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Extraction of alkali metals using emulsion liquid membrane by nano-baskets of calix[4]crown

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Abstract−Nano-assisted inclusion separation of alkali metals from basic solutions was reported by inclusion-facilitated emulsion liquid membrane process. The novelty of this study is the application of nano-baskets of calixcrown in the selective and efficient separation of alkali metals as both the carrier and the surfactant. For this aim, four derivatives of diacid calix[4]-1,2-crowns were synthesized, and their inclusion-extraction parameters were optimized including the calixcrown scaffold (**13**, 4 wt%) as the carrier/demulsifier, the commercial kerosene as diluent in membrane, sulphonic acid (0.2 M) and ammonium carbonate (0.4 M) as the strip and the feed phases, the phase and the treat ratios of 0.8 and 0.3, mixing speed (300 rpm), and initial solute concentration (100 mg/L). The selectivity of membrane over more than ten interfering cations was examined and the results revealed that under the optimized operating condition, the degree of inclusion-extraction of alkali metals was as high as 98-99%.

Key words: Nano-basket, Inclusion, Calixcrown, Emulsion Liquid Membrane

INTRODUCTION

Emulsion liquid membrane (ELM), which was invented by Li [1] in 1968, is one of the most promising separation methods for trace extraction of metal contaminants [2-4] and hydrocarbons [5,6], owing to the high mass transfer rate, high selectively, low solvent inventory and low equipment cost. Frankenfeld et al. [7] reported that the ELM could be up to 40% cheaper than that of other solvent extraction methods. This process combines both extraction and stripping stage to perform a simultaneous purification and concentration. However, this method has been limited by the emulsion instability [8-14].

The lack of emulsion stability will decrease the extraction efficiency. In the ELM process, three steps are followed including an emulsification, extraction, and demulsification. In the first step, the emulsions are prepared by mixing the membrane and the internal phases as water-in-oil (W/O) droplets. In this step, water is dispersed into the oil phase as fine globules. The second step is followed by permeation of solutes from the feed phase, through the liquid membrane, to the receiving phase. In the third step, the emulsions are settled and demulsified to release the internal phase containing the concentrated solutes. This step is associated with the recovery of the membrane phase. Some of the ELM's applications include separation of sugars [15], organic acids [16,17], amino acids [18-21], proteins [22] and antibiotics [23,24].

Nano-baskets of calixarenes are a versatile class of macrocycles, which have been subject to extensive researches and extractions [25,26], stationary phases [27], transporters [28] and optical and electrochemical sensors [29] over the past years. Baeyer, in the nineteenth century, synthesized the calixarenes by reaction of *p*-substituted phenols with formaldehyde in basic or acidic environment [30]. However, the limited analytical instrumental techniques at that time were unable to interpret the structure of the synthesized products.

Zinke and Ziegler [31], in the 1940s, discovered that the products possessed cyclic tetrameric structures. Gutsche [32], in 1975, introduced the presently accepted name of calixarene. After that, new advances in the field of metal extraction by calixarenes led to introducing new groups such as the ionizable moieties [33-35] and crown ethers [36-38] in their scaffolds. The ionizable moieties not only participate in cooperative metal ion complexation, but also eliminate the need to transfer the anions from the aqueous phase into the organic phase by acting in a cation-exchange mode with the metal cation [39-42]. Introducing the crown ether ring on the lower-rims not only increased the cation binding ability of the calixarenic scaffolds [43-48] but also enhanced their selectivity [49-53]. Nano-baskets have been widely used and identified (such as gas chromatograph, Teif Gostar Faraz Co., Iran) in recent years [54-59].

In this study, four nano-baskets of calixcrown were used as bifunctional surfactant/carrier, and the method of "once at a time" was used to study the influences of different factors on ELM performance. The objective of this study is feasibility study of the application and optimization of calixcrowns (as carrier/surfactant) in ELM separation of alkali metals. This is the first work dealing with (1) using calixcrowns in ELMs, (2) assimilation of carrier and surfactant as one scaffold (calixcrown) and eliminating their destructive interactions, (3) optimizing the extraction efficiency of this novel approach, and (4) experimental application of the novel approach for ELM extraction of alkali metals, etc. In this approach, the experiments were designed to study the effect of a tuned variable at a time while keeping all other independent factors constant. By the method of once at a time, the ELM process for selective extraction of alkali metals was investigated. The process factors such as calixcrown type and concentration (as surfactant and carrier), strip phase type

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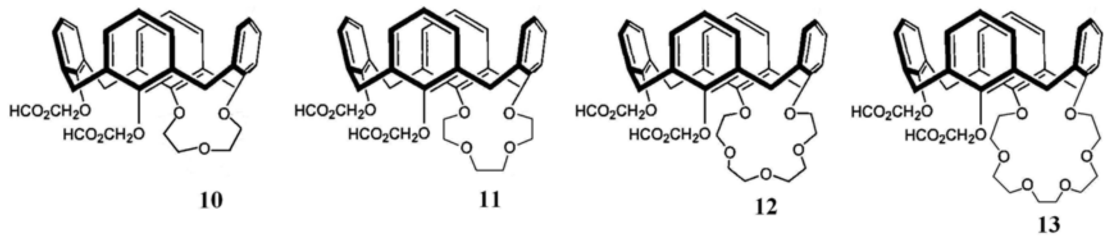

Fig. 1. Chemical structure of calixcrown derivatives.

and concentration, base type and concentration in feed, phase and treat ratios, membrane type and selectivity, mixing speed, and solute concentration in feed were investigated and optimized.

EXPERIMENTAL

1. Chemicals and Reagents

The liquid membrane consists of a diluent and a calixcrown (as surfactant and extractant). The calixcrowns were synthesized as described below. Commercial kerosene (Shell, USA) was used as diluent, which was a complex mixture of aliphatics and aromatics. Sulfuric acid, hydrochloric acid and nitric acid were purchased from Fluka. Sodium chloride, sodium carbonate and potassium chloride (99%) were purchased from Mallinckrodt; cesium chloride and ammonium carbonate (99%) were obtained from Alfa Aesar, and ithium chloride, rubidium chloride. 1.0 N hydrochloric acid were purchased from J. T. Baker; chloroform from EM Science, Lithium hydroxide and sodium hydroxide from Fisher Scientific, n-Decane from Sigma-Aldrich, and 2.0 N sulfuric acid from Mallinckrodt. The chloroform was shaken with deionized water to remove the stabilizing ethanol and was stored in a dark position.

The experiments carried out using four derivatives of diacid calix [4]-1,2-crowns [38] and their chemical structures are presented in Fig. 1.

2. Analytical Instruments

Determinations of alkali metals were accomplished by Dionex DX-120 ion chromatographs with a CS12A column, a conductivity detection and membrane suppression. The eluent was 0.011 M sulfuric acid after filtration through a Millipore 0.22 μm filtration membrane, while the pump flow rate at 1,700 psi was about 1 mL/min. Nitrogen pressure for the eluent was set at 50 psi. To obtain a stable baseline, the eluent was flowed through the column for 1 h, and then 2.0 mL of standard solutions were injected and they were repeated two other times. PeakNet software was used to manipulate the outputs from the Dionex ion chromatograph. The pH meter was equipped with a Corning 476157 combination pH electrode.

3. Preparation of ELM

The specific amounts of calixcrown were solved in the specific amount of kerosene and thus membrane solutions were prepared. $(NH_4)_2CO_3$ solution (25 mL, 0.5 M) was used as stripping solution. In 100-mL beaker, stripping solution was added dropwise to the stirred membrane solution and the two-phase system was stirred continuously for 30 min at mixing speed of 1,500 rpm by a variable speed mixer equipped with a turbine-type Teflon impeller. The mixture of the membrane and the stripping solution was emulsified.

4. Characterization of ELM

The size, size distribution and stability of emulsions were characterized to examine the method. Size and size distribution of droplets were obtained by optic microscopy (Mettler FP). The digital format of captured micrographs was analyzed by means of image analyzer software (Digital Micrograph TM, Gatan Inc.). Using a Neubauer camera, the volume of analyzed samples was controlled. By size distribution changes at constant times, the stability of w/o droplets was monitored and evaluated by image analyses from photographs obtained during the diafiltration experiments.

5. Batch ELM Experiment

In 500-mL beaker, the ELM prepared was added to some volumes of the feed solution and stirred by a variable speed mixer equipped with a turbine-type impeller at speed of 500 rpm for extraction time of 30 min. The speed of the mixer was regulated by a voltage regulator. To determine the important variables governing the permeation and separation of alkali metals, calixcrown's type and concentration, strip phase's type and concentration, base type and concentration in feed, the phase and the treat ratios, membrane's diluent type and selectivity, mixing speed, initial solute concentration in the feed phase were varied to observe their effects on the extraction and separation. The samples were taken from the stirred cell periodically during the course of the run. The feed phase of the samples was separated from the emulsions by filtration with a filter paper. The emulsion was demulsified by freezing. The concentration of alkali metals was analyzed by ion chromatography.

RESULTS AND DISCUSSION

Several studies have shown that calixcrown is an appropriate carrier for extraction of alkali metals in the organic phase. At the basic internal interface of the membrane phase, alkali metals (as their cations) are stripped by the internal agent and transformed into a new species that cannot penetrate the membrane reversibly. The reversible reactions at both interfaces of the membrane phase with non-ionizable and ionizable calixcrown as surfactant/carrier in an ELM system are depicted in Eqs. (1) and (2), respectively.

$$M(ClO_4)_n + Calix \leftrightarrow [M:Calix]^{+n} \cdot n(ClO_4)^- \quad (1)$$

$$M^{n+} + CalixH_n \leftrightarrow [M:Calix] + nH^+ \quad (2)$$

Where M_n^+ depicted the alkali cation (n=1), $CalixH_n$ shows the calixcrown scaffold in the molecular form, and M : Calix presents the calixcrown complex with alkali metal.

Calixarenes and di-ionizable calixarenes in the acidic solutions are formed as molecular state, while are hydrolyzed in the basic solutions. The ionic form includes the cationic species, while the molecular form cannot capture them. After that, the new uncharged complex state diffuses throughout the organic membrane. In the side of

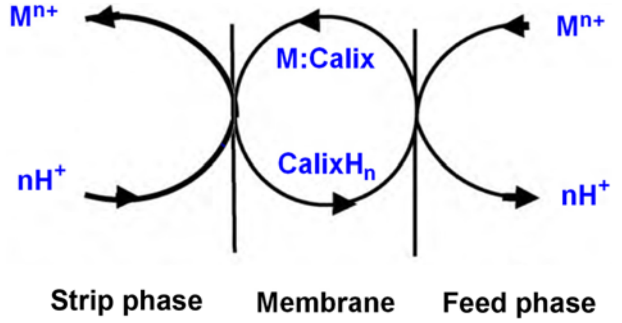

Fig. 2. Facilitated transport mechanism of alkali metals in ELM using ionizable calixarenes.

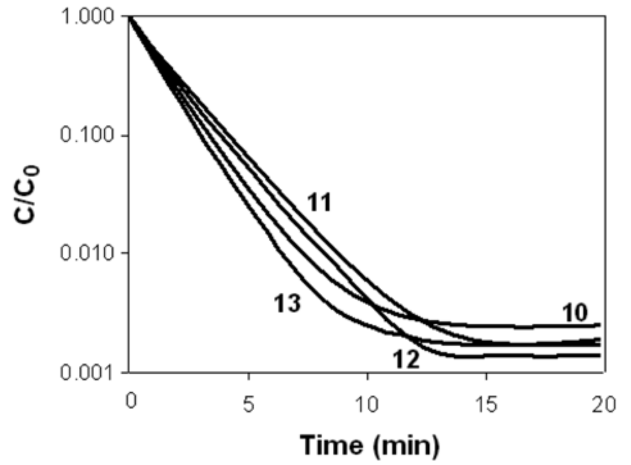

Fig. 3. Effect of calixcrown type on the extraction efficiency of alkali metals in the ELM process.

acidic striping phase, the calixcrown complex is dissociated as an uncharged molecular calixcrown and diffuses into the organic membrane again. This transportation is repeated during the extraction until the chemical potentials in both sides are equal. Fig. 2 depicts the mechanism of facilitated transport of alkali metals with ELM process.

The optimum conditions for the extraction of alkali metals were determined by the method of once at a time. Table 1 presents all test conditions as well as the optimum conditions in bold. The methodology of optimizations is discussed as the following sections.

1. Effect of Calixcrown Type

The type of calixcrown is the most important factor that influences the selectivity of an inclusion-ELM system, and can often be used in related liquid-liquid extractions. The effect of calixcrown type on the extraction efficiency of alkali metals was studied in the ELM process and the results obtained are shown in Fig. 3. According to the results, although calixcrown **13** gives higher rate of extraction in the first 10 min compared to calixcrowns **10-12**, it gradually deteriorates with time. Examination of these results indicates that calixcrown **13** was more favorable than calixcrowns **10-12** as emulsifier/carrier. Therefore, calixcrown **13** was selected among all scaffolds.

There are many factors that affect the complexation strength of calix[4] crown derivatives and mobility of resulted complexes, including (1) size of calix[4] crown cavity, (2) size of cations, (3) charge density on cations (or hard/soft issues), (4) complex stability (or 10dQ), (5) steric arrangement of proximal moieties (like carboxylic acids or crown ether), and (6) kind, number, size and position of those proximal moieties, etc.

In the present study, the attempt was reducing the degree of freedom or the effect of most above-mentioned factors by equalization of experiments that differed in minimum factors. The main controlling factor was the size of a proximal moiety, 1,2-crown ether, which was tuned from 1,2-crown-3 to 1,2-crown-6. Calixcrown derivative bearing 1,2-crown-6 moiety showed the highest complexation tendency, stability and mobility. It was owing to proper sitting of alkali metal cations in calixcrown cavity, more stability of produced complex and high mobility from outer side to inner side of membrane and vice versa.

2. Effect of Calixcrown Concentration

The extraction of alkali metals increased by increasing of calixcrown concentration from 1-5%, while more increase from 5-10% hardly affected the extraction performance. As depicted in Fig. 4, further increase of calixcrown concentration decreased the efficiency of extraction, due to the access of molecular calixcrown in mem-

Table 1. The experimental and optimum conditions for the extraction of alkali metals

1	Calixcrown type	10	11	12	**13**	-
2	Calixcrown concentration (wt%)	1	3	**4**	5	10
3	Acid type in strip phase	H_2SO_4	HCl	HNO_3	-	-
4	Acid concentration in strip (M)	0.1	**0.2**	0.3	0.4	0.5
5	Base type in feed	NaOH	NH_4OH	Na_2CO_3	**$(NH_4)_2CO_3$**	-
6	Base concentration in feed (M)	0.1	0.2	0.3	**0.4**	0.5
7	Phase ratio	0.4	0.6	**0.8**	1.0	1.2
8	Treat ratio	0.1	0.2	**0.3**	0.4	-
9	Membrane type	Kerosene	n-Decane	k : d*	-	-
10	Membrane selectivity					
11	Stirring rate (rpm)	100	200	**300**	400	500
12	Solute concentration in feed (mg/L)	10	**100**	1000	-	-

The **bold** items were obtained and used as the optimum conditions, M: Mole/Liter
*Kerosene/n-decane 1 : 1

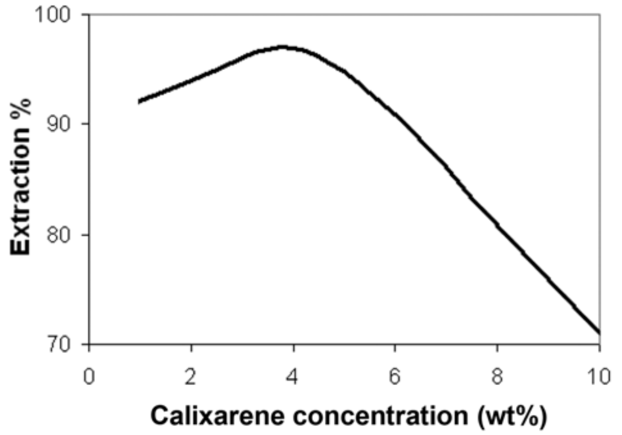

Fig. 4. Effect of calixcrown 13 concentration on the extraction % of alkali metals in the ELM process.

brane phase. Under the optimum concentration, the molecular form of calixcrown is considered enough for forward extraction. Increasing of calixcrown concentration to 5% increased the stability of emulsion liquid membrane, which led to the decrease in the break-up rate, hence the extraction of solutes was increased. Further increase in the concentration of calixcrown leads to the decrease in the rate of capturing and stripping reaction. This is because the metallic cations remain in the complex form (in the membrane) without being stripped. This affects the final recovery by the ELM process.

The excessive calixcrown tends to increase the interface's resistance and increase the viscosity of membrane. This increasing from 5% increased the emulsion stability, but the mass transfer was adversely decreased. Similar results have been reported by other researchers [60,61]. Hence, there is an optimum in the concentration of calixcrown around 4%. The excess of calixcrown concentration leads to osmotic swelling and membrane breakdown. Hence, the concentration of 4% was accepted as the optimum concentration. Another criterion is the financial aspects, in which the calixcrowns are the most expensive agents among the other components of ELM process, and lower concentrations are preferred.

3. Effect of Acid Type in Strip Phase

The stripping agent in the internal aqueous phase is an important factor that influences the selectivity of an ELM system. A suitable stripping agent dissociates the complex of calixcrown:alkali metal to the desired cation directly, and thus shortens the recovery process. The type of the acids used in the acidic solution is a parameter influencing the extractant efficiency. Selection of a mineral acid in the strip phase solution is suitable for the protonation of calixcrown and exchange interaction. The effect of the presence of 0.05 M of different acids; sulfuric acid, hydrochloric acid and nitric acid in the acidic solution on the transport of calixcrown complex was investigated. Fig. 5 depicts the results, in which there is a little difference in the extraction efficiency between the acids used. Obviously, the extraction rates of alkali metals up to 10 min followed the order: sulfuric acid<hydrochloric acid<nitric acid. However, at 10-15 min interval, the acidic feed solutions yielded near quantitative extraction, and the highest extraction efficiency was obtained with sulfuric acid. Thus, 0.05 sulfuric acid solution was accepted as the best acid and was used as the strip phase solution in the following experiments.

After-test results revealed that the concentration of nitrate ion-

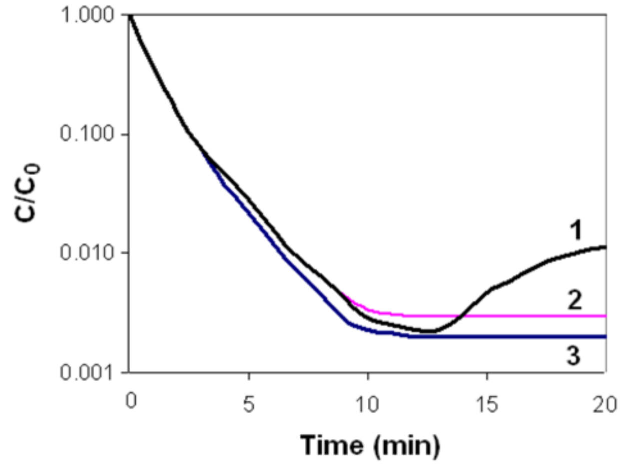

Fig. 5. Effect of acid type in the strip phase on the extraction efficiency of alkali metals in the ELM process.
1. Nitric acid 2. Hydrochloric acid 3. Sulfuric acid

pairs was more than twice in comparison to sulfate or chloride ion-pairs (as the anions of two other acids) in the membrane (CCl_4) media. According to the results of experiments and repetitions, as it is presented in Fig. 5, nitrate anions concentrated more in the membrane media and affected the emulsion stability in that the emulsions lost their stability by the time of mixing.

4. Effect of Acid Concentration in Strip

The effect of sulfuric acid concentration in the strip phase on the extraction of alkali metals was studied. To determine the influence of sulfuric acid concentration on the extraction of solutes, experiments were performed with various concentrations of sulfuric acid in the range 0.1-0.5 M. Fig. 6 depicts the effect of acid concentration on the extraction of alkali metals. Obviously, below 0.2 M, the extractions decreased with decrease in acid concentration. The decrease in the extraction with the decrease in proton concentration can be explained by the fact that the protonation rate of calixcrown complexes decreases due to the less availability of protons for the reaction [62-64]. On the other hand, the extractions were maximum at 0.2 M. Above this concentration, the extraction decreased, since the increase in proton concentration in the strip phase will form spe-

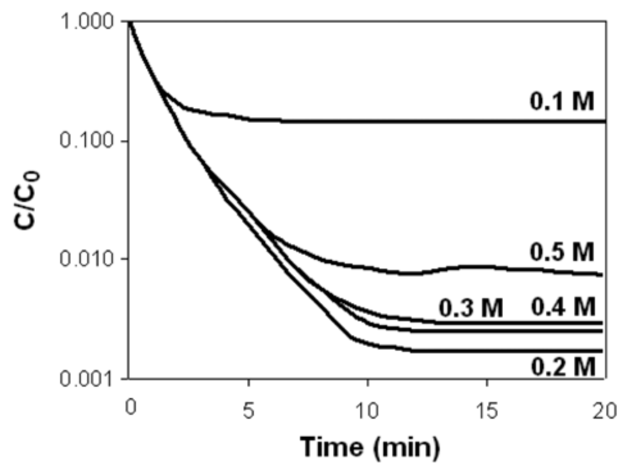

Fig. 6. Effect of sulfuric acid concentration in the strip phase on the extraction efficiency of alkali metals in the ELM process.

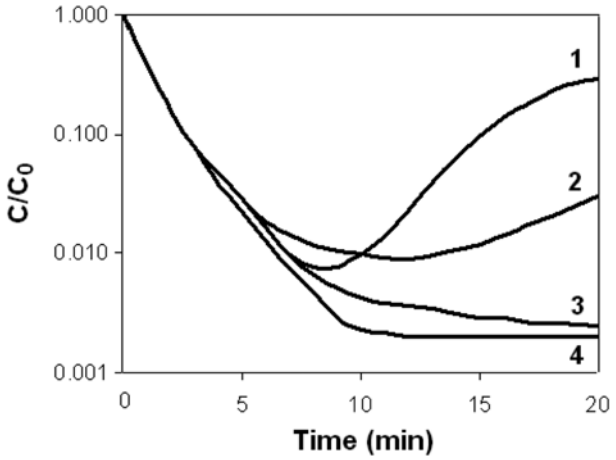

Fig. 7. Effect of base type in the feed phase on the extraction efficiency of alkali metals in the ELM process.
1. NaOH 2. NH_4OH 3. Na_2CO_3 4. $(NH_4)_2CO_3$

cies like $(CalixH_{n+m})^{m+}$, which may not mobilize to the membrane completely at higher acid concentrations. Hence, the extraction will decrease with the more increase in acid concentration.

5. Effect of Base Type in Feed

As the extraction occurs in the interface between the basic solution and the liquid membrane, the transport of metal necessarily requires a simultaneous back-extraction step at the opposite side of the membrane. In the stage of back-extraction, the calixcrown is regenerated and the alkali metal is stripped. As reported in the beforementioned literatures [8-14], the stability of emulsions is the main factor in ELM. In addition to mixing speed, extractant type and concentration, and surfactant type and concentration, another parameter is the agent's types in the feed phase. Therefore, the selection of suitable feed solution is considered one of the key factors for cation extraction. Hence, NaOH, NH_4OH, Na_2CO_3, and $(NH_4)_2CO_3$ were used and the results are shown in Fig. 7. According to this figure, $(NH_4)_2CO_3$ solution was more preferable in making the feed solution since it stabilized the emulsions during the extraction process. Therefore, the proper concentration of ammonium carbonate was selected as the best base in the feed phase.

Different extraction efficiencies were achieved using different base types: 1, 2, 3, and 4. The reason was their counter ions. NaOH, NH_4OH, Na_2CO_3 and $(NH_4)_2CO_3$, released OH^- and $(CO_3)^{2-}$ anions in feed phase. According to Fig. 7, bases 1 and 2 released OH^- and led to decreasing the extraction efficiency. In the other side, bases 3 and 4 released $(CO_3)^{2-}$ and led to increasing the extraction efficiency. Therefore, the effect of counter ion was confirmed.

However, concerning the difference of traces for bases 1 and 2, NH_4 cations were responsible too.

6. Effect of Base Concentration in Feed

The literature contains many options for accomplishing the ELM process by cation complex. Among them, solutions of ammonium carbonate, sodium carbonate and sodium hydroxide have been used in the feed phase. From our list, ammonium carbonate solution was used as the best feed phase. The molarity of ammonium carbonate was varied between 0.1-0.5 M and the results obtained are shown in Fig. 8, in which there is difference in the extraction efficiency in the concentration range aforementioned. Obviously, the extraction

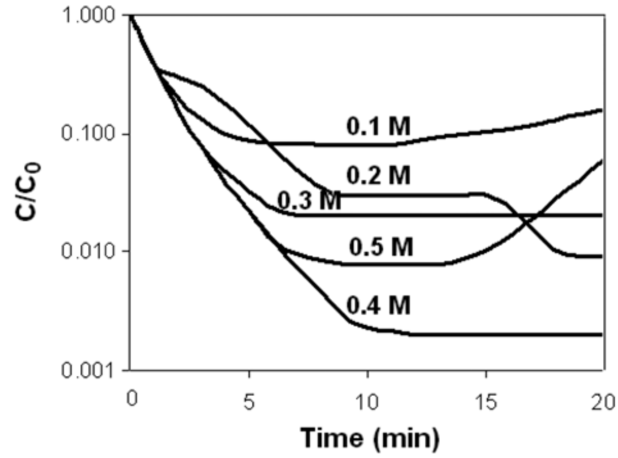

Fig. 8. Effect of base concentration in the feed phase on the extraction efficiency of alkali metals in the ELM process.

rate of solutes up to about 10 min increased with the increase of base concentration in the feed solution. However, at 10 min, the efficiency of extraction decreased with the increase of base concentration in the feed solution owing to instability of emulsion droplets. Therefore, at tenth minute, the highest extraction efficiency was obtained with 0.4 M $(NH_4)_2CO_3$ solution. Thus, 0.4 M $(NH_4)_2CO_3$ solution was selected as the best concentration for feed phase.

7. Effect of Phase Ratio (Strip Phase Volume/Membrane Volume)

The phase ratio is defined as the volume of stripping solution to volume of membrane. Fig. 9 shows the effect of phase ratio on the extraction of alkali metal cations, in which it increases with an increase of phase ratio up to 4 : 5. At 4 : 5 phase ratio, the maximum extractions were observed. By increasing the volume of the strip phase, the thickness of film in the emulsion was reduced owing to dispersion of strip phase in the membrane by mixing. This was favorable in extractions and resulted in an increase in the extraction of alkali metal cations. Beyond 4 : 5, the further increase in the volume of strip phase caused the instability of globules.

8. Effect of Treat Ratio (Feed Volume/Emulsion Volume)

The treatment ratio, defined as the volume ratio of the emulsion

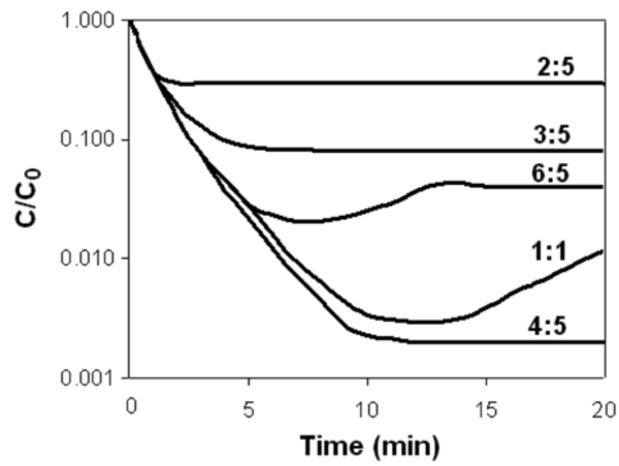

Fig. 9. Effect of phase ratio on the extraction efficiency of alkali metals in the ELM process.

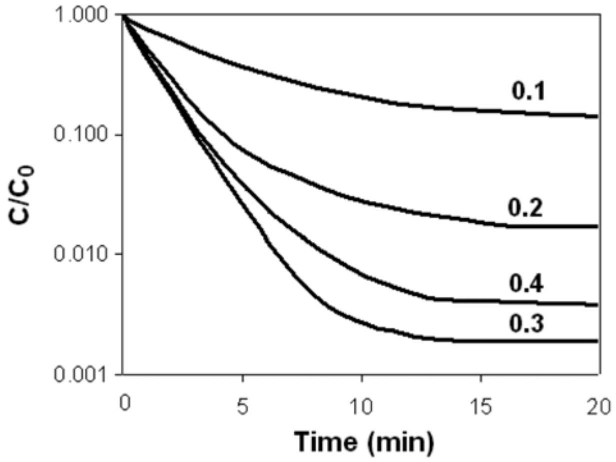

Fig. 10. Effect of treat ratio on the extraction efficiency of alkali metals in the ELM process.

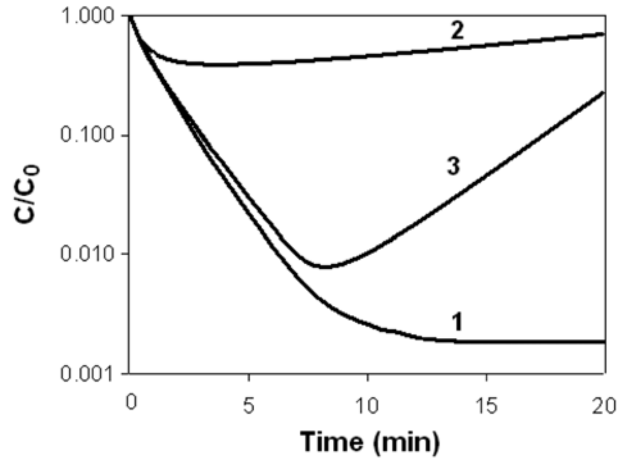

Fig. 11. Effect of diluent (membrane) type on the extraction efficiency of alkali metals in the ELM process.
1. Kerosene 2. n-Decane 3. Their blend (1 : 1)

phase to the feed phase, plays an important role in determining the efficiency of ELM process. By increasing the amount of emulsion in the feed phase, the number of available droplets and interfacial surface area per unit volume of the feed solution increases. This leads to increasing the mass transfer of solutes from the feed to the membrane, and more efficiency. Increasing of treat ratio slightly increased the size of emulsion droplets and inversely caused a reduction in interfacial surface area. The increment in the size of droplets was suppressed by the increment in the number of droplets. The results are depicted in Fig. 10, in which the extraction efficiency was improved by increasing the treat ratio from 0.1 to 0.3. Beyond 0.3, the further increase in the ratio caused the instability of globules and less extraction efficiency.

9. Effect of Membrane Type

The most crucial task in all types of LM processes is the choice of the membrane phase. The interactions of membrane toward the carrier as well as its viscosity are two main parameters controlled by choosing the membrane type. The membrane phase viscosity determines the rate of transport of carrier or solutes and the residence or contact time of the emulsion with the feed phase. Note that residence time is system specific and varies for each organic phase under the given conditions. In this work the effect of three organic phases on the extraction performance were investigated. Kerosene, n-decane and their blend 1 : 1 were investigated as the diluent. The results are presented in Fig. 11. According to the results, kerosene was selected as the best diluent in the following experiments.

10. Membrane Selectivity

The selectivity of membrane was examined as the enrichment factor (EF). The enrichment factors of alkali metals with respect to the other cations that exist in the solutions were determined and the results are given in Table 2. In inclusion separations, the enrichment factor is the factor by which the ratio of the amounts of two compounds in the solution must be multiplied to give their ratio after extraction. Eq. (3) depicts how to calculate the enrichment factor.

$$\frac{C_A^f}{C_B^f} = \mathrm{EF} \cdot \frac{C_A^i}{C_B^i} \tag{3}$$

Where, C_A^i and C_B^i are the initial amounts of species A and B in the feed solution. C_A^f and C_B^f depict the final amounts of them, respectively in the strip solution. The EF factor represents the enrichment factor. At the end of the experiments, except for calcium, at interval 4-10 min, liquid membrane selectivity of alkali metals with respect

Table 2. Separation factors of alkali metals over other cations at the optimum conditions

Intervals	2-6 min					6-12 min					12-20 min				
Cations	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
Ca	074	112	134	102	094	076	112	136	102	099	077	114	144	102	102
Ba	218	314	442	208	158	222	306	475	303	196	230	298	480	176	186
Ag	146	180	145	198	223	188	202	209	270	176	190	214	210	283	180
Pb	280	324	166	207	332	334	217	247	319	298	330	220	242	308	290
Mn	304	314	298	323	362	318	315	300	384	311	320	311	301	383	311
Zn	288	319	299	257	296	330	303	288	302	288	334	300	280	308	280
Cd	305	248	313	260	200	240	340	205	243	240	244	338	205	245	241
Cr	428	389	367	360	408	355	369	328	434	370	355	360	325	438	370
Cu	414	376	329	300	310	370	380	289	326	385	375	375	259	320	377
Co	366	325	310	203	213	303	300	244	189	290	300	305	244	188	293
Ni	300	284	309	362	340	202	288	350	322	273	202	285	355	322	270

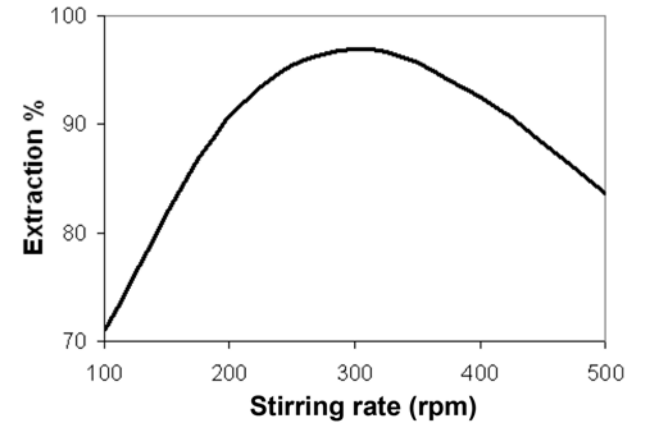

Fig. 12. Effect stirring rate on the extraction efficiency of alkali metals in the ELM process.

to other ions was high.

11. Effect of Stirring Rate

The speed of mixing is a key factor in the rate of mass transfer through emulsion liquid membranes. The effect of stirring speed in the basic solution was investigated in the range of 100-500 rpm to obtain optimal speed with effective extraction of alkali metal cations in the ELM process. As depicted in Fig. 12, when the mixing speed was increased from 100 to 300 rpm, an increase in extraction rate was observed. Above 300 rpm the extraction rate again was reduced. As a result, an increase in the mixing speed would increase the interfacial area, and this was true up to a certain level of mixing speed, beyond which an increase in the speed was likely to break the emulsions and thereby reduce overall enrichment and the efficiency of extraction. As discussed by Thien et al. [65], the impact on the wall of a contactor on the emulsion droplets or the shear induced breakage of fragile emulsion droplets near the tip of the impeller imposes an upper limit on the speed of agitation. At the same time, swelling was also increased owing to transport of water from feed to strip phase. Some particles are broken owing to shear after reaching larger size. The swollen droplets break down on their own or are induced by shear. Therefore, the extraction performance is a trade-off between two effects of swelling phenomena and mixing speed.

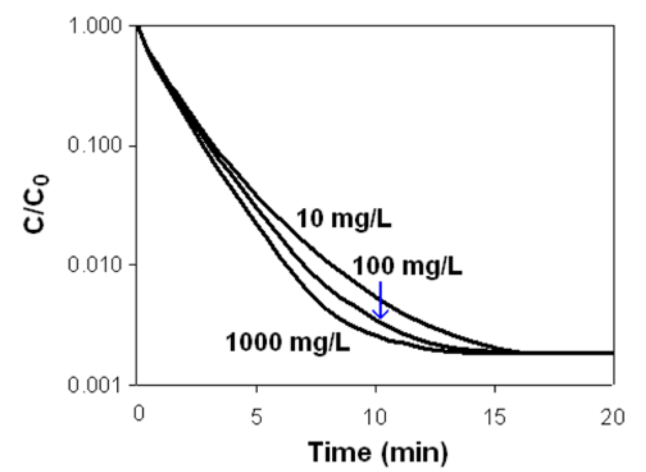

Fig. 13. Effect of solute concentration in the feed phase on the extraction efficiency of alkali metals in the ELM process.

12. Effect of Solute Concentration in Feed

The effect of initial concentration of solutes on the degree of extraction was studied. The results are presented in Fig. 13. Obviously, the concentration of alkali metal cations in the feed solution varied from 10 to 1,000 mg/L. Within 10 min, the concentration of solutes in the feed solution was reduced from 10 to 1.0 mg/L, from 100 to 6.0 mg/L, and from 1,000 to 35 mg/L, with the extraction efficiencies of 90, 94, and 96.5%, respectively.

CONCLUSION

Alkali metals in basic and dilute water can be recovered by an ELM process using nano-baskets of calixcrown. An ELM using four derivatives of diacid calix[4]arene-1,2-crowns as both the extractant and the demulsifier has been investigated to extract and concentrate alkali metals from the basic solutions. The selectivity of this novel approach was assessed over interfering cations containing Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), etc. From this work the following conclusions can be drawn:

1. The optimum conditions of inclusion ELM process have been determined experimentally and tabulated in Table 1.

2. The membrane selectivity of inclusion-extraction of alkali metals from the basic solutions containing interfering cations has been performed by ELM process using calixcrown derivative **13** (4 wt%) and the results are in Table 2.

3. The highest efficiency for inclusion-extractions was obtained when the acid type and concentration in the strip solution was sulfuric acid (0.2 M).

4. The best stirring speed was determined to be 300 rpm and increasing from 300 to 500 rpm resulted in deterioration of emulsion stability the efficiency of inclusion-extractions.

5. The optimum conditions of both the phase and the treat ratios were determined to be 0.8 and 0.3, respectively.

6. At the optimum conditions, the extraction of alkali metals has been achieved with an efficiency of about 98.0-99.0% from the basic solution (ammonium carbonate, 0.4 M) within almost 10-20 min.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Extraction of alkali metals using emulsion liquid membrane by nano-baskets of calix[4]crown

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SYNTHESIS PROCEDURE

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH_2 and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. Cs_2CO_3 was activated by heating at 150 °C overnight under high vacuum and stored in a desiccator. Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH_2Cl_2 solution on NaCl plates. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (^{1}H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with Me_4Si as internal standard unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants (J) values are in Hz. The synthesis scheme for preparation of cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (**10-13**) are presented in Scheme 1.

1. Synthesis of Calixcrown 1

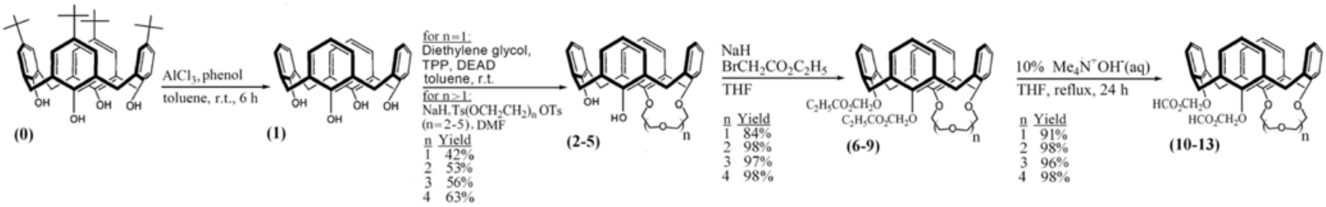
p-tert-butylcalix[4]arene (**0**) (10.00 g, 13.5 mmol), toluene (100 mL) and phenol (1.75 g, 18.60 mmol) were added to a flask and the solution was stirred under argon for 10 min. With vigorous mechanical stirring, aluminum trichloride (10.00 g, 75.0 mmol) was added. The mixture was stirred at room temperature for 5 h. The mixture was poured into a 500-mL beaker containing crashed ice (200 g) and extracted with CH_2Cl_2 (400 mL). The organic layer was washed with 1 N HCl (3×100 mL) and water (2×100 mL), and dried over $NaSO_4$. The solvent was evaporated *in vacuo.* Diethyl ether (50 mL) was added to the oily orange residue and the heterogeneous mixture was kept at −15 °C for 1 h. The precipitated solid was filtered and triturated with diethyl ether (100 mL). The mixture was kept at −15 °C for 1 h and filtered to provide 5.54 g (90%) of light yellow powder: mp 314-317 °C (lit 315-318 °C). IR (deposit on NaCl plate from CH_2Cl_2 solution): 3136 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.54 (br s, 4H), 4.24 (br s, 4H), 6.73 (t, 4H, J=7.6 Hz), 7.04 (d, 8H, J=7.6 Hz), 10.20 (s, 4H).

2. Synthesis of Calixcrown 2

To a mixture of calix[4]arene **1** (6.00 g, 10 mmol), diethylene glycol (1.59 g, 15 mmol) and TPP (8.00 g, 30 mmol) in 200 mL of toluene, a 40% solution of DEAD (5.22 g, 30 mmol) in toluene was added dropwise. The mixture was stirred at room temperature for 1 h. Then the solution was evaporated to dryness and the residue was extracted with hexane (3×30 ml) followed by evaporation and subsequent stirring in hexane and ethyl acetate. The precipitate was filtered and the filtrate was purified by chromatography on silica gel with hexane-EtOAc (9 : 1) as eluent to give a white solid (2.70 g, 42%) with mp 119-121 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3340 (O-H), 1248 and 1125 (C-O); ^{1}H NMR ($CDCl_3$): δ 3.22-3.48 (m, 4 H, $ArCH_2Ar$), 4.04 (t, *J*=10.5 Hz, 2 H, OCH_2CH_2O), 4.10 (t, *J*=11.0 Hz, 2 H, OCH_2CH_2O), 4.32-4.48 (m, 7 H, OCH_2CH_2O, $ArCH_2Ar$), 4.80 (d, *J*=12.0 Hz, 1 H, $ArCH_2Ar$), 6.96-7.10 (m, 10 H, ArH), 7.16 (d, *J*=2.0 Hz, 2 H, ArH), 8.86 (s, 2 H, OH); ^{13}C NMR ($CDCl_3$): δ 33.92, 34.16, 75.30, 125.33, 125.57, 125.61, 126.44, 128.34, 128.82, 129.12, 133.86, 134.60, 142.80, 147.40, 149.16, 150.32. Anal. Calcd for $C_{32}H_{30}O_5$: C, 54.18; H, 4.29. Found: C, 54.06; H, 4.21%.

3. Synthesis of Calixcrown 3

25,26-dihydroxycalix[4]arene-crown-4 was synthesized as the following. To a mixture of NaH (5.00 eq, 1.80 g, 75 mmol) in DMF (1,300 mL) in a 2,000 mL, three-necked flask under nitrogen was added dropwise a solution of 25,26,27,28-tetrahydroxycalix[4]arene (**1**) (1.00 eq, 6.36 g, 15 mmol) in DMF (100 mL). The mixture was stirred for 30 min. A solution of triethylene glycol di-*p*-toluenesulfonate (1.05 eq, 7.22 g, 15.75 mmol) in DMF (100 mL) was added dropwise and the mixture was stirred for 10 h at 70 °C. The reaction was quenched by addition of 1 N HCl (50 mL) at 0 °C. The DMF was removed by mixing with 3 N HCl and CH_2Cl_2 (volume ratio is 1 : 1 : 1). The remaining DMF in the organic layer was evaporated under high



Scheme 1. Synthesis of cone 25,26-di(carboxymethoxy)calix[4]arene-1,2-crown-3,4,5,6 (10-13).

vacuum. The residue was dissolved in CH_2Cl_2 (350 mL). The resulting organic solution was dried over $MgSO_4$. The crude product was chromatographed on silica gel with hexanes-EtOAc (2 : 1) as eluent to obtain 4.28 g (53%) of white solid with a melting point of 225-227 °C (lit.: 226-228 °C). 10 IR: 3318 (br, O-H), 1259, 1150, 1055 (C-O) cm^{-1}. ^1H NMR: δ 8.89 (s, 2H, OH), 7.11 (dd, *J* 7.5, 1.5, 2H, ArH), 7.05-6.90 (m, 8H, ArH), 6.81 (t, *J* 7.57, 2H, ArH), 6.64 (t, *J* 7.4, 2H, ArH), 4.71 (d, *J* 12.3, 1H, ArCH_2Ar, *ax*), 4.38-4.22 (m, 9H (ArCH_2Ar, *ax* (3H) and OCH_2 (6H)), 4.17-4.10 (m, 2H, OCH_2), 4.08-4.01 (m, 2H, OCH_2), 3.96-3.90 (m, 2H, OCH_2), 3.42 (d, *J* 12.33, 1H, ArCH_2Ar, *eq*), 3.41 (d, *J* 13.1, 2H, ArCH_2Ar, *eq*), 3.38 (d, *J* 13.6, 1H, ArCH_2Ar, *eq*). ^{13}C NMR: δ 153.45, 151.14, 134.92, 133.97, 129.21, 129.15, 129.00, 128.85, 128.82, 128.06, 124.99, 120.65 (Ar), 75.67, 71.59, 69.83 (OCH_2), 31.95, 31.78, 29.44 (ArCH_2Ar).

4. Synthesis of Calixcrown 4

25,26-dihydroxycalix[4]arene-crown-5 was synthesized as the following. To a mixture of NaH (5.00 eq, 2.16 g, 90.0 mmol) and DMF (1,300 mL) in a 2,000 mL, three-necked flask under nitrogen was added a solution of 25,26,27,28-tetrahydroxycalix[4]arene (**1**) (1.00 eq, 7.64 g, 18.0 mmol) in DMF (100 mL) over a 1 h period. The mixture was stirred for an additional hour. Tetraethylene glycol dimesylate (2.20 eq, 13.88 g, 39.6 mmol) in DMF (100 mL) was added over a 1-h period. The mixture was stirred at 50 °C for 72 h. The reaction was quenched by addition of H_2O (50 mL) at 0 °C. The DMF was removed by mixing the reaction mixture with 3 N HCl and CH_2Cl_2 (volume ratio is 1 : 1 : 1). The remaining DMF in the organic layer was evaporated under high vacuum. Addition of MeOH to the residue generated 5.87 g (56%) of white precipitate with a melting point of 215-217 °C (literature: 216-218 °C). 7 IR: 3317 (br, OH), 1262, 1128, 1047 (C-O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 2H, OH), 7.13-6.87 (m, 8H, ArH), 6.80 (t, *J* 7.5, 2H, ArH), 6.60 (t, *J* 7.5, 2H, ArH), 4.62-4.41 (m, 6H (ArCH_2Ar, *ax* (4H) and OCH_2 (2H)), 4.41-4.28 (m, 2H, OCH_2), 4.11 (t, *J* 9.0, 2H, OCH_2), 4.06-3.88 (m, 6H, OCH_2), 3.87-3.65 (m, 4H, OCH_2), 3.39 (d, *J* 12.3, 1H, ArCH_2Ar, *eq*), 3.36 (d, *J* 13.5, 2H, ArCH_2Ar, *eq*), 3.32 (d, *J* 13.8, 1H, ArCH_2Ar, *eq*).

5. Synthesis of Calixcrown 5

25,26-dihydroxycalix[4]arene-crown-6 was synthesized as the following. To a mixture of NaH (5.00 eq, 1.58 g, 65.85 mmol) and DMF (1,067 mL) in a 2,000 mL, three-necked flask under nitrogen was added a solution of 25,26,27,28-tetrahydroxycalix[4]arene (**1**) (1.00 eq, 5.59 g, 13.17 mmol) in DMF (150 mL) over a 40 min period. The mixture was stirred for 1 h. A solution of pentaethylene glycol di-*p*-toluenesulfonate (2.50 eq, 18.00 g, 32.93 mmol) in DMF (100 mL) was added over a 1 h period. The mixture was stirred overnight at 50-55 °C. The reaction was quenched by addition of H_2O (30 mL). The DMF was removed by mixing the reaction mixture with 3 N HCl and CH_2Cl_2 (volume ratio is 1 : 1 : 1). The remaining DMF in the organic layer was evaporated under high vacuum. The residue was chromatographed on silica gel with CH_2Cl_2-acetone (19 : 1) as eluent to obtain a solid. EtOAc was added to the solid to get 5.18 g (63%) of white precipitate with a melting point of 182-184 °C (literature: 180-182 °C). 7 IR: 3317 (br, O-H), 1264, 1124, 1050 (C-O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.68 (s, 2H, OH), 7.06-6.88 (m, 8H, ArH), 6.76 (t, *J* 7.5, 2H, ArH), 6.60 (t, *J* 7.5, 2H, ArH), 4.55 (d, *J* 12.6, 1H, ArCH_2Ar, *ax*), 4.45 (d, *J* 12.9, 2H, ArCH_2Ar, *ax*), 4.44-4.36 (m, 2H, OCH_2), 4.33 (d, *J* 13.5, 1H, ArCH_2Ar, *ax*), 4.25-4.14 (m, 2H, OCH_2), 4.13-3.97 (m, 4H, OCH_2), 3.96-3.74 (m, 10H, OCH_2), 3.74-3.61 (m, 2H, OCH_2), 3.66 (d, *J* 12.6, 1H, ArCH_2Ar, *eq*), 3.35 (d, *J* 13.2, 3H, ArCH_2Ar, *eq*).

6. Synthesis of Calixcrown 6

Calix[4]arene-1,2-crown-3 (**2**) (4.58 g, 7 mmol) in 50 mL of THF was added dropwise into a mixture of NaH (0.85 g, 35.4 mmol) in 50 mL of THF. After stirring for 1 h, ethyl bromoacetate (6.95 g, 41.7 mmol) was added and the reaction mixture was stirred overnight. The reaction was monitored by TLC. After 48 h, the reaction was quenched by careful addition of dilute HCl and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, the solution was washed with dilute HCl and water, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. Chromatographic purification on silica gel with hexane-EtOAc (2 : 8) as eluent gave an oil (1.82 g, 42%). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1758 (C=O), 1250 and 1126 (C-O); ^1H NMR ($CDCl_3$): δ 1.34 (t, *J*=7.0 Hz, 6 H, OCH_2CH_3), 3.09 (d, *J*=12.0 Hz, 1 H, ArCH_2Ar), 3.18 (d, *J*=12.0 Hz, 2 H, ArCH_2Ar), 3.24 (d, *J*=13.0 Hz, 1 H, ArCH_2Ar), 3.83-3.92 (m, 2 H, OCH_2CH_2O), 4.07 (d, *J*=12.2, 2 H, OCH_2CH_2O), 4.22 (m, 2 H, OCH_2CH_2O), 4.27 (q, *J*=7.0, 4 H, OCH_2CH_3), 4.42 (d, *J*=10.5 Hz, 2 H, OCH_2CH_2O), 4.51-4.63 (m, 3 H, ArCH_2Ar, OCH_2Ar), 4.88 (d, *J*=15.5 Hz, 2 H, OCH_2CO), 4.98 (d, *J*=12.0 Hz, 1 H, ArCH_2Ar), 6.78-6.88 (m, 8 H, ArH), 6.84 (d, *J*=2.5 Hz, 2 H, ArH), 6.92 (d, *J*=2.0 Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.08, 33.80, 33.86, 53.44, 60.60, 72.02, 73.02, 75.22, 124.36, 125.38, 125.54, 132.74, 134.04, 134.36, 134.80, 144.86, 145.32, 152.86, 152.92, 170.26. Anal. Calcd for $C_{40}H_{42}O_9$: C, 53.47; H, 4.76. Found: C, 53.20; H, 4.43%.

7. Synthesis of Calixcrown 7

25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-4 in the cone conformation was synthesized as the following. A mixture of NaH (10.00 eq, 2.01 g, 83.92 mmol) and 20 mL of THF-DMF (9 : 1) in a 250-mL, three-necked flask under nitrogen was stirred for 30 min. A solution of 25,26-dihydroxycalix[4]arene-crown-4 (**3**) (1.00 eq, 4.52 g, 8.39 mmol) in 100 mL of THFDMF (9 : 1) was added dropwise. The mixture was stirred for 1 h. Ethyl bromoacetate (8.00 eq, 11.21 g, 7.44 mL, 67.13 mmol) in 10 mL of THF-DMF (9 : 1) was added to the flask over a 1-h period. The mixture was refluxed for 48 h. The reaction was quenched by addition of 1 N HCl (20 mL) at 0 °C. The organic solvent was evaporated *in vacuo.* The residual aqueous layer was extracted with CH_2Cl_2 (200 mL). The organic solution was washed with H_2O (2×150 mL) and then dried over $MgSO_4$. The solvent was evaporated *in vacuo* to give a solid. The solid was chromatographed on silica gel with hexanes-EtOAc (1 : 1) as eluent to obtain 5.25 g (88%) of white solid with a melting point of 126-128 °C. IR: 1757 (C=O), 1240, 1094, 1024 (C-O) cm^{-1}. ^1H NMR: δ 6.90-6.30 (m, 12H, ArH), 4.97 (d, *J* 13.1, 1H, ArCH_2Ar, *ax*), 4.76 (d, *J* 16.2, 2H, OCH_2C(O)), 4.73 (d, *J* 15.6, 1H, ArCH_2Ar, *ax*), 4.69 (d, *J* 16.2, 2H, OCH_2C(O)), 4.64 (d, *J* 13.4, 2H, ArCH_2Ar, *ax*), 4.35-4.19 (m, 6H, OCH_2), 4.19-4.10 (m, 2H, OCH_2), 3.94-3.77 (m, 6H, OCH_2), 3.77-3.67 (m, 2H, OCH_2), 3.24 (d, *J* 12.8, 1H, ArCH_2Ar, *eq*), 3.22 (d, *J* 13.2, 2H, ArCH_2Ar, *eq*), 3.13-3.11 (d, *J* 12.9, 1H, ArCH_2Ar, *eq*), 1.30 (t, *J* 7.1, 6H, CH_3). ^{13}C NMR: δ 170.10 (C=O), 156.11, 155.61, 135.78, 134.81, 134.54, 134.23, 128.54, 128.49, 128.32, 128.13, 122.79, 122.34 (Ar), 73.49 (OCH_2), 71.14 (OCH_2C(O)), 70.53, 70.16 (OCH_2), 60.53 (OCH_2CH_3), 31.28, 31.15, 29.84 (ArCH_2Ar), 14.22 (CH_3). Anal. Calcd for $C_{42}H_{46}O_{10}$: C, 70.97;

H, 6.52. Found: C, 70.86; H, 6.76.

8. Synthesis of Calixcrown 8

25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-5 in the cone conformation was synthesized as the following. To a stirred mixture of NaH (10.00 eq, 2.04 g, 85 mmol) and DMF (20 mL) in a 250 mL, three-necked flask under nitrogen was added dropwise a solution of 25,26-dihydroxycalix[4]arene-crown-5 (**4**) (1.00 eq, 4.95 g, 8.50 mmol) in DMF (100 mL). The mixture was stirred for 1 h. A solution of ethyl bromoacetate (8.00 eq, 11.36 g, 7.54 mL, 68 mmol) in DMF (10 mL) was added over a 1 h period. The mixture was stirred for 60 h at 80 °C. The reaction was quenched by addition of 1 N HCl (20 mL) at 0 °C. The solvent was evaporated *in vacuo.* CH_2Cl_2 (100 mL) was added to the residue. The resulting organic solution was washed with H_2O (2×100 mL) and dried over $MgSO_4$. After filtration, the filtrate was evaporated *in vacuo*. The resulting solid was chromatographed on flash silica gel with hexanes-EtOAc (3 : 2) as eluent to give 1.73 g (27%) of slightly yellow solid with a melting point of 51-53 °C. IR: 1757 (C=O), 1266, 1095, 1064 (C-O) cm^{-1}. ^{1}H NMR: δ 6.73-6.52 (m, 12H, ArH), 4.87 (d, *J* 13.43, 1H, Ar*CH$_2$*Ar, *ax*), 4.75 (s, 4H, O*CH$_2$*C(O)), 4.61 (d, *J* 13.6, 2H, Ar*CH$_2$*Ar, *ax*), 4.58 (d, *J* 15.2, 1H, Ar*CH$_2$*Ar, *ax*), 4.22 (q, *J* 7.1, 4H, O*CH$_2$*CH$_3$), 4.30-4.10 (m, 2H, OCH$_2$), 4.09-3.92 (m, 6H, OCH$_2$), 3.80-3.59 (m, 8H, OCH$_2$), 3.23 (d, *J* 13.4, 1H, Ar*CH$_2$*Ar, *eq*), 3.22 (d, *J* 13.5, 2H, Ar*CH$_2$*Ar, *eq*), 3.14 (d, *J* 13.4, 1H, Ar*CH$_2$*Ar, *eq*), 1.29 (t, *J* 7.2, 6H, CH$_3$). ^{13}C NMR: δ 170.13 (C=O), 156.24, 155.65, 135.34, 134.67, 134.64, 128.45, 128.42, 128.32, 128.21, 122.70, 122.34 (Ar), 73.50 (OCH$_2$), 71.31 (O*CH$_2$*C(O)), 71.15, 70.56, 70.27 (OCH$_2$), 60.51 (O*CH$_2$*CH$_3$), 31.25, 31.22, 30.60 (Ar*CH$_2$*Ar), 14.20 (CH$_3$). Anal. Calcd. for C_{44}H50O$_{11}$•0.3CH$_2$Cl2: C, 69.37; H, 6.65. Found: C, 69.22; H, 6.77.

9. Synthesis of Calixcrown 9

25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-6 in the cone conformation was synthesized as the following. A stirred mixture of NaH (10.00 eq, 0.65 g, 27.1 mmol), 25,26-dihydroxycalix[4]arene-crown-6 (**5**) (1.00 eq, 1.70 g, 2.71 mmol), and 45 mL of THF-DMF (9 : 1) in a 100 mL, one-necked flask under nitrogen was stirred for 30 min. Ethyl bromoacetate (8.00 eq, 3.62 g, 21.68 mmol) was added to the flask with a syringe. The mixture was refluxed for 24 h. The reaction was quenched by addition of 1 N HCl (10 mL). THF was evaporated *in vacuo* and 1 N HCl (75 mL) was added to the residue. The resulting aqueous solution was extracted with CH_2Cl_2 (100 mL). The organic layer was separated, washed with H_2O (100 mL), and dried over $MgSO_4$. The CH_2Cl_2 was evaporated *in vacuo*. The crude product was chromatographied on silica gel with hexanes-EtOAc (1 : 2) as eluent to give 1.72 g (80%) of slightly yellow viscous oil. IR 1758 (C=O), 1246, 1093, 1066 (C-O) cm^{-1}. ^{1}H NMR: δ 6.80-6.30 (m, 12H, ArH), 4.80 (d, *J* 13.43, 1H, Ar*CH$_2$*Ar, *ax*), 4.74 (d, *J* 16.2, 2H, O*CH$_2$*C(O)), 4.68 (d, *J* 17.1, 2H, O*CH$_2$*C(O)), 4.65 (d, *J* 13.7, 2H, Ar*CH$_2$*Ar, *ax*), 4.60 (d, *J* 13.43, 1H, Ar*CH$_2$*Ar, *ax*), 4.22 (q, *J* 7.1, 4H, O*CH$_2$*CH$_3$), 4.18-4.07 (m, 4H, OCH$_2$), 4.07-3.98 (m, 2H, OCH$_2$), 3.96-3.85 (m, 2H, OCH$_2$), 3.79-3.60 (m, 12H, OCH$_2$), 3.24 (d, *J* 13.7, 1H, Ar*CH$_2$*Ar, *eq*), 3.19 (d, *J* 13.6, 2H, Ar*CH$_2$*Ar, *eq*), 3.15 (d, *J* 13.4, 1H, Ar*CH$_2$*Ar, *eq*), 1.295 (t, *J* 7.1, 6H, CH$_3$). ^{13}C NMR: δ 170.00 (C=O), 156.30, 155.58, 135.24, 134.82, 134.81, 134.42, 128.48, 128.44, 128.26, 128.12, 122.75, 122.28 (Ar), 73.18 (OCH$_2$), 71.15 (O*CH$_2$*C(O)), 70.89, 70.87, 70.51, 70.26 (OCH$_2$), 60.53 (O*CH$_2$*CH$_3$), 31.36, 31.04, 30.81 (Ar*CH$_2$*Ar), 14.22 (CH$_3$). Anal. Calcd. for $C_{46}H_{54}O_{12}$: C, 69.16; H, 6.81. Found: C, 68.83; H, 7.05.

10. Synthesis of Calixcrown 10

Calix[4]arene-1,2-crown-3 diester (**6**) (2.60 g, 3.05 mmol) in 60 mL of THF and 60 mL of 10% Me_4NOH was refluxed overnight. The solvent was evaporated *in vacuo* and the residue was dissolved in 100 mL of CH_2Cl_2. The organic layer was washed with 1 N HCl solution until pH 1, and then washed with 60 mL of brine and 60 mL of water, dried over $MgSO_4$, and evaporated *in vacuo* to give a white solid (2.12 g, 91%) with mp 196-200 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3212 (O-H), 1760 (C=O), 1204 (C-O); ^{1}H NMR (CDCl$_3$): δ 3.14 (d, *J*=12.0 Hz, 1 H, ArCH$_2$Ar), 3.20-3.38 (m, 3 H, ArCH$_2$Ar), 3.80-3.94 (m, 2 H, OCH$_2$CH$_2$O), 4.12 (d, *J*=12.5 Hz, 2 H, OCH$_2$CH$_2$O), 4.22 (t, *J*=11.0 Hz, 2 H, OCH$_2$CH$_2$O), 4.22-4.36 (m, 4 H, OCH$_2$CH$_2$O, ArCH$_2$Ar), 4.46 (d, *J*=13.0 Hz, 1 H, ArCH$_2$Ar), 4.56 (d, *J*=16.5 Hz, 2 H, OCH$_2$CO), 4.78 (d, *J*=16.5 Hz, 2 H, OCH$_2$CO), 5.18 (d, *J*=12.5 Hz, 1 H, Ar CH$_2$Ar), 6.803-6.92 (m, 8 H, ArH), 6.92 (d, *J*=2.0 Hz, 2 H, ArH), 6.98 (d, *J*=2.5 Hz, 2 H, ArH); ^{13}C NMR (CDCl$_3$): δ 31.32, 33.92, 33.96, 53.40, 71.60, 73.64, 124.50, 125.48, 126.10, 126.18, 133.14, 133.23, 133.53, 134.96, 145.46, 146.82, 151.22, 152.74, 171.54. Anal. Calcd for $C_{36}H_{34}O_9$: C, 51.79; H, 4.10. Found: C, 51.52; H, 4.15%.

11. Synthesis of Calixcrown 11

25,26-bis(carboxymethoxy)calix[4]arene-crown-4 in the cone conformation was synthesized as the following. A solution of 25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-4 (**7**) (5.23 g, 7.36 mmol) in THF (65 mL) was mixed with 10% aq tetramethylammonium hydroxide (65 mL) and the solution was refluxed for 24 h. After cooling to room temperature, the reaction was quenched by addition of 6 N HCl (35 mL). The mixture was stirred for 1 h. The organic solvent was evaporated *in vacuo* and the precipitate was filtered. The precipitate was dissolved in CH_2Cl_2 (100 mL). The aqueous filtrate was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 solutions were dried over $MgSO_4$ and evaporated *in vacuo* to provide 4.72 g (98%) of white solid with a melting point of 178-180 °C. IR: 3400-2700 (br, CO$_2$H), 1750 (C=O), 1266, 1098, 1055 (C-O) cm^{-1}. ^{1}H NMR: δ 10.13 (br, s, 2H, CO$_2$H), 6.96-6.53 (m, 12H, ArH), 5.23 (d, *J* 12.9, 1H, Ar*CH$_2$*Ar, *ax*), 4.85 (d, *J* 16.1, 2H, O*CH$_2$*C(O)), 4.60 (d, *J* 16.1, 2H, O*CH$_2$*C(O)), 4.53 (d, *J* 13.9, 1H, Ar*CH$_2$*Ar, *ax*), 4.49 (dd, *J* 11.5, 4.2, 2H, OCH$_2$), 4.34 (d, *J* 13.3, 2H, Ar*CH$_2$*Ar, *ax*), 4.06 (t, *J* 9.4, 2H, OCH$_2$), 3.91-3.63 (m, 8H, OCH$_2$), 3.34 (d, *J* 12.9, 1H, Ar*CH$_2$*Ar, *eq*), 3.31 (d, *J* 13.1, 2H, Ar*CH$_2$*Ar, *eq*), 3.14 (d, *J* 13.1, 1H, Ar*CH$_2$*Ar, *eq*). ^{13}C NMR: δ 171.90 (C=O), 154.95, 154.76, 136.13, 134.20, 133.96, 133.60, 129.13, 128.96, 128.74, 128.37, 123.86, 123.15 (Ar), 74.82 (OCH$_2$), 71.62 (O*CH$_2$*C(O)), 69.89, 69.80 (OCH$_2$), 31.11, 29.38 (Ar*CH$_2$*Ar). Anal. Calcd for $C_{38}H_{38}O_{10}$·0.4CH$_2$Cl$_2$: C, 66.74; H, 5.72. Found: C, 67.02; H, 5.66.

12. Synthesis of Calixcrown 12

25,26-bis(carboxymethoxy)calix[4]arene-crown-5 in the cone conformation was synthesized as the following. A solution of 25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-5 (**8**) (1.70 g, 2.25 mmol) in THF (20 mL) was mixed with 20 mL of 10% aq tetramethylammonium hydroxide. The mixture was refluxed for 24 h. After cooling to room temperature, the reaction was quenched by addition of 6 N HCl (10 mL). The mixture was stirred for 1 h. The organic solvent was evaporated *in vacuo* and the precipitate was filtered. The precipitate was dissolved in CH_2Cl_2 (50 mL). The aqueous filtrate was extracted with CH_2Cl_2 (2×30 mL). The combined CH_2Cl_2 solutions were dried over $MgSO_4$ and evaporated *in vacuo* to give 1.51 g (96%) of white solid with a melting point of 128-130 °C. IR: 3500-2700 (br, CO_2OH), 1752 (C=O), 1248, 1130, 1058 (C-O) cm^{-1}. ^1H NMR: δ 10.17 (br, s, 2H, CO_2H), 7.00-6.50 (m, 12H, ArH), 4.78 (d, *J* 16.1, 2H, OCH_2C(O)), 4.65 (d, *J* 15.9, 2H, OCH_2C(O)), 4.65 (d, *J* 15.9, 1H, ArCH_2Ar, *ax*), 4.61 (d, *J* 13.8, 1H, ArCH_2Ar, *ax*), 4.35 (d, *J* 13.2, 2H, ArCH_2Ar, *ax*), 4.29-4.15 (m, 2H, OCH_2), 4.15-4.04 (m, 2H, OCH_2), 4.04-3.86 (m, 4H, OCH_2), 3.86-3.73 (m, 4H, OCH_2), 3.73-3.59 (m, 4H, OCH_2), 3.30 (d, *J* 11.5, 1H, ArCH_2Ar, *eq*), 3.28 (d, *J* 13.3, 2H, ArCH_2Ar, *eq*), 3.18 (d, *J* 13.2, 1H, ArCH_2Ar, *eq*). ^{13}C NMR: δ 171.97 (C=O), 155.04, 154.67, 135.39, 134.11, 134.02, 133.94, 128.94, 128.86, 128.56, 128.46, 123.79, 123.10 (Ar), 74.59 (OCH_2), 71.62 (OCH_2C(O)), 70.89, 70.44, 69.76 (OCH_2), 31.12, 30.83, 30.40 (ArCH_2Ar). Anal. Calcd. for $C_{40}H_{42}O_{11}$: C, 68.76; H, 6.06. Found: C, 68.94; H, 6.11.

13. Synthesis of Calixcrown 13

25,26-bis(carboxymethoxy)calix[4]arene-crown-6 in the cone conformation was synthesized as the following. A solution of 25,26-bis[(ethoxycarbony)methoxy]calix[4]arene-crown-6 (**9**) (1.70 g, 2.13 mmol) in THF (30 mL) was mixed with 10% aq tetramethylammonium hydroxide (30 mL). The mixture was refluxed for 24 h. After cooling to room temperature, the reaction was quenched by addition of 6 N HCl (15 mL). The mixture was stirred for 1 h. The organic solvent was evaporated *in vacuo* and the precipitate was filtered. The precipitate was dissolved in CH_2Cl_2 (50 mL). The aqueous filtrate was extracted with CH_2Cl_2 (2×30 mL). The combined CH_2Cl_2 solutions were dried over $MgSO_4$ and evaporated *in vacuo* to give 1.55 g (98%) of white solid with a melting point of 120-122 °C. IR: 3400-2700 (br, CO_2H), 1757 (C=O), 1273, 1130, 1062 (C-O) cm^{-1}. ^1H NMR: δ 10.14 (br, s, 2H, CO_2H), 6.99-6.50 (m, 12H, ArH), 4.78 (d, *J* 16.1, 2H, OCH_2C(O)), 4.65 (d, *J* 13.3, 1H, Ar*CH2*Ar, *ax*), 4.61 (d, *J* 16.0, 2H, OCH_2C(O)), 4.61 (d, *J* 16.0, 1H, ArCH_2Ar, *ax*), 4.40 (d, *J* 13.2, 2H, ArCH_2Ar, *ax*), 4.28-4.08 (m, 4H, OCH_2), 4.06-3.93 (m, 2H, OCH_2), 3.93-3.83 (m, 2H, OCH_2), 3.83-3.53 (m, 12H, OCH_2), 3.31 (d, *J* 13.7, 1H, ArCH_2Ar, *eq*), 3.26 (d, *J* 13.3, 2H, ArCH_2Ar, *eq*), 3.20 (d, *J* 13.3, 1H, ArCH_2Ar, *eq*). ^{13}C NMR: δ 171.74 (C=O), 155.19, 154.72, 135.17, 134.25, 134.19, 133.82, 128.93, 128.86, 128.68, 128.21, 123.76, 123.02 (Ar), 74.30 (OCH_2), 71.64 (OCH_2C(O)), 70.88, 70.75, 70.32, 69.73 (OCH_2), 31.12, 30.67 (ArCH_2Ar). Anal. Calcd. for $C_{42}H_{46}O_{12}$: C, 67.91; H, 6.24. Found: C, 67.58; H, 6.54.