Supported ionic liquid membranes (SILMs) as a contactor for selective absorption of CO₂/O₂ by aqueous monoethanolamine (MEA)

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ABSTRACT

Application of membrane contactors in a combination of monoethanolamine as a solvent system for post-combustion CO₂ capture has been extensively studied in the last decades. Due to the better performance to capture CO₂ at low concentration, the potentialities of novel technology of supported ionic liquids membranes (SILMs) for absorption process in gas-liquid membrane contactor system are currently being explored to improve and compliment previous technology. In this study, a modified hydrophobic gas-liquid membrane contactor system was prepared using Liqui-Cel® parallel flow module as a membrane support and 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [emim] [NTf₂] ionic liquid as a supporting phase. Under moderate operating conditions, parallel flow mode and use of monoethanolamine (MEA) as an absorbent, the effects of absorbent temperature and gas velocity on the CO₂ absorption efficiency and CO₂/O₂ selectivity were determined using this modified module. Further investigation to compare the performances of blank and modified membrane module was implemented at different temperatures (303–348 K) and gas velocities (4.63 × 10⁻⁶ to 3.70 × 10⁻⁵ m s⁻¹). Results revealed that efficiency of the CO₂ absorption process of the modified module is almost doubled with an average selectivity factor of CO₂/O₂ around 5 times compared to blank contactor system. Thus, this modified membrane contactor system had shown a great potential for further used in the real industrial CO₂ capture and beneficial to bottleneck the issue of MEA oxidation that usually occurred in previous gas-liquid membrane contactor system.

1. Introduction

In the recent years, the development of robust and eco-friendly technologies in the reduction of CO₂ emission becoming extremely crucial. In order to minimize the emissions of carbon dioxide, CO₂ capture and storage is one of the popular strategies being employed worldwide. Chemical absorption using amine solutions can be considered as one of the most effective CO₂ capture methods to remove CO₂ after combustion, i.e. during post-combustion CO₂ capture [1]. This method has recently reached a commercial stage and being recognized as the most mature method for post-combustion CO₂ capture [2–4]. Monoethanolamine (MEA) can be considered as a standard solvent in chemical absorption of CO₂, due to its excellent properties towards CO₂ absorption, which exhibits high reactivity of CO₂, a CO₂ absorption capacity of 1:2 mol of CO₂ per mole of solvent ratio, relatively low solvent cost, low molecular weight, special ease of reclamation and reasonable volatility [3–6]. However, solvent degradation has become one of the main concerns in CO₂ capture processes. It is an irreversible transformation of an absorbent solution into other compounds or by-products. These by-products can cause problems to the absorption process such as corrosion of the equipment, fouling, amine loss, foaming and reduction of CO₂ absorption capacity [7]. While the degradation of amines can be either oxidative or thermal, some of the degradation products can be corrosive agents. In pilot plants, oxidative degradation due to dissolved O₂ was found to be more dominant than the thermal degradation [8].

Another main limitation in post-combustion CO₂ capture is the requirement of membrane with high selectivity characteristics to extract a relatively low concentration CO₂ from flue gases [9]. Hence, the selectivity of membrane is a huge challenge in commercializing this process. Due to this reason, membrane properties play an important role not only in the effectiveness of CO₂ capture [10], but also in the separation and absorption of O₂, H₂S, SO₂ and other volatile organic compounds (VOC) [11,12]. Since membrane materials play the most

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crucial role in governing the gas transport through the membrane, there is a need to wisely select the membrane materials to fulfill the requirement of the processes. Up to date, the most prominent way to gain excellent selectivity is the incorporation of liquid into polymers membranes, which yield to supported liquid membranes (SLMs) [13]. In supported liquid membranes, the liquid is either supported on the surface of a solid or filled inside the pores. The transport mechanism for the SLMs is solution diffusion, while the main factor that controls the selectivity is the affinity of the membrane towards the particular gas of interest. Quite a number of studies have been found to report on the investigations of the performance of various solvents in these membranes [14–17].

Meanwhile, ionic liquids (ILs), offer attractive transport properties due to low resistance to diffusion [18], while the selectivity can be tuned by choosing appropriate functional groups [19]. The combination of ILs with membranes for CO2 separation is a relatively new concept [20]. Many different types of membranes and membrane processes containing ILs have been reported, including supported IL membranes (SLMs). A large number of publications and significant attention by engineering communities relating to the use of ILs in SLMs for CO2 gas separations clearly show that research in this field has grown dramatically over the last decade. This IL-based platform has opened a new door for exploring next-generation CO2 separation membrane materials and membrane processes, which give a nearly infinite range of possibilities concerning membrane design and lead us to the goal of technological sustainability. Despite the rapid development of SLMs in recent years, there is still a big margin for the further improvement especially its application for CO2 absorption process in membrane contactor system using MEA as a solvent [21]. Its unique characteristics such as high interfacial area per unit volume, small size, easiness to scale up and down, and independent control of gas and liquid flow rates make the membrane contactors as a superior option [22]. The combination of the high efficiency absorbent (high efficiency), as well as high surface area and compact structure SLMs in the membrane gas absorption process is the main advantage of this hybrid technology. This process can achieve a better selectivity and higher removal rate than a normal gas separation membrane due to the continuous high driving force. Thus, research must be done to tackle the challenges associated with the tendency of SLMs for selective CO2 absorption which leads to prevention of MEA oxidation degradation [21]. This study reports the preparation of SLMs for high CO2 performance and an improved CO2/O2 selectivity. To our best knowledge, this is the first article that reports the preparation and application of SLMs as an absorption process to capture CO2 from flue gases, while preventing oxidative degradation of MEA solvent during this process. To evaluate the performance of the SLMs prepared, a Liqui-Cel® parallel flow supported with [emim][NTf2] IL has been chosen as the contactor equipment to conduct the parametric study and long-term performances of the CO2 absorption process.

2. Experimental

2.1. Materials

1-ethyl-3-methylimidazolium bis ( trifluoromethylsulfonyl) imide [emim][NTf2] is the IL used in this research as a supporting phase, with a molecular weight of 391.31, a melting point above −15 °C, and a purity level over 97% (Merck, Germany). Monoethanolamine (MEA) and acetone were purchased and used with the highest purity level available (Merck, Germany). A polypropylene (PP) Liqui-Cel® parallel flow membrane contactor (Hoechst Celanese Corp., Charlotte, NC, USA) was used as a membrane support system (Fig. 1). Specifications of the hollow fiber are given in membrane Table 1.

![Fig. 1. Parallel flow Liqui-Cel gas-liquid membrane contactor.](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Hollow fiber membrane contactor characteristics for parallel Liqui-Cel type.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane material</td>
<td>Polypropylene (PP)</td>
</tr>
<tr>
<td>Fiber o.d., d1 (m)</td>
<td>3 × 10⁻⁴</td>
</tr>
<tr>
<td>Fiber i.d., d2 (m)</td>
<td>2.2 × 10⁻⁴</td>
</tr>
<tr>
<td>Fiber length, l (m)</td>
<td>0.115</td>
</tr>
<tr>
<td>Number of fibers, n</td>
<td>2300</td>
</tr>
<tr>
<td>Effective inner membrane area, A (m²)</td>
<td>0.18</td>
</tr>
<tr>
<td>Membrane thickness, δ (m)</td>
<td>0.4 × 10⁻⁴</td>
</tr>
<tr>
<td>Membrane pore diameter, dp (µm)</td>
<td>0.04</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>40</td>
</tr>
<tr>
<td>Packing factor</td>
<td>0.39</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>2.5</td>
</tr>
<tr>
<td>Diameter of the contactor, d_contact (m)</td>
<td>2.54 × 10⁻²</td>
</tr>
</tbody>
</table>

2.2. Preparation of supported ionic liquid membranes (SLMs)

Based on our previously reported work [21], a binary mixture with a composition of 80% [emim][NTf2] IL: 20% acetone (v/v) was selected as a supporting phase. At this composition, the IL was also found to be homogeneously distributed. In this process, IL was supplied to the shell side of the membrane. The process duration was set to 24 h to provide sufficient time for the diffusion of the IL into the membrane structure. Then, any remaining solvent on the membranes from the surface was eliminated, and the drying process was done for 1–2 days in dry air (N2) at a flow rate of 1 LPM, for the removal of the residual acetone.

2.3. CO2 absorption using gas-liquid membrane contactor system

Fig. 2 shows the schematic diagram of CO2 absorption process using a prepared [emim][NTf2]-SLMs gas-liquid membrane contactor with various composition range of flue gas. In preparation of the aqueous MEA solution, MEA of 99.5% purity level was dissolved in deionized water. The gas and liquid circulated in opposite directions over the module (the absorbent passed through the shell side, while the gas also circulated countercurrently through the lumen side of the hollow fibers). In the experiments, the introduction of gas mixtures into the process from compressed gas containers and the adjustment of the flow rates using mass flow controller (GFC17, Aalborg, Aalborg Instrument and Control, Inc.) were made, which can put accurate control on the gas flow rate. After being channeled through a pressure gauge, the gas mixtures flowed into the membrane module from the lumen side. An analysis of the inlet and outlet gas compositions was analyzed using CO2 analyzer (Guardian, Edinburgh Instrument Ltd.). A vessel that had been submerged in a water bath was provided, in order to keep the absorbent solution. The control of the absorbent solution temperature was made through adjustment on the temperature of the water bath. Moreover, in order to drive the absorbent into the shell side of the membranes from the absorbent solution vessel with a controlled liquid flow rate, a pump drive (PD5201, Heidolph Instruments GmbH & Co. KG, Germany) was used. Through the application of chemical titration method and the usage of oxygen meter, the outlet concentration of CO2 and O2 in a liquid absorbent from the membrane contactor were measured respectively.
2.3.1. Determination of CO₂ loading
For the purpose of obtaining the CO₂ loading of the sample after the reaction, 5 ml sample of the carbonated solution was taken over the sample point. The sample was then mixed with 50 ml solution of 0.5 M BaCl₂ and 50 ml solution of 0.5 M NaOH. In this experiment, NaOH solution was added to convert all the free dissolved gas into non-volatile ionic species, while BaCl₂ solution was used to precipitate all the CO₂ existed in the sample solution. The mixtures were then stirred for 3 h at 343 K and at atmospheric pressure. The sample was then cooled down to room temperature before filtration and washed thoroughly to eliminate all traces of NaOH.

BaCO₃ was precipitated as a white crystalline solid residue using Glass microfiber filter paper in order to ensure that the whole solid carbonate was collected during this process. Solid BaCO₃ was then mixed with 300 ml of distilled water and stirred for 3 h to ensure complete dissolution of the solid. It was then titrated with a standard solution of 1 M HCl using a computer controlled auto-titrator (Metrohm 716 DMS Titrino). The data obtained were used to calculate the CO₂ loading. This method of determining CO₂ loading was verified by conducting a similar experiment on a sample containing a known amount of NaHCO₃. The tests were repeated three times for each sample to ensure the accuracy of the data.

The volume of HCl used to neutralize the basic species in the solution is determined from the endpoints using the first derivative of the titration curve. The CO₂ loading of the solution is defined as total mol of CO₂ absorbed per mol of amine (Eq. (2.1)):

\[
\alpha_{\text{CO}_2} = \frac{V_{\text{HCl}} \times M_{\text{HCl}}}{2(M_{\text{MEA}})(V_{\text{Sample}})}
\]

where

\[
\alpha = \text{CO}_2 \text{ loading in mol of CO}_2 \text{ per mol of amine}
\]

\[
V_{\text{HCl}} = \text{Volume of HCl needed to neutralized the basic species in ml}
\]

\[
V_{\text{Sample}} = \text{Volume of sample taken for analysis in ml}
\]

\[
M_{\text{MEA}} = \text{Molarity of the alkanolamine solution in mol per litre}
\]

2.4. Performances and selectivity of CO₂/O₂ using blank and supported ionic liquid membranes (SILMs) contactor system

CO₂ absorption performances of blank and supported ionic liquid membranes contactor system were performed as per described in Section 2.3 using parallel (Fig. 1) membrane module. Meanwhile, the ideal selectivity of CO₂/O₂ for both systems are determined by the ratio of the outlet concentration of the gases in the absorbent of the membrane modules.

2.4.1. Mass transfer calculations
In order to relate the overall mass transfer resistance to the individual mass transfer resistance, the resistance in series approach is used (Eq. (2.2)).

\[
R_{\text{overall}} = R_g + R_{\text{mg}} + R_l
\]

A hollow fiber configuration is selected, with the gas phase flowing through the lumen side and the liquid phase in the shell side. The outer diameters of the tubes are the location where the liquid-gas interface is located. The Eq. (2.3) as follows considers the chemical reaction in the liquid side (as expressed by the enhancement factor, Eₐ):

\[
\frac{1}{K_{\text{overall}}} = \frac{d_o}{k_o d_l} + \frac{d_o}{k_{\text{mg}} d_{\text{mg}}} + \frac{1}{k_h E_a}
\]

where \(d_{\text{mg}}, d_l\), and \(d_o\) are the log mean, inside and outside diameters in (m) of the hollow fiber, with \(H_d\) representing the Henry constant that is dimensionless, \(k_{\text{mg}}, k_i, k_s\), are the individual mass transfer coefficients for the membrane, liquid phase and gas phase, correspondingly (m s⁻¹) and \(K_{\text{overall}}\) is the overall mass transfer coefficient (m s⁻¹). Henry’s law constant \(H_d\) which is dimensionless, is the important factor in modeling the process of mass transfer. The below equation for Henry constant had been defined in previous researches (Eq. (2.4)):

\[
H_d = \frac{C_{\text{gas}}}{C_i} = \frac{y^* P_f}{x^* RT}
\]

with \(x^*\) and \(y^*\) being the molar fractions in the liquid and gas and phases correspondingly and \(P_f\) is the pressure for overall. The mass...
transfer flux of carbon dioxide is determined as per Eq. (2.5):

\[ N_{CO_2,i} = \frac{Q_i}{A}(C_{CO_2,\text{in}} - C_{CO_2,\text{out}}) = \frac{K_{\text{overall}} \Delta ylm P_f}{RT} \]  

(2.5)

Fluxes are equal in the liquid and gas, in the steady state of CO2. The overall mass transfer \( K_{\text{overall}} \) is able to assessed through an experiment from the flux through the concentration gradient and membrane. \( \Delta ylm \) is the logarithmic mean of the driving force that is based on gas phase molar fractions, \( P_f \) is the entire pressure in the gas phase, \( A \) is the membrane area (m²) and \( Q_i \) is the gas flow rate (m³s⁻¹). In view of the carbon dioxide concentration in the outlet \( (y_{CO_2,\text{out}}) \) and the inlet \( (y_{CO_2,\text{in}}) \) of the hollow fiber membrane contactor, it is assumed that CO2 concentration in the solvent is quite a distance far from the saturation in the experiments, the calculation for \( \Delta ylm \) are as per Eq. (2.6):

\[ \Delta ylm = \frac{(y_{CO_2,\text{out}}) - (y_{CO_2,\text{in}})}{\ln((y_{CO_2,\text{out}})/(y_{CO_2,\text{in}}))} \]  

(2.6)

Quite a few authors have recommended other empirical correlations for the parallel flow in shell-side mass transfer in hollow fiber membrane contactors [23]. Kartohardjono’s correlation is being used in this study to estimate \( k_i \), due to the Reynolds number and packing factor are in a similar range \((0.029 < \varphi < 0.53; \text{Re} > 4000) \) (Eq. (2.7)):

\[ Sh = \left( \frac{k_i d_i}{D_{CO_2}} \right) = 0.1879(\varphi^{0.66})Re^{0.34}Sc^{0.7} \]  

(2.7)

\[ d_i = \frac{d_{\text{outside}}^2 - d_{\text{inside}}^2}{na_o} \]  

(2.8)

where

- \( Re \) = Reynolds number
- \( Sc \) = Schmidt number
- \( Sh \) = Sherwood number
- \( D_{CO_2} \) = diffusion coefficient of carbon dioxide in the liquid
- \( d_i \) = hydraulic diameter (m)
- \( d_{\text{outside}} \) = outside diameter of the fiber (m)
- \( d_{\text{cont}} \) = diameter of the contactor (m)
- \( n \) = number of fibers

The membrane contactor characteristics and the physical properties of the absorbent determines the mass transfer coefficient in the liquid phase \( (k_i) \). Morgan et al. (2005) [24] have established a correlation that expresses the liquid viscosity with the dependency of gas diffusivity as per Eq. (2.9):

\[ D_{CO_2} = 2.66 \times 10^{-3} \frac{1}{\mu_{\text{MEGA}}^{0.4} C_{CO_2}} \]  

(2.9)

with \( V_{CO_2} \) being the molar volume of carbon dioxide at the normal boiling point \((33.3 \text{ cm}^3 \text{ mol}^{-1})\), \( \mu_{\text{MEGA}} \) being the viscosity of solvent in cP, and the diffusivity found in \text{cm}^2 \text{s}^{-1}. The gas and liquid velocities were also calculated based on Eqs. (2.10) and (2.11).

\[ \frac{Q}{A} = \frac{V_{\text{MEGA}}}{\lambda_{\text{MEGA}}} \]  

(2.10)

where \( Q \) being an inlet volume flow rate to both tube or shell sides of the membranes (ml min⁻¹), \( A \) is the inner surface of the hollow fiber membranes (m²) and \( \lambda_{\text{MEGA}} \) is the average velocity (m s⁻¹). Substituting and converting the known values and units produces,

\[ \lambda_{\text{MEGA}} = \frac{X(\text{ml/min})(10^{-6} \text{ m}^3/\text{ml})(1 \text{ min}/60 \text{ s}) = Y \text{ m s}^{-1}}{A(\text{m}^2)} \]  

(2.11)

Prediction of the calculation for this membrane absorption process is basically follows several assumptions such as:

(a) The operating system is under isothermal and steady-state conditions
(b) Consideration of the gas phase as an ideal gas
(c) Incompressible liquid phase and Newtonian-type flow
(d) Negligible axial diffusion
(e) The Henry’s law is appropriate for the gas-liquid surface

3. Results and discussion

3.1. CO2 absorption performance of the SILM contactor in parallel flow mode

To evaluate the process efficiency of both systems at different temperatures and gas velocities, carbon dioxide absorption experiments were carried out in a blank and supported ionic liquid membrane (SILM) contactors. The CO2 absorption flux of the module can be calculated as per Eq. (3.1):

\[ J_{CO_2} = \frac{(C_i - C_o)Q_i}{A_i} \]  

(3.1)

where \( J_{CO_2} \) is the CO2 absorption flux (mol m⁻² s⁻¹), \( Q_i \) is the liquid flow rate (m³ s⁻¹), \( A_i \) is the inner surface of the hollow fiber membranes (m²), \( C_i \) and \( C_o \) are the liquid phase CO2 concentrations (mol m⁻³) at inlet and outlet of the membrane module, respectively. The experimental CO2 absorption efficiency can be calculated as per Eq. (3.2):

\[ \text{Efficiency, } \eta(\%) = (1 - C_o/C_i) \times 100 \]  

(3.2)

Figs. 3 and 4 show the results of both systems being conducted at different temperatures (303, 318, 333 and 348 K) with a gas velocity of \( 4.63 \times 10^{-6} \text{ m s}^{-1} \). The outlet concentration dimensionless of carbon dioxide is calculated as \( C_{o(i)/C_{o*out}} \). Meanwhile, Figs. 5 and 6 demonstrate the trend of carbon dioxide outlet concentration operated with gas velocity, ranges from \( 4.63 \times 10^{-6} \) to \( 3.70 \times 10^{-5} \text{ m s}^{-1} \) (gas flow rate = 50, 100, 200, 300 and 400 ml min⁻¹) at 303 K using blank (Fig. 5) and a supported ionic liquid membrane (Fig. 6) contactor, respectively. The outlet concentration dimensionless of CO2 was calculated for each experiment at pseudo-steady-state, ranges between (a) 0.61–0.64 for blank contactor and 0.19–0.21 for supported ionic liquid membrane contactor at different temperatures, while approximately (b) 0.61–0.99 for blank contactor and 0.19–0.96 for supported ionic liquid membrane contactor in the case of different gas velocities.

The CO2 removal efficiencies were calculated from inlet and outlet concentrations at different temperatures and gas velocities.
CO₂ concentrations of the experiments. In Fig. 7, the efficiency and mass transfer rate of CO₂ is plotted as a function of absorbent temperature for both membrane contacting systems. The gas and liquid velocities were considered as constant at 4.63 × 10⁻⁶ and 9.26 × 10⁻⁶ m s⁻¹, respectively. For blank membrane, when absorbent temperature was increased from 303 to 348 K, the CO₂ absorption efficiency and mass transfer rate was slightly decreased from 39.13 to 36.23% and from 2.15 × 10⁻⁶ to 1.99 × 10⁻⁶ mol m⁻² s⁻¹. Meanwhile for the SILM system, data had shown that the CO₂ absorption efficiency decreases from 80.68 to 79.23%; with the increase of absorbent temperature of 303–348 K. By increasing the absorbent temperature, the absorption flux decreases from 4.43 × 10⁻⁶ to 4.36 × 10⁻⁶ mol m⁻² s⁻¹. It is known that the increase in temperature favoured reaction rate, according to the Arrhenius expression of reaction rate constant [25,26], and diffusion [27,28]. In addition, the increase in temperature also resulted in a decrease in CO₂ solubility [29] and an increase in evaporation of absorbent; which are not conducive to absorption [30]. In previous study, it was observed that by increasing the temperature of amine solutions, the effects of temperature on reaction rate and diffusion rate are higher than that on CO₂ solubility [31]. However, the temperature effect was found to be reversed in this study. A more favourable CO₂ removal condition can be seen with a low temperature operation. The reduction of mass transfer rate with an increase in temperature especially in lower CO₂ removal condition can be seen with a low temperature operation. The reduction of mass transfer rate with an increase in temperature especially in lower CO₂ loading, and was confirmed by previous works [29,30]. As discussed above, it should be noted that increasing the absorbent temperature of 2M MEA have been known to reversely influence the efficiency and mass transfer rate of CO₂. Therefore, a relatively lower value of temperature should be selected for this study.

On the other hand, the impact of gas velocities on the mass transfer rate and absorption efficiency of CO₂ is studied and demonstrated in Fig. 8. When the gas velocity increases from 4.63 × 10⁻⁶ to 3.70 × 10⁻⁵ m s⁻¹, the residence time of CO₂ in the membrane
CO₂ loading attributed to the low solubility of CO₂ in MEA solution at temperatures, (iii) the temperature had a minor impact towards CO₂ absorption process when compared to the dominant impact of gas velocities, and more importantly (iv) the efficiency and residence time in supported ionic liquid membrane was slightly higher as compared to a blank contactor system; which doubles the efficiency from 303 to 348 K and from 4.63 × 10⁻⁶ to 3.70 × 10⁻⁵ m s⁻¹.

3.2. Selectivity of the SILM contactor in parallel flow mode

It is with high regards, that the information that was obtained from previous COSMO-RS predictions is valuable to identify the selectivity of CO₂/O₂ in a gas-liquid membrane contactor system for selected ionic liquids. The outcome from the predictions have demonstrated that [emim][NTf₂] IL could be a good candidate as supporting material for SILMs, which was attributed to higher CO₂/O₂ selectivity characteristics as compared to others [21]. For the parallel flow mode system, selectivity data was obtained by plotting the outlet concentration profiles of CO₂ and O₂ for each run at different absorbent temperatures and gas velocities. Typical CO₂ and O₂ loadings at steady state with selectivity data at various operating conditions for the blank and SILM system are provided in Figs. 9, 10 and Table 2 respectively. To investigate the absorbent temperature effects towards the selectivity of CO₂/O₂, a profile of CO₂ and O₂ loading as shown in Fig. 9 was evaluated. The outlet concentrations of CO₂ and O₂ were calculated for each experiment at pseudo-steady-state that ranged between (a) 1.81–1.67 mol m⁻³ of CO₂ and 0.13–0.18 mol m⁻³ of O₂ for blank system and (b) 3.72–3.66 mol m⁻³ of CO₂ and 0.05–0.09 mol m⁻³ of O₂ for SILM system. It is obvious that the loading of CO₂ of the run that was conducted at 303 K was higher than those carried out at the higher temperatures of 318, 333 and 348 K. The loading of O₂ was found to have increased, if the temperature increase was due to the reduction of CO₂ loadings attributed to the low solubility of CO₂ in MEA solution at higher temperatures. Therefore, selectivity of CO₂/O₂ of the run at 303 K measured at 13.9 was slightly higher than those at 318, 333 and 348 K, respectively, measured at 11.7, 10.8 and 9.3 for blank membrane; and declined from 74.4 to 40.7 for SILM system (Table 2). Based on initial analysis, MEA have shown a tendency to degrade if

Table 2
Selectivity of CO₂/O₂ for (a) blank and (b) SILM contactor system at different temperatures and gas velocities.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Gas velocity (m s⁻¹)</th>
<th>Selectivity (a)</th>
<th>Selectivity (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>4.63 × 10⁻⁶</td>
<td>13.90</td>
<td>74.40</td>
</tr>
<tr>
<td>318</td>
<td>4.63 × 10⁻⁶</td>
<td>11.70</td>
<td>52.90</td>
</tr>
<tr>
<td>333</td>
<td>4.63 × 10⁻⁶</td>
<td>10.80</td>
<td>46.00</td>
</tr>
<tr>
<td>348</td>
<td>4.63 × 10⁻⁶</td>
<td>9.30</td>
<td>40.70</td>
</tr>
<tr>
<td>303</td>
<td>9.26 × 10⁻⁶</td>
<td>8.50</td>
<td>20.80</td>
</tr>
<tr>
<td>303</td>
<td>1.85 × 10⁻⁵</td>
<td>2.60</td>
<td>9.90</td>
</tr>
<tr>
<td>303</td>
<td>2.78 × 10⁻⁵</td>
<td>1.10</td>
<td>5.60</td>
</tr>
<tr>
<td>303</td>
<td>3.70 × 10⁻⁵</td>
<td>0.40</td>
<td>2.00</td>
</tr>
</tbody>
</table>
temperature in the system were increased [32]. This is due to the reduction of CO$_2$ loading that would lead to the enhancement of MEA degradation attributed to the increase of O$_2$ loading in the solvent system [33]. The MEA degradation rate was higher at a lower CO$_2$ loading, than at a higher CO$_2$ loading. Then again, the degradation rate in the MEA-CO$_2$-O$_2$ system was found to be 8.3 times higher as that in the MEA-CO$_2$ system. This shows that MEA is more prone to degradation in the presence of O$_2$, as compared to the presence of only CO$_2$ [34].

Meanwhile, in the case of different gas velocities, the measured loading of CO$_2$ and O$_2$ was (a) 1.81 to 0.07 mol m$^{-3}$ of CO$_2$ and 0.13 to 0.19 mol m$^{-3}$ of O$_2$ for blank system and (b) 3.72 to 0.18 mol m$^{-3}$ of CO$_2$ with 0.05 to 0.09 mol m$^{-3}$ of O$_2$ for SILM system. As a result, the effect of gas velocities on the selectivity of CO$_2$/O$_2$ was evaluated using a similar approach that was used for absorbent temperature. The loadings of CO$_2$ and O$_2$ in 2M MEA is shown in Fig. 10, while selectivity data of CO$_2$/O$_2$ was presented in Table 2. The runs were conducted at 303 K with gas velocities ranging from $4.63 \times 10^{-6}$ to $3.70 \times 10^{-5}$ m s$^{-1}$. The results have shown that the selectivity for the run with $4.63 \times 10^{-6}$ m s$^{-1}$ was 37 times higher than that of the run carried out at a gas velocity of $3.70 \times 10^{-5}$ m s$^{-1}$ for both systems. From the results obtained as shown in Figs. 9 and 10, some remarks are pointed out for both systems: (i) the CO$_2$ loading significantly influences the loading of O$_2$; (ii) lower O$_2$ loading attributed to the higher loading of CO$_2$ in the 2ME, due to the fact that the higher CO$_2$ loading causes a reduction in the solubility of O$_2$ in the MEA solution and (iii) selectivity of CO$_2$/O$_2$ using supported ionic liquid membrane were always higher than that of a blank contactor system with an average selectivity factor of about 5 for both parameters.

### 3.3. Mass transfer calculations

The overall mass transfer coefficient $K_{\text{overall}}$ is calculated from the experimental results of CO$_2$ fluxes at different temperatures and gas velocities using Eq. (3.1). Table 3 shows the different trends in the $K_{\text{overall}}$ for both systems. For both contactor systems, the $K_{\text{overall}}$ value remains constant around $4.60 \times 10^{-6}$ to $4.17 \times 10^{-6}$ m s$^{-1}$ (blank) and $1.52 \times 10^{-5}$ to $1.46 \times 10^{-5}$ m s$^{-1}$ (supported ionic liquid membrane) for the temperature interval of 303 to 348 K. Despite that, in the case of decreasing gas velocities from $4.63 \times 10^{-6}$ to $3.70 \times 10^{-5}$, the $K_{\text{overall}}$ value increases significantly from $1.35 \times 10^{-7}$ to $4.60 \times 10^{-7}$ m s$^{-1}$ (blank) and $3.65 \times 10^{-7}$ m s$^{-1}$ to $1.52 \times 10^{-5}$ (supported ionic liquid membrane). Under optimal operating conditions, the mass transfer coefficient using supported ionic liquid membrane contactor is 3.3 times higher as compared to the blank system. This behavior correlates with the presence of [emim] [NTf$_2$] ionic liquid as an immobilized liquid in the pores of the membrane, where it would result in improved process efficiency for CO$_2$ capture.

### 3.4. Long-term performances of SILM contactor in parallel flow mode

The effects of operation time on the CO$_2$ absorption performances of blank membrane and SILM membrane were investigated by running the system continuously for 72 h, followed by heating in combination with drying the membranes at 373 K for 24 h. This entire process is known as one cycle. For the blank membrane, the CO$_2$ absorption efficiency and CO$_2$ mass transfer rate were maintained around 39.13% and 3.76 $\times$ 10$^{-6}$ mol m$^{-2}$ s$^{-1}$, respectively, within the first 72 h (Cycle 1). This cycle is illustrated in Figs. 11 and 12. The CO$_2$ removal efficiency and CO$_2$ mass transfer rate were decreased with the increase in the number of cycles. This is due to the fact that heating and drying could not recover the performance of the blank membrane. In addition, this is also attributable to the irreversible changes of the membrane surface morphologies, due to swelling caused by long-term exposure to the
MEA aqueous solution [35–37]. After long-term operations, some slit-like pores in the blank membrane sample shrank longitudinally and became almost circular. The average pore diameter had increased with the time of operation resulting in more MEA aqueous solution being penetrated into the membrane pores [37–41]. Hence, the performance of blank membrane deteriorated with the operational time. For the SILM, the CO2 absorption efficiency maintained at 80.68% for 72 h with CO2 mass transfer rate of 7.75 × 10^{-6} mol m^{-2} s^{-1} until the end of the process of Cycle 1 (Fig. 11). A similar trend was observed for other cycles as well. In this work, the transport mechanism of gases through SILM can be explained by solution-diffusion process principles. After the heating and drying process at 373 K, the membrane’s performance was resumed and slightly doubled the performance of blank membrane. This observation suggests that the membrane’s surface was not destroyed during the exposure of the membrane to the MEA aqueous solution. Selectivity of CO2/O2 for both contactors systems using 2M MEA as a solvent system has been calculated, with the detailed results shown in Fig. 13. Blank membrane has displayed distinct changes in the selectivity values for CO2/O2 with the membrane process, and the stability of the membrane process was retained until the 3rd day of operation. However, in the case of SILM, the selectivity had improved significantly since the CO2/O2 selectivity of the SILM and is more than 4 times higher than the blank membrane even after the 3rd cycle. Meanwhile, the decrease of CO2/O2 selectivity of SILM after each cycle could be caused by the loss of IL during the regeneration process; and the IL used was not fully regenerated as there was still O2 that remained in the gas mixture. CO2 loading, which in turn causes a reduction of O2 in the MEA solution. In addition, it has been suggested that [emim] [NTf2] IL has displayed a higher affinity to CO2 [42–44] as compared to other gases in the gas mixture.

4. Conclusion

In this study, SILM system did not show any significant effect of temperature on the CO2 absorption performance (removal efficiency decreased from 80.68 to 79.23% for the temperature rise from 303 to 348 K). As for the blank membrane contactor system, the process was compensated by chemical reaction and diffusion with temperature, whereas in SILM system, the effect of solubility and chemical reaction become controlling stages of the process. It should be noted that the effect of wetting was not significant in this study because at each pseudo-steady-state conditions, no wetting was observed. Therefore, low temperatures in combination with low gas velocities should be selected as an optimal operating conditions for long term absorption performance. On the other hand, results indicated that, at optimal operating conditions, the overall mass transfer coefficient, \(k_{\text{av}}\), of the modified supported ionic liquid membranes contactor was 70% higher than that of the blank module. In addition, this modified system demonstrates the better capability for CO2 absorption process with an average CO2/O2 selectivity factor of 5 in comparison with the blank contactor. Thus, these behaviours are beneficial for capturing CO2 with high tendency, while preventing the oxidative degradation of monoethanolamine (MEA). There are still a number of on-going works which are focusing on development of SILMs for membrane contactor. Success in this area will definitely open the door widespread application of SILMs technology in CO2 absorption applications.

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Appendix A. Supplementary material

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