Influence of Physicochemical Properties on Gas Transport Properties of Silver-Containing Ionic Liquid Mixtures for Olefin/Paraffin Membrane Separation

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Influence of Physicochemical Properties on Gas Transport Properties of Silver-containing Ionic Liquid Mixtures for Olefin/Paraffin Membrane Separation

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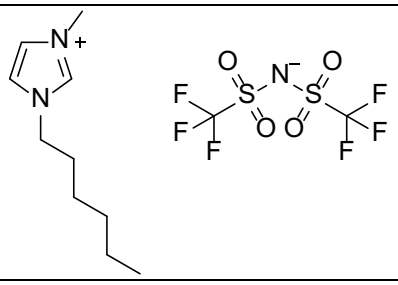
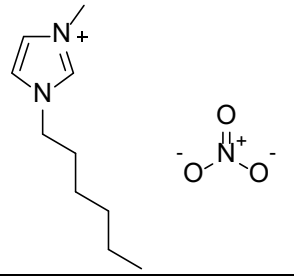
Physicochemical properties, including viscosity and density, of silver salt-containing ionic liquids were measured and used to rationalize the permeability of ethane, ethylene, and helium through supported ionic liquid membranes (SILMs). Mixtures investigated included 1-hexyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([hmim][Tf_2N]) and 1-hexyl-3-methylimidazolium nitrate ([hmim][NO_3]) and their corresponding silver salts. The gas transport properties were very different for the two different ionic liquid/silver salt mixtures, consistent with very different behavior of viscosity and density upon silver salt dissolution. The distinctive dependence of both viscosity and density on temperature and silver salt concentration suggests different inter-ion interactions and molecular arrangements in the two ionic liquids. Free volume and physical/chemical interactions between the anion and the gas solutes are critical in determining gas permeabilities.

Introduction

Olefin/paraffin separation by cryogenic distillation is one of the most energy-intensive processes, not only within the chemical industry, but also among all human activities. Specifically, the purification of propylene and ethylene accounts for 0.3% of global energy use (1). Membrane separation is an attractive alternative, owing to its high energy-efficiency compared to conventional distillation processes. Many kinds of membrane materials, such as carbon (2-6), polymer composites (7, 8), and metal-organic frameworks (MOFs), have been utilized for olefin/paraffin membrane separation (9-11). Among them, liquid membranes that utilize gas transport through the liquid phase confined in the pore structures have shown promising performance due to faster transport than that of solid membrane materials (12-14). In liquid membranes, the liquid phase is physically held in membrane pores by capillary forces. In addition to physical stability, chemical and thermal stabilities of the liquid phase material are needed for stable long-term separation performance. In that sense, ionic liquids (ILs) are a suitable material because they have the potential to provide stable separation performance, owing to their extremely low vapor pressure, and good thermal/chemical stability. Moreover, the limitless tunability of ionic liquids can be manipulated to enhance molecular interaction with target gas molecules and thus yield better gas solubility. For olefin/paraffin separation, silver ions can be added to further improve olefin solubility (15-18). The silver ions can form complexes with olefin molecules via interaction between the double bonds of olefins and the orbitals of silver ions (19). Thus, understanding the interactions between ionic liquids and silver salts is essential for designing liquid membrane systems with improved separation performance.

Here, we report the physiochemical properties of silver ion-containing ionic liquid mixtures with two different anions and their gas transport properties when used in supported ionic liquid membranes (SILMs). Two ionic liquids, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]) and 1-hexyl-3-methylimidazolium nitrate ([hmim][NO_3]), were studied, and their chemical structures are shown in Table 1. Silver bis(trifluoromethylsulfonyl)imide ($AgTf_2N$) and silver nitrate ($AgNO_3$), silver salts with the same anion as each ionic liquid, were added to the ILs to study the effect of the silver ion addition on IL mixtures. We measured densities and viscosities of silver-containing IL mixtures at five different silver ion concentrations for each IL. In addition, we determined pure gas permeabilities of ethane, ethylene, and helium in SILMs, using an Anopore disc as support, with pure ILs and 1M Ag^+ IL mixtures.

TABLE I. Chemical structures of ionic liquids in this study.

Abbreviation	Chemical Structure	Molecular Weight (g/mol)
[hmim][Tf_2N]		447.4
[hmim][NO_3]		229.3

Experimental

Ionic Liquid Synthesis

Both ILs used in this work were synthesized in our laboratory. The synthesis method has been reported in previous work (23). Silver nitrate was purchased from Alfa Aesar. Silver bis(trifluoromethylsulfonyl)imide was synthesized in our laboratory.

Mixture Preparation

Five IL mixtures at five different Ag^+ concentrations were prepared for each anion by combining the salt and IL at a certain weight ratio. The weight ratios corresponding to the five molar concentrations considered were determined by dissolving 0.25 mmol, 0.5 mmol, 0.75 mmol and 1 mmol of silver salt with IL in separate 1-ml amber volumetric flasks. The determined weight ratios of silver salt to ionic liquid were used to prepare the mixtures on a larger scale to meet the volume required for the measurements. All mixtures were

prepared in amber vials to mitigate reduction of silver ions from Ag^+ to Ag^0 by ambient light. The vials were additionally wrapped with aluminum foil and stored in the desiccator.

Viscosity/Density Measurement

The density and the viscosity measurements were conducted using a DMA 4500 Anton Paar oscillating U-tube densitometer and a Lovis 2000 M/ME Anton Paar rolling-ball viscometer. The temperature was varied from 20 °C to 50 °C with an interval of 5 °C. The uncertainties in the measurements are estimated as ±0.0001 g/cm^3 for density and ± 0.5% for viscosity.

SILM Preparation and Gas Permeation

Two concentrations (0 M and 1 M Ag^+) for two anion conditions were used to prepare SILMs. Multiple droplets of the prepared mixtures were dropped on both sides of the porous supports (Whatman Anodisc inorganic filter membrane, dia. 13 mm, pore size 0.02 μm, thickness 60 μm). Full wetting was confirmed by checking the consistency of the weight difference before and after wetting. The wetted samples were attached to a brass disc with epoxy. A piece of porous polytetrafluoroethylene filter was placed on the underside of the SILM for mechanical support. The gas permeating area for gas permeation was imaged by a scanner and calculated using image-processing software.

Pure gas permeabilities of the SILMs were measured using a constant-volume, variable pressure gas permeator. Initially, the permeator was evacuated until the vacuum level of both upstream and downstream volumes was below 30 mTorr. After evacuation, a leak test on the downstream volume was performed for 1 hour to take into account the underlying leak rate of the instrument. All measurements were carried out at 35 °C, and the upstream pressure ranged between 10 and 30 psia. The rate of increase of the downstream pressure was measured at a given upstream pressure when steady-state was achieved. The gas permeabilities were calculated as follows (24):

$$P_{app} = \frac{V_d l}{p_1 ART}\left[\left(\frac{dp_2}{dt}\right)_{SS} - \left(\frac{dp_2}{dt}\right)_{leak}\right] \quad [1]$$

where P_{app} is the apparent permeability, V_d is the downstream volume, l is the membrane thickness, A is the gas permeating area, R is the gas constant, T is the temperature, p_1 is the upstream pressure, $(dp_2/dt)_{ss}$ is the steady-state rate of the downstream pressure rise, and $(dp_2/dt)_{leak}$ is the leak rate of the downstream volume. The estimated uncertainty in the permeability measurements is 2~4%.

Results and Discussion

Figure 1 presents the densities of silver-containing mixtures with five different silver ion molar concentrations. For ILs with both anions, addition of silver salt increased mixture density, due primarily to the presence of the heavier silver ions in the silver salts. The densities of both ILs and their mixtures with silver salts decreased linearly with increasing temperature, due to the thermal expansion of the mixtures. The densities of the IL and IL mixtures with Tf_2N^- anions are greater and increase more upon silver salt addition than do

the equivalent IL and IL mixtures with NO_3^- anions, due to the presence of the heavy fluorine atoms. The molar volumes of the mixtures were calculated by converting the density results using the weight ratios of IL and silver salt and the molecular weights. All the IL mixtures with Tf_2N^- anions have larger molar volumes than any of the IL mixtures with NO_3^- anions.

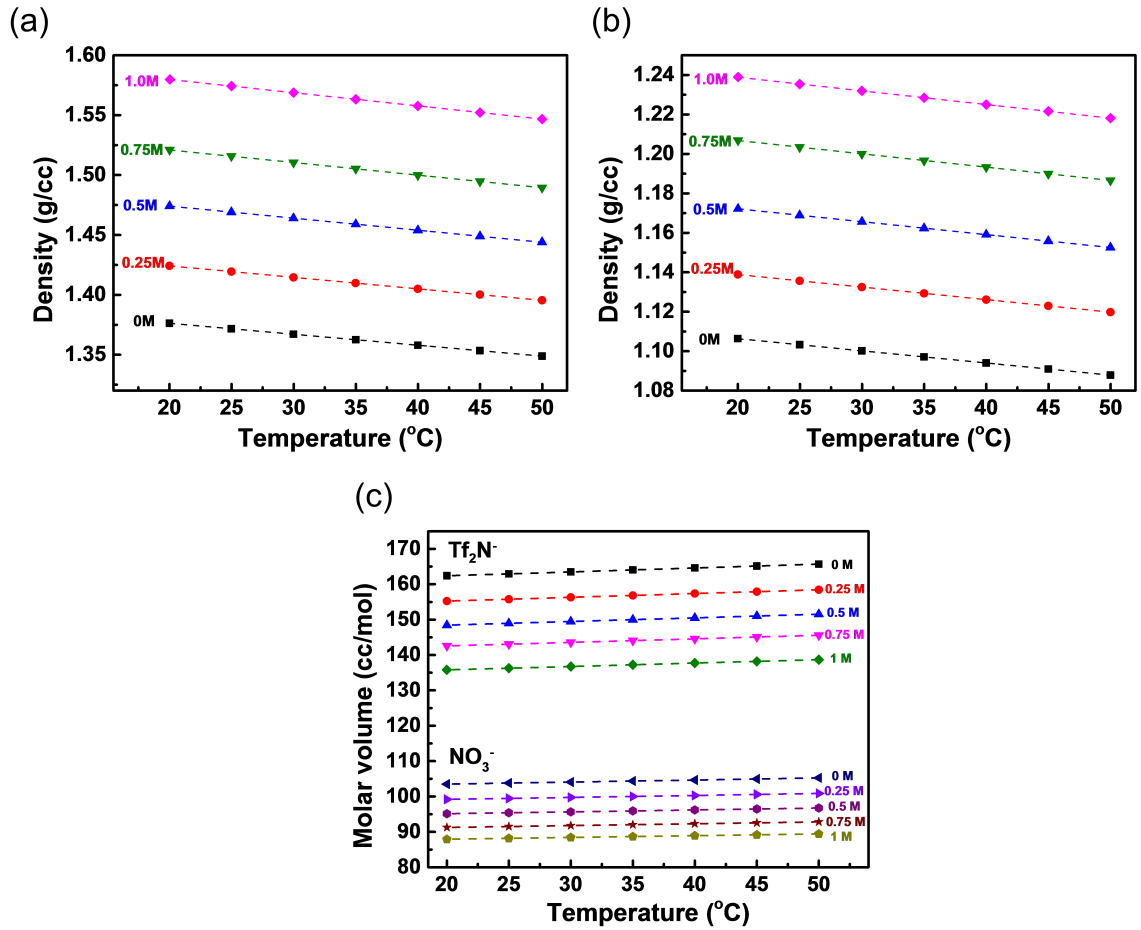


Figure 1. Densities of silver containing ionic liquid mixtures with (a) Tf_2N^- anions and (b) NO_3^- anions, as a function of silver salt concentration and temperature. (c) Calculated molar volumes of the silver-containing ionic liquid mixtures.

As shown in Figure 2, the viscosities of both ILs increased with increasing silver salt concentration. However, silver salt addition resulted in a significant increase in viscosity for the IL mixtures with Tf_2N^- anions, but only a very small increase in viscosity for the IL mixtures with NO_3^- anions. Based on this dramatic difference in viscosity behavior, the inter-ion interactions and molecular structure resulting from silver salt dissolution must be very different for the two ILs. As expected, the viscosities exponentially decrease with increasing temperature for both pure ILs and their mixtures. The temperature dependence of the viscosity becomes much more pronounced at higher silver ion concentration for the IL mixtures with Tf_2N^- anions. A change in the temperature dependence of liquid viscosity indicates a free volume change in the liquid (20). Clearly, the addition of $AgTf_2N$ to [hmim][Tf_2N] results in increased inter-ion interactions and increased ordering in the mixture. This does not occur when $AgNO_3$ is added to [hmim][NO_3]. We interpret this as the formation of molecular structures in the $AgTf_2N$/[hmim][Tf_2N] mixture. It is as if there

are strong interactions (reminiscent of hydrogen bonds), that form, resulting in increasing viscosity.

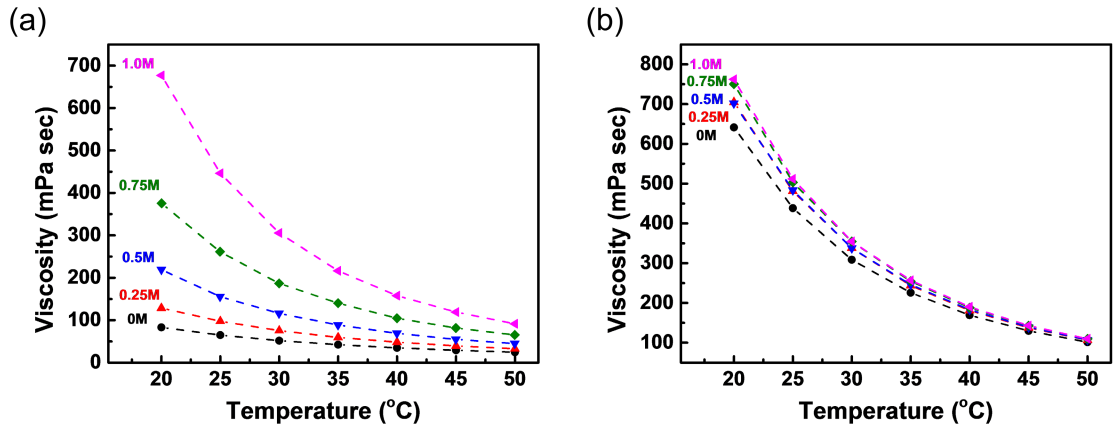


Figure 2. Viscosities of silver-containing IL mixtures with (a) Tf_2N^- anions and (b) NO_3^- anions, as a function of silver salt concentration and temperature.

Transport of gases through the IL and mixtures of IL and silver salts was examined by measuring gas permeation through supported IL membranes, where alumina oxide Anodiscs were used as the support. Two Ag^+ ion concentrations (i.e., 0 and 1 M) were investigated for each IL (cf. Figure 3). Three pure gases (helium, ethylene, and ethane) were permeated through the SILMs. The rate of increase in downstream pressure at steady-state was used to calculate the gas permeabilities.

As shown in Figure 3a and 3c, the permeability of all three gases in the pure ILs is independent of pressure. The permeability of ethylene and ethane is greater than that of helium. The ethylene/ethane selectivity in pure [hmim][Tf_2N] is about 1.5, whereas it is about 2.2 in pure [hmim][NO_3]. The addition of 1 M $AgTf_2N$ to [hmim][Tf_2N] (Figure 3b) substantially increases the ethylene permeability and decreases the ethane permeability, resulting in ethylene/ethane selectivities greater than 5.0. The addition of 1 M $AgNO_3$ to [hmim][NO_3] (cf. Figure 3d) did not increase the ethylene permeability, although it did decrease the ethane solubility, resulting in ethylene/ethane selectivities of about 3.0.

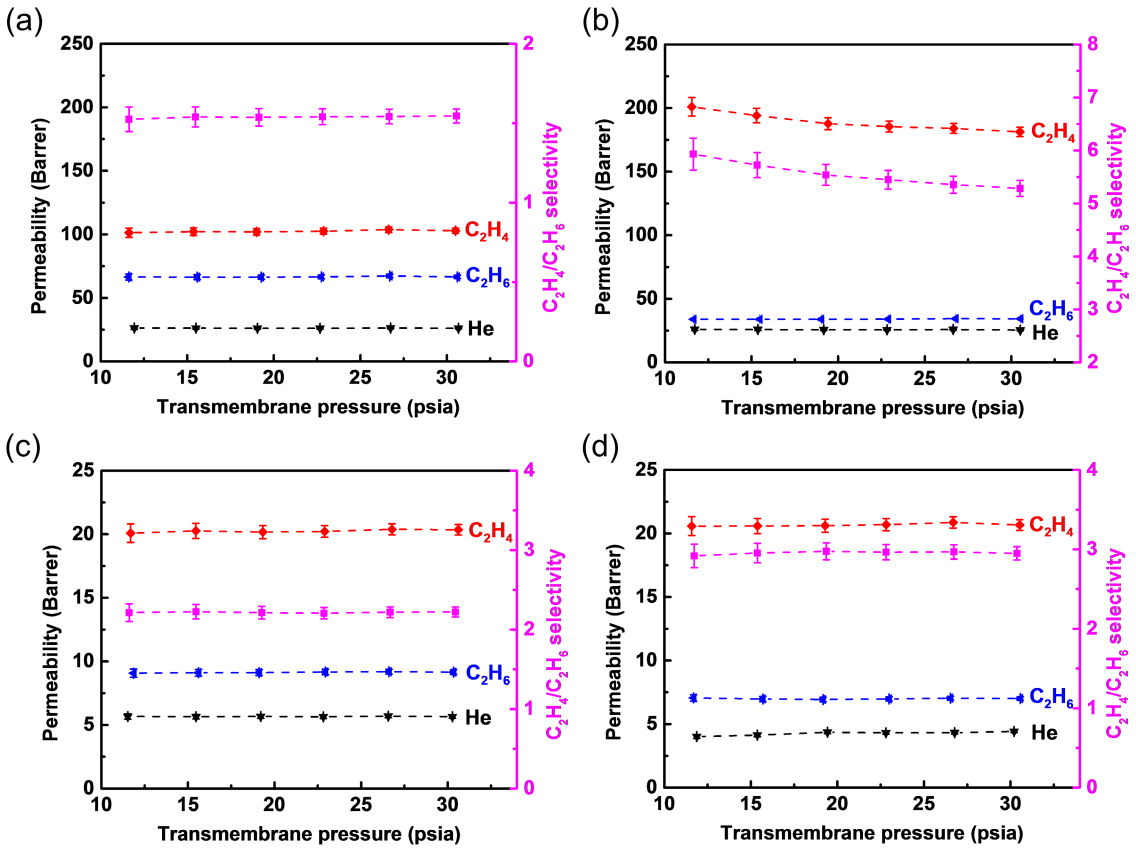


Figure 3. Gas permeabilities of ethane, ethylene, and helium in the SILM containing Tf_2N^- anions at (a) 0 M and (b) 1 M Ag^+ and NO_3^- anions at (c) 0 M and (d) 1 M Ag^+.

In general, one would expect the permeability (P) of a gas through the liquid in a SILM to be the product of solubility (S) and diffusivity (D): P = S x D. The Stokes-Einstein equation predicts that the diffusivity of a solute will be inversely proportional to the viscosity of the liquid. Since the viscosity of pure [hmim][Tf_2N] is significantly less than that of pure [hmim][NO_3] (cf. Figure 2), the diffusivities of gas solutes in [hmim][Tf_2N] should be higher than diffusivities in [hmim][NO_3]. This hypothesis is consistent with the permeabilities of all three gases being significantly higher in pure [hmim][Tf_2N] than in pure [hmim][NO_3], as shown in Figure 3a and 3c.

Using the measured values of the permeabilities and viscosities (to estimate diffusivity), one can compute the change in gas solubility due to addition of 1 M of silver salt to each of the ILs. The Stokes-Einstein equation predicts that diffusivity is inversely proportional to viscosity, but it was developed for large solute molecules diffusing through relatively small solvent molecules (22). A weaker viscosity dependence has been reported in the literature for the diffusivity of small gas molecules through large solvent molecules (21, 22). In this case, the diffusivity depends on the viscosity raised to the power of -0.7, instead of -1. To examine how the solubility changes upon addition of 1 M silver salt to both [hmim][Tf_2N] and [hmim][NO_3], the apparent ratios of the solubilities of ethane, ethylene, and helium in 1 M silver solutions to neat ILs were calculated using the -0.7-power relationship. As shown in Figure 4, the solubility of ethylene in both SILMs increases upon addition of 1 M silver salt, owing to chemisorption of ethylene by the silver ions. The ethylene solubility ratio in [hmim][Tf_2N] increases by a factor of ~6 upon silver salt addition, but it increases only slightly (~1.1) when the silver salt is added to [hmim][NO_3].

The increase in ethylene solubility in the 1 M Ag^+ SILM with Tf_2N^- anions is slightly greater in the low-transmembrane pressure range. We attribute this decrease in the solubility ratio with increasing transmembrane pressure to saturation of the olefin-silver complexation at the higher pressures.

The solubilities of both non-complexing gases (ethane and helium) decrease slightly upon addition of 1 M $AgNO_3$ to the [hmim][NO_3] (Figure 4b). We attribute this to the reduced free volume in the 1 M $AgNO_3$ in [hmim][NO_3] mixture (see Figure 1c). Moreover, the mixture contains a higher concentration of the high charge density NO_3^- anions, which would not interact favorably with non-polar solute molecules.

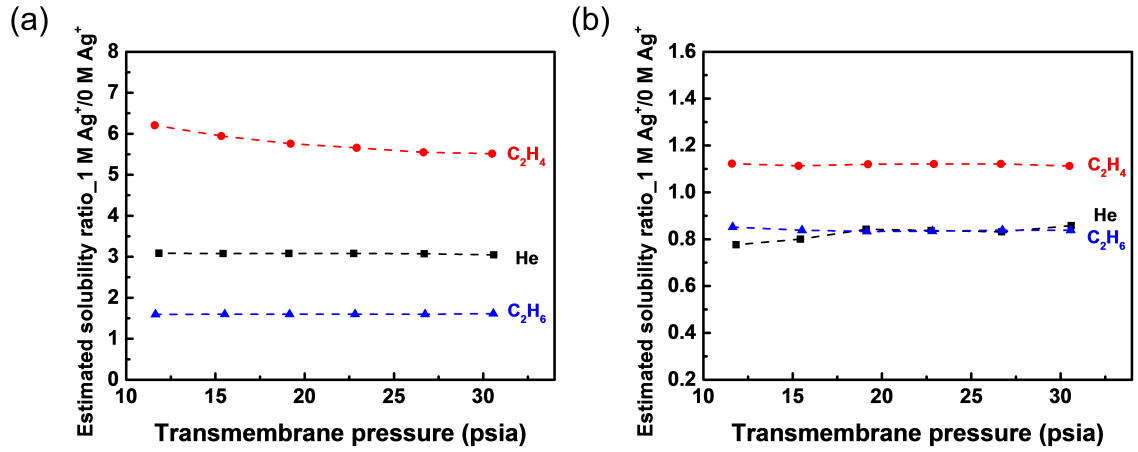


Figure 4. Calculated solubility ratios of SILMs with different anion conditions: (a) Tf_2N^- anion and (b) NO_3^- anion using -0.7 power relationship of diffusivity with viscosity.

By contrast, the solubility of both ethane and helium increase when 1 M $AgTf_2N$ is added to [hmim][Tf_2N]. Like [hmim][NO_3], the molar volume (and, subsequently, free volume) of [hmim][Tf_2N] decreases when $AgTf_2N$ is added. However, the absolute values of the molar volume in [hmim][Tf_2N] mixtures are always greater than those of the [hmim][NO_3] mixtures. In addition, the charge on the Tf_2N^- anion is highly dispersed, providing better opportunities for attractive van der Waals type interactions with nonpolar molecules like ethane and helium.

Conclusions

Neat 1-hexyl-3-methylimidazolium ILs and mixtures containing up to 1 M silver salt were studied using physicochemical property and gas permeation measurements. Upon salt dissolution, the density of both ILs increased significantly. Likewise, the viscosity of the [hmim][Tf_2N] increased dramatically upon silver salt addition, but the viscosity of the [hmim][NO_3] did not. Thus, the two mixtures likely have very different inter-ion interactions and molecular structure. The presence of silver in the [hmim][Tf_2N] significantly increased ethylene permeability through a supported ionic liquid membrane (SILM) using this mixture, greatly enhancing olefin/paraffin selectivity. However, this was not observed for [hmim][NO_3]. The macroscopic properties (viscosity and density) were used to rationalize the gas permeability results in terms of their effect on gas diffusivity and solubility.

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