



Removal of NaCl using facilitated up-hill transport through bulk liquid membranes containing dibenzo-18-crown-6

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ABSTRACT

Desalination using liquid membranes (LMs) has been investigated in our laboratory using emulsion, supported and flowing LMs. However, bulk liquid membranes (BLMs) have not yet been applied as is clear from the literature cited. Accordingly, in the present work, the aforementioned technique was investigated for removal of sodium chloride from solutions of different concentrations as an attempt for desalination. Variables investigated included: type and quantity of LM, quantity of mobile carrier (MC) in LM, and type and quantity of sequestering agent in receptor phase (RP). Results indicated that: a mixture of 1:1 b.v. dichloroethane (DCE) plus chlorobenzene (CB) was a better LM than CB alone, and that DCE was almost equivalent to nitrobenzene (NB). As to the effect of sequestering agent, soluble starch gave better complexation with NaCl than sorbitol in the RP. It was also shown that the presence of the selected MC was efficient. An optimum quantity of MC led to the highest percentage of extraction of NaCl. The smaller volume of LM leads to higher extraction due to shorter diffusion path of the complex of NaCl plus MC through the LM. The highest extraction obtained was about 75%.

Keywords: Bulk liquid membranes; Crown ether (dibenzo-18-crown-6); Chlorobenzene; Dichloroethane; Nitrobenzene; Facilitated up-hill transport

1. Introduction

In recent years, membranes and membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact. Today membranes are used on a large scale to produce potable water from seawater by reverse osmosis, to clean industrial efflu-

ents and recover valuable constituents by electro dialysis, to fractionate macromolecular solutions in the food and drug industry by ultrafiltration, to remove urea and other toxins from the blood stream by dialysis in an artificial kidney, and to release drugs such as scopolamine, nitroglycerin, etc. at a predetermined rate in medical treatment [1].

Liquid membranes (LMs), however, have gained wide interest since their discovery by Li [2], since they

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offer great potential and merits compared to solid membranes, such as higher permeability, simplicity in separation, higher selectivity, low energy consumption, and absence of pores to be blocked or fouled as in solid membranes. They have been shown to have great potential for wastewater treatment [3–10], separation of hydrocarbons [11–14], hydrometallurgy [15–20], removal of metals [21,22], and in biotechnological and biomedical applications [23,24]. LMs, however, cannot be fouled by pore blocking or adsorption of foulant, and are cost effective since they consume little energy while permitting high rates of mass transfer than solid membranes. They can be mainly divided into emulsion-(ELMs), supported-(SLMs), and bulk-(BLMs) LMs. The former suffer from emulsion instability, swelling of the internal phase, and difficulty of breaking the emulsion following extraction operation.

In general, no literature cites desalination of seawater by LMs, except by Naim [25] and by Naim and Moneer by SLM and flowing LM [25–27], respectively. However, numerous work on the transport ability of various cations through bulk liquid membranes (BLMs) containing mobile carriers (MCs) has been done. Izatt et al. [28] investigated the cation fluxes of binary cation mixtures in water–chloroform–water BLM systems using different macrocyclic ligands as carriers for the separation of silver ion. The stabilities of the cation–carrier complexes were found to significantly influence the flux of single cations through the LM, and a very stable complex results in extraction of the cation from the DP, but little, if any release of it to the receptor phase (RP), and therefore the movement of the cation through the membrane may be blocked. A certain range existed for the values of the equilibrium constants within which maximum transport occurs. Frensdorff [29] provided a quantitative measure of the strength of complexing in solution as a function of cyclic polyether (MC) structure, cation size and type, and solvent. He proved that there is an optimum ring size for different ions depending on their size. Lamb et al. [30] studied the effects of salt concentrations, in the dilute ranges, and type of anion, on the rate of carrier-facilitated transport of metal cations through BLMs containing crown ethers. They stated that since macrocyclic ligands are neutral, the cation carries its co-anion with it across the membrane to maintain electrical neutrality in the system, which was also confirmed by Igawa et al. [31] and Dermeni et al. [32]. The rate of cation transport through the membranes by macrocyclic ligands has been shown to be influenced by the nature of the salt anion [30–33]. It is worth mentioning that chloroform was the LM of choice in many lab investigations [26,28,33]. As Pederson [34] has observed, complexing is expected to be

weak when the polymer ring is either too small for the cation or too large compared to the cation size.

Optimal application of BLM technology in special aspects requires detailed knowledge of their mechanism of action scale [35–40]. The large number of publications concerning BLMs was focused on systems in which metal ions are being removed mainly for economical reasons and also carried out to determine the transport mechanism showing their importance in separation [35–40].

Misra and Sharma [41] studied the extraction and carrier facilitated transport of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} picrates, dinitrophenolates, orthonitrophenolates, and thiocyanates using triethylene glycol monomethyl ether as a carrier through chloroform, 1,2-dichloroethane (DCE), and carbontetrachloride BLMs. K^+ and Ca^{2+} were selectively extracted into the organic phase over Na^+ and Mg^{2+} . They found that the ionophore is an efficient carrier for transport of Na^+ and Ca^{2+} over K^+ and Mg^{2+} . Higher extraction of cations was observed in 1,2-DCE than in chloroform and carbon tetrachloride. They also found that the anion has no effect on extraction and transport of cations. This ionophore is an efficient extractant and carrier for transport of both alkali and alkaline earth metal ions.

Fluxes and selectivities for competitive alkali metal cation transport across BLMs by the lipophilic crown ether carboxylic acid carrier syn-(octyl)dibenzo-16-crown-5-oxyacetic acid have been determined in a variety of chlorinated hydrocarbon and aromatic hydrocarbon solvents by Bartsch et al. [42]. The membrane solvents used were: dichloromethane, chloroform, carbontetrachloride, 1,2-DCE, 1,1,1-trichloroethane, *o*-dichlorobenzene, toluene, and *p*-xylene. The total alkali metal cation and Na^+ fluxes, as well as the Na^+/K^+ and Na^+/Li^+ transport selectivity ratios, are compared with selected properties of these organic solvents using the Schmidt, Swain, Kemper-Palm and Kamlet-Taft models. The best correlations were obtained for the Na flux and Na /K transport selectivity.

A kinetic study of the facilitated transport of sodium and chloride ions through BLMs containing, respectively, di(2-ethylhexyl)phosphoric acid and tri-n-octyl methyl ammonium hydroxide as carriers, and using, respectively, hydrogen and hydroxyl ions as counter-ions in the product phase, is described by León et al. [43]. The authors found that after 24 h, the ion content of the DP was reduced by more than 95% in both cases, obtaining recoveries in the RP of 81% for sodium ion and 89% for chloride. The transport kinetics was analyzed by means of a kinetic model involving two consecutive irreversible first-order reactions. The rate constants of the extraction and

stripping reaction were experimentally determined. Model curves of time dependence for the reduced concentrations of sodium and chloride ion in feed, membrane, and product phases showed good agreement with experimental data.

Altin et al. [44] studied the effects of the RP and the DP properties on sodium ion transport in BLM system. They used toluene and a mixture of toluene–dichloromethane (90–10% v/v) containing 1×10^{-3} M dibenzo-18-crown-6 as the membrane. In order to examine the effects of different RP, firstly H_2SO_4 , HCl , HNO_3 , CH_3COOH , and distilled water were used as RP. Furthermore, the experiments were performed by using various acid concentrations such as 2, 0.2, and 0.02 M of acids, as the RP. They also studied the effect of DP on sodium ion transport. For this examination, Na_2SO_4 , NaNO_3 , NaOH , and NaCl were applied. And to determine the effect of the DP concentration, the experimentation was performed using 1.08×10^{-2} , 2.17×10^{-2} , 3.26×10^{-2} , and 4.34×10^{-2} M concentrations of Na^+ in the form of NaCl . It was determined that the type and the concentration of the RP and the DP solutions were significant for transport efficiency in LM systems. They also found that the most efficient transport was obtained by applying 2 M H_2SO_4 and 2.17×10^{-2} M Na^+ in the form of NaCl . It was observed that there was a significant effect of the anion attached to the cation on transport efficiency.

Based on what has been aforementioned, in order that NaCl diffuses through the LM, a suitable MC has to be added to the LM to facilitate its transport under favorable conditions through the membrane, and then the transported NaCl has to be sequestered in the RP by a suitable trapping agent as used in the present work.

2. Experimental

2.1. Materials used

Sodium chloride (Analar product of Fluka, USA) as DP; chlorobenzene (CB), nitrobenzene (NB), and DCE (products of BDH laboratory reagents, England) as LMs; dibenzo-18-crown-6 (product of Fluka, USA) as MC; sorbitol (product of Republic Co., Egypt) and soluble starch (product of Fluka, USA) as sequestering agents; distilled water as RP were used.

2.2. Apparatus

BLM is the simplest design for performing LM processes. The device is made from Pyrex glass and is divided in two parts as illustrated in Fig. 1: a common

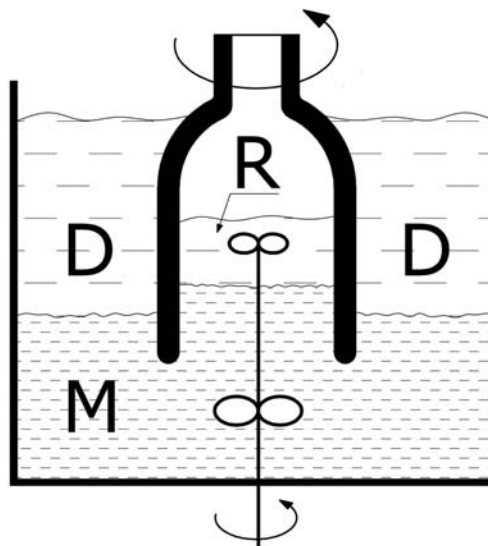


Fig. 1. Schematic diagram of apparatus, D: donor phase; R: receptor phase; and M: membrane phase.

part, containing the membrane liquid and a second part, in which, the donor solution and the receptor solution are separated by a solid impermeable barrier. The membrane liquid contacts with the two other liquids and affects the transfer between them. All three liquids are stirred with an appropriate intensity avoiding mixing of both DP and RP [45].

2.3. Methods

The apparatus as described earlier consists of 50 mL distilled water as RP, 50 mL of aqueous sodium chloride solution as DP, and 50 or 100 mL of an organic LM phase, which completely separated both RP and DP from each other. The NaCl concentration is measured using a conductivity meter (Model: 3200 Conductivity Instrument-YSI, USA).

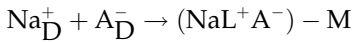
2.4. Variables investigated

The rate of diffusion and transport of Na^+ and Cl^- ions is expected to be affected by numerous variables which are: type and quantity of LM used, quantity of MC (complexation agent) to LM, and type and quantity of additive (sequestering agent) to RP.

2.5. Kinetic procedure

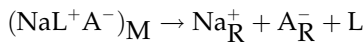
In this study, the transport occurring in the BLM system is a carrier-facilitated up-hill simple transport. This type of transport occurs in four steps:

(1) The complex formation of carrier molecules with sodium ions at donor–membrane phase interface (D/M).



(2) Transport of the complex towards membrane–receptor phase interface (M/R) due to concentration gradient.

(3) Decomposition of the complex at membrane–receptor phase interface (M/R).



(4) Back diffusion of free carrier molecule to donor–membrane interface (D/M). where L is macrocycle ligand and A^- is anion.

In this study, the nonsteady-state kinetics approach was applied similarly to kinetic analysis of BLMs in many other studies [46–50]. In this approach, it was assumed that consecutive irreversible first-order reaction occurred in the (carrier-facilitated)-LM systems Eq. (1).



where D , M , and R represent the donor, the membrane, and the RPs, respectively.

At time t , the sodium ion concentration in donor, membrane, and RPs is C_d , C_m , and C_r , respectively. Since the dimensionless concentration changes are very small, reduced concentrations (R) are used for practical reasons and defined as:

$$R_d = \frac{C_d V_d}{C_{d0} V_{d0}}, \quad R_m = \frac{C_m V_m}{C_{d0} V_0}, \quad R_r = \frac{C_r V_r}{C_{d0} V_0} \quad (2)$$

where C_{d0} is the initial concentration of sodium ion in DP at $t=0$. Then, the material balance equation can be written as:

$$R_d + R_m + R_r = 1 \quad (3)$$

The following kinetic equations can be written by using the above kinetic analysis:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (4)$$

$$\frac{dR_d}{dt} = k_1 R_d - k_2 R_m \quad (5)$$

$$\frac{dR_r}{dt} = k_3 R_m \equiv J_r \quad (6)$$

If the differential Eqs. (4)–(6) are integrated, the following equations are obtained [2]:

$$R_d = \exp(-k_1 t) \quad (7)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (8)$$

$$R_r = 1 - \frac{1}{k_3 - k_1} [k_3 \exp(-k_1 t) - k_1 \exp(-k_3 t)] \quad (9)$$

The maximum value of R_m ($dR_m/dt=0$) can be written as:

$$R_m^{\max} = \left(\frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)} \quad (10)$$

If the logarithm of Eq. (10) is taken and the result is rearranged, the following equation is obtained:

$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2} \quad (11)$$

In order to obtain the values of the parameters, a nonlinear numerical analysis is carried out by a BASIC iteration program. The membrane entrance rate constant k_1 is obtained by using Eq. (7). Then, the membrane exit rate constant k_2 and k_3 are obtained by using Eqs. (8) and (9).

3. Results and discussions

The present work deals with removal of sodium chloride from solutions of different concentrations using the BLM technique. Different variables were investigated for their effect on the degree of the removal, which included: type and quantity of organic BLM, type and quantity of additive to RP, quantity of MC, and type and quantity of LM. The results were plotted as weight of NaCl solution in both DP and RP on the ordinates vs. time of operation on the abscissa. The weight of NaCl in the LM was computed by conducting an overall material balance between the three different phases constituting the system.

3.1. Effect of volume of LM and the presence of sequestering agent in RP

Fig. 2 which explains the results of two experiments, in both of them 1,2 DCE was used as LM and

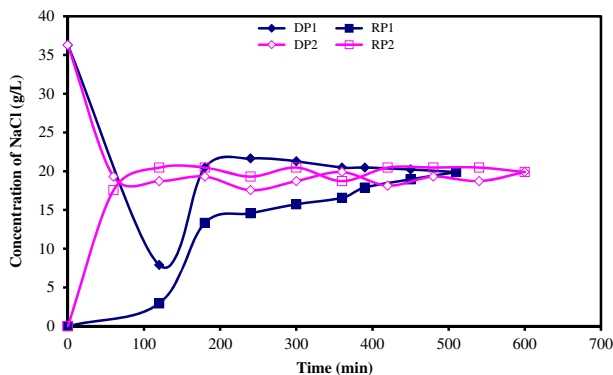


Fig. 2. Effect of volume of LM, $C_i=36.27$ g NaCl/L, DP=50 mL, RP₁=50 mL H₂O+3 g sorbitol, LM₁=100 mL DCE, RP₂=50 mL H₂O, and LM₂=50 mL DCE.

3 g of sorbitol was added to RP in the first experiment while no sorbitol was added to RP in the second one. In each experiment, volume of DP was 50 mL, but LM was 100 and 50 mL respectively, while C_i in both was 36.27 g NaCl/L solution. In experiment 1, it was observed that the rate of drop of concentration in the DP was great at first then smoothed out, while at the same time the concentration of NaCl in the RP increased simultaneously but at much lower rate proving that diffusion in the LM was slow due to two reasons: that the volume was 100 mL which would obviously need more time for the NaCl to diffuse through from the DP to RP (longer diffusion path), in addition, there was no MC in the LM which should have assisted in more rapid diffusion. After prolonged time, diffusion continued from the LM so the concentration increased on prolonged stirring to equal almost that of the DP. Later on, the DP slightly decreased while the RP simultaneously increased giving a slightly higher concentration than that of the DP meaning that complete removal of NaCl took place but needed improvement in the experimental conditions.

In experiment 2, due to LM being only 50 mL, this caused the initial drop in concentration to be faster than in experiment 1 due to the shorter diffusion path. The extraction in this case was over 50%. A final observation is that the concentration of NaCl in the LM was steadier in this experiment and was almost zero throughout the experiment which lasted for 600 min due to the aforementioned explanation.

3.2. Effect of adding starch in RP

The effect of addition of 1 g soluble starch as sequestering agent in the RP is illustrated in Fig. 3. The figure indicates that more rapid mass transfer

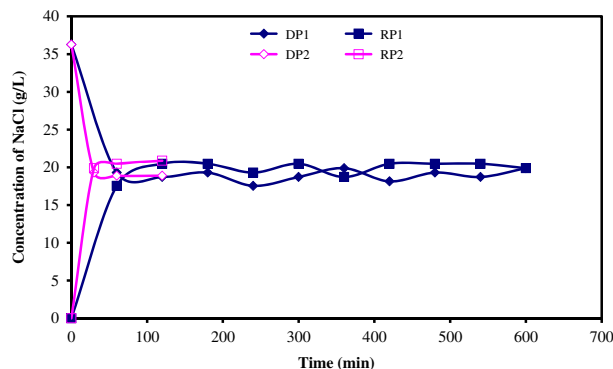


Fig. 3. Effect of adding starch to RP, $C_i=36.27$ g NaCl/L, DP=50 mL, RP₁=50 mL H₂O, LM₁=50 mL DCE, RP₂=50 mL H₂O+1 g soluble starch, and LM₂=50 mL DCE.

took place in the presence of soluble starch because it can form complexes with NaCl through a coordinate bond between the latter and the OH groups [51]; thus extraction increased to about 65% which took place in only 120 min.

3.3. Effect of quantity of MC in LM:

3.3.1. Effect of presence of small quantity of MC in LM:

Fig. 4 confirms that the presence of a small amount of crown ether causes rapid mass transfer to take place from DP to RP due to a great number of complexation sites available in the 0.3 g crown ether used. It should be noted that had soluble starch been used instead of sorbitol in the RP, stronger coordinate bonds between the hydroxyl groups and the Na ions would have taken place [51].

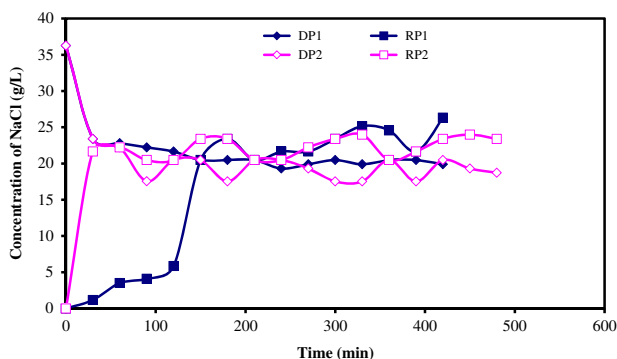


Fig. 4. Effect of small quantity of MC in LM, $C_i=36.27$ g NaCl/L, DP=50 mL, RP=50 mL H₂O+1 g sorbitol, LM=100 ml CB, MC₁=0.1 g, and MC₂=0.3 g.

3.3.2. Effect of presence of high quantity of MC in LM:

Fig. 5 proves that 0.6181 g in 100 mL LM causes steric hindrance due to large molecular volume of the dibenzo-18-crown-6 which occupies a large space. Accordingly, the NaCl in the DP was not capable of diffusing in the LM due to the crowding of the molecules in the LM phase. Thus, the increase of NaCl in the RP was very slow and negligible, and at the same time, the NaCl was almost constant in the LM phase which proves that complexation was poor between the NaCl and MC due to crowding in the LM. One last point is that DP dropped slightly in concentration and the latter remained almost constant until after 600 min, it started decreasing gradually with a simultaneous gradual increase in the concentration of the RP. This proves that there is an optimum dose of the MC which is yet to be investigated.

3.3.3. Effect of varying quantity of MC in LM:

The effect of different quantities of MC in the LM is clearer on examining Fig. 6 in which 0.1, 0.3, and 0.6181 g of MC are shown for their effect on the behavior of the different RPs with time. The figure clarifies that 0.3 g gave the highest kinetics among the three quantities tested. The reason must be due to the LM not being that viscous to delay diffusion of the NaCl via the LM and that the quantity of MC was sufficient to assist in rapid mass transfer to the RP. On the other hand, 0.1 g resulted in a slower transport of NaCl through the LM indicating that it was rather insufficient. However, on prolonged times, extraction in this case reached 75% in 400 min, while 0.3 g reached lower percentage of extraction. This result suggests that 0.2 g may have been the optimum dose.

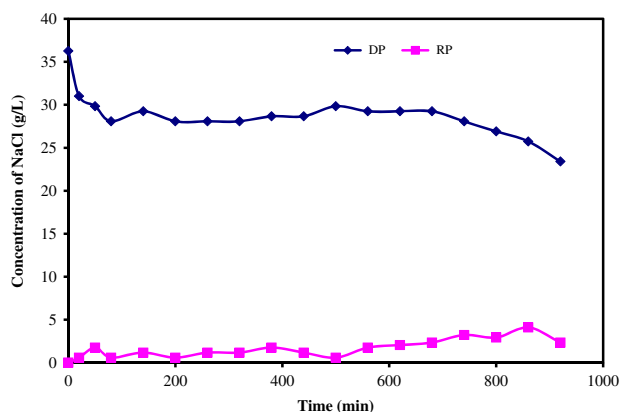


Fig. 5. Effect of large quantity of MC in LM, $C_i=36.27$ g NaCl/L, DP=50 mL, RP=50 mL H_2O+2 g sorbitol, LM=100 mL DCE, and MC=0.6181 g.

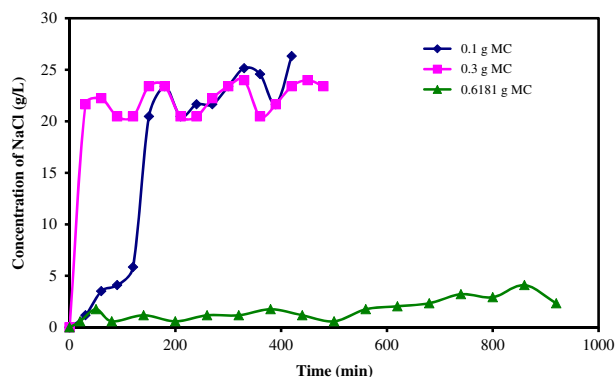


Fig. 6. Effect of varying quantities of MC in LM, $C_i=36.27$ g NaCl/L, DP=50 mL, RP=50 mL, and LM=100 mL.

Finally, the 0.6181 g MC resulted in a very poor extraction which increased extremely slowly but regularly reaching almost 13% extraction after 850 min due to the very high viscosity and crowding of the complex in the LM, and therefore, this dose is completely unrecommended.

3.4. Effect of type of LM

Fig. 7 shows the effect of type of LM from which it is clear that DCE gave a higher percentage of extraction (about 65%) on prolonged operation. However, percentage extraction was almost identical for both DCE and NB after 300 min of the experiment. However, in case of DCE, prolonged operation resulted in an extraction that was about 60% but during the first 250 min, the NaCl accumulated in the LM due to the absence of an MC, then when diffusion of the accumulated NaCl took place to the RP, a sudden jump in

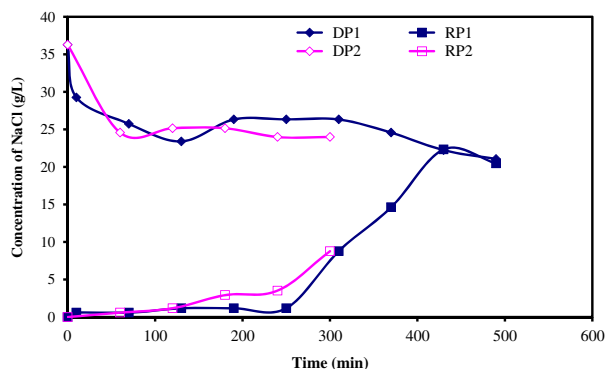


Fig. 7. Effect of type of LM, $C_i=36.27$ g NaCl/L, DP=50 mL, RP=50 mL, LM₁=100 mL DCE, and LM₂=100 mL NB.

concentration took place until almost 500 min when the percentage extraction reached almost 65%. The same observations could be applied to NB when it was used as LM except that the initial drop in concentration in the DP was sharper than in the other case, which may be attributed to the higher viscosity and dielectric constant of the NB.

3.5. Effect of mixed LM

Fig. 8 in which sorbitol functioned as sequestering agent in the RP and MC was 0.1 g crown ether, while the only variable which varied among the two experiments was that in one experiment DCE + CB was used in equal amounts, while CB alone was used in the other experiment. The figure illustrates that the mixed organic liquids gave rapid mass transfer, however, the NaCl kept accumulating until 150 min when it was released to the RP by rapid transfer due to complexation with the crown ether followed by release to the RP in which the sorbitol complexed with it thus trapping the NaCl in the RP. Maximum extraction achieved was around 70%. Actually, had the operation been terminated at this point a highest percentage of extraction could have been achieved. It is clear that the use of suitable water-insoluble organic solvents as LM and the presence of an optimum sequestering agent in the RP and MC in the LM, altogether led to increased percentage of extraction of the NaCl, and thus there is always the ability of improving desalination by LMs. On the other hand, CB alone led to lower rates of mass transfer from the DP but the same observation of the sudden jump in the RP concentration took place for the same aforementioned reasons. It is realized that the concentration in the RP gradually increased with time until after 420 min, reaching about 70% extraction; however, a longer time was required in this case. This result shows that there is

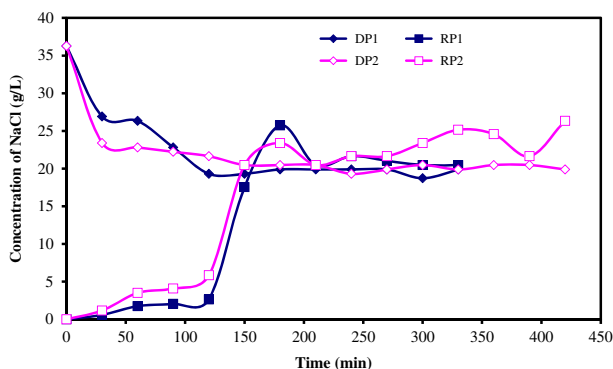


Fig. 8. Effect of mixed LM, $C_i = 36.27$ g NaCl/L, DP = 50 mL, RP = 50 mL $H_2O + 1$ g sorbitol, $LM_1 = 100$ mL DCE + CB, $LM_2 = 100$ mL CB, and MC = 0.1 g.

more work to do in the near future in which other solvent mixtures may be used, together with various masses and types of crown ethers and MC, different trapping agents in the RP, and actual seawater as DP.

3.6. Physicochemical interpretation of phenomena of LM permeation

Based on the results arrived, it could be stated that sodium chloride cannot diffuse through LM except in the presence of a suitable MC which has to be added to the LM in order to facilitate its transportation through the membrane, under favorable conditions. This can only take place when the optimum quantity and quality of MC is present in the LM. The MC in the present work is chosen based on its cavity size which ensures that the sodium ion fits perfectly into the cavity according to the atomic size of the Na ion. In addition, the two benzene rings one on each side of MC molecule render the MC less hydrophilic and therefore decreases its solubility in the aqueous phases, nullifying the solubilizing effect of the ether moieties. The presence of a small quantity of MC does not result in a rapid rate of diffusion through the LM, while a large quantity may cause crowding of the $MC-Na^+$ complex within the LM. Accordingly, there exists an optimum dose which results in the best mass transfer rate. Since the macrocyclic ligands are neutral, the cation carries its co-anion with it across the membrane to maintain electrical neutrality in the system which was also confirmed by Lamb et al. [30], Igawa et al. [31], and Dermeni et al. [32]. The rate of cation transport through the membranes by macrocyclic ligands has been shown to be influenced by the nature of the salt anion [30]. It is noteworthy that the complex diffuses from the DP/LM interface to the LM/RP interface owing to the concentration gradient and backwise due to the gradient of the MC alone after dissociating into MC and NaCl, the latter being sequestered by the sequestering agent due to the formation of a coordinate bond between it and the sodium ions.

4. Conclusion

From the present work, the following conclusions were arrived at:

- BLM is a simple way by which a study on desalination can be conducted.
- The type of LM material was found to be very important in determining the performance of the removal process of NaCl, and a mixture of DCB

+CB was a better LM than DCE and the latter better than NB.

- Complete insolubility of LM in water is one factor of prime importance in affecting the process performance.
- The presence of MC is essential in complexing with NaCl and facilitating diffusion of the latter from DP to RP.
- The quantity of MC is crucial in determining the rate of diffusion of NaCl through the LM; if too little it will not be sufficient for making all the NaCl diffuse rapidly to the RP, while if too much, it will cause an increase in the viscosity and crowding of the LM, thus decreasing the diffusion rate. Therefore, an optimum quantity has to be found which is proportional to the quantity of LM.
- The RP should contain a complexing agent in order to sequester the NaCl in the RP and prevent its back diffusion to the LM.
- Soluble starch followed by sorbitol were found to be suitable sequestrants for NaCl in the RP due to formation of coordinate bond between Na⁺ ion and the hydroxyl groups in the sequestrants. The first is found to be optimum due to the greater number of hydroxyl groups, higher solution viscosity, and its larger molecular weight which prevents its back diffusion.
- Speed of stirring assisted in transfer of the NaCl from DP via LM to RP. High speed caused vortex formation which resulted in swirling of the LM. Therefore, medium speed is recommended.
- The present work proved that desalination is possible in spite that very highly concentrated NaCl solution (36.27 g/L) was used, and that diffusion from DP to RP took place opposite to the direction of concentration gradient by facilitated up-hill transport.

5. Recommendations

It is recommended that future work should be directed towards:

- Studying desalination by other LM techniques such as hollow fiber contained LM (HFCLM) and electrostatic pseudo LM (ESPLM).
- Brackish water of much lower concentration should be investigated in desalination by BLM as well as the last two aforementioned techniques.
- Testing other MCs and other sequestrants in the RP.
- Studying the increasing volume ratio of DP: RP, (e.g. 2:1, 3:1, etc.).

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