Separating miscible liquid-liquid mixture using supported ionic liquid membranes (SILMs)

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ABSTRACT Supported Liquid Membranes (SLMs) are promising in separating miscible liquid-liquid mixtures, which has been a key challenge in wastewater treatment and other applications. However, SLMs suffer from the poor durability due to the loss of liquid phase. In current work, ionic liquids (ILs) with high stability have been impregnated into polyvinylidene fluoride (PVDF) membranes to separate miscible benzene-heptane mixture. The two-imidazolium based ILs, i.e., 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([BMIM][FAP]), were tested in Supported ionic liquid membranes (SILMs) for the benzene-heptane separation. Both ILs show successful separation within 48 hours as indicated by Nuclear Magnetic Resonance (NMR) results. Compared to the SILM with [BMIM][FAP], the SILM with [BMIM][PF_6] has lower throughput and higher selectivity. The higher selectivity can be attributed to the higher hydrophilicity of [BMIM][PF_6], which results in strong repulsion against heptane. The lower throughput can be attributed to the higher hydrophilicity as well since it lowers the solubility of benzene in

[BMIM][PF_6]. The stability of IL in SILMs has also been investigated via multiple separation cycles. The SEM, weight change of SILM and separation results indicate that the separation efficiency of [BMIM][PF_6] SILM does not degrade for up to 144 hours. The SILM has been further optimized with curvature design (i.e., curved SILM) to increase the interfacial area and thus increase the separation throughput, where the curved SILM separation device was 3D-printed. The findings here have important implications on design and application of SILMs in separating miscible liquid-liquid mixtures.

INTRODUCTION

Supported Liquid membranes (SLMs), i.e., porous solid membranes filled with liquid, are promising for separating miscible liquid-liquid mixture because they combine both extraction and stripping process. [1] Moreover, compared to conventional bulk solvent extraction, the amount of solvent required in SLMs is far less. Meanwhile, compared to the distillation process that is widely utilized in separating miscible liquid mixture, SLMs process is expected to have lower energy consumption, easier operation, less waste, and more flexibility in system design[2]. Nevertheless, to date commercial application of SLMs is limited due to insufficient durability of SLMs, which results from the loss of liquid phase within the pores of the membrane due to evaporation or mass transport from the surface of the membrane. [3] Various studies have been conducted to increase the durability of the SLMs[2] and different methods have been proposed, including gelling the liquid phase[4] in the pores of the membrane, interfacial polymerization[5], and plasma polymerization of surface coatings[6], etc.

Ionic liquids (ILs), organic salts with the melting temperatures below 100° C, have been extensively studied for application in separation. Due to their low vapor pressure and high chemical stability compared to conventional organic solvents[7], ILs are ideal candidate to replace conventional solvents in SLMs. [8,9] Low vapor pressure significantly reduces the loss of ILs due to evaporation. Meanwhile, it also renders the separation of ILs and the dissolved liquid afterwards much easier. The SILM are also perfect candidates for miscible liquid-liquid separation where boiling points of two liquids are very similar so that distillation is difficult. Indeed, separating miscible liquid mixture with supported ionic liquid membranes (SILMs) has been reported by several authors. In one of the earliest works, Branco et al. [10] reported the successful separation of secondary and tertiary amines with similar boiling points using [BMIM][PF_6] immobilized in PVDF and nylon membranes. Later Matsumoto et al.[11] separated aromatic hydrocarbons, i.e., benzene, toluene and p-xylene, using imidazolium based SILMs (i.e., [BMIM][PF_6], [HMIM][PF_6], and [OMIM][PF_6]) and found that the permeation rate increases with the hydrophobicity of ILs. Similar experimental setup[12] was used for simultaneous separation of the products of transesterification reaction, i.e., vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid, with six different imidazolium based ILs immobilized in Nylon membrane. Chakraborty et al. [13] reported a highly selective and efficient toluene separation from *n*-heptane using the SILM with Ag^+ carrier. Fallanza et al. [14] also found that PVDF supported imidazolium IL membrane containing Ag^+ carrier is efficient in separating the mixture of propylene and propane. Zhang et al. [15] demonstrated the successful separation of toluene-cyclohexane mixture with hollow fiber supported ionic liquid membrane based on [BPy][BF_4]. Later Zhang et al. [16] also reported the efficient toluene-heptane separation using imidazolium based SILM. Branco et al. [17]reported good durability of imidazolium based SILMs in the separation of secondary amines over primary and

tertiary amines. Koók et al. [17] demonstrated that SILM based on 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) is very efficient in microbial fuel cell application. Liquid-liquid extraction of methanol from it mixtures with hexane using three imidazolium based ILs were discussed by Zhu et al.[18] and based on their study 1-decyl, 3-methylimmidazolium bis(trifluoromethylsulphonyl)amide ([DMIM][NTf_2]showed promising extraction results. Moreover, the effect of alkyl length and variation of anions on liquid-liquid equilibrium data was discussed. Recently, Shen et al.[19] have studied abilities of imidazolium based ILs in extraction processes of n-heptane/n-propanol and concluded that [dmim][MP] (1,3-dimethylimmidazolylphosphonate) has the strongest hydrogen bonding with n-propanol based on the quantum chemistry calculations. In 2021, Chen et al. [20] have studied three imidazolium based ILs ([HMIM][OTF], [OMIM][OTF], and [BMIM][OTF]) by molecular dynamics simulation for n-heptane- t-butanol separation application and they concluded that [HMIM][OTF] is the best candidate for the desired separation. Kamaz et al. [21] studied three different imidazolium based SILMs in separating benzene, naphthalene, phenanthrene in tetradecane solution. Based on the experimental results, Kamaz et al. [21] concluded that benzene has the highest flux in all three ILs used, followed by naphthalene and phenanthrene. They [21] also reported that the hydrophilic ILs were stable in SILMs after immersion in water, hexane and tetradecane up to 165 hours.

Although much progress has been made on SILMs in the separation of miscible liquid mixture, the effect of IL structure on the separation efficiency and durability has yet to be fully uncovered. Meanwhile, the relatively low throughput in SILMs separation remains a concern for commercial application. To address these issues, in the current paper, we have studied two imidazolium based SILMs in separating the benzene/*n*-heptane mixture. The two imidazolium-based ILs are 1-butyl-

3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([BMIM][FAP]). The two ILs have the same cation but different anion. Since [PF_6] is hydrophilic and [FAP] is hydrophobic, the two ILs are expected to have different selectivity in benzene/heptane separation. Interestingly, the experimental results also show that the stability of two ILs in SILMs are different, which can be attributed to the different solubility of ILs in benzene. The SILM has been further optimized with curvature design (i.e., curved SILM) to increase the interfacial area and thus increase the throughput, where the curved SILM separation device was 3D-printed. The findings here have important implications in designing SILMs with higher selectivity, throughput, and durability for future application in the separation of miscible liquid-liquid mixtures.

2. MATERIALS AND METHODS

2.1 Materials.

Benzene (≥99%) was purchased from Sigma-Aldrich. n-hexadecane (≥99%), n-heptane (≥99%) were purchased from Fisher Scientific. 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]; 98+%) was obtained from Fisher Scientific and tris(pentafluoroethyl)trifluoro-phosphate ([BMIM][FAP]; high purity) was purchased from Millipore Sigma. These chemicals were used as received. Viton fluoroelastomer rubber sheet (chemical-resistant, 12" x 12", 1/32") were purchased from McMaster-Carr. PVDF (Polyvinylidene fluoride) membrane filters (MilliporeSigma™ Durapore™: hydrophilic: 0.65µ pore size) was purchased from Fisher Scientific.

2.2 SILMs Preparation

The porous PVDF membrane were filled with the IL by simply placing the membrane in a Petri dish and then adding ILs dropwise onto the surface of the membrane. This process of membrane preparation was conducted under room temperature and ambient pressure. With time, white membrane will turn colorless as the ILs were distributed evenly in the membrane. To ensure that all the pores of the membrane were filled with the IL, the SILM went into the vacuum chamber for 24 hours to render all the air within the pores to be replaced with IL. Afterwards, the SILM was removed from the vacuum chamber and the excess IL were wiped off the membrane surface.

2.3 Membrane Characterization

The surface topography and the composition of PVDF membrane were characterized by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX), respectively. Scanning electron microscopy (SEM) imaging was conducted using a Zeiss SIGMA VP scanning electron microscope. The accelerating voltage utilized was 10 kV, and the imaging was performed under high vacuum. SEM analysis was conducted with bare PVDF membranes as well as with IL impregnated membranes. The purpose for this analysis is to understand the pore structures, pore sizes of the PVDF membranes, and how the topography changes in the presence of ILs and after they were used in the separation. EDX analysis was performed to characterize the amount of ILs within the membrane pores before and after they have been used for multiple cycles of separation.

2.4 SILM Separation Experiment

The separation setup is schematically shown in Figure 1, using glass cylindrical compartments that contains feed solution, receiving solution, and the SILM in between. The SILM were inserted in the middle of two compartments and were clamped with an O-ring to prevent leaking. The feed

solution contains *n*-heptane and benzene mixture 50/50% by volume, total of 150 ml. The 50/50% volume ratio is typical in separation study to understand the selectivity of two ILs for benzene. The receiving solution contains 150 ml of hexadecane. The reason that hexadecane is selected as the receiving solvent is due to the fact that benzene is highly soluble in hexadecane. Moreover, the large difference in boiling points between hexadecane and benzene (i.e., the boiling point of benzene is 80.1C^{o} while the boiling point of hexadecane is 286.9C^{o}.) renders the separation of benzene and hexadecane easier. The separation experiments were conducted at room temperature and ambient pressure with the solution on both sides stirred at 500 rpm. The separation experiments were 48 hours long and samples were taken at 3, 6, 24 and 48 hours on the receiving solution side to determine the amount of benzene and heptane by Nuclear Magnetic Resonance (NMR) Bruker Advance -III 300MHz spectrometer with 1H inverse probe. In H^1-NMR analysis, approximately 10-15 mg of sample was mixed with 500 mg of acetone D-6.

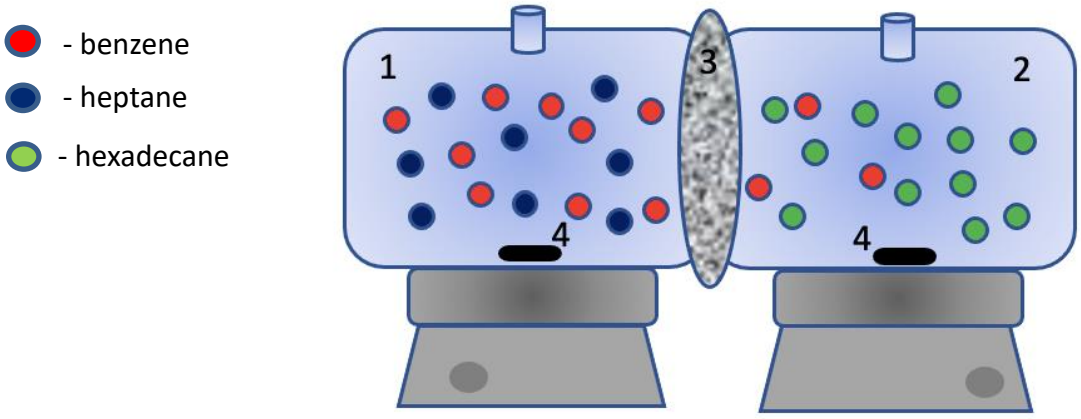

Figure 1. Schematic of separation setup: 1-feed compartment, 2- receiving compartment, 3-SILM, 4-stirrer bars

The stability of ILs in SILMs were evaluated by 6-cycle separation tests with each cycle of 24 hours. Every cycle of separation was conducted with fresh feed and receiving solutions. Samples

were taken at 3, 6 and 24 hours from the receiving solution to determine the amount of benzene and heptane by NMR analysis.

2.5 Curved SILM

Curved SILM was designed using Solidworks software and 3D printed with Formlab Form2 3D printer. Main criterion in 3D design was to have high surface area of the membrane to increase the benzene throughput. As shown in Figure 2, the length, width and the height of the 3D designed box was optimized to get the optimal surface area (SA)/Volume (V) ratio. The chemical-resistant Viton sheet (1/32 thickness) was used in the middle of the box to prevent leaking. The 3D printed box was clamped on all 4 sides.

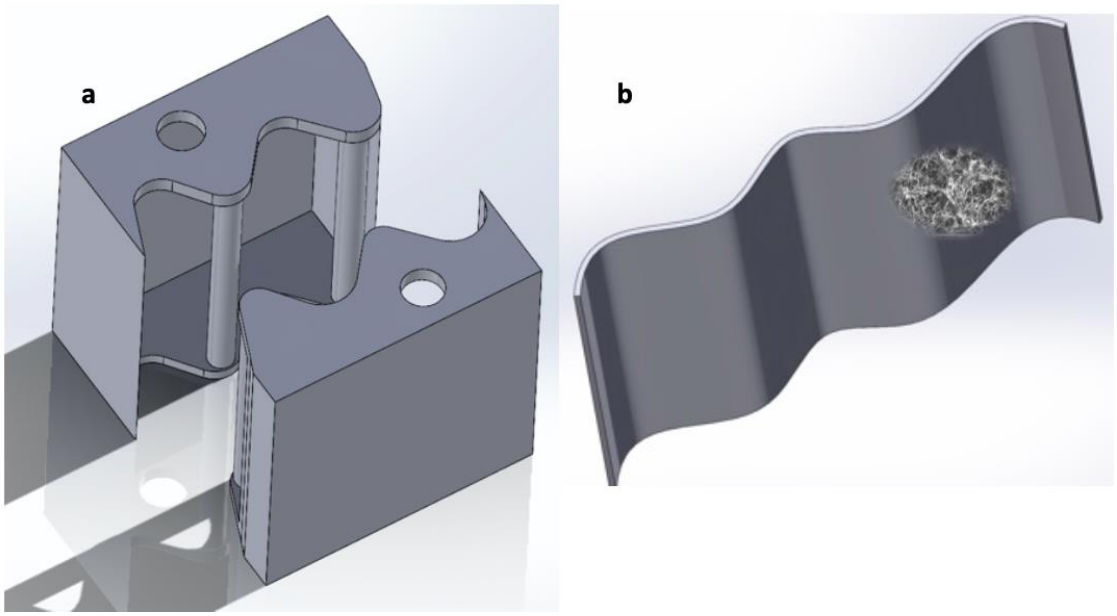

Figure 2. (a) 3D design of curved SILM with two compartments for feed and receiving solutions, (b) SILM sliding in between these two compartments.

3. RESULTS AND DISCUSSION

The separation of benzene/heptane was conducted using SILMs with two different ILs, i.e., [BMIM][FAP] and [BMIM][PF_6], under the same condition. The separation lasted for 48 hours and volumes of feed and receiving solutions were the same, i.e., feed solution of 75ml benzene and 75ml heptane and the receiving solution of 150 ml hexadecane. The volume of benzene and heptane in the receiving solutions was determined by NMR and the results are shown in Figure 3. For both ILs, the volume of benzene in the receiving solution steadily grows with time. As shown in Figure 3 (right) , the volume of benzene in the receiving solution using [BMIM][FAP] is higher than [BMIM][PF_6] on Figure 3 (left). For the SILM using [BMIM][PF_6], the volume of heptane in the receiving solution is ~ 0 over 48 hours, whereas for [BMIM][FAP] SILM the volume of heptane is ~1.1 ml after 48 hours. Compared to the SILM with [BMIM][FAP], the SILM with [BMIM][PF_6] has lower benzene throughput and higher selectivity. The higher selectivity can be attributed to the higher hydrophilicity of [BMIM][PF_6], which results in strong repulsion against heptane. The lower throughput can be attributed to the higher hydrophilicity as well since it lowers the solubility of benzene in [BMIM][PF_6]. Similar results of [BMIM][PF6] IL in benzene separation was published by Matsumoto et al. [11] where benzene volume in the receiving solution grew with time and heptane volume remained zero.

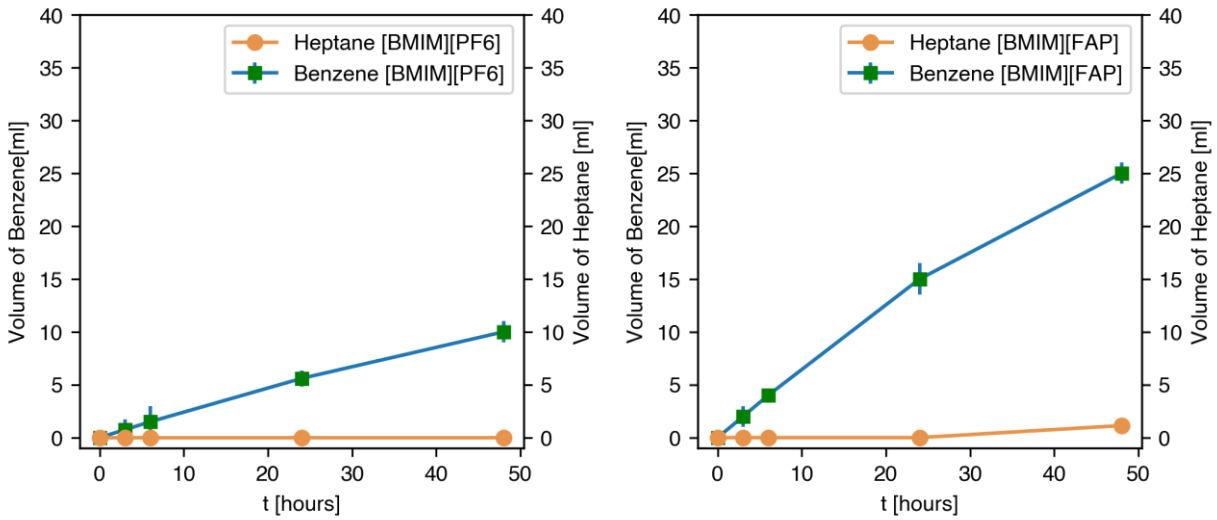

Figure 3. Volume of benzene and heptane in the receiving solution over 48 hours w/ [BMIM][PF_6] (left) and [BMIM][FAP] (right) SILMs.

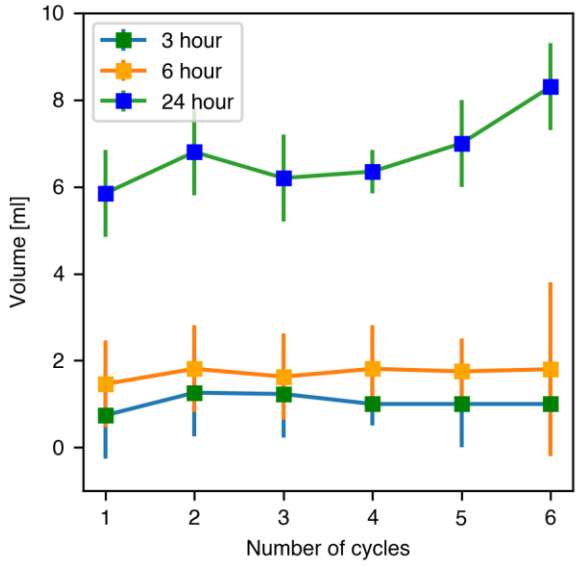

Figure 4. The volume of benzene in the receiving solution over 6 cycles of separation using [BMIM][PF_6] SILM.

To understand the stability of IL in the SILM, the separation using [BMIM][PF_6] SILM was repeated for 6 cycles of 24 hours. In each cycle, the volume of benzene in the receiving solution was measured after 3 hours, 6 hours and 24 hours. The volume of heptane in the receiving solution was measured after 24 hours. As shown in Figure 4, there is little change in the volume of benzene in the receiving solution after 3 hours and 6 hours over 6 cycles. After 24 hours' separation, the volume of benzene in the receiving solution increases slightly with the number of cycles. As for the volume of heptane in the receiving solution, it does not change over number of cycles and stays as ~0. The results indicated that the selectivity of SILM with [BMIM][PF_6] does not degrade after up to 144 hours of separation. The excellent stability of [BMIM][PF_6] SILM could be explained by the poor miscibility of the IL with heptane and hexadecane as discussed above, where high hydrophilicity of [BMIM][PF_6] results in strong repulsion towards heptane and hexadecane for up to 144 hours.

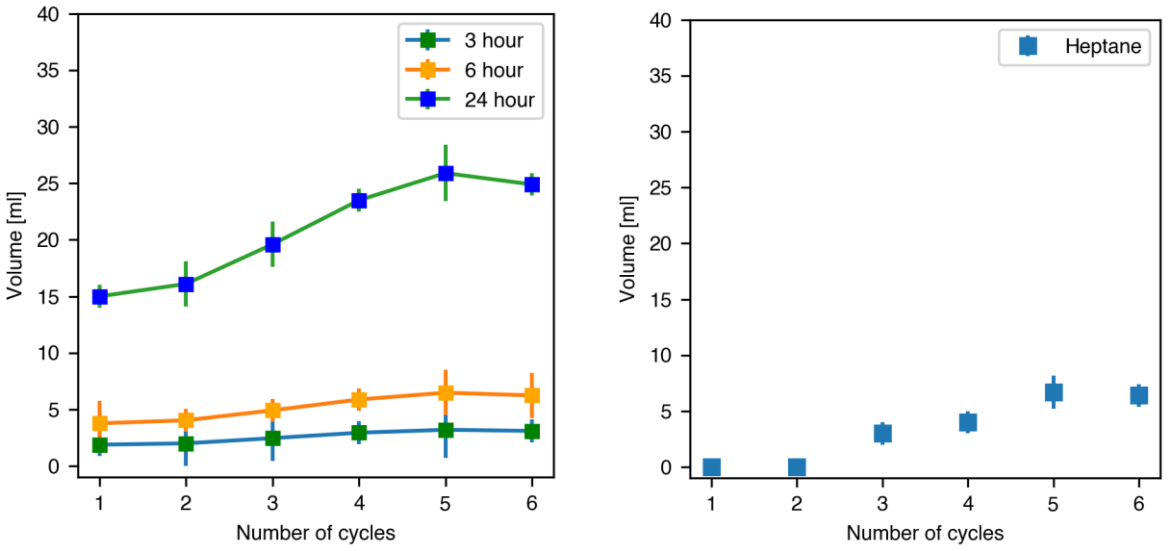

Figure 5. The volume of benzene (left) and heptane (right) in the receiving solution over 6 cycles of separation using [BMIM][FAP] SILM.

To understand the stability of [BMIM][FAP] in the SILM, 6 cycles of 24 hours' separation of benzene/heptane was conducted. As shown in Figure 5, compared to [BMIM][PF_6] SILM, the volume of benzene in the receiving solution grows more significantly with the number of cycles for [BMIM][FAP] SILM. Meanwhile, the volume of heptane in the receiving solution becomes non-zero after 2nd cycle and increases with the number of cycles afterwards. These results show that, with the increase of separation cycles, the selectivity of [BMIM][FAP] SILM towards benzene decreases. Although the selectivity of [BMIM][FAP] SILM decreases with number of separation cycles, the amount of benzene separated in one cycle is ~3 times of that with [BMIM][PF_6] SILM.

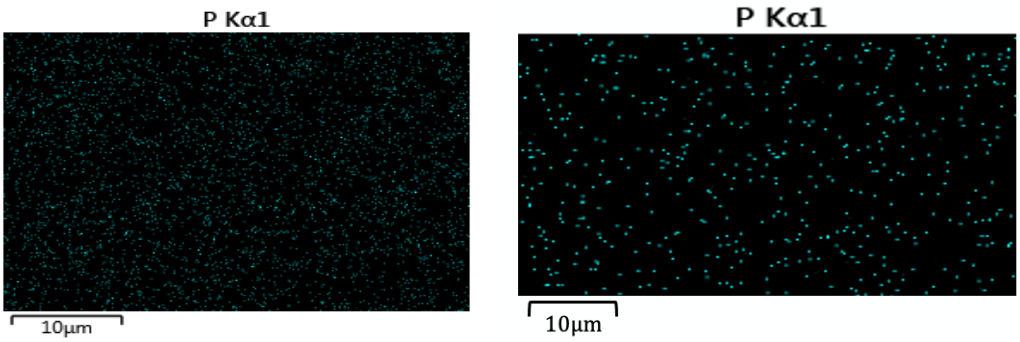

Figure 6. EDX results of [BMIM][FAP] SILM after 2nd (left) and 4th (right) separation cycle.

Since the selectivity of [BMIM][FAP] SILM decreases with increasing number of separation cycles, EDX analysis were carried out on the SILM to characterize the amount of [BMIM][FAP] within the pores of PVDF membrane after each separation cycle. Figure 6 shows the EDX results

of phosphorous content for [BMIM][FAP] in the membrane after 2nd and 4th separation cycles. As shown in Figure 6, the phosphorous content is much higher after 2nd cycle than after 4th cycle, indicating the loss of the IL. The EDX results correlate well with the weight measurement carried out during the separation cycles. Weight measurement results of bare PVDF membrane, after impregnation with IL and after each separation cycle is shown in Table 1. Both EDX analysis and weight measurement indicate the IL loss with the separation cycle, which results in the decreased selectivity of [BMIM][FAP] SILM.

Table 1. Weight measurement results of [BMIM][FAP] SILM

Membrane	Weight (mg)	Weight loss (%)
PVDF Membrane bare	135.3	N/A
PVDF after impregnation	335	N/A
After 1st separation cycle	293.3	12.4%
After 2nd separation cycle	272.4	18.7 %
After 3rd separation cycle	249.0	25.7 %
After 4th separation cycle	257.0	23.3%

To further understand the IL loss from the pores of PVDF membrane after each cycle of separation, SEM analysis were carried out. The SEM results of [BMIM][FAP] SILM after 2nd and 4th separation cycles are shown in Figure 7A and 7B, respectively. For comparison, the SEM result of bare PVDF membrane is shown in Figure 7C. As shown in Figure 7A, IL is clearly present within the membrane pores, which is consistent with our EDX results shown in Figure 6. After 4th cycle, as shown in Figure 7B, more IL are lost. For further comparison, the SEM result of [BMIM][PF_6] SILM after 2 separation cycles is shown in Figure 7D. There is significantly more

IL within the pores of the PVDF membrane. There is a dramatic difference between Figure 7A and 7D, where presence of two ILs within the membrane pores significantly vary. [BMIM][PF_6] SILM (Figure 7D) has more IL within the pores of the membrane, where most of the pores of the membrane cannot be seen clearly since they are covered with IL. On the other hand, [BMIM][FAP] SILM (Figure 7A) shows significantly less IL within the pores of the membrane. The lower stability of [BMIM][FAP] can be attributed to the higher solubility of benzene in the IL as discussed above.

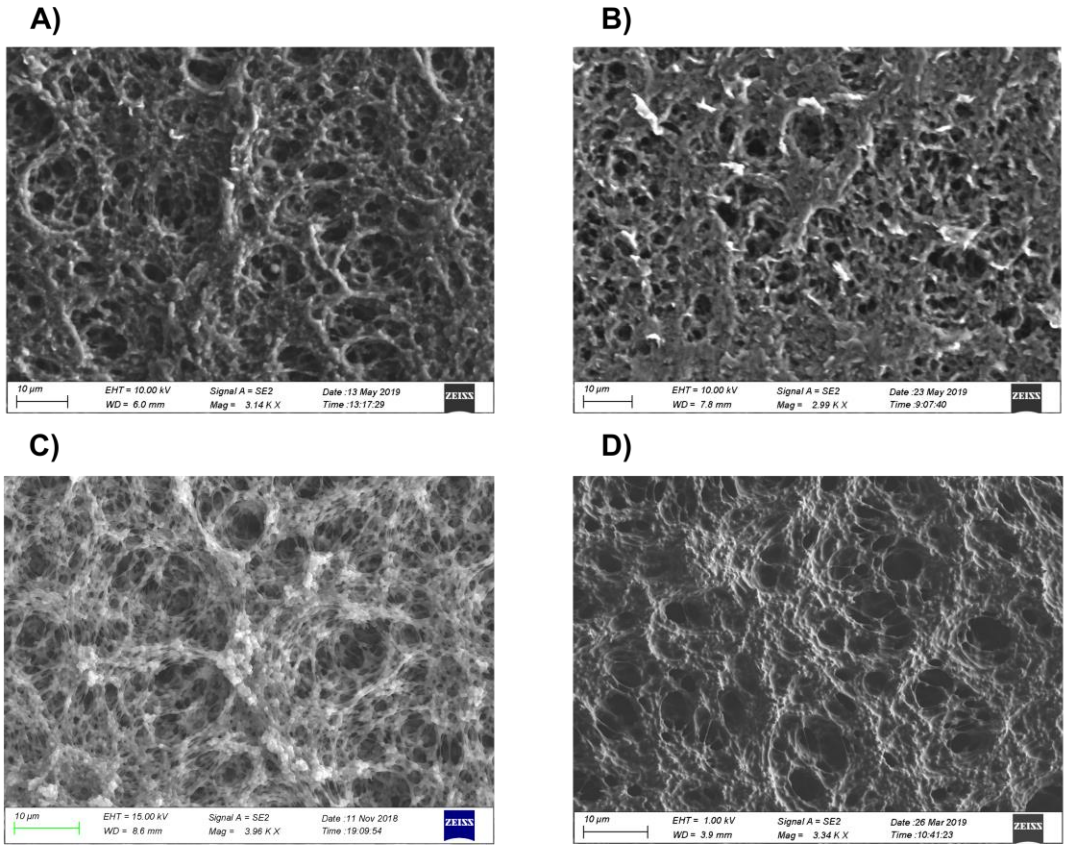

Figure 7. SEM results of [BMIM][FAP] SILM after 2nd (A) and 4th (B) separation cycles, PVDF membrane (no IL) (C), and [BMIM][PF_6] SILM (D) after 2 separation cycles

The throughput of SILMs is low and this is a serious concern for commercial applications. To this end, curved SILM was designed to increase the surface area of SILM per volume of feed solution to increase the benzene throughput in the separation. The curved SILM has a ratio of SA/V=2.5 cm^2/ml, whereas the flat SILM has a ratio of SA/V= 0.1cm^2/ml. This increase in SA/V ratio is expected to increase the benzene throughput in the separation.

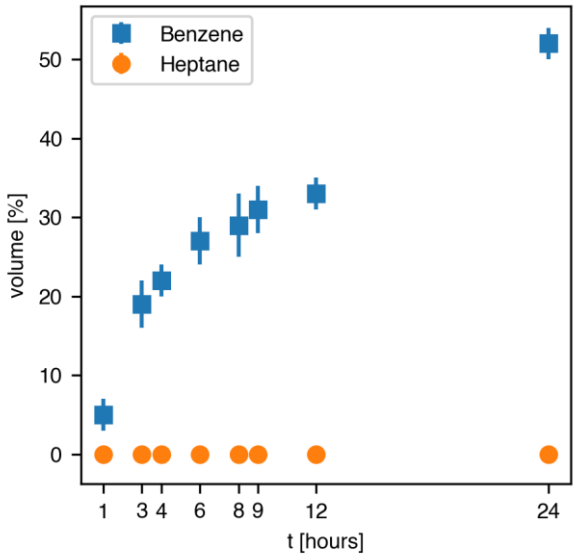

Figure 8. Curved surface SILM separation results

Figure 8 shows the separation results of curved [BMIM][PF_6] SILM, where both benzene and heptane volume percentage in the receiving solution (over initial feed volume) are plotted over time. Similar to flat SILM, the amount of benzene in the receiving solution steadily increases with time and approximately 50% of benzene transports to the receiving solution in 24 hours. The percentage of heptane in the receiving solution stays zero over time, as expected.

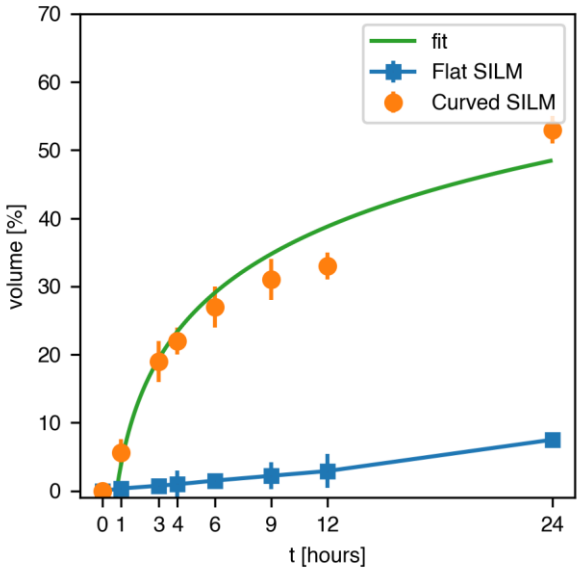

Figure 9. Comparison of two SILM surfaces with [BMIM][PF_6] ionic liquid

Our separation results with [BMIM][PF_6] SILMs were compiled in Figure 9 to further compare the flat SILM to the curved SILM. As expected, the curved SILM has higher benzene throughout compared to the flat SILM, i.e., ~50% vs. ~7% after 24 hours. Regarding the surface area, the ratio between the curved and flat SILM is ~25. Interestingly, the ratio of benzene percentage in the receiving solution between the curved and flat SILM after 24 hours is ~7, which is lower than ~25. This decrease can be attributed to the decrease in the driving force with the separation, i.e., the concentration difference of benzene between the feeding and receiving sides decrease more significantly for the curved SILM. The benzene diffusion rate (dC/dt), from the feed to the receiving solution can be described by Eqn. 1 shown below[21]:

$$Ak(C_f - C_r) = V\frac{dC}{dt} \quad (1)$$

Here A is the surface area of the membrane that is in contact with the solution, k is mass transfer coefficient of the solute, C_f and C_r are concentrations of benzene in the feed solution and in the

receiving solution, respectively, V is the volume of the receiving solution, t is time. For flat SILM, since the benzene throughput is very limited, $(C_f - C_r)$ changes little and thus dC/dt almost stays as a constant. For curved SILM, the benzene throughout increases significantly and $(C_f - C_r)$ decreases dramatically with time. As a result, dC/dt also decreases with time and the overall throughput after 24 hours is not ~25 times of that of the flat SILM. If the above hypothesis is correct, at ~ 0 hour, the ratio between the slopes of the V-t plot (Figure 9) of the curved SILM and the flat SILM should be ~ 25. The curve fitting results using Eqn. 1 are shown in Figure 9. As expected, the ratio is ~25. Our results suggest that, with appropriate design to increase the total interfacial area, the throughput in SILMs separation can be increased dramatically.

CONCLUSION

Two imidazolium-based ILs, i.e., 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([BMIM][FAP]), were studied in SILMs for benzene-heptane separation. Experimental results show a lower separation throughput and higher selectivity for the [BMIM][PF_6] SILM. The lower throughput can be attributed to the higher hydrophilicity of [PF_6] anion since it reduces the solubility of benzene in [BMIM][PF_6]. The higher selectivity can be also attributed to the higher hydrophilicity of [BMIM][PF_6], which results in strong repulsion against heptane. The stability of ILs in the SILM was investigated over 6 separation cycles. The SEM, EDX, weight change of SILM and separation results indicate that [BMIM][PF_6] SILM can be used to separate benzene-heptane for up to 144 hours without degradation in separation efficiency. Last but not least, the SILM is further optimized with curvature design (i.e., curved SILM) to increase the interfacial area and thus increase the separation throughput, where the curved SILM separation device was

3D-printed. Our results highlight the importance of the structure of ILs on selectivity, throughput and reliability in SILMs separation of miscible liquid mixture.

ASSOCIATED CONTENT

Supporting Information

The followings are available free of charge.

NMR results (at 1, 3, 6, 12 hours) and detailed discussion on the analysis of NMR results.

AUTHOR INFORMATION

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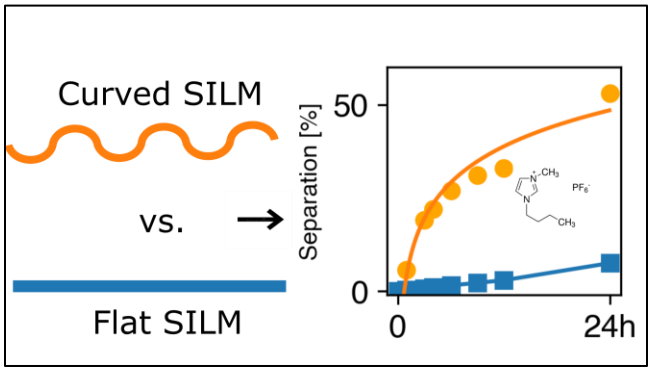
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