Emulsion-Liquid-Membrane Extraction of Alkali Metals by Nano-baskets

B. Mokhtari*, K. Pourabdollah†

Razi Chemistry Research Center (RCRC), Shahreza Branch, Islamic Azad University, Shahreza, Iran

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 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]-1,3-crowns-4,5 were synthesized, and their inclusion-extraction parameters were optimized including the calixcrown scaffold (**4**, 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 results reveled that under the optimized operating condition, the degree of inclusion-extraction of alkali metals was as high as 98-99%.

Keywords: Nano-baskets, Calixcrown, Emulsion Liquid Membrane, Alkali Metals.

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1. INTRODUCTION

Emulsion liquid membrane (ELM) was invented by Li [1] in 1968 and is known as one of the most promising separation methods for trace extraction of metal contaminants [2] and hydrocarbons [3] owing to the high mass transfer rate, high selectively, low solvent inventory and low equipment cost. Frankenfeld et al. [4] reported that the ELM could be up to 40% cheaper than that of other solvent extraction methods. However, this method has been limited by the emulsion instability [5].

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, organic acids [6], amino acids [7], proteins [8] and antibiotics [9]. Nano-baskets of calixarenes are a versatile class of macrocycles, which have been subject to extensive researches and extractions [10], stationary phases [11], transporters [12] and optical and electrochemical sensors [13] over the past years.

Zinke and Ziegler [14], in the 1940s, discovered that the products possessed cyclic tetrameric structures. Gutsche [15], 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 and crown ethers in their scaffolds.

In this study, four nano-baskets of calixcrown 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.

2. EXPERIMENTAL

2.1 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. 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 ithium chloride, rubidium chloride. hydrochloric acid (1.0 N) 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 diacid calix[4]-1,3-crowns-4,5 [16].

2.2 Analytical instruments

Determinations of alkali metals were accomplished by Dionex DX-120 ion chromatograph. 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

* mokhtari@iaush.ac.ir
† pourabdollah@iaush.ac.ir

was used to manipulate the outputs from the Dionex ion chromatograph. The pH meter was equipped with a Corning 476157 combination pH electrode.

2.3 Preparation and Characterization 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 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.

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). 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.

2.4 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, 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 using a filter paper. The emulsion was demulsified by the freezing. The concentration of alkali metals was analyzed using ion chromatography.

3. RESULTS AND DISCUSSION

In several studies, it was shown that calixcrown 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.

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 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 be equal. 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.

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

calixcrown type	**1**	2	3	**4**	-
calixcrown concentration (wt%)	1	3	**4**	5	10
acid type in strip phase	**H₂SO₄**	HCl	HNO₃	-	-
acid concentration in strip (M)	0.1	**0.2**	0.3	0.4	0.5
base type in feed	NaOH	NH₄OH	Na₂CO₃	**(NH₄)₂CO₃**	-
base concentration in feed (M)	0.1	0.2	0.3	**0.4**	0.5
phase ratio	0.4	0.6	**0.8**	1.0	1.2
treat ratio	0.1	0.2	**0.3**	0.4	-
membrane type	**kerosene**	n-decane	k:d*	-	-
Membrane selectivity					
stirring rate (rpm)	100	200	**300**	400	500
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

3.1 Effect of calixcrown type

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. According to the results, although calixcrown **4** gives higher rate of extraction in the first 10 min compared to calixcrowns **1-3**, it gradually deteriorates with time. Examination of these results indicates that calixcrown **4** was more favorable than calixcrowns **1-3** as emulsifier/carrier. Therefore calixcrown **4** was selected as among all scaffolds.

3.2 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. Further increase of calixcrown concentration decreased the efficiency of extraction, owing to the access of molecular calixcrown in membrane phase. Under the optimum concentration, the molecular form of calixcrown is considered enough for forward extraction. Increasing of calixcrown 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 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 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 been reported by other researchers. 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 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 the lower concentrations are preferred.

3.3 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. 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.

3.4 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, the experiments were performed with various concentrations of sulfuric acid in the range 0.1–0.5 M. 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 decrease due to the less availability of protons for the reaction. 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 $(CalixH_{n+m})^{m+}$, which may not mobilize to the membrane completely at higher acid concentrations. Hence, the extraction will decrease with the more increase in acid concentration.

3.5 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 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, 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. According to this figure, $(NH_4)_2CO_3$ solution was more preferable in making the feed solution since it stabled the emulsions during the extraction process. Therefore, the proper concentration of ammonium carbonate was selected as the best base in the feed phase.

3.6 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 there is difference in the extraction efficiency in the concentration range aforementioned. Obviously, the extraction 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.

3.7 Effect of phase ratio

The phase ratio is defined as the volume of stripping solution to volume of membrane. The phase ratio 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 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.

3.8 Effect of treat ratio

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 revealed 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.

3.9 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 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 tree organic phases on the extraction performance were investigated. Kerosene, n-decane and their

blend 1:1 were investigated as the diluent. According to the results, kerosene was selected as the best diluent in the following experiments.

4. CONCLUSION

The optimum conditions of inclusion ELM process have been determined experimentally and tabulated in Table 1. The highest efficiency for inclusion-extractions was obtained when the acid type and concentration in the strip solution was sulfuric acid (0.2 M). 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. The optimum conditions of both the phase and the treat ratios were determined to be 0.8 and 0.3, respectively. 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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