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Supported ionic liquid membranes for the separation of methanol/dimethyl carbonate mixtures by pervaporation

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ABSTRACT

Two supported ionic liquid membranes (SILM) based on 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_8MIM][NTf_2]) and N-octyl-N-methylpyrrolidinium bis(triuoromethanesulfonyl)imide ([C_8C_1Pyrr][NTf_2]) were prepared and studied for the pervaporation separation of binary mixtures of dimethyl carbonate (DMC)/methanol. Scanning electron microscope (SEM) analyses were carried out to evaluate the cross section morphology of the porous membranes before and after incorporating the ionic liquids. The pervaporation performance of SILMs was found to be highly concentration dependent. At low methanol concentration (0.2 M fraction), both SILMs tend to preferentially permeate DMC. In general, the SILM based on [C_8MIM][NTf_2] exhibited a better performance than the one with [C_8C_1Pyrr][NTf_2]. Under optimal conditions, the SILM composed of [C_8MIM][NTf_2] enabled a transmembrane flux of 0.739 kg/m^2h, a DMC/methanol selectivity of 67 and separation factor of 21 at 30 °C at 0.8 M fraction of DMC. However, at high concentration of methanol, the permeance of methanol increased due to coupling effects therefore decreasing the membrane selectivity to around 2.

1. Introduction

Membrane technology has been recognized as an environmentally friendly technology thanks to its low energy consumption and low waste generation [1]. Pervaporation is generally used to separate challenging mixtures which separation with conventional methods, such as distillation, requires high energy consumption. These complicated cases typically include azeotropic mixtures or close-boiling point compounds. In the present work, a binary mixture of dimethyl carbonate (DMC) and methanol has been studied. It is of interest as dimethyl carbonate is an important biodegradable "green chemical" with low toxicity with an increasing number of applications [2–4]. Methanol appears in different dimethyl carbonate synthesis routes [5–7], as for example DMC can be produced by the reaction of CO_2 and methanol, by the transesterification of ethylene carbonate and methanol [8–11] or by the reaction of urea again with methanol [12,13]. In addition, methanol is also a by-product in different syntheses involving DMC, such as the production of glycerol carbonate via the transesterification reaction between glycerol and DMC [14,15]. In both cases, an efficient separation of DMC and methanol is needed to get a sustainable and economically favorable process. However, methanol forms an azeotrope with dimethyl carbonate at 30/70 wt% DMC/methanol concentration [16], making the separation process energetically intensive by conventional distillation [17]. Hence, the development of energy-efficient processes for the separation of DMC and methanol is an important challenge to be addressed.

The application of pervaporation is a very attractive approach. Commercial pervaporation membranes based on polyvinyl alcohol from Sulzer have been previously studied by our group for the separation of a quaternary mixture including DMC and methanol [18], showing that methanol is concentrated in the permeate at 44 mol% concentration of methanol in the feed, with a separation factor of 14 (methanol relative to DMC), a selectivity of 5.7 (methanol relative to DMC) and a permeance of methanol of 723 GPU. The pervaporation separation of a DMC/methanol binary mixture was also studied by using self-made PEEK membranes [19]. It was shown that good separation could be achieved at low concentration of methanol (0.1 M fraction): separation factor of 13.4 (methanol relative to DMC), selectivity of 3.5 (methanol relative to DMC) and permeance of methanol 293 GPU.

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Supported liquid membranes (SLMs) have been introduced in pervaporation as potential solutions to increase the selectivity and transmembrane flux by tuning the affinity of the liquid to the target compound and the higher diffusivity through the liquid phase immobilized inside the membrane pores [20]. The mass transport mechanism in SLM involves three stages: 1) the molecules are sorbed from the feed solution into the solvent in the SLM; 2) the sorbed molecules diffuse through the liquid membrane to the permeate side; 3) the molecules are desorbed into the permeate side [21]. The solubility and diffusion coefficients of different solutes in a liquid leads to high flux if compared to dense membranes since diffusion coefficients in liquids are much higher than in polymers [22]. However, the stability of SLMs remains the major limitation for a large scale commercial application [23,24]. Low stability of supported liquid membranes has been observed in the literature, with a loss of immobilized solvent after relatively short application time, leading to a dramatic increase of flux and decrease of selectivity [25]. Solvent evaporation, dissolution into contiguous phases and pressure gradient are the major factors leading to the loss of solvent [26]. In order to solve this issue, ionic liquids have been used as the active separation medium in SLMs, leading to the so-called supported ionic liquid membranes (SILMs) [27].

Ionic liquids are generally defined as organic salts containing an organic cation and an inorganic or organic anion that have a melting temperature below 100 °C [28]. They can be designed by combining different cation and anion therefore modifying both their chemical and physical properties, such as their solubility properties. Such tunability gives these solvents a very good potential to achieve a good selectivity toward target component [29]. In addition, ionic liquids have high chemical and thermal stabilities and negligible vapor pressure [30]. Therefore, they are often considered as "green solvents" to replace volatile organic solvents in the chemical industry. Ionic liquids have wide applications in chemistry for instance as catalysts or additives [30–33], for extraction [32–35], as electrolytes [38–41], or in gas purification [42–44]. In fluid-fluid separation processes, ionic liquids are good media for extraction. However, the high price of most of ionic liquids and the high energy consumption needed to purify ionic liquids for reuse are important factors for the limitation of their application in separation processes [45]. These shortcomings can be solved by using SILMs since only a small amount of IL is required to fill the membrane pores and the recycling of ionic liquid for further reuse is not necessary. Due to their negligible vapor pressure and high viscosity, ionic liquids in SILMs can be more stable than organic solvents.

In the literature, SILMs have been extensively used for gas separation, such as SO_2/CO_2, $CO_2/H_2/N_2$, $H_2S/CO_2/CH_4$ and natural gas purification [27,46–52]. While their application in pervaporation is not as widespread, SILMs have received increasing attention in recent years, for example for the separation of transesterification reaction mixtures containing alcohols, organic acids, hydrocarbons and amines [53–61].

The use of SILMs for the separation of transesterification mixtures has been studied based on ionic liquids such as $[C_4MIM][BF_4]$, $[C_8MIM][BF_4]$, $[C_4MIM][PF_6]$ or $[C_8MIM][PF_6]$ [55,62]. In addition, the ionic liquids $[C_2MIM][Cl]$ and $[C_4MIM][Cl]$ have been investigated to be used as carriers for breaking the azeotrope of methanol and DMC [63]. These two ionic liquids showed their capability to separate the azeotrope when the molar fraction of ionic liquids in the methanol, DMC and ionic liquid ternary system increased up to certain level, such as 0.1168 M fraction of $[C_4MIM][Cl]$. However, the application of SILMs for the separation methanol/DMC mixtures has not been reported yet.

In this work, two ionic liquids were synthesized and impregnated in a porous polyacrylonitrile (PAN) support membrane to prepare the corresponding SILMs. These materials have been tested for the separation of DMC/methanol mixtures by pervaporation. The ionic liquids, 1-octyl-3-methylimidazolium bis(triuoromethanesulfonyl)imide $[C_8MIM][NTf_2]$ and N-octyl-N-methylpyrrolidinium bis(triuoromethanesulfonyl)imide $[C_8C_1Pyrr][NTf_2]$ characterized as hydrophobic ionic liquids [64], were used. Their molecular structures are presented in Fig. 1. The ionic liquid $[C_8MIM][NTf_2]$ was selected taken as reference the works by Hernández-Fernández and de los Ríos [56–58], which showed the interest of this ionic liquid for organic-organic separations. In addition, in order to investigate the impact of the structure of the cation on the separation performance, the ionic liquid $[C_8C_1Pyrr][NTf_2]$, containing the pyrrolidinium cation and the same anion and alkyl chain, was selected [65]. The performance of the SILMs prepared with those ionic liquids was evaluated in terms of flux, separation factor, permeance and selectivity.

2. Materials and methods

2.1. Materials

The support membrane used for the preparation of the SILMs is a PAN flat ultrafiltration hydrophilic membrane (Type: PX), which was purchased from Synder Filtration (USA). Polypropylene (PP) flat sheet membrane (hydrophobic) model ACCUREL PP 1E (R/P) was purchased from 3 M GmbH (Germany). Dimethyl carbonate (purity >99%) and methanol (purity >99.8%) were purchased from VWR International and Alfa Aesar, respectively.

Lithium bis(triuoromethanesulfonyl)imide (purity>99%) was purchased from Abcr GmbH, Germany. 3-methylimidazole (purity 99%) was purchased from Alfa Aesar and N-methylpyrrolidine (purity >98%) was purchased from Acros Organics. These chemicals were used for the synthesis of the ionic liquids without further purification.

2.2. Ionic liquid synthesis

The ionic liquids have been synthesized in a two-step process based on known procedure from the literature, namely a quaternarization of a tertiary amine [66] followed an anion metathesis using lithium bis(trifluoromethanesulfonyl)imide [67]. The first step was the quaternization of N-methylimidazole or N-methylpyrrolidine using 1-chlorooctane in acetonitrile at 80 °C. The second step consists in an anion metathesis using lithium bis(triuoromethanesulfonyl)imide at room temperature. The purity of the different ionic liquids was assessed based on ^1H and ^{13}C Nuclear magnetic resonance (NMR) analyses. No signal for starting materials or eventual by-products were observed.

2.3. Membrane preparation

First, hydrophobic and hydrophilic porous membranes were tested as supports. On one hand, the hydrophobic membrane (polypropylene) could not hold the ionic liquid inside the membrane pores. The high vacuum applied in the permeate side during the immobilization proce-

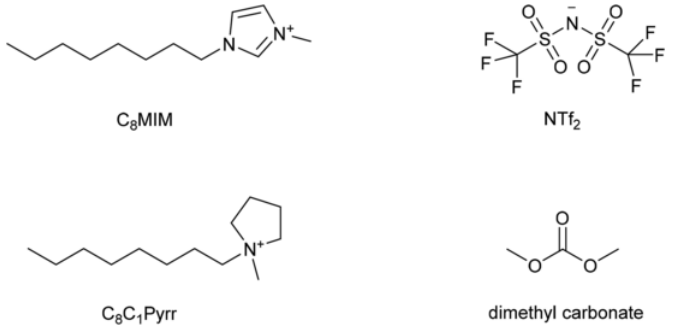

Fig. 1. The molecular structure of the cations and anion forming the ionic liquids studied here, together with dimethyl carbonate (DMC).

dure and its larger pore size could explain why the polypropylene membrane was not able to hold the ionic liquids. On the other hand, the hydrophilic (PAN) membrane was able to hold the ionic liquids inside its pores thanks to intramolecular interactions of the sulfoxide group (S=O) from $[NTf_2]^-$ anion and the cyano groups (C≡N) [68,69]. Therefore, the hydrophilic PAN flat sheet membrane was used as a supporting membrane.

All the SILMs used through this study were prepared by the following immobilization procedure: a commercial circular flat sheet ultrafiltration membrane (PAN) was placed inside the membrane cell. The ionic liquid was added on top of the membrane using a pipette. The quantity of the IL added was sufficient to cover entirely the surface of the porous membrane. An O-ring was installed on the circular membrane and pressed gently on it. Then, the cell was fixed and tightened by closing the bolts. The structure of the membrane cell is shown in Fig. 2. Vacuum was applied for 2 h using a rotatory pump (50 mbar) on the permeate side to remove the air from the pores of the membrane and suck the ionic liquids into the pores. When the immobilization was completed, the excess of IL on the membrane surface was removed carefully using a tissue. To determine the amount of ionic liquid immobilized in the supported membrane, all the membranes were weighted before and after impregnation with an analytical balance (AE 260 METTLER TOLEDO, Belgium) with precision ± 0.0001 g.

2.4. Scanning electron microscopy (SEM) analysis

In order to evaluate the quality of the immobilization of the ionic liquid inside the membrane pores, the morphology of the cross section before (raw PAN membrane) and after adding the ILs was analyzed by SEM (Zeiss, ULTRA). The membranes were cut in small rectangular pieces and immersed into liquid nitrogen. As the polymeric material from which they are made is very brittle at such low temperatures, samples were broken without deforming the cross section. Before analysis, all the samples were sputter coated with a thin layer of gold (BALZERS UNION FL 9460 BALZERS SCD 030) to make them conductive.

Fig. 2. The cell for preparing supported ionic liquid membrane.

2.5. Gas chromatography analysis

The composition of feed and permeates was analyzed by gas chromatography (Interscience TRACE 1300) equipped with a flame ionization detector (FID), split/splitless injection (SSL) unit, thermal conductivity detector (TCD) and a capillary column (Stabilwax, 30 m, 0.32 mm, 1 μm). The carrier gas was Helium and the injection was performed in split mode with a split ratio of 100. Initially, the oven temperature was set at 50 °C and it was increased at the rate of 20 °C/min until it reached 150 °C. Then, it was maintained at this temperature for 1 min. The FID and injection temperatures were 250 °C and 300 °C, respectively. A calibration curve was obtained by performing GC analysis of samples of known concentrations. Three trials were done for each of the data points.

2.6. Pervaporation experiments

The pervaporation experiments were performed in a 3″ round cell unit (Sulzer Chemtech GmbH, Switzerland), the same unit used to prepare the SILMs (Fig. 3). The scheme of the pervaporation system is shown in Fig. 3.

The experimental temperature inside the membrane cell was kept at 30 °C (±0.3 °C) using a heating circulator (Julabo, Germany). A vacuum pump was used at the permeate side giving a vacuum pressure of 1–2 mbar. The surface area of installed SILM was 38.48 cm^2 (diameter 7.0 cm). Sampling of the permeate was started after running the system for 2 h to reach stable conditions. The permeate was collected and weighed every 30 or 60 min depending on the amount of permeate. The composition of the permeate samples was analyzed every 120 min by means of gas chromatography as indicated in section 2.5. The membranes prepared were tested with different compositions of binary mixtures methanol/DMC. The feed compositions were 0.2, 0.5, or 0.8 mol fraction of methanol. In this work, each experiment was carried out twice in order to check the reproducibility of experimental results.

The performance of SILMs was evaluated in terms of transmembrane flux J (kg/m•h), separation factor $\beta_{i/j}$, permeance $\frac{P_i}{l}$ and selectivity $\alpha_{i/j}$, expressed as follows:

$$J = \frac{Q}{\Delta t \times A} \tag{1}$$

$$\beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{2}$$

$$\frac{P_i}{l} = \frac{J_i}{(x_i \times \gamma_i \times P_i^0 - y_i \times P_p)} \tag{3}$$

$$\alpha_{i/j} = \frac{P_i/l}{P_j/l} = \frac{P_i}{P_j} \tag{4}$$

where A is the membrane effective area (m^2), Δt is the permeate collecting time (h) and Q is the weight of permeate (kg). x and y are molar fraction of components, the subscript indicates the components i and j in the permeate (y_i, y_j) and feed (x_i, x_j) solutions, respectively. J_i is the partial flux of component i (kg/m [2]•h) and P_p is the pressure at permeate side. Aspen Plus 11 was used to calculate the vapor pressure P_i^0 (atm) and activity coefficients γ_i of component i at different concentrations. The NRTL method was employed to estimate the thermody-

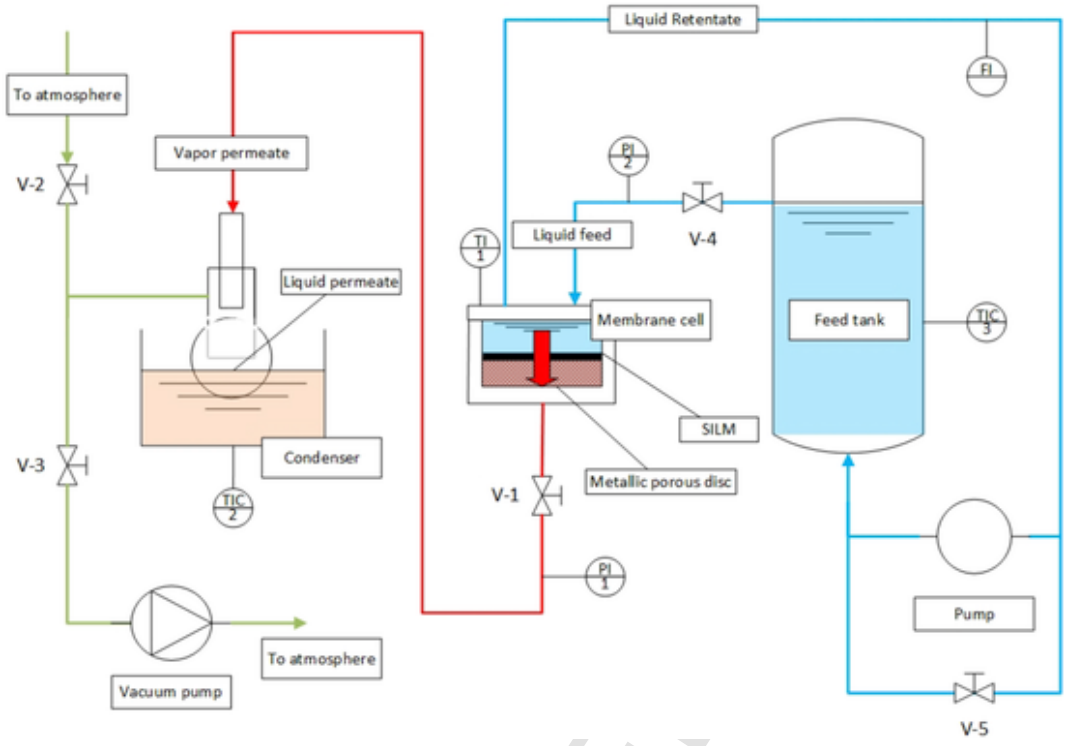

Fig. 3. The scheme of pervaporation separation experimental equipment.

namic parameters since it shows good approach for DMC/methanol mixtures [70,71]. l is the membrane thickness. The unit of permeance is expressed in GPU $1\ GPU = 1 \times 10^{-6}\ cm^3\ (STP)/(cm^2 s\ cmHg)$ and $1\ m^3/m^2 s\ kPa = 1.33 \times 10^8\ GPU$; the unit conversion can be found in Baker et al. [72]. The selectivity ($\alpha_{i/j}$) is the ratio of permeance of component i and j. If the value of selectivity ($\alpha_{i/j}$) is larger than 1, this indicates that component i is more permeable to the membrane than component j.

The SILMs performance results are interpreted by analyzing the Kamlet-Taft solvatochromic parameters, the Hildebrand solubility parameters and the chemical structure of the molecules.

2.7. Kamlet-Taft solvatochromic parameters and Hildebrand solubility parameters

The Kamlet-Taft solvatochromic parameters were used to provide a comprehensive insight into the solvent-space structure regarding to the similarity of solute and solvent interactions [73]. Kamlet–Taft solvatochromic parameters are the most comprehensive and frequently used quantitative measure of solvent properties, such as polarity and hydrogen-bonding ability. Three Kamlet–Taft parameters include: α, β and π^*, which quantify hydrogen-bond donating ability (acidity), hydrogen-bond accepting ability (basicity) and polarity/polarizability, respectively.

The Hildebrand solubility parameter is derived from the square root of the cohesive energy density of the solvent, in terms of the heat of vaporization divided by the molar volume, a more detailed explanation can refer to Barton et al. [74]. Table 2 shows the Hildebrand solubility parameters of ionic liquids, pure methanol and DMC, and their mixtures at different molar fraction. The solubility parameter of a mixture is estimated by the following equation (5) [74]:

$$\delta_H = \sum_i \varphi_i \delta_{Hi} \tag{5}$$

the δ_H is Hildebrand solubility parameter and δ_{Hi} is the Hildebrand solubility parameter of pure component i. φ_i is the volume fraction of the pure component i in the mixture. A shorter distance of δ_H between component A and component B indicates a stronger affinity between them.

3. Results and discussion

3.1. SEM analysis

The cross section morphologies of the raw PAN membrane and the prepared supported ionic liquid membranes are shown in Fig. 4. Before immobilization, regular empty pores can be clearly observed in the raw PAN porous membrane (Fig. 4a). After immobilization, the membranes with the ionic liquids [C_8MIM][NTf_2] and [C_8C_1Pyrr][NTf_2] are shown in Fig. 4b and c, respectively. It shows that the PAN porous membrane can hold the ionic liquids inside membrane pores, being present in all the membrane thickness.

3.2. Pervaporation separation performance

The separation performances of SILMs prepared with [C_8C_1Pyrr][NTf_2] and [C_8MIM][NTf_2] immobilized in PAN membranes were determined for binary mixtures at different concentrations of methanol/DMC. The transmembrane flux, separation factor, permeance and selectivity of these two SILMs are shown in Fig. 5.

Fig. 5a, e and f shows that the total transmembrane flux and partial flux of both SILMs are strongly dependent on the concentration in methanol. The raw flux value does not reflect the real interaction between the feed components and ionic liquids due to the presence of driving force [72]. Therefore, the permeance is discussed instead because permeance removes the effect of the driving force. Fig. 5b shows the permeance of DMC and methanol of both SILMs. It is clear that the permeance, selectivity and separation factor are strongly dependent on the feed composition, which indicates the presence of strong coupling effects (the presence of one compound changes the permeability properties of the other). A phenomenon of coupled transport happens in per-

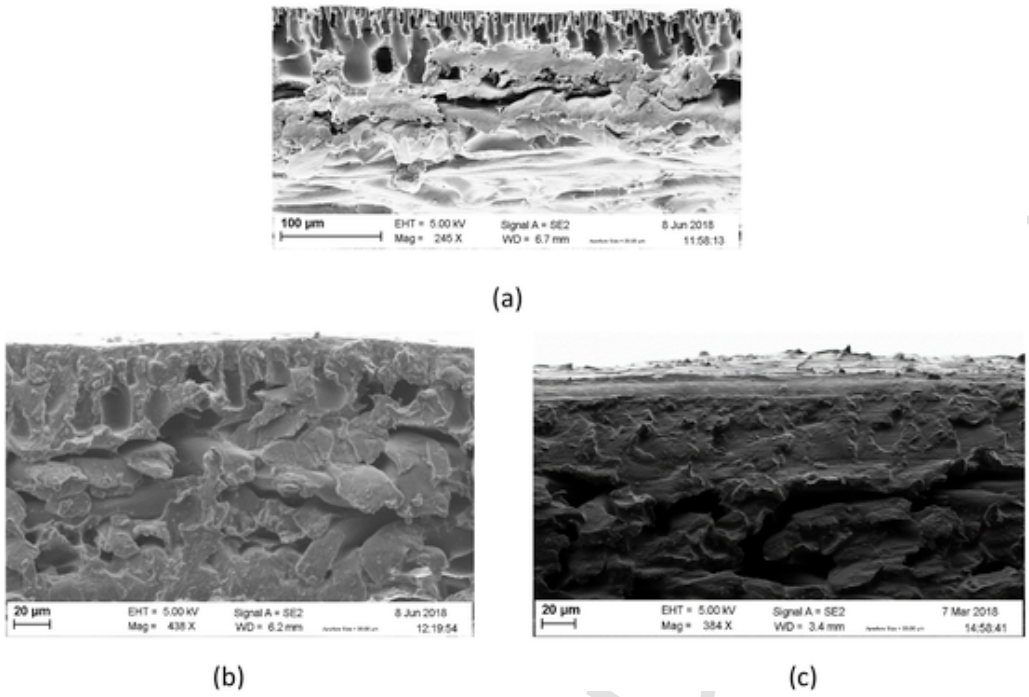

Fig. 4. The PAN membrane before immobilization (a); immobilization of $[C_8MIM][NTf_2]$ (b); and immobilization of $[C_8C_1Pyrr][NTf_2]$ (c).

vaporation resulting from strong interaction among membrane and penetrants [75].

Regarding the separation factor and selectivity, both of them are larger than 1. The high selectivity means that both membranes are favorable to permeate DMC rather than methanol, which can be also observed when comparing the permeance values. However, as indicated before, the permeation behavior is highly concentration dependent. At high concentration of methanol (0.8 M fraction), the separation factor and selectivity remain only between 1.77 and 3, respectively. With an increase of the concentration of DMC in the feed solution, the separation factor and selectivity increase. Both SILMs can achieve a separation factor around 21, and selectivity of 67 for $[C_8MIM][NTf_2]$ (0.2 M fraction of methanol) and 48 for $[C_8C_1Pyrr][NTf_2]$ (0.5 M fraction of methanol).

Fig. 6 shows the vapor liquid equilibrium behavior of DMC/methanol mixture along with the pervaporation DMC permeate concentrations vs. its feed concentration. The separation performance of the permeation selectivities of the two types of SILMs $[C_8MIM][NTf_2]$ and $[C_8C_1Pyrr][NTf_2]$ is compared with distillation separation based on vapor-liquid equilibrium. It illustrated that both SILMs exhibit excellent separation behavior when DMC concentration is higher (80 mol%). The selectivities of both SILMs are slightly poor at low concentration of DMC (<20 mol%), but the SILMs can still break the azeotropic balance. Therefore, the SILMs prepared in this work may be used to separate DMC/MeOH mixtures by pervaporation.

3.3. Kamlet-Taft solvatochromic parameters analysis

In Table 1, solvatochromic parameters of solvents and ionic liquids were given. In Table 1, by comparing solvatochromic parameters of solvents and ionic liquids, it appears that methanol is not only a hydrogen bond acceptor but also a stronger hydrogen bond donor than DMC and ILs. Therefore, methanol could preferably form hydrogen bonds with DMC rather than ILs in the feed solution because DMC has a higher hydrogen bond acceptor (β) value than that of ionic liquids. At low concentration of methanol in the feed solution, most methanol molecules tend to form hydrogen bonds with DMC. As a result, methanol molecules have less opportunity to contact ionic liquids and to pass through the membrane. In this case, the major interaction takes place between the DMC molecules and ionic liquids. In addition, the permeance of DMC at low methanol concentration is $[C_8C_1Pyrr][NTf_2] > [C_8MIM][NTf_2]$. This is consistent with the α value of ILs. $[C_8C_1Pyrr][NTf_2]$ has higher hydrogen bond donor capacity than $[C_8MIM][NTf_2]$. Hence, DMC/$[C_8C_1Pyrr][NTf_2]$ have stronger affinity than DMC/$[C_8MIM][NTf_2]$ and $[C_8C_1Pyrr][NTf_2]$ is prone to permeate DMC. When the concentration of methanol increases, in this case, methanol molecules have more opportunity to contact ionic liquids then permeating through the membranes because methanol is not only hydrogen bond donor but also hydrogen bond acceptor.

3.4. Solubility parameter analysis

Two distinct values of the Hildebrand solubility parameter have been found in the literature for DMC; thus, the calculation of Hildebrand solubility parameter of the mixture methanol/DMC includes two values. The data concerning the Hildebrand solubility parameter of ionic liquids are limited and different sources can provide different values. From Table 2, it can be seen that the Hildebrand solubility parameters of both ionic liquids are around 20–25. On the other hand, the Hildebrand solubility parameter of mixture increases with increasing methanol concentration. When the concentration of methanol increases up to 0.5–0.8 M fraction, the Hildebrand solubility parameter of the mixture is closer to the ones of ionic liquids. This indicates that the compatibility of the mixture and ionic liquids is higher at a higher concentration of methanol. Therefore, it can be deduced that the coupling effect is more likely to appear at high concentration of methanol due to the variation of the solubility parameters of a mixture [82].

From the analysis of solubility parameter, it can be observed that the Hildebrand solubility parameter (δ_H in Table 2) increases with the increase of methanol concentration, being closer to the value for the ionic liquids. This implies a stronger affinity between them due to a shorter distance of δ_H between ionic liquids and solution. The concentration effect on the permeation behavior follows this prediction. Thus, the selectivity and separation factor become lower at higher concentra-

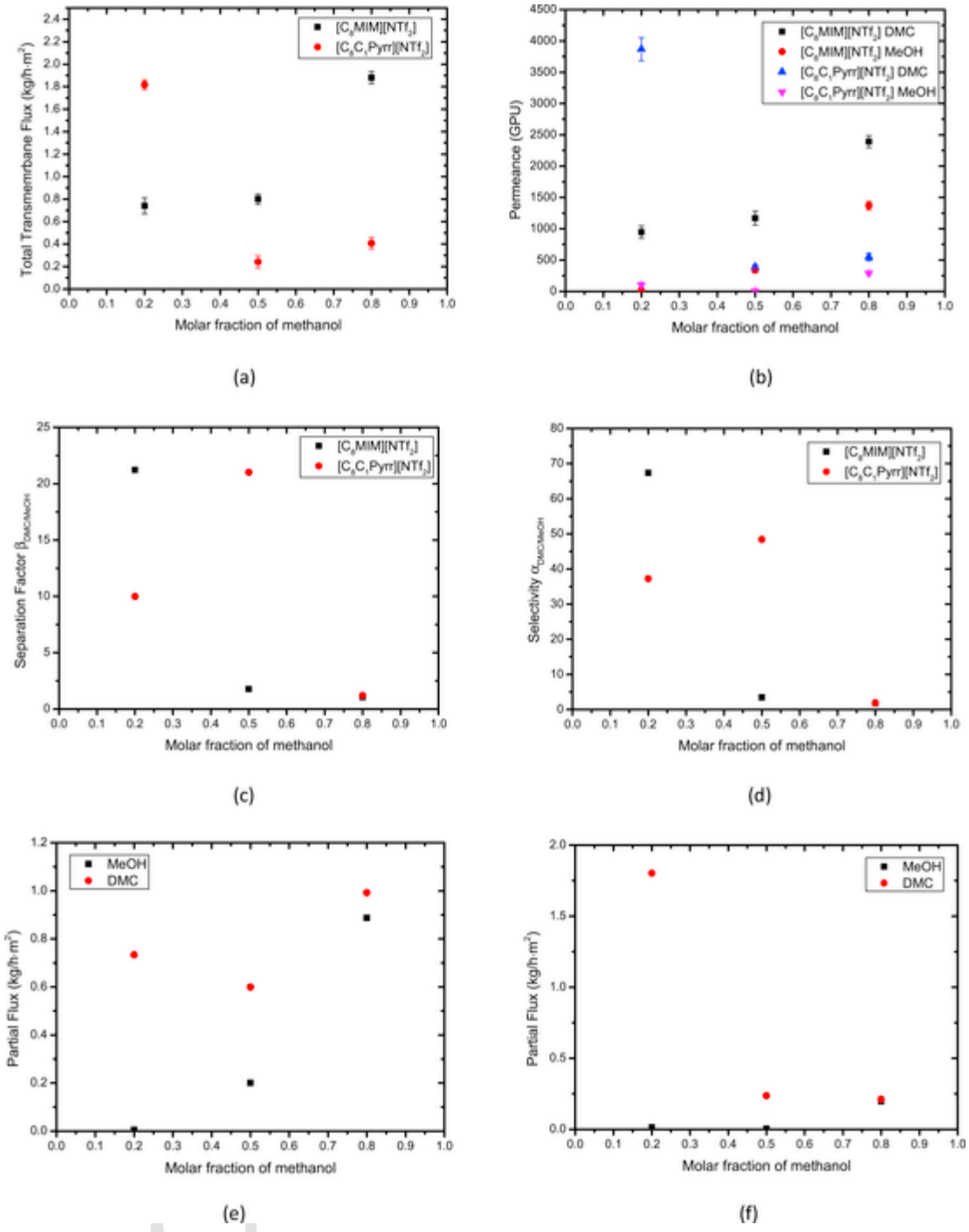

Fig. 5. Performance of SILMs based on ionic liquid [C_8C_1Pyrr][NTf_2] and [C_8MIM][NTf_2] at 30 °C, (a) Total transmembrane flux, (b) Permeance of DMC and methanol, (c) Separation factor, (d) Selectivity, (e) the partial flux of DMC and methanol for [C_8MIM][NTf_2] and (f) [C_8C_1Pyrr][NTf_2].

tion of methanol. This is consistent with an increase of permeance of both compound as methanol concentration in the feed solution increases.

3.5. Impact of the molecular structure of DMC and methanol on coupling effects

The molecular structures of all components studied in this work were shown in Fig. 1. In the DMC-methanol-ionic liquid system, different molecular interactions occur. The hydroxy group (-OH) of methanol can generate a hydrogen bound and dipole-dipole attraction to the group (C═O) in the DMC molecule. DMC has a stronger interaction with both ionic liquids than methanol, because both ionic liquids are hydrophobic.

Thus, at low concentration of methanol in the feed solution, most methanol could form hydrogen bonding with DMC due to this interaction. Therefore, the formation of intermolecular attraction between DMC and methanol makes them difficult to permeate through the membrane. However, the other DMC molecules which do not interact with methanol can permeate through the membrane much easier. In addition, because of the existing interaction between DMC and methanol, methanol has less opportunity to contact ionic liquids. As a

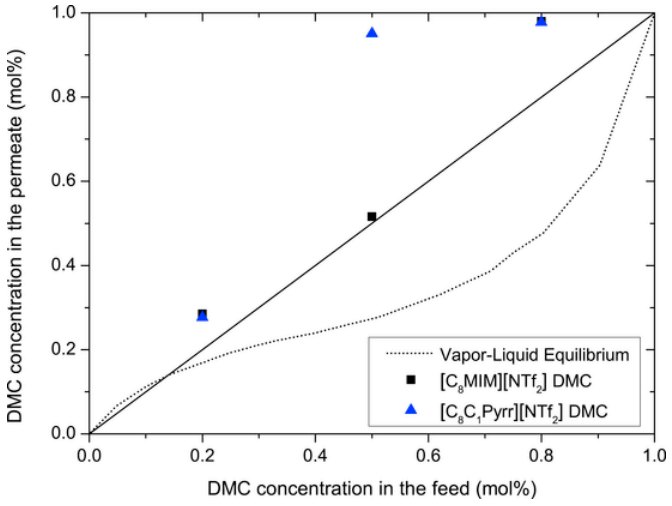

Fig. 6. Relationship of DMC concentrations in feed side and in permeate side.

Table 1
Solvatochromic parameters (Kamlet-Taft solvation parameters), α, β and π^*, which quantify hydrogen-bond donating ability (acidity), hydrogen-bond accepting ability (basicity) and polarity/polarizability, respectively.

Component	Hydrogen bond donor (α)	Hydrogen bond acceptor (β)	Dipolarity/ polarizability (π^*)	Ref.
$[C_8MIM][NTf_2]$	0.60	0.29	0.96	[76]
$[C_8C_1Pyrr][NTf_2]$	0.80	0.08	0.73	[77]
Methanol	1.05	0.61	0.73	[77–79]
DMC	0	0.38	0.47	[78,80,81]

Table 2
Hildebrand solubility parameter of ionic liquids, pure methanol, pure DMC and their mixtures.

Material	δ_H	Ref.
$[C_8MIM][NTf_2]$	20, 22, 25	[83–85]
$[C_8C_1Pyrr][NTf_2]$	20	[85]
Methanol	29.7	[86]
Dimethyl carbonate	12.7/15.9	[86]
Mixture		
0.2 MeOH + 0.8 DMC	14.5/17.4	This work [a]
0.5 MeOH + 0.5 DMC	18.2/20.4	This work [a]
0.8 MeOH + 0.2 DMC	23.9/25.0	This work [a]

[a] Calculated using equation (5).

result, most of methanol remains in the feed solution and the permeance of methanol through both supported ionic liquid membranes is very low at low concentration of methanol.

When the concentration of methanol increases, methanol has more opportunity to contact ionic liquids leading to methanol permeation. On the other hand, the ionic liquids prefer to permeate DMC. As a result, coupling effect takes place during the permeation, methanol also permeates through the membrane with DMC due to hydrogen bonding interaction between them. From Fig. 5 (b), it can be seen that the permeance of methanol in both supported ionic liquid membranes increased dramatically but it is still lower than permeance of DMC for each SILM. The selectivity and separation factor showed very low value at high methanol concentration.

In addition, the structure of the cation has an impact on the permeation behavior. The only difference between the structure of the two ionic liquids lays into their cationic heterocycles (pyrrolidine vs. imidazole). As mentioned before, at low concentration of methanol, the interaction between methanol and ionic liquids are weak due to the presence of large amount of DMC. When the concentration of methanol increases, the methanol can interact more easily with $[C_8MIM]^+$ than $[C_8C_1Pyrr]^+$. It may be ascribed to the presence of a tertiary amine in the imidazolium cation that does not exist in the pyrrolidinium one therefore leading to hydrogen bonds between hydroxyl groups of methanol and the pair of non-bounding electrons borne by the nitrogen atom of the tertiary amine [87].

3.6. Membrane stability

A frequent major issue with SILMs is their low stability due to ionic liquid loss during operation. Hence, a long-term stability test was carried out for both SILMs. The prepared membrane was tested for 120 h under the concentration of 0.2 M fraction of methanol. The stability test is shown in Fig. 7, showing stable fluxes during the experimental time. The test confirms that both ionic liquids were kept in the pores of supported PAN membrane and gives stable transmembrane flux and separation factor.

3.7. Comparison with DMC/methanol pervaporation separation in the literature

A comparison of pervaporation separation of methanol DMC mixtures is shown in Table 3. In the literature, most of study of separation methanol/DMC mixture is to maximize to permeation of methanol. Therefore, the separation factor and selectivity are reported by means of methanol relative to DMC as the methanol is usually concentrated in the permeate in the literature. In this work, the ILs were in favor of permeating DMC.

Comparing with other studies, the SILMs evaluated in this work have an outstanding separation performance at low temperature (30 °C) with high selectivity (DMC towards methanol) of 67 and 48 for $[C_8MIM][NTf_2]$ (0.2 M fraction of methanol) and $[C_8C_1Pyrr][NTf_2]$ (0.2 M fraction of methanol) based SILMs, respectively. $[C_8C_1Pyrr][NTf_2]$-SILM can also keep good separation performances at 0.5 M fraction of methanol in the feed.

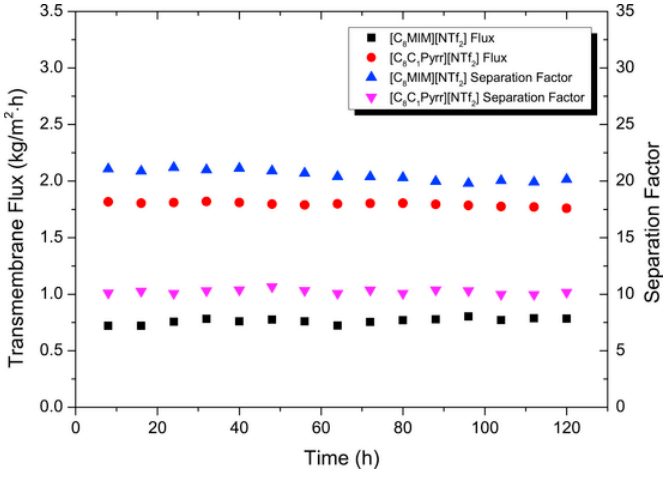

Fig. 7. Operational stability of SILMs based on PAN membrane with supported $[C_8MIM][NTf_2]$ and $[C_8C_1Pyrr][NTf_2]$ under 0.2 M fraction of methanol at 30 °C.

Table 3
Comparison of pervaporation performances for the separation of methanol/DMC mixtures reported in the literature (only optimal conditions are shown in this table).

Membrane material	Feed Methanol concentration (wt%)	Temperature (°C)	Total Flux (g/m [2].h)	Separation Factor	Permeance	Selectivity	Ref.
Methanol-selective membranes [a]							
Chitosan/silica	70	50	1265	30.1	–	–	[88]
Poly (vinyl alcohol)	50	70	248	37	–	–	[89]
Nano-Silica/polydimethylsiloxane	70	40	702	3.97	–	–	[90]
Silicotungstic acid hydrate/ Chitosan	10	50	1163	67.3	–	–	[91]
Chitosan hollow fiber membrane	20	50	150	23	~30 DMC; ~800 MeOH	~15	[92]
Poly (acrylic acid)/poly (vinyl alcohol)	70	60	577	13	~20 DMC; ~80 MeOH	~4	[93]
Crosslinked chitosan	70	55	480	60	–	–	[94]
DMC-selective membranes [b]							
PDMS/PVDF	72	40	487.2	3.95	–	–	[95]
$[C_8MIM][NTf_2]$ SILM	13 (0.2 mol%)	30	739.8	21.2	947 DMC; 14 MeOH	67	This work
$[C_8C_1Pyrr][NTf_2]$ SILM	26 (0.5 mol%)	30	241	21.0	395 DMC; 8.2 MeOH	48.41	This work

[a] Separation factor and selectivity are methanol relative to DMC.
[b] Separation factor and selectivity are DMC relative to methanol.

4. Conclusions

In this work, two SILMs containing the ionic liquids $[C_8MIM][NTf_2]$ and $[C_8C_1Pyrr][NTf_2]$ were studied for the separation of a binary mixture of DMC and methanol. It was found that at high concentration of DMC (0.8 M fraction), the SILMs show good separation performances with high selectivity. However, the membrane performance is highly dependent on concentration. At high concentration of methanol, the separation performance decreases due to strong coupling effects as the coupled transport of DMC and methanol through the membrane because of their hydrogen bonding. The ionic liquid structure has an impact on the permeation behavior. For both of the studied cation structures there are quite significant differences in permeation behavior of DMC and methanol.

Uncited references

[]; [].

CRediT authorship contribution statement

Wenqi Li: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review editing, Visualization. **Cristhian Molina-Fernández:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - review editing. **Julien Estager:** Writing - review editing, Funding acquisition. **Jean-Christophe M. Monbaliu:** Writing - review editing, Funding acquisition. **Damien P. Debecker:** Conceptualization, Writing - review editing, Funding acquisition. **Patricia Luis:** Conceptualization, Methodology, Formal analysis, Resources, Writing - review editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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