

## Inclusion Extraction of Alkali Metals by Emulsion Liquid Membranes and Nano-baskets of *p*-tert-Calix[4]arene Bearing Di-[N-(X)sulfonyl Carboxamide] and Di-(1-propoxy) in *ortho*-cone Conformation

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Received December 20, 2011, Accepted January 1, 2012

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 application of nano-baskets of calixarene in the selective and efficient separation of alkali metals as both the carrier and the surfactant. For this aim, four derivatives of *p*-tert-calix[4]arene bearing different sulfonamide moieties were synthesized and their inclusion-extraction parameters were optimized including the calixarene scaffold **3** (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, Calixarene, Emulsion liquid membrane, Alkali metals

### Introduction

Emulsion liquid membrane (ELM) was invented by Li<sup>1</sup> in 1968 and is known as one of the most promising separation methods for trace extraction of metal contaminants<sup>2-4</sup> and hydrocarbons<sup>5,6</sup> owing to the high mass transfer rate, high selectivity, low solvent inventory and low equipment cost. Frankenfeld *et al.*<sup>7</sup> 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.<sup>8-14</sup>

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 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,<sup>15</sup> organic acids,<sup>16,17</sup> amino acids,<sup>18-21</sup> proteins<sup>22</sup> and antibiotics.<sup>23,24</sup>

Nano-baskets of calixarenes are a versatile class of macrocycles, which have been subject to extensive researches and extractions,<sup>25,26</sup> stationary phases (using gas chromatograph, Teif Gostar Faraz Co.),<sup>27</sup> transporters<sup>28</sup> and optical and elec-

trochemical sensors<sup>29</sup> 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.<sup>30</sup> However, the limited analytical instrumental techniques at that time were unable to interpret the structure of the synthesized products.

Zinke and Ziegler,<sup>31</sup> in the 1940s, discovered that the products possessed cyclic tetrameric structures. Gutsche,<sup>32</sup> 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<sup>33-35</sup> and crown ethers<sup>36-38</sup> 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.<sup>39-42</sup> Introducing the crown ether ring on the lower-rims, not only increased the cation binding ability of the calixarenic calixarene scaffolds but also enhanced their selectivity.<sup>43-50</sup>

The recent developments about the medical aspects of calixarene scaffolds have been reviewed by Mokhtari and Pourabdollah<sup>41</sup> in six medical divisions including hematology, pathology, pharmacy and pharmacology, infectious diseases, nuclear medicine, and chemotherapy. Calixarenes enable to encapsulate the guest drugs and show different biological activities.

The role of calixarene's scaffolds and substitutions in the field of pharmacology including anti-cancer, anti-mycobacterial, anti-proliferativity, catalytic and inhibitory activities as well as solubility control, drug analysis, drug purification,

drug supports and structural studies have been reviewed.<sup>42</sup> The importance of calixarene nano-baskets in controlling their toxicity comes back to their ability to encapsulate the biological compounds. New complexes show improved physical characteristics such as more solubility in water and enhanced chemical properties like less toxicity in biological systems. Moreover, the covalent bonding, inclusion encapsulation and induction activities of calixarenes lead to improve the activity of drug molecules.

Owing to interests in calixarene-based bonded-phases, different applications of them in the main fields of molecular and ionic species as well as the mobile and stationary phases have been reviewed recently.<sup>27</sup> In this review, a variety of research data dealing with the synthesis, preparation and behavior of calixarene-based liquid chromatographic phases has been collected and compared. The rapid growth of calixarenes in extraction of ionic and molecular species, has been reviewed by focusing on the bindings of alkali and alkaline earth metals, *p*-block cations, transition metals, actinides and lanthanides,<sup>39</sup> molecular species,<sup>43</sup> organic cations and anions.<sup>29</sup>

In this study, nano-baskets of calixarene were used as bi-functional surfactant/carrier and the method of "once at a time" was used to study of the influences of different factors on ELM performance. In this approach, the experiments are 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 calixarene type and concentration (as surfactant and carrier), strip phase type 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

**Chemicals and Reagents.** The liquid membrane consists of a diluent and a calixarene (as surfactant and extractant). The calixarenes were synthesized as described below. Commercial kerosene (Shell, USA) was used as diluent, which was a complex mixture of aliphatics and aromatics. Sulphuric 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 lithium chloride, rubidium chloride. 1.0 N hydrochloric acid was 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 *p*-*tert*-butyl-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide] di-propoxy, *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-hydroxy phenyl)sulfonyl carboxamide] di-propoxy, *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide] di-propoxy, and *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulfonyl carboxamide] di-propoxy. The synthesis procedures were given in the previously work.<sup>26</sup> The chemical structure of calixarene scaffolds **01-04** were used in the experiments are presented in Figure 1.

**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 1700 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.

**Preparation of ELM.** The specific amounts of calixarenes were solved in the specific amount of kerosene and thus membrane solutions were prepared. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 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 1500 rpm by a variable speed mixer equipped with a turbine-type Teflon impeller. The mixture of the membrane and the stripping solution was emulsified.

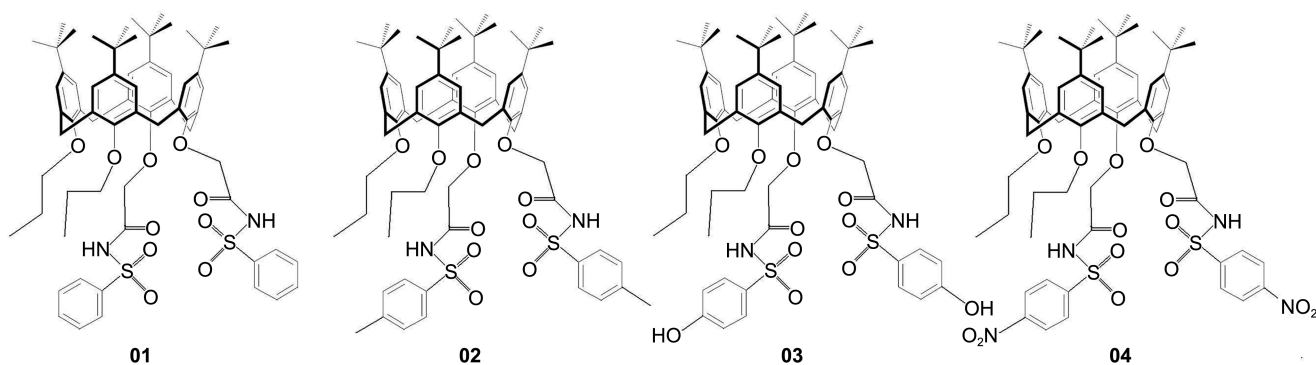


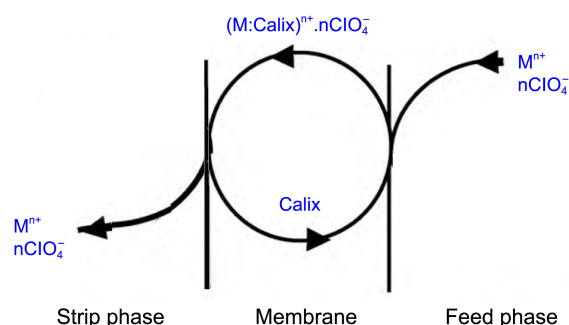
Figure 1. Chemical structure of derivatives **01-04**.

**Characterization of ELM.** The size, size distribution and stability of emulsions were characterized to examine the method. Size and size distribution of (w/o) droplets obtained by optic microscopy (Mettler FP). The digital format of captured micrographs were analyzed by means of image analyzer software (Digital Micrograph TM, Gatan Inc.). Using a Neubauer camera, the volume of analyzed samples were 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.

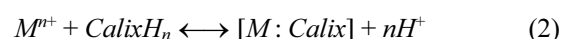
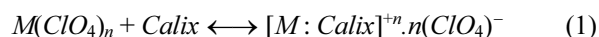
**Batch ELM Experiment.** In 500-mL beaker, the ELM prepared was added to some volumes of the feed solution and were stirred by a variable speed mixer equipped with a turbine-type impeller at speed of 500 rpm for extraction time of 30 min. The speed of the mixer was regulated by a voltage regulator. To determine the important variables governing the permeation and separation of alkali metals, calixarene'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 using a filter paper. The emulsion was demulsified by the freezing. The concentration of alkali metals was analyzed using ion chromatography.

## Results and Discussion

In several studies, it was shown that calixarenes are 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) were 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 calixarenes as surfactant/carrier in an ELM system are depicted in Eqs. (1) and (2), respectively.



**Figure 2.** Facilitated transport mechanism of alkali metals in ELM.



Where  $M_n^+$  depicted the alkali cation ( $n = 1$ ),  $CalixH_n$  shows the calixarene scaffold in the molecular form, and  $M:Calix$  presents the calixarene 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 can't capture them. After that, the new uncharged complex state diffuses throughout the organic membrane. In the side of acidic strip phase, the calixarene complex dissociates as an uncharged molecular calixarene and diffuses into the organic membrane again. This transportation is repeated during the extraction until the chemical potentials in both sides be equal. Figure 2 depicts the mechanism of facilitated transport of alkali metals with ELM process.

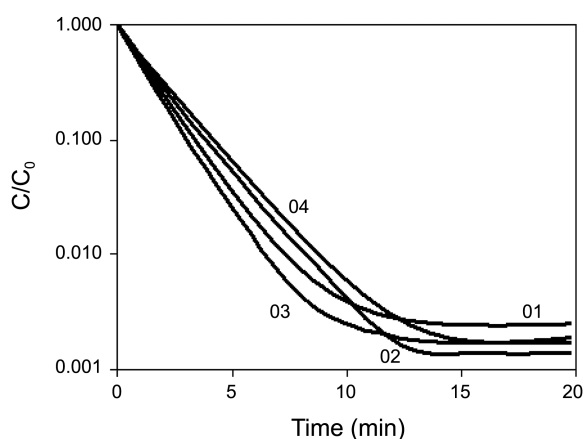
The optimum conditions for the extraction of alkali metals were determined by the method of once at a time. Table 1 presented all conditions were tested as well as the optimum conditions in bold. The methodology of optimizations is discussed as the following sections.

**Effect of Calixarene Type.** Type of calixarene 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 calixarene type on the extraction efficiency of alkali metals was studied in the ELM

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

1	calixarene type	01	02	<b>03</b>	04	-
2	calixarene concentration (wt %)	1	3	<b>4</b>	5	10
3	acid type in strip phase	<b>H<sub>2</sub>SO<sub>4</sub></b>	HCl	HNO <sub>3</sub>	-	-
4	acid concentration in strip (M)	0.1	<b>0.2</b>	0.3	0.4	0.5
5	base type in feed	NaOH	NH <sub>4</sub> OH	Na <sub>2</sub> CO <sub>3</sub>	<b>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub></b>	-
6	base concentration in feed (M)	0.1	0.2	0.3	<b>0.4</b>	0.5
7	phase ratio	0.4	0.6	<b>0.8</b>	1.0	1.2
8	treat ratio	0.1	0.2	<b>0.3</b>	0.4	-
9	membrane type	<b>kerosene</b>	n-decane	k:d*	-	-
10	Membrane selectivity					
11	stirring rate (rpm)	100	200	<b>300</b>	400	500
12	solute concentration in feed (mg/L)	10	<b>100</b>	1000	-	-

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

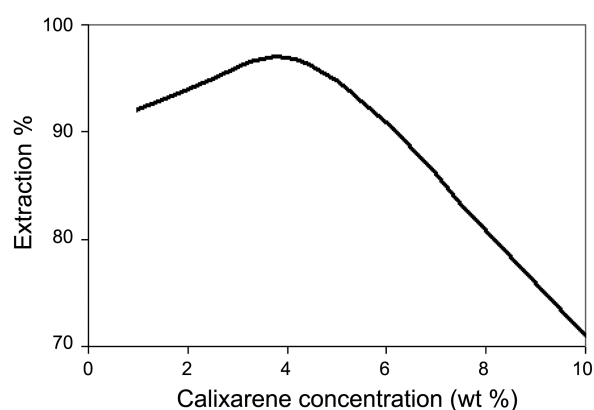


**Figure 3.** Effect of calixarene type on the extraction efficiency of alkali metals in the ELM process. **01:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide] di-propoxy, **02:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-hydroxy phenyl)sulfonyl carboxamide] di-propoxy, **03:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide] di-propoxy, and **04:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulfonyl carboxamide] di-propoxy.

process using **01:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide] di-propoxy, **02:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-hydroxy phenyl)sulfonyl carboxamide] di-propoxy, **03:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide] di-propoxy, and **04:** *p*-*tert*-butyl-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulfonyl carboxamide] di-propoxy. *C* and *C*<sub>0</sub> depict the concentration of alkali metals after and before the ELM process. The results obtained are shown in Figure 3. According to the results, although calixarene **03** gives higher rate of extraction in the first 10 min compared to calixarenes **01**, **02**, **04**, it gradually deteriorates with time. Examination of these results indicates that **03** was more favorable than **01**, **02**, **04** as emulsifier/carrier. Therefore **03** was selected as among all scaffolds.

**Effect of Calixarene Concentration.** The extraction of alkali metals increased by increasing of calixarene concentration from 1-5%, while more increase from 5-10% hardly affected the extraction performance. As depicted in Figure 4, further increase of calixarene concentration decreased the efficiency of extraction, owing to the access of molecular calixarene in membrane phase. Under the optimum concentration, the molecular form of calixarene is considered enough for forward extraction. Increasing of calixarene concentration up 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 calixarene 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.

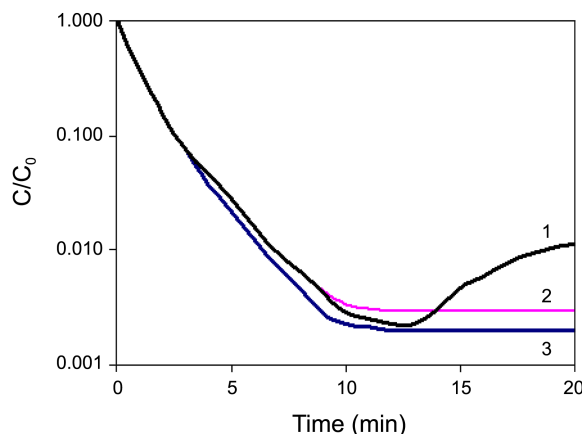
The excessive calixarenes tend to increase the interface's resistance and increase the viscosity of membrane. This increasing from 5% increased the emulsion stability but the mass transfer was adversely decreased. Similar results have



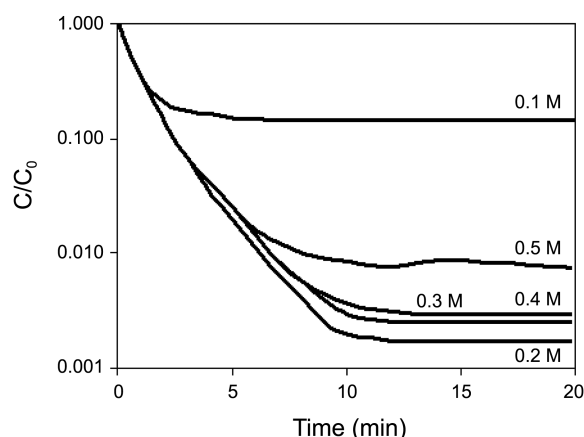
**Figure 4.** Effect of calixarene concentration on the extraction efficiency of alkali metals in the ELM process.

been reported by other researchers.<sup>51,52</sup> Hence, there is an optimum in the concentration of calixarenes around 4%. The excess of calixarenes concentration leads to osmotic swelling and membrane breakdown. Hence, the concentration of 4% was accepted as optimum concentration. Another criterion is the financial aspects, in which the calixarenes are the most expensive agents among the other components of ELM process, and the lower concentrations are preferred.

**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 calixarene: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 calixarene 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 including **1:** nitric acid, **2:** hydrochloric acid and **3:** sulfuric acid, on the transport of calixarene complex was investigated. Figure 5 depicts the results, in which there is a little difference in the extraction efficiency between the



**Figure 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.

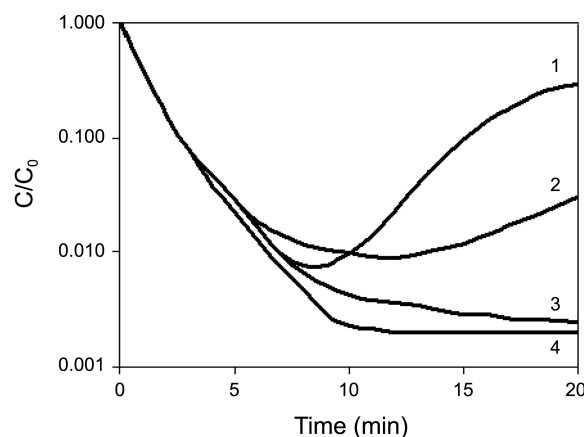


**Figure 6.** Effect of sulfuric acid concentration in the strip phase on the extraction efficiency of alkali metals in the ELM process.

acids used.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. 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.

**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, the experiments were performed with various concentrations of sulfuric acid in the range 0.1-0.5 M. Figure 6 depicted the effect of acid concentration on the extraction of alkali metals.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. Noticeably, 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 calixarene complexes decrease due to the less availability of protons for the reaction.<sup>53-55</sup> 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 species like  $(\text{CalixH}_{n+m})^{m+}$ , which may not mobilize to the membrane completely at higher acid concentrations. Hence, the extraction will decrease with the more increase in acid concentration.

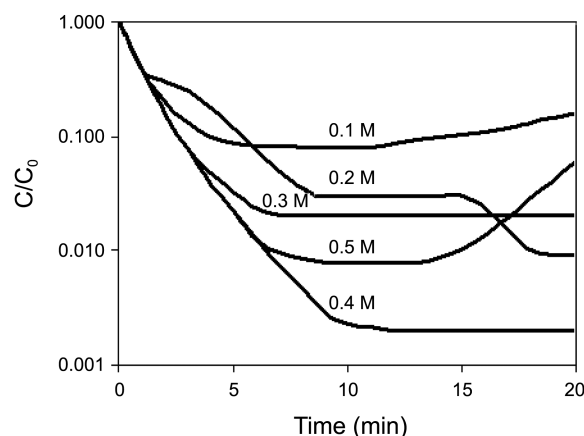
**Effect of Base Type in Feed.** As the extraction occurs in the interface between the basic solution and the liquid membrane, the transport of metal necessarily requires a simultaneous back-extraction step at the opposite side of the membrane. In the stage of back-extraction, the calixarene is regenerated and the alkali metal is stripped. As reported in literature, 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,



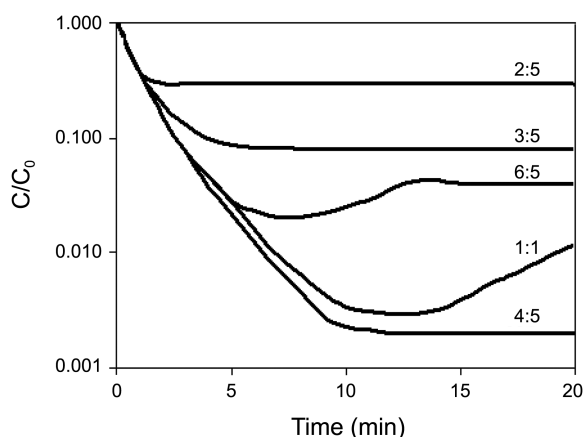
**Figure 7.** Effect of base type in the feed phase on the extraction efficiency of alkali metals in the ELM process. **1:** NaOH, **2:**  $\text{NH}_4\text{OH}$ , **3:**  $\text{Na}_2\text{CO}_3$ , and **4:**  $(\text{NH}_4)_2\text{CO}_3$ .

the selection of suitable feed solution is considered one of the key factors for cation extraction. Hence, **1:** NaOH, **2:**  $\text{NH}_4\text{OH}$ , **3:**  $\text{Na}_2\text{CO}_3$ , and **4:**  $(\text{NH}_4)_2\text{CO}_3$  were used and the results are shown in Figure 7.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. According to this figure,  $(\text{NH}_4)_2\text{CO}_3$  solution was more preferable in making the feed solution since it stables the emulsions during the extraction process. Therefore, the proper concentration of ammonium carbonate was selected as the best base in the feed phase.

**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 were shown in Figure 8, in which there is difference in the extraction efficiency in the concentration range aforementioned.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. Obviously, the extraction rate of solutes up to about



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

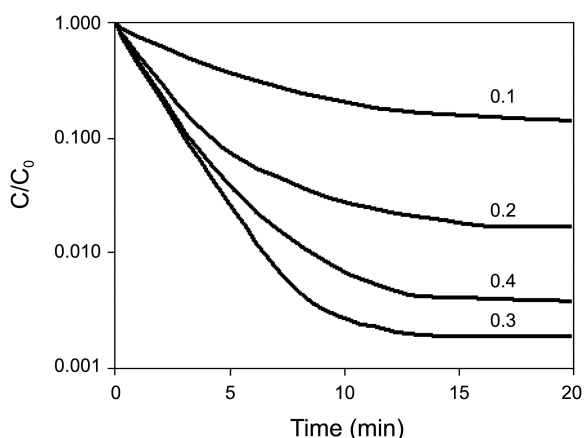


**Figure 9.** Effect of phase ratio on the extraction efficiency of alkali metals in the ELM process.

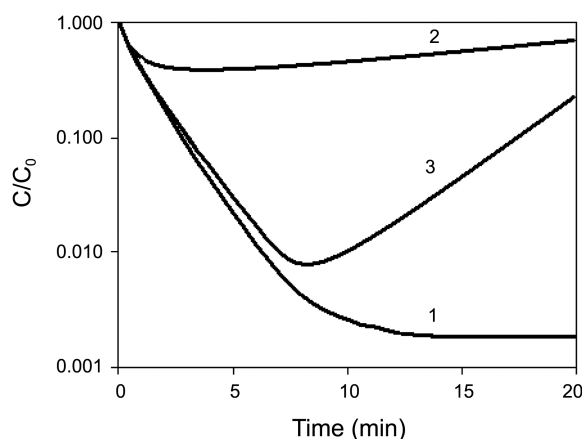
10 min increased with the increase of base concentration in the feed solution. However, at 10 min, the efficiency of extraction decreased with the increase of base concentration in the feed solution owing to instability of emulsion droplets. Therefore, at tenth minute, the highest extraction efficiency was obtained with 0.4 M  $(\text{NH}_4)_2\text{CO}_3$  solution. Thus, 0.4 M  $(\text{NH}_4)_2\text{CO}_3$  solution was selected as the best concentration for feed phase.

**Effect of Phase Ratio (Strip Phase Volume/Membrane Volume).** The phase ratio is defined as the volume of stripping solution to volume of membrane. Figure 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.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. 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 results 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.

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



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



**Figure 11.** Effect of diluent (membrane) type on the extraction efficiency of alkali metals in the ELM process. **1:** Kerosene, **2:** *n*-decane and **3:** their blend (1:1).

The treatment ratio, defined as the volume ratio of the emulsion 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 caused inversely 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 Figure 10, in which the extraction efficiency was improved by increasing the treat ratio from 0.1 to 0.3.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. Beyond 0.3, the further increase in the ratio caused the instability of globules and less extraction efficiency.

**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 that is 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. It is important to 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. **1:** Kerosene, **2:** *n*-decane and **3:** their blend 1:1 were investigated as the diluent. The results are presented in Figure 11.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. According to the results, kerosene was selected as the best diluent in the following experiments.

**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

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

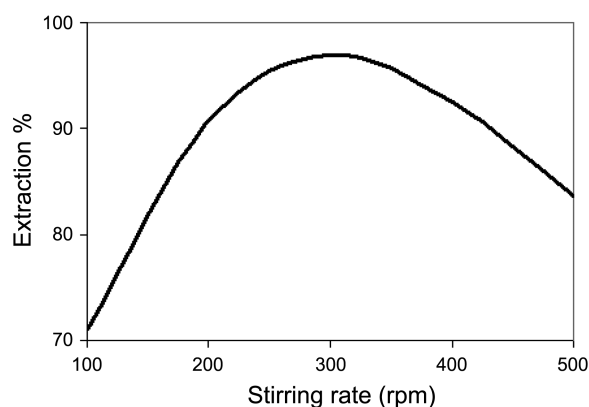
Intervals	2-6 min					6-12 min					12-20 min				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
Ca	074	112	134	102	094	076	112	136	102	099	077	114	144	102	102
Ba	218	314	442	208	158	222	306	475	303	196	230	298	480	176	186
Ag	146	180	145	198	223	188	202	209	270	176	190	214	210	283	180
Pb	280	324	166	207	332	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

compounds in the solution must be multiplied to give their ratio after extraction. Eq. (3) depicted how to calculate the enrichment factor.

$$\frac{C_A^f}{C_B^f} = EF \cdot \frac{C_A^i}{C_B^i} \quad (3)$$

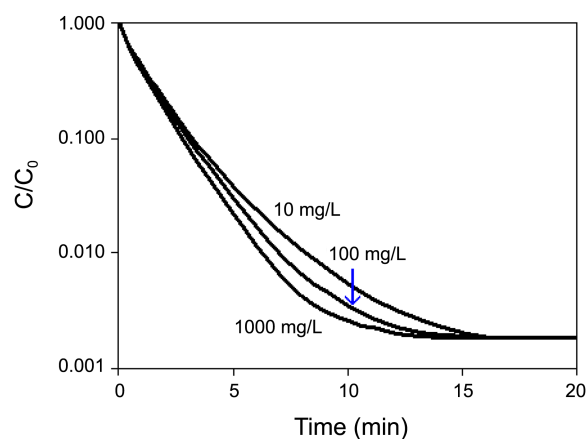
Where,  $C_A^i$  and  $C_B^i$  are the initial amounts of species A and B in the feed solution.  $C_A^f$  and  $C_B^f$  depict the final amounts of them, respectively in the strip solution. The EF factor represents the enrichment factor. At the end of the experiments, except for calcium, at interval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

**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 in order to obtain optimal speed with effective extraction of alkali metal cations in the ELM process. As depicted in Figure 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 reduced. As a result, an increase in the mixing speed would increase the interfacial area, and this was true up to certain level of mixing speed beyond which

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

an increase in the speed was likely to break the emulsions thereby reducing overall enrichment and the efficiency of extraction. As discussed by Thien *et al.*,<sup>56</sup> 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 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 are breakdown on their own or induced by shear. Therefore, the extraction performance is a trade-off between two effects of swelling phenomena and mixing speed.

**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 Figure 13.  $C$  and  $C_0$  depict the concentration of alkali metals after and before the ELM process. Noticeably, the concentration of alkali metal cations in the feed solution was varied from 10 to 1000 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 1000 to 35 mg/L, with the extraction efficiencies of 90, 94, and 96.5%, respectively.

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



### Conclusion

Alkali metals in basic and dilute water can be recovered by an ELM process using nano-baskets of calixarene. Hence, an ELM using derivatives of *p*-tert-calix[4]arene bearing different sulfonamide moieties 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 calixarene derivative **03** (4 wt %) and the results are tabulated 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.

**Acknowledgments.** This work was supported by Islamic Azad University (Shahreza branch) and Iran Nanotechnology Initiative Council.

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