The effects of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [emim] [NTf$_2$] IL: acetone compositions on the amount, homogeneity and chemical stability of immobilized IL in hollow fiber-supported ionic liquid membranes (SILMs)

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ABSTRACT

The use of supported ionic liquid membranes and solvents that possess good selectivity on capturing carbon dioxide from flue gases would have a potential to replace conventional absorption method. However, common good solvents for carbon dioxide capture will undergo degradation due to the presence of oxygen. In this work, the effect of binary mixtures of [emim] [NTf₂] ionic liquid: acetone at different composition on the morphology of the supported ionic liquid membranes (SILMs) was investigated using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray (EDX) analysis. To test the stability of the SILMs, membranes were submerged in a pure and aqueous solution of monoethanolamine (MEA) at 70 °C for 14 days. The maximum amount of ionic liquid immobilized within the particular membranes was acquired at [emim] [NTf₂] IL: acetone; (80:20) composition and found to be homogeneously distributed. Based on the study, the SILMs were found to be more stable with 2 M MEA as its surrounding phase. These remarks were in agreement with the ionic liquid losses, as ascertained by mass balance. Results in this work ultimately suggest promising potentials of [emim] [NTf₂]-SILMs for further evaluation work, especially for the prevention of oxidative degradation of the amine solvents in membrane contactor applications for CO_2 capture.

Introduction

To date, supported liquid membrane (SLM) has been among the most favored methods of modifying membranes. It is believed that the usage of ionic liquids will work to control the challenges of the system due to their distinctive characteristics, such as broad liquidus range, trivial vapor pressure, stable thermal properties, and practicable gas solubilities (Hasib-ur-Rahman et al. 2012; Ramli et al. 2018). Previously, SLM systems are mainly comprised of common solvents such as monoethanolamine (MEA), diethanolamine (DEA), ethylenediamine (EDA), diisopropylamine (DIPA), polyethylene glycol (PEG), diglycolamine (DGA), and glycerol solutions as a supporting phase (Bara et al. 2009; Chen et al. 1999, 2001;

Davis and Sandall 1993; Donaldson and Nguyen 1980; Francisco et al. 2010; Matsumiya et al. 2005; Park et al. 2000; Saha and Chakma 1995; Teramoto et al. 1996; Yamaguchi et al. 1996). However, the major technical constraint of these systems has been determined to be associated with the stability of the membrane, which could be due to the possible leakage of the solvent from the pores or as a result of transmembrane pressure and evaporation process (Gorji and Kaghazchi 2008; de los Rios et al. 2009).

Ionic liquids with less vapor pressure (i.e., low volatility) can suppress the membranes' stability issues, which could eventually lead to more stable supported ionic liquid membranes (SILMs) (Luis et al. 2009; Noble and Gin 2011; Scovazzo 2009).

The ionic liquid within the SILMs can enhance the selectivity for a particular element, for instance, organic (Branco et al. 2002; Martak et al. 2008; Matsumoto et al. 2005), gases (Ilconich et al. 2007; Park et al. 2009; Scovazzo et al. 2009), ions (Alguacil et al. 2009, 2010), and liquid or vapor mixtures (Bryant et al. 1997; Izak et al. 2006, 2008; Matsumoto et al. 2009). Despite the ionic liquids' ability to prevent liquid loss from the pores, the high viscosity of the ionic liquids weakens the filling of the porous support (Kemperman et al. 1996). In response to this, viscosity has become a salient indicator of SILMs preparation procedure through the application of pressure (Hernandez-Fernandez et al. 2009), vacuum (Fortunato et al. 2005), and direct immersion or dipping method (Scovazzo et al. 2004) approach. The stability of the SILMs is an important aspect of industrial application related to the existence of leaching process after a long term of operation. Although this phenomenon's frequency could be ceased, it cannot be eliminated. Several reports have been found on the stability of SILMs at several operating conditions (e.g., surrounding phases, pressure, and temperature) (Bijani et al. 2009; Cserjesi et al. 2009; Hanioka et al. 2008; Ilconich et al. 2007; Myers et al. 2008) and based on the results, the performance of the membranes is significantly influenced by the viscosity of the ionic liquid (de los Rios et al. 2007; Hernandez-Fernandez et al. 2009).

The use of ionic liquids has solved the issue of solvent evaporation, which may happen in typical SLM which aim toward high thermal stability; however, issues regarding the role of viscosity on membrane performances and its chemical stability are still unsolved. Apart from that, there had been less report and discussions made in the preparation of SILMs using direct immersion or dipping method (easiest preparation technique) and its stability studies. Therefore, for more new insights into the issue of SILMs, in the recent experiment, preparation will be made on the SILMs from a different composition of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide: acetone as carriers. ILs containing bis(tri-fluoro-methylsulfonyl)imide ($[NTf_2]^-$) anion are selected due to their good hydrophobicity,

chemical stability, and widely ranged liquidity (Anwar et al. 2016).

Our work aims to get a better fundamental understanding in the effect of preparation method of supported liquid membranes on the stability of the SILM, which would be of great interest in designing a highly stable-supported ionic liquid membranes system. The chemical stability of a SILM based on [emim] [NTf_2] IL in different surrounding phases (pure MEA and 2 M MEA) will be microscopically characterized by using FESEM and EDX analysis. MEA solution is used as a surrounding phase, since our future interest is to extend the use of these SILM in the field of CO_2 absorption where MEA has been long recognized to be the benchmark solvent for this process. Besides, our previous experimental results have shown that the selectivity of CO_2/O_2 had been improved, with the presence of [emim] [NTf_2] IL within the membrane's pores (Ramli et al. 2018). The results have also demonstrated that the selectivity of CO_2/O_2 using [emim] [NTf_2]-SILMs was always higher than that of blank membrane with an average selectivity factor of 3. The potentialities for further evaluation work especially for the prevention of oxidative degradation of amine solvents using gas–liquid membrane contactor system will be useful in the field of CO_2 capture using SILMs. Thus, the analysis is made in three stages; the effects of the varying composition of IL on structures of membrane support will be investigated, and the amount of immobilized ionic liquid will be determined by mass balance. In addition, the surface structures and chemical stability of fresh membranes, including the membranes after being in contact with a pure and aqueous solution of monoethanolamine at 70 °C for 14 days of operation in a diffusion cell, will be compared and evaluated through FESEM-EDX analysis.

Methodology

Materials

1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [emim] [NTf_2] IL with a molecular weight of 391.31 g/mol, monoethanolamine (MEA), and acetone were purchased and used

Table 1. Specifications of the [emim] [NTf$_2$] IL.

|	
Purity (high-performance liquid chromatography)	≥98.0%
Halides (ion chromatography)	≤0.1%
Water (Karl Fischer)	≥1.0%
Melting point (°C)	−15

Table 2. Characteristics of hydrophobic PP hollow fiber membrane.

Parameter	Value
Fiber o.d. d_o (m)	3×10^{-4}
Fiber i.d. d_i (m)	2.4×10^{-4}
Membrane pore diameter, d_p (μm)	0.03
Porosity (%)	40

with the highest purity level available (Merck, Germany). A commercial polypropylene (PP) hollow fiber membrane (Seawell Industrial Limited, China) served as a membrane support in this research. Specifications of the [emim] [NTf$_2$] as an ionic liquid supporting phase, hollow fiber membrane and molecular structures of [emim] [NTf$_2$], acetone, and monoethanolamine are displayed in Tables 1 and 2 and Figure 1, respectively.

Preparation of supported ionic liquid membranes (SILMs)

Different amounts of IL and acetone were blended with different volume ratios of [emim] [NTf$_2$] IL: acetone; 100:0, 90:10. 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90, and 0:100 at 30 °C. Using VT550 rotary viscometer (HAAKE, Germany) and RE50 refractometer (Mettler Toledo, USA), measurements are made on viscosity and refractive index (RI) of binary mixtures, respectively. A total of 11 types of SILMs were then prepared via immobilization process of the binary mixtures onto the hollow fiber membranes. The duration of this process was set up to 24 hours to provide sufficient time for the IL's diffusion into the membrane structure. Twenty-four hours were considered as an adequate and optimal membrane immersion time due to unchanged amount of immobilized IL after this time (weight of immobilized IL was stable). Excess IL and acetone were then removed from the prepared SILMs using blotting paper and thoroughly dried over 12 days in dry air, respectively. The weights of all membranes prepared were measured before and after
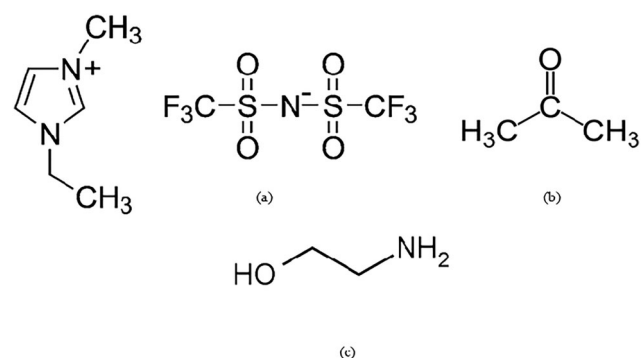
Figure 1. Molecular structures of [emim] [NTf$_2$] IL, acetone and monoethanolamine (MEA).

impregnation, in order to measure the loading of immobilized IL in the supporting membrane (Equation (2.1)).

Loading of immobilized IL (mg)
= weight of SILMs after impregnation of IL (mg)
− 17.00 mg (weight of each membrane before impregnation of IL (mg)

(2.1)

Characterization and stability of SILMs

The surface structure and elemental analysis of SILMs were examined using a field emission scanning electron microscope (FESEM) AURIGA cross beam workstation (Carl Zeiss, Germany), which was equipped with EDAX (AMETEK, advanced microanalysis solutions), at an accelerating voltage of 1.5 kV. On the other hand, the measurement of the individual pore diameters was determined from the enlarged micrographs using a computer program "Gatan: Digital Micrograph." The average pore size (d) and standard deviation (σ) were obtained from at least 200 membrane pores. In addition, the EDX analysis was also used to examine the elemental loss, after the membranes were immersed into pure MEA and 2 M MEA solutions individually via dipping method for 14 consecutive days at 70 °C.

Results and discussion

Physical properties of binary mixtures

Dynamic viscosities and refractive index (η_D) of [emim] [NTf$_2$] IL and acetone binary mixtures
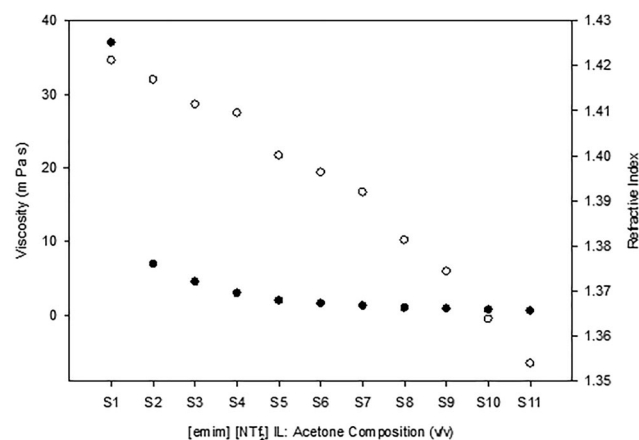
Figure 2. Viscosity (●) and RI (○) value of binary mixtures at various [emim] [NTf₂] IL: acetone compositions.

Table 3. Viscosity, RI, and the amount of immobilized IL at various [emim] [NTf₂] IL: acetone composition.

SILMs	ILs: Acetone (% v/v)	Viscosity (mPas)	RI	Immobilized ILs (mg)
S1	100:0	37.00	1.4212	3.00
S2	90:10	6.91	1.4169	9.50
S3	80:20	4.50	1.4114	58.50
S4	70:30	2.94	1.4095	55.50
S5	60:40	1.95	1.4000	50.80
S6	50:50	1.57	1.3963	47.50
S7	40:60	1.24	1.3919	40.00
S8	30:70	0.97	1.3813	30.80
S9	20:80	0.85	1.3744	20.80
S10	10:90	0.69	1.3638	6.80
S11	0:100	0.57	1.3539	0.00

were determined at 30 °C. Triplicate determinations were applied for the data reported. The measured parameters of the binary mixtures are presented in Figure 2 and Table 3. From this study, a significant decrease of viscosities was discovered with a decrease of [emim] [NTf₂] IL composition, which was from 37 to 0.57 mPa s. The viscosity values changed significantly at greater volume fraction when compared to lesser volume fractions of [emim] [NTf₂] IL. This was due to the viscosity of IL, which is higher than the viscosity of acetone. In addition, the results also showed that interactions between the protons of the ring, the methyl and methylene next to the nitrogen of ionic liquids, and the carbonyl oxygen of acetone weakened the strong interaction between the cation and anion of the ionic liquid, and thus increased the motion and decreased the viscosity of the ionic liquid (Zhai et al. 2006). Similarly, the decrease of the refractive index of mixtures in Figure 2 from 1.42 to
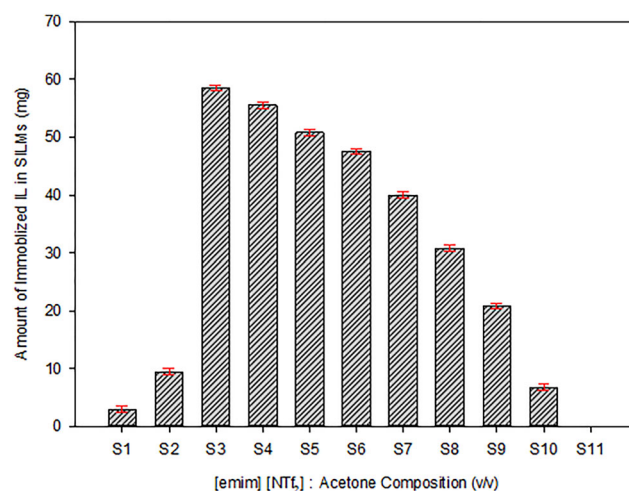

Figure 3. Effect of [emim] [NTf₂] IL: acetone composition (v/v) on the amount of immobilized IL of SILMs preparation.

1.35 occurs due to the increase of acetone composition in the mixture. Viscosity and refractive index were linearly correlated by the less presence of bigger chains of IL as they have less opportunity to interact with each other and move freely. The decrease of refractive index was due to the existence of highest density of electrons without involving any physical changes.

Supported ionic liquid membranes (SILMs)

Figure 3 shows the amount of ionic liquid embedded in SILMs as classified by weight differences. Based on the figure, the greatest extent of ionic liquid immobilized was acquired with S3; hence, this condition was taken as the optimal composition for SILMs preparation. The liquid membrane phase weight increased from 3 (S1) to 58.50 mg (S3) and then dropped continuously to 6.80 mg (S10). The reduction in viscosity of the ionic liquid due to the decline of the capillary force is a basis to elucidate the increase in the amount of immobilized IL on the membrane support of S1 to S3, for which consequently allowing the ionic liquid to penetrate through the porous membrane more efficiently (refer Table 3). Nevertheless, it was found that the increase of acetone composition from 30% to 90% in the binary mixtures had caused the loading of immobilized IL on the S4 to S10 membranes to decrease. This is due to the decrease of IL composition and insufficient amount of IL to be supported in the SILMs (Ramli et al. 2018).
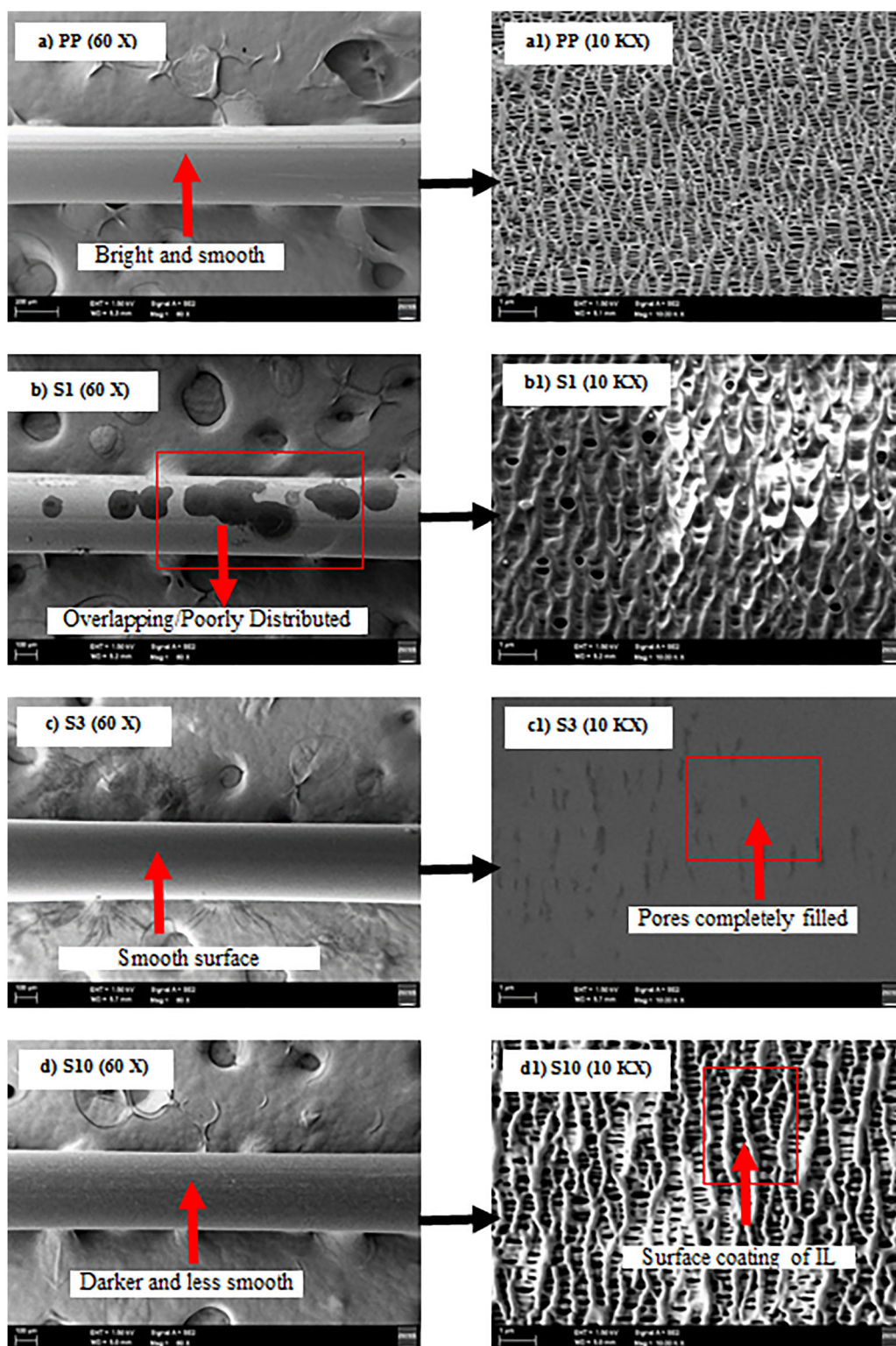
Figure 4. Micrographs of scanning electron of blank PP and prepared SILMs membranes (Outer layer) at different magnifications (Secondary Electron).

The microscopic characterization of the surface structures of the membranes was conducted using FESEM. Figure 4 consists of FESEM micrographs of the PP and SILMs membranes, which were based on (100:0), (80:20), and (10:90) of IL: acetone volume ratio, and prepared via the dipping method. Initial analysis of the structure of the PP polymeric membrane in the FESEM micrographs
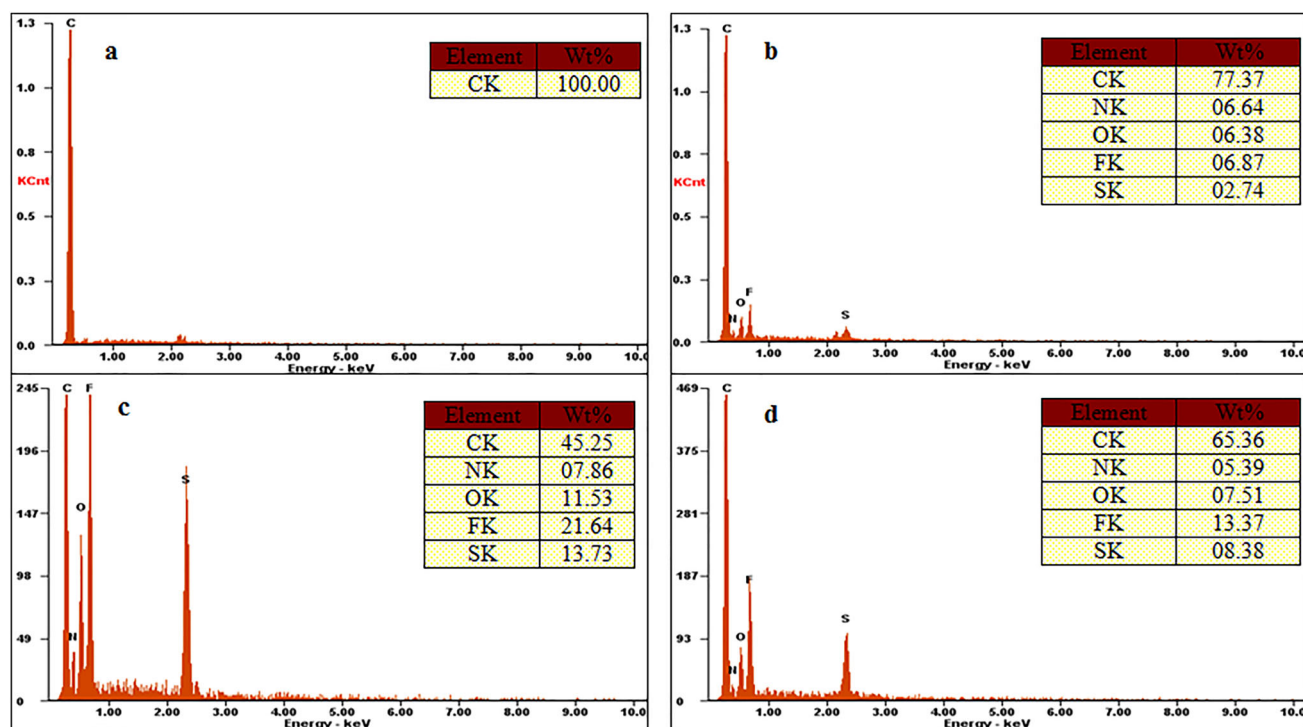
Figure 5. EDX spectra of (a) PP, (b) S1, (c) S3, and (d) S10 membranes.

shows a highly porous material composing of a network of microspores with a mean size of 0.079 μm (refer to Figure 4(a,a1)). After the immobilization of the [emim] [NTf₂] ionic liquid on the blank PP membrane, the SILMs were examined to verify their homogeneity and distribution.

Based on FESEM micrograph analysis presented in Figure 4(d,d1), it can be seen that after the impregnation with low [emim] [NTf₂] IL: acetone composition (10:90), homogenous distribution of the IL on the membrane was not observed and the pores of the membranes were occupied with few IL filling. In addition, the existence of an inadequate amount of ionic liquid on the outer membrane surfaces was apparent in this condition, since the membrane wall was clearly visible in **micrograph** Figure 4(d1). However, the immobilization of 80% of [emim] [NTf₂] IL: 20% of acetone (v/v) into membrane support appeared to have completely filled the membrane pores and homogeneously distributed (refer to Figure 4(c,c1)).

On the other extreme, Figure 4(b,b1) indicates immobilization and poor distribution (overlapping) of the ionic liquid on the outermost layers of the membranes when pure [emim] [NTf₂]

ionic liquid was used. The possible factor to this was the great capillary force associated with the highly viscous liquid, which increased makes it inconvenient to diffuse into the pores of the membrane. The significance of liquid viscosity on the degree of IL immobilization was validated, provided that there be correlations between these observations and the viscosity of the ionic liquid. Thus, in this study, SILMs based on 80:20 of [emim] [NTf₂] IL: acetone composition (S3) prepared at optimal composition for SILMs were selected for further investigation. Selection of S3 membranes for the operation was supported by the facts that leakage of ILs outside of the membrane would occur during the absorption process with the use of pure ILs as a supporting phase, due to an excessive supply of ILs into the membrane. In order to resolve the problem, the ILs were diluted through the use of co-solvent (Kim et al. 2011).

Based on Figure 5(a), the characteristic peak assigned to C (Carbon) Kα line is shown by the EDX spectrum of the PP membrane. The comparative peak height of equivalent elements in a different membrane is associated with their particular concentrations. The existence of these chemical elements corresponds to the predicted
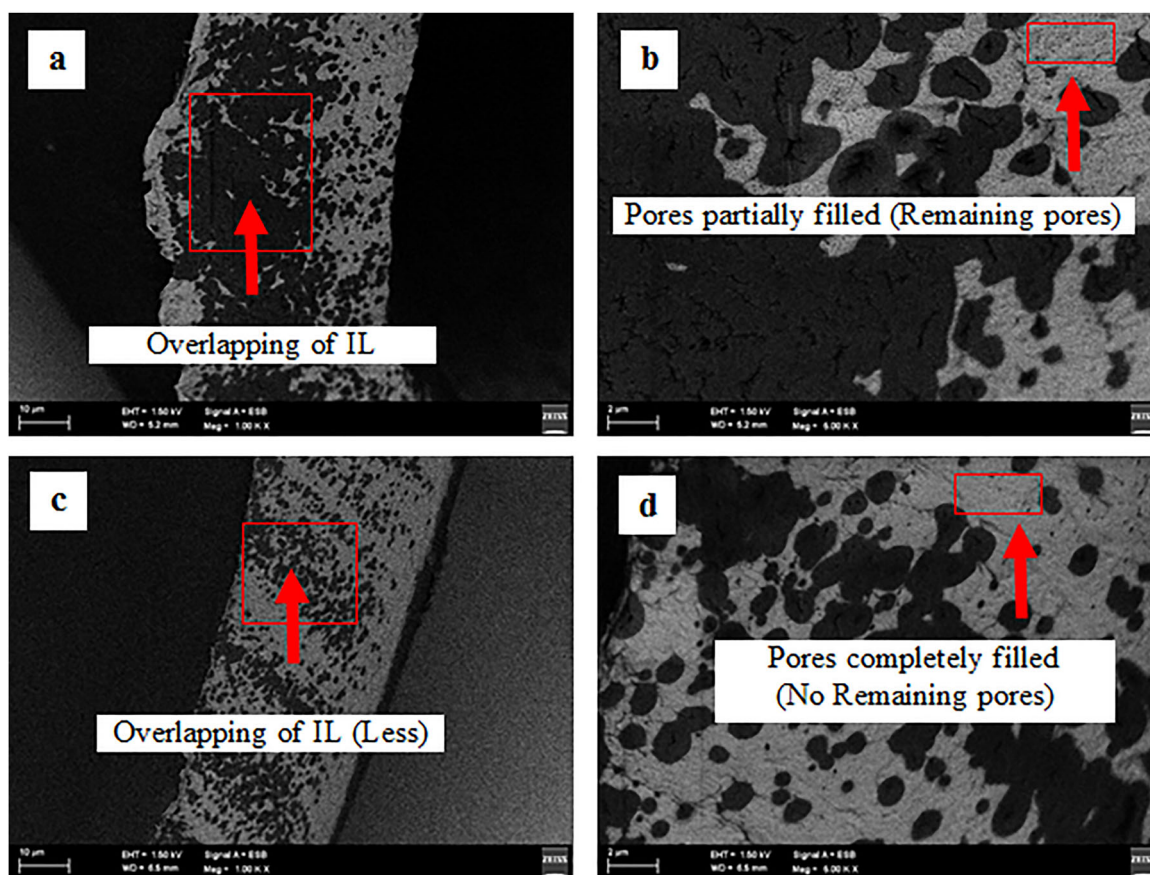
Figure 6. Micrographs of scanning electron (interior side) of (a) S10 at 1000X, (b) S10 at 5000X, (c) S3 at 1000X, and (d) S3 membranes at 5000X magnification (Backscattered).

chemical formulation of polypropylene. Nonetheless, hydrogen is a lighter chemical element; hence, it could not be detected by EDX. In Figure 5(b–d), the presence of F (Fluorine), S (Sulfur), O (Oxygen), and N (Nitrogen) elements from [NTf$_2$] anion, or peaks spectrum of the SILMs, signified the absorption of IL in the PP membranes. Therefore, the differences in the elemental composition of the SILMs have provided quantitative results, which significantly corroborated FESEM's morphological and EDX spectral results.

Based on Figure 6, through the use of back-scattered electrons (ESB) imaging mode – results have shown that the C, F, S, N, and O elements from [emim] [NTf$_2$] ionic liquid scattered more effectively, compared to the lighter C element that existed in porous supports. Therefore, the contrast from IL elements should appear brighter than the contrast of the C element in PP membranes. However, the overlapping of the IL amount within the membrane pores (interior) led

to the increase of the contrast's darkness, compared to the presence of light elements in the membranes. On the other hand, no remaining pores were observed in the case of (80: 20 – S3) compared to (10: 90 – S10) [emim] [NTf$_2$] IL: acetone compositions as noticeably shown in Figure 6(b,d), respectively. From this observation, it was clearly seen that IL has successfully been immobilized into the external and internal sides of the membranes.

SILMs stability

Since CO_2 absorption efficiency in membrane contactors depends on the changes occurring in the pores of membranes, the stability of the SILMs was also examined by submerging the membranes in amine solutions before analyzed using FESEM microscopy. The purpose of this approach was to identify the specific alterations of the membranes structure, the form and dimension of the pores in particular, and potential
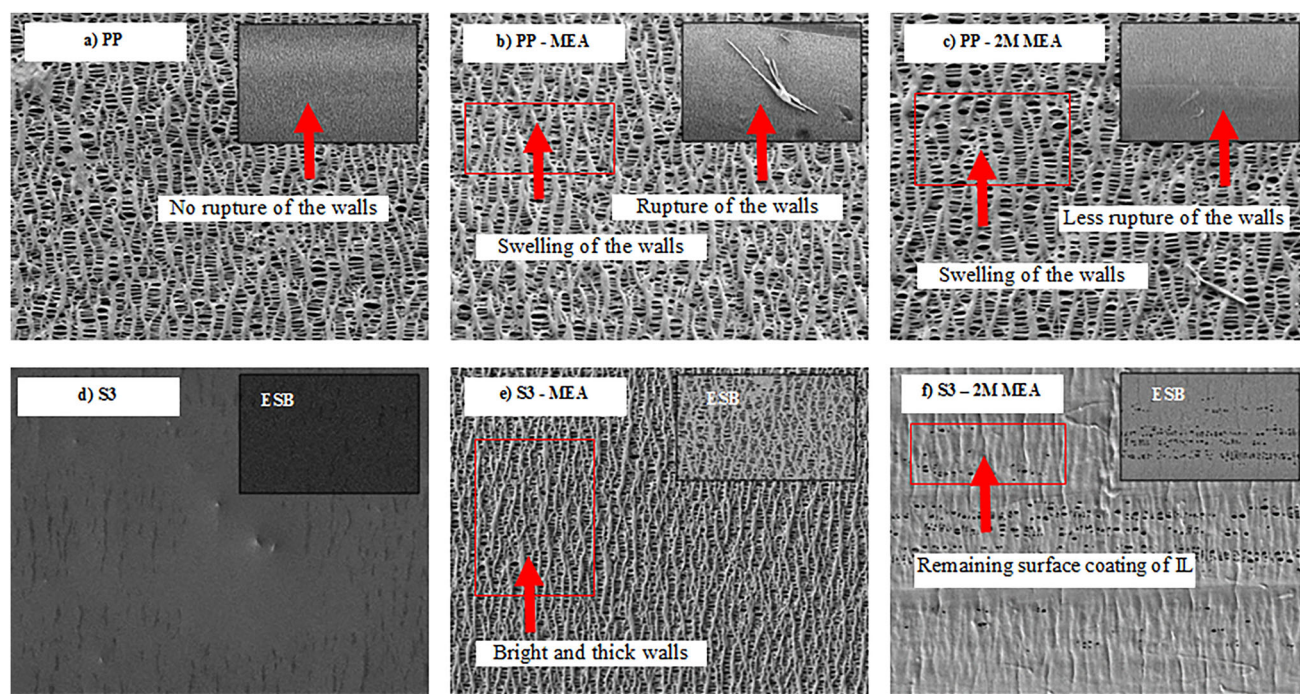
Figure 7. Micrographs of scanning electron of blank PP and S3 membranes before and after immersion with MEA solution for 14 days at 70°C (10000X magnification).

harms to the cell walls. Figure 7 illustrates the FESEM images, which depicts the porous structure of hollow fiber membranes 14 days before and after submersion in amine solutions (pure MEA and 2 M MEA). Prior to the submersion, the cell walls within the neat fiber were fairly identical and small (Figure 7(a)). After 14 days in contact with the MEA solutions, enlargement of the membrane pores was observed while the membrane's surface experienced morphological degradation, as illustrated in Figure 7(b,c). To support these observations, Table 4 describes the data related to the pore enlargement process, with the presence of liquids.

The surface tension of 2 M MEA (56.52 mN m^{-1}) was greater than that of pure MEA (48.14 mN m^{-1}) (Vázquez et al. 1997), which were consistent with the extent of degradation perceived in the FESEM images. These experimental findings suggest a significant relationship between the structural stability of membrane pores and the surface tension of the surrounding phase (Lv et al. 2010; Wang et al. 2005). The solutions with lesser surface tension could penetrate the pores more efficiently (Mansourizadeh et al. 2010; Zhao et al. 2012). Upon diffusion, the liquid meniscus enforced the pore walls and

eliminated them. The FESEM images also portrayed that pure MEA could penetrate into the neat PP membrane pores easily, enlarging the pores and breaking the walls of the membrane pores. All of these observations and findings were in an agreement with the previous reported studies (Kladkaew et al. 2011; Saiwan et al. 2011).

Studies on membrane stability were also conducted to substantiate the potential displacement of ionic liquids from the membrane pores to the surrounding media throughout the absorption process. Figure 7(d–f) demonstrates the morphological appearance of the PP membrane infused with 80:20 (S3) of [emim] [NTf$_2$] ILs: acetone before and after a 14-day cell operation in pure MEA and 2 M MEA, respectively. It was also perceived that a minimal amount of [emim] [NTf$_2$] ionic liquid remained perpetually on the external surface (bright areas). In addition, some pores of

Table 4. Mean sizes of membrane pores before and after immersion with MEA solutions for 14 days at 70ºC.

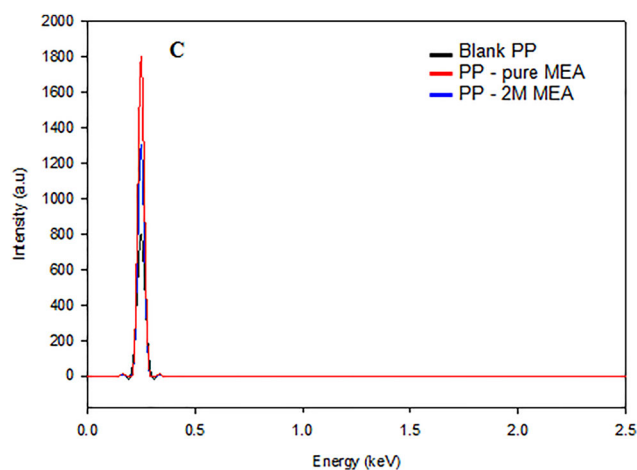| Types of membranes	Mean sizes of membrane pores (nm)
PP	30.00 ± 2.20
PP-MEA	50.85 ± 3.50
PP-2M MEA	37.55 ± 2.40
S3	0.05 ± 0.01
S3-MEA	6.10 ± 2.70
S3-2M MEA	1.25 ± 0.50

Figure 8. EDX spectra of PP membranes before and after immersion in MEA solution for 14 days at 70°C where (–) blank PP, (–) PP – pure MEA, and (–) PP – 2 M MEA.
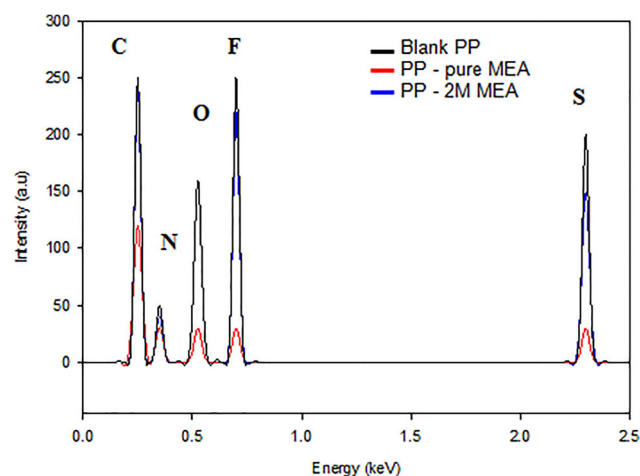

Figure 9. EDX spectra of S3 membranes before and after immersion in MEA solution for 14 days at 70°C where (–) S3 – 2 M MEA, (–) S3 – pure MEA, and (–) S3.

the membrane were partly filled after a long-term operation, while aqueous phase of MEA was used as surrounding phase as shown in Figure 7(f).

Figures 8 and 9 illustrate a comparison of EDX spectra of PP and SILMs based on 80:20 of [emim] [NTf$_2$] IL: acetone composition (S3), before and after the immersion in pure and aqueous solutions of MEA for 14 days. For SILMs (see Figure 9), it was shown by the results that there were extensive losses of ionic liquid from the membrane after the immersion in pure MEA. In the case of immersion in an aqueous solution of MEA, less substantial losses of IL occurred from this process, which indicated that a large amount of the IL persisted within the pores of the membranes. Accordingly, the membranes could be regarded as more stable in 2 M MEA solution. However, the losses of immobilized ionic liquid attained by weight differences can be elucidated by the fact that some of the ionic liquid deposited on the exterior surface of SILMs was mainly miscible with the solvent used, and the immobilized ionic liquid is simply eliminated during the process (Kislik 2010; Matsumoto et al. 2010). The percentages of IL losses are tabulated in Table 5. Therefore, the use of [emim] [NTf$_2$] IL as supporting phase in SILMs had increased the stability of the PP membrane by reducing solution penetration into the pores and stabilizing the pore structures. In terms of SILMs, the structural degradation has been found to be less significance. Therefore, [emim] [NTf$_2$] IL also acts as a stabilizer. In addition, SILMs stability and

Table 5. Amount of immobilized IL in S3 membranes before and after immersion in MEA solution for 14 days at 70°C.

Types of membrane	SILMs weight before immersion (mg)	SILMs weight after immersion (mg)	% of IL losses SILMs
S3-MEA	75.50	10.20	86.50
S3-2M MEA	75.50	60.50	19.90

performances studied by Kim et al. (2011) for CO$_2$/N$_2$ separation process verified that SILMs immobilized via dipping method for 24 hours is more effective in comparison with forced immobilization, with good stability under pressure up to 1.5 bars, and exhibited high permeability and selectivity as well as good reproducibility (Zhai et al. 2006).

Conclusions

The highlight of this research is a comparative study on the preparation of SILMs with the use of various [emim] [NTf$_2$] IL: acetone compositions under dipping technique. It was carried out in two stages: the impregnation of fresh membranes with IL and after the immersion in an MEA solution after 14 days. The number of immobilized IL was influenced by the viscosity and RI of the binary mixtures. Additionally, less IL was absorbed into the membranes with the use of pure [emim] [NTf$_2$] IL, compared to diluted IL.

A FESEM-EDX study was conducted for PP and SILMs, based on (80:20) of [emim] [NTf$_2$] IL: acetone composition (S3) in different

surrounding phases. In terms of SILMs, when 2 M MEA was used as a surrounding phase, the membranes experienced less substantial IL loss after 14 days of operation. On the contrary, when MEA was used as contacting phases; almost all of the immobilized IL was lost from the membranes. Apart from that, the stability of the resulting SILMs increased when the surface tension of the surrounding phases increased, as demonstrated and confirmed by FESEM-EDX technique. In conclusion, the vital role played by the binary mixture viscosity for the preparation of supported ionic liquid membranes has been highlighted in this research. With the added advantage that this preparation method is also more easily prepared, our preparation of SILMs technique constitutes useful and practical approaches for CO_2 capture applications, as required by industrial sectors.

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