Transport of Ca^{2+} Ion through a Bubbling Pseudo-emulsion Liquid Membrane with Calixarenes and Calixcrowns as Carriers

WANG, Li[a](王丽) ZHENG, Qi-Yu[b](郑企雨) CAO, Yan-Yan[a](曹炎炎) LIU, Yu[a](刘宇)
JIANG, Zhong-Liang[a](蒋忠良) SHI, Xian-Fa*,[a](施宪法)
[a] *Department of Chemistry, Tongji University, Shanghai 200092, China*
[b] *Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

Several new calixcrowns were synthesized and characterized. The transport of Ca^{2+} ion was investigated through a bubbling pseudo-emulsion liquid membrane with these calixcrowns, the parent calix[*n*]arenes (*n* = 4, 6, 8) and the ester, acid derivatives of calix[4]arene as mobile carriers. The effects of the initial concentrations of Ca^{2+} ion in the source phase and the initial pH difference (ΔpH) between the receiving phase and the source phase were studied. The results suggest that there are two different transport mechanisms. The transports using calixarenes and their ester, acid derivatives as carriers represent a proton-coupled co-transport with a flow of protons in the opposite direction, while the transports using the calixcrowns as carriers exhibit the characteristics of an anion-coupled co-transport with a flow of anion in the same direction.

Keywords calixarene, calixcrown, Ca^{2+} ion, pseudo-emulsion liquid membrane, transport

Introduction

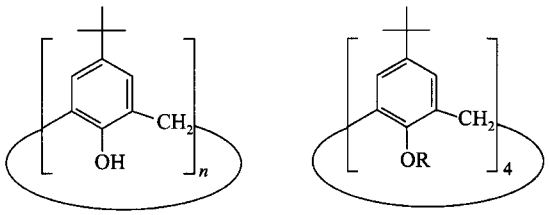
Calixarenes constitute a versatile class of macrocyclic compounds that can be easily functionalized, thus affording a large variety of new multifunctional receptors.[1] In the past two decades, they have played an important role in supramolecular chemistry as useful building blocks for the synthesis of ionic or molecular receptors and carriers. Calixcrowns, in which an oligo(ethylene oxide) chain is capped on the lower rim of calixarene ring, are one of the most important calixarene derivatives. In this kind of derivatives, the structural features of the calixarene and crown ether are combined and thus it may introduce a double control of selectivity. Due to this unique characteristic, the interest in calixcrowns has increased continuously since Ungaro and his co-workers' first report appeared.[2] So far, a great deal of work has been done and several research groups have succeeded in demonstrating that these compounds can serve as excellent selective receptors or carriers for metal ions.[3-5]

Transport of ionic species is a fundamental and essential process in many biological systems and is of increasing importance for the recovery and ungrading of resources using artificial membranes. Since Izatt *et al*. reported the transport of alkali metal ion through liquid membranes with a series of calixarenes as carriers,[6] transports of ions or molecules have been extensively studied using calixarenes as mobile carriers in bulk liquid membranes[7,8] or supported liquid membranes (SLM).[5,9-11] However, most transport researches concerning calixarenes or their derivatives were concentrated on alkali metals. To the best of our knowledge, up to now, no related report has ever appeared dealing with the transport of Ca^{2+}, Mg^{2+} or other alkaline earth metals, although some studies have been conducted in relation to the recognition of alkaline earth metals.[12-15]

In this paper, the syntheses of several calixcrowns **4a**, **4b** and **5a**, **5b** were reported. As an extension of our studies on the transports of Na^+, K^+ and Fe^{3+} ions,[16,17] the transport of Ca^{2+} ion was studied by means of a bubbling pseudo-emulsion liquid membrane with these new calixcrowns and the parent calixarenes (**1a**—**1c**),

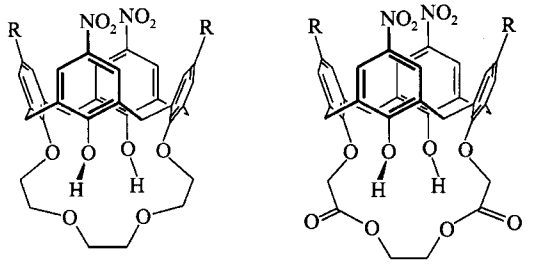
* E-mail: xfshi@mail.tongji.edu.cn
Received September 25, 2001; revised December 4, 2001; accepted January 10, 2002.
Project supported by the National Natural Science Foundation of China (No. 29971023).

calix[4]arene ester (**2**) and calix[4]arene acid (**3**). Although the transport of Ca^{2+} ion is not high compared with those of K^+, Na^+ and Fe^{3+},[16,17] the study could at least offer an enlightening insight into the transport of alkaline earth metals with the calixarenes.



1a $n = 4$
1b $n = 6$
1c $n = 8$

2 R = CH_2COOEt
3 R = CH_2COOH



4a R = *t*-butyl
4b R = H

5a R = *t*-butyl
5b R = H

Fig. 1 Structures of the calixarenes and their derivatives **1**—**5**.

Experimental

Instrumentation and materials

^1H NMR and ^{13}C NMR spectra were recorded at 500 MHz using an AM500 spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were obtained on a Nicolet FT-IR170SX spectrometer. Elemental analysis was performed on a Perkin Elmer 240 instrument. UV-vis spectrophotometer (No. 3 Shanghai Analysis Instrumentation Factory, Type 731) was used to determine the concentration of Ca^{2+} ion.

p-tert-Butylcalix[*n*]arenes ($n = 4$, 6, 8) (**1a**—**1c**),[18] calix[4]arene ester (**2**)[19] and calix[4]arene acid (**3**)[19] were prepared according to methods reported. All these compounds were characterized by IR, ^1H NMR spectra and elemental analysis. Water used in this study was de-ionized with a de-ionized water fabricator (Shanghai Hezi Medical Instrumentation Factory, Type 70) and treated with EDTA to remove the Ca^{2+} and other metal ions. Other chemicals used were of A.R. grade.

Syntheses of calix[4]crowns **4a**—**4b** *and* **5a**—**5b**

Calix[4]crowns **4a**—**4b** or **5a**—**5b** were synthesized by nitration or ipso-nitration of calix[4]crowns-4 **6a**—**6b** or calix[4]crowns containing ester groups **7a**—**7b** with 65% HNO_3 and glacial acetic acid in CH_2Cl_2 according to the known method.[20]

5,17-*Bis*(*tert-butyl*)-25,27-*dihydroxy*-11,23-*dinitrocalix*[4]*arene-crown*-4 (**4a**) Yield: 66%; ^1H NMR ($CDCl_3$/TMS) δ: 1.22 (s, 18H, $C(CH_3)_3$), 3.50 and 4.36 (AB, 8H, J = 13.0 Hz, $ArCH_2Ar$), 3.99 (s, 4H, OCH_2CH_2O), 4.18—4.26 (m, 8H, $ArOCH_2CH_2O$), 7.18 (s, 4H, ArH), 7.96 (s, 4H, ArH), 9.89 (s, 2H, OH); ^{13}C NMR ($CDCl_3$/TMS) δ: 31.27 ($C(CH_3)_3$), 31.89 ($ArCH_2Ar$), 34.44 ($C(CH_3)_3$), 68.56, 68.77, 74.82 (OCH_2), 124.42, 126.40, 129.00, 132.48, 140.03, 149.10, 149.83, 159.46 (ArC); IR (KBr) ν: 3150 (OH), 2920, 1495 and 1320 (NO_2) cm^{-1}; MS (FAB) *m/z* (%): 739 ($[M-1]^+$); Anal. calcd for $C_{42}H_{48}N_2O_{10}$: C 68.09, H 6.53, N 3.78; found C 67.75, H 6.44, N 3.89.

25,27-*Dihydroxy*-11,23-*dinitrocalix*[4]*arene-crown*-4 (**4b**) Yield: 43%; ^1H NMR ($CDCl_3$/TMS) δ: 3.51 and 4.35 (AB, 8H, J = 13.0 Hz, $ArCH_2Ar$), 3.98 (s, 4H, OCH_2CH_2O), 4.16—4.28 (m, 8H, $ArOCH_2CH_2O$), 6.89—7.15 (m, 6H, ArH), 8.00 (s, 4H, ArH), 9.85 (s, 2H, OH); ^{13}C NMR ($CDCl_3$/TMS) δ: 31.62 ($ArCH_2Ar$), 68.96, 69.02, 74.64 (OCH_2), 124.46, 126.28, 128.84, 129.61, 132.87, 139.79, 151.65, 159.65 (ArC); IR (KBr) ν: 3180 (OH), 1490 and 1320 (NO_2) cm^{-1}; MS (FAB) *m/z* (%): 627 ($[M-1]^+$); Anal. calcd for $C_{34}H_{32}N_2O_{10}\cdot 0.4CHCl_3$: C 61.09, H 4.83, N 4.14; found C 61.07, H 5.04, N 4.09.

5,17-*Bis*(*tert-butyl*)-25,27-*dihydroxy*-11,23-*dinitro*-26,28-(3′,6′-*dioxa*-2′,7′-*dioxo*-*octylene*) *dioxycalix*[4]*arene* (**5a**) Yield: 64%; ^1H NMR ($CDCl_3$/TMS) δ: 1.19 (s, 18H, $C(CH_3)_3$), 3.54 and 4.25 (AB, 8H, J = 13.0 Hz, $ArCH_2Ar$), 4.65 (s, 4H, OCH_2CH_2O), 4.73 (s, 4H, OCH_2CO), 7.15 (s, 4H, ArH), 8.01 (s, 4H, ArH), 9.30 (s, 2H, OH); ^{13}C NMR ($CDCl_3$/TMS) δ: 31.19 ($C(CH_3)_3$), 31.59 ($ArCH_2Ar$), 34.49 ($C(CH_3)_3$), 62.86 (OCH_2CH_2O), 73.04 ($ArOCH_2$), 124.61, 126.76, 128.17, 131.59, 140.11, 148.11, 149.90, 159.15 (ArC), 166.98 (CO_2); IR (KBr) ν: 3330 (OH), 2960, 1750 (CO_2),

1520 and 1335 (NO_2) cm^{-1}; MS (FAB) *m/z* (%): 767 ([M − 1]$^+$); Anal. calcd for $C_{42}H_{44}N_2O_{12}$: C 65.62, H 5.77, N 3.64; found C 65.05, H 5.69, N 3.55.

25,27-*Dihydroxy*-11,23-*dinitro*-26,28-(3,6′-*dioxa*-2′,7′-*dioxooctylene*) *dioxycalix*[4]*arene* (**5b**) Data of this compound have already been reported.[20]

Experimental methods for transport

Membrane transport experiments were carried out with a specially designed "bubbling pseudo-emulsion liquid membrane system" (illustrated in Fig. 2), which has been described in detail before.[16]

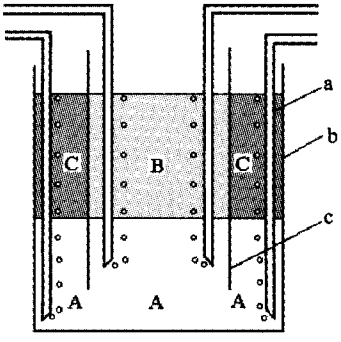


Fig. 2 Liquid membrane transport cell. A: liquid membrane phase, B: receiving phase, C: source phase, a: air inlet, b: outer cylinder, c: inner cylinder

In this study, the source phase was aqueous solution of calcium gluconate and the receiving phase was that of HCl with various concentrations. The liquid membrane phase was the solution of calixarene or calixarene derivative in $CHCl_3$ + CCl_4 (*V*/*V* = 1/9) with concentrations about 1.0×10^{-3} mol/L for **1a**—**1c**, **2**, **3** and about 1.0×10^{-4} mol/L for **4a** , **4b** and **5a**, **5b**. The volume of the source phase and the receiving phase was both 75 mL and that of the membrane phase was 130 mL.

The concentration of Ca^{2+} was determined by means of the UV-vis spectrometric analysis using arsenazo III as chromogenic agent with a detection limit of 1.0×10^{-7} mol/L.

In this paper, the transport results are expressed as the change of Ca^{2+} ion concentration in the receiving phase after transport. The transport time was determined by "transport time curve", which reveals the relation between the transport time and the transport result. When the total transport amount does not vary with the transport time, the transport balance is achieved. The corresponding balance time was determined as transport time. In this study, the longest balance time of all carriers was used as transport time (6 h) to make the results comparable.

According to our previous experimental results, the effect of temperature on the transport results might be ignored within the temperature range of 18—30 ℃. Therefore the transports were conducted at room temperature without taking the effect of temperature into account.

During each transport experiment, a control experiment involving no carrier in the membrane phase was conducted. All results reported here are the net transport results, with the corresponding blank value already deducted from the original experimental results. They are the average results of three parallel transport experiments. After the transport process was completed, the changes in the pH value of the source phase were also measured (the receiving phase was a highly acidic solution, so the change in the pH value could not be detected).

Results and discussion

Transport experiments were first carried out under four conditions with different initial concentrations of Ca^{2+} in the source phase and the varying initial pH difference (ΔpH) between the receiving phase and the source phase using each compound as a carrier.

The data, summarized in Table 1, indicate that all these compounds have visible transport ability for Ca^{2+} ions, although their transport percentages are not high. The transport ability of the different parent calix[*n*]-arenes decreased in the order **1a** > **1b** > **1c**. The approximate hydroxyl-end cavity diameters of **1a**—**1c** are reported as follows:[6] **1a** 0.068—0.092 nm, **1b** 0.21—0.28 nm, **1c** 0.40—0.41 nm. The ionic radius of Ca^{2+} is 0.099 nm. These facts described here indicate that some factors rather than size-related selectivity are responsible for the transport ability. Comparing the results of the similar calixcrowns listed in the Table 1, it could be seen that dealkylation of **4a** and **5a** in the *para* position of the phenolic group, leading to **4b** and **5b**, resulted in a remarkable increase of the transport (**4b** > **4a**, **5b** > **5a**). This implies that the presence of substituent on the upper rim of calixarenes might have some effect on the transport.

The results in Table 1 also suggest that both the initial concentration of Ca^{2+} in the source phase and the

ΔpH between the receiving phase and the source phase can affect the transport. Further studies performed with calixcrown **4b**, which transports the Ca^{2+} most efficiently, indicate that the bigger the initial ΔpH and the initial concentration of Ca^{2+} in the source phase were, more Ca^{2+} ions were transported into the receiving phase as shown in Figs. 3 and 4.

After each transport was completed, the pH value of the source phase was measured. It decreased obviously after transport when the compounds **1a**—**1c** and **3** were used as carriers. This means that a number of H^+ ions had flowed into the source phase from the receiving phase during the transport. The increases of H^+ in the source phase after transport and the corresponding transport of Ca^{2+} are listed together in Table 2. Comparison of the data in Table 2 shows that for each transport the increase of H^+ in the source phase was approximately twice as big as the transported Ca^{2+}. Therefore, it can be conjectured that the transport mechanism is not different from the mechanism of the transports of alkaline metal ions by calixarenes,[6,16] which is a proton-coupled co-transport with a flow of protons in the opposite direction. As for ester derivative **2**, though it has not any potential ionizable proton, the slight increases of H^+ in the source phase were observed, too. So we guess that under the transport conditions provided by us, the ester derivative **2** could transport Ca^{2+} as a result of the above mentioned mechanism. This can be explained in that one of the four ester groups of **2** might turn into a carboxyl group on the phase-surface between the acidic receiving phase and the membrane phase.[21] Thus the transport ability **3** > **1a** > **2** and the fact that the transport of Ca^{2+} ion is much smaller than that of K^+, Na^+[16] can easily be made clear by this mechanism. The transport ability **3** > **1a** > **2** is ascribed to their acidity (**3** > **1a** > **2**). pK_a measurements of calixa-[4]rene reveal that the first proton is very acidic (a so-called super proton) and that a considerably large gap exists between the pK_a values for the first deprotonation step and those for the second deprotonation step.[22] Transport of Na^+ or K^+ needed only one proton deprotoned while Ca^{2+} needed two H^+ ions deprotoned to keep the complex neutral. So it is easier to transport K^+ or Na^+ than to transport Ca^{2+} with the similar calixarenes as carriers. The transport procedure can be described as follows: at the interface of the source phase and the membrane, the carrier is deprotoned and cation complexation occurs to give a neutral complex, which can diffuse across the membrane; at the interface of the receiving phase (acidic) and the membrane, the reverse process occurs. Ca^{2+} ions are delivered into the receiving phase while the calixarenes reprotonate to generates the carrier and complete the cycle.

In contrast to the results of **1a**—**1c**, **2** and **3**, no obvious change was observed in the pH value of the source phase after transport when compound **4a**, **4b** and **5a**, **5b** were used as carriers. This means that H^+ had not participated in the transport process. Obviously, here Ca^{2+} ions were transported by another mechanism. It has been reported that a counter anion (picrate anion) can participate in the coordination of Rb^+ ion and calix-

Table 1 Transport of Ca^{2+} with different initial ΔpH between the receiving and the source phase and different initial concentration of Ca^{2+} in the source phase

Carrier	$\Delta c_{Ca^{2+}}$ (mol·L^{-1})			
	A	B	C	D
1a	1.06×10^{-5}	6.07×10^{-6}	6.98×10^{-6}	3.02×10^{-6}
1b	7.42×10^{-6}	3.46×10^{-6}	4.51×10^{-6}	1.76×10^{-6}
1c	3.40×10^{-6}	*	1.65×10^{-6}	*
2	6.05×10^{-6}	3.46×10^{-6}	3.90×10^{-6}	2.31×10^{-6}
3	1.65×10^{-5}	6.43×10^{-6}	1.02×10^{-5}	4.84×10^{-6}
4a	8.90×10^{-6}	4.45×10^{-6}	5.66×10^{-6}	2.86×10^{-6}
4b	2.72×10^{-5}	1.54×10^{-5}	1.80×10^{-5}	7.80×10^{-6}
5a	7.70×10^{-6}	*	3.79×10^{-6}	*
5b	9.12×10^{-6}	5.57×10^{-6}	5.88×10^{-6}	3.35×10^{-6}

Conditions: A. initial ΔpH: 6.80, c_s^0: 1.12×10^{-2} mol/L; B. initial ΔpH: 6.80, c_s^0: 1.12×10^{-3} mol/L; C. initial ΔpH: 4.80, C_s^0: 1.12×10^{-2} mol/L; D. initial ΔpH: 4.80, c_s^0: 1.12×10^{-3} mol/L, c_s^0: the initial concentration of Ca^{2+} in the source phase. $\Delta c_{Ca^{2+}}$: the net transport of Ca^{2+}; * the transport of Ca^{2+} is too small to be detected precisely.

Table 2 Increases of H^+ ion (Δc_{H^+}) in source phase and the increase of Ca^{2+} ion ($\Delta c_{Ca^{2+}}$) in the receiving phase after transport

Carrier	Δc_{H^+} ($\Delta c_{Ca^{2+}}$) (mol·L^{-1})			
	A	B	C	D
1a	2.07×10^{-5}	1.24×10^{-5}	1.43×10^{-5}	4.72×10^{-6}
	(1.06×10^{-5})	(6.07×10^{-6})	(6.98×10^{-6})	(3.02×10^{-6})
1b	1.40×10^{-5}	4.85×10^{-6}	6.23×10^{-6}	2.16×10^{-6}
	(7.42×10^{-6})	(3.46×10^{-6})	(4.51×10^{-6})	(1.76×10^{-6})
1c	7.10×10^{-6}	*	3.02×10^{-6}	*
	(3.40×10^{-6})	(*)	(1.65×10^{-6})	(*)
3	5.60×10^{-5}	1.57×10^{-5}	2.79×10^{-5}	9.34×10^{-6}
	(1.65×10^{-5})	(6.43×10^{-6})	(1.02×10^{-5})	(4.84×10^{-6})

Conditions: A. initial ΔpH: 6.80; c_s^0: 1.12×10^{-2} mol/L; B. initial ΔpH: 6.80; c_s^0: 1.12×10^{-3} mol/L; C. initial ΔpH: 4.80; c_s^0: 1.12×10^{-2} mol/L; D. initial ΔpH: 4.80; c_s^0: 1.12×10^{-3} mol/L; c_s^0: the initial concentration of Ca^{2+} in the source phase. $\Delta c_{Ca^{2+}}$: the net transport of Ca^{2+}; Δc_{H^+}: the increase of H^+ ion in source phase; * the transport of Ca^{2+} is too small to be detected precisely.

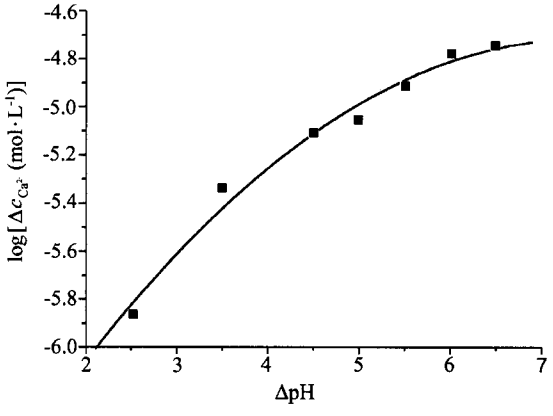


Fig. 3 Effect of the initial ΔpH between the receiving and resource phases. (Conditions: membrane phase: 1.0×10^{-4} mol/L solution of **4b**; source phase: 1.12×10^{-3} mol/L calcium gluconate; receiving phase: the solution of HCl with different pH value; $\Delta c_{Ca^{2+}}$: the concentration of transported Ca^{2+}).

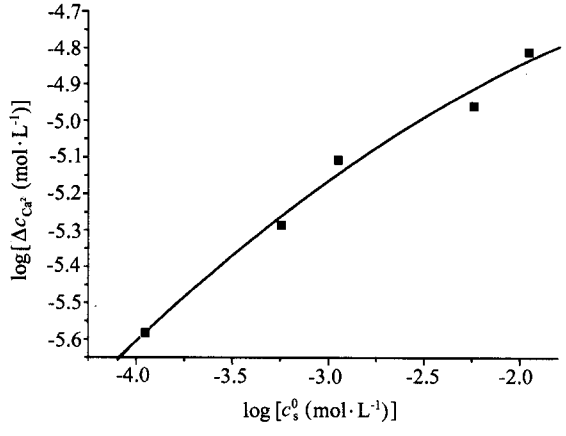


Fig. 4 Effect of the initial concentration of Ca^{2+} in source phase (Conditions: membrane phase: 1.0×10^{-4} mol/L soluion of **4b**; receiving phase: 0.01 mol/L HCl; source phase: solution of calcium gluconate with different Ca^{2+} conncentration; c_s^0: the initial concentration of Ca^{2+} in source phase; $\Delta c_{Ca^{2+}}$: the concentration of the net transported Ca^{2+}).

crown.[23,24] From this, it can be conjectured that the counter anions should have been transported simultaneously when the Ca^{2+} was transported by the carriers **4a**, **4b** and **5a**, **5b**. In other words, the counter anion had also participated in the transport. So further transport experiments were also performed with different counter anions using calixcrown **4b** as carrier for the purpose of gaining an in-depth knowledge of the influence of the counter anion. The data in Table 3 show that the counter anions in the source phase have an effect on the transport results. The gluconate anion worked better than the acetic anion. When the anion is a chloride anion, the transport can be insignificant.

Table 3 Transport of Ca^{2+} using different anion in the source phase with **4b** as carrier

Anions	Gluconate anion	Acetic anion	Chloride anion
$\Delta c_{Ca^{2+}}$ (mol/L)	7.80×10^{-6}	3.24×10^{-6}	1.26×10^{-6}

Conditions: rceiving phase: 0.01 mol/L aqueous solution of HCl; membrane phase: 1.0×10^{-4} mol/L solution of **4b**; source phase: 1.12×10^{-3} mol/L solution of Ca^{2+} ion; initial ΔpH: 4.8; $\Delta c_{Ca^{2+}}$: the net transport of Ca^{2+}.

So it is evident that the mechanism, for which the calixcrowns transported Ca^{2+} ion, is similar to that in the case of crown ether. By that mechanism, the counter an-

ions participate in the transport.[25] The carriers that transported the Ca^{2+} ions bore the counter anions through the membrane, which attracted each other together by an electrostatic force. Therefore, the nature of the counter anion used can affect the results of the transport. The bigger the organic group in the anion was, the easier it could be solved in the membrane phase, and the more effectively the Ca^{2+} ion was transported.

Conclusion

Several new calixcrowns were synthesized and characterized. The transport of Ca^{2+} ion was investigated through a bubbling pseudo-emulsion liquid membrane with these calixcrowns and the calix[n]arenes ($n = 4, 6, 8$) and their derivatives as carriers. The results show that both the initial concentration of Ca^{2+} in the source phase and the initial pH difference between the receiving phase and the source phase can affect the transport. The change in pH value of the source phase after the transport represents a proton-coupled co-transport mechanism when using calixarenes and their ester, acid derivatives as carriers. The facts that no changes in pH value of the source phase were observed and that the anion used in source phase could affect the transport result when the calixcrowns were used as carriers may imply an anion-coupled mechanism.

References

1 (a) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713. (b) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.

2 Alfieri, C.; Dradi, E.; Pochini, A.; Ungaro, R.; Andreetti, G. D. *J. Chem. Soc., Chem. Commun.* **1983**, 1075.

3 Kim, J. S.; Yu, I. Y.; Suh, H.; Ra, D. Y.; Kim, J. W. *Synth. Commun.* **1998**, *28*, 2937.

4 Zheng, Q.-Y.; Chen, C.-F.; Huang, Z.-T. *Chin. J. Chem.* **2000**, *18*, 104.

5 Nijenhuis, W. F.; Buitenhuis, E. G.; Jong, F.; Sudhölter; E. J. R.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 7963.

6 (a) Izatt, R. M.; Lamb, J. D.; Hawkins, R. T.; Brown, P. R.; Izatt, S. R.; Chistensen, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 1782. (b) Izatt, S. R.; Hawkins, R. T.; Christensen, J. J.; Izatt, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 63.

7 Shinkai, S.; Shiramama, Y.; Satoh, H.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1167.

8 Arnaud-Neu, F.; Fanni, S.; Guerra, L.; McGregor, W.; Ziat, K.; Schwing-weill, M.; Barrett, G.; Mckervey, M. A.; Marrs, D.; Seward, E. M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 113.

9 Yaftian, M.; Burgard, R. M.; Dieleman, C. B.; Matt, D. *J. Membr. Sci.* **1998**, *144*, 57.

10 Asfari, Z.; Bressot, C.; Vicens, J.; Hill, C.; Dozol, J.-F.; Rouquette, H.; Eymard, S.; Lamare, V.; Tournois, B. *Anal. Chem.* **1995**, *67*, 3133.

11 Reichwein-buitenhuis, E. G.; Visser, H. C.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 3913.

12 Arnaud-Neu, F.; Barret, G.; Fanni, S.; Marrs, D.; McGregor, W.; McKervey, M. A.; Schwing - Weill, M.- J.; Vetrogon, V; Wechsler, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 453.

13 Chang, S.-K.; Kwon, S.; Cho, I. *Chem. Lett.* **1987**, 947.

14 Ogata, M.; Fujimoto, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 4505.

15 Muzet, N.; Wipff, G.; Casnati, A.; Domiano, L.; Ungaro, R.; Ugozzoli, F. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1605.

16 Ye, Z.-F.; Wang, Y.-P.; Liu, Y.-S.; Jiang, Z.-L.; Shen, X.; Zhu, L.-G.; Shi, X.-F. *J. Membr. Sci.* **1999**, *163*, 367.

17 Wang, L.; Sun, H.-B.; Fu, H.-Y.; Jiang, Z.-L.; Shi, X.-F. *Chem. J. on Internet* **2000**, *2*, 44.

18 (a) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234. (b) Gutsche, C. D.; Dhawan, B.; Leonis, M.; Steward, D. *Org. Synth.* **1990**, *68*, 238. (c) Munch, J. H.; Gutsche, C. D. *Org. Synth.* **1990**, *68*, 243.

19 Arnaud-Neu, A.; Collins, E. M.; Deasy, M.; Ferguson, G.; Harris, S. J.; Kaitner, B.; Lough, A. J.; McKervey, M. A.; Marques, E.; Ruhl, B. L.; Schwing-Weill M. J.; Seward, E. M. *J. Am. Chem. Soc.* **1989**, *111*, 8681.

20 Zheng, Q.-Y.; Chen, C.-F.; Huang, Z.-T. *Tetrahedron* **1997**, *53*, 10345.

21 Barratt, G.; Böhmer, V.; Ferguson, G.; Gallagher, J. F.; Harris, S. J.; Leonard, R. G.; McKervey, M. A.; Owens, M.; Tabatabai, M.; Vierengel A.; Vogt, W. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1595.

22 (a) Shinkai, S.; Araki, K.; Shibata, J.; Tsugawa, D.; Manabe, O. *Chem. Lett.* **1989**, 931. (b) Shinkai, S.; Araki, K.; Koreishi, H.; Tsubaki, T.; Manabe, O. *Chem. Lett.* **1986**, 1351.

23 Reinhoudt, D. N.; Dijkstra, P. J.; Veld, P. J. A.; Bugge, K. E.; Harkema, S.; Ungaro, R.; Ghidini, E. *J. Am. Chem. Soc.* **1987**, *109*, 4761.

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

25 Dulyea, L. M.; Fyles, T. M.; Whitfield, D. M. *Can. J. Chem.* **1984**, *62*, 498.

(E0109251 SONG, J. P.; LING, J.)