Separation and Purification Technology 236 (2020) 116237

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

π Electron induced separation of organic compounds using supported ionic liquid membranes

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ARTICLE INFO

Keywords:
Aromatic compounds
Flux
Membrane stability
Nucleobase
Stereoisomers

ABSTRACT

Supported ionic liquid membranes have been tested for fractionation of organic compounds. Imidazolium based ionic liquids; 1-allyl-3-vinylimidazolium bromide, 1-hexyl-3-vinylimidazolium bromide and 1-octyl-3-vinylimidazolium bromide were trapped in the pores of a polypropylene membrane. Fractionation of a feed stream consisting of benzene, naphthalene and phenanthrene in tetradecane and *cis*- and *trans*-stilbene in hexane were investigated. The receiving phase was hexane. Differences in the π electron cloud density of the aromatic solutes influence their interactions with the imidazolium cation, which can affect the rates of transport. In the case of the three aromatic solutes, the degree of conjugation and molecular weight increase in order benzene, naphthalene and phenanthrene. These opposing effects result in similar mass transfer coefficients for the three solutes for the three ionic liquids tested. However, for *cis*-and *trans*-stilbene, the mass transfer coefficient was larger for all three ionic liquids. It is likely that enhanced aromatic stacking of the *trans*- isomer led to a higher mass transfer coefficient. In addition, 1-hexyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide was used as the liquid membrane phase to fractionate two nucleobases: thymine and cytosine in water. The receiving phase was also water. The membrane mass transfer coefficient for thymine was 5.5 times greater than cytosine indicating the possibility of exploiting multimodal interactions with the imidazolium group to fractionate compounds.

1. Introduction

Supported liquid membranes where a liquid phase is trapped within the pores of a microporous membrane represents one of the early membrane contactors [1,2]. Supported liquid membranes are attractive as a solute can be selectively extracted into the liquid phase that is trapped within the membrane pores and then back extracted into the strip solution. Numerous module configurations have been described. Other potential advantages include low capital cost, low operating cost and energy consumption. Further the process is modular and easy to scale up.

Commercialization of supported liquid membranes has been slow as the stability of the liquid membrane is limited. The liquid phase within the membrane pores can be lost to the bulk feed and strip phases on either side of the membrane as well as by evaporation. Even if the solubility of the phase within the membrane pores in the two bulk phases that contact the membrane is minimal, given the large difference in the volume of the liquid membrane phase and the bulk phases, loss of the liquid membrane occurs. Various attempts, such as strip dispersion, have been proposed to increase membrane stability [3–5].

Room temperature ionic liquids are salts in which formation of a crystal lattice is suppressed at room temperature. They have been referred to as designer solvents as the properties can be tuned by using different ion pair combinations. Ionic liquids have negligible vapor pressure, thus there will be no evaporation losses. By choosing appropriate ion pairs, hydrophobic ionic liquids with very low water solubility can be prepared. Further, due to their high surface tension and viscosity, which can be modified by choice of the ion pairs used, very stable supported ionic liquid membranes (SILMs) may be prepared.

Abejón et al. [6] indicated that interest in SILMs has increased rapidly since 2005. In general, four main applications for SILMs have been considered: carbon dioxide separation, separation of other gases and pervaporation represent gas phase feed streams. Here we focus on liquid phase feed streams where numerous potential applications have

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https://doi.org/10.1016/j.seppur.2019.116237
Received 26 August 2019; Received in revised form 20 October 2019; Accepted 21 October 2019
Available online 22 October 2019
1383-5866/

Table 1
Summary of diffusion experiments.

Ionic liquid phase	Aromatic solutes in tetradecane	Stereoisomers of stilbene in hexane	Nucleobases: cytosine, thymine
1-allyl-3-vinylimidazolium bromide	Solute concentration: benzene 0.819 M, naphthalene 0.650 M, phenanthrene 0.468 M, experiment run for 2 hr, strip solution was hexane	Solute concentration: *cis*-stilbene and *trans*-stilbene 0.0556 M, experiment was run for 2.6 hr, strip solution was hexane	
1-hexyl-3-vinylimidazolium bromide	Solute concentration: benzene 0.819 M, naphthalene 0.650 M, phenanthrene 0.468 M, experiment run for 2 hr, strip solution was hexane	Solute concentration: *cis*-stilbene and *trans*-stilbene 0.0556 M, experiment was run for 2.6 hr, strip solution was hexane	
1-hexyl-3-vinylimidazolium bis (trifluoromethylsulfonyl)imide			Solute concentration: cytosine and thymine 0.0218 M, experiment was run for 48 hr, strip solution was water
1-octyl-3-vinylimidazolium bromide	Solute concentration: benzene 0.819 M, naphthalene 0.650 M, phenanthrene 0.468 M, experiment run for 2 hr, strip solution was hexane	Solute concentration: *cis*-stilbene and *trans*-stilbene 0.0556 M, experiment was run for 2.6 hr, strip solution was hexane	

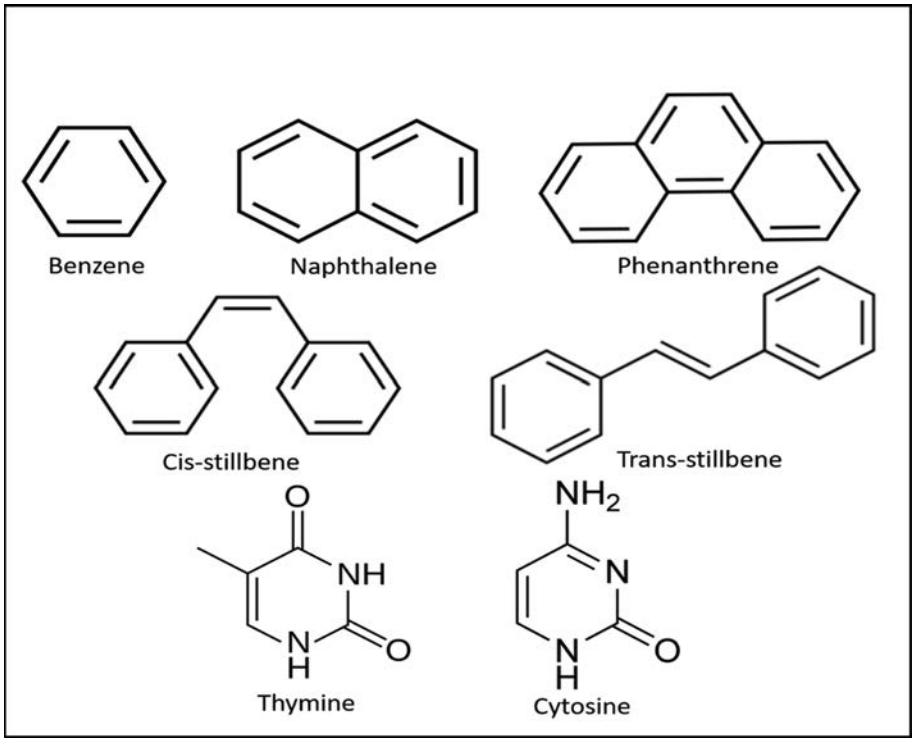

Fig. 1. Chemical structure of solutes.

been described.

Chakraborty et al. reported highly efficient and selective separation of toluene using an ionic liquid membrane with Ag^+ carrier [7]. Branco et al. reported mutual separation of several organic compounds (1,4-dioxane, propan-1-ol, butan-1-ol, cyclohexanol, cyclohexanone, morpholine and methyl morpholine) using imidazolium based ionic liquid membranes [8]. Removal of phenol, amino acids, ketones and acetic acid have also been reported using bulk ionic liquid membranes [9–12]. The transport and experimental design were optimized for achieving higher efficiency without any compromise in ion selectivity [13]. Ionic liquid based membranes have also been used in microbial fuel cell applications [14,15]. One of the advantages was the specific energy gained from substrates (i.e. glucose and acetate) was found to be more in ionic liquid based membranes compared to the nafion based membrane [16].

Nevertheless, most interest has focused on hydrocarbon separations, recovery of products from fermentation broths, desulfurization of crude oil and fuels [17] and metal ion recovery [18–20]. Here we focus on separation of organic compounds.

Perhaps the first use of an SILM for separation of organic compounds was described by Branco et al. [21]. They indicated selective separation of secondary amines over tertiary amines using ionic liquids based on 1-n-alkyl-3-methylimidazolium as a cation and hexafluorophosphate and tetrafluoroborate as anions. The high selectivity for secondary amines is a result of preferential interactions with the imidazolium ring. This is due to the formation of hydrogen bonds with the protons at the C-2 position [22]. In an early publication, Matsumoto et al. [23] indicated that SILMs may be used for selective transport of aromatic hydrocarbons. Hanke et al. [24] showed that electrostatic interactions between the solute and ionic species in the solvent, in this case the ionic liquid cation and π electrons in the aromatic solute, are important. For benzene and other aromatic compounds, with electron density on both sides of the plane of the aromatic ring, quadrupole and other higher order electrostatic moments arise. These quadrupole moments interact with the cations present in the solvent.

Chakraborty et al. [25] extended the work by Matsumoto et al. [23]

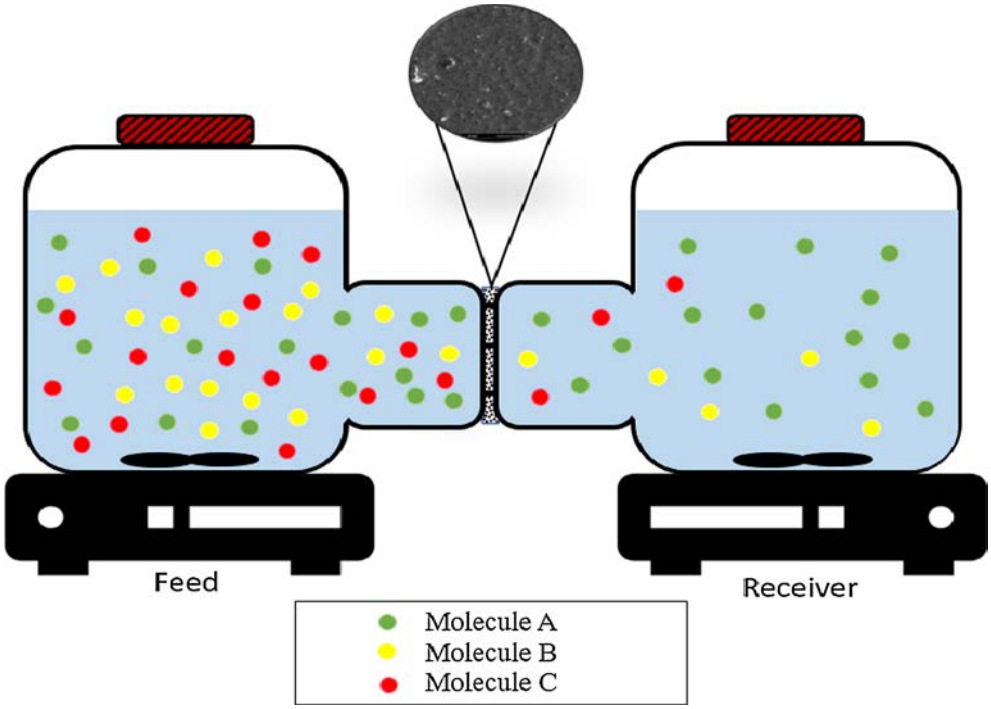

Fig. 2. Schematic diagram of diffusion cell.

Table 2
HPLC detection wavelengths and retention time for solutes.

Compound	Wavelength (nm)	Retention time (min)
Benzene	220	7.7
Naphthalene	250	8.5
Phenanthrene	300	10.0
Trans-stilbene	310	7.0
Cis-stilbene	310	9.3
Thymine	220	12.6
Cytosine	220	9.8

by investigating the separation of various aromatic hydrocarbons using different imidazolium based ionic liquids as the liquid membrane phase. They also show that ionic liquids may be used to separate aromatic hydrocarbons from aromatic-aliphatic mixtures. Further studies by Zhang et al. [26] and Zhang et al. [27] have explored the feasibility of toluene/cyclohexane and toluene/n-heptane separations. Again, the enhanced solubility of aromatic hydrocarbons led to recovery of toluene in the strip solution. Wang et al. [28] have determined solubility parameters and selectivity for a range of organic solutes in ionic liquids. They show that ionic liquids show great promise for separation of alkanes from aromatics. Further, by selecting the cation and anion of the ionic liquid, the properties of the liquid membrane phase can be tailored for a specific separation. Lozano et al. [29], Han and Row [30] and Martínez-Palou et al. [31] provided reviews of the use of SILMs for liquid phase separations.

Marták et al. [32] investigated the extraction of lactic acid using an SILM. These authors provide a detailed mass transfer analysis of the extraction process. They indicate that the protonated form of lactic acid may be extracted via hydrogen bonding with the ionic liquid [33]. On the other hand, the anionic form of lactic acid could also be extracted by ion exchange with the lactate anion.

Here, we further explore the ability of imidazolium based ionic liquids to fractionate aromatic compounds. We consider separation of a three-component mixture consisting of benzene, naphthalene and phenanthrene in tetradecane. The three imidazolium based ionic liquids we investigate in the membrane phase are: 1-allyl-3-vinlyinidazoliumbromide, 1-hexyl-3-vinlyinidazolium bromide and 1-octyl-3-vinlyinidazolium bromide. The strip solution consisted of hexane. The difference between the three solutes is their degree of conjugation. We also investigated the separation of two stereoisomers, *cis*- and *trans*-stilbene, using the same three imidazolium based ionic liquids as the membrane phase. The feed and strip solutions consisted of hexane. Finally, we have investigated the separation of two nucleobases cytosine and thymine. The feed and strip solutions consisted of water. In order to render the ionic liquid water insoluble, the bromide anion in 1-hexyl-3-vinylimidazolium bromide was exchanged with bis(trifluoromethylsulfonyl)imide. The membrane phase consisted of 1-hexyl-3-vinlyimidazolium bis(trifluoromethylsulfonyl) imide. Our results highlight the importance of interactions between the π electrons above and below the aromatic ring and the cation present in the ionic liquid.

2. Material and methods

2.1. Materials

1-vinylimidazole (99%), lithium bis(trifluoromethylsulfonyl)imide (98 + %), *cis*-stilbene, *trans*-stilbene, n-hexane (ACS grade), n-octane and n-tetradecane (99%) were purchased from Alfa-Aesar (Ward Hill, MA). Allylbromide (99%), bromooctane (99%), toluene (ACS grade), naphthalene and phenanthrene were bought from Sigma-Aldrich (Munich, Germany). Thymine (> 98.0%) and cytosine (> 98.0%) were obtained from Tokyo Chemical Industry Co., Ltd (Chuo-ku, Tokyo, Japan). Acetonitrile (HPLC grade) and ethyl acetate (ACS grade) were sourced by Macron Fine Chemicals TM (Radnor, PA). 1-bromohexane (≥98%) was obtained from Merck KGaA (Kenilworth, NJ). Deionized water used in all the experiments was produced using a Thermo Fisher 18MΩ Barnstead Smart2Pure system (Schwerte, Germany). Polypropylene (PP) membranes were provided by 3M Corporation (Maplewood, MN) and had a thickness of 135 μm, a pore size of 0.45 μm and a porosity of 0.76.

2.2. Preparation of ionic liquids

Imidazolium based ionic liquids were prepared from an equimolar

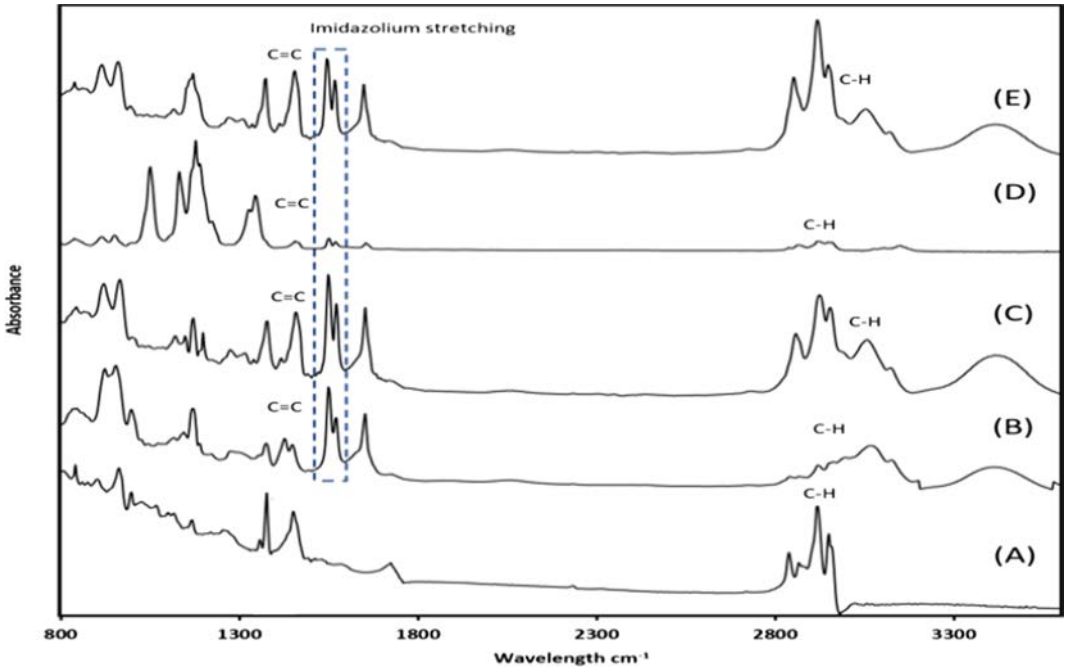

Fig. 3. FTIR spectra for: (A) base polyrpopylene membrane and membrane pores filled with: (B) $[C_3vim^+][Br^-]$; (C) $[C_6vim^+][Br^-]$; (D) $[C_6vim^+][NTf_2^-]$; (E) $[C_8vim^+][Br^-]$.

mixture of vinyl imidazole and one of the following alkyl halides (allyl bromide, bromohexane and bromooctane). The resulting mixture was heated to 60 °C and stirred at 150 rpm for 3 h. The mixture phase separated during reaction forming an ionic liquid phase consisting of 1-allyl-3-vinylimidazolium bromide ($[C_3vim^+][Br^-]$), 1-hexyl-3-vinylimidazolium bromide ($[C_6vim^+][Br^-]$) or 1-octyl-3-vinylimidazolium bromide ($[C_8vim^+][Br^-]$) and a phase containing the residual reactants [34]. To remove residual reactants and impurities, the mixture was rinsed three times with an equal volume of ethyl acetate. After each rinse, the mixture was shaken, and the residual precursors were removed after phase separation. After rinsing, the ionic liquid was placed in a vacuum oven set to ~40 °C for at least 5 h to remove any remaining impurities.

To obtain a more hydrophobic ionic liquid (1-hexyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide), an ion exchange procedure was carried out using 1-hexyl-3-vinylimidazolium bromide and lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) as described earlier [35]. Prior to anion exchange, separate aqueous solutions of 1-hexyl-3-vinylimidazolium bromide and $LiNTf_2$ were prepared using equimolar amounts (100 mM) of each reactant. To initiate the ion exchange, the $LiNTf_2$ solution was added dropwise to the aqueous solution of 1-hexyl-3-vinylimidazolium bromide. After stirring and phase separation, a hydrophobic ionic-liquid phase (clear) and an aqueous phase were obtained, and the latter was removed. The remaining ionic liquid $[C_6vim^+][NTf_2^-]$ was rinsed with deionized (DI) water multiple times. To ensure that no water remained, the ionic liquid was placed in a vacuum oven at temperature of 40 °C for about 3 h.

2.3. Preparation of SILMs

The pores of PP microfiltration membranes were filled with one of the ionic liquids as described earlier [35]. A PP membrane was added to a 5-mL Amicon® ultrafiltration cell EMD Millipore (Bedford, MA, USA) along with 3 mL of each ionic liquid. Pressurized nitrogen (1.0–1.4 bar) was used to push the ionic liquid through the membrane. The process was stopped after 2 mL of ionic liquid were collected as permeate. This process was repeated three times to ensure all the membrane pores were filled with the ionic liquid. The membranes were removed from the cell and their surfaces were wiped to remove as much excess ionic liquid as possible. Thus, we assume there is minimal excess ionic liquid on the membrane surface. This method was shown in earlier studies to minimize excess ionic liquid on the membrane surface [35].

2.4. Membrane characterization

Fourier Transform Infrared (FTIR) spectroscopic analysis of the surface of the PP membranes was conducted to verify incorporation the ionic liquid in the membrane pores. An IRAffinity-1 and a ZnSe crystal (Shimadzu) were used for these measurements. Prior to analysis, the surface of the membrane was wiped to remove residual ionic liquid. For each measurement, 300 scans were done in the range of 600 cm^{-1} to 4000 cm^{-1} at a resolution of 8 cm^{-1}.

2.5. Membrane stability

For SILMs containing $[C_3vim^+][Br^-]$, $[C_6vim^+][Br^-]$ and $[C_8vim^+][Br^-]$, the stability in hexane, tetradecane and water was determined. 50 mL of each of these liquids was added to a container and the initial conductivity was recorded using a Cond 3310 Conductivity Meter, Cole-Parmer (Vernon Hills, IL). Next, the SILM was added and the liquid gently shaken. The conductivity was measured over a 165hour period. For the more hydrophobic ionic liquid, $[C_6vim^+][NTf_2^-]$, the stability in water was determined using the same method.

2.6. Membrane performance

Table 1 summarizes the experiments that were conducted. Fig. 1 gives the structure of the various solutes investigated. In the case of the three aromatic compounds, different feed concentrations were used. The experiments were run for 2 h. As can be seen the degree of conjugation of these three solutes is very different. For the two stereoisomers of stilbene, the concentration of both stereoisomers was the same and the experiments were run for 2.6 h. Finally, the concentration of the two nucleobases in the feed was the same. This experiment was run for 48 h. Data points are reported based on the average of triplicate measurements. All readings were within 10% of the mean value.

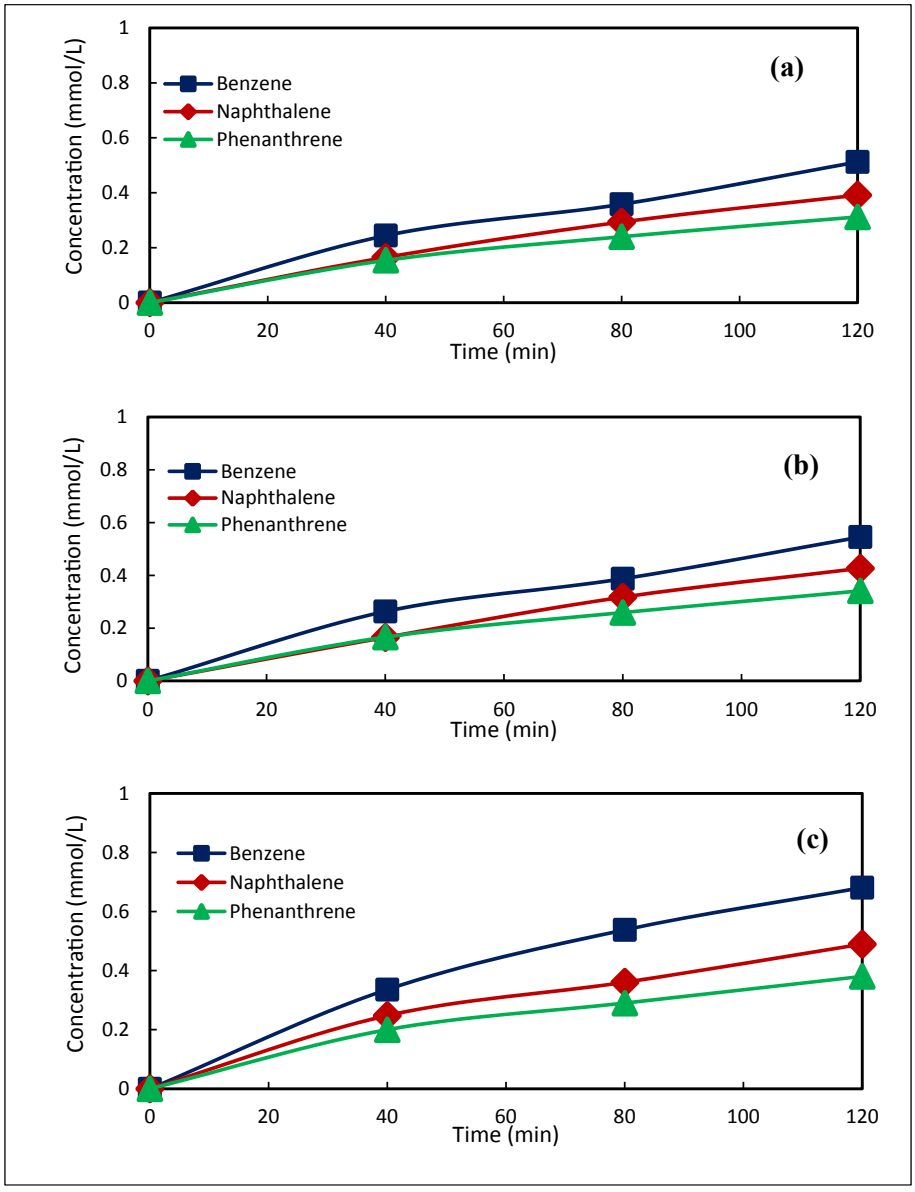

Fig. 4. Variation of benzene, naphthalene and phenanthrene concentration in the receiving solution as a function of time for membrane pores containing (a) $[C_3vim^+][Br^-]$, (b) $[C_6vim^+][Br^-]$ and (c) $[C_8vim^+][Br^-]$.

Diffusion experiments were conducted in a glass diffusion cell consisting of two separable cylindrical compartments with a volume of 30 mL each (Fig. 2). The SILM was placed between the two compartments and O-rings were inserted on both sides of the SILM. The two compartments were put together using threaded connector. The active area of the membrane was 1.27 cm^2. Due to the low solubility of aliphatic compounds in the ionic liquid [25], tetradecane and hexane were used as the feed and receiving solvents. The solution in both compartments was stirred at 500 rpm. All experiments were conducted at room temperatures. The variation of solute concentration in the receiving cell (strip solution) was determined by collecting 100 μL samples at various times for analysis.

A mass balance over the receiving reservoir for the solute species is given by

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

where A is the membrane surface area, k the solute mass transfer coefficient, V the volume of the receiving solution, t the time, C_f the feed concentration and C the receiving solution solute concentration. The feed concentration is given by $C_0 - C$ where C_0 is the initial feed concentration. Eq. (1) may be integrated to give

$$Ln\left[\frac{C_0}{C_0 - 2C}\right] = \frac{2Akt}{V} \quad (2)$$

The overall mass transfer coefficient is given by

$$\frac{1}{K} = \frac{1}{k_F} + \frac{1}{k_M} + \frac{1}{k_s} \quad (3)$$

where $1/k_F$, $1/k_M$, $1/k_S$ are the individual mass transfer coefficients for solute transfer through the feed side concentration boundary layer, through the membrane pores and through the receiving (strip) side concentration boundary layer. For stirred cell diffusion experiments the membrane phase mass transfer coefficient dominates [2]. The membrane mass transfer coefficient is given by

$$k_{M=\frac{\varepsilon D_M H}{\delta\tau}} \quad (4)$$

where ε, δ and τ are the void fraction, thickness and tortuosity of the membrane and H is partition coefficient that relates the concentration

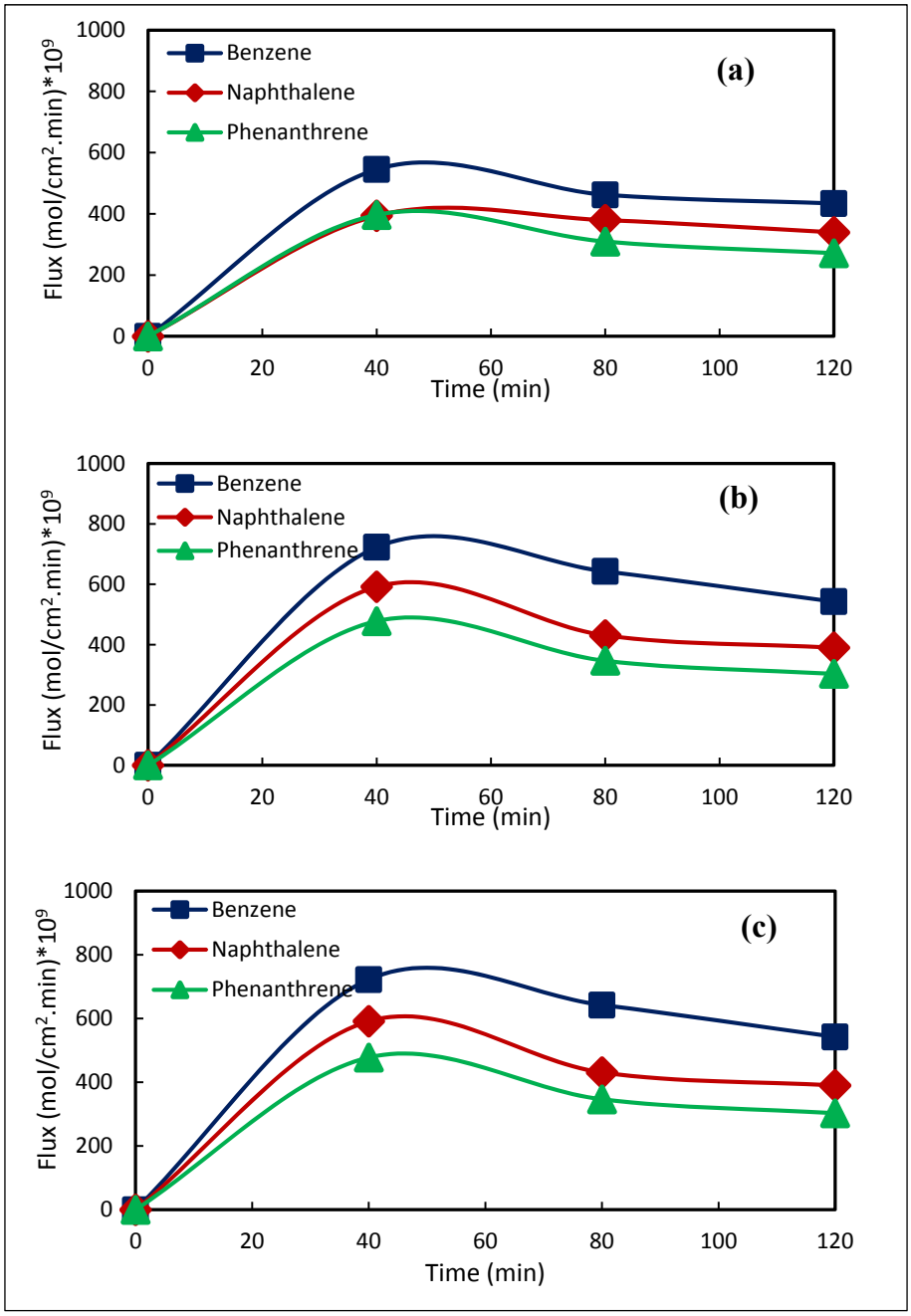

Fig. 5. Variation of benzene, naphthalene and phenanthrene flux with time for membrane pores containing (a) $[C_3vim^+][Br^-]$, (b) $[C_6vim^+][Br^-]$ and (c) $[C_8vim^+][Br^-]$.

between phases.

The separation factor is also calculated to express the relative separation under the specified conditions, which is defined as follows.

$$\mathscr{B} = \frac{\left(\frac{\text{mole fraction of the more permeable inpermeate}}{\text{mole fraction of the less permeable in permeate}}\right)}{\left(\frac{\text{mole fraction of the more permeable in feed}}{\text{mole fraction of the less permeable in feed}}\right)} \quad (5)$$

2.7. Solute detection

High Performance Liquid Chromatography (HPLC) equipped with Luna C_{18} column (5 µm, size 250 * 4.6 mm, from Phoenix, USA) was used to detect all the solutes. A water/acetonitrile mixture was used as the mobile phase at a flow rate of 0.5 mL min^{-1}. This mixture was pumped through the column at a linear gradient started as 0% acetonitrile in water to 100% acetonitrile in water during a 40 min period. The column temperature was kept at 29 °C. The injection sample volume was 20 µL. A diode array detector was used to detect the selected compounds. UV scan was conducted for each compound and the maximum wavelength identified. Distinctive retention times for each compound were obtained. The results are summarized in Table 2.

3. Result and discussion

3.1. Membrane characterization

The presence of ionic liquid within the membrane pores was verified by FTIR spectroscopic analysis as shown in Fig. 3. Spectra of the synthesized ionic liquids are given in the supplementary data. The

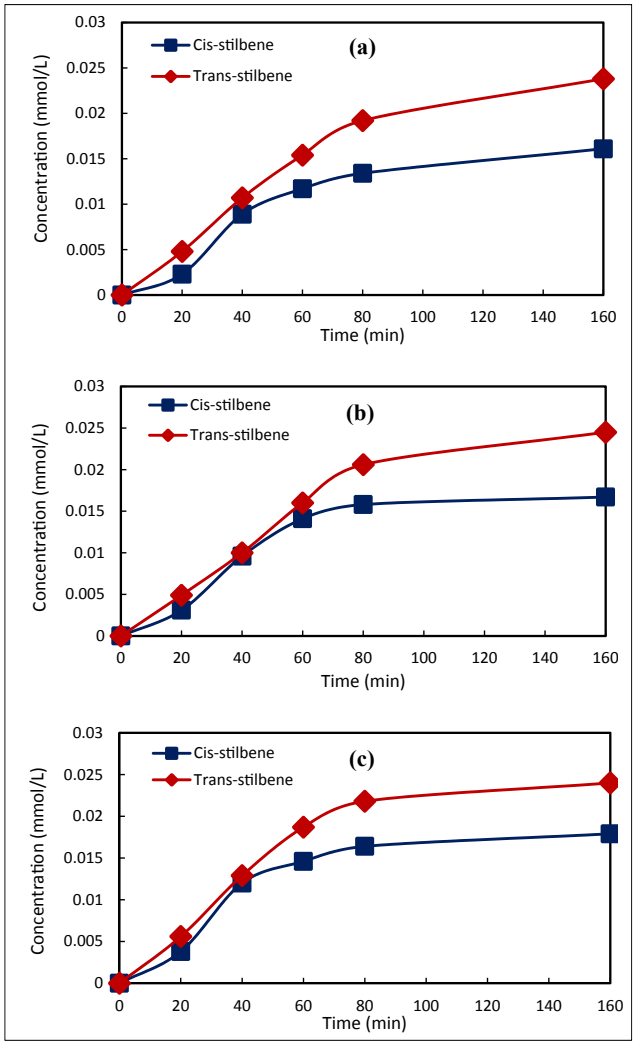

Fig. 6. Variation of *cis*-stilbene and *trans*-stilbene concentration in the receiving solution as a function of time for membrane pores containing (a) [C_3vim^+][Br^-], (b) [C_6vim^+][Br^-] and (c) [C_8vim^+][Br^-].

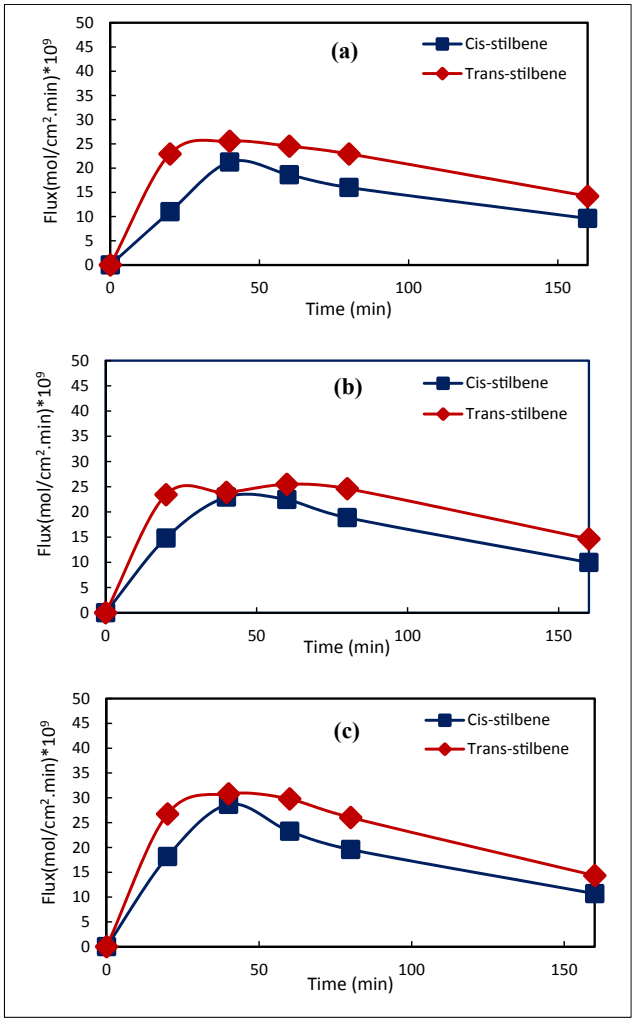

Fig. 7. Variation of *cis*-stilbene and *trans*-stilbene flux with time for membrane pores containing (a) [C_3vim^+][Br^-], (b) [C_6vim^+][Br^-] and (c) [C_8vim^+][Br^-].

spectrum for the base PP membrane showed peaks corresponding to C-H bond stretching. For membranes with ionic liquid filled prores, extra peaks were observed in the range of 1500 cm^{-1} to 1700 cm^{-1}, which were attributed to the stretching frequency of imidazolium ring [36].

3.2. SILM performance

Fig. 4(a), (b) and (c) give the change in concentration in the receiving solution as a function of time for benzene, naphthalene and phenanthrene for membranes filled with [C_3vim^+][Br^-], [C_6vim^+][Br^-] and [C_8vim^+][Br^-] respectively. Since Table 1 indicates that the initial feed concentrations increase in order phenanthrene, naphthalene and benzene, it is not surprising that the increase in concentration in the receiving solution follows the same order. The concentration increases approximately linearly with time.

Fig. 5(a), (b) and (c) give the benzene, naphthalene and phenanthrene flux defined as the moles of solute in the receiving solution divided by the membrane area and time for membrane pores filled with [C_3vim^+][Br^-], [C_6vim^+][Br^-] and [C_8vim^+][Br^-] respectively. As can be seen, there is an initial rapid increase in flux followed by a slow decrease. The slow decrease in flux occurs as the driving force for diffusion decreases with increasing solute concentration in the receiving solution and decreasing concentration in the feed solution.

Results for the stereoisomers of stilbene are given in Figs. 6 and 7.

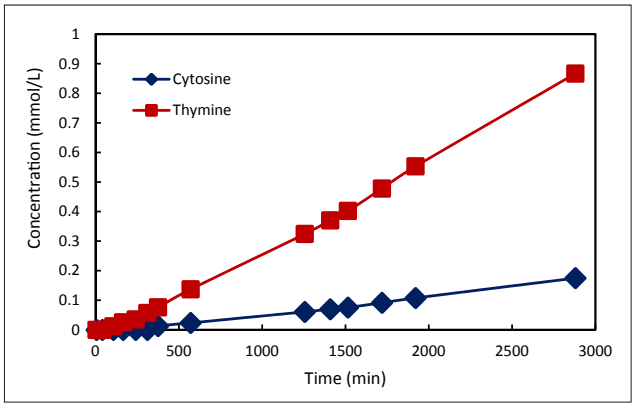

Fig. 8. Variation of cytosine and thymine concentration in the receiving solution as a function of time for membrane pores containing [C_6vim^+][NTf_2^-].

Fig. 6(a), (b) and (c) give the change in concentration in the receiving solution as a function of time for the two stereoisomers of stilbene for membranes pores filled with [C_3vim^+][Br^-], [C_6vim^+][Br^-] and [C_8vim^+][Br^-] respectively. Fig. 7(a), (b) and (c) give the corresponding flux values. The results are analogous to Figs. 4 and 5. The concentration of both isomers increases with time. Again, the slow

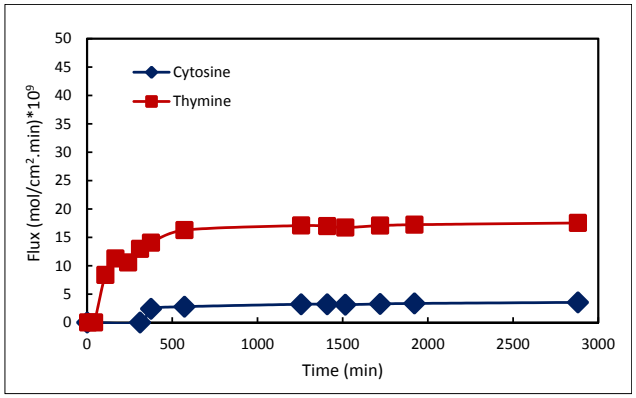

Fig. 9. Variation of cytosine and thymine flux with time for membrane pores containing $[C_6vim^+][NTf_2^-]$.

Table 3
Calculated mass transfer coefficients.

Solute	SILM	Mass transfer coefficient, K × 10^9 m s^{-1}
Benzene	$[C_3vim^+][Br^-]$	2.78
Naphthalene	$[C_3vim^+][Br^-]$	2.78
Phenanthrene	$[C_3vim^+][Br^-]$	3.06
Benzene	$[C_6vim^+][Br^-]$	3.06
Naphthalene	$[C_6vim^+][Br^-]$	3.33
Phenanthrene	$[C_6vim^+][Br^-]$	3.33
Benzene	$[C_8vim^+][Br^-]$	3.89
Naphthalene	$[C_8vim^+][Br^-]$	3.61
Phenanthrene	$[C_8vim^+][Br^-]$	3.89
Cis-stilbene	$[C_3vim^+][Br^-]$	1.67
Trans-stilbene	$[C_3vim^+][Br^-]$	2.50
Cis-stilbene	$[C_6vim^+][Br^-]$	1.94
Trans-stilbene	$[C_6vim^+][Br^-]$	2.50
Cis-stilbene	$[C_8vim^+][Br^-]$	2.22
Trans-stilbene	$[C_8vim^+][Br^-]$	2.78
Thymine	$[C_6vim^+][NTf_2^-]$	18.89
Cytosine	$[C_6vim^+][NTf_2^-]$	3.33

Table 4
The separation factor ($\mathscr{B}$) using different SILMs.

Parameter	SILM	$\mathscr{B}$
Thymine to Cytosine	$[C_6vim^+][NTf_2^-]$	5.12
Trans stilbene to Cis stilbene	$[C_3vim^+][Br^-]$	1.49
Trans stilbene to *Cis* stilbene	$[C_6vim^+][Br^-]$	1.47
Trans stilbene to *Cis* stilbene	$[C_8vim^+][Br^-]$	1.34
Phenanthrene to Benzene	$[C_3vim^+][Br^-]$	1.07
Phenanthrene to Benzene	$[C_6vim^+][Br^-]$	1.10
Phenanthrene to Benzene	$[C_8vim^+][Br^-]$	0.98
Naphthalene to Benzene	$[C_3vim^+][Br^-]$	0.96
Naphthalene to Benzene	$[C_6vim^+][Br^-]$	0.99
Naphthalene to Benzene	$[C_8vim^+][Br^-]$	0.91

decrease in flux after about 60 min is due to the decrease in driving forces for diffusion with increasing solute concentration in the receiving solution and decreasing concentration in the feed solution. Though the initial feed concentration of the two stereoisomers is the same, Fig. 6 indicates that for all three SILMs, the transport of *trans*-stilbene is faster than *cis*-stilbene.

Finally, Figs. 8 and 9 give analogous results for the two nucleobases. The rate of solute transfer as well as the initial solute concertation is lower. Consequently, no decrease in flux is observed at longer run times. Though the initial nucleobase concentration in the feed is the same, the rate of transport of thymine is much faster than cytosine.

The results in Figs. 4–7 indicate that as the length of the carbon chain present on the imidazolium ring increases, the rate of transport of all solutes increases. The rate of diffusion through the liquid membrane will depend on the viscosity and density of the ionic liquid as well as interactions between the solute and the ionic liquid. Recent studies indicate that the groups on the imidazolium ring can alter viscosity in unpredictable ways [37]. In the case of increasing hydrocarbon chain length, it is likely the viscosity increases while the density decreases [38].

The anion of the ionic liquid is generally weakly coordinating in nature. Therefore, it will have a much weaker interaction with the ionic liquid cation or the solutes of interest. However, the anion can be used to tune the properties of the ionic liquid such as solubility and viscosity as we have done in this work. It is the interplay between these effects that results in the observed rate of mass transport. This observation highlights the tremendous potential for tailoring the properties of the liquid membrane phase.

Using Eq. (2), mass transfer coefficients were calculated and are given in Table 3. For stilbene and the nucleobases, the feed and receiving solutions consisted of the same liquid phase. However, for benzene, naphthalene and phenanthrene, the feed liquid was tetradecane while the receiving solute was hexane. Though very similar, the solubility of the three solutes will be slightly different in the two different liquid phases. We have ignored these effects (assumed the partition coefficient is 1) in determining the overall mass transfer coefficient.

The mass transfer coefficient for benzene, naphthalene and phenanthrene are the same for a given ionic liquid though they increase slightly for all solutes with increasing length of the carbon chain attached to the imidazolium ring. In the case of the two stilbene stereoisomers, the mass transfer coefficient for *trans*-stilbene is always larger than for *cis*-stilbene. Finally, the mass transfer coefficient is larger for thymine compared to cytosine.

The separation factor were calculated using equation (4)(5). It can be seen that the separation factors of phenanthrene to benzene and naphthalene to benzene using different SILMs are almost the same. However, the concentration of these solutes in the feed is very different. The separation factor for *trans*-stilbene to *cis*-stilbene for the same feed concentration of the two solutes indicates preferential transport of trans stilbene. A large separation factor is obtained in the case of thymine to cytosine (see Table 4).

The results indicate that the degree of conjugation and hence electron cloud density by itself does not imply faster transport. Though the degree of conjugation increases in order benzene, naphthalene, phenanthrene, the molecule weight of these compounds also increases as follows benzene, 78.11 g mol^{-1}; naphthalene, 128.17 g $mol^{-1;}$ phenanthrene 178.23 g mol^{-1}. Thus, the mass transfer coefficient for all three compounds, which in the stirred diffusion cell used here is dominated by diffusion through the SILM, is the same.

The situation is different for the two stereoisomers of stilbene which have the same molecular weight. The presence of two phenyl rings on the same side of carbon double bond in the *cis*- isomer (see Fig. 1) may lead to deviations from planarity between the two groups and result in deterioration in aromatic stacking with the cation present on the ionic liquid [39–41]. As a result, the effects of extended conjugation of the π electron cloud is reduced. On the other hand, the *trans*- isomer does not have such stereo-chemical constraints and does not lose the effects of extended conjugation. This leads to preferential transport of *trans*-stilbene.

Thymine and cytosine have similar molecular weights; 126.11 and 111.1 g mol^{-1} respectively. However, thymine is preferentially transported through the SILM; its mass transfer coefficient is more than 5 times as large as that for cytosine and $\mathscr{B}$ for this separation is 5.12. It is known that imidazole groups play an important role in nature [42]. They can form hydrogen bonds with both thymine and cytosine. It is likely that differences in the hydrogen bonding interactions between the cation in the ionic liquid and thymine, which contains two nitrogen and two oxygen atoms, compared to cytosine, which contains three nitrogen and one oxygen atoms, resulted in the enhanced transport of

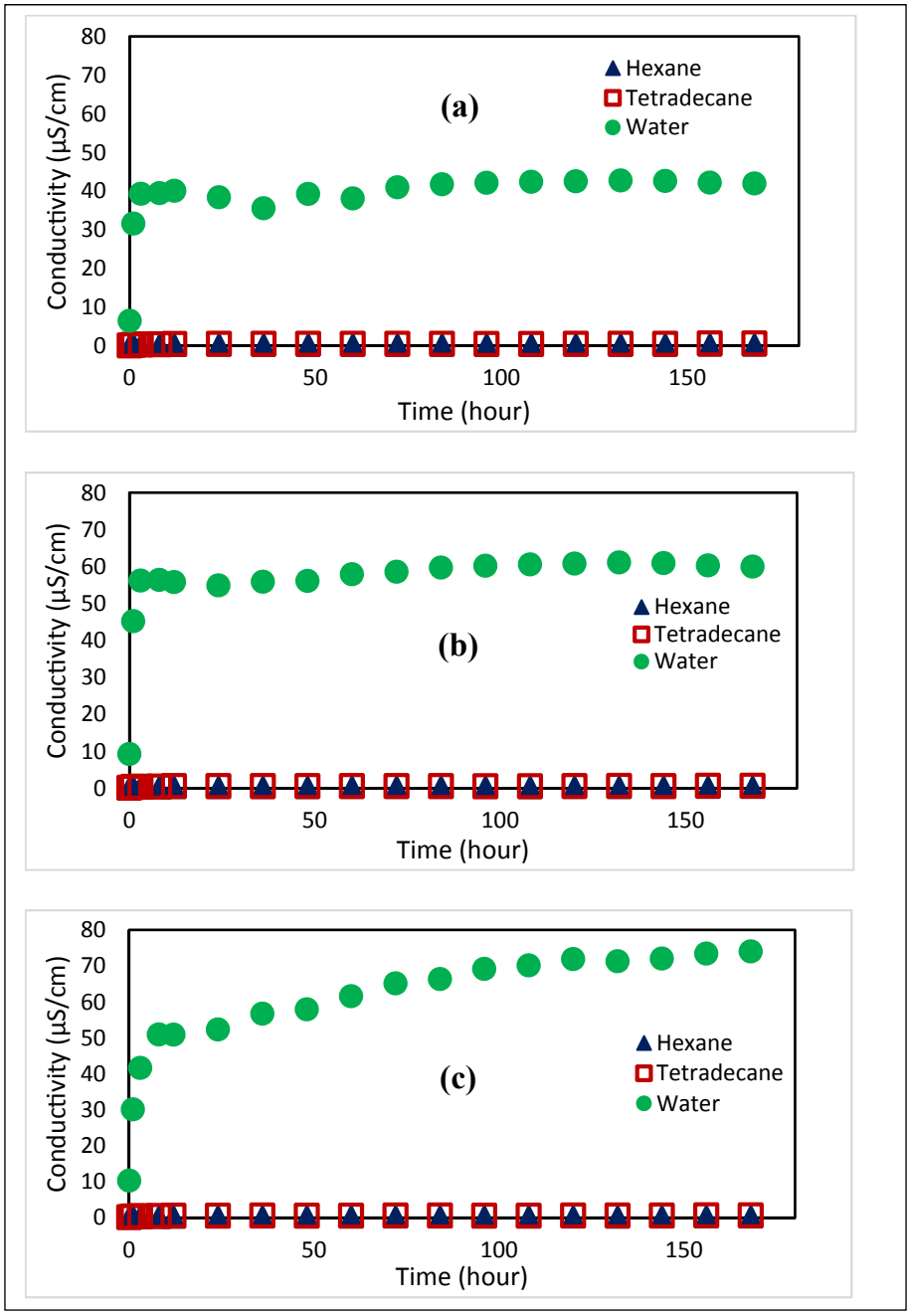

Fig. 10. Variation of conductivity with time for hexane, tetradecane and water containing membranes with pores filled with (a) $[C_3vim^+][Br^-]$, (b) $[C_6vim^+][Br^-]$ and (c) $[C_8vim^+][Br^-]$.

thymine.

The results indicate that cation-π interactions may be used to enhance the selectivity of the SILM for given solute. However, simply increasing the degree of conjugation of the solute species does not imply enhanced rates of transport through the SILM; factors such as molecular weight can also play a role in this regard. In the case of fractionation of stereoisomers, our results suggest that an SILM could be used to enhance the concentration of one of the of isomers. Our results for the two nucleobases indicate that exploiting multimodal interactions (hydrogen bonding, cation - π interactions etc.) could result in very high selectivities for a given solute. A molecular-level simulation study could identify the importance of these different interactions. A major advantage of SILMs over conventional supported liquid membranes is the ability to tune the properties of the cation and anion of the ionic liquid membrane.

The stability of the SLIMs, like all supported liquid membranes, is a major concern. The stability of an SILM containing water soluble ionic liquids $[C_3vim^+][Br^-]$, $[C_6vim^+][Br^-]$ and $[C_8vim^+][Br^-]$ was determined by incubating them in hexane, tetradecane and water for up to 165 h and measuring the conductivity of the solution. Fig. 10 gives the results for (a) $[C_3vim^+][Br^-]$, (b) $[C_6vim^+][Br^-]$ and (c) $[C_8vim^+][Br^-]$. As can be seen over 165 h, the conductivity of tetradecane and hexane did not increase due to loss of the liquid membrane phase. However, as expected, the conductivity of the water continually increased for the SILMs containing water soluble ionic liquids. Thus, the SILMs containing the water-soluble ionic liquids were stable in the organic solutions tested here.

As discussed by Koók et al, for aqueous phase application, hydrophobic ionic liquids are relatively stable [43]. Further, by increasing the length of the alkyl side chain attached to the imidazolium cation, the

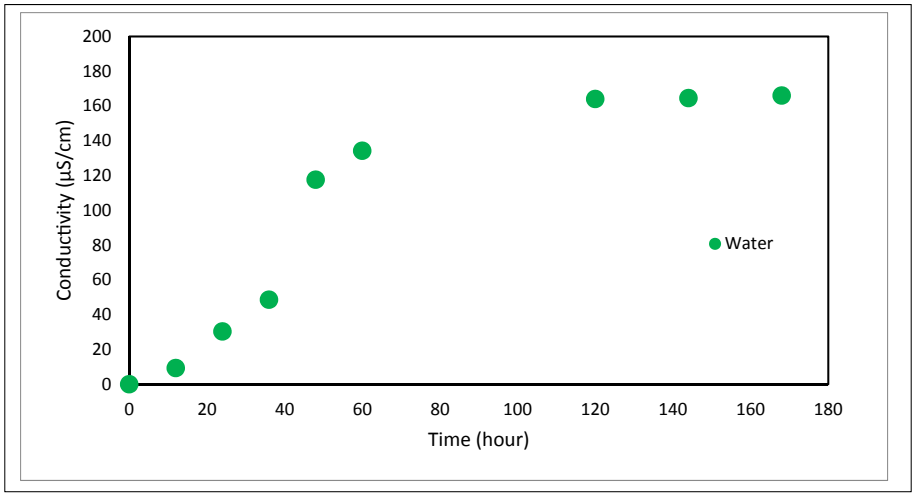

Fig. 11. Variation of conductivity with time for water containing a membrane with pores filled with $[C_6vim^+][NTf_2^-]$.

hydrophobicity is increased and hence aqueous miscibility decreases. The nature of anion also plays vital role in the stability of the SILM [44]. Similarly, the reverse is true for present case, where an organic solvent is used. Previous studies indicate minimal loss of the ionic liquid from the pores under mild stirring conditions. However, some loss is observed due to excess ionic liquid on the membrane surface [45,46]. Our results are in keeping with these observations.

The stability of water insoluble $[C_6vim^+][NTf_2^-]$ was determined in water. The result is shown in Fig. 11. As can be seen this SILM is less stable as over a 165-hour period the conductivity of the water gradually increased. However, our mass transfer results (see Figs. 8 and 9) indicate that over 48 h, loss of the ionic liquid did not lead to failure of the SILM.

Taken together these results indicate that the ability to tune the properties of ionic liquids make them very attractive for highly specific separations. Development of an SILM is attractive as it minimizes the volume of expensive ionic liquid that is required. By combining extraction and back extraction, significant process intensification is possible. Nevertheless, significant engineering challenges remain regarding module design and the stability of the SILM. For practical processes, highly stable SILMs will be required.

If traces of ionic liquid are lostduring the separation it will contaminate the component(s) to be purified and hence removal of the trace amounts of ionic liquid may be necessary. Though not part of the current investigation, an additional unit operation may be required. For example, as ionic liquids are known for their very low vapour pressure, while most of the organic compounds are highly volatile distillation could be feasible. Importantly, inclusion of an SILM based separation in a manufacturing process will depend on the cost of any additional purification steps that may be required.

4. Conclusion

The results of the investigation conducted here indicate that SILMs may be developed for very specific separations. Here we have focused on interaction between π electrons in the solute and the ions present in the ionic liquid that form the liquid membrane phase. Given the ability to tailor the properties of the ionic liquid through choice of the cation and anion as well as groups attached to these ions, tremendous potential exists to develop SILMs for highly specific separations. Our results indicate however that the rate of mass transfer will depend on the interplay of a number of factors. Simply increasing the degree of conjugation of the solute species does not guarantee faster rates of mass transfer.

Though supported liquid membranes are attractive for energy efficient separations that can lead to significant process intensification, stability of the liquid membrane remains a major challenge. Ionic liquids are attractive as their properties can be tailored to minimize loss of the liquid membrane. Our results indicate that it will be essential to optimize the properties of the ionic liquid in order to maximize the stability in practical applications of SILMs for liquid phase separations.

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.

Acknowledgements

Funding for this work was provided by the National Science Foundation USA (1659653), the Arkansas Research Alliance USA and the University of Arkansas USA through the Ross E Martin Chair in Emerging Technologies.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2019.116237.

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