

INCLUSION SEPARATION OF ALKALI METALS IN EMULSION LIQUID MEMBRANES BY NANO- BASKETS OF CALIX[4]CROWN-3

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(Submitted: December 28, 2011 ; Revised: April 16, 2012 ; Accepted: April 18, 2012)

Abstract - Nano-assisted inclusion separation of alkali metals from basic solutions was reported by an inclusion-facilitated emulsion liquid membrane process. The novelty of this study is application of nano-baskets of calixcrown in the selective and efficient separation of alkali metals as both the carrier and the surfactant. For this purpose, two diacids, *p-tert*-butylcalix[4]arene-1,2-crown-3 in the cone and the 1,2-alternate conformation, as well as another diacid, *p-tert*-butylcalix[4]arene-1,2-thiacrown-3 in the cone conformation, were synthesized. Their inclusion-extraction parameters were optimized, including the calixcrown scaffold (0.4, 4 wt%) as the carrier/demulsifier, commercial kerosene as the diluent in the 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 were 0.8 and 0.3, mixing speed (300 rpm), and initial solute concentration (100 mg/L). The selectivity of the membrane was examined for 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%.

Keywords: Nano-basket; Inclusion; Calixcrown; Emulsion liquid membrane; Alkali metals.

INTRODUCTION

The emulsion liquid membrane (ELM) was invented by Li (1968) and is known as one of the most promising separation methods for trace extraction of metal contaminants (Kumbasar and Sahin, 2008; Chakraborty *et al.*, 2003; Ortiz *et al.*, 2003; Biscaia Junior *et al.*, 2001; Ferraz *et al.*, 2007) and hydrocarbons (Correia and de Carvalho, 2003; Park *et al.*, 2006) owing to the high mass transfer rate, high selectivity, low solvent inventory and low equipment cost. Frankenfeld *et al.* (1981) reported that the ELM could be up to 40% cheaper than other solvent extraction methods. This process combines both an extraction and stripping stage to perform a simultaneous purification and concentration. However, this method has been limited by the emulsion

instability (Hou and Papadopoulos, 1996; Zihao *et al.*, 1996; Bandyopadhyaya *et al.*, 1998; Xuan-cai and Fu-quan, 1991; Li *et al.*, 1988; Florence and Whitehill, 1981; Wan and Zhang, 2002).

The lack of emulsion stability decreases the extraction efficiency. In the ELM process, three steps are employed 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 the 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

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the membrane phase. ELM applications include separation of sugars (Ikeda *et al.* 2003), organic acids (Yordanov and Boyadzhiev, 2007; Demirci *et al.*, 2003), amino acids (Kaghazchia *et al.*, 2006; Mohagheghi *et al.*, 2008; Oshima *et al.*, 2003; Bayraktar, 2001), proteins (Vasudevan and Wiencek, 1996) and antibiotics (Habaki *et al.*, 2008; Lee, 2002).

Nano-baskets of calixarenes are a versatile class of macrocycles, which have been the subject of extensive research (Mokhtari *et al.*, 2011 a-d) over the past years. Baeyer (1872) synthesized the calixarenes by the reaction of *p*-substituted phenols with formaldehyde in basic or acidic environment. However, with the limited analytical instrumental techniques available at that time, he was unable to interpret the structure of the synthesized products.

Zinke and Ziegler (1944) discovered that the products possessed cyclic tetrameric structures. Gutsche (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 ionizable moieties and crown ethers in their scaffolds (Mokhtari and Pourabdollah, 2012 a-o). 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. Introducing the crown ether ring on the lower-rims not only increased the cation binding ability of the calixarenic scaffolds, but also enhanced their selectivity (Mokhtari and Pourabdollah, 2011 a-g).

In this study, three nano-baskets of calixcrown were used as bi-functional surfactant/carrier and the method of "one 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 one tuned variable at a time, while keeping all other independent factors constant. By the method of one at a time, the ELM process for selective extraction of alkali metals was investigated.

Avoiding the possibility of mutual dependences of the variables is the disadvantage of "one at a time". However, this approach is worth using since it has some advantages, in which it is not necessary to perform many experiments. On the other hand, using

this approach, the number of experiments and consequently the expense and time decrease.

Moreover, the users can test the validity of this approach by reversing the priority of stages. This was done in the present study and no differences in the results were observed. Therefore, it was confirmed that mutual dependences of the variables played no vital role in the present experiments.

The process factors such as calixcrown type and concentration (as surfactant and carrier), strip phase type and concentration, base type and concentration in the feed, the phase and treat ratios, membrane type and selectivity, mixing speed, and solute concentration in the feed were investigated and optimized.

EXPERIMENTAL

Chemicals and Reagents

The liquid membrane consists of a diluent and a calixcrown (as surfactant and extractant). The calyx-crowns 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 the dark.

The experiments carried out using three derivatives of the diacid calix[4]-1,2-crowns-3 and the synthesis procedures were given in previous work (Mokhtari and Pourabdollah, 2011 e). The chemical structures of calixcrown scaffolds 04, 06 and 09 used in the experiments are presented in Figure 1.

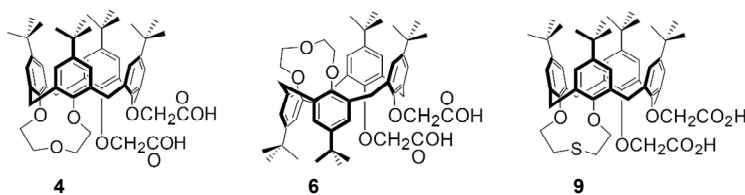


Figure 1: Chemical structure of derivatives.

Analytical Instruments

Determinations of alkali metals were accomplished by Dionex DX-120 ion chromatography with a CS12A column, a conductivity detector 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 repeated twice. 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 the ELM

The specific amounts of calixcrown were dissolved in kerosene to prepare the membrane solutions. $(\text{NH}_4)_2\text{CO}_3$ solution (25 mL, 0.5 M) was used as the stripping solution. Stripping solution was added dropwise to the stirred membrane solution in a 100-mL beaker and the two-phase system was stirred continuously for 30 min at a mixing speed of 1500 rpm with a variable speed mixer equipped with a turbine-type Teflon impeller. The mixture of the membrane and the stripping solution was emulsified.

Characterization of the ELM

The size, the size distribution and the stability of the emulsions were characterized to examine the method. Size and size distribution of (w/o) droplets was obtained by optical 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 the analyzed samples was controlled. The stability of w/o droplets was monitored by size distribution changes at constant times, evaluated by image analyses from photographs obtained during the diafiltration experiments.

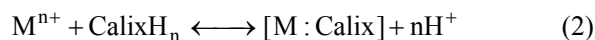
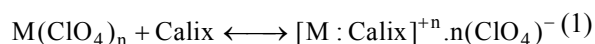
Batch ELM Experiments

In a 500-mL beaker, the prepared ELM was added to several volumes of the feed solution and were stirred by a variable speed mixer equipped with a turbine-type impeller at a speed of 500 rpm for an 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, the calixcrown's type and concentration, the strip phase type and concentration, the base type and concentration in the feed, the phase and the treat ratios, the membrane diluent type and selectivity, the mixing speed, and the 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. Each run was repeated three times and the error bars were determined based upon $N=3$. The feed phase of the samples was separated from the emulsions by filtration using a filter paper. The emulsion was demulsified by freezing. The concentration of alkali metals was analyzed using ion chromatography.

RESULTS AND DISCUSSION

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



where M^{n+} depicts the alkali cation ($n=1$), CalixH_n the calixcrown scaffold in the molecular form, and $\text{M}:\text{Calix}$ the calixcrown complex with the alkali metal.

Calixarenes and di-ionizable calixarenes in acidic solutions are in the molecular state, but are hydrolyzed in the basic solutions. The ionic form includes the cationic species, while the molecular form does not capture them. The new uncharged complex state then diffuses throughout the organic membrane. At the side of the acidic stripping phase, the calixcrown complex is dissociated as an uncharged molecular calixcrown and diffuses back into the organic membrane again. This transport is repeated during the extraction until the chemical potentials on both sides are equal. Figure 2 depicts the mechanism of facilitated transport of alkali metals via the ELM process.

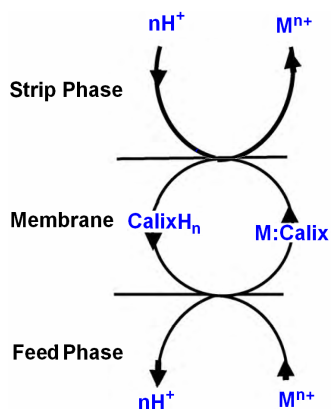


Figure 2: Facilitated transport mechanism of alkali metals in ELM using ionizable calixarenes.

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

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 Figure 3(a). According to the results, although calixcrown 04 gave a higher rate of extraction in the first 10 min compared to calixcrown 06 and 09, it gradually deteriorates with time. Examination of these results indicates that 04 was more favorable than 06 or 09 as emulsifier/carrier.

Therefore, 04 was selected as the preferred scaffold.

Effect of Calixcrown Concentration

The extraction of alkali metals increased upon increasing of calixcrown concentration from 1-5%, but a further increase from 5-10% hardly affected the extraction performance. As depicted in Figure 3(b), a further increase of calixcrown concentration decreased the efficiency of extraction, owing to the excess of molecular calixcrown in the membrane phase. At the optimum concentration, the molecular form of calixcrown is enough for forward extraction. Increasing the calixcrown concentration up to 5% increased the stability of the emulsion liquid membrane, which led to a decrease in the break-up rate, hence the extraction of solutes was increased. Further increase in the concentration of calixcrown leads to a decrease in the rate of the capturing and stripping reactions. This is because the metal cations remain in the complex form (in the membrane) without being stripped. This affects the final recovery by the ELM process.

The excess calixcrown increases the interface's resistance and the viscosity of the membrane. This increase above 5% increased the emulsion stability, but the mass transfer was adversely decreased. Similar results have been reported by other researchers (Reis and Membr, 1993; Othman *et al.*, 2006). Hence, there is an optimum concentration of calixcrown around 4%. The excess calixcrown concentration leads to osmotic swelling and membrane breakdown. Hence, a concentration of 4% was accepted as the optimum concentration. Another criterion is the financial aspect, the calixcrowns being the most expensive reagents among the components of the ELM process, making lower concentrations preferred.

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

1	Calixcrown Type	04	06	09	-	-
2	calixcrown concentration (wt%)	1	3	4	5	10
3	acid type in strip phase	H ₂ SO 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 ₄ OH	Na ₂ CO ₃	(NH ₄) ₂ CO 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

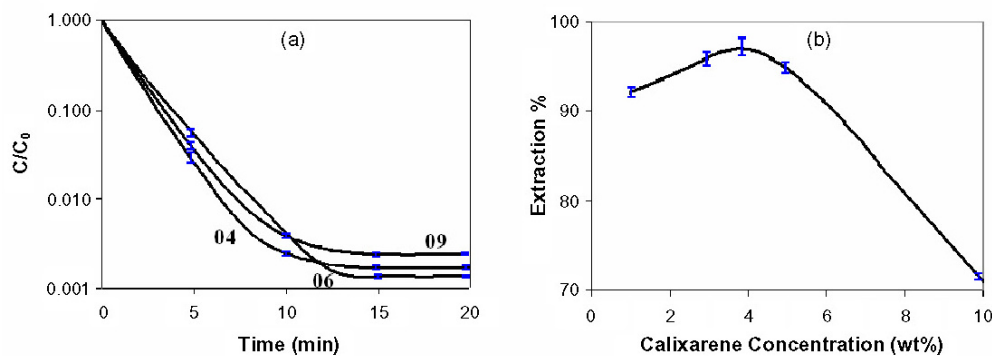


Figure 3: Effect of calixcrown type (a) and concentration of derivative 04 (b) on the extraction efficiency and extraction percent of alkali metals in the ELM process.

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 acid 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 solutions of different acids

(sulfuric acid, hydrochloric acid and nitric acid) on the transport of calixcrown complex was investigated. Figure 4(a) depicts the results, in which there is only 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, in the 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 M sulfuric acid solution was accepted as the best acid and was used as the strip phase solution in the following experiments.

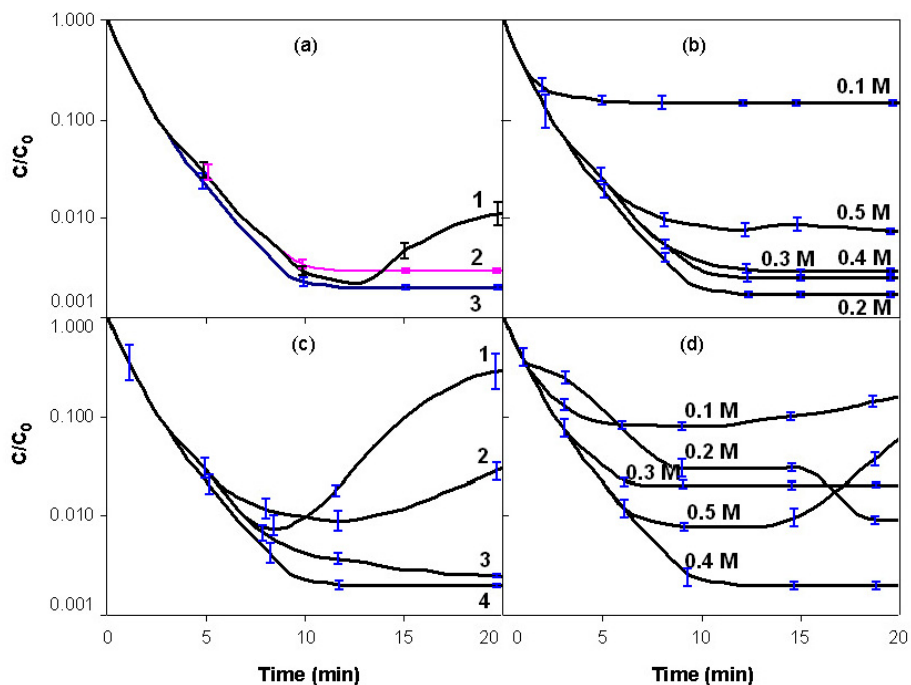


Figure 4: Effect of acid type (a) and concentration of sulfuric acid (b) in the strip phase, and base type (c) and concentration of ammonium carbonate (d) in the feed phase on the extraction efficiency of alkali metals in the ELM process.

(a) 1: nitric acid, 2: hydrochloric acid, 3: sulfuric acid; (c) 1: NaOH, 2: NH₄OH, 3: Na₂CO₃, 4: (NH₄)₂CO₃

Effect of Acid Concentration in the Strip Phase

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 of 0.1–0.5 M. Figure 4(b) depicts the effect of acid concentration on the extraction of alkali metals. Obviously, below 0.2 M, the extractions decreased with a 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 lower availability of protons for the reaction (Bhowal and Datta, 2001; Venkateswaran and Palanivelu, 2005; Strzelbicki *et al.*, 1984). 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 a further increase in acid concentration.

Effect of Base Type in the Feed

Because the extraction occurs at 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 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 base type in the feed phase. Therefore, the selection of a suitable feed solution is considered one of the key factors for cation extraction. Hence, NaOH, NH_4OH , Na_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$ were used and the results are shown in Figure 4(c). According to this figure, $(\text{NH}_4)_2\text{CO}_3$ 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.

Effect of Base Concentration in the Feed

The literature contains many options for accomplishing the ELM process by cation complexation. Among them, solutions of ammonium carbonate,

sodium carbonate and sodium hydroxide have been used in the feed phase. In our case, 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 Figure 4(d), in which there is a difference in the extraction efficiency in the aforementioned concentration range. Obviously, the extraction rate of solutes up to about 10 min increased with the increase in base concentration in the feed solution. However, at 10 min, the efficiency of extraction decreased with the increase in base concentration in the feed solution owing to the instability of the emulsion droplets. Therefore, at the 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 the feed phase.

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

The phase ratio is defined as the ratio of the volume of stripping solution to the volume of the membrane. Figure 5(a) shows the effect of phase ratio on the extraction of alkali metal cations, which increases with an increase of the phase ratio up to 4:5. At a 4:5 phase ratio, the maximum extractions were observed. By increasing the volume of the strip phase, the thickness of the film in the emulsion was reduced owing to dispersion of the 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, a further increase in the volume of strip phase caused the instability of globules.

Effect of Treat Ratio (Feed Volume/Emulsion Volume)

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 the ELM process. By increasing the amount of emulsion in the feed phase, the number of available droplets and the interfacial surface area per unit volume of the feed solution increase. This leads to increasing the mass transfer of solutes from the feed to the membrane and more efficiency. Increasing the treat ratio slightly increased the size of the emulsion droplets and caused inversely a reduction in interfacial surface area. The increment in the size of the droplets was suppressed by the increment in the number of droplets. The results are depicted in Figure 5(b), in

which the extraction efficiency was improved by increasing the treat ratio from 0.1 to 0.3. Beyond 0.3, a further increase in the ratio caused the instability of the globules and a lower 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 the membrane with the carrier as well as its viscosity are two main parameters that are controlled by choosing the membrane type. The membrane phase viscosity determines the rate of transport of the carrier or solutes and the residence or contact time of the emulsion with the feed phase. It is important to note that the 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 1:1 blend were investigated as the diluent. The results are presented in Figure 6(a). According to the results, kerosene was selected as the best diluent in the following experiments.

Membrane Selectivity

The selectivity of the membrane was examined via 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 the calculation of the enrichment factor (EF).

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

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. At the end of the experiments, except for calcium in the interval of 4–10 min, the liquid membrane selectivity for alkali metals with respect to other ions was high.

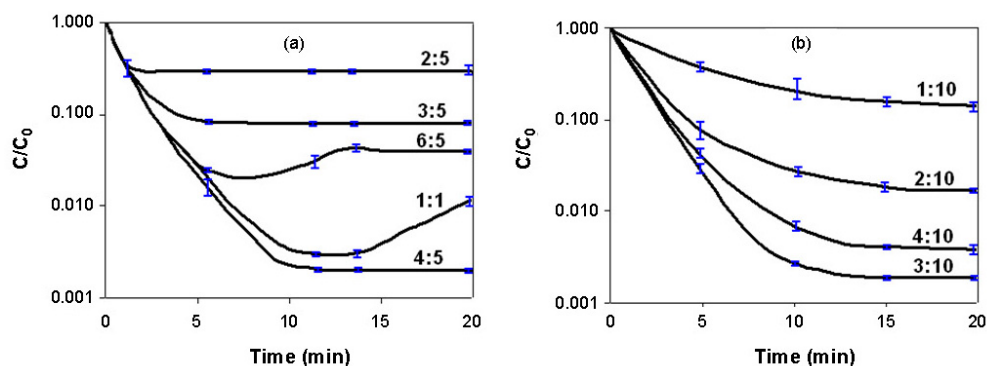


Figure 5: Effect of phase- (a) and treat-ratios (b) on the extraction efficiency of alkali metals in the ELM process.

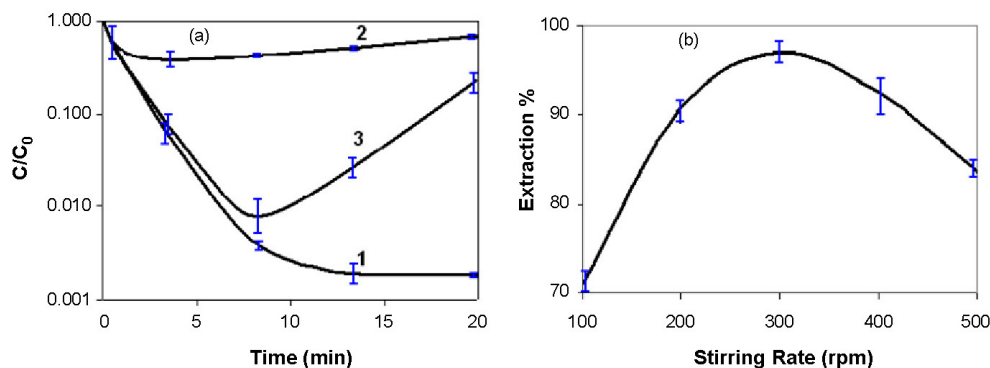


Figure 6: Effect of membrane type (a): curve 1 = kerosene, curve 2 = n-decane, curve 3 = their blend 1:1 and stirring rate (b) on the extraction efficiency of alkali metals in the ELM process.

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

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 6(b), 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 increases the interfacial area. This was true up to certain level of mixing speed, beyond which 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.* (1990), 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 the feed to the strip phase. Some particles are broken due to shear after reaching larger size. The swollen droplets break down on their own or this is induced by shear. Therefore, the extraction performance is a trade-off between the two effects of swelling phenomena and mixing speed.

Effect of Solute Concentration in the Feed

The effect of initial concentration of solutes on the degree of extraction was studied. The results are presented in Figure 7. 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 extraction efficiencies of 90, 94, and 96.5 %, respectively.

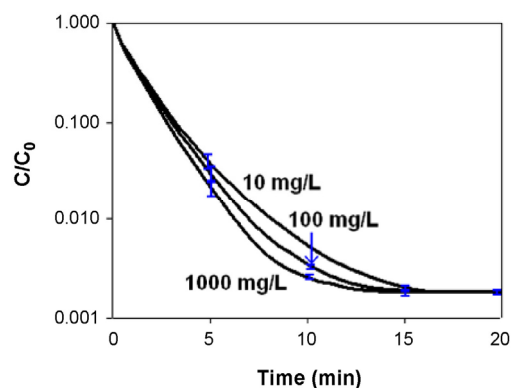


Figure 7: Effect of solute concentration in the feed phase on the extraction efficiency of alkali metals in the ELM process.

Diffusion of ammonia across the membrane is not supported by the carrier (calixcrowns) since this kind of carrier just captures and delivers those species that are (1) cationic and (2) have the proper size with respect to the size of calixcrown's bowl. Therefore, diffusion of other species like ammonia is carried out just by conventional diffusion across the membrane at a low rate and is not accelerated by inclusion of carriers like calixcrown. To be sure, the content of ammonia was measured in the strip-phase just after finishing the experiments by breaking the emulsions. This content was negligible.

Precipitation of Ca(II) as well as other alkaline earth metals in the strip-phase of sulfuric acid did not present any problem for the extraction efficiency of alkali metals or for the emulsion stability. The main

subject was enhancement of mass transfer through the membrane and raising its selectivity towards alkali metals. Precipitation of alkaline earth metals did not affect the mass transfer rate of alkali metals since there were not any differences in the efficiency and quality of extractions with and without added alkaline earth metals. Moreover, such probable precipitations did not affect the emulsion stability since there were not any differences in the efficiency, time and quality of extractions with and without added alkaline earth metals.

CONCLUSION

Alkali metals in basic and dilute water can be recovered by an ELM process using nano-baskets of calixcrown. Hence, an ELM using three derivatives of the diacid *p-tert-butylcalix[4]arene-1,2-crown-3* 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 with the potentially interfering cations 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 for the inclusion ELM process have been determined experimentally and tabulated in Table 1;
2. The results of membrane selectivity for inclusion-extraction of alkali metals from the basic solutions containing interfering cations performed by ELM process using calixcrown derivative 04 (4 wt%) are tabulated in Table 2;
3. The highest efficiency for inclusion-extraction 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; increasing from 300 to 500 rpm resulted in deterioration of emulsion stability and 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 was achieved with an efficiency of about 98.0-99.0% from the basic solution (ammonium carbonate, 0.4 M) within almost 10-20 min.

ACKNOWLEDGEMENTS

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

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