Desalination using modified configuration of supported liquid membrane with enhancement of mass transfer of NaCl
Mona M. Naim, Abeer A. Moneer, Mahmoud M. Elewa and Ahmed A. El-Shafei

ABSTRACT
Supported liquid membranes (SLM) suffer from very slow mass transfer of the solute from the donor phase (DP) to the receptor phase (RP) through the liquid membrane (LM). In the present work, an attempt was made to accelerate the mass transfer in SLM by creating a modified configuration in which the DP and RP are made to flow either co- or counter-currently to each other. Variables, which could affect the removal of NaCl, were the volume ratio of DP to RP, type and quantity of sequestering agent (SA), presence of mobile carrier (MC), type of LM, and flow rate of DP and RP. The results showed that the higher the flow rate of DP and RP, the higher the mass transfer of NaCl. Quantity and type of SA and type of LM were prime important factors. Remarkably, the time required for transfer of NaCl from DP to RP was reduced from several hours in the case of stagnant SLM to several minutes in the present work. The mass transfer of NaCl was analysed based on kinetic laws of two consecutive irreversible first-order reactions. The values achieved establish the process is diffusion controlled, and the membrane entrance rate constants increase directly with initial concentration (Ci) and inversely with quantity of SA.

Key words | desalination, mobile carrier, sequestering agent, supported liquid membrane

NOMENCLATURE

\[ C_d, C_m, C_r \] NaCl concentrations in the DP, LM, and RP
\[ CB \] chlorobenzene
\[ Ci \] initial concentration
\[ Co \] concentration at time \( t = 0 \) min
\[ Ct \] concentration at time \( t \)
\[ DCB \] 1,2-dichlorobenzene
\[ DP \] donor phase
\[ DW \] distilled water
\[ FSSLM \] flat sheet supported liquid membrane
\[ HFSLM \] hollow fiber supported liquid membrane
\[ k_1, k_2 \] apparent membrane entrance and exit rate constants
\[ LM \] liquid membrane
\[ MC \] mobile carrier
\[ NaCl \] sodium chloride
\[ R_d, R_m, R_r \] reduced NaCl concentrations in DP, LM and RP
\[ RP \] receptor phase
\[ SA \] sequestering agent
\[ SLM \] supported liquid membranes
\[ SS \] soluble starch
\[ TR \] treatment ratio
\[ V_{d}, V_{m}, V_{r} \] volumes of DP, LM, and RP
\[ W/O \] water in oil emulsion

INTRODUCTION
The supported liquid membrane (SLM) technology is theoretically one of the most efficient membrane-based methods of separation. It does not use pressure or voltage, but is based on difference of chemical energy as a driving factor of the process; for example, it can use simple \( H^+ \) concentration difference. Coupled co- or counter-ion transport...
allows an active transport of the targeted species from dilute solutions into more concentrated ones, and collection of toxic or precious species in a small volume of the receptor solution. Remarkably, in recent years, SLMs have become an alternative for the currently used wastewater treatments (Izak et al. 2008; Hernandez-Fernandez et al. 2015). SLMs are used for elimination of amino acids (Wieczorek et al. 1997a, 1997b), phenol compounds (Venkateswaran & Palanivelu 2006) and metal ions from aqueous solutions (Kozłowski & Walkowiak 2005; Swain et al. 2015). The basic mechanism for SLMs is facilitated transport (Lothongkum et al. 2009). It consists of two aqueous phases called the donor phase (DP) and receptor phase (RP), which are separated by a porous membrane containing an organic liquid phase (LM) as a carrier to selectively transport ions from the DP side to the RP side (Muthuraman & Palanivelu 2006). The most considerable advantages of SLMs over other techniques are low cost, low energy consumption, small amounts of extractant, high separation efficiencies, one step mass transfer, easy scalability, simple scale up (Venkateswaran & Palanivelu 2006; Szczepanski et al. 2014; Wannachod et al. 2014), higher extraction efficiency of the target solute from diluted solutions, more effective separation of elements with similar properties, simultaneous extraction and stripping using a one-step procedure and simple operation. Beside the important advantages, a common problem of SLMs is low durability of the process.

In an SLM, usually organic liquid (LM) is embedded in the small pores of a polymer support and is kept there by capillary forces. If the LM is immiscible with the DP and RP, SLM can be used to separate the two aqueous phases. It may contain a mobile carrier (MC) or an organic solvent to adjust viscosity. Generally little volume of LM in the membrane and instantaneous extraction and re-extraction in one step offers the benefits of conceivable utilization of costly MC, high separation factors, simple scale-up, low energy necessities, low capital and working expenses (Chakraborty et al. 2010).

Common configurations of SLM are flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM). Experimental laboratory setup generally comprises of a two-compartment cell, isolated by a flat membrane. If the SLM is not steady and LM does not remain in the pores, it is conceivable to use cells with three compartments where two porous supports of the same (Wodzki & Sionkowski 1995) or different nature (Kislik & Eyal 1996) are used to separate the LM, DP and RP. The support in this case is often hydrophilic and is filled with aqueous solutions. The organic solution (LM) with the carrier (MC) can be mixed or circulated in the inner compartment to decrease mass transfer resistance (Kocherginsky et al. 2007).

Generally, SLMs depend on organic liquid separating two aqueous solutions; however, in some systems, aqueous solution separating two organic liquids, and the pores in the membrane support were impregnated by water (Miyako et al. 2005). The issue with this course of action is that water has relatively high volatility and the membrane is not stable. It appears that this issue can be treated by utilizing moderately new materials, so-called ionic liquids. For this situation, a bulk organic cation, being apart from its anion, is chemically more active and able to form complexes with olefins (Hong et al. 2000; Kim et al. 2004), in this way encouraging their separation from saturated hydrocarbons through the membrane (Kocherginsky et al. 2007).

The breakthrough in the present work is the use of the flowing DP and RP and also the use of distilled water (DW) as LM as a replacement for ordinary organic solvents such as chlorobenzene, di-chloroethane, chloroform, and so on, the latter being hazardous to human and animal health plus aquatic life, due to the solvents’ sparingly soluble nature and consequently the presence of them in desalinated fresh water intended for municipal, irrigation and industrial purposes. Accordingly, using DW avoids the need for further post-treatment of the produced water to get rid of any contaminants. The aim of the present work was to investigate the possibility of desalination of saline water by the application of SLMs. A laboratory-scale set-up, which includes the module, was constructed as a modification of the ordinary SLM configuration. Experiments are then conducted to investigate the different variables on the extent of desalination, which were: flow rates of both DP and RP, volume ratio of DP to RP, initial salt solution concentration, presence and quantity of MC in organic LM, type and quantity of sequestering agent (SA) in the RP, and type of LM. Moreover, a kinetic study of the results was implemented.

**MATERIALS AND METHODS**

**Materials**

Sodium chloride (NaCl) (Fluka Chemica, Switzerland) was used for preparation of saline water and di-benzo-18-crown-6 (Fluka Chemica, Switzerland) was used as MC. A polysaccharide (soluble starch (Fisher Chemical, USA)), several monosaccharides (glucose (Chemajet, Egypt),...
sorbitol (Comperion Co., UK), mannose (Chemajet, Egypt), polyhydric alcohols (glycerol (Chemajet, Egypt)) and dibasic acids (tartaric acid (National Co., Egypt)) were investigated as SA in the RP. DW, 1,2-dichlorobenzene (DCB) (BDH Chemicals Ltd, UK) and chlorobenzene (CB) (Chemajet, Egypt) were chosen as LM.

Module

The module, as shown in Figure 1, was made of Plexiglas (PMMA) and consisted of two identical slabs, each 2 cm thick, 25 cm long and 10 cm wide. Each slab contains an inlet and outlet manifold at its top and bottom ends. They also contain hexagonal grooves on one face of each slab (4.4 cm width and 1.5 cm depth). The two slabs are made to face each other and two cellophane membranes are held between two rubber gaskets, which are made to fit into the grooves, and the cellophane membranes are separated from each other by a thin Plexiglas frame to allow space for LM to be contained between them. In the frame, two small holes are drilled at the top to admit the LM through one hole, while the other is for the sake of

![Figure 1](https://iwaponline.com/wst/article-pdf/79/1/175/589507/wst079010175.pdf)
equalizing the pressure outside and inside the LM cavity. Rubber gaskets are placed between each slab and frame and on both sides of the membrane to prevent liquid leakage. The inlet and outlet manifolds in each slab are fitted with threaded stainless steel tubes to which polyethylene tubing could be attached. All the parts of the module (slab, gasket, membranes and frames) were assembled by a set of eight bolts and nuts with plastic washers on either side of the module. The flow rate of water at DP and RP were measured via flowmeter (Nxtop 1/2’ PT Thread 0.05–0.5GPM 0.2–2LMP), and were adjusted by a control valve. A uniform flow of DP and RP along the membrane surface within the module is ascertained by the streamlined shape of the hexagonal flow channels.

Set-up

The set-up consists of the module, two plastic centrifugal pumps with power of 200 W, DP and RP circuits, and the necessary polyethylene tubing. The DP or RP circuit is contained in a 1 L Pyrex beaker, flow meter controller and a bypass for control feed flow rate. Figure 1 presents a schematic diagram of the set-up.

Procedure

The saline water as DP (physical and chemical properties of DW used for preparation of DP are illustrated in Table 1) and DW with SA as RP were added to the beakers and rapid flow rates were controlled. The NaCl concentration of each phase was traced vs. time from the onset of the experiment by sampling 2 mL of each phase at regular time intervals, and the experiment was terminated when the concentrations remain constant for four consecutive readings. The concentrations of DP and RP were analysed by conductivity meters (inoLab 7310P advanced conductivity bench top meter with printer), concentration of salt in the LM is then determined by material balance. The dimensionless reduced concentrations in both phases are each plotted versus time of operation.

Theory

In the present study; two types of LM were used for comparison: DW as eco-friendly LM and CB and DCB as ordinary organic LM. Consequently, there are two transport mechanisms controlling the transport of NaCl. In the case of using DW as LM, and since MC is insoluble in water and was not used, the transport of NaCl was simple up-hill transport. On the other hand, when using organic LM containing MC, the NaCl transport was due to facilitated up-hill transport mechanism. In simple up-hill transport, the NaCl is extracted from the DP due to its selective solubility in the DW. Simultaneously, the RP containing the SA strips and irreversibly binds each molecule of NaCl. In this mechanism, the solute NaCl is pumped from the DP to the RP, apparently counter to its concentration gradient. The term ‘apparently’ is used, since the concentration of the permeate NaCl in the RP always remains lower than that in the DP, irrespective of the high concentration of the transformed product SA-NaCl (Boyadjiev & Lazarova 1995). While, for the facilitated up-hill transport mechanism, the LM contains a MC, which complexes with NaCl, the complex diffuses to RP due to its concentration gradient, where it decomplexes at the LM/RP interface. The MC diffuses back to the DP/LM interface due to its concentration gradient. This mechanism of NaCl transport from DP to RP through LM was discussed thoroughly in previous work (El-Shafei et al. 2016; Naim et al. 2016), Schematic representation of NaCl transport through the SLM is illustrated in Figure 2.

RESULTS AND DISCUSSION

Effect of flow rate of both DP and RP

The effect of flow rate is shown by examining Figure 3, in which reduced concentrations (Rd, Rm, and Rr), defined according to Altin et al. (2007) and Léon et al. (2004), are plotted vs. time of operation. The numerical analyses of the kinetic models for Rd, Rm, and Rr were carried out by non-linear curve fitting using a JavaScript iteration program presented by Pezzullo (2006) using the non-steady state kinetic regimes and then followed by calculating the different

### Table 1 | Chemical and physical properties of distilled water used for preparation of DP

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.2</td>
</tr>
<tr>
<td>EC (μs/cm)</td>
<td>28</td>
</tr>
<tr>
<td>NO3⁻ (mg/L)</td>
<td>0.21</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>12.6</td>
</tr>
<tr>
<td>B (mg/L)</td>
<td>0.78</td>
</tr>
<tr>
<td>CO₃²⁻ (mg/L)</td>
<td>0</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>2.4</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>11</td>
</tr>
</tbody>
</table>

Figure 3, in which $C_i$ was 35 g/L, volume ratio of DP:RP = 3:1, LM is DW, no MC in LM, no SA in RP, indicates that $\Delta C$ between both streams is greater at lower flow rate (17.3 mL/s) than that at higher flow rate (30 mL/s). It is clear that the rate of change of concentration is higher in the latter than the former case. It is also clear that accumulation of salt in the LM is very high at low flow rates, which is expected due to stagnancy of the LM, accompanied with high resistance in the laminar boundary layers on both sides of the cellophane sheets facing the two flowing phases. Thus it can be stated that the higher the flow rate (with Reynolds number of 1,061 and 2,141 for 17 mL/s and 30 mL/s, respectively), the greater is the mass transfer. This was also concluded by Neplenbroek et al. (1992), who observed an increase in solute diffusion for FSSLMs when the velocity of the solution was increased in a specific module (Neplenbroek et al. 1992). By inspecting Table 2, it is obvious that the membrane entrance ($k_{1d}$) rate constant was higher in case of high flow rate. The same observation was also concluded for both ($k_{2m}$) and ($k_{2r}$) rate constants, which were much higher; additionally, using a high flow rate led to a great decrease in $t_{max}$ and great increase in $J_{max}$, which clarifies the importance of the flow rate of both DP and RP in the transfer of the NaCl molecules from DP to RP.

**Effect of ratio of DP:RP**

This factor is illustrated by comparing Figure 4(a) and 4(b), in which the ratio was 3:1 and 3:2, respectively, at the optimum flow rate arrived at and with DW as LM with no MC in LM and no SA in RP. It is clear that when the ratio of DP:RP was 3:1, the rates $R_d$, $R_r$, and $R_m$ were more rapid than when the ratio was 3:2. On the other hand, the percentage desalination in the two cases were almost close to each other with no accumulation of NaCl in the LM in the case of ratio 3:2, which indicates that using higher ratios will lead to more percentage desalination and which is more

<table>
<thead>
<tr>
<th>Flow rate (mL/s)</th>
<th>$k_{1d} \times 10^3$ (min$^{-1}$)</th>
<th>$k_{2m} \times 10^3$ (min$^{-1}$)</th>
<th>$k_{2r} \times 10^3$ (min$^{-1}$)</th>
<th>$R_{max}^m$ (min)</th>
<th>$t_{max}$ (min)</th>
<th>$k_{1d}/k_{2m}$</th>
<th>$J_{max}^m \times 10^3$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.3</td>
<td>1.278</td>
<td>5.918</td>
<td>5.768</td>
<td>0.14</td>
<td>330.4</td>
<td>0.2158</td>
<td>0.835</td>
</tr>
<tr>
<td>30</td>
<td>1.5461</td>
<td>54.91</td>
<td>148.97</td>
<td>0.03</td>
<td>66.9</td>
<td>0.0281</td>
<td>1.449</td>
</tr>
</tbody>
</table>
appropriate for industrial applications, in which it is preferable to transfer salts from large volumes to smaller ones and free the DP from solute while containing the solute in a much smaller volume, since the latter will be contaminated with the diffused solute. Thus the higher the ratio, the more beneficial is the desalination process. It is worth noting that no SA was present in the RP, which would assist in trapping the solute, preventing it from back diffusion from RP to DP, since the larger the ratio of DP:RP, the higher the reverse operation leading to back diffusion from the more concentrated RP to the much more diluted DP. Conclusively, the ratio 3:1 is much more preferred to be applied.

By inspecting Table 3, in which the same previous conditions were used, it is clear that the ratio of 3:1 is more preferred to 3:2. From the table it is noticeable that $k_{1d}$, $k_{2r}$ rate constants were much higher in the case of ratio 3:2, this confirms the fact that no accumulation of salts in the LM took place. On the other hand, for the rest of the rate constants the values were close to each other. The most important remark is that $J_{max}$ was less in the case of ratio 3:2 than that for ratio 3:1, which indicates that the higher the ratio of DP:RP the faster the flux for the desalination process to take place.

### Effect of initial concentration of NaCl

The effect of initial NaCl concentration varying from 10 through 15 to 36 g/L in the feed phase on the percentage desalination is illustrated in Figures 5 and 4(a) in which optimum flow rate (30 mL/s) and ratio of DP:RP (3:1) were applied, without using either MC in LM or SA in RP. It is clear that percentage desalination increased from 20 through 40 to 55% with the increase of initial concentration from 10 through 15 (Figure 5(a) and 5(b)) to 36 g/L (Figure 4(a)), respectively, and it is obvious that the driving force was the concentration gradient, even though no MC and no SA were used. This result proves that in the present technique, the LM supported on cellophane sheet allowed NaCl to diffuse through it from DP to RP, since the LM is very thin. Accordingly, the resistance to diffusion in the LM is very low. This is a very promising result, which indicates that the liquid membrane is a very applicable technique for desalination of saline water with high concentration (similar to sea water concentration) rather than brackish water. On the other hand, in a study of separation selectivity of rare earth elements in flat sheet SLMs by Martínez et al. (2018), they concluded that the higher the initial ion concentrations in the DP, which means a larger amount of metal ions to be transferred, the longer the process time required to reach to complete removal. By inspecting Table 4, it is obvious that $k_{1d}$ rate constant was higher in case of high initial concentration of NaCl. The same observation was also concluded for both $(k_{2m})$ and $(k_{2r})$ rate constants, which were much higher; additionally, using high initial concentration led to a great decrease in $t_{max}$ and great increase in $f_{max}$ which clarifies the importance of the initial NaCl concentration in the transfer of the NaCl molecules from DP to RP.

### Effect of quantity of glucose as SA in RP

This is revealed from Figure 6, in which zero, 10, 15, 20, 25 and 30 g of glucose were added to the RP, respectively. It is clear that the lowest rate of transfer of NaCl (lowest membrane exit rate constants $(k_{2m}$ and $k_{2r}$), highest $t_{max}$ and lowest flux $(f_{max})$) was in the case at 20 g glucose

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**Table 3** Kinetic parameters at different ratios of DP:RP (average $C_i$ = 38.39 g/L, LM is DW, no MC in LM, no SA in RP, flow rate of DP and RP = 30 mL/s)

<table>
<thead>
<tr>
<th>Ratio of DP:RP</th>
<th>$k_{1d} \times 10^{-3}$ (min$^{-1}$)</th>
<th>$k_{2m} \times 10^{-3}$ (min$^{-1}$)</th>
<th>$k_{2r} \times 10^{-3}$ (min$^{-1}$)</th>
<th>$t_{max}$ (min)</th>
<th>$R_{max}$</th>
<th>$k_{1d}/k_{2m}$</th>
<th>$f_{max} \times 10^{3}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>1.5461</td>
<td>54.91</td>
<td>148.97</td>
<td>0.030</td>
<td>66.9</td>
<td>0.0281</td>
<td>1.449</td>
</tr>
<tr>
<td>3:2</td>
<td>1.3</td>
<td>209.9</td>
<td>141</td>
<td>0.017</td>
<td>56.4</td>
<td>0.018</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Figure 4** Time variation of reduced concentrations of NaCl in DP, LM, and RP (Rd, Rm, and Rr) at $C_i$ = 38.39 g/L, LM is DW, no MC in LM, no SA in RP, flow rate 30 mL/s for volume ratio of DP:RP: (A) 3:1 and (B) 3:2.
Addition of 10 g glucose shows an improved rate of diffusion through LM due to the availability of greater complexation sites in the RP. On comparing the points of the two quantities of 10 and 15 g glucose, it is noticed that higher rates of transfer of NaCl are obtained when 15 g glucose was present in the RP, in spite of the initial NaCl solution concentration being relatively high. Addition of 20 g glucose on the other hand results in a decrease in the rate of mass transfer. It is clear that there is an optimum glucose concentration at which maximum rate of complexation takes place. The accumulation of salt in the LM proves that crowding of the complex adjacent to the cellophane in the RP interface due to slow diffusion of heavy complex away from the cellophane membrane, results in the free glucose molecule being unable to replace the complex adjacent to the cellophane, and therefore complexation is retarded, which results in a NaCl accumulation in the LM. A further increase in glucose (25 g) resulted in an improved result. However, 30 g glucose resulted in a slower rate of mass transfer and a larger \( \Delta C \) was attained at the end of the experiment. Furthermore, by investigating Table 5 it can be concluded that \( k_{1d} \) rate constant was higher in case of absence of glucose as SA. The same observation was also concluded for both \( k_{2m} \) and \( k_{2r} \) rate constants which were much higher, this will be clear from studying different types of SA and which will lead to the conclusion that glucose is not the preferred SA. On the other hand, on comparing the other quantities with each other, it can be concluded that the use of 15 g was the optimum. By comparing the values of \( k_{1d} \), they were close to each other, but values of \( k_{2m} \) and \( k_{2r} \) were much higher in the case of using 15 g glucose. Additionally, using 15 g glucose led to a great decrease in \( t_{max} \) and an increase in \( J_{max} \), which clarifies that using 15 g of glucose was an optimum quantity as SA in RP.

Effect of type of sequestering agent

The effect of type of SA is shown in Figures 6(b) and 7 in which 10 g of different types of carbohydrates such as glucose, mannose, sorbitol, glycerol and starch were added to the RP, respectively. It is clear that the effect of the presence of glucose and mannose is almost identical, \( \Delta C \) between the two streams being equal after about 600 min, and the rate of change of concentration being almost the same. This result is expected, since glucose and mannose have equal number of hydroxyl groups, which for coordinate bonds with NaCl. However, sorbitol led to an improved result, due to the presence of one extra primary hydroxyl group in its molecule. It is also noticed that the amount of NaCl in the LM is closer to the zero value, indicating higher rate of mass transfer across the LM due to rapid sequestration of NaCl with the sorbitol. However, when glycerol (a trihydric alcohol) was used, the initial rates of mass transfer were high, but as diffusion progressed the rate decreased then became constant. This result may be due to the higher viscosity of the glycerol solution in spite of the flow rate in this case being almost equal to the three previous cases (30 mL/s). However, starch gives a better result compared to the other SA. Starch typically consists of amylose (10–20%) and amylopectin (80–90%), which have a molecular weight of 10–60 K and 30–1,000 K, respectively (Brautlecht 1973), although composition varies greatly depending on the source. Sequentially arranged hydroxyl groups in starch molecules form a relatively

![Figure 5](https://iwaponline.com/wst/article-pdf/79/1/175/589507/wst079010175.pdf)
stable complex with cations such as the sodium ion (Rendleman 1967; Angyal 1989) to lower the activities of ions in the aqueous phase. Furthermore, it is relatively inexpensive and highly biodegradable to minimize environmental concerns for concentrate treatment and disposal. By inspecting Table 6, it is clear that the $k_{1d}$ rate constant was higher in the case of using starch as SA than for all other sequestering agents tried in the present work. It is also the case for both ($k_{2m}$) and ($k_{2r}$) rate constants, which were much higher. Additionally, using starch as SA in the RP led to a great decrease in $t_{max}$ and an increase in $J_{max}$.

Inspecting Figures 6(b) and 7(e), it is clear that starch and glucose gave almost equal percentage desalination despite the rate being a little faster in the case of glucose as SA. On the other hand, from Table 5 and 6 and comparing the results of adding 10 g of both glucose and starch to RP, it is obvious that the rate constant in the case of using starch is much higher and that $t_{max}$ was much less in the same case, which clarifies that starch is the preferred SA.

**Effect of type LM**

It is known that the organic LMs used in the literature have a high effect on membrane stability. From numerous studies it can be concluded that to increase the durability of LMs, the organic LMs should have a minimum solubility in water (Shinbo et al. 1993), and also water should possess a minimum solubility in the organic LMs (Dozol et al. 1993). The LMs from organic origin should have a high interfacial tension between the LM and the water phases (Neplenbroek et al. 1995) and a high boiling point (Lamb et al. 1988). The effect of type of LM on the transport efficiency of NaCl was evaluated by using DCB, CB and DW, comparing them to each other, and also comparing organic LMs with DW as an environmentally friendly LM instead of the hazardous organic LMs. The results are shown in Figures 8(a), 8(b) and 9(a), in which CB, DW and DCB were used, using the optimum conditions arrived at in the present experiments, which were: flow rate (30 mL/s), ratio of DP:RP (3:1) and 20 g starch as SA in RP. It is clear that the physico-chemical characteristics of the solvent affected the diffusion processes (see Table 7). By comparing organic LMs to each other, it is clear that DCB resulted in a slightly better though unacceptable result than when CB was used as LM. This result emphasizes the importance of the kind of organic LM solvent in effecting proper performance, which may be due to the fact that two chlorine atoms are present per benzene ring to
coordinate with NaCl molecules, whereas in the case of CB there is only one chlorine atom. By inspecting Figures 8 and 9(a), it is clear that the rate of diffusion of NaCl from DP to RP is faster in the case of using DW as LM than with using either DCB or CB, and that ΔC is smaller in the same case, which proves that using DW as LM is very efficient in conducting desalination using SLM with the present configuration. Moreover, percentage desalination was in the region of 50% in the case of using DW as LM, while when using both DCB and CB it was 38 to 40%, respectively.

Table 8 illustrates that the $k_{1d}$ rate constants for both DCB and CB were almost equal, while for both ($k_{2m}$) and ($k_{2r}$) rate constants they were much higher in the case of CB; additionally, using CB as LM led to a decrease in $t_{max}$ with a small value and the $J_{max}$ value being equal in both cases, which clarifies that using either DCB or CB as LM will give almost the same results. On the other hand, when using DW as LM, it is clear that the aforementioned values were not that much different. Conclusively, using DW as LM is much better as an eco-friendly LM without sacrificing any of the process parameters, especially $t_{max}$, which was only 13 minutes more than the lowest value which was 40 minutes when using CB as LM.

**Effect of presence of MC in organic LM**

Gu *et al.* (1992) revealed that the key criterion in selecting an MC is that it and the complex formed must be soluble in the membrane phase, but not soluble in both the RP and DP. Further, from an economic point of view, a lower concentration of MC is always preferred since it is the most expensive agent among the other components of the membrane. A macrocyclic ligand (crown ether) was specifically chosen to be the carrier for NaCl transport. Peterson & Lamb (1996) managed to prepare numerous crown ethers that contain cavities of different sizes formed of ether groups linked to each other, within which positive cations may be held by attraction of the negative ether groups in the cyclic polyether structure. If the atomic volume of the cation is larger than the cavity size of the polyether ring, the former cannot be contained within the polyether cavity; accordingly the crown ether is unable to complex with the cation and the latter will not be transported.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Kinetic parameters at different quantities of glucose as SA (Average Ci = 35 g/L, ratio of DP:RP = 3:1, LM is DW, no MC in LM, flow rate of DP and RP = 30 mL/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of glucose (g)</td>
<td>$k_{1d} \times 10^3$ (min$^{-1}$)</td>
</tr>
<tr>
<td>0</td>
<td>1.5461</td>
</tr>
<tr>
<td>10</td>
<td>1.059</td>
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<td>15</td>
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<td>25</td>
<td>1.3</td>
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<td>30</td>
<td>1.6</td>
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</table>

**Figure 7** Time variation of reduced concentrations of NaCl in DP, LM, and RP (Rd, Rm, and Rr) at average Ci = 35 g/L, ratio of DP:RP = 3:1, LM is DW, no MC in LM, flow rate of DP and RP = 30 mL/s for 10 g of different types of SA in RP: (A) sorbitol, (B) mannose, (C) glycerol and (D) starch.
across the LM phase. On the other hand, if the cation volume is smaller than the cavity size, the attraction between the positive cation and the negative ether moieties will be weak, such that the required complex between them will not be possible due to the larger distance between both cation and negative ether moieties resulting in a weak electrostatic bond, causing a poor complex unable to transfer the cations to the RP. To this end, dibenzo-18-crown-6 was specifically chosen for the extraction of the NaCl molecules from the DP, in which the Na ion will exactly fit inside the polyether cavity and can be decomplexed at the same time. In other words, complexation and decomplexation can be easily effected when conditions are favourable (Naim et al. 2019). It remains to be mentioned that the presence of the two benzene rings on either side of the polycyclic ring assists in making the MC less soluble in water; consequently the study of the effect of MC in LM was not conducted when using DW as LM.

Figure 9 presents the effect of the presence of the same concentration of MC (0.0269 mol/L of LM that was decided based on previous work (El-Shafei et al. 2016; Naim et al. 2016)), in both DCB and CB as organic LMs. The figure shows that the presence of MC accelerates diffusion of NaCl via the LM in the case of using DCB as LM and that

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### Table 6

Kinetic parameters at 10 g of different types of SA (average Cl = 35.1 g/L, ratio of DP:RP = 3:1, LM is DW, no MC in LM, flow rate of DP and RP = 30 mL/s)

<table>
<thead>
<tr>
<th>Type of SA</th>
<th>( k_{df} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{dm} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{rf} \times 10^{-3} ) (min(^{-1}))</th>
<th>( R_{max} )</th>
<th>( t_{max} ) (min)</th>
<th>( k_{df}/k_{dm} )</th>
<th>( j_{max} \times 10^{1} ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>1.059</td>
<td>20.8</td>
<td>66.02</td>
<td>0.043</td>
<td>150.8</td>
<td>0.051</td>
<td>0.965</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>1.3</td>
<td>41.4</td>
<td>58.85</td>
<td>0.029</td>
<td>85.7</td>
<td>0.032</td>
<td>1.3</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.1</td>
<td>13</td>
<td>24.5</td>
<td>0.065</td>
<td>210.1</td>
<td>0.081</td>
<td>0.9</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1.3</td>
<td>38.6</td>
<td>24.3</td>
<td>0.030</td>
<td>90.8</td>
<td>0.034</td>
<td>1.1</td>
</tr>
<tr>
<td>Starch</td>
<td>1.2</td>
<td>75.8</td>
<td>177.6</td>
<td>0.015</td>
<td>55.3</td>
<td>0.016</td>
<td>1.2</td>
</tr>
</tbody>
</table>
the time required for reaching the highest reduced concentration of NaCl in the LM was 42.1 and 44.5 minutes using DCB and DCB + MC, respectively (Table 9). Remarkably, the time required for transfer of NaCl from DP to RP was reduced from several hours in the case of stagnant SLM (El-Shafei et al. 2016) to several minutes in the present work. Also, percentage desalination increased with the presence of MC in the DCB. On the other hand, using CB as LM led to an increase in the rate of NaCl diffusion to RP compared to DCB and DCB + MC. While the addition of MC to CB decreased the rate to a high degree and also the percentage desalination was decreased to only 20%. A final note is that ΔC in this case is higher than the former three cases. These observations may be attributed to the fact that crown ether is less soluble in CB than in DCB. On the other hand, the absence of MC led to the to and fro diffusion of NaCl in the DP, since no complexation in the LM will occur and thus mass transfer from DP to LM will not take place. As shown in Table 9, it was demonstrated that the rate constants were not that different in the three cases DCB, DCB + MC and CB. However, \( k_{1d} \) and \( k_{2m} \) was lower with CB + MC, which indicated that the presence of MC in CB retarded the diffusion of NaCl through CB as LM. Finally, \( t_{max} \) increased to 70.4 minutes in this case and \( J_{max}^{\text{eff}} \) value was minimum, which ensures that using MC with CB was not favorable in this system. It is noteworthy that no MC was added when DW was used as LM because crown ether is insoluble in water; accordingly, the transfer in this case was simple transfer with chemical reaction in RP, which is preferable to avoid using chemicals which may affect the quality of the desalinated water.

### CONCLUSIONS

In the present work, a novel configuration of the SLM technique was assembled in which both DP and RP were made to flow either co- or counter-currently to each other while being separated by two cellophane sheets that are made to contain either the DW or organic membrane liquid. It was concluded that this configuration enhanced the mass transfer of solute to a great extent compared to ordinary SLM configurations in which both DP and RP are stagnant. The results showed that the higher the flow rate of DP and RP, the higher the mass transfer of NaCl; a volume ratio of DP to RP 3:1 gave better results. The type of SA in RP has a pronounced effect on the degree of desalination achieved. The number of coordinating hydroxyl groups in all the sequestrants tested has a marked effect on the mass transfer process of the NaCl, since the greater the number of OHs available for coordination, the higher the efficiency in complexing and trapping NaCl in RP. Consequently, it was concluded that using starch as SA was optimum and 15 g glucose was an efficient replacement for starch as SA.

<table>
<thead>
<tr>
<th>LM</th>
<th>( \varepsilon_0 )</th>
<th>( n_0 )</th>
<th>M</th>
<th>( \eta )</th>
<th>( V_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>9.93</td>
<td>1.55</td>
<td>2.27</td>
<td>0.84</td>
<td>113</td>
</tr>
<tr>
<td>CB</td>
<td>5.62</td>
<td>1.52</td>
<td>1.54</td>
<td>0.8</td>
<td>101.8</td>
</tr>
<tr>
<td>DW</td>
<td>80.1</td>
<td>1.33</td>
<td>1.82</td>
<td>1</td>
<td>18.01</td>
</tr>
</tbody>
</table>

Table 7: Physicochemical characteristics of LMs

Note: \( \varepsilon_0 \), dielectric constant (20°C); \( n_0 \), refractive index, (20°C); \( \mu \), dipole moment (D); \( \eta \), viscosity (cP); \( V_m \), molar volume (ml/mol).

<table>
<thead>
<tr>
<th>Type of organic LM</th>
<th>( k_{sd} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{sm} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{dr} \times 10^{-2} ) (min(^{-1}))</th>
<th>( k_{mr} \times 10^{-4} )</th>
<th>( J_{max} )</th>
<th>( J_{max}^{\text{eff}} \times 10^3 ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>1.2</td>
<td>100.2</td>
<td>70</td>
<td>0.012</td>
<td>44.5</td>
<td>0.012</td>
</tr>
<tr>
<td>CB</td>
<td>1.1</td>
<td>115.8</td>
<td>274.7</td>
<td>0.009</td>
<td>40.3</td>
<td>0.010</td>
</tr>
<tr>
<td>DW</td>
<td>1.2</td>
<td>79.4</td>
<td>206.5</td>
<td>0.015</td>
<td>53.2</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 8: Kinetic parameters at different organic LM (Cl = 35 g/L, flow rate 30 mL/s, 20 g starch as SA, no MC in LM, volume ratio of DP:RP: 3:1)

<table>
<thead>
<tr>
<th>Type of LM system</th>
<th>( k_{sd} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{sm} \times 10^{-3} ) (min(^{-1}))</th>
<th>( k_{dr} \times 10^{-2} ) (min(^{-1}))</th>
<th>( k_{mr} \times 10^{-3} )</th>
<th>( t_{max} )</th>
<th>( k_{mr}/k_{2m} )</th>
<th>( J_{max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>0.9</td>
<td>115.1</td>
<td>118.2</td>
<td>0.008</td>
<td>42.1</td>
<td>0.008</td>
<td>0.9</td>
</tr>
<tr>
<td>DCB + MC</td>
<td>1.2</td>
<td>100.2</td>
<td>70</td>
<td>0.012</td>
<td>44.5</td>
<td>0.012</td>
<td>1.1</td>
</tr>
<tr>
<td>CB</td>
<td>1.1</td>
<td>115.8</td>
<td>274.7</td>
<td>0.009</td>
<td>40.3</td>
<td>0.01</td>
<td>1.1</td>
</tr>
<tr>
<td>CB + MC</td>
<td>0.7</td>
<td>64.5</td>
<td>311.7</td>
<td>0.011</td>
<td>70.4</td>
<td>0.011</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 9: Kinetic parameters at different organic LM with and without MC (Cl = 35 g/L, flow rate 30 mL/s, 20 g starch as SA, volume ratio of DP:RP: 3:1)
Using DW as LM was very efficient, giving remarkable results compared to ordinary organic LMs. It was found that the flow rate of the DP and RP along the cellophane membranes has a strong effect on enhancing the diffusion of NaCl from DP to RP through its effect on the boundary layer thickness. The presence of MC is of great importance, since it facilitates the mass transfer of NaCl from DP to RP.

Finally, initial NaCl concentration has a remarkable effect on the mass transfer rate, the higher the initial concentration, the higher the mass transfer rate according to the concentration driving force effect.

**REFERENCES**


aqueous solution using carrier-mediated transport.

Environmental Technology 37 (4), 495–504.

Neplenbroek, A. M., Bargeman, D. & Smolders, C. A. 1992


Swain, B., Mishra, C., Jeong, J., Lee, J. C., Hong, H. S. & Pandey, B. D. 2015 Separation of Co(II) and Li(I) with Cyanex 272 using hollow fiber supported liquid membrane: a comparison with flat sheet supported liquid membrane and dispersive solvent extraction process. Chemical Engineering Journal 271, 61–70.


