Viscosity and Self-Diffusivity of Ionic Liquids with Compressed Hydrofluorocarbons: 1-Hexyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)Amide and 1,1,1,2-Tetrafluoroethane.

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Abstract

The viscosity and self-diffusivity of mixtures of the ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf₂N]), and the compressed gas, 1,1,1,2-tetrafluoroethane (R-134a), were measured at three different temperatures (298.15 K, 323.15 K, 343.15 K) and pressures to 21 bar. The high-pressure vapor-liquid equilibrium (VLE) of the ionic liquids with R-134a was measured to calculate the composition of the liquid phase at the various pressures encountered in the viscosity and diffusivity measurements. The viscosity of the ionic liquid decreases significantly with increased composition of R-134a at VLE. The “excess” viscosity demonstrates positive values that are believed to represent relatively strong intermolecular forces of the polar R-134a and [HMIm][Tf₂N]. The self-diffusivity of mixtures of [HMIm][Tf₂N] and liquefied R-134a (298.15 K and 6.7 bar) was measured and increases significantly with increases in the composition of R-134a. The self-diffusivity of [HMIm][Tf₂N] in vapor-liquid equilibrium with compressed R-134a gas was measured and indicates similar increases in diffusivity with composition of R-134a. The diffusivity demonstrates close Stokes-Einstein behavior using the measured mixture viscosity data and ambient pressure self-diffusivity.

Keywords: compressed hydrofluorocarbon gas, imidazolium ionic liquids, viscosity, self-diffusivity, 1, 1, 1, 2-tetrafluoroethane (R-134a)

Graphical Abstract:

1. Introduction

Coupling ionic liquids with compressed gases have been demonstrated in diverse applications in chemistry and engineering. The extremely low to immeasurable volatility of most ionic liquids inhibits them from entering a gas phase. However, ILs often have large solubility of certain gases in the ionic liquid-rich phase. Coupling ILs with compressed CO₂ forms an interesting platform for combining catalyzed reactions and separations [1, 2]. For instance, we have investigated the effect of CO₂ pressure/composition on the range of kinetic and mass-transport limited regimes in rhodium-catalyzed olefin hydrogenation and hydroformylation in biphasic IL/CO₂ systems [3, 4]. These IL/compressed gas systems are a subset of what are currently called gas-expanded liquids (GXLs) or CO₂-expanded liquids (CXLs) [5, 6]. There is currently a tremendous amount of research to use ionic liquids for pre- or post-combustion CO₂ capture [7-10].

In addition to CO₂, ionic liquids can be involved with a variety of other gases. ILs have been proposed as lubricants in gas compressors which would bring any number of gases in contact with the ionic liquid lubricant [11, 12]. Ionic liquids can improve the efficiency of absorption refrigeration processes where the IL absorbs the refrigerant gas (usually hydrofluorocarbons) in one stage and releases the high pressure gas with heat in another stage to produce a high pressure gas without the need for a mechanical compressor [13, 14]. Here the liquid solvent needs to have a high solubility of the gas at lower temperatures and no volatility. Current liquid solvents for absorption refrigeration are not optimal as often bulky equipment is needed to remove their contamination of the high-pressure gas. Non-volatile ionic liquids in these systems with refrigerants may help solve these problems.

While a considerable amount of research has involved the phase equilibrium thermodynamics of gas/ionic liquid systems, the transport properties of these mixtures, such as viscosity and diffusivity, are important equally as important to understand some of these vast applications in chemical dynamics to mass transfer. We [15] and other groups such as Harris and Kanakubo [16, 17], and Tomida [18, 19] have measured the high-pressure (>1000 bar) viscosity of pure ionic liquids. Several studies have appeared in the literature for the viscosity of ionic liquids saturated with compressed CO₂. We have measured the viscosity of three *n*-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([R-MIm][Tf₂N]) ionic liquids saturated with compressed CO₂ at temperatures of 298.15 K, 323.15 K, and 343.15 K and pressures to 287 bar

[20]. The dissolution of CO₂ significantly reduces the viscosity of the ionic liquid. Liu *et al.* [21] measured the viscosity of mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]), methanol, and CO₂ using the falling ball viscometer. Laurenczy and Dyson [22] measured the viscosity of 1-butyl-3-methylimidazolium [Tf₂N] ([BMIm][Tf₂N]) and [BMIm][PF₆] under subcritical CO₂ pressure with a falling ball method. Tomida *et al.* [23, 24] measured the viscosity of non-saturated CO₂ mixtures with 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIm][BF₄]) and [BMIm][PF₆] by a rolling ball viscometer. However, the viscosity of ionic liquids saturated with compressed hydrofluorocarbons could not be found in the literature despite possible applications in absorption refrigeration [14], etc.

The diffusivity of gases has mainly been measured for CO₂ at low and high pressures into ionic liquids. All current reports represent the so-called *Fickian* diffusion, or more precisely the *inter-* or *mutual*-diffusion for binary systems [25], of gases into ionic liquids in a chemical potential (fugacity) gradient, *i.e.* away from saturation. This is opposed to *self-* or *intra*-diffusion measured in this study at phase equilibrium, *i.e.* constant chemical potential (composition) [26]. Some examples are demonstrated from the groups of Shiflett at DuPont [27], Noble [28], Baltus [29-31], Kroon [32], Rodriguez [33, 34], Jalili [35, 36], Li [37-39], Scovazzo [40, 41], etc. However for fluorocarbon gases, only Shiflett *et al.* [42, 43] also measured and correlated the inter-diffusivity of several hydrofluorocarbons into [BMIm][PF₆] and [BMIm][BF₄] using a gravimetric microbalance. There are currently no known self-diffusivity measurements for fluorocarbon gases and ionic liquids.

In present work, the viscosity, self-diffusivity, and phase equilibrium of the ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf₂N]), with compressed 1,1,1,2-tetrafluoroethane (its refrigerant designation is R-134a) (see Figure 1) were measured at three different temperatures (298.15 K, 323.15 K, and 343.15 K) and pressures to approximately 21 bar. These temperatures allow an understanding of the temperature effects of the IL/gas system. These viscosity and self-diffusion coefficients are some of the first for a hydrofluorocarbon and ionic liquid. [HMIm][Tf₂N] is a common ionic liquid in the literature and has been selected by an IUPAC ionic liquid committee to be used as a model and standard ionic liquid [44, 45].

a)

b)

Figure 1. Structure of a) 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf₂N]) and b) 1,1,1,2-tetrafluoroethane (R-134a)

2. Experimental Methods

2.1 Ionic Liquid Synthesis

1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf₂N]), was prepared by anion exchange from the corresponding bromide salt of the imidazolium cation ([HMIm][Br]) with lithium bis(trifluoromethylsulfonyl)amide (Li[Tf₂N]) in deionized water as described in the literature [46, 47]. Further details and spectroscopic characterization, etc. are given in the Supplemental Data file. From NMR and elemental analysis, the estimated purity is 99+%. The water content is less than 125 ppm(mass) and the Br content is lower than 8 ppm(mass).

2.2 Viscosity Measurements

The high pressure viscosity of the ionic liquid and R134a mixture was measured with a modified Cambridge Applied Systems (currently Cambridge Viscosity) high pressure viscometer (ViscoPVT/ViscoPro 2000 System 4- SPL-440 with Viscolab software). The apparatus and measurement procedure has been described in detail previously [20], however, an overview will be given here. An equilibrium view cell is used to mix the ionic liquid with R-134a vapor. A recirculation pump takes liquid from the equilibrium cell through the viscosity measurement device and then back to the top of the view cell thus contacting the liquid with the gas phase. After thermodynamic equilibrium is obtained, the pump is turned off and readings are taken. At a new pressure the process is repeated. The viscosity measurement device is based on the movement of a piston (rod) inside of a chamber and described in detail in Aghosseini and Scurto [15]. Two magnetic coils inside the sensor body oscillate the piston over a fixed distance, forcing the fluid to flow through the annular space between the rod and chamber. The time

required for the rod to complete a round trip is directly related to the viscosity of the fluid. The current equilibrium system is capable of measuring viscosity from 0.2 to 10,000 mPa s (cP), at a maximum pressure of 300 bar and in a temperature range of -40 to $+110^{\circ}\text{C}$. The viscosity reading is the average of 20 viscosity measurements and is reported with the standard deviation of those measurements with the uncertainty nominally estimated at less than $\pm 1.0\%$. The nominal uncertainty of the pressure gauge is 0.07% full-scale (FS=206.8 MPa); but the NIST-traceable calibration was accurate to 0.0084% full-scale. The maximum deviation of temperature from the set-point temperature for all data was less than 0.1 K.

2.3 Diffusivity

A proton NMR method is used here to determine the self-diffusion of the ionic liquid or specifically the cation (the anion has no protons) and the dissolved refrigerant gas. A Bruker 400 MHz ^1H NMR was used to measure the translational diffusion with a pulsed-field gradient (PFG) method. In a pulsed-field gradient, the reduction of a signal intensity resulting from the combination of molecular diffusion and magnetic force gradient pulses on nuclear spins can be measured. The reduction of the signal intensity is based on the diffusion time as well as the gradient parameters: gradient strength and length of gradient. The intensities for the sample are given by the following equation [48]:

$$\ln\left(\frac{I}{I^{\circ}}\right) = -(\gamma \delta g)^2 D^* \left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right) \quad \text{Eqn. 1}$$

where, I is the intensity of the NMR peak, I° is Initial intensity of NMR Peak, γ is the gyromagnetic ratio equal to $26750 \text{ Gauss}^{-1}\text{sec}^{-1}$ for ^1H NMR, g is the gradient strength (G/m), δ is the length of gradient (sec), Δ is the diffusion time (sec), τ is the time between rf gradients (sec), and D^* is Self-Diffusion coefficient (m^2/s). For a more detailed description of the NMR method used for diffusion see references [49, 50].

2.3.1 Calibration

For diffusion measurements, the NMR must be calibrated and the applied gradient strength (g) determined by knowing all other parameters in equation (1). The signals for the $\text{CH}_3\text{-N}$ group and the $-\text{CH}_2\text{F}$ were followed for the diffusion of the cation and R-134a respectively. Two standards were utilized to determine the parameters: hexane ($D^*_{\text{o}} = 4.15 \times 10^{-9} \text{ m}^2/\text{sec}$) [51] and water ($D^*_{\text{o}} = 2.3 \times 10^{-9} \text{ m}^2/\text{sec}$) [52] at 298.15 K . All measurements were performed without

deuterated solvents by manual shimming. For the calibrations, all the time parameters, Δ , δ , and τ remained constant, while the applied gradient strength was altered. To protect the gradient coil from damage, the maximum gradient strength used was $g=70\% \times g_{max}$ [53]. The applied gradient strength alteration was between $g=5\%$ to $g=70\%$ of the total applied gradient strength using [49, 53] equal increments. From the two calibrations, the total applied gradient strength was determined as 49.5 Gauss per meter (G/m). The standard deviation of the diffusion coefficients measurements out of five different experiments for both hexane and water are less than 3%. It is believed that the uncertainty in the ionic liquid measurements are 5% or less. We have also tested the following systems and confirmed the stated accuracy: ethanol in water [54], dilute benzene in acetonitrile [55], and aniline and acetone [56]. It should be noted that the self-diffusion coefficients of ionic liquids from NMR methods are actually averages of different species as ILs may exist as ion pairs or higher aggregates in a pure phase and additionally in a mixture, fully solvated ions, solvated contact ion pairs, etc. etc. Here, a ^1H signal from the cation ($\text{CH}_3\text{-N}$) is used to determine the self-diffusivity of the IL. However, this measurement is really an average of the cation in different molecular species with different diffusivity, *e.g.* fully solvated cation, ion pairs, etc. Determining the exact extent of solvation and nature of the solution at each composition is beyond the scope of these studies.

2.3.2 Measurement Procedure

To measure the diffusion coefficient of molecules of a liquid mixing with a compressed gas, medium pressure NMR tube from Wilmad Lab Glass, Inc. (Model PV-ANV Pressure/Vacuum NMR Valve) which is capable of pressures to 13 bar. A sample of ionic liquid is injected to the tube to the height of 3 cm. The valve assembly is connected to the tube and a pressure gauge and then to an Isco high-pressure syringe pump (260M) by a 1/8 inch OD PEEK tube. A certain amount of the R-134a is injected and the valve on the NMR tube is closed. The tube is rocked back and forth to increase mixing and reduce the time to equilibrium. After several hours, the tube is placed in the NMR. For vapor-saturated liquid, the liquid is contacted at a certain pressure, mixed and repeated until the pressure remains constant. For the diffusivity involving liquid R-134a mixtures with the IL, the Isco pump is used to meter in a certain quantity of liquid. The pump is jacketed to a water bath to a constant ($\pm 0.1\text{K}$). The pump is set in constant pressure mode (± 0.1 bar), therefore constant T and P for constant density). The pump is then used to meter in a certain volume (± 10 nL) of liquid R-134a to the gravimetrically measured ionic liquid

in the NMR tube. The density of R-134a is from the equation of state found within the REFPROP program [57]. From density and volume delivered, the mass can be obtained. The cell was placed within the NMR and allowed to come to thermal equilibrium at the desired temperature for 30-60 minutes to avoid temperature gradients and artifacts of natural convection. Data regression was performed with SigmaPlot 11.

2.4 High-Pressure Vapor-Liquid Equilibrium

The solubility of 1,1,1,2-tetrafluoroethane in the ionic liquids at various temperatures and pressures were measured in a static equilibrium apparatus. Details of the apparatus and extensive error analysis are described in Ren and Scurto [58, 59], and an overview will be given here. The system consists of a custom built high-pressure windowed equilibrium cell, a high-pressure and high-precision syringe pump (Teledyne-Isco, Inc. 100DM), a water bath and high-precision temperature measurement and a high-precision pressure gauge (Heise DXD Series 3711). The apparatus is able to determine the solubility (mole fraction, molarity, etc.), density of the liquid solution, molar volume, and volume expansion simultaneously. These calculations are based on the mass balance of the gas in the system, by determining R-134a delivered from the pump, the moles/mass of R-134a in the headspace above the liquid and in the tubing/lines to the equilibrium cell and the volume of the liquid with dissolved gas. This method can yield high resolution of solubility data (often better than ± 0.001), pressure with accuracy of ± 0.2 bar, temperature of $\pm 0.01^\circ\text{C}$, density up to $\pm 0.4\%$, and volume expansion to $\pm 0.05\%$. As significant quantities of R-134a are soluble in the ionic liquid even at 1 bar of pressure, a vacuum is used to remove most of the gas dissolved in the IL for approximately 30 minutes to achieve a steady pressure of approximately 0.2 bar absolute.

2.5 Materials

1-Methyl-imidazole, (CAS#616-47-7) 99+%, acetonitrile $\geq 99.9\%$, and lithium bis(trifluoromethylsulfonyl)amide (CAS# 90076-65-6) 99.95% were purchased from Sigma-Aldrich. Bromohexane (CAS# 111-25-1) 99+% and aluminum oxide (activated, acidic, for column chromatography; 100-500 micron) were obtained from Acros. 1-Bromohexane and 1-methylimidazole were vacuum distilled directly prior to use. Activated carbon 50-200 mesh was obtained from Fisher Scientific. 1,1,1,2-Tetrafluoroethane (R-134a, 99.99%) was purchased

from Linweld, Inc and used as received. Compressed argon (CAS# 7440-37-1) (Ultra High Purity (UHP) grade) was obtained from Airgas, Inc. See sample description table, Table S1.

3 Results and Discussion

3.1 Phase Behavior and Equilibrium of [HMIm][Tf₂N] and R-134a

We have previously investigated the global phase behavior (pressure-temperature projection) of binary mixtures of 1,1,1-tetrafluoroethane (R-134a) and various imidazolium ionic liquids, including [HMIm][Tf₂N], between approximately 273.15 K to 378.15 K and pressure to 330 bar [60, 61]. These systems with R-134a exhibit Type V behavior according to the classification of Scott and van Konynenburg [62]. This is characterized by regions of vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE) between lower critical and upper critical endpoints (LCEP and UCEP respectively) temperatures and pressures, liquid-liquid equilibrium (LLE), and mixture critical points that emanate from the lower critical endpoint and extend theoretically to the pure critical point of the component with lower volatility, *i.e.* the IL. Thus at higher pressures, regions exist where the ionic liquids are miscible or even critical with R-134a. This single-phase behavior is quite unique for hydrofluorocarbon refrigerant gases and ionic liquids, as most compressed gases (CO₂, CO, ethane, etc.) have no reported miscibility or criticality with ILs [63-66]. At temperatures below the LCEP (approximately 335.75 K), vapor-liquid equilibrium exists with complete liquid miscibility above the vapor pressure of R-134a. Thus, our results presented here for 298.15 K and 323.15 K are below the LCEP and would become miscible liquids at and above the vapor-pressure of pure R-134a. However, the isotherm at 343.15 K is between the LCEP and UCEP (approximately the pure R-134a critical point) and would exhibit VLE at lower pressures, then a pressure producing vapor-liquid-liquid (VLLE) equilibrium, followed by liquid-liquid equilibrium (liquid immiscibility) and finally a mixture critical point at higher pressures. These different phase transitions make it imperative to understand phase behavior in compressed gas systems before attempting to measure other chemical or physical properties: here, viscosity and diffusivity. As such, the viscosity and diffusivity measurements below are conducted in the VLE region below the VLLE region, and one example in the single phase liquid region.

As will be discussed below, the viscosity and diffusivity of R-134a saturated [HMIm][Tf₂N] were measured at 298.15 K, 323.15 K and 343.15 K at various pressures of R-134a. In order to determine the composition of R-134a in the liquid phase at these points, the phase equilibrium must be quantified. We have previously measured isotherms at 298.15 K and 323.15 K [67]. New data at 343.15 K for the solubility, liquid molar volume and volume expansion are presented here and listed in Table S2. Figure 2 illustrates that the two lower isotherms represent VLE across the entire pressure/composition region. All points in the Figure at a $x_{R1234a} = 1$ are the pure component vapor pressures of R-134a from REFPROP of Lemmon *et al.* [57] at their respective temperatures. At the lower two temperatures, the two components become miscible at pressures above the vapor pressure of R-134a. However, at 343.15 K, the VLE behavior becomes vapor-liquid-liquid equilibrium (VLLE) at 21.0 bar and 87.1% mole R-134a. Here an IL-rich liquid and a R-134a-rich liquid are in equilibrium with a R-134a-rich vapor phase. Above this pressure, liquid-liquid equilibrium occurs followed by a mixture critical point that was measured at 37.78 bar and 94.4% mole R-134a.

Figure 2. Experimental vapor-liquid equilibrium data for [HMIm][Tf₂N] and R-134a at 298.15 K (●) [67]; 323.15 K (■) [67]; and 343.15 K (▲) (this work). Experimental VLLE point (∇) and LLE critical point (◇) at 343.15 K. All points at a $x_{R1234a} = 1$ are the vapor pressure of R-134a from the accurate correlation of Lemmon *et al.* [57] at their respective temperatures.

As significant quantities of the gas dissolve into the ionic liquid, the volume of the mixture expands significantly over the initial volume of the liquid. As shown in Table S, between approximately 0.2 bar and 20.8 bar, the volume increases by over 50%. However as the amount of R-134a entering the liquid is greater than the corresponding volume increase, the molar volume decreases (molar density increases).

3.2 Viscosity of R-134a saturated [HMIm][Tf₂N]

The viscosity of [HMIm][Tf₂N] with 1,1,1,2-tetrafluoroethane (R-134a) has been measured to pressures of approximately 20 bar and three temperatures: 298.15 K, 323.15 K, and 343.15 K; the results are listed in Table 1. Regions of multiphase behavior, miscibility and criticality, as discussed above, are avoided, so that only 2-phase VLE or LLE regions are investigated. The pure IL viscosity was measured as 71.0, 24.9, and 14.1 at 298.15, 323.15, and 343.15 K. From the literature, Widegren and Magee [68] from NIST measured 70.2, 26.3, and 14.6 respectively at the same temperatures; this is a deviation of approximately 3%. Even closer agreement was found with other datasets at the same temperatures in the literature [69-71]. Figure 3a illustrates that at lower temperatures the viscosity decreases considerably with the pressure of the R-134a gas. Again, this decrease corresponds to the large increase of R-134a solubility in the IL. The viscosity at 343.15 K, which was measured to just below the multi-phase VLLE region, demonstrates a nearly linear trend with the R-134a pressure. However, this is not a primarily a pressure effect, but a composition effect, as the pure IL viscosity or pure liquid R-134a increase little under this pressure regime [15].

The phase equilibrium data was interpolated at the pressures of the viscosity measurements to calculate the saturated R-134a compositions at the corresponding conditions. Figure 3b now demonstrates the relationship between the viscosity and the composition of the R-134a in the ionic liquid. It appears from this plot that the viscosity decreases relatively linearly with lower compositions of R-134a. However, there seems to be a higher order response at high compositions of the gas in the liquid phase. When the data is normalized to the pure [HMIm][Tf₂N] viscosity at the temperature of the isotherm, similar relative behavior is observed as demonstrated in Figure S2 in the supplemental data file. The relative behavior is similar at similar compositions of the R-134a, especially at low and high compositions despite the large

absolute differences between isotherms. However, there is more scatter at intermediate compositions, *viz.* 0.35-0.7 mole fraction R-134a.

Table 1. Measured Dynamic Viscosity (η) and calculated Kinematic Viscosity (ν) of [HMIm][Tf₂N] phase with pressure and composition of R-134a.

T	P	x_{R134a}	η	$\pm^e$	$\underline{V}^L$	ρ	ν
[K]	[bar]		[mPa·s]		[cm ³ /mol]	[g/cm ³]	[cSt]
298.15 ^a	1 ^c	0.000	71.0	0.7			
	2.9	0.387	55.8	0.5	238	1.316	42.4
	3.9	0.511	51.3	0.5	207	1.310	39.1
	5.2	0.672	35.5	0.3	166	1.299	27.3
	5.6	0.725	18.7	0.2	152	1.294	14.5
	6.65 ^d	1.000	0.195		84.6	1.207	0.162
323.15 ^a	1 ^c	0.000	24.9	0.3			
	3.0	0.223	22.2	0.2	280	1.322	16.8
	4.9	0.349	19.3	0.3	248	1.318	14.6
	7.0	0.473	15.8	0.3	216	1.312	12.0
	8.8	0.575	12.3	0.1	190	1.307	9.4
	10.9	0.701	8.98	0.1	158	1.296	6.9
343.15 ^b	13.18 ^d	1.000	0.142		92.6	1.102	0.129
	1 ^c	0.000	14.07	0.1	299	1.325	9.5
	3.1	0.148	12.62	0.1	267	1.321	9.1
	6.1	0.276	11.97	0.1	244	1.317	7.1
	8.5	0.364	9.33	0.1	220	1.313	6.2
	11.3	0.459	8.09	0.1	190	1.307	5.4
	14.7	0.575	7.06	0.1	130	1.283	2.5
	20.3	0.813	3.24	0.03	299	1.325	9.5
	21.17 ^d	1.000	0.107		102.4	0.996	0.107

Standard Uncertainties: $u(T)=0.1\text{K}$; $u(P)=0.1\text{ bar}$; $u(\underline{V}^L)=1\text{ ml/mol}$;

$$u(\rho)=0.001 \text{ g/cm}^3; u(\nu)=0.1 \text{ cSt.}$$

^a compositions, molar volume, density were interpolated from the data of Ren and Scurto [67]; ^b interpolated from data presented here; ^c pure IL at ambient pressure, not at 1 bar of R-134a. ^d Properties of pure saturated liquid R-134a from REFPROP database [57]; ^e Standard deviation of 20 measurements.

a)

b)

Figure 3. The viscosity of [HMIm][Tf₂N] with pressure (a) and composition (b) of R-134a at 298.15 K (●); 323.15 K (■); and 343.15 K (▲); note that lowest pressure/composition viscosity points are free of R-134a at ambient pressure.

Using the molar volumes and compositions from the phase equilibrium studies to compute the liquid phase density, the kinematic viscosity can be calculated. As shown in Table 1 and Figure S1 in the supplemental data file, the kinematic viscosity behaves very similarly as the dynamic viscosity. This is despite the large increase in volume and decrease in molar volume with increased dissolution of R-134a. However as the average molecular weight also decreases similarly with molar volume, the density only slightly decreases across the compositions as shown in Table (<5% decrease); also the *specific* volume only slightly increases. Thus, the kinematic viscosity differs from the dynamic viscosity by nearly a constant factor, *i.e.* specific volume, at all compositions.

A method to compare the viscosity of mixtures to their pure component values is the concept of “excess viscosity”. While not a true *excess* property in the thermodynamic sense, it is a method to observe the differences in behavior between the real mixture and that of an “ideal solution” of the components. The viscosity of an ideal solution is characterized by having values equal to the mole fraction average of the pure component viscosity. The excess viscosity (η^{EX}) is defined as:

$$\eta^{EX} = \eta_m - (x_1\eta_1 + x_2\eta_2)$$

where η_m is the experimental mixture viscosity and η_i is the pure component viscosities at the temperature, pressure, and state of aggregation of the mixture. While usually computed at the same pressure throughout the composition range, the viscosity of the pure liquids will change little for the pressures investigated here [15]. As the pure R-134a is a gas at the conditions investigated, the viscosity of its corresponding pure saturated liquid at the system temperature is used; thus the pure viscosity at its saturation pressure, not system pressure, is used. It should be noted that the order of the excess viscosity is usually small and thus it is a strong function of the pure component values and any errors in the measurements. As high accuracy data and values were used, we believe that the calculations are both qualitatively (sign) and quantitatively accurate enough for this discussion. Figure 4 illustrates the excess viscosity of the [HMIm][Tf₂N] with various compositions of R-134a for each of the isotherms. As shown, the excess viscosity is positive indicating that the mixture viscosity is larger than that of an ideal mixture. As is typical, the excess viscosity decreases significantly with increasing temperature. This positive behavior is quite different than the viscosity of CO₂ saturated solutions of [HMIm][Tf₂N] from our previous work [20]. While CO₂ also decreases the viscosity of ionic

liquids significantly, the excess viscosity at all isotherms investigated with CO₂ is actually negative (see Figure 4 for an example at 298.15 K); *i.e.* lower viscosity than an ideal solution. For the [HMIm][Tf₂N]/R-134a system, the positive excess viscosity which decreases with temperature may indicate that relatively strong intermolecular interactions exist between the polar R-134a (1,1,1,2-tetrafluoroethane) and the IL liquid which has coulombic forces, polar forces and regions of mainly dispersion forces (*i.e.* hexyl- group). This is in contrast to CO₂ with a negative excess viscosity that has mainly dispersion and quadrupole forces. As an example for liquid mixtures, Salinas *et al.* [72] have measured the viscosity and excess viscosity of [HMIm][Tf₂N] and ethanol at 298.15K. They found large negative excess viscosity. The dielectric constant of ethanol is large enough to potentially solvate the ions in solution. Hoffmann and coworkers found negative excess viscosity for [HMIm][Tf₂N] and chloroform [73, 74].

Figure 4. The variation of excess viscosity with the mole fraction of R134a in [HMIm][Tf₂N] at three different isotherms. The corresponding data for CO₂ in [HMIm][Tf₂N] at 298.15 K [20] is shown for comparison (♦).

3.3 Diffusivity [HMIm][Tf₂N]/R-134a Mixtures

3.3.1 Pure Component Self-Diffusivity

The pure component self-diffusivity (D^*_0) was measured for the ionic liquid and the compressed liquid R-134a at 298.15K, 323.15 K, and 343.15 K. From our NMR method for self-diffusivity, the cation diffusion coefficient for pure [HMIm][Tf₂N] at 298.15 K was determined to be 1.79×10^{-11} m²/s and compares well with the literature values of 1.75×10^{-11} m²/s [75] and 1.73×10^{-11} m²/s [76]; about a 3.5% deviation. For comparison with other ILs, Kanakubo *et al.* determined the self-diffusion coefficient of [BMIm][PF₆] at 298.15K at 6.92×10^{-12} m²/sec [77]. However, Palmer *et al.* measured the self-diffusion coefficient for [BMIm][PF₆] at approximately 1.97×10^{-11} m²/s which is an order of magnitude higher than the Kanakubo results and higher than the [HMIm][Tf₂N] measured here [78]. However as the ambient pressure viscosity of [BMIm][PF₆] is approximately 282% higher than [HMIm][Tf₂N][15], one would expect the diffusivity of [BMIm][PF₆] to be less. Palmer *et al.* also determined the diffusivity at 300 bar (pure) and found that it decreased approximately 23% over the ambient pressure diffusivity [78]. Similar pressure effects were reported by Kanakubo *et al.* [77]. However, below 20 bar very little decrease in diffusivity was observed. Thus, the effect of pressure on the *pure* IL diffusivity was not considered here and only composition effects were investigated.

For 1,1,1,2-tetrafluoroethane (R-134a), the self-diffusion coefficient at 298.15K and 6.7 bar is 594.9×10^{-11} m²/s, and, thus, several orders of magnitude higher than the IL. The self-diffusion coefficient of liquid R-134a at saturation (~6.7 bar) reported from the literature [79] is approximately 6.2×10^{-9} m²/s; a difference of approximately 4%. Thus, good agreement has been obtained for both pure IL (cation) and liquid R-134a.

3.3.2 Diffusivity in Liquid Mixtures of [HMIm][Tf₂N] and compressed Liquid R-134a

The self-diffusion coefficients for liquid mixtures of R-134a (1) and [HMIm][Tf₂N] (2) system at 298.15 K and 6.7 bar were measured across the composition range. The results are shown in Figure 5 and Table 2. These conditions are just above the vapor pressure of R-134a (~6.7 bar) and thus represent liquid mixtures. As discussed above, this temperature is below the LCEP and thus miscible liquids form above the vapor pressure of R-134a. Here, the composition of R-134a was increased and the self-diffusivity was measured of both the [HMIm][Tf₂N] (cation, D^*_2) and

R-134a (D^*_1). As seen in Figure 5, the diffusivity of [HMIm][Tf₂N] (D_{21}) significantly increases with increasing composition of the R-134a. For instance at 50 mole% R-134a, D^*_2 increases over ~250% from the pure ionic liquid (1.7×10^{-11} m²/s). However, the self-diffusivity of pure liquid R-134a is 594.9×10^{-11} m²/s and decreases to 30.8×10^{-11} m²/s at 50 mole% in the mixture. [HMIm][Tf₂N] has an acidic hydrogen at the bridge carbon between the nitrogens of the imidazolium ring and the anion has both fluorine and sulfonyl groups which may also participate in hydrogen bonding with the R-134a. At the higher compositions of the R134a, both the IL and R134a have more mobility due to decreases in R-134a/IL interactions. From the plot, it appears that certain regions have a near logarithmic relationship with the composition of R-134a dissolved in the liquid phase. Palmer *et al.* investigated the self-diffusion coefficient of [BMIm][PF₆] in mixtures with methanol and ambient and elevated pressures [78]. They also noticed a rise in diffusivity in the dilute range of the IL in methanol similar to the dilute range here.

Table 2. Self-diffusivity R-134a (1) and [HMIm][Tf₂N] cation (2) at various compositions of liquid R-134a at 298.15 K and 6.7 bar.

x_{R134a}	$D^*_2 \times 10^{-11}$ [m ² /s]	$D^*_1 \times 10^{-11}$ [m ² /s]
0.00	1.79 ^a	
0.30	4.49	18.6
0.50	5.87	30.8
0.70	10.4	52.2
0.86	12.9	
0.98	141.4	498.6
1.00		594.9 ^b
Standard Uncertainties: $u(x)=0.005$; $u(P)=0.1$ bar; $u(D)=5\%$; ^a self-diffusivity of pure IL cation ($D^*_{0,2}$) at ambient pressure; ^b self-diffusivity of pure liquid R-134a $D^*_{0,1}$.

Figure 5. The self-diffusion coefficients of [HMIm][Tf₂N] (cation; D_2^*) and R-134a (D_1^*) with composition of compressed *liquid* R-134a at 298.15 K and 6.7 bar. The values at $x=0,1$ are the pure component self-diffusion coefficients, $D_{0,i}^*$.

There is only one other study known to the authors for the diffusivity of R-134a in ionic liquids. Shiflett and Yokozeki [42] measured the inter-diffusivity (*i.e.* in a chemical potential/concentration gradient versus self-diffusion here) of gaseous R-134a dissolving into the ionic liquid [BMIm][PF₆] using a microbalance and measured a diffusivity of $4 \times 10^{-11} \text{ m}^2/\text{s}$ at 3.5 bar (approximately 0.46 mole fraction of R-134a at saturation). Interpolating the data of our IL system in Table 2 and Figure 5 for a similar composition of 0.46, the self-diffusivity of R-134a in [HMIm][Tf₂N] would be approximately $30 \times 10^{-11} \text{ m}^2/\text{s}$; almost an order of magnitude higher than the R-134a in [BMIm][PF₆]. As the ambient pressure viscosity of [BMIm][PF₆] is approximately 282% higher than [HMIm][Tf₂N][15], one would expect the diffusivity (even inter-diffusivity) of [BMIm][PF₆] to be less as is the case here. The vast majority of published diffusivity of gases into ionic liquids concern carbon dioxide at both low and high pressure; For example, the inter-diffusivity of CO₂ into a related IL, [BMIm][Tf₂N] was reported as $7.8 \times 10^{-10} \text{ m}^2/\text{s}$ at 298.15 K and near ambient pressure (*i.e.* low CO₂ compositions).

3.3.3 Diffusivity of [HMIm][Tf₂N] Saturated with Compressed R-134a Gas.

The self-diffusivity of the ionic liquid saturated with R-134a at various pressures (compositions) was measured and listed in Table 2. As opposed to the above study of miscible liquids, these data are in vapor-liquid equilibrium and only the liquid phase diffusivity was measured. Figure 6a illustrates the diffusivity of the cation of [HMIm][Tf₂N] (D_2^*) at three temperatures with pressure of R-134a as measured. Figure 6b illustrates the diffusivity at the corresponding compositions of R-134a. The diffusion coefficient at 298.15 K increases about 42% with increasing pressure of R134a from ambient to 3 bar; 3.5 bar corresponds to approximately 40 mole% R-134a in the IL phase (see Figure 6b). This enhancement, at similar conditions at 323.15 K and 343.15 K, is around 25 % and 20%, respectively. Table 3 demonstrates that the diffusivity at 323.15 K and 343.15 K is two and three fold larger than at 298.15 K.

Table 3. Self-diffusivity of [HmIm][Tf₂N] (2) saturated with R-134a (1), D_2^* .

298.15 K				323.15 K				343.15 K			
P [bar]	x _{R-134a} a	η^b [mPa·s]	$D_2^* \times 10^{11}$ [m ² /s]	P [bar]	x _{R-134a} a	η^b [mPa·s]	$D_2^* \times 10^{11}$ [m ² /s]	P [bar]	x _{R-134a} a	η^b [mPa·s]	$D_2^* \times 10^{11}$ [m ² /s]
1.0 ^c	0	71.0	1.79	1.0 ^c	0	24.9	5.54	1.0 ^c	0	14.07	10.66
3.15	0.42	55.3	2.50	3.14	0.23	22.0	6.86	4.06	0.19	13.06	12.91
4.19	0.55	47.7	2.55	4.12	0.3	20.2	6.97	5.11	0.24	12.36	13.15
				5.15	0.36	18.4	6.85	6.08	0.28	11.78	13.41

Standard Uncertainties: $u(T)$ =0.1K; $u(P)$ =0.1 bar; $u(\eta)$ =0.5 mPa.S; $u(D)$ =5%. ^a interpolated from vapor-liquid equilibrium data; ^b interpolated from mixture viscosity data; ^c ambient pressure viscosity with no R-134a.

c)

Mixture Viscosity, η [mPa.s]

Figure 6. The effect of R134a (1) on diffusivity of ionic liquid (cation) (D^*_2) at different temperatures: a) with pressure of R-134a (note 0 bar indicates ambient pressure data of pure component); b) at the corresponding composition interpolated from VLE data. The lines represent the Stokes-Einstein prediction from the mixture viscosity data and the pure IL diffusivity; c) *log-log* plot of diffusivity (D^*_2) versus mixture viscosity with correlation.

Figure 6c is a traditional *log-log* plot of the diffusivity and the interpolated mixture viscosity at the same conditions. As shown, the log of diffusivity and viscosity are highly correlated ($R^2 > 0.99$); however this is not particularly surprising on a *log-log* plot. From hydrodynamic theory, the liquid self-diffusivity, D^* , of pure components and mixtures can be connected to viscosity through the Stokes-Einstein equation [80]:

$$D^* = \frac{k_B T}{n \pi a \eta}$$

where, n is often 4 for smooth spherical object (slip-boundary condition) and 6 for a rough object; a is the hydrodynamic radius characteristic of the diffusing object; T is temperature; η is

the viscosity; and k_B is the Boltzmann constant. Assuming that the hydrodynamic radius, a , and shape parameter, n , remain constant for [HMIm][Tf₂N] in the mixture with R-134a, the following equation can be derived to relate the diffusivity and viscosity of the pure ionic liquid at ambient pressure (0) with that of the mixture properties (m):

$$D_m^* = \frac{D_0^*}{\eta_m / \eta_0}$$

At each pressure, the mixture viscosity interpolated from above is used. This prediction is based entirely from the ambient pressure diffusivity and viscosity, and the mixture viscosity data. As shown in Figure 6, a fair correlation exists between this expression and the data with differences reported in Table S3. However, the above diffusivity expression assumes that the intermolecular interactions remain constant and only the viscosity changes. Obviously, the real system experiences differences in local solvation with changes in composition which would subsequently affect the transport properties for this IL/-R-134a system. However, diffusivity at high pressures is more difficult to obtain than viscosity. Thus, the Stokes-Einstein approach would allow reasonable predictions from limited data. However, it should be noted that other systems in the literature seem to deviate from Stokes-Einstein behavior. Hoffmann and coworkers measured the viscosity and diffusivity of [HMIm][Tf₂N] and chloroform [73, 74]. They found deviations from Stokes-Einstein even at very dilute conditions (~ 0.01 mole fraction of the IL).

4. Conclusions

The viscosity, diffusivity and solubility in the system of [HMIm][Tf₂N] with the hydrofluorocarbon gas, 1,1,1,2-tetrafluoroethane (R-134a) was measured at 298.15 K, 323.15 K, and 343.15 K with pressures up to 20 bar. Increasing the R134a composition increases the transport properties of ionic liquid phase, *i.e.* decreasing viscosity and increasing diffusivity. Positive excess viscosity may also indicate particularly strong molecular interaction among the IL and R-134a, which is not seen with nonpolar gases such as CO₂. The increase in diffusivity correlates with the decrease in the viscosity of the mixture in a Stokes-Einstein relationship. This level of understanding would help facilitate the development and design of applications, such as absorption refrigeration, etc.

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Notes

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