

Polymeric CTA membrane with calixarene

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ABSTRACT

Carboxylic acid and carboxamide-appended calix[6]arene in an alternative way has been synthesized. Transport rates of alkali and alkaline-earth metal ions through the bulk liquid membrane and polymer inclusion membrane were tested. Ba²⁺ ion was found to give the highest transport rate among tested metal ions in both BLM and PIM systems. In PIM system, high durability of the membrane was observed. Thermodynamic study gives a same propensity for the Ba²⁺ ion selectivity.

Key words : calix[6]arene; membrane; transport experiment; polymer inclusion membrane.

Introduction

Calixarenes has gained much attention as inclusion hosts for ions and specific molecules.¹⁻³ Among them, calix[4]arenes have been also used as 3-D molecular building blocks for the synthesis of receptors with specific properties.¹ They can exist in four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate.² Calix[4]arenes constrained to the 1,3-alternate conformation and more particularly to 1,3-calix[4]-*bis*-crowns and aza-crown systems have received much attention because of their structural peculiarities. They present two binding sites departed on both sides of the calixarene and are linked to each other by a π -basic benzene tunnel.

While crown ethers and azacrown ether attached calix[4]arenes have long been interesting to chemists for synthesis as well as for their metal ion recognition,⁴ calix[6]arene was not that attractive not only because synthesis of the calix[6]arene derivatives is difficult but also because

the conformations of the product is too complicated to be assigned. Recently, these calix[6]arenes having both carboxamide and carboxylic acid tails by alternative pattern have been intensively studied in selective separation of the lanthanides and actinides which can exist in atomic nuclear wastes.⁵ Am³⁺ selectivity (separation factor) over lanthanides in two-phase extraction experiment was found to be 108 at pH 3.0.⁵ However, transport through polymer inclusion membrane (PIM) and bulk liquid membrane (BLM) of the metal ions using the calix[6]arene derivatives have not been reported yet.

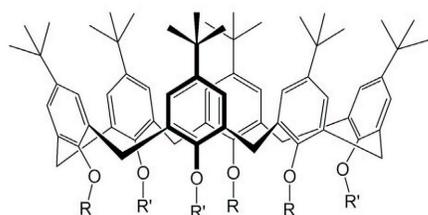
Two phase extraction, BLM, and SLM using those calixarene derivatives have been explored to investigate binding capabilities, transport rates, and transport permeability for the cesium ion.⁶ As one of the membrane technologies, polymeric inclusion membrane (PIM) system has been recently investigated taking advantages of (i) easy setup, (ii) high selectivity, and (iii) high durability, has been developed.^{7,8} PIMs with cellulose triacetate (CTA) polymer as a supporter, together with a hydrophobic non-volatile organic solvent (e.g., NPOE) as a plasticizer and an organic carrier were found to cover the several problems occurred in SLM system such as loss of organic carrier with plasticizer-

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into aqueous solution, slow transport rate, and low durability.^{6,8}

Results and Discussion

We began synthesis with *para-tert*-butylcalix[6]arene for **1**. Synthetic procedures for the target molecule were followed the method for *para-tert*-octylcalix[6]arene derivatives already reported.⁵ To attach the three carboxylic acids on lower rim of the calix[6]arene unit by 1,3,5-alternative type, selective methylation should be carried out in advance. Alkylation of ethyl 2-bromoacetate in the presence of metal carbonate gave a low yield. So, we carried out amidoalkylation using *N,N*-diethyl 2-chloroacetamide prior to attaching the three carboxylic acids, then we obtained compound in 80 % yield. Demethylation of using iodotrimethylsilane and sodium perchlorate and alkylation using 2-bromoacetic acid and NaH as a base in THF gave the desired target molecule **1** as a white solid.



1

To measure the binding ability of the **1** toward alkali and alkaline-earth metal ions, firstly we used a bulk liquid membrane (BLM) system. The results of the measurement of single ion transport rate are described in Table 1. Among alkali metal ions, K^+ ion was found to move the most rapidly from source into receiving phase through bulk organic medium by a rate of $14.28 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$. For alkaline-earth metal ions, the transport rate of Ba^{2+} ion was the largest by $21.33 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$. So, it is presumed that Ba^{2+} ion is selectively bound to the calix[6]arene **1**, then demetalation rate from organic medium into the receiving phase is also fast although the rate-determining step between two process

(complexation and decomplexation) could not be determined.

Table 1. Single ion transport values for alkali metal ions and alkaline-earth metal ions through a bulk liquid membrane using **1**.^a

Metal	Transport rate ($10^{-8} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$) ^b								
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
	5.94	7.18	14.28	2.05	1.24	2.23	8.93	14.75	21.33

^aTransport condition: source phase (aqueous solution of metal nitrate, 0.8mL, 0.1M); membrane phase ($\text{ClCH}_2\text{CH}_2\text{Cl}$, 3.0mL), (carrier)=1.0mM; i.d. of glass vial=18mm, stirred by 13mm Teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 mL). ^bThe average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

To study the binding ability of the **1** considering transport rate from source phase into receiving phase by an organic medium, we used a polymeric inclusion membrane (PIM) which is modeled after the diketone-containing membranes developed by Sugiura.⁷ They are formed by the polymerization of cellulose triacetate (CTA) to give a thin film.⁷ The PIM is then placed between an aqueous source and a receiving phase. While PIM can effectively separate two aqueous phases, they are independent of the organic solvents in maintaining phase separation and in allowing continuous transport. Transport rates of the alkali and alkaline-earth metal ions through PIM when ligand **1** were used are listed in Table 2. Like in the case of BLM, Ba^{2+} ion was found to give a selective transport through the PIM. Selectivity of $\text{Ba}^{2+}/\text{Mg}^{2+}$ is more than 40 which is the largest value ever known so far. In a control experiment, no transport rate was detected in the absence of the ligands during more than 60-hour continuous run.

Table 2. Transport rates of alkali metal ions and alkaline-earth metal ions through a PIM using **1**.

ligand	Transport rate ($10^{-5} \text{ mol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$) ^a								
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
	0	6.10	8.45	0	1.64	3.22	6.73	10.57	124.88

^aTransport condition: source phase (aqueous solution of metal nitrate 10 mM); membrane phase (CTA membrane), [carrier]=1.0 mM; receiving phase: deionized water.

Permeability coefficient (P , $\text{m} \cdot \text{s}^{-1}$) was determined by plotting the logarithm of Cs/Co vs time according to Eq. (1)

$$\ln(C_s/C_o) = - (P S/V) t \quad (1)$$

where C_o is the initial concentration of the cation in the source phase, C_s denotes the metal ion concentration in the source phase as a function of time. V and S are for volume of source phase and for membrane area, respectively.⁸ To obtain the permeability coefficient of the alkali and alkaline-earth metal ions, several different experimental sets were performed. The results are listed in Table 3 and depicted in Figure 1 and Figure 2.

Table 3. Logarithm of permeability coefficients of alkali metal ions and alkaline-earth metal ions using 1.

Metal	Log P (m·s ⁻¹) ^a								
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
	0	-5.10	-5.00	0	-5.70	-5.40	-5.10	-5.00	-4.00

^a Transport condition: source phase (aqueous solution of metal nitrate 10mM); membrane phase (CTA membrane); [carrier]=1.0 mM; receiving phase: deionized water.

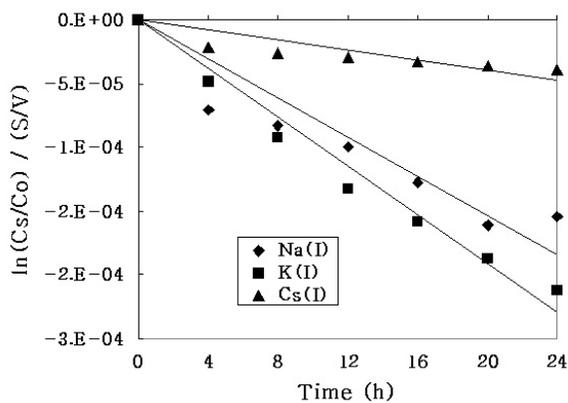


Fig 1. Kinetic plot of the permeability for alkali metal ions as a function of time (h) through a PIM. Source phase: aqueous solution of 10 mM metal nitrate; membrane phase: CTA membrane; [carrier]=1.0 mM; receiving phase: deionized water.

The slope for $\ln(C_s/C_o)/(S/V)$ vs time (h) indicates the permeability coefficient (P). Potassium ion provided the largest permeability coefficient (-5.0) among alkali metal ions. In the case of alkaline-earth metal ions, barium ion gave -4.0 of permeability coefficient that is the largest among alkaline-earth metal ions. The Log P values increased with carrier concentration and reach a maximum at 10 mM of 1.

This relationship also complies with the diffusion-based mathematical model for organic ligand across a liquid membrane described by McBride.¹⁰

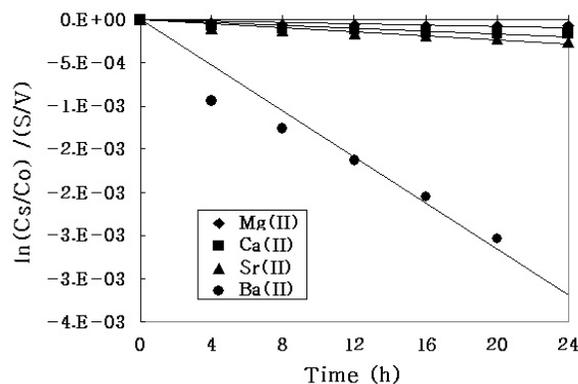


Fig 2. Kinetic plot of the permeability for alkaline-earth metal ions as a function of time (h) through a PIM. Source phase: aqueous solution of 10 mM metal nitrate; membrane phase: CTA membrane; [carrier]=1.0 mM; receiving phase: deionized water.

The enthalpy changes (ΔH) of the ligand for metal ion complexation was determined by titration calorimetry in 90 % (v/v) methanol. Complexation of the cations with the ligand is exothermic as shown in Table 3, implying that the interaction of the ligand with cations is enthalpy driven. Based upon this thermodynamic study, we found that carrier 1 forms the strongest complex with Ba²⁺ over other cations, which is in good agreement with those obtained from BLM, SLM, and PIM.

Table 3. Enthalpy changes for complexation of metal cation by various organic ligands.

Compound	ΔH (Kcal/mole)					
	Ba ²⁺	Mg ²⁺	Sr ²⁺	Na ²⁺	K ²⁺	Cs ²⁺
1	-10.02	-8.91	-3.18	-2.71	-1.86	-3.81

Titrate : 0.001 M ligands in 90 % (v/v) methanol.
 Titrant : 0.01 M metal cations in 90 % (v/v) methanol.

To examine the long-term stability of the PIMs, same membrane containing 1 was repeatedly reloaded in successive experiments. Measurement of the transport flux every 4-hour gave constant values up to 30 days. After 30 days we observed some rust in the membrane, then observed small

decline of permeability. PIM system retained a transparent solution without any loss of the organic materials into aqueous solutions during 30-days of stirring, indicating its excellent durability.

Experimental

Unless specified otherwise, reagent-grade reactants and solvents were obtained from chemical suppliers and used as received. Deionized water was prepared by passing distilled water through an Organo G-10 cartridge. Dry solvents were prepared as follows: acetonitrile was freshly distilled from calcium hydride; DMF was dried over 4 Å molecular sieves. ^1H NMR and ^{13}C NMR spectra were obtained from the Korea Basic Science Research Institute, Daejeon, Korea. Calix[6]arene derivative 1 was prepared by the adaptation of the reported procedures.⁵

Syntheses

1,3,5-Trimethyl-2,4,6-tricarboxamide-*p*-*tert*-butylcalix[6]arene

A mixture of 1.0 g (0.98 mmole) of 1,3,5-trimethyl-*p*-*tert*-butylcalix[6]arene, 0.497 mL (3.92 mmole) of *N,N*-diethyl-2-chloroacetamide, and 0.542 g (3.92 mmole) of K_2CO_3 in 150 mL of acetonitrile refluxed for 20 hrs. The crude mixture was dissolved in CH_2Cl_2 and the treated with 10 % HCl solution. The organic layer was dried over MgSO_4 . Recrystallization of the product from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (9:1) gave a white crystal in 80 % yield. IR (KBr pellet, cm^{-1}): 3452, 2985.5, 2370.8, 1637.2, 1482.7, 1019.4. ^1H NMR (300 MHz, CDCl_3): δ 7.2-7.3 (d, 6 H, ArH), 6.59-6.68 (s, 6 H, ArH), 4.6 (s, 6 H, OCH_2C), 3.56-4.55 (m, 12 H, ArCH_2Ar), 2.2 (s, 9 H, $-\text{CH}_3$), 1.15-1.33 (q, 9 H, NCH_2CH_3), 1.38 (s, 27 H, *t*-Bu), 0.77 (s, 27 H, *t*-Bu). FAB-MS m/z (M^+) calcd. 1454.92, found 1454.90.

1,3,5-Tricarboxamide-*p*-*tert*-butylcalix[6]arene

Under nitrogen atmosphere, a mixture of 1.0 g (0.74 mmole) of 1,3,5-trimethyl-2,4,6-tricarboxamide-*p*-*tert*-butylcalix[6]arene, 0.70 mL (4.94 mmole) of iodotrimethylsilane, 0.36 g (2.95 mmole) of sodium perchlorate in 150 mL of chloroform re-

fluxed for 4 hrs. After the chloroform was removed *in vacuo*, the crude mixture was dissolved in CH_2Cl_2 and the treated with 10 % HCl solution. The organic layer was dried over MgSO_4 . Recrystallization of the product from EtOAc:hexane (1:4) gave a white crystal in 66 % yield. IR (KBr pellet, cm^{-1}): 3414.3, 2965.5, 2347.7, 1652.6, 1482.7, 1204.7; ^1H NMR (CDCl_3): δ 7.26-6.84 (t, 12 H, ArH), 4.59-4.47 (m, 6 H, $-\text{CH}_2\text{C}$), 4.28-3.44 (m, 12 H, ArCH_2Ar), 3.38-3.28(m, 12 H, NCH_2CH_3), 1.25-0.99 (m, 9 H for NCH_2CH_3 , 54 H for *t*-Bu). FAB-MS m/z (M^+) calcd. 1312.84, found 1312.80.

1,3,5-Tricarboxylic acid-2,4,6-tricarboxamide-*p*-*tert*-butylcalix[6]arene (1)

Under nitrogen atmosphere, to a solution of 1.0 g (0.76 mmole) of 1,3,5-triamide-*p*-*tert*-butylcalix[6]arene in THF, 0.547 g (22.8 mmole) of sodium hydride was added slowly at 0 °C. 0.63 g (4.56 mmole) of bromoacetic acid in 10 mL of THF was added dropwise at 0 °C. Upon the complete addition, the reaction mixture was refluxed for 10 hrs. After the THF was removed *in vacuo*, the crude mixture was dissolved in CH_2Cl_2 and the treated with 10 % HCl solution. The organic layer was dried over MgSO_4 . Recrystallization of the product from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (9:1) gave a colorless crystal in 82 % yield. IR (KBr pellet, cm^{-1}): 2965.5, 1753, 1644.9, 1482.7, 1197, 1119.8, 1058; ^1H NMR (CDCl_3): δ 7.12-7.0 (s, 6 H, ArH), 6.9-6.8 (s, 6 H, ArH), 5.3 (s, 3 H -OH), 4.5 (s, 12 H, OCH_2C), 3.8 (m, 6 H, ArCH_2Ar), 3.4 (m, 6 H, for ArCH_2Ar , 12 H for NCH_2CH_3), 1.21-1.16 (m, 18 H for NCH_2CH_3 , 27 H for *t*-Bu), 1.05 (s, 27 H, *t*-Bu). FAB MS m/z (M^+): calcd 1486.95, found 1486.60.

BLM Membrane

Membrane transport experiments were carried out using a bulk liquid membrane cell based on the concept of the Schulman bridge at 25 °C.⁹ The bottom half of the cell was filled with 3.0 mL of 1.0 mM solution of the organic ligand 1 in chloroform and a glass tube is inserted. The interior of the tube above the organic media is filled with a 0.8 mL of 0.1 M metal ion solution as a source phase. The outer cylinder is filled with 5.0 mL of deionized water as a receiving phase. The details of the transport conditions are summar-

ized in the footnotes of Table 1. The receiving phase was sampled after 24 hours stirring with 120 rpm at 25 °C and analyzed for cation concentration using an atomic absorption spectrometer.

SLM Membrane

The single stage SLM measurement was carried out with a simple two compartments permeation cell which consisted of a source phase (200 mL of transition metal nitrate) and receiving phase (200 mL of deionized water) separated by a membrane phase. The membrane phase was prepared by soaking a sheet of Celgard 2400 (Celanese Separation Product Co.) in 2-nitrophenyloctyl ether (NPOE) containing 1.0 mM of acyclic polyethers as carrier. The total membrane area exposed to the aqueous phase is 19.6 cm². The thickness of the membrane film was 25 μm. 200 mL source phase was prepared by dissolving transition metal nitrate in distilled deionized water (AgNO₃, Cd(NO₃)₂, Co(NO₃)₂, Cu(NO₃)₂, Ni(NO₃)₂, Pb(NO₃)₂, Zn(NO₃)₂). Receiving phase consisted of distilled deionized water. Both source and receiving phase were stirred with glass propellers at 600 rpm. In competitive transport experiments, we prepared the source phases as 0.01 M of seven component metal ions in deionized water. In permeability coefficient experiment, 1 mL of solution was periodically taken from receiving phase to monitor the transport process and 1 mL of distilled deionized water was replaced. The measurement of the concentration of transported ions was performed on a AAS (Perkin Elmer 2380). Each experiment was repeated three times in room temperature (25 °C).

CTA Membrane and transport experiment

Cellulose triacetate, CTA (0.062 g) in 5.0 mL of CH₂Cl₂ was mixed with 3.0 mL of 10 % (v/v) NPOE (2-nitrophenyloctyl ether) in CH₂Cl₂ and 0.50 mL of 10 % (v/v) tris(2-butoxyethyl) phosphate (TBEP) in CH₂Cl₂, and 2.0 mL of the ligand **1** (1.0 mM) in CH₂Cl₂. The NPOE and TBEP were used as membrane plasticizers. The solvent of this mixed solution was allowed to slowly evaporate in a 9.0 cm diameter petri dish which was covered by a watch glass. After 18-hour

evaporation, a few drops of water were swirled on top of the film to help loosen it from the glass.⁷ The polymer film was then carefully peeled off the petri dish. The thickness of the membrane film was 30 μm. The membrane was placed between 200 mL of two cylindrical glass vessels. The area of the membrane was 19.6 cm². Both source and receiving aqueous phase were stirred with glass stirrers at about 600 rpm by synchronous motors at 25 °C. The initial concentration of LiNO₃, NaNO₃, KNO₃, RbNO₃, CsNO₃, Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂, and Ba(NO₃)₂ was 0.010 M, respectively. 5.0 mL from the receiving phase was periodically taken and the metal cations transported from source phase into receiving phase through PIM were determined by atomic absorption spectrometer. Three independent experiments were employed in the determination of each cation transport rate and permeability constant. The standard deviations were less than ±10 %.

Calorimetric titration

The calorimetric titration were carried out using TRONAC Model 1250 isothermal isoperibol titration calorimeter equipped with a 25-mL glass Dewar flask and a 10 mL-precision constant-rate burette for titrant delivery. The thermostat was maintained at 25 ± 0.02 °C with a TRONAC model 40 precision temperature controller. Procedures, calibrations, and data analyses including determinations of ΔH value by non-linear regression methods were adapted from earlier recommendation. The ligand solution (1.0 mM of calixcrown ether, 25 mL) was titrated with 10 mM of titrant in 90 % (v/v) MeOH solution.

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