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Viscosity and Diffusivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide with 1-Octene

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ABSTRACT: In order to correlate and predict interfacial mass transfer rates for ionic liquids and organic components, transport properties are required at various temperatures and, importantly, compositions. Here, the viscosity of mixtures of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf_2N]) with 1-octene to the liquid−liquid saturation limit were measured at four different isotherms [(10, 25, 50, and 75) °C]. The viscosity of a [HMIm][Tf_2N] + 1-octene mixture decreases up to 33 % over the pure ionic liquid in the temperature range studied. The computed viscosity deviation ("excess viscosity") demonstrates a negative trend throughout the composition range and diminishes with increasing temperature. The self-diffusivity of both 1-octene and [HMIm][Tf_2N] (cation) were measured at (25 and 50) °C and increased up to 40 % with increasing composition of 1-octene. The self-diffusivities were of the order of (10^{-11} and 10^{-10}) $m^2 \cdot s^{-1}$ for the cation and 1-octene, respectively.

INTRODUCTION

Room temperature ionic liquids (ILs) are organic salts with a combination of cation/anion that are liquid at a wide range of temperatures. The physicochemical properties of ILs can be molecularly designed to positively affect different kinds of processes by varying these anions and cations.[1] The ILs' negligible vapor pressure and low flash point make them relatively safer solvents. Various applications of ionic liquids are often based upon biphasic liquid−liquid systems which are being developed for extraction,[2−4] absorption -desorption in chromatography,[5] chemical reactions[6−8] and even biochemical reactions.[9,10] However, there is a lack of information for systems involving ionic liquids in interfacial mass transfer. Therefore, fundamental studies on interfacial mass and momentum transfer for biphasic systems are necessary for any process intensification and implementation.

We have recently reported[11] on the thermodynamic and phase equilibrium properties of 1-octene (**1**) and a model ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf_2N]) (**2**; see Figure 1). [HMIm][Tf_2N] is a common ionic liquid and was selected by the IUPAC committee on "Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems" to be used as a model and standard ionic liquid.[12,13] From the liquid−liquid equilibrium, 1-octene is fairly soluble in the IL (≈ 0.2 mol fraction at 25 °C), whereas the solubility of the IL in the octene phase is very small (< 0.0001 mol fraction at 25 °C). Thus, in a dynamic liquid−liquid contracting system, the mass transfer will occur in virtually one direction, i.e., 1-octene into the IL. As the 1-octene is fairly soluble, the density of the mixture changes with increasing composition of 1-octene. The surface tension of mixtures was also measured at different compositions and temperatures in addition to the saturated interfacial tensions of the two-phase system. We have also reported on the homogeneously catalyzed hydrogenation and hydroformylation of 1-octene in [HMIm][Tf_2N] with and without compressed CO_2.[6−8]

This contribution represents further studies into the mass and momentum transport properties for a biphasic system of 1-octene and a model ionic liquid, [HMIm][Tf_2N]. The viscosity and self-diffusivities of both an IL-rich phase and a 1-octene rich phase is reported at temperatures of (10, 25, 50, and 75) °C and compositions to the saturation condition.

EXPERIMENTAL METHODS

Synthesis of Ionic Liquid. [HMIm][Tf_2N] was prepared by anion exchange from the corresponding bromide salt of the imidazolium cation ([HMIm][Br]) with lithium bis(trifluoromethylsulfonyl)amide (Li[Tf_2N]) in deionized water as described in the literature.[14,15] The bromide salt of the imidazolium cation was prepared from a quaternization reaction of 1-methylimidazole with a slight excess amount of the corresponding 1-bromohexane in acetonitrile at 40 °C under an argon atmosphere with stirring for three days. Caution: This reaction is highly exothermic, and adequate solvent volumes and/or cooling must be provided during the reaction. The bromide salt of 1-hexyl-3-methyl-imidazolium was purified with activated charcoal (10 %) by stirring the mixture for 24 h. Acetonitrile was added to reduce the viscosity of the ionic liquid, and the mixture was filtered. The mixture was then passed through a plug of Celite (depth = 7 cm, diameter = 3 cm) and through a short column (height = 20 cm, diameter = 2.5 cm) of acidic alumina. The solvent was removed on a rotary evaporator under reduced pressure at 40 °C and then connected to a high vacuum (< 0.1 Pa) at 50 °C for at least 48 h. [HMIm][Tf_2N] was synthesized by anion exchange between the [HMIm][Br] and Li[Tf_2N]. The denser hydrophobic IL phase was decanted and washed with water 6 to 8 times until the bromide concentration was less than $8 \cdot 10^{-6}$ weight fraction. The sample was dried under a high vacuum (< 0.1 Pa) at 50 °C for at least 48 h and contained less than $50 \cdot 10^{-6}$ mass fraction in

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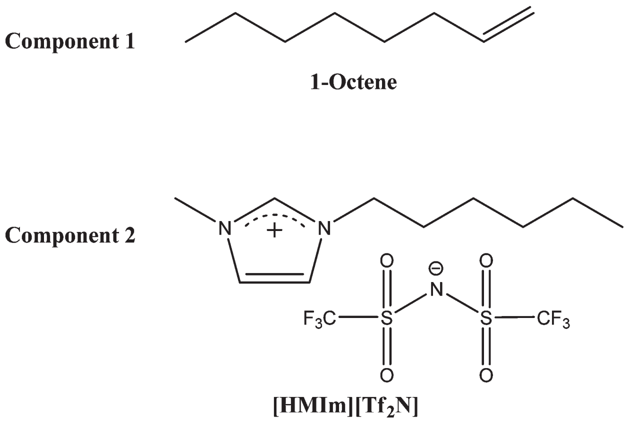

Figure 1. Structure of 1-octene and 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf_2N]).

mass of water. The original sample of ionic liquid was then stored in a Schlenk tube under an atmosphere of dry argon.

^{1}H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: δ = 8.65 (s, 1H), 7.39 (t, 1H, J = 1.76), 7.37 (t, 1H, J = 1.48), 4.17 (t, 2H, J = 7.4), 3.93 (s, 3H), 1.87 (m, 2H), 1.32 (m,6H), 0.87 (t, 3H, J = 6.53). Analysis calculated for $C_{12}H_{19}N_3F_6S_2O_4$: C, 32.2; H, 4.28; N, 9.39; S, 14.33. Found: C, 32.21; H, 4.27; N, 9.25; S, 14.19. From NMR and elemental analysis, the estimated purity is 99+ %.

Analysis. Elemental analysis was performed by Desert Analytics Transwest Geochem. ^{1}H NMR spectra were recorded on a Bruker 400 NMR Spectrometer using TMS as a reference for ^{1}H chemical shifts. The water content was determined by a Mettler Toledo DL32 Karl Fisher Coulometer and the Br content was measured by a Cole Parmer Bromide Electrode (27502-05) read with an Oakton Ion 510 series meter.

Materials. 1-Methyl-imidazole, (CAS no. 616-47-7) 99+ %, acetonitrile ≥ 99.9 %, 1-octene (CAS no. 111-66-0) 98 %, and lithium bis(trifluoromethylsulfonyl)amide (CAS no. 90076-65-6) 99.95 % were purchased from Sigma-Aldrich. Bromohexane (CAS no. 111-25-1) 99+ % and aluminum oxide (activated, acidic, for column chromatography; (100 to 500) μm) were obtained from Acros. Bromo-hexane and 1-methylimidazole were vacuum distilled directly prior to use. Activated carbon 50 to 200 mesh was obtained from Fisher Scientific. Compressed argon (CAS no. 7440-37-1) (ultra high purity (UHP) grade) was obtained from Airgas, Inc.

Interfacial Transport Properties. *Viscosity.* The viscosity at ambient pressure (at different temperatures) was measured using a Wells-Brookfield Cone/Plate (DV-III ULTRA) viscometer/rheometer. The relative uncertainty of the apparatus is within ± 1.0 %. Reproducibility is to within ± 0.2 %. The temperature range is from (0 to 100) °C with an uncertainty of ± 0.1 °C. The standard gravimetric method is used to make the solutions of 1-octene in ionic liquid. The mixture is prepared by weighing a specific amount of each part into a 25 mL vial with an uncertainty of ± 0.0002 g with an uncertainty in mole fraction of better than 0.01.

Diffusivity. Self-diffusion is the random translational movement of molecules from internal energy.[16] A proton NMR method is used here to determine the self-diffusion of the ionic liquid or specifically the cation (as the anion has no protons) and the dissolved 1-octene. A Bruker 400 MHz ^{1}H NMR was used to measure the translational diffusion with a pulsed-field gradient (PFG) method. The software used to analyze the data was Topspin version 1.3. In a pulsed-field gradient (PFG), 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:[16]

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

where I is the intensity of the NMR peak, I^0 is initial intensity of NMR peak, γ is the gyromagnetic ratio equal to 26 750 $G^{-1}\cdot s^{-1}$ for ^{1}H NMR, g is the gradient strength ($G\cdot m^{-1}$), δ is the length of gradient (sec), Δ is the diffusion time (s), τ is the time between rf gradients (s), and D = diffusion coefficient ($m^2\cdot s^{-1}$). For a more detailed description of the NMR method used for diffusion see other related references.[17,18]

For diffusion measurements, the NMR spectrometer must be calibrated and the applied gradient strength (g) determined by knowing all other parameters in eq 1. Two standards were utilized to determine, e.g., hexane ($D = 4.15\cdot 10^{-9}\ m^2\cdot s^{-1}$)[19] and water ($D = 2.30\cdot 10^{-9}\ m^2\cdot s^{-1}$)[20] at 298.15 K. All measurements were performed without deuterated solvents by manual shimming. For the calibrations, all of 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 $g = 0.7g_{\max}$.[21] The applied gradient strength alteration was between $g = 0.05g_{\max}$ to $g = 0.7g_{\max}$ using equal increments.[17,21] From the two calibrations, the total applied gradient strength was determined as 49.5 ($G\cdot m^{-1}$). To validate the gradient strength obtained from experiments the cation diffusion coefficient for pure [HMIm][Tf_2N] at 298.15 K was determined to be $1.79\cdot 10^{-11}\ m^2\cdot s^{-1}$ and compared with the literature, $1.75\cdot 10^{-11}\ m^2\cdot s^{-1}$.[22] The relative standard deviation of the diffusion coefficients measurements out of five different experiments are less than 3 %.

Table 1. Comparison of Viscosity (η) of Pure [HMIm][Tf_2N] and 1-Octene from Our Laboratory and Literature Sources

η [mPa·s] [HMIm][Tf_2N]	ref	η [mPa·s] 1-octene	ref
		t = 25 °C	
70.1 ± 0.8	*a*	0.47 ± 0.01	*b*
68	23	0.478	28
69.7	22	0.447	43
70.2	25	0.48	29,44
		t = 50 °C	
25.8 ± 0.3	*a*	0.37 ± 0.01	*b*
26.25	25	0.365	28
25.8	22	0.351	43
24.76	24	0.346	27

[a] From our previous report ref 45. [b] This work.

■ RESULTS AND DISCUSSION

Viscosity of the 1-Octene and [HMIm][Tf_2N] System. The experimental results of dynamic viscosity for pure 1-octene and [HMIm][Tf_2N] and their mixtures to saturation at different

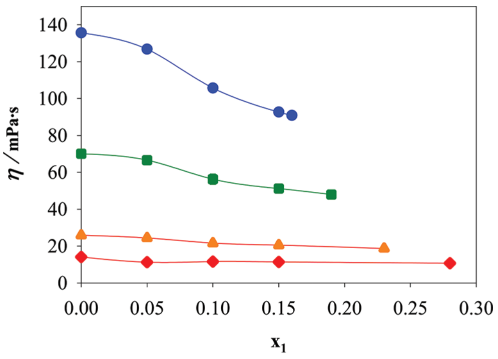

Figure 2. Viscosity of [HMIm][Tf_2N] with increasing amounts of 1-octene (1) at 10 °C (blue circle), 25 °C (green square), 50 °C (orange triangle), and 75 °C (red diamond). Lines are smoothed data.

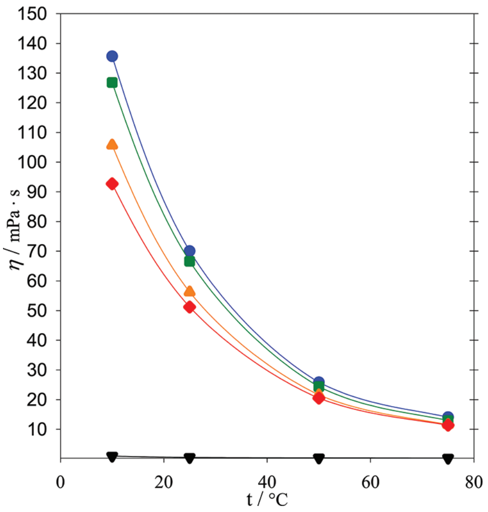

Figure 3. Effect of temperature and composition on viscosity of [HMIm][Tf_2N] at different concentrations of 1-octene (x_1): x_1 = 0 (blue circle), x_1 = 0.05 (green square), x_1 = 0.1 (orange triangle), x_1 = 0.15 (red diamond), and x_1 = 1 (black triangle). Lines are smoothed data.

temperatures were measured at (10, 25, 50, and 75) °C at ambient pressure. IL in the 1-octene phase is generally very small ($x_1 < 0.001$) except at the highest temperature investigated (75 °C), where $x_1 = 0.04$. These small concentrations render the viscosity of the 1-octene phase virtually identical to the pure component values within experimental error. The saturation compositions in the IL-rich phase as determined in our previous study[11] were x_1 = 0.16, 0.19, 0.23, and 0.28 at (10, 25, 50, and 75) °C, respectively. Table 1 lists the viscosity of both pure components at (25 and 50) °C from our method and from the literature. As shown, the relative viscosity of [HMIm][Tf_2N] at the two temperatures is within 3% of several literature reports.[22−25] The relative viscosity of pure 1-octene is between 0.2% and 5.8% of several literature reports.[26−30]

Figure 2 illustrates the mixture viscosity of the liquid phase with increasing composition of the 1-octene at the four isotherms. At all isotherms, the viscosity decreases with increasing composition of 1-octene. For instance at 25 °C, the viscosity at x_1 = 0.15 1-octene is 27 % lower than the pure ionic liquid. However, at 75 °C, the viscosity decrease at the same composition is only ≈ 16 % lower. The last data point at each isotherm represents the saturated conditions, after which a two-phase system emerges. Initially, adding 1-octene only slightly decreases the liquid viscosity, but after approximately x_1 = 0.05, the decrease becomes larger. At higher temperatures, the composition effect appears relatively linear. At the saturated composition, the viscosity of [HMIm][Tf_2N] phase decreases by 34 % at 10 °C, 35 % at 25 °C, 28 % at 50 °C, and 21 % at 75 °C over the pure component at the same temperature.

Figure 3 illustrates that the viscosity of the IL-phase with temperature at five compositions: x_1 = 0, 0.05, 0.10, 0.15, and 1. The classic exponential decay with temperature is observed at each composition. As shown, pure 1-octene is significantly less viscous than [HMIm][Tf_2N] or mixtures thereof. The cation and anion of ionic liquids have molecular forces of electrostatics, dispersion, and dipoles that interact with each other and the neutral nonpolar solute. The electrostatic interactions between cations and anions in IL (or between the ion pairs and other ion pairs) are affected by the neutral molecules of 1-octene which decreases the frictional forces during flow.

From our previous report, we have measured the density of the mixture at the same compositions as in the current study. Thus, the kinematic viscosity can be computed and is listed in Table 2. The kinematic viscosity follows similar qualitative trends as the dynamic viscosity. However, the relative percent decreases may be slightly different. For instance, the difference in the saturated viscosity and pure IL viscosity at 25 °C is approximately 35 % lower for dynamic viscosity and approximately 29 % lower for the kinematic viscosity.

Few reports exist in the literature of the mixture viscosity of [HMIm][Tf_2N] or other ILs with partially miscible (LLE) organic compounds. The viscosity of water-saturated [HMIm][Tf_2N] has been reported[31] and other studies of the effect of water on the viscosity of other ILs.[32,33] [HMIm][BF_4] and 1-pentanol form a liquid−liquid system at room temperature. Wagner et al.[34] measured the viscosity of a mixture at the upper critical solution composition (0.31 mass fraction of the IL) at temperatures just above the critical solution temperature of 41.8 °C, i.e., 1-phase. Andreatta et al.[35,36] measured the viscosity of mixtures of 1-octyl-3-methylimidazolium [Tf_2N] with alcohols and alkyl esters (ethyl acetate, etc.) across the full composition range.

Due to the wide range of possible molecular interactions between the two components, deviations can occur from ideal behavior. These viscosity deviations can be quantified by the viscosity deviation, $\Delta\eta$, also known as "excess viscosity" in other sources:

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

where η_m is the mixture viscosity and η_1 and η_2 are the pure component properties. This is not a strict "excess" property in the thermodynamic sense which is defined as the difference between a mixture property and its ideal solution value. The results for the viscosity deviation of 1-octene and [HMIm][Tf_2N] solutions are presented in Figure 4. Plots of the viscosity deviation with mole fraction of 1-octene for a binary 1-octene and [HMIm][Tf_2N] system at different temperatures demonstrates negative values throughout the composition range. Low compositions of 1-octene have nearly ideal mixture behavior ($\Delta\eta \approx 0$) as the 1-octene possibly resides in the free volume of ionic liquid structure changing little the electrostatic and dipolar interactions of the cation and anions. However, as more 1-octene dissolves, the

Table 2. Dynamic Viscosity, η, Density, ρ, and Computed Kinematic Viscosity, ν, for Mixtures of 1-Octene + [HMIm][Tf$_2$N]

	10 °C			25 °C			50 °C			75 °C		
x_1	η [mPa·s]	ρ^b [g·cm^{-3}]	$10^6\nu$ [m^2·s^{-1}]	η [mPa·s]	ρ^b [g·cm^{-3}]	$10^6\nu$ [m^2·s^{-1}]	η [mPa·s]	ρ^b [g·cm^{-3}]	$10^6\nu$ [m^2·s^{-1}]	η [mPa·s]	ρ^b [g·cm^{-3}]	$10^6\nu$ [m^2·s^{-1}]
0	136 ± 2	1.3854 ± 0.0004	98.17 ± 1.44	70.1 ± 0.8	1.3711 ± 0.0006	51.1 ± 0.6	25.8 ± 0.3	1.348 ± 0.002	19.14 ± 0.22	13.5 ± 0.2	1.324 ± 0.002	10.20 ± 0.15
0.05	127 ± 1	1.3721 ± 0.0008	92.56 ± 0.73	66.6 ± 0.7	1.360 ± 0.006	48.9 ± 0.5	24.4 ± 0.3	1.336 ± 0.002	18.26 ± 0.23	13.0 ± 0.2	1.313 ± 0.005	9.9 ± 0.16
0.1	106 ± 1	1.356 ± 0.005	78.17 ± 0.79	56.2 ± 0.8	1.344 ± 0.003	41.8 ± 0.6	21.6 ± 0.3	1.319 ± 0.006	16.38 ± 0.24	11.6 ± 0.2	1.3 ± 0.01	8.92 ± 0.17
0.15	93 ± 1	1.34 ± 0.01	69.4 ± 0.91	51.2 ± 0.6	1.326 ± 0.007	38.6 ± 0.5	20.5 ± 0.3	1.303 ± 0.002	15.73 ± 0.23	11.4 ± 0.2	1.279 ± 0.011	8.91 ± 0.17
0.16^a	91 ± 1	1.34 ± 0.009	67.91 ± 0.87									
0.19^a				48.0 ± 0.6	1.3204 ± 0.003	36.3 ± 0.5						
0.23^a							18.7 ± 0.3	1.300 ± 0.002	14.38 ± 0.23			
0.28^a										10.7 ± 0.2	1.267 ± 0.012	8.45 ± 0.18
1	0.56 ± 0.01	0.7235 ± 0.0006	0.77 ± 0.01	0.47 ± 0.01	0.7112 ± 0.0001	0.66 ± 0.01	0.37 ± 0.01	0.69 ± 0.01	0.54 ± 0.02	0.30 ± 0.01	0.668 ± 0.012	0.45 ± 0.02

[a] Saturated composition at respective temperature. [b] Density data from our previous report ref 11.

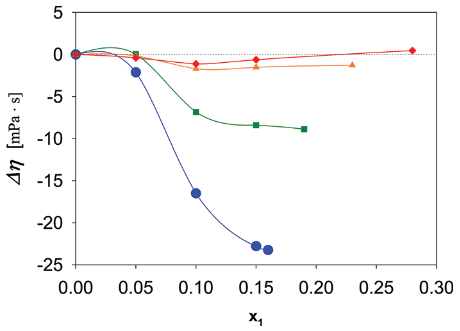

Figure 4. Effect of 1-octene composition on viscosity deviation of mixtures with [HMIm][Tf$_2$N] at 10 °C (blue circle), 25 °C (green square), 50 °C (orange triangle), and 75 °C (red diamond). Lines are smoothed data.

Table 3. Self-Diffusivity for Mixtures of 1-Octene +-[HMIm][Tf$_2$N] at (25 and 50) °C to the Saturation Limit

	$10^{11}D_{12}$ [m^2·s^{-1}]		$10^{11}D_{21}$ [m^2·s^{-1}]^a	
x_1	25 °C	50 °C	25 °C	50 °C
0	5.4^c	24.3^c	1.7 ± 0.1	5.5 ± 0.4
0.01	5.5 ± 0.6	24.9 ± 2.0	1.8 ± 0.1	5.7 ± 0.4
0.05	6.5 ± 0.5	26.3 ± 1.8	2.0 ± 0.1	6.5 ± 0.5
0.1	7.4 ± 0.5	29.3 ± 2.1	2.1 ± 0.2	7.3 ± 0.5
0.15	9.0 ± 0.6	31.3 ± 2.2	2.3 ± 0.2	7.7 ± 0.5
0.19^b	9.1 ± 0.6		2.4 ± 0.2	
0.23^b		31.0 ± 2.2		7.7 ± 0.5
1	228 ± 16	344 ± 24		

[a] Diffusivity of cation only. [b] Saturated composition at respective temperature. [c] Extrapolated infinite dilution value (D_{12}^{∞})

electrostatic and dipolar forces of the cation and anion (or ion pair) possibly become more screened and thus decrease long-range interactions. Without these long-range interactions, the barrier to motion decreases. However, the excess viscosities at higher temperatures (50 °C and 75 °C) are very close to zero indicating that the kinetic energy may overcome any solvation and simply act as a diluent of relatively low viscosity. Negative excess molar volume was computed for this system in our previous paper.[11] Similar to the viscosity deviation, the excess molar volume changes very little from zero with small amounts of 1-octene. However, larger negative values occur approaching the saturation limit at all temperatures, not just at the lower temperatures as seen in the viscosity deviation measurements. Wang et al.[37] measured both the excess molar volume, V^E, and viscosity, $\Delta\eta$, in the miscible system, 1-butyl-3-methylimidazolium [PF$_6$] and 3-pentanone, and found that the composition that produces a maximum in V^E produces a minimum in $\ln(\eta^E)$, which they discuss in terms of ion−dipole interactions. However, with few systems available with both excess volume and viscosity, clear trends are difficult to infer.

Self-Diffusivity in the 1-Octene and [HMIm][Tf$_2$N] System. The self-diffusivities of 1-octene and the cation of [HMIm]-[Tf$_2$N] at (25 and 50) °C were measured at different compositions and listed in Table 3. As shown in Figure 5, the self-diffusivity of 1-octene in a mixture with [HMIm][Tf$_2$N] increases as the composition of 1-octene is increased. From a x_1 of 0.01 to

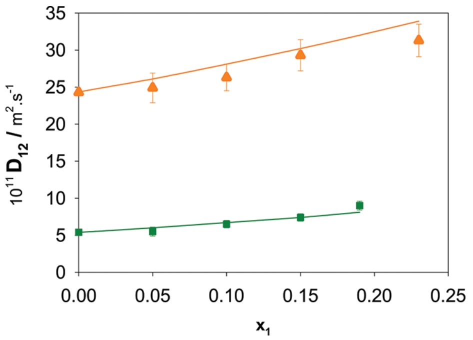

Figure 5. Self-diffusivity of 1-octene in a mixture with [HMIm][Tf_2N]: D_{21} at 25 °C (green square) and 50 °C (orange triangle). Lines are Stokes–Einstein predictions.

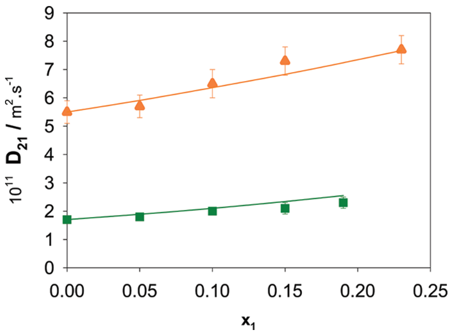

Figure 6. Self-diffusivity of the cation of [HMIm][Tf_2N] with a mixture of 1-octene: D_{21} at 25 °C(green square) and 50 °C (orange triangle). Lines are Stokes–Einstein predictions.

0.15, the self-diffusivity at 25 °C increases by approximately 64 % in the range of approximately $(25 \text{ to } 30)\cdot 10^{-11}$ $(m^2\cdot s^{-1})$. At the same compositions and at 50 °C, diffusivities increased just ≈ 26 %. The infinitely dilute diffusivity of 1-octene in the IL mixture, $D_{12}{}^{\infty}$, was estimated by extrapolating the experimental data to a mole fraction of 0 and presented in Table 3. As the solubility of the IL in the 1-octene phase was so low, a corresponding $D_{21}{}^{\infty}$ could not be experimentally obtained using the current technique. Morgan et al.[38] measured the tracer diffusion coefficient of the olefin, 1-butene, in [BMIm][Tf_2N] and obtained a value of $27\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 30 °C. However, these mixture diffusivities are over an order of magnitude less than the diffusivity of pure 1-octene: $228.3\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 25 °C and $344.2\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 50 °C. Literature reports of the self-diffusivity of pure 1-octene are unknown to the authors. However, Kasahara et al.[39] report the self-diffusivity of 1-hexene at 40 °C is approximately $500\cdot 10^{-11}$ $(m^2\cdot s^{-1})$. Smuda et al.[40] report the self-diffusivity of n-octane at 20 °C as approximately $230\cdot 10^{-11}$ $(m^2\cdot s^{-1})$.

Figure 6 illustrates that the diffusivity of the [HMIm] cation of [HMIm][Tf_2N] increases with increasing composition of 1-octene at (25 and 50) °C. The self-diffusion coefficients for the pure IL (cation) are $1.67\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 25 °C and $5.54\cdot 10^{-11}$ $m^2\cdot s^{-1}$ at 50 °C. These results compare favorably with literature reports of $1.75\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 25 °C and $5.05\cdot 10^{-11}$ $(m^2\cdot s^{-1})$ at 50 °C.[22] At 25 °C, the diffusivity of the IL cation in the mixture increases by ≈ 35 % from the pure component to 0.15 mol fraction of 1-octene. However, at 50 °C, the increase is approximately 40 % to the same composition. This lower percent increase at 25 °C may be due to a larger influence on specific interactions of the unsaturated 1-octene with the cation's delocalized electron system. This interaction would create a stronger complex at lower temperatures than at 50 °C, which has higher kinetic energy. The infinite dilution diffusion coefficients using a Taylor-dispersion technique have been reported for [HMIm][Tf_2N] in water, methanol, and acetonitrile by Sarraute et al.[41] with values on the order of 10^{-9} $(m^2\cdot s^{-1})$.

The Stokes–Einstein relationship, which relates the self-diffusivity to the viscosity and hydrodynamic radius, σ, is given by[42]

$$D = \frac{k_B T}{6\pi\sigma\eta} \tag{3}$$

where k_B is the Boltzmann constant. Assuming the hydrodynamic radius remains constant, the diffusivity is inversely related to the viscosity of the mixture and can be rearranged to the form of

$$D_{ij} = \frac{D_0}{\left(\dfrac{\eta}{\eta_0}\right)} \tag{4}$$

Here, D_0 and η_0 are taken as the pure IL self-diffusivity and viscosity respectively. For the case of the self-diffusivity of 1-octene in the mixture, the infinitely dilute diffusivity is utilized for $D_0 = D_{12}{}^{\infty}$. The mixture viscosities, η, were interpolated by an exponential function from the data in Table 2. This prediction is illustrated for each of the self-diffusivities in Figures 5 and 6. As shown, a relatively good prediction is achieved using the initial diffusivities and mixture viscosity data. The average absolute relative deviations (AARD) for both D_{12} and D_{21} from the prediction over both isotherms was less that 5 %. However, the assumption of constant hydrodynamic radius is probably not entirely valid across all of the conditions.

■ CONCLUSIONS

Transport properties are necessary for ultimate understanding and designing important chemical processes including reactions and separations. However, there is a distinct lack of data in this area for biphasic systems involving ionic liquids, which inhibit their implementation as a potential sustainable media. In this work, the system of 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ([HMIm][Tf_2N]) and 1-octene was investigated and the mixture viscosity and self-diffusivities were measured. These transport properties of the ionic liquid phase experience a significant improvement, i.e., lower viscosity and higher diffusivity, with the addition of 1-octene up to its saturation value. This is important as ionic liquids generally have a higher viscosities and lower diffusivities than conventional organic solvents. It appears that small additions of the octene may first fill the free volume of the ionic liquid followed by some level of interaction or solvation by the alkene group, which reduces the electrostatic and dipolar interactions of the cation and anion. Realistic applications will invariably feature mixtures whose properties will be superior to simply the pure component properties. These properties and the thermodynamic properties are being utilized in current interfacial mass transfer experiments.

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REFERENCES

(1) Holbrey, J. D.; Seddon, K. R. Ionic Liquids. *Clean Prod. Proc.* **1999**, *1* (4), 223–236.

(2) Zhao, H.; Xia, S.; Ma, P. Use of ionic liquids as 'green' solvents for extractions. *J. Chem. Technol. Biotechnol.* **2005**, *80* (10), 1089–1096.

(3) Roettger, D.; Nierlich, F.; Krissmann, J.; Wasserscheid, P.; Keim, W., Method for separation of substances by extraction or by washing them with ionic liquids. U.S. Patent No. 7,304,200, 2007.

(4) Smith, R. S.; Herrera, P. S.; Reynolds, J. S.; Krzywicki, A. Use of ionic liquids to separate diolefins. U.S. Patent App. 10/308,307, 2002.

(5) Pandey, S. Analytical applications of room-temperature ionic liquids: A review of recent efforts. *Anal. Chim. Acta* **2006**, *556* (1), 38–45.

(6) Ahosseini, A.; Ren, W.; Scurto, A. M. Homogeneous Catalysis in Biphasic Ionic Liquids/CO_2 Systems. *Chem. Today* **2007**, *25* (2), 40–42.

(7) Ahosseini, A.; Ren, W.; Scurto, A. M. Understanding Biphasic Ionic Liquid/CO_2 Systems for Homogeneous Catalysis: Hydroformylation. *Ind. Eng. Chem. Res.* **2009**, 95–101.

(8) Ahosseini, A.; Ren, W.; Scurto, A. M. Hydrogenation in biphasic ionic liquid/CO_2 systems. In *Gas Expanded Liquids and Near-Critical Media: Green Chemistry and Engineering*; Hutchenson, K., Scurto, A. M., Subramaniam, B., Eds.; ACS Symposium Series 1006; American Chemical Society: Washington, DC, 2009; Chapter 11, pp 218—234.

(9) Gangu, S. A.; Weatherley, L. R.; Scurto, A. M. Whole-Cell Biocatalysis with Ionic Liquids. *Curr. Org. Chem.* **2009**, *13* (13), 1242–1258.

(10) Fehér, E.; Illeová, V.; Kelemen-Horváth, I.; Bélafi-Bakó, K.; Polakovič, M. L. G. Enzymatic production of isoamyl acetate in an ionic liquid-alcohol biphasic system. *J. Mol. Catal. B.* **2008**, *50*, 28–32.

(11) Ahosseini, A.; Sensenich, B.; Weatherley, L.; Scurto, A. Phase Equilibrium, Volumetric, and Interfacial Properties of the Ionic Liquid, 1-Hexyl-3-Methyl-Imidazolium Bis(Trifluoromethylsulfonyl)amide and 1-Octene. *J. Chem. Eng. Data* **2010**, *55* (4), 1611–1617.

(12) Anon., Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems. *Chem. Int.* **2005**, *27*, (5), 22-23.

(13) Marsh, K. N.; Brennecke, J. F.; Chirico, R. D.; Frenkel, M.; Heintz, A.; Magee, J. W.; Peters, C. J.; Rebelo, L. P. N.; Seddon, K. R. Thermodynamic and thermophysical properties of the reference ionic liquid: 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]-amide (including mixtures). Part 1. Experimental methods and results (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81* (5), 781–790.

(14) Nockemann, P.; Binnemans, K.; Driesen, K. Purification of imidazolium ionic liquids for spectroscopic applications. *Chem. Phys. Lett.* **2005**, *415* (1—3), 131–136.

(15) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35* (5), 1168–1178.

(16) Price, W. Pulse-Field Gradient Nuclear Magnetic Resonance as a Tool for Studying Translational Diffusion: Part 1. *Basic Theory, Concepts Magn. Reson.* **1997**, *9*, 299–336.

(17) Price, W. S. Pulse-field gradient nuclear magnetic resonance as a tool for studying translational diffusion. II. Experimental aspects. *Concepts Magn. Reson.* **1998**, *10*, 197–237.

(18) Schleicher, J. C., Kinetics and Solvent Effects in the Synthesis of Ionic Liquids. MS Thesis, 2007.

(19) Harris, K. R. Temperature and density dependence of the self-diffusion coefficient of n-hexane from 223 to 333 K and up to 400 MPa. *J. Chem. Soc., Faraday Trans.* **1982**, *78* (7), 2265–2274.

(20) Krynicki, K.; Green, C. D.; Sawyer, D. W. Pressure and temperature dependence of self-diffusion in water. *Faraday Discuss. Chem. Soc.* **1978**, *66*, 199–208.

(21) Kerssebaum, R. DOSY and diffusion by NMR. *Bruker BioSpin, Rheinstetten, Germany* **2002**, 3–23.

(22) Tokuda, H.; Ishii, K.; Susan, M.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. Physicochemical Properties and Structures of Room-Temperature Ionic Liquids. 3. Variation of Cationic Structures. *J. Phys. Chem. B* **2006**, *110* (6), 2833–2839.

(23) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37* (6), 559–568.

(24) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation. *J. Phys. Chem. B* **2005**, *109* (13), 6103–6110.

(25) Widegren, J. A.; Magee, J. W. Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* **2007**, *52* (6), 2331–2338.

(26) Crossley, J. Dielectric relaxation of l-alkenes. *J. Chem. Phys.* **1973**, *58* (12), 5315–5318.

(27) Naziev, Y. Study of the dynamic viscosity of 1-heptene and 1-octene at high pressures. *Chem. Technol.* **1976**, *28* (12), 736–738.

(28) Wright, F. J. Influence of Temperature on Viscosity of Non-associated Liquids. *J. Chem. Eng. Data* **1961**, *6* (3), 454–456.

(29) Yarranton, H. W.; Satyro, M. A. Expanded Fluid-Based Viscosity Correlation for Hydrocarbons. *Ind. Eng. Chem. Res.* **2009**, *48* (7), 3640–3648.

(30) Yaws, C. L. *Handbook of Viscosity*; Gulf Publishing Company: Houston, TX, 1995; Vol. 3, p 52.

(31) Fitchett, B. D.; Knepp, T. N.; Conboy, J. C. 1-Alkyl-3-methylimidazolium Bis(perfluoroalkylsulfonyl)imide Water-Immiscible Ionic Liquids. *J. Electrochem. Soc.* **2004**, *151* (7), E219–E225.

(32) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. Density and viscosity of serveral pure and water-saturated ionic liquids. *Green Chem.* **2006**, *8*, 172–180.

(33) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72* (12), 2275–2287.

(34) Wagner, M.; Stanga, O.; Schroer, W. Critical viscosity near the liquid liquid phase transition in the solution of the ionic liquid 1-methyl-3-hexylimidazolium tetrafluoroborate in 1-pentanol. *Phys. Chem. Chem. Phys.* **2004**, *6* (8), 1750–1757.

(35) Andreatta, A.; Arce, A.; Rodil, E.; Soto, A. Physical and excess properteis of (methylacetate + methanol + 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) and its binary mixtures at $T = 298.15$ K and atmospheric pressure. *J. Chem. Thermodyn.* **2009**, *41*, 1317–1323.

(36) Andreatta, A.; Arce, A.; Rodil, E.; Soto, A. Physical properties of binary and ternary mixtures of ethylacetate, ethanol and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) at 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 1022–1025.

(37) Wang, J.; Zhu, A.; Zhuo, K. Excess molar volumes and excess logarithm viscosities for binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with some organic compounds. *J. Solution Chem.* **2005**, *34*, 585–596.

(38) Morgan, D.; Ferguson, L.; Scovazzo, P. Diffusivities of gases in room-temperature ionic liquids: data and correlations obtained using a lag-time technique. *Ind. Eng. Chem. Res.* **2005**, *44*, 4815–4823.

(39) Kasahara, Y.; Suzuki, Y.; Kabasawa, A.; Minami, H.; Matsuzawa, H.; Iwahashi, M. CH/π interaction between benzene and hydrocarbons having six carbon atoms in their binary mixture. *J. Oleo Sci.* **2010**, *59* (1), 21–29.

(40) Smuda, C.; Busch, S.; Gemmecker, G.; Unruh, T. Self-diffusion in molecular liquids: medium-chain n-alkanes and coenzyme Q_{10} studied by quasielastic neutron scattering. *J. Chem. Phys.* **2008**, *129*, 014513.

(41) Sarraute, S.; Gomes, M. F. C.; Padua, A. A. H. Diffusion coefficients of 1-alkyl-3-methylimidazolium ionic liquids in water, methanol, and acetonitrile at infinite dilution. *J. Chem. Eng. Data* **2009**, *54* (9), 2389–2394.

(42) Atkins, P. *Physical Chemistry*, 6th ed.; W.H. Freeman and Company: New York, 1998.

(43) See ref 30.

(44) Crossley, J. Dielectric relaxation of l-alkenes. *J. Chem. Phys.* **1973**, *58* (12), 5315–5318.

(45) Ahosseini, A.; Scurto, A. M. Viscosity of Imidazolium-Based Ionic Liquids at Elevated Pressures: Cation and Anion Effects. *Int. J. Thermophys.* **2008**, *29*, 1222–1243.