# Cation Complexation by Chemically Modified Calixarenes. Part 7.† Transport of Alkali Cations by *p-tert*-Butylcalix[*n*]arene Esters and Amides

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The co-transport of alkali thiocyanates, at 20 °C, from an aqueous source solution into an aqueous receiving solution through a bulk liquid dichloromethane solution, is facilitated by *p-tert*-butylcalix[*n*]arene esters of lower rim calixarene acetic acids, named ethyl esters ($n = 4, 5, 6, 8$), by *p*-dealkylated calix[6]arene ethyl ester and the diethyl and pyrrolidine amides of a *p-tert*-butylcalix[4]arene. The transport rates show that all derivatives, except the octamer, are efficient and selective neutral ionophores for alkaline cations. The amides are better carriers than the esters and the pyrrolidinyl amide is more efficient for $Li^+$, $Na^+$ and $K^+$ than the diethyl amide. Among the esters, the most efficient, by far, is the pentamer. The tetra- and penta-esters are selective for $Na^+$, the hexaester for $Cs^+$ and the tetraamides for $K^+$. The $Cs^+/Na^+$ selectivity of the hexaester is increased by dealkylation in the *para* position. The same is shown to be displayed in extraction. The data are compared with existing stability constant values in methanol and extraction equilibrium constants for alkali picrates, from water to dichloromethane. New extraction data are provided for alkali thiocyanates.

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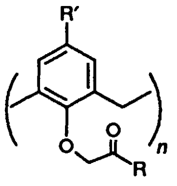
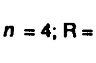
Macrocycles are known to be able to mediate selectively the transport of metal cations through a membrane. The bulk liquid membrane technique has been used extensively for the study of transport by crowns[1,2] and cryptands.[3,4] We now report a study of transport of alkali cations by calixarenes—chemically modified on the lower rim by esters and amides—using the bulk liquid membrane technique.

Prior to this study, very little has been done on the subject and the few existing studies mainly concern ionizable calixarenes bearing either free OH groups or acetic acid groups. Izatt and co-workers reported in 1983 their pioneering work on the tetra-, hexa- and octa-meric parent calixarenes.[5,6] They showed that transport of alkali cations does not occur from an aqueous source phase into an aqueous receiving phase, through a dichloromethane membrane, unless the source solution is made sufficiently alkaline to ensure deprotonation of the phenolic groups and subsequent transport is that of a neutral phenolate–cation complex. In 1983, Ungaro and co-workers[7] found that a crowned *p-tert*-butylcalix[4]arene, in which two opposite phenolic oxygens are linked by a polyether chain, is able to act as a neutral carrier for metal and ammonium picrates. These authors report that this chemically modified calixarene is also a very efficient carrier in its anionic form, transporting alkali cations from a basic aqueous solution (pH 12–13); they relate this property to the previous observation of one of us (M. A. McK.) that the presence in the same molecule of ionisable phenolic OH groups and a crown macrocycle greatly improves the transport ability of the carrier.[8] Böhmer and co-workers[9] have studied a series of bridged parent calix[4]arenes with two opposite *para* positions on the upper rim linked by an aliphatic chain. They report that this class of parent calixarenes transport $Cs^+$ from a 1 mol dm$^{-3}$ CsOH aqueous solution, with an efficiency depending upon the length of the aliphatic chain.



**1**: $n = 4$; R = OEt; R′ = Bu$^t$
**2**: $n = 5$; R = OEt; R′ = Bu$^t$
**3**: $n = 6$; R = OEt; R′ = Bu$^t$
**3a**: $n = 6$; R = OEt; R′ = H
**4**: $n = 8$; R = OEt; R′ = Bu$^t$
**5**: $n = 4$; R = NEt$_2$; R′ = Bu$^t$
**6**: $n = 4$; R = ; R′ = Bu$^t$

There have been, up to now, few systematic studies of ion transport with chemically modified non-ionizable calixarenes. Reinhoudt and co-workers using the supported liquid membrane technique have demonstrated the use of calixcrowns as selective potassium ion carriers.[10] In our first study of the physico-chemical aspects of complexation by calixarene esters and ketones, we reported a few preliminary transport experiments of alkali cations with symmetrical calixarenes chemically modified on the lower rim, namely the *p-tert*-butylcalix-[4]-, -[6]- and -[8]-arene ethyl esters, derivates **1**, **3** and **4**.[11,12] These ligands, L, are neutral and consequently their metallic complexes $ML^+$ are charged and the species transported is the neutral pair $ML^+A^-$ formed by the complex and the counter ion $A^-$. The main conclusions of our preliminary study were: (*i*) these symmetrically functionalised calixarenes do transport alkali cations from a neutral aqueous solution through a $CH_2Cl_2$ bulk membrane; (*ii*) in the ethyl ester series the tetramer and the hexamer appear to be quite efficient carriers with a maximum transport occuring for $Na^+$ with the tetramer and for $Cs^+$ with the hexamer; (*iii*) the octameric ethyl ester shows very little ionophoric activity and poor discrimination between the alkali cations. These features have been observed also in extraction of alkali metal picrates from an aqueous 1 mol dm$^{-3}$ alkali hydroxide solution into a dichloromethane solution of the receptor.[11,12] An earlier study by Chang and Cho[13] reveals trends in transport similar to those reported by us for the three esters **1**, **3** and **4**. However, Chang and Cho were unable to prepare the

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† For Part 6, see ref. 15.

‡ Preliminary studies were performed by E. M. S. in the Department of Chemistry, University College Cork, Irish Republic (1981–1985).

**Table 1** Influence of the composition of the receiving phase on the transport rate by 18-crown-6 and two calixaryl esters (each figure relates to the mean of three experiments and the precision given between brackets is the standard deviation $\sigma_{n-1}$ on the mean)

| | | Composition of the receiving phase | |
|---|---|---|---|
| Ligand | Cation | According to Thoman[a] | Twice distilled water |
| 18-crown-6 | $K^+$ | 8.3 (0.3) | 8.25 (0.25) |
| **3** | $Na^+$ | 1.2 (0.1) | 1.17 (0.01) |
| | $K^+$ | 5.6 (0.5) | 2.5 (0.1) |
| | $Cs^+$ | 10.6 (0.8) | 8.0 (0.7) |
| **4** | $K^+$ | 0.40 (0.003) | 0.37 (0.06) |
| | $Rb^+$ | 0.30 (0.04) | 0.28 (0.01) |

[a] Ref. 19.

pure tetraester and, for this derivative, their transport study was carried out using the sodium bromide complex. Thus it is not clear how the presence of bromide ion in the membrane influences the rate of transport of picrates.

Our first results were sufficiently interesting to justify further investigations in the field of transport. We have thus developed a more controlled experimental technique and tried to characterise the nature of the transport process involved. We have repeated the studies of transport of these three esters and we have now included the pentaester **2** and the dealkylated hexaester **3a** and have extended the study to two representative amides: the *p-tert*-butylcalix[4]arene diethyl and pyrrolidinyl amides **5** and **6**. Chang and Cho conducted a study of three secondary amides[14] and found very low efficiencies for $Na^+$, $K^+$ and $Cs^+$. We now show that tertiary amides are very efficient in transport as we have already shown in extraction.

The present paper reports our results and conclusions which we analyse in the light of our earlier studies. The complexation properties of these ligands have already been characterised by the percentage cation extracted from a neutral aqueous alkali picrate solution[14,15-17] and by the stability constants $\beta$ of the 1:1 metallic complexes in methanol.[11,12,15-17]

## Experimental

The synthesis of the calixarene derivatives **1**,[12] **2**,[15] **3**,[12] **3a**,[11] **4**,[12] **5**[16] and **6**[16] have been described elsewhere.

The instrumentation used for the transport rate measurements has already been described by Burgard and co-workers.[2,18] It consists of a thermostatted glass cell ($T$ = 20.0 ± 0.1 °C) into which a glass bell cylinder is inserted to separate the inner aqueous source phase (phase I = 30 $cm^3$) from the outer aqueous receiving phase (phase III = 70 $cm^3$). A synchronous motor (Digitronic, from Framo) provided a constant and well controlled rotation of the cylinder around its axis, which ensured stirring of the phases. A static mixer immersed in both the organic phase (phase II = 100 $cm^3$) and phase I ensured a rapid homogenisation of the concentrations in the phases. The second II–III interface had a surface twice as large (21.4 $cm^2$) as the first I–II interface (10.7 $cm^2$).

For a standard experiment, phase I was a $5 \times 10^{-2}$ mol $dm^{-3}$ ($C^\circ_m$) aqueous solution of alkali cation thiocyanate, phase II was a $7 \times 10^{-4}$ mol $dm^{-3}$ ($L^\circ$) solution of calixarene in dichloromethane and phase III was twice distilled water. The stirring rate was fixed at 100 runs $min^{-1}$.

The appearance of the cation in the receiving phase III was monitored by titration of the $SCN^-$ anion simultaneously appearing as the counter-ion. An aliquot of 2 $cm^3$ was pipetted out of phase III every second hour and diluted to a suitable volume by a $Fe(NO_3)_3$ solution, *ca.* 0.02 mol $dm^{-3}$ in aqueous 0.2 mol $dm^{-3}$ $HNO_3$, for a spectrophotometric titration of $SCN^-$ as $FeSCN^{2+}$ at 480 nm and 25 °C according to the procedure of Thoman.[19] The variation of the volume of phase III due to the successive removal of 2 $cm^3$ aliquots was of course taken into account in the calculations.

Thiocyanate can form two successive complexes with $Fe^{3+}$: $FeSCN^{2+}$ and $Fe(SCN)_2{}^+$. According to previous studies of their stability constants,[20-23] the experimental conditions of our titrations should allow the formation of only $FeSCN^{2+}$. We have measured the apparent molar extinction coefficients $\varepsilon_{app}$ of $FeSCN^{2+}$ under our experimental conditions with thiocyanate salts of all alkali cations and have found mean values from 27 determinations, in the concentration range of total thiocyanate $5.10^{-5}$–$7.10^{-4}$ mol $dm^{-3}$ of 2820 ± 40 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 480 nm and 3100 ± 30 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 457.5 nm, the latter being the wavelength of maximum absorption.

In order to see whether our measurements of $\varepsilon_{app}$ are consistent with the results of the previous studies of the $Fe^{3+}$–$SCN^-$ system,[20-23] we have calculated, in two different ways, the stability constants $K_1$ and molar extinction coefficient $\varepsilon$ of $FeSCN^{2+}$ in our experimental conditions. First, it was necessary to correct the thermodynamic stability constant $K^\circ_1$ (25 °C) = 865 mol $dm^{-3}$ of $FeSCN^{2+}$ (at zero ionic strength and 25 °C) determined by Betts and Dainton,[22] in order to take into account our experimental conditions. For this purpose, the equation of Rabinowitch and Stockmayer was used.[24] We found log $K_1^{0.192}$ (25 °C) equal to 2.20, at the ionic strength 0.192 of our titration solutions. A further correction of this value to take into account the hydrolysis of $Fe^{3+}$ [$Fe^{3+} + H_2O \rightleftharpoons FeOH^+ + H^+(K_H)$], as explained in ref. 20, with $K^\circ_H = 6.10^{-3}$ mol $dm^{-3}$,[25] *i.e.* $K_H^{0.192} = 6.10^{-3}$, only slightly changed log $K_1^{0.192}$ from 2.20 to 2.19. This value corresponds to a percentage of complex formation of 64–65% in our $SCN^-$ concentration range of $5.10^{-5}$–$3.10^{-4}$. Our measured value of $\varepsilon_{app}$ at 457.5 nm, of 3100 ± 30 $dm^3$ $mol^{-1}$ $cm^{-1}$ corresponds to $\varepsilon_{457.5}$ = 4800 ± 50 $dm^3$ $mol^{-1}$ $cm^{-1}$, a value in good agreement with the value of 5000 given by Betts and Dainton.[22] Secondly, we have corrected, using the Van't Hoff isochore equation, the stability constant $K_1^{0.2}$ (18 °C) = 196 ± 8 mol $dm^{-3}$ determined by McDonald and co-workers at 18 °C in a nitric acid medium. With $\Delta H = -1.6$ kcal $mol^{-1}$,[22] we found $K_1^{0.2}$ (25 °C) = 184 mol $dm^{-3}$, at 25 °C. This value corresponds to an extent of complex formation of 67%. Our measured value of $\varepsilon_{app}$ at 480 nm, of 2820 ± 40, combined with this result, leads to $\varepsilon_{480}$ = 4210 ± 60, a value in good agreement with $\varepsilon_{480}$ = 4474 given in ref. 22.

A standard transport experiment was followed during 10 h. In most cases, the plot of the number $n$ of μmol $SCN^-$ appearing in phase III *vs.* $t$ was an excellent straight line for the 10 h period, indicating that the stationary state was reached (correlation coefficients of at least 0.999). The transport rate was taken as the slope of these lines. In some cases (*e.g.*, with the system **3**–$Cs^+$ and **1**–$Na^+$) the $n$ *vs.* $t$ plots were curved after some time and only that interval from 0 to 4 h was considered as linear (correlation coefficient of 0.96). The absence of passive transport without ligand was confirmed.

Thoman has worked with phase III already containing the species necessary to obtain $FeSCN^{2+}$, *i.e.* consisting of an aqueous solution 0.02 mol $dm^{-3}$ in $Fe(NO_3)_3$ and 0.2 mol $dm^{-3}$ in $HNO_3$. We performed transport experiments with both types of receiving phase: either twice distilled water or Thoman's solution. The results, reported in Table 1, show that the two methods gave the same transport rates $V$ of $K^+$ with 18-crown-6 but sometimes gave different results for the transport of alkali cations by calixarenes. The rates were identical for $V$ values roughly below 0.3 μmol $h^{-1}$, but differed significantly for larger values, the bigger rates corresponding to the acidic ferric receiving phase. In order to avoid any uncontrolled side-effect,

**Table 2** Rate of transport $V$/μmol h$^{-1}$ of alkali thiocyanates through a bulk dichloromethane liquid membrane, at 20 °C.[a] The values between brackets are the standard deviations $\sigma_{n-1}$ on the mean.

| Ligand | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| **1** | 0.07 (0.02) | 3.9[b] (0.9) | 0.50 (0.06) | 0.056 (0.007) | 0.030 (0.002) |
| log $\beta$ (MeOH)[c] | 2.6 | 5.0 | 2.4 | 3.1 | 2.7 |
| **2** | 1.25 (0.18) | 11.8 (1.2) | 9.1 (0.5) | 2.9 (0.6) | 8.3 (0.5) |
| log $\beta$ (MeOH)[d] | 1.0 | 4.4 | 5.3 | 5.6 | 5.5 |
| **3** | 0.3 (0.1) | 1.81[b] (0.02) | 3.7 (0.2) | 7.6 (0.2) | 12 (1) |
| **4** | 0.070 (0.005) | 0.15[b] (0.01) | 0.5 (0.1) | 0.42 (0.01) | 0.46 (0.02) |
| **5** | 11 (3) | 0.87 (0.04) | 12 (2) | 9.96 (0.06) | 7.1 (0.2) |
| log $\beta$ (MeOH)[c] | 3.9 | 7.9 | 5.8 | 3.8 | 2.4 |
| **6** | 15.4 | 1.25 (0.05) | 16 (2) | 5.18 (0.01) | 0.37 (0.03) |
| log β (MeOH)[c] | 3.0 | 7.2 | 5.4 | 3.0 | < 1 |
| **3a** |  | *e* |  |  | 14.8 (0.6) |
| log $\beta$ (MeOH) |  | < 1 |  |  | > 6 |
| %$E$ |  | 0.8 |  |  | 46.4 |

[a] The transport fluxes in μmol h$^{-1}$ cm$^{-2}$ can be obtained by dividing these data by 21.7. [b] Initial concentration of sodium, in the source phase $C_1^0$ = 0.07 mol dm$^{-3}$. [c] Ref. 11, 12. [d] Ref. 16. [e] Too low to be determined.

we decided to use pure distilled water and to proceed as already described in this paper.

## Results and Discussion

Table 2 summarises the transport rates $V$, in μmol h$^{-1}$, for all systems investigated. Table 2 also contains the stability constants for these systems in methanol. The data correspond to the mean of two or three experiments and the precision given between brackets is the $\sigma_{n-1}$ on the mean. Under the same experimental conditions, we have measured $V = 13.1 \pm 0.7$ μmol h$^{-1}$ for the reference system 18-crown-6–K$^+$ and 16.4 ± 0.5 μmol h$^{-1}$ for the reference system dicyclohexyl-18-crown-6–K$^+$. The corresponding fluxes are 13.1/21.4, and 16.4/21.4, *i.e.* 0.61 and 0.77 μmol h$^{-1}$ cm$^{-2}$.

The uncertainties reported in Table 2 lead to the conclusion that the reproducibility, expressed as $\sigma_{n-1}$ on the mean, is in the usually admitted range of ± 15%.[5] Only four results have a standard deviation higher than 15%. It is interesting to note that, despite the poor reproducibility, the results were confirmed by repeat experiments performed over a short time period.

*Transport Efficiency and Selectivity.*—Table 2 shows that all the ligands studied are *efficient* and *selective* neutral carriers for alkali cations, with the exception of the larger octaester **4**. This had already been indicated by our preliminary transport experiments with esters **1**, **3** and **4**.[12]

Their efficiency, with $V$ ranging from 0.03 μmol h$^{-1}$ for the system **1**–Rb$^+$ up to 16 μmol h$^{-1}$ for the system **6**–K$^+$, is inferior or, at best, equal to that of dicyclohexyl-18-crown-6–K$^+$ (16.4 μmol h$^{-1}$). Three systems have an efficiency very close to that of 18-crown-6–K$^+$ ($V$ = 13.1 μmol h$^{-1}$), namely **2**–Na$^+$, **3**–Cs$^+$ and **5**–K$^+$, which are characterised by a value $V$ = 12 μmol h$^{-1}$. The amides are better carriers than the esters and the tetrapyrrolidinyl amide is more efficient for Li$^+$, Na$^+$ and K$^+$ than the tetradiethyl amide, whereas the opposite trend is observed in complexation and in extraction.[16] Among the esters, the most efficient, by far, is the pentamer **2**. The decreasing order of highest transport rate for a given ester is pentamer (Na$^+$ : 11.8) $\approx$ hexamer (Rb$^+$ : 12) > tetramer (Na$^+$: 3.8) > octamer (K$^+$ : 0.5). The tetra- and penta-esters **1** and **2** are selective for Na$^+$; the hexaester **3** is selective for Cs$^+$ and the tetraamides **5** and **6** are selective for K$^+$. It should be noted however that the two amides are only slightly less efficient for Li$^+$ than for K$^+$ and that the very low extent of transport of Na$^+$ with both amides is a remarkable finding considering their well established selectivity for Na$^+$ in both extraction and stability constants.[16]

According to Lehn,[26] a ligand is a selective carrier when the most efficiently bound cation is also the one which is carried fastest. On the other hand, it will be a selective receptor when the best bound cation is the one most slowly transported. On the basis of these definitions, the tetraester **1** may be considered as a 'selective carrier': even in the presence of other alkali cations Na$^+$ will be selectively transported. On the contrary, the two tetraamides, which transport K$^+$ selectively but complex Na$^+$ selectively,[16] may be considered as 'selective receptors': the transport selectivity for K$^+$ may be reduced or even cancelled in the presence of Na$^+$. The pentaester **2** may also be regarded as a selective receptor.[15]

Such conclusions cannot be drawn from the complexation data of the hexaester **3**, as they were measured in acetonitrile and not in methanol for solubility reasons. In acetonitrile, **3** displays a plateau selectivity in favour of the largest cations K$^+$, Rb$^+$, Cs$^+$ with a slight preference for K$^+$. If this was also the case in methanol, one could conclude that **3** is a selective receptor. But as there are no data in methanol and as acetonitrile has properties very different from those of methanol,[12] we cannot make any conclusion, but just note that the extraction selectivity mirrors the transport selectivity with a maximum for Cs$^+$.[17]

In Table 3 are shown some transport selectivities of the cations M$^+$ with respect to the cation M$'^+$, expressed as $V$(M$^+$)/$V$(M$'^+$), for the calixarenes investigated, except **4**, and, for comparison purposes, for cryptand 222, 18-crown-6, and the natural ionophores valinomycin, monensin and nigericin. As already stated, the esters **1** and **2** are sodium selective, but less so than cryptand 222. The compound most selective for K$^+$ with respect to Na$^+$ is the tetradiethyl amide **5**, followed by **6** and, to a lesser extent, by **3**, which displays the same K$^+$/Na$^+$ selectivity as valinomycin and nigericin. The compounds **5** and **6** are selective for Li$^+$ with respect to Na$^+$, comparably to cryptand 221. Ligands **3**, **3a** and **5** are selective for Cs$^+$ with respect to Na$^+$, more so than cryptand 222 or 18-crown-6. As **5** and **6** are selective receptors and not carriers, one must keep in mind that their selectivities observed in single ion transport

**Table 3** Transport selectivities $S = V(M^+)/V(M'^+)$ for the calixarene derivatives and other known synthetic and natural carriers

| Compounds | $K^+/Na^+$ | $Li^+/Na^+$ | $Cs^+/Na^+$ |
|---|---|---|---|
| **1** | 0.13 | 0.018 | 0.008 |
| **2** | 0.77 | 0.105 | 0.703 |
| **3** | 2.04 | 0.166 | 6.63 |
| **5** | 13.8 | 12.6 | 8.16 |
| **6** | 12.8 | 12.3 | 0.30 |
| 222[a] | 0.05 | | 4.83 |
| 221[b] | | 14 | |
| 18-Crown-6[c] | 24.8 | | 3.00 |
| Valinomycin[b] | 2 | | |
| Monensin[b] | | 0.5 | |
| Nigericin[b] | 2 | | |

[a] Ref. 3. [b] Ref. 27. [c] Ref. 1.

experiments may be changed when competitive experiments are performed.

The dealkylation of **3** in the *para* position, leading to **3a**, results in a remarkable increase of the $Cs^+/Na^+$ selectivity as shown in Table 2. We have observed the same effect of the *para* dealkylation in biphasic picrate extraction experiments from a neutral aqueous solution to a dichloromethane solution of the calixarene (concentrations of cation salt and carrier = $2.5 \times 10^{-4}$ mol dm$^{-3}$). For the *p-tert*-butylcalix[6]arene hexaethyl ester **3**, the percentage cation extracted, %*E*, is 2.7 with $Na^+$ and 33.0 for $Cs^+$ whereas for the *p*-dealkylated calix[6]arene hexaethyl ester **3a**, it is 0.8 with $Na^+$ and 46.4 with $Cs^+$.

*Transport Rate* versus *Stability Constant* $\beta$.—Lehn and Kirch were the first to show the existence of a relationship between the value of $\beta$ and the transport rate and found that maximum transport rates for alkali picrates by cryptands occurred when the log $\beta$ value in methanol was about 5 log units.[3] Izatt *et al.* developed a theoretical model of the transport in diffusion controlled systems which confirmed these observations.[1] Our results show that the optimum transport value, for a given ligand, coincides with a log $\beta$ value in methanol at 25 °C of *ca.* 5, more precisely 5.1 ± 0.7.

*Transport Rate* versus *Extraction Equilibrium Constant* $K_e$.—The dependence of $V$ upon the extraction equilibrium constant $K_e$ has been studied theoretically by Behr, Kirch and Lehn[4] who showed that, for diffusion controlled co-transport processes, the plot of $V$ *vs.* $K_e$ is, in principle, bell-shaped.

Our first attempt was to use the $K_e$ values which we had determined in earlier work for the picrate extraction. The use of $K_e(Pi^-)$ instead of $K_e(SCN^-)$ is justified by the assumption that there is a linear correlation between both, an assumption which we verified with compound **6**: $\log K_e(Pi^-) = 3.87 \log K_e(SCN^-) - 15.94$. The resulting plot is shown in Fig. 1 which represents the transport rates of thiocyanates *vs.* log $K_e(Pi^-)$. Indeed, the plot suggests a bell-shaped curve; the best transport occurs for log $K_e(Pi^-)$ *ca.* 7.8. The reversal of the $Na^+/K^+$ transport selectivity of the amides **5** and **6** with respect to the extraction selectivity is explained by the excessively high extractability of the sodium systems; the points which correspond to the systems **5**–$Na^+$ and **6**–$Na^+$ are on the descending branch of the curve.

The existence of a bell-shaped curve is based upon the assumptions (*i*) that the steady state is reached and (*ii*) that the co-transport process is totally diffusion controlled, *i.e.* the rate limiting step is the diffusion of the species in the unstirred Nernst layers and the complexation and decomplexation processes at both interfaces are rapid compared to the diffusion rate.

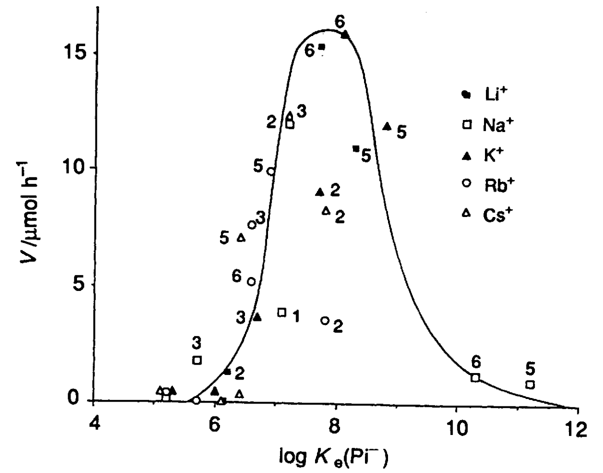

**Fig. 1** Variation of the transport rate of alkali thiocyanates, in μmol h$^{-1}$, with log $K_e(Pi^-)$

Assumption (*i*) concerning the steady-state is confirmed by the linearity of the graphs giving the number of μmol $n$ in the receiving phase *vs.* time, with nearly all systems. An exception is observed with the system **1**–$Na^+$ where the graph $n$ *vs.* $t$ is not linear, but curved, with a slope decreasing with time. We have observed that the deviation from linearity increases with increasing initial carrier concentration $L_o$ in the membrane. This fact could be consistent with the formation of monolayers of the carrier at the first interface, leading to a saturation of the interface (see below).

In order to check the validity of assumption (*ii*) concerning the diffusion limited transport regime, we undertook the following investigations. (*a*) Dependence of $V$ upon the stirring rate (in revolutions per minute, rpm). $V$ should increase linearly as a function of the stirring speed if the process is totally diffusion controlled, but should be independent of the stirring speed if the process is totally kinetically controlled. (*b*) Dependence of $V$ upon the initial concentration $L_o$ of the carrier in the membrane. As claimed by Fyles,[28] the linearity of this plot has been widely assumed and is now regarded as substantiated. (*c*) Dependence of $V$ upon the initial concentration $C_I^o$ of the cation in the aqueous source phase I. Due to the formal similarities between enzyme kinetics and transport kinetics, the transport rate obeys a law of the Michaelis–Menten type, which suggests that the plot of $V$ *vs.* $C_I^o$ should correspond to a saturatable process and $1/V$ should be a linear function of $1/C_I^o$, at least on the ascending part of the bell-shaped curve.

Fig. 2 reports the three types of graphs for the system **6**–$K^+$, which corresponds to $V_{max}$. All three plots are linear and we can conclude that this system is purely diffusion-controlled. The same behaviour is displayed by the dealkylated hexamer **3a**.

Fig. 3 is related to the system **1**–$Na^+$, which is on the ascending part of the curve in Fig. 1. We get a linear plot of $1/V$ *vs.* $1/C_I^o$, but the plot of $V$ *vs.* the stirring speed forms a horizontal line up to 100 rpm and mounts linearly with the rpm between 100 and 200 rpm. The plot of $V$ *vs.* $L_o$ is definitely not linear but corresponds to a saturation of the process which might be attributable to the surfactant properties of the tetraethylester already invoked above when we discussed the attainment of the steady state. Indeed, the tetraester has been shown to facilitate the formation of Langmuir monolayers.[29,30]

Fig. 4 is related to the system **6**–$Na^+$, situated on the tail of the descending part of the bell-shaped curve. Neither $V$ *vs.* $L_o$ nor $V$ *vs.* stirring speed is linear. This is an indication that the process is no longer diffusion controlled. In this case, the extraction equilibrium constant is so large that the extraction at the first interface is high, but the stripping at the second interface is too slow for an efficient global transport process.

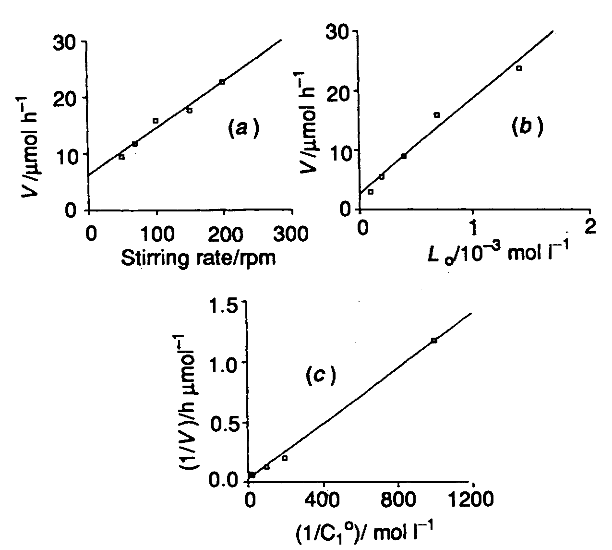

**Fig. 2** System **6**–K$^+$. Variation of $V$ in µmol h$^{-1}$, with (*a*) the stirring rate; (*b*) the initial carrier concentration in the membrane $L_0$ in mol dm$^{-3}$; (*c*) variation of $1/V$ with the inverse of the initial carrier concentration in the source phase.

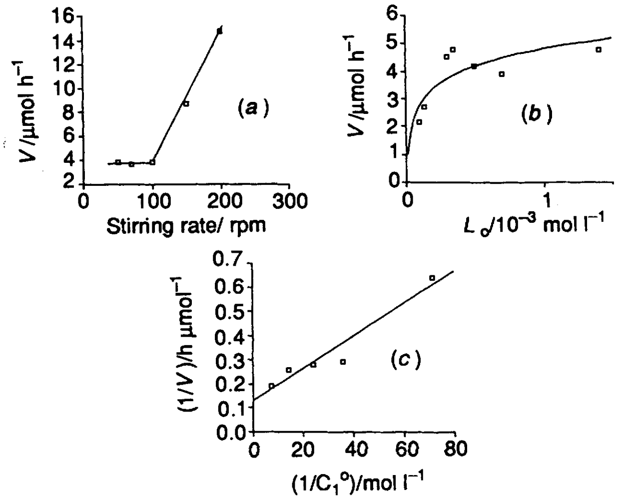

**Fig. 3** System **1**–Na$^+$. Variation of $V$, in µmol h$^{-1}$, with (*a*) the stirring rate; (*b*) the initial carrier concentration in the membrane $L_0$; (*c*) variation of $1/V$ with the inverse of the initial carrier concentration in the source phase.

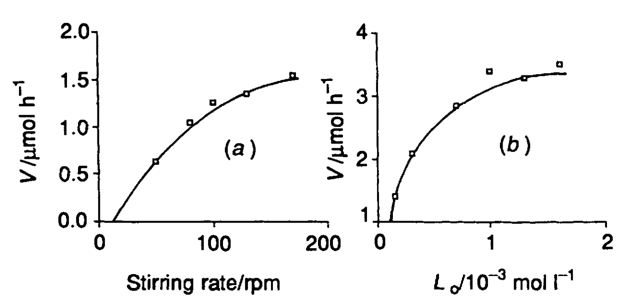

**Fig. 4** System **6**–Na$^+$. Variation of $V$, in µmol h$^{-1}$, with (*a*) the stirring rate; (*b*) the initial carrier concentration in the source phase.

Consequently, among the systems tested for the nature of the transport regime, only two of them, the systems **6**–K$^+$ and **3a**–Cs$^+$ display the behaviour expected for a totally diffusion controlled process.

It may also be seen on Fig. 1 that some of the points lie significantly outside the bell curve, especially **1**–Na$^+$, **2**–Rb$^+$, **2**–K$^+$ and **2**–Cs$^+$ in which the ligands are all esters. This suggests that (*i*) all systems may not obey the same linear relationship between log $K_e$(Pi$^-$) and log $K_e$(SCN$^-$) and (*ii*) amides and esters should be treated separately.

**Table 4** Log $K_e$ values for the extraction of alkali thiocyanates. The values for picrate extraction, given between brackets, are calculated from the percentage extraction reported in our earlier work. The thiocyanate extracts used 2.5 × 10$^{-3}$ mol dm$^{-3}$ ligand solutions, except for the pyrrolidinyl amide with which the standard conditions of our picrate extraction measurements were used (see Experimental)

| | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| **1** | < 4.5<br>(6.1)[a] | 5.2<br>(7.1)[a] | < 4.5<br>(6.0)[a] | < 4.5<br>(5.7)[a] | < 4.5<br>(6.1)[a] |
| **2** | < 4.5<br>(6.2)[a] | 4.7<br>(7.2)[b] | 5.0<br>(7.7)[b] | 5.2<br>(7.8)[a] | 5.2<br>(7.8)[b] |
| **3** | < 4.5<br>5.2)[a] | < 4.5<br>(5.7)[a] | < 4.5<br>(6.7)[a] | < 4.5<br>6.6)[a] | < 4.5<br>(7.2)[a] |
| **5** | 5.7<br>(8.3)[c] | 7.7<br>(11.2)[c] | 5.8<br>(8.8)[c] | 5.3<br>(6.9)[c] | 5.4<br>(6.4)[c] |
| **6** | 6.0<br>(7.7)[c] | 6.8<br>(10.3)[c] | 6.2<br>(8.1)[c] | 5.9<br>(6.6)[c] | 5.8<br>(6.4)[c] |

[a] Ref. 17. [b] Ref. 15. [c] Ref. 16.

In order to understand further the correlation of the transport rate with the extraction equilibrium constant, we determined the latter for the thiocyanate systems. The results are given in Table 4 as log $K_e$, together with the picrate extraction data calculated from our earlier work. $K_e$ was obtained from the measured percentages of extraction $P$ ($0 \leqslant P \leqslant 1$) by eqn. (1).

$$K_e = PC_1^\circ/(C_1^\circ - PC_1^\circ)^2(L_0 - PC_1^\circ) \qquad (1)$$

In fact eqn. (1) gives the product $K_e(\gamma_\pm)^2$, $\gamma_\pm$ being the mean activity coefficient of the metal salt which we assumed to equal 1 in our very dilute experimental conditions.

The extent of extraction of the thiocyanates is so small in our standard experimental conditions that even with $L_0$ ten times higher than $C_1^\circ$, we observed no extraction for the tetra- and hexa-esters and the cations K$^+$, Rb$^+$ and Cs$^+$, which corresponds under our conditions to log $K_e \leqslant 4.5$. This does not leave many points to test the dependence of $V$ *vs.* log $K_e$(SCN$^-$) for the esters. Nevertheless, the results summarised in Table 4 allow the following conclusions concerning our two assumptions stated above. (*i*) Effectively, the correlation between log $K_e$(Pi$^-$) and log $K_e$(SCN$^-$) is always linear, but the equation of the line depends upon the carrier. In consequence, the bell-shaped curve of Fig. 1 cannot have theoretical justification as we first thought, because the shift from log $K_e$(Pi$^-$) to log $K_e$(SCN$^-$) varies from one carrier to the other. (*ii*) Contrary to what was expected, the plot of all data $V$ *vs.* log $K_e$(SCN$^-$) is not at all bell-shaped.

If we consider the two amides only, most of the data fit a bell-shaped curve, but not as well as in the plot of $V$ *vs.* log $K_e$(Pi$^-$). Nothing can be deduced from the plot of $V$ *vs.* log $K_e$(SCN$^-$) when restricted to the esters' series, which consists of five points only.

*Conclusions.*—Although our attempts to apply the theory of transport developed for diffusion controlled processes have not been entirely successful, contrary to what we had anticipated from first results, we have demonstrated that calixarene esters and amides do possess significant cation dependent ionophoric properties. It may well prove to be the case that esters and amides need to be treated separately. Furthermore, the systems themselves may not be totally diffusion controlled.

## Acknowledgements

Portions of this work were conducted within the European Community's RTD Programme on Nuclear Waste Management and Storage (Contract F12W-CT90-0062). We thank the EC Commission for financial support.

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*Paper* 4/03558E
*Received* 13*th June* 1994
*Accepted* 8*th September* 1994