified by Figure 3 for the Na-picrate complexation by **1** and **2**. For each experiment, except for the complexation of cesium by **2**, the formation of a 1 : 1 complex ($n = 1$) could unambiguously be determined. Because of the weak bathochromic shift observed for Cs complexation by **2**, this method did not allow precise determination of the stoichiometry of the resulting complex. The formation of a 1 : 1 complex in this case could nevertheless be demonstrated by showing that the K_{ex} value, assumed to be of the form, $[CsL^+, Pic^-]_{org} \cdot [L]_{org}^{-1} \cdot [Cs^+]_{aq}^{-2}$ (i.e. corresponding to a 1 : 1 complex), does not vary significantly in the concentration range: $2.5 \times 10^{-4} < [Cs^+] < 3.5 \times 10^{-4}$ M.

The logarithms of the stability constants were determined by means of the Rose-Drago method [20]. The calculated values are: 5.37, 4.42, 5.48, 5.23 and 4.18 for **1** and 5.85, 5.77, 5.40, 4.49, and *ca.* 3.5 for **2**, with, respectively, Li, Na, K, Rb and Cs.

Proton NMR spectra were run to obtain structural information about the sodium and potassium thiocyanate complexes obtained from **2** (Table II). The addition of NaSCN or KSCN solutions in CD_3OD to a solution of **2** in $CDCl_3$ was followed
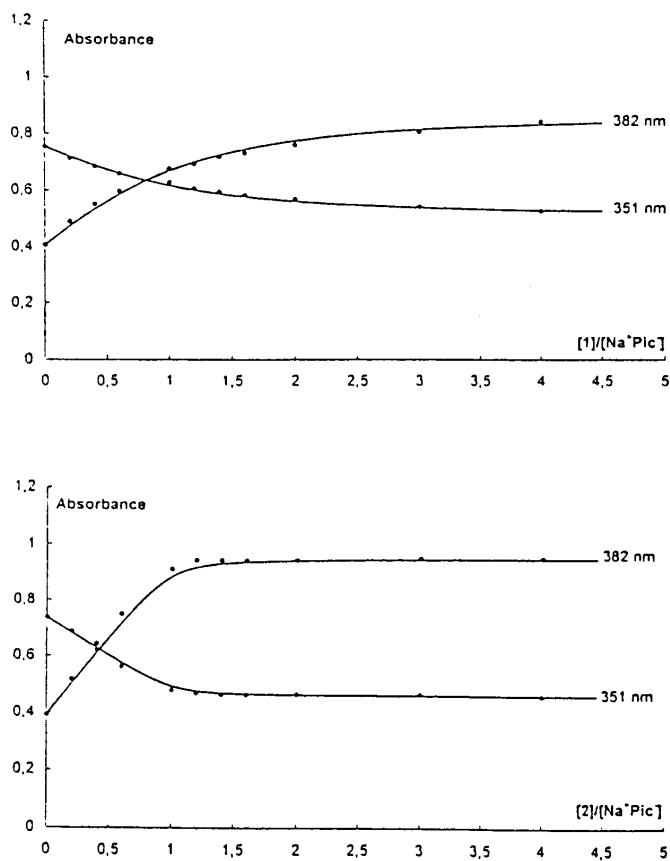
Figure 3. Plot of the absorbance vs. [L]/[Na$^+$Pic$^-$] at λ_{max} of the tight sodium picrate (351 nm) and ligand separated sodium picrate (382 nm).

by NMR. The NMR spectra of mixtures containing a M$^+$/**2** ratio $<$ 1 display signals corresponding to the free ligand and to the complex formed. When the M$^+$/**2** ratio reaches 1, the signals due to **2** disappear completely, suggesting the formation of a highly stable 1 : 1 complex. The NMR spectra of the thus formed complexes indicate a C_2 symmetrical structure. Note, the ^{1}H NMR spectrum of Na-**2** displays a single Bu^t signal (whereas the potassium complex shows, as expected, two Bu^t signals) suggesting a symmetry close to C_4 for the calixarene matrix in this complex.

Participation of the phenolic oxygen atoms in cation binding appears very likely in view of the observed downfield shift of the m-ArH hydrogen atoms upon complexation (Table II). These results are consistent with those reported for **3** and **5**, two ligands whose Na and K complexes were shown to have the metal ions encapsulated [3, 5].

Table II. ^{1}H NMR chemical shifts (ppm) of selected signals of ligand **2** and its complexes with NaSCN and KSCN.

Proton	Ligand	Na-**2**	$\Delta\delta^{a}$	K-**2**	$\Delta\delta^{a}$
H_A^b	4.78	4.51	−0.27	4.06	−0.72
H_B^c	2.86	3.01	+0.15	2.76	−0.10
m-ArH	6.63	6.96	+0.33	6.97	+0.34
(of calixarene)	6.39	6.78	+0.39	6.80	+0.41
$-CH_2CON(Et)_2$	4.63	4.75	+0.12	4.45	−0.18
$-CH_2P(O)Ph_2$	5.94	5.09	−0.85	5.30	−0.64

^{a} $\Delta\delta = \delta_{complex} - \delta_{free\ ligand}$. ^{b} Axial ArC$H_2$ hydrogen atom. ^{c} Equatorial ArCH_2 hydrogen atom.

Table III. Extraction percentage and logarithm of equilibrium^a extraction constants of alkali metal picrates^b from water to 1,2-dichloroethane at 20 $^\circ$C.

Ligand	M^+Pic^-				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	14.5	5	27	21	6.5
	(6.7)	(6.0)	(7.1)	(6.8)	(6.1)
2	64.5	58	45	20	5
	(8.3)	(8.1)	(7.6)	(6.8)	(6.0)
3^c	63	95.5	74	24	12
	(8.3)	(11.2)	(8.8)	(6.9)	(6.4)

^{a} The logarithm of extraction constants is given in parentheses below the value expressing the extraction percentage. ^{b} $[M^+Pic^-]_0 = [Ligand]_0 = 2.5 \times 10^{-4}$ M. ^{c} Ref. 16 (determined for a water to CH_2Cl_2 extraction).

The phase transfer ability of ligands **1** and **2** was examined by studying the extraction of alkali picrates from water to 1,2-dichloroethane at 20°C. Analysis of the extraction data shows that the extraction takes place via the following heterogeneous equilibrium:

$$M_{aq}^+ + Pic_{aq}^- + L_{org} \rightleftharpoons LM^+, Pic_{org}^-$$

(M = Li, Na, K, Rb, Cs and L = **1** and **2**).

The calculated extraction percentages as well as the corresponding K_{ex} are given in Table III together with data published by other authors [16] on tetra-amide **3**.

As shown in Figure 4, the variation of the extraction equilibrium constants vs. the ionic radius of the alkali cations parallels that of the corresponding formation constants in THF.
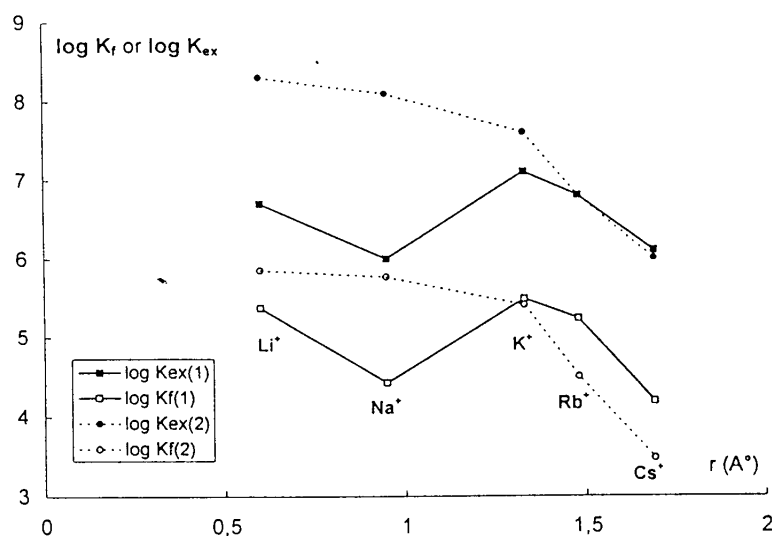
Figure 4. Plot of variation of the formation constants in THF and extraction constants for the water to 1,2-dichloroethane system of alkali picrates at 20 °C vs. the ionic radius of the alkali cations.

Comparison of the extraction properties of **1** and **2** (Figure 5) gives some indications about the relative contribution of the amide and the PO functions in the extraction by **2**. For Li^+, Na^+ and K^+, the extracting properties of the mixed amide-phosphine oxide calixarene **2** are superior to those of the tetra(phosphine oxide) **1**, the most significant effect being observed for Na^+ extraction. Full replacement of the phosphoryl groups by amide functions still increases the extracting power of the calixarene in the case of Na^+ and K^+. Ligands **1–3** show comparable extraction properties towards Rb^+ (Table III). The extracting ability of ligands **1** and **2** towards cesium is poor, presumably because the size of the receptor cavity is too small.

Interesting behaviour was observed when extracting lithium with **2**. Indeed, this compound exhibits higher extraction properties than **1**, but similar ones to that of **3**. This suggests that the crucial point for lithium complexation is the presence of two amide groups in these systems. However, participation of the phosphoryl groups in complexation appears likely, considering the observed downfield shift of the ^{31}P NMR signal on going from **2** to Li-**2** ($\Delta\delta \approx +10$ ppm). It is noteworthy that the ^1H NMR spectrum of Li-**2** displays broad signals, thus contrasting with the corresponding Na and K complexes. This suggests dynamic behaviour of the Li-**2** complex.

Transport of alkali thiocyanates through a bulk liquid membrane mediated by **1**, **2** and DC18C6 in 1,2-dichloroethane was investigated in the early stages of transfer kinetics by plotting the variation of the salt concentration in the receiving (C_{II}) and membrane phases (C_m) vs. time (Figure 6). As shown by these diagrams, the early
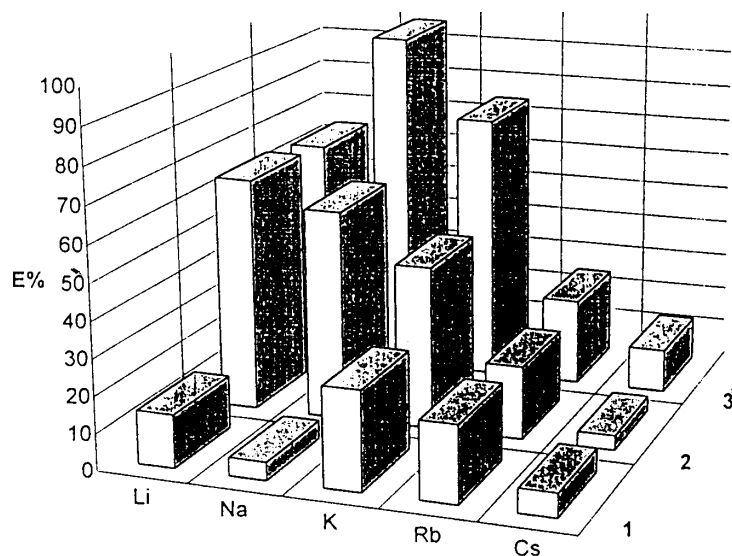
Figure 5. Extraction percentages (E%) of the alkali picrates with **1, 2** and **3** at $20°$C. $[M^+Pic^-]_0$ = [ligand]$_0$ = 2.5 × 10^{-4} M. * Ref. 16 (for water to dichloromethane system).

stage of the transport is a non steady state process. This is due to the non negligible volume of the membrane.

A mathematical description of the transfer is carried out by assuming a pure diffusion process and by applying to the system the conventional mass conservation law: entering rate − leaving rate = accumulating rate, leading to the following equation:

$$S_1 \cdot J_1 - S_2 \cdot J_2 = V_m \frac{dC_m}{dt} \tag{1}$$

where S_1 and S_2 are interfacial area, J_1 and J_2 are fickian fluxes through the membrane stagnant layers at the first and second interfaces respectively.

By introducing a transfer coefficient (k_{org}) and the complex concentration gradient, Equation 1 can be rewritten as:

$$S_1 k_{org1}(C_{1i} - C_m) - S_2 k_{org2}(C_m - C_{2i}) = V_m \frac{dC_m}{dt} \tag{2}$$

where C_{1i} and C_{2i} are interfacial concentrations and V_m is the membrane phase volume.

For symmetry reasons,

$$S_1 = S_2 = S, \qquad k_{org1} = k_{org2} = k_{org}.$$

To a first approximation, C_{1i} can be considered as the equilibrium complex concentration, C_1. This concentration can be determined by performing an extraction
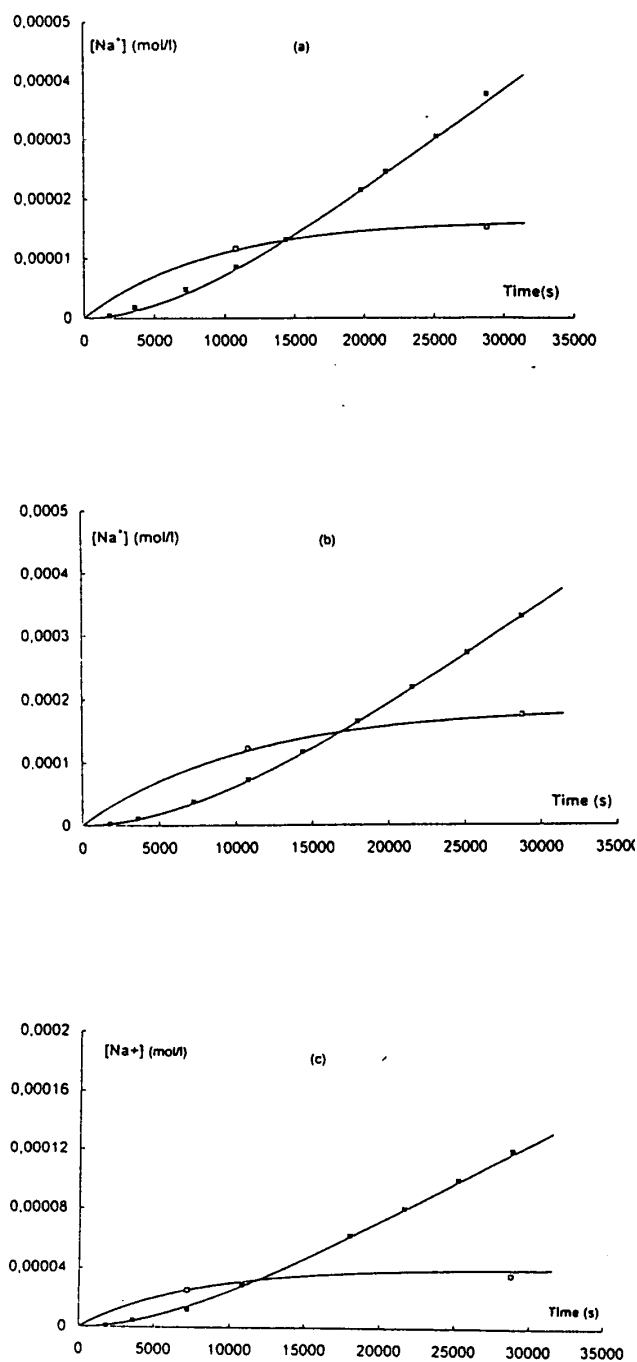
Figure 6. Evolution of the sodium thiocyanate concentration in the receiving (filled squares) and membrane (empty squares) phases as a function of time using **1** (a), **2** (b) and DC18C6 (c) as carriers at 25 °C. Feed phase: 0.1 M sodium thiocyanate (80 ml); receiving phase: distilled water (80 mL); membrane phase: 7×10^{-4} M of carriers in 1,2-dichloroethane (160 mL); stirring speed: 100 cycles/min.

experiment under transport conditions. At the early stages of the transfer $C_{2i} = 0$; it follows:

$$J_2 = k_{\text{org}} C_m = \frac{V_{\text{II}}}{S} \cdot \frac{\mathrm{d}C_{\text{II}}}{\mathrm{d}t} \tag{3}$$

(V_{II} is the receiving phase volume).

Integration of Equations (2) and (3) lead to the following expressions for $C_{m(t)}$ and $C_{\text{II}(t)}$:

$$C_{m(t)} = \frac{C_1}{2}\left(1 - \exp\left[-\frac{2k_{\text{org}} \cdot S \cdot t}{V_m}\right]\right) \tag{4}$$

$$C_{\text{II}(t)} = \frac{k_{\text{org}} \cdot S}{2V_{\text{II}}} \cdot C_1 \cdot t - \frac{C_1 \cdot V_m}{4V_{\text{II}}} + \frac{C_1 \cdot V_m}{4V_{\text{II}}}\exp\left[-\frac{2S \cdot k_{\text{org}} \cdot t}{V_m}\right]. \tag{5}$$

This model was tested by fitting Equations 4 and 5 with the corresponding experimental data and by introducing an appropriate value of k_{org}. It also provides the equation for the steady state regime (linear part of Equation 5):

$$C_{\text{II steady}} = \frac{k_{\text{org}} \cdot S}{2V_{\text{II}}} \cdot C_1 \cdot t - \frac{C_1 \cdot V_m}{4V_{\text{II}}} \tag{6}$$

the slope of which is proportional to the steady state regime rate (v_s):

$$v_s = \frac{k_{\text{org}} \cdot C_1 \cdot S}{2}. \tag{7}$$

The determined k_{org}, C_1 and v_s values are given for all alkali cations and for **1** and **2** in Table IV. The corresponding data for DC18C6 are also presented for comparison.

The reliability of the model was supported by the fact that for **1** or **2** the calculated k_{org} values are nearly the same (mean value 6.1×10^{-5} dm/s). This was confirmed by the v_s vs. C_1 plot (Figure 7).

In the two–film theory, k_{org} is related to the diffusional coefficient, D, by the relation:

$$k_{\text{org}} = D/\delta_{\text{org}} \tag{8}$$

(δ_{org} is the stagnant film thickness at the interfaces which is constant for a given stirring speed).

According to the Wilke–Chang equation [21] the diffusion coefficient is related to the molar volume, V, of the diffusing species:

$$D \propto V^{-0.6}$$

Table IV. Results of the alkali thiocyanates extraction and transport through a solution of **1**, **2** and DC18C6 in 1,2-dichloroethane at 25°C.[a]

M$^+$	$V_s \times 10^9$ (mol/s)			$C_1 \times 10^4$ (mol/l)			$k_{org} \times 10^5$ (dm/s)		
	1	**2**	DC18C6	**1**	**2**	DC18C6	**1**	**2**	DC18C6
Li$^+$	0.77	1.39	0.06	1.95	3.70	0.09	6.0	5.7	10.2
Na$^+$	0.14	1.40	0.44	0.33	3.71	0.81	6.7	5.7	8.2
K$^+$	1.13	1.34	1.91	3.05	3.66	3.82	5.6	5.6	7.6
Rb$^+$	1.01	0.96	1.50	2.56	2.41	2.84	6.0	6.0	8.0
Cs$^+$	0.27	0.16	0.90	0.54	0.40	1.64	7.6	6.1	8.4

[a] Ligand concentration: 7×10^{-4} M (160 ml); feed alkali thiocyanate concentrations: 0.1 M (80 ml); receiving phase: distilled water (80 ml); stirring: 100 cycles/min.
V_s: transport rate of solute at steady state; C_1: equilibrium extraction concentration of solute in the transport conditions; k_{org}: coefficient of transfer.
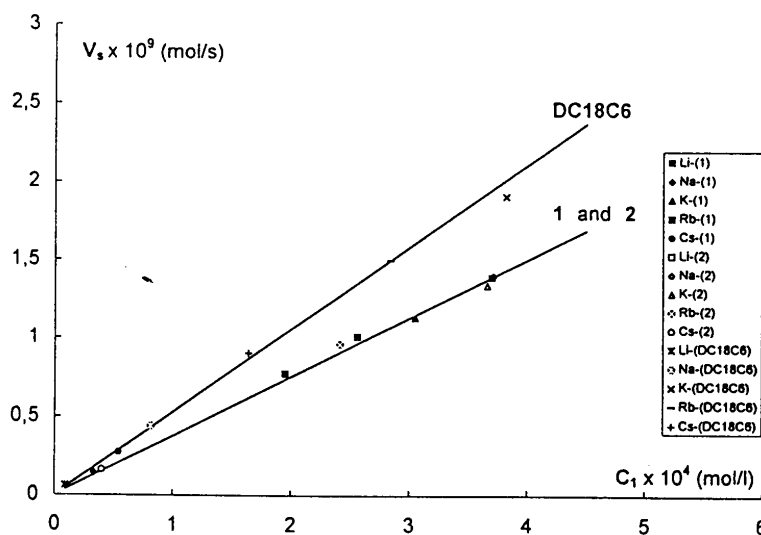

Figure 7. Plot of the steady state transport rate of alkali thiocyanates by **1**, **2** and DC18C6 as carriers vs. extraction equilibrium concentrations at 25 °C. Feed phase: 0.1 M alkali thiocyanate (80 mL); receiving phase: distilled water (80 mL), membrane phase 7×10^{-4} M of carriers in 1,2-dichloroethane (160 mL); stirring speed: 100 cycles/min.

hence similar values of k_{org} are expected for diffusing species having the same size. This is certainly the case for all the MLSCN species (M = alkali cations, L = **1** and **2**). Consequently in these systems the extraction selectivity parallels the transport selectivity (see Figure 7).

It should be noted that the k_{org} values observed for DC18C6-MSCN systems are significantly higher (mean value 8.5×10^{-5} dm/s) within the considered model; this effect is to be related to a significant decrease of the complex size.

In transport studies by macrocyclic carriers the effect of transfer coefficient (k) on the transport rate is generally not considered. This study illustrates the fact that the size of the carrier should also be taken into account in analysis of the transport processes.

4. Conclusion

The tetra(phosphine oxide) **1** and the mixed amide-phosphine oxide **2** are both suitable for alkali complexation. They form 1 : 1 complexes with the alkali cations. Hybrid **2** displays higher binding properties towards Li, Na, and K than **1**, confirming that amide groups are strong complexing agents for alkali cations. As shown by the NMR study, encapsulation of Na and K by **2** resulted in formation of a C_2-symmetrical complex. The transport efficiency of **1** and **2** towards alkali cations varies in the same order as the extraction; K>Rb>Li>Cs>Na for **1**; Na≈Li>K>Rb>Cs for **2**. The transport rates are shown to depend on both the extraction efficiency of the ligands and the size of the transported complex.

Acknowledgment

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