Transport of K\textsuperscript{+} from Seawater Using Dibenzo-l8-crown-6 via Carbon Nanotube Based Pseudo Supported Liquid Membrane

Ghafoor Mihandoost, Mir Mahdi Zahedi* and Morteza Ziyaadini
Department of Marine Chemistry, Faculty of Marine Sciences, Chabahar Maritime University, P. O. Box: 99717-56499, Chabahar, Iran
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In the present study, the transport of potassium salt as an important agricultural fertilizer is reported through a pseudo carbon nanotube supported liquid membrane using dibenzo-l8-crown-6 as the carrier. Single wall carbon nanotube was utilized as an additive to liquid membrane to form a pseudo support, while the extraction result showed a noticeable increase in the process rate. In order to find the best transport conditions, affecting parameters such as the feed pH and receiving phases, type of membrane solvent, concentration of the carrier, stripping solution conditions, time, and temperature were investigated. In the optimum working conditions and after 80 min, 23.0(±0.1) % of K\textsuperscript{+} from the feed phase (containing K\textsuperscript{+} = 0.01 M, NaCl = 0.01 M, pH = 5.6) across a dichloromethane membrane (DB18C6 = 0.01 M) was transported into the receiving phase (containing HCl 1 M and NaCl = 0.01 M). The selectivity of the method was evaluated by performing the competitive transport experiments on the simulated mixtures containing the main ions with conservative concentration of seawater.

Keywords: Potassium, Seawater, Pseudo supported liquid membrane, Carbon nanotube, Dibenzo-l8-crown-6

INTRODUCTION

Potassium has been extensively used as agriculture fertilizers with an annual consumption of 60 million tons, and its production is known as one of the oldest mineral industries. It is one of the required three nutrient elements (nitrogen, phosphates, and potassium) for plants. K is the electrochemical regulator in the live membrane of cells. So, it is essential for manufacturing fertilizers required to ensure continuous production of crops and hence global food security [1]. Currently, a main contribution of potash needed is supplied through mining; however, most countries in the world do not have reliable and economically sustainable resources of potash minerals. In these countries, the necessity for finding other alternative sources of potassium is inevitable to meet their needs. Meanwhile, the amount of potassium and other useful metals in seawater is very considerable [2,3]. The potassium content in seawater is as high as 0.399 g l\textsuperscript{-1} with total reserves of 550 trillion tons [4].

One cost effective extraction method for separating potassium from seawater could easily provide coastal countries with a large amount of this element. Accordingly, potassium separation from seawater and brines has been reported via a number of different processes including; precipitation and solvent extraction [5], adsorption by Magnetic P zeolites [6], manganese nodules [7], zeolite W by ion-exchange properties [8], K-phillipsite (K-PHI) membrane [9], ionic sieve membrane [10] and liquid membrane separation [11].

Membrane methods has been accomplished to separate the dissolved metals with high efficiency [12-13]. These methods which have been also used in the chemical separations are simple and easy techniques that do not demand much raw materials and operating costs. At the same time, the membrane methods are energy efficient techniques that offer a high pre-concentration factor with a high degree of selectivity [14]. Facilitated liquid membrane transport uses suitable chelates as the carrier [15]. However,
crown ethers have attracted much attention as carrier due to their high selectivity and stability in complexation with alkali metal ions [16]. They include unique complexation characteristic for metal ions. Their size selectivity originates from the correct fit of a metal ion into their cavity [17]. It is mentioned that some of the crown ethers such as dibenzo-18-crown-6 have favorable binding sites for selective complexation with potassium [18,19,20,21,22] making them appropriate carriers for the separation purposes. However, in some of these studies, the focus has been on extracting potassium nitrate ion pair from environmental resources except sea water, which is full of the chloride ions.

Nanomaterials with precise size and geometry have been gained a lot of attention recently [23,24] due to their capacities for utilization in diverse scientific and technological fields i.e., cosmetics, medication, composites and ceramics, pigments, catalysts, and electronic devices [25,26]. Carbon nanotubes are one of the most important and most widely used structures which have been recently discovered. The unique structure of carbon nanotubes, including small dimensions, high atomic scale strengths, surface area, excellent permeability and flexibility, in addition to their high mechanical and thermal stability, have made them suitable for being used in transport processes [27] and it seems that it can be tested as a membrane additive to accelerate their transport rate. The use of nanomaterials such as carbon nanotube in membrane progress has been developed for different purposes. Application of carbon nanotubes as additive in supported liquid membrane in the extraction of europium [28], in cellulose acetate membrane for water desalination [29], and water purification [30] has been reported.

The focus of the present research is on the increased permeability and improved membrane performance. As part of the present research, we have used carbon nanotube as an additive to membrane composition which has created pseudo supported conditions. The aim of the present work is to investigate the extraction ability of potassium ions from seawater via carbon nanotube-based pseudo supported liquid membrane using dibenzo-18-crown-6 as the carrier. Affecting parameters such as the feed pH and receiving phases, type of membrane solvent, concentration of carrier, stripping solution conditions, time, and temperature were studied to achieve the most optimum transport conditions.

In these conditions, the efficiency of liquid membrane transport method in the presence and absence of carbon nanotube is investigated and compared with several synthetic mixture seawater solutions containing different ions with reported conservative concentration.

EXPERIMENTAL

Reagents and Instruments

Dichloromethane, chloroform, carbon tetrachloride as organic solvents of membrane were purchased from Merck (Darmstadt, Germany). These solvents were washed three times with deionized/distilled water to remove the stabilizers and aqueous soluble impurities. Dibenzo-18-crown-6 ether (DB18C6) was purchased from Sigma-Aldrich (Steinheim, Germany). Analytical grade metal salts (most of them chloride as KCl) were purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland) and used for preparing Mg2+, Cr3+ and Na+ solution. Metal ions working solutions were prepared by dilution of their stock solutions in deionized/distilled water. All other chemicals such as hydrochloric acid (HCl), sodium hydroxide (NaOH), sulfuric acid, nitric acid in analytical grade were prepared by dissolving in deionized water. Multi walled carbon nanotube (outside diameter (OD): 10-20 nm (from HRTEM, Raman), inside diameter (ID): 5-10 nm, purity: > 95 wt% (from TGA & TEM)), and single walled carbon nanotube (OD:1-2 nm (from HRTEM, Raman), ID: 0.9-2 nm 1-3 nm (from HRTEM, Raman), purity: Carbon nanotubes >95 wt%) were provided by US NANO.

Concentration of metal ions in the aqueous media was determined using flame photometer spectrometry (Fater Electronic model 620 C, Iran). For separating the two aqueous phases, a transport cell (Fig. 1) was utilized. It is comprised of a cylindrical glass with internal diameter of 3.7 cm and an internal glass tube with a diameter of 2 cm. The temperature of the transport cell was adjusted using ThermoHaak C10 thermostatic water bath. A TPS pH meter model wp-80 (Brisbane, Australia) equipped with a glass combination electrode was used in pH measurements. One ALFA magnetic stirrer was used for stirring the bulked membrane solvent.

Transport Procedure

In transport cell (Fig. 1) whose temperature was kept constant at 30 °C, the feed phase (total volume of 8 ml) contained K$^+$ (0.01 M) and NaCl (0.01 M) was adjusted by HCl solution at pH = 5.6, while monitored by a pH meter. The receiving phase (total volume of 12 ml) was comprised of HCl solution of 1 M. These aqueous phases were separated physically by 17 ml dichloromethane solution of DB18C6 (0.01 M) in the presence of carbon nanotubes as the additive. Facilitated liquid membrane transport process was started by stirring the organic phase (speed of 100 rpm and using of a teflon-coated magnetic bar). After a given time, concentration of potassium in the aqueous phases, was separated and determined by flame photometer spectrometry. The extraction (E %) and stripping percentage (S%) were calculated from the following formulas [31]:

$$E\% = \left( \frac{C_{0f} - C_f}{C_{0f}} \right) \times 100$$

$$S\% = \left( \frac{C_R - C_{0f}}{C_{0f}} \right) \times 100$$

$C_{0f}$ and $C_f$ are initial and final concentrations of K$^+$ in the feed phase and $C_R$ is the concentration of K$^+$ in the receiving phase after transportation.

RESULTS AND DISCUSSION

Effect of the Feed Solution pH on Extraction Efficiency

The influence of feed phase pH on transport of potassium ion as an extraction factor was studied. For this purpose, the pH of feed phase was adjusted in the range of

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**Fig. 1.** PSLM and schematic representation of the ion exchange mechanism.
2-10, using concentrated NaOH and HCl solutions and by the application of a pH meter. The results of potassium extraction in different pH values have been plotted in Fig. 2. As is clear, in pH = 5.6, the extraction percentage of potassium (82%) is maximum compared with other points. Since the dibenzo-l8-crown-6 cavity diameter is not suitable for the proton ion, and because of the ability of H⁺ to pull crown ether to the boundary zone of membrane, it seems that in this pH there is a better potassium ion complexation with dibenzo-l8-crown-6 [18]. Thus, pH of 5.6 was selected as optimum point for future work.

Selection of Membrane Solvent

The right choice of organic solvents plays an important role in liquid membrane. The selection of solvents to be used in the membrane can be performed based on the low volatility and viscosity, suitable dielectric constant, polarity and also the ability to good exchange phase by high distribution coefficient [32]. So, some solvents heavier than water such as carbon tetrachloride, dichloromethane, and chloroform were selected to be studied in pseudo supported liquid membrane (PSLM) procedure. The results of this experiment (Table 1) show that dichloromethane has a higher extraction percentage than the other solvents. Dielectric constants of these solvents changes in order of carbon tetrachloride < chloroform < dichloromethane. It seems that in higher dielectric constant of solvent, the membrane’s ability to get K⁺-DB18C6-Cl⁻ ion pair is better. Also, the viscosity of solvents changes as carbon tetrachloride > chloroform > dichloromethane, which leads to a better membrane mobility by using dichloromethane. Thus, as dichloromethane provides a more suitable condition for the extraction of potassium into the membrane, it was chosen as the optimum solvent of the present study.

Choice of Carrier Ligand and its Concentration

The use of crown ethers as ligands to isolate the alkali metals has been well recorded [18]. In most of these reports [19], the effectiveness of dibenzo-l8-crown-6 (Fig. 1) is mentioned to be appropriate for using as a ligand for potassium ion extraction. Considering the structure and size of the cavity, dibenzo-l8-crown-6 can make a potassium complex with higher selectivity. Dibenzo-l8-crown-6 has a

Fig. 2. Effect of pH on K⁺ transport. Experiment conditions: [K⁺] = 0.01 M, membrane = 0.01 M of DB18C6 in dichloromethane, [Cl⁻] = 0.01, temperature = 30 °C, stripping reagent = HCl 1 M, and extraction time = 80 min.

limited water solubility to prevent carrier loss in the water phases. The rate of cation transport depends on the stability constant values of K$^+$-dibenzo-18-crown-6 complex which needs to be in an optimum range for the suitable extraction, not at higher or lower values [20]. The reported values for the transport rates and stability constants of dibenzo-18-
crown-6 with potassium, compared to sodium and calcium [21], make this ligand suitable carrier in a PSLM system including seawater environment. According to the materials mentioned in the previous section, dibenzo-18-crown-6 was selected as the carrier ligand of PSLM for transporting potassium ions. It should be emphasized that the authors

<table>
<thead>
<tr>
<th>Solvent</th>
<th>E%$^a$</th>
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<tbody>
<tr>
<td>Dichloromethane</td>
<td>82 ± 6</td>
</tr>
<tr>
<td>Chloroform</td>
<td>50 ± 4</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>11 ± 5</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of DB18Crown 6 concentrations in membrane on K$^+$ transport. Experiment conditions: [K$^+$] = 0.01 M, membrane = DB18C6 in dichloromethane, [Cl$^-$] = 0.01, temperature = 30 °C, stripping reagent = HCl 1 M, and extraction time = 80 min.
have devoted all their efforts to optimize the method for extracting potassium from seawater, so there are many differences between the conditions in the present study and the existing reports.

Optimum concentration of the carrier in PSLM is another important factor. In facilitated transport procedure, the carrier forms a complex with the guest cation helping its transport with more selective and higher rate through the hydrophilic membrane [19]. In this part of the experiment, the concentration of dibenzo-l8-crown-6 is evaluated in the range of 0.001-0.1 M. The results (Fig. 3) show that 0.01 M of dibenzo-l8-crown-6 has the best performance and in higher amounts, the effect of ligand concentration on transport is almost constant. Therefore, this concentration is chosen as the optimal amount throughout the rest of the present research.

The Effect of Type and Concentration of the Counter Ion in the Feed

The movement of charged species through a hydrophobic membrane is accomplished by the presence of a macrocyclic ligand acting as a cation carrier. Since macrocyclic ligands are neutral, the cation carries are coupled with a co-anion and go through the membrane to maintain electrical neutrality in the system. Transport rate of the potassium salts (including Cl\(^{-}\), I\(^{-}\), SCN\(^{-}\), NO\(_3\)^{-}) is already studied [20]. In other transport studies using crown ether as carrier [18,19], some of the inorganic and organic anions such as picrate (PA\(^{-}\)), trinitrobenzene sulfonate (TNBS), nitrophenols, etc. have been investigated as the counter anions. According to the reported papers, in the transport of potassium using dibenzo-l8-crown-6 through the membrane, via predicted mechanism of Fig. 1, applying the counter anion is necessary. In the present study, due to the tendency toward potassium separation from seawater and the environmental considerations, important anions in the seawater have been sought as the counter anions. For this purpose, different types of 0.01 M of sodium salts solution such as Cl\(^{-}\), I\(^{-}\), NO\(_3\)^{-}, Br\(^{-}\) and ClO\(_4\)^{-} were applied in the feed phase in the presence of potassium ions to find a better counter ion behavior. According to the results presented in Table 2, in the presence of Cl\(^{-}\), potassium transport efficiency is higher. Due to the presence of a high concentration of Cl\(^{-}\) in seawater (about 55% of the total dissolved solids in seawater is chloride), and its desirable accessibility, it was selected as the counter ion for the transport of potassium through the membrane. In order to determine the optimum concentration of counter ion, NaCl at a concentration range of 0-1 M was tested in the membrane containing dibenzo-l8-crown-6. The results indicate that maximum extraction percentage is 0.1 M. Therefore, this concentration of Cl\(^{-}\) was chosen to be utilized in the rest of the present research. However, additional experiments indicate that higher amounts of chlorine ion do not have a bad effect on the potassium transport process.

The Effects of Type and Concentration of Stripping Reagent on the Receiving Phase and Cell Temperature

The nature and concentration of the stripping agent in the aqueous receiving phase could have a significant effect on the efficiency of the transport of the cations. In the absence of suitable stripping reagent, the transport is negligible and reaches to steady state [32]. The transport of K\(^{+}\) in the above mentioned membrane is based on the reaction between dibenzo-l8-crown-6 as a chelating agent and this cation. The K\(^{+}\)-dibenzo-l8-crown-6-Cl\(^{-}\) complex after passing through the two of aqueous/organic interfaces is transported to the receiving phase. To find the best stripping reagents, 0.1 M of nitric acid, oxalic acid, citric acid, hydrochloric acid, and sulfuric acid were tested and the stripping percentage (S\%) was evaluated (Fig. 4). As a result, it was observed that hydrochloric acid illustrates a better stripping behavior rather than other ones. Optimum concentration of HCl was investigated in a range of 0.0001-2 M and the concentration of 1 M HCl of was chosen to continue the transport study. It seems that H\(^{+}\), by approaching the donor group of dibenzo-l8-crown-6, helps releasing potassium ion in the receiving phase.

The temperature in the liquid membrane transport is an effective factor affecting the kinetic of membrane interface reactions. To study the effect of the temperature on transport, three points at 25, 30 and 35 °C, close to home temperature and lower than solvent boiling temperature, were selected. The results show that, with increasing temperature, both extraction and stripping process are increased, however, due to instability in the
dichloromethane as a membrane solvent, the temperature of 30 °C was selected and set throughout the rest of the present study.

**Table 2.** Effect of the Contour Ion Type.

<table>
<thead>
<tr>
<th>Counter ion</th>
<th>E%</th>
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<tbody>
<tr>
<td>NO₃⁻</td>
<td>43 ± 5</td>
</tr>
<tr>
<td>I⁻</td>
<td>40 ± 1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>85 ± 3</td>
</tr>
<tr>
<td>Br⁻</td>
<td>83 ± 4</td>
</tr>
<tr>
<td>ClO₄²⁻</td>
<td>38 ± 6</td>
</tr>
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*Concentration of salts = 0.01 M.

**Fig. 4.** Effect of stripping reagent type in receiving phase with concentration of 0.1 M for every reagent.

Experiment conditions: [K+] = 0.01 M, membrane = 0.01 M of DB18C6 in dichloromethane, temperature = 30 °C, Feed pH = 5.6, stripping reagent = HCl 1 M, and extraction time = 80 min.

**Effect of Time on Transport Procedure in the Presence and Absence of Carbon Nanotube**

The unique structural features of carbon nanotubes including small dimensions, high atomic scale strengths,
surface area, excellent permeability and flexibility, in addition to their high mechanical and thermal stability, have made them suitable for being used in transport processes [23,33,34]. On the other hand, the process of liquid membrane transport is time consuming, so finding the optimal time [16] and some additive materials which could accelerate the transport, are very important and worthwhile. It seems that the carbon nanotubes are capable of this accomplishment.

In this part of the experiment, the effect of transport time and addition of carbon nanotubes to the liquid membrane on the transport rate are examined. To this end, potassium ions extraction and stripping percentage via time are evaluated in minutes and the results are shown in Fig. 5 in the presence and absence of carbon nanotube. As the results show, maximum extraction and maximum stripping occur respectively within 40 min and 80 min when no additive is used. According to the specifications of the solvent and ligand type, the membrane is the most effective factor in the transport process. Assuming the two-step transition in the membrane, the following equation can be proposed for this operation [35],

\[ K^+ (fp) \xrightarrow{K_s} K^+ L(mp) \xrightarrow{K_e} K^+ (sp) \]

where \( K_s \) and \( K_e \) are stripping and extraction kinetic constants. Therefore, it is necessary to pay attention to these optimum times to achieve an efficient \( K^+ \) transport. It seems that the potassium ion transport into the membrane is a limiting factor which, as we will see, is accelerated by adding single wall carbon nanotubes.

To study the influence of single wall carbon nanotube, in optimum condition of transport, CNT was added into the organic membrane to evaluate its effect on the time of \( K^+ \) transport. To this end, a certain amount of carbon nanotube was added to the membrane solvent. To homogenize the mixture, it was placed under an ultrasonic irradiation for 5 min and a contribution for 10 min with 1000 rpm. After the phase separation, the remaining nanotubes were dried and then weighed to calculate the nanotube amount in the membrane (0.03 mg ml\(^{-1}\) single carbon nanotubes). The results of \( K^+ \) transport experiment in the presence and absence of nanotube are plotted in Fig 5. The figure shows the effects of nanotubes on the extraction and stripping rate (while the best stripping time was 40 min). According to the

![Fig. 5. Effect of time on liquid membrane transport of K\(^+\) in the presence and absence of CNT. Experiment conditions: [K\(^+\)] = 0.01 M, membrane = 0.01 M of DB18C6 in dichloromethane, [Cl\(^-\)] = 0.1 M, temperature = 30 °C, feed pH = 6.2, and stripping reagent = 1 M of HCl.](image-url)
results, single wall carbon nanotube shows a better performance and increases the stripping rate twice as much as the absence of CNT. It seems that by adding the carbon nanotube into the membrane, complex of K\(^{+}\)-dibenzo-18-crown-6-Cl\(^{-}\)is received quicker at the membrane border line. On the other hand, the selectivity study (following section) suggests that there is a little interference in the potassium transport. It should be noted that the multi-wall carbon nanotube was also studied as a membrane additive, but no significant change was observed in the transport rate.

### The Selectivity of Liquid Membrane System

In an optimum working condition, the selectivity of the pseudo supported liquid membrane system for K\(^{+}\) transport in the presence and absence of carbon nanotube was evaluated in several feed mixture solutions containing Ca\(^{2+}\) (450 mg l\(^{-1}\)), Na\(^{+}\) (13680 mg l\(^{-1}\)), and Mg\(^{2+}\) (1433 mg l\(^{-1}\)) ions. Concentrations were chosen near the reported amount of these ions in seawater. Table 3 shows the extraction and stripping percentage of K\(^{+}\) (0.01 M) and foreign cations in optimum transport conditions. Observations show that there is a little interference in the presence of other interfering ions in the receiving phase, and in the presence of carbon nanotubes, the stripping percentage of potassium in the receiving phase has increased without rising the interference of other ions.

### CONCLUSIONS

Currently, most countries in the world do not have...
reliable and economically sustainable resources of potash minerals, and finding other alternative sources of potassium is inevitable to meet the needs especially for agricultural use. Here, the transport of potassium ion from simulated seawater through a carbon nanotube-based pseudo supported liquid membrane was investigated using DB18C6 as a carrier. Operational conditions leading to K⁺ transport established were: 0.1 M of sodium chloride, pH of feed = 5.6, membrane comprised of dichloromethane solution of DB18C6 (0.01 M) containing single wall carbon nanotube, stripping reagent of 1 M HCl, and overall transport time of 40 min. As discussed, the optimized method has a good selectivity for the transport of potassium in the presence of other major ions in seawater, such as sodium, magnesium and calcium. The transport rate of K⁺, especially in stripping, is doubled by using single-wall carbon nanotubes as membrane additive, while the selectivity of the proposed method is not adversely affected. Finally, we can say that the proposed method is simple and has good results for potassium transport with high ability for industrializing.

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REFERENCES


