Separation study of Mg^{+2} from seawater and RO brine through a facilitated bulk liquid membrane transport using 18-Crown-6

Mir Mahdi Zahedi and Somayeh Mohamad Ghasemi

ABSTRACT

A facilitated bulk liquid membrane transport approach is studied for Mg(II) extraction from seawater and reversed osmosis brine simulated media using 18-Crown-6 and dibenzo (DB)-18-Crown-6. The work is based on investigating the experimental parameters affecting the transport efficiency, such as pH of feed and receiving phase, type of membrane solvent, temperature, type and concentration of the carrier, and stripping solution conditions. The transported amount of magnesium ions from feed phase (Mg(II) = 0.059 M, NaCl = 0.01 M, pH = 3.3) across a chloroform membrane (18C6 = 0.001 M) into the receiving phase (SCN$^-$ 0.1 M pH 3) was found to be %97 ($\pm$0.7) after 2.5 hr. The selectivity of the method was evaluated by performing competitive transport experiments on the mixtures containing Ca^{2+}, Na$^+$, K$^+$, and Mg^{2+} ions.

Key words | bulk liquid membrane transport, crown ethers, Mg^{2+}, RO brine, seawater

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INTRODUCTION

Magnesium is the third most plentiful element dissolved in seawater, with an average of 0.13%. Most magnesium and magnesium compounds are produced from seawater, well and lake brines and bitterns (Al-Mutaz & Wagialla 1990), as well as from minerals such as dolomite, magnesite, brucite, carnallite. Elemental magnesium alloys are increasingly used as a lightweight metal in the manufacture of engine parts, jet engines, missiles, and rockets. Likewise, dry magnesium salts and solutions are widely used in industrial, agricultural, medical, and environmental contexts (Kramer 2000).

The most common method for the initial separation of magnesium from seawater and brines is solar evaporation which induces a chemical precipitation. Solar evaporation is usually applied for processing highly concentrated brines such as the Dead Sea and Great Salt Lake waters

(Epstein 1976; Tripp 2009). This method is based on the fact that MgCl$_2$ is more soluble than NaCl. The chemical precipitation method is typically applied to low concentrated brines, such as seawater (Bhatti *et al.* 1984).

Traditional methods of magnesium production, i.e., processing of the hydromineral sources, despite their profitability, do not satisfy increasing ecological standards (Mero 1965). Consequently, new alternative ecological clean technologies, based on ion exchange of desalinated seawater with Mg^{2+} ions (Birnhack & Lahav 2007), nanofiltration/crystallization process (Drioli *et al.* 2004; Lahav *et al.* 2013) from desalination brines, precipitation of Mg(OH)$_2$(s) on the surface area of self-synthesized magnetite (Fe$_3$O$_4$) micro-particles (Lehmann *et al.* 2014), and use of positively charged polyamide composite nanofiltration hollow-fiber membranes for lithium and magnesium separation (Li *et al.* 2015) have been developed. Furthermore, as the worldwide need for metals increases and the grades of ore decreases, the incentive to find more effective and efficient separation and purification methods grows.

Extraction techniques for metal separation (Mohite & Khopkar 1988) are of increasing interest due to the importance of environmental protection problems. In recent years, the use of various types of liquid membranes has attracted increasing attention due to their ability for selective metal ions separation in aqueous solutions (Danesi et al. 1981; Kamiński & Kwapiński 2000). Transport of metal ions across a membrane has an important role in industrial processes and has useful practical applications in separation science (Jafari et al. 2009). This type of membrane has been widely utilized for carrier facilitated separations and acquired significant importance for its use in separation, purification, or analytical application in diverse areas like water and waste water treatment (Shamsipur et al. 2010; Dalali et al. 2012). In liquid membranes, the extraction, stripping, and regeneration operations are combined in one single step which has the advantages of low cost and low energy consumption (León & Guzmám 2004; Revathi Reddy et al. 2010).

It seems that the main challenge to do an efficient liquid membrane transport process with unlimited feed like seawater (containing the macro components of Mg^{2+}, Ca^{2+}, K$^+$, and Na$^+$) is finding alternative carriers, and membrane conditions (Rounaghi et al. 1997), such as solvent type, stripping reagent, etc. Effective transport requires the carrier, which is distributed primarily to the membrane phase, to provide a selective complex with the desired metal ion (Kikuchi & Sakamoto 2000). Macrocyclic ligands, i.e., crown ethers as carrier (Izatt et al. 1986), have been developed to be used in several transport procedures for their selectivity to cation ions. In some studies (Heo 2012), selectivity of crown ethers to alkaline and alkaline earth ions is mentioned.

In this study, an attempt has been made to use facilitated bulk liquid membrane (BLM) transport using crown ethers 18-Crown-6 and DB-18-Crown-6 to find optimum conditions, such as pH, temperature, type and concentration of the carrier, solvent and ionic strength for extraction of magnesium ion from the simulated seawater media. Results show that the best extraction of magnesium was carried out at an acidic feed and received phase using 18-Crown-6 dissolved in chloroform as transport membrane in the presence of 0.01 M of sodium chloride. The selectivity of method was evaluated by performing competitive transport experiments on simulated seawater mixtures containing Ca^{2+}, Na$^+$, K$^+$, and Mg^{2+} ions.

EXPERIMENTAL

Reagents

Dichloromethane, chloroform, and carbon tetrachloride as organic solvent membrane were purchased from Merck (Darmstadt, Germany). These solvents were washed three times with distilled water to remove the stabilizers and impurities. 18-Crown-6 ether (18C6) and dibenzo-18-Crown-6 ether (DB18C6) were purchased from Sigma-Aldrich (Steinheim, Germany). Analytical grade metal salts (mainly chloride such as MgCl$_2$.6H$_2$O) were purchased from Merck or Fluka (Buchs, Switzerland) and used for preparation of Mg^{2+} Ca^{2+}, K$^+$, and Na$^+$ stock solution. Metal ions working solutions were prepared by dilution of their stock solutions in deionized water. Solutions of ethylene diamine tetra acetic acid (EDTA for metal ion standardizing), hydrochloric acid (HCl), and sodium thiocyanate were prepared by dissolving respective analytical reagent grade chemicals in deionized water.

Transport procedure

For separating the two aqueous phases, one transport cell (Figure 1), including a cylindrical glass with inside diameter of 3.7 cm and holding a glass tube inside it with a diameter of 2 cm (Jabbari et al. 2001) was utilized. By placing it in a thermostated water bath, the temperature of the transport cell was kept constant at 30 °C. A feed phase (total volume of 5 mL) was included of Mg^{+2} (0.059 M) and NaCl (0.01 M), and adjusted by HCl solution at pH = 3.3. The receiving phase (total volume of 5 mL) was included of SCN$^-$ solution (0.1 M) and set at pH of 3. These aqueous phases were separated by 20 mL chloroformic solution of 18C6 (0.001 M). Facilitated BLM transport work was performed by stirring the organic phase with a speed of 100 rpm using a Teflon-coated magnetic bar. After a given time, concentration of Mg^{2+} in the aqueous phases was separated and determined by EDTA titration to end point with Eriochrome Black T (pH = 10).
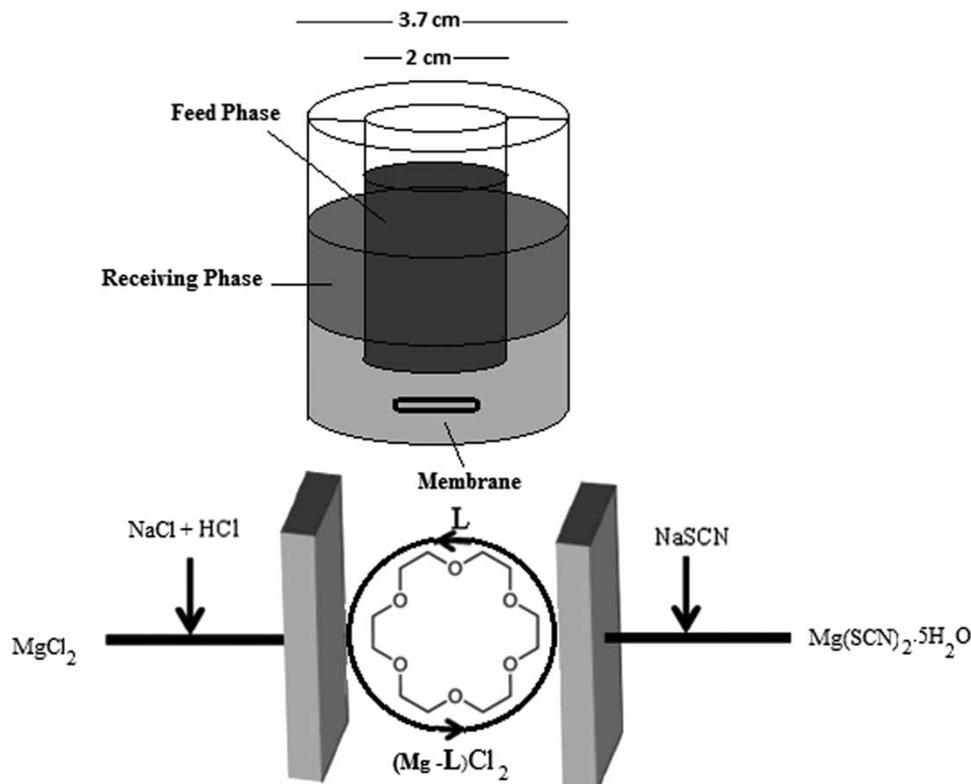
Figure 1 | BLM and schematic representation of the ion exchange mechanism.

RESULTS AND DISCUSSION

Selection of membrane solvent

The main objective of this study is identification of the best conditions for magnesium separation from seawater and reversed osmosis (RO) brine. Organic solvents have an important role in BLM transport (Ajwani et al. 2012). According to the high concentration of magnesium ions in these samples and in order to prevent evaporation of the solvent, the organic phase with a higher density was selected. The organic phase should include features such as low volatility and viscosity, suitable dielectric constant, polarity and also the ability for a good exchange phase with high distribution coefficient (Zidi et al. 2011). Therefore, several heavy solvents, such as dichloromethane, chloroform, and carbon tetrachloride were tested. Results of this study are shown in Table 1. It appears that suitable dielectric constant and polarization ability of chloroform leads to better behavior in magnesium

Table 1 | Effect of membrane solvent type on transport procedure

%E	Solvent
16.95	Dichloromethane
20.34	Chloroform
8.47	Carbon tetrachloride

Experiment conditions: $[Mg^{+2}] = 0.059$ M; temperature $= 25\,^{\circ}$C; feed pH $= 4$; stripping reagent $= 0.1$ M of SCN$^-$; pH of the receiving solution $= 3$; extraction time $= 2$ hr.

transport than other solvents. Extraction percent (%E) and stripping (%S) are calculated from the following formulas (Fakhari et al. 2006):

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

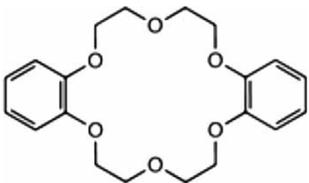where, C_{0f}, C_f are initial and final concentration of Mg^{2+} in the feed phase and C_R is concentration of Mg^{2+} in the receiving phase after the transport process.

The type and concentration of the carrier

The type and concentration of the carrier for metal ion transporting is another important factor that should be selected properly. In facilitated BLM transport, the carrier forms a complex with the guest cation and helps it to transfer through the hydrophilic membrane (Ajwani *et al.* 2012). For this purpose, the behavior of two crown ethers (18-Crown-6 and DB-18-Crown-6) was studied and the results are shown in Table 2. It seems the greater flexibility of 18-Crown-6 works better than the hydrophobicity of DB-18-Crown-6 (possessing two benzenes) in the chloroform membrane for magnesium transport. It should be noted that DB-18-Crown-6, due to possessing two benzene groups, is more hydrophobic than 18-Crown-6. For the same reason, it is easier for 18-Crown-6 ether to adjust its structure for better reacting with Mg^{2+}, and this leads to its greater flexibility.

In the next stage of this study, the concentration of 18-Crown-6 as carrier in the range of 0.0001 to 0.1 M was evaluated. Results show that 0.001 M with an extraction of 20.33% has the best performance. It seems that at higher concentration of carriers, due to increasing irreversible interaction between metal cations and 18-Crown-6 in membrane, the extraction efficiency was decreased. In the facilitated BLM transport process, the complexation reaction between the carrier and the cation should not be so

strong, since its delivery is not done in receiving phases. A high concentration of carrier ligand leads to irreversible reaction with the metal ions and the transfer process will be stopped.

Effect of type and concentration of the counter ion

Transport of Mg^{2+} across the membrane via the predicting mechanism of Figure 1, needs to apply a contour ion. For this purpose, different types of 0.01 M salt solution, such as KCl, KI, $KClO_3$, $NaNO_3$, NaBr, and NaCl, were studied against 0.059 M of magnesium ions to find a better contour ion. According to the results of Table 3, in the presence of Br^-, magnesium transport is higher. However, due to economic reasons and the abundant presence of Cl^- in seawater and RO brine, which are our target samples, Cl^- was selected as the contour ion. In order to determine the optimum concentration of contour ion, NaCl at a concentration range of 0.0001–2 M was tested in the membrane containing 18-Crown-6. As a result (Figure 2), the maximum extraction percent of magnesium ion was found at the concentration of 0.01 M of NaCl.

Effect of pH of feed solution on extraction efficiency

At this stage, the pH of the feed phase was adjusted in the range of 1–10, using concentrated NaOH and HCl solutions. Results of magnesium ions transport in different pH values are plotted in Figure 3. As is clear, at pH = 3.3, the extraction percent of magnesium (22.8%) is

Table 2 │ Effect of carrier type, tested concentration is 0.01 M in chloroform

%E	Structure	Crown type
11.86		DB18C6
18.36		18C6

Experiment conditions: $[Mg^{+2}]$ = 0.059 M; membrane solvent = chloroform; temperature = 25 °C; feed pH = 4; stripping reagent = 0.1 M of SCN^-; pH of the receiving solution = 3; extraction time = 2 hr.

Table 3 │ Effect of type of the counter ion

%E	Contour ion (0.01 M)
16.59	KCl
16.59	KI
20.34	$KClO_3$
15.25	$NaNo_3$
22.03	NaBr
20.34	NaCl

Experiment conditions: $[Mg^{+2}]$ = 0.059 M; membrane = 0.001 M of 18 crown 6 in chloroform; temperature = 25 °C, feed pH = 4; stripping reagent = 0.1 M of SCN^-; pH of the receiving solution = 3; extraction time = 2 hr.
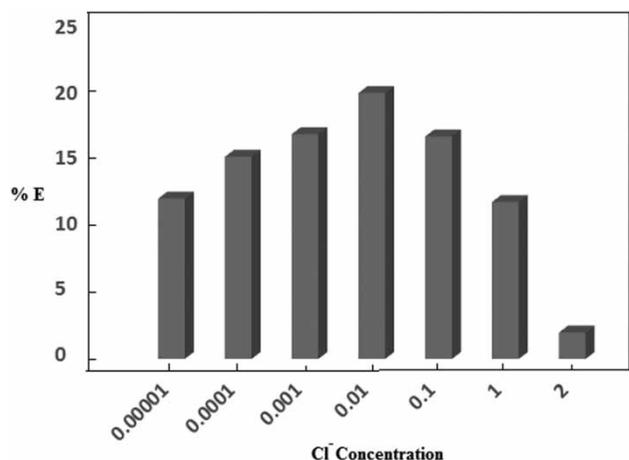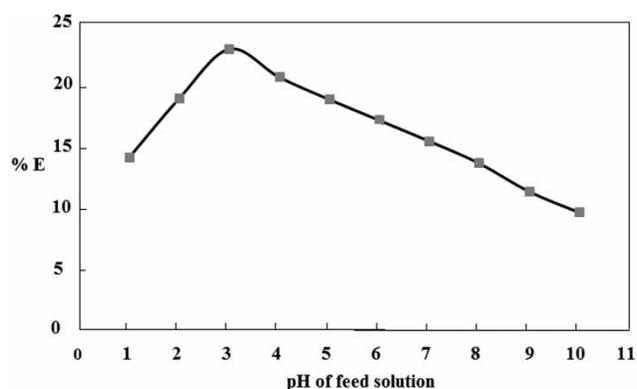
Figure 2 | Effect of Cl⁻ concentration in feed phase, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; temperature $= 25\,^{\circ}$C, feed pH $= 4$; stripping reagent $= 0.1$ M of SCN⁻; pH of the receiving solution $= 3$; extraction time $= 2$ hr.

Figure 3 | Effect of feed pH on Mg^{2+} transport, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; $[Cl^-] = 0.01$ M; temperature $= 25\,^{\circ}$C; stripping reagent $= 0.1$ M of SCN⁻; pH of the receiving solution $= 3$; extraction time $= 2$ hr.

maximum compared with the other points. This is due to the ability of H^+ to pull crown ether to the boundary zone of the membrane, and the increase of Cl^- for the contour ion role. Therefore, this pH was selected as the optimum point for future work.

The effects of type and concentration of stripping reagent in receiving phase

Transport of Mg^{2+} in the mentioned membrane is based on reaction between 18-Crown-6 as a chelating agent and this cation. The complex after passing through the

aqueous/organic interface is transferred to the receiving phase, but in the absence of stripping reagent, transport is negligible. For this purpose, the effect of several stripping reagents (0.1 M of EDTA, SCN⁻, sodium citrate, nitric acid, oxalic acid, and citric acid) on the stripping percent (%S) was studied. Figure 4 presents the results of this experiment, which accordingly show SCN⁻ with the best behavior as stripping reagent. To find the optimum concentration of SCN⁻, its concentration was investigated in a range of 0.0001–2 M and a concentration of 0.1 M was chosen as the optimum amount.

Effect of pH of receiving phase on stripping process

Here, due to the importance of the role of pH of the receiving phase on the stripping process, this parameter was adjusted at different amounts by using concentrated NaOH and HCl solutions in the presence of 0.1 M SCN⁻ as the optimum stripping reagent. Results of this study are shown in Figure 5, and as is clear, the best stripping percent was obtained at pH $= 3$. Therefore, this pH was selected as the optimum pH of the receiving phase. It seems that the main role of acidic media is establishing a tendency for the metal complex to be present between the aqueous/ organic boundary zone.

Effect of time and cell temperature on transport

Since BLM transport is time-consuming, finding the optimal time for the work is very important. Figure 6 shows the
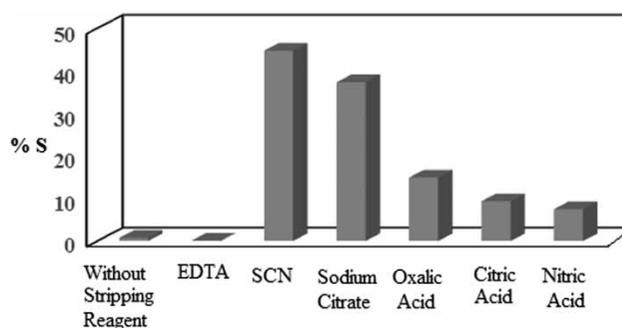

Figure 4 | Effects of type of stripping reagent in receiving phase with concentration of 0.1 M for every reagent, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; $[Cl^-] = 0.01$ M; feed pH $= 3.3$; temperature $= 25\,^{\circ}$C; pH of the receiving solution $= 3$; extraction time $= 2$ hr.
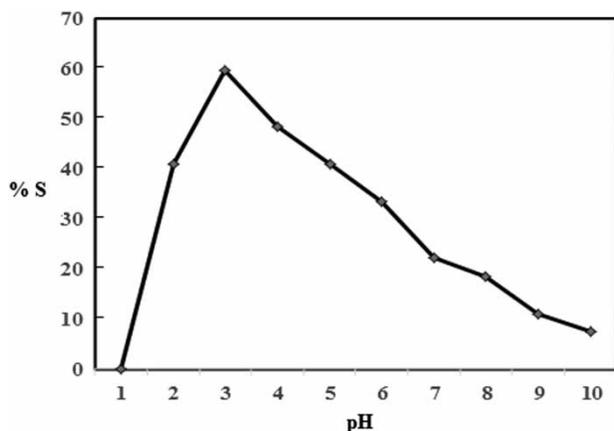
Figure 5 │ Effect of receiving pH on Mg^{2+} stripping, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; $[Cl^-] = 0.01$ M; feed pH $= 3.3$; stripping reagent $= 0.1$ M of SCN^-; temperature $= 25\ ^\circ$C; extraction time $= 2$ hr.

Figure 6 │ Effect of time on BLM transport of Mg^{2+}, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; $[Cl^-] = 0.01$ M; feed pH $= 3.3$; stripping reagent $= 0.1$ M of SCN^-; pH of the receiving solution $= 3$; temperature $= 25\ ^\circ$C.
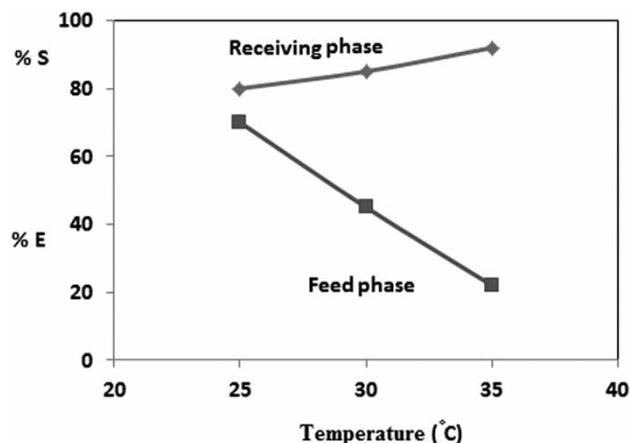

Figure 7 │ Effect of temperature on BLM transport of Mg^{2+}, experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18-Crown-6 in chloroform; $[Cl^-] = 0.01$ M; feed pH $= 3.3$; stripping reagent $= 0.1$ M of SCN^-; pH of the receiving solution $= 3$; extraction time $= 2.5$ hr.
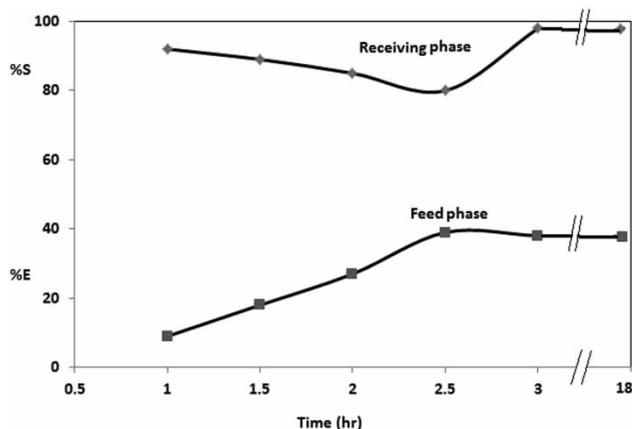
Table 4 │ Selectivity study of BLM transport of Mg^{2+} in several interference mixture simulated seawater

No.	Mixture	% Transported into receiving phase
1	Mg^{2+}	98
	Ca^{2+}	nd
2	Mg^{2+}	98
	Na^+	7.8
3	Mg^{2+}	98
	K^+	2.1
4	Mg^{2+}	97
	Ca^{2+}	nd
	Na^+	8.3
	K^+	3.7

Experiment conditions: $[Mg^{+2}] = 0.059$ M; membrane $= 0.001$ M of 18 crown 6 in chloroform; $[Cl^-] = 0.01$ M; feed pH $= 3.3$; stripping reagent $= 0.1$ M of SCN^-; pH of the receiving solution $= 3$; extraction time $= 2.5$ hr. nd: not detected.

changes in extraction and stripping percent of magnesium ions via time in hours. As can be seen, maximum extraction and stripping efficiency can be achieved at 2.5 hours and at higher times there are no great changes. Therefore, this time was selected for further work.

Temperature of the transport cell is the next factor whose effect was investigated at the three points of 25, 30, and 35 °C. To do this work, the transport cell was inserted into a water bath and the results of this study are plotted in Figure 7 for the feed phase as extraction percent and receiving phase as stripping percent.

Selectivity of BLM system

As the aim of this study was separation and extraction of magnesium ion from seawater and RO brine, the selectivity of the BLM system was evaluated by Mg^{2+} transport studies in the presence of Ca^{2+} (450 mg/L), Na^+ (13,680 mg/L), and K^+ (800 mg/L) ions in the feed solution close to the reported concentration of these ions in seawater. Table 4 shows the percentage transport of Mg^{2+} (0.059 M) and these cations into the receiving phase. As is observed, in the absence of

any masking agents, the interfering effects of these foreign metals ions are low.

CONCLUSIONS

As mentioned before, with the increasing consumption of metals such as magnesium, extraction has become important, especially from the easy to access source, seawater. Here, a facilitated BLM transport method is presented for extraction of Mg(II) from simulated seawater using 18-Crown-6 as carrier. The operational conditions leading to Mg(II) transport were established as: 0.01 M of sodium chloride, pH of feed = 3.3, membrane consisting of chloroform solution of 18C6 (0.001 M), 0.1 M SCN$^-$ as stripping reagent and pH = 3 in the receiving phase and overall transport time of 2.5 hours. Despite the good results of the selectivity study of the method in the mixture solutions, it seems we need to find a more selective carrier or extraction condition for magnesium, even if its extraction efficiency is lower, because the used feed phase material (seawater) is completely unlimited.

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