

The Viscosity and Density of Ionic Liquid + Tetraglyme Mixtures and the Effect of Tetraglyme on CO₂ Solubility

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Supporting Information

ABSTRACT: We show that the addition of tetraglyme (TG), which is a low viscosity liquid with relatively low vapor pressure, is effective in reducing the viscosity of ionic liquids (ILs). In particular, we measure the viscosities of mixtures of 18 ionic liquids with tetraglyme at temperatures between 278.15 and 323.15 K, with a focus on mixtures that are primarily ionic liquid. Thirteen of the ionic liquids contain aprotic heterocyclic anions (AHA ILs) paired with tetra-alkylphosphonium and imidazolium cations, which we have developed for cofluid vapor compression refrigeration and postcombustion CO₂ capture applications. Three bis(trifluoromethylsulfonyl)amide ($[Tf_2N]^-$) ionic liquids are included for comparison, as well as trihexyltetradecylphosphonium acetate and trihexyltetradecylphosphonium dicyanamide ([P₆₆₆₁₄][acetate] and [P₆₆₆₁₄][DCA]). In addition, we present the densities of trihexyltetradecylphosphonium 1,2,3-triazolide ([P₆₆₆₁₄][3-Triz]) + tetraglyme mixtures at temperatures



between 283.15 and 353.15 K. Finally, we show that the solubility of CO_2 in mixtures of $[P_{66614}]$ [3-Triz] + 30 mol % tetraglyme and trihexyltetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄][4-Triz]) + 30 mol % tetraglyme at 313.15, 333.5, and 353.6 K and pressures to 34 bar can be represented reasonably well by a mole fraction weighted sum of the solubilities (on a mole ratio basis) in the two pure components.

1. INTRODUCTION

The viscosities of many ILs (salts with melting points below $373.15 \text{ K})^1$ are quite high, leading to poor mass transfer and increased pumping costs if they were to be used in flow processes. One way to reduce the viscosity is judicious choice of cations, anions, and substituents, which is a major reason for the popularity of ILs containing the bis(trifluoromethylsulfonyl)amide ($[Tf_2N]^-$) anion.^{2–4} For cofluid vapor compression refrigeration and postcombustion CO₂ capture applications, we have developed ILs containing aprotic heterocyclic anions (AHAs).⁵⁻⁸ Unfortunately, some of the AHA ILs have relatively high viscosities, especially at low temperatures.² Therefore, here we consider the use of a low viscosity additive or diluent as a way to lower the viscosity.

Many research groups have measured properties of ILs mixed with solvents such as water,^{9–24} ethanol,^{12,13,25} diethyl ether,¹² acetone,^{12,25} methanol,^{25,26} 1-methylimidazole,¹⁰ toluene,^{10,24,25} 1,4-dimethylbenzene,¹⁰ 1,2-dimethoxyethane,¹⁰ ethanenitrile,¹⁰ 2-propenenitrile,¹⁰ trimethylethanenitrile,¹⁰ hexane,^{12,25,27} ben-zene,^{25,27} phenol,²⁷ anisole,²⁷ acetophenone,²⁷ benzoic acid,^{24,27} methylbenzoate,²⁷ benzaldehyde,²⁷ 1-chlorohexane,²⁷ 1-hexa-nol,^{25,27–29} 1-propanol,^{25,28,29} 1-butanol,^{25,28,29} 1-octanol,^{16,23,28} butyl ethyl ether,²⁷ cyclohexane,^{25,27} 2-hexanone,²⁷ hexanoic acid,²⁷ methyl pentanoate,²⁷ and 1,4-butanediol.²⁷ Some of the solvents used were chosen because they are completely miscible with the ILs, whereas others were chosen because they are not and might be candidates for separation using the IL in a liquid-liquid extraction system.^{12,24,27,30-32} Tetraglyme is not a common additive for ionic liquids. Our group has previously used it to reduce viscosity and eliminate mass transfer

resistances so that we could determine the kinetics of CO₂ reacting with amino acid and AHA-based ILs. In this case, the ILs were very dilute in the tetraglyme, and associated viscosity measurements were focused on these dilute solutions in that study.³³ Nonetheless, tetraglyme is a very good choice as a diluent for ILs because it has low vapor pressure³⁴ and low viscosity.35

A common way to correlate viscosity data as a function of temperature is the Vogel-Fulcher-Tamman equation,³⁷

$$\mu = \mu_o \exp\left(\frac{B}{T - T_o}\right) \tag{1}$$

where μ_{o} , *B*, and T_0 are the fitting parameters. T_0 should be close to the glass transition temperature, ^{40–43} but here it is used as an adjustable parameter. A discussion of the origin and theoretical basis of the Vogel-Fulcher-Tamman (VFT) equation can be found elsewhere.^{44,45} The modified Vogel-Fulcher–Tamman equation adds a factor of $T^{0.5}$ in order to try to fit experimental data better.¹⁵ Subsequently, the Litovitz⁴⁶ and other equations⁴⁷ have been proposed by different researchers.^{48,49}

In addition, there are multiple ways to represent the viscosity of a mixture of two liquids. Arrhenius⁵⁰ proposed an equation based on the logarithm of the viscosity, which is

$$\log(\mu_{\rm m}) = x_1 \log \mu_1 + x_2 \log \mu_2 \tag{2}$$

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Table 1. Structure of the Family of Cations and Anions Investigated in This Study. Bracket Denotes It Is Not a Family of Ions, But the Specific One Used in This Study



where x_1 and x_2 are the mole fractions of the two liquids, μ_1 and μ_2 are the viscosities of the two pure liquids, and μ_m is the viscosity of the mixture. This equation is entirely predictive and does not always adequately represent experimental data. Therefore, Grunberg and Nissan⁵¹ added an additional term containing an adjustable parameter, which leads to

$$\log(\mu_{\rm m}) = x_1 \log \mu_1 + x_2 \log \mu_2 + x_1 x_2 G \tag{3}$$

where *G* is a constant for a particular binary mixture. Alternatively, *G* can be assumed to be a slight function of temperature.¹⁸ Katti and Chaudhri⁵² incorporated the molar volume into the equation

$$\log(\mu_{\rm m} V_{\rm m}) = x_1 \log(\mu_1 V_1) + x_2 \log(\mu_2 V_2) + x_1 x_2 \frac{W_{\rm visc}}{RT}$$
(4)

where w_{visc} is the interaction parameter for the activation of flow. Redlich–Kister⁴⁶ and other groups^{53–56} have proposed additional correlations for the viscosity of mixtures of two liquids.

As mentioned above, the cations and anions of an IL can be adjusted in numerous ways in order to obtain desired physical properties. Unfortunately, adjustments can improve some properties while worsening others. For instance, cations with long alkyl chains, such as $[P_{66614}]^+$, suppress melting points but are relatively viscous.² Reducing the size of the cation tends to reduce the viscosity, but could lead to the appearance of a melting point. Previously, we have shown² that the triethyloctylphosphonium ($[P_{2228}]^+$) cation is a good compromise for many AHA anions. As mentioned above, AHA ILs with the [4-NO₂pyra]⁻ and [3-Triz]⁻ anions are of particular interest for cofluid vapor compression refrigeration applications. Unfortunately, the melting point of $[P_{2228}]$ [3-Triz] is above room temperature² because of easy stacking of the anion, so longer alkyl chains are required. Moreover, the viscosities of [P₆₆₆₁₄][3-Triz] and [P₂₂₂₈][4-NO₂pyra] (as well as [P₆₆₆₁₄][4-NO₂pyra]) are higher than desired, so tetraglyme is investigated as an additive to reduce the viscosity. The data were fit with the empirical equations described above in order to estimate how much tetraglyme would be required to achieve a particular viscosity. A variety of IL + tetraglyme mixtures are investigated to establish trends in the data. The effect of tetraglyme on mixture density and the solubility of CO_2 in the mixtures is also of interest. Therefore, we present detailed measurements of density for the $[P_{66614}]$ [3-Triz] + tetraglyme system and CO₂ solubility measurements for $[P_{66614}]$ [3-Triz] + tetraglyme and $[P_{66614}]$ [4-Triz] + tetraglyme.

2. EXPERIMENTAL SECTION

Materials. Table 1 and Table 2 show the structure, name, abbreviation, and purity of the ILs used in this work. The materials and synthesis have been reported previously for $[P_{66614}][Tf_2N]$,

Table 2. Materials Used, Including Full Name and Abbreviation for All Ionic Liquids Investigated

		purity (mass %)
carbon dioxide, Praxair, CAS no. 124-38-9 ^a	CO ₂	99.995
2,5,8,11,14-pentaoxapentadecane, Sigma-Aldrich, CAS no. 143-24-8 ^a	tetraglyme, tetraethylene glycol dimethyl ether	99
trihexyl(tetradecyl)phosphonium 4-nitro imidazolide b	[P ₆₆₆₁₄][4-NO ₂ imid]	98
trihexyl(tetradecyl)phosphonium 4,5-dicyano imidazolide ^b	[P ₆₆₆₁₄][4,5-CNimid]	99
trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imi- de ^b	$[P_{66614}][Tf_2N]$	99
trihexyl(tetradecyl)phosphonium 2-methyl-5-nitro imidazolide ^b	[P ₆₆₆₁₄][2-CH ₃ ,5-NO ₂ imid]	99
trihexyl(tetradecyl)phosphonium dicyanamide, Sigma-Aldrich ^a	[P ₆₆₆₁₄][DCA]	95
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide b	$[hmim][Tf_2N]$	99
trihexyl(tetradecyl)phosphonium 6-bromo-benzimidazolide b	[P ₆₆₆₁₄][BrBnim]	99
trihexyl(tetradecyl)phosphonium acetate b	[P ₆₆₆₁₄][Acetate]	99
1-hexyl-2-methyl-3-methylimidazo- lium bis(trifluoromethylsulfonyl) imide b	$[hmmim][Tf_2N]$	97
trihexyl(tetradecyl)phosphonium 1,2,4 triazolide ^b	[P ₆₆₆₁₄][4-Triz]	99
trihexyl(tetradecyl)phosphonium 1,2,3 triazolide ^b	[P ₆₆₆₁₄][3-Triz]	99
tributyl(dodecyl)phosphonium 1,2,3 triazolide ^b	[P ₄₄₄₁₂][3-Triz]	99
octyltriethylphosphonium 4-nitro pyrazolide ⁶	[P ₂₂₂₈][4-NO ₂ pyra]	97
octyltriethylphosphonium 4-nitro imidazolide ^b	[P ₂₂₂₈][4-NO ₂ imid]	95
octyltriethylphosphonium 2-methyl-5-nitro imidazolide b	[P ₂₂₂₈][2-CH ₃ ,5-NO ₂ imid]	99
1-butene-2-methyl-3-methylimida- zolium 4-nitro pyrazolide ^b	[mm(butene)im][4-NO ₂ pyra]	98
butyltriethylphosphonium 2-methyl- 5 -nitro imidazolide ^b	[P ₂₂₂₄][2-CH ₃ ,5-NO ₂ imid]	95
1-propyl-2-methyl-3-methylimidazo- lium 4-nitro pyrazolide b	[pmmim][4-NO ₂ pyra]	97
^{<i>a</i>} Used without further purificati	on. ^b Synthesized in house.	

 $\begin{array}{l} [P_{66614}][acetate], [hmim][Tf_2N], [P_{66614}][3-Triz], [P_{44412}][3-Triz], \\ [P_{2228}][4-NO_2pyra], [P_{2228}][4-NO_2imid], [P_{2228}][2-CH_3, \\ S-NO_2imid], [P_{2224}][2-CH_3, \\ S-NO_2imid], [P_{2224}][2-CH_3, \\ S-NO_2imid], [mm(butene)im] \\ [4-NO_2pyra], [pmmim][4-NO_2pyra], [P_{66614}][BrBnim] and \\ [P_{66614}][4-Triz].^{2,57} [P_{66614}][DCA] was ordered from Sigma- \\ Aldrich (95\% purity) and dried under vacuum prior to measurements. \end{array}$

The synthesis of [hmmim][Tf₂N] involves a two-step procedure. The first step of mixing dimethylimidazole (Sigma-Aldrich, 98% purity) with 1-bromohexane (Acros Organics, 98% purity) takes place in toluene (Sigma-Aldrich, 99.8% purity) at about 273 K for 1 to 2 days. This is the same alkylation procedure used in our previous work.² When the stirring is stopped, the mixture separates into two liquid phases. More toluene is added, and the toluene-rich phase is decanted. This process is repeated to remove residual alkyl halide. NMR confirms the purity of the [hmmim][Br] product. The second step involves dissolving [hmmim][Br] in water, adding lithium bis(trifluoromethylsulfonyl)imide (3M, trace impurities) and stirring overnight. The [hmmim][Tf₂N] product is not miscible with water so it forms a separate liquid phase. The water containing the LiBr byproduct is removed by decanting. More water is added and decanted until LiBr is no longer present, as determined by testing the aqueous phase with AgNO₃ solution and observing no precipitate. $[hmmim][Tf_2N]$ is dried on a vacuum line to remove the remaining water, and then the purity is determined with NMR spectroscopy. The NMR spectrum for this IL is shown in the Supporting Information.

Prior to preparation of any mixtures, the water content of the IL was measured using a Brinkman 831 Karl Fischer coulometer. If the water content was high (above weight fraction of 0.0005), the IL was dried further under vacuum (~0.013 Pa at 323 K). Tetraethylene glycol dimethyl ether (Sigma-Aldrich, 99% purity, IUPAC name 2,5,8,11,14-pentaoxapentadecane), also known as tetraglyme, was used without drying unless it was above 0.0005 weight fraction. Each mixture was made in a glovebox under nitrogen to prevent absorption of water from the atmosphere and then stirred for about an hour. The mixture was examined to ensure it was completely mixed and that only one phase existed. If two phase are present, no measurements are taken for that overall composition. Prior to any measurements, the water content of the mixture is measured to make sure it is below 0.0005 weight fraction.

Viscosity. The viscosity of each mixture was measured with an ATS viscoanalyzer under a flow of dry nitrogen. A parallel plate spindle with 30 mm diameter was used, and the gap was set at 0.300 mm. The stress was varied from 0.1 to 25 Pa. The instrument requires 0.3-0.4 mL of sample. The estimated uncertainty is $\pm 6\%$. The lower limit of the viscosity apparatus is 50 mPa·s. Between 50 and 100 mPa·s the viscosity tends to be overestimated. Above 150 mPa·s, the apparatus tends to

Table 3a. Viscosity of [P₆₆₆₁₄][4-NO₂imid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			μ/mPa ·s								
IL mole fraction	water content before/after (weight fraction ×10²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0173/0.1055	3376	2222	1497	1036	735	533	396	298	230	180
0.811	0.0233/0.0597	1503	1036	726	522	384	290	222	173	138	111
0.596	0.0302/0.0488	443	324	240	180	135	107	85	70	57	
0 ⁵⁹		5.91	5.06	4.37	3.84	3.4	2.99	2.77	2.44	2.24	2.02

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3b. Viscosity of [P₆₆₆₁₄][4,5-CNimid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			μ/mPa ·s									
IL mole fraction	water content before/after (weight fraction ×10 ²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	
1 ²	0.0151/0.0764	2489	1628	1092	754	535	391	291	220	171	135	
0.799	0.0258/0.0430	1051	723	507	365	269	203	156	123	98	79	
0.599	0.0285/0.0496	389	283	209	158	122	97	77	63			
^a Standard u	ncertainties u are $u(T) = 0.1$ K	and $u(p)$	= 0.005 M	Pa, and rel	ative stand	ard uncerta	unty <i>u_r</i> is <i>u</i>	$u_{\rm r}(\mu) = 0.00$	6 for new v	alues repo	rted here.	

Table 3c. Viscosity of [P₆₆₆₁₄][Tf₂N] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			$\mu/\mathrm{mPa}\cdot\mathrm{s}$										
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	<i>T</i> /K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 313.15	T/K = 323.15				
1 ²	0.0061/0.0169	1210	841	594	430	318	241	145	92				
0.809	0.0259/0.1078	589	414	299	221	168	130	83	60				
0.634	0.0322/0.0458	281	207	157	121	96	77	52					
0.441	0.0300/0.0824	111	85	67	54								
0.336	0.0226/0.0863	64	51										

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3d. Viscosity of [P₆₆₆₁₄][2-CH₃,5-NO₂imid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			$\mu/\mathrm{mPa}\cdot\mathrm{s}$										
IL mole fraction	water content before/after (weight fraction ×10 ²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15		
1 ²	0.0193/0.1286	5887	3730	2421	1619	1114	786	569	420	317	244		
0.849	0.0215/0.0725	2535	1685	1140	791	563	411	306	232	179	141		
0.601	0.0310/0.0692	595	425	308	228	173	134	106	85	69	57		
^a Standard u	ncertainties u are $u(T) = 0.1$ K	and $u(p)$	= 0.005 M	Pa, and rel	ative stand	ard uncerta	ainty <i>u_r</i> is <i>u</i>	$q_{\rm r}(\mu) = 0.0$	6 for new v	alues repo	rted here.		

Table 3e. Viscosity of [P₆₆₆₁₄][DCA] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			$\mu/\mathrm{mPa}\cdot\mathrm{s}$									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	
158		1646.8	1144.9	816.36	592.93	438.57	329.68	251.71	195.00	153.15	121.78	
1	0.0068/0.0501	1750	1210	842	603	442	331	253	196	155	124	
0.901	0.0122/0.0519	1130	794	566	413	308	234	182	143	115	93	
0.797	0.0171/0.0487	708	508	370	275	209	162	128	103	83	69	
0.701	0.0156/0.0414	479	348	258	195	151	119	96	78	64	54	
0.499	0.0225/0.0651	160	122	95	75	61						
0.348	0.0207/0.1263	73	57									

"Standard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3f. Viscosity of $[hmim][Tf_2N]$ Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures.^{*a*} The Data Are Consistent with Higher Temperature Mixture Data Published Elsewhere⁶⁰

			μ/m	Pa∙s	
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15
1 ²	0.0031/0.0134	203	150	113	87
1	0.0053/0.0220	204	151	115	89
0.901	0.0208/0.0429	171	126	96	74
0.810	0.0169/0.0292	130	97	74	57
0.724	0.0148/0.0304	109	81	63	
0.587	0.0250/0.0272	78	60		
0.456	0.0142/0.0624	50			

^{*a*}Standard uncertainties *u* are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

underestimate the viscosity by about 3%. The viscosity of the mixtures were measured from 278.15 to 323.15 K in 5 K increments. The viscosity of $[P_{66614}][DCA]$ matches previously published data within the experimental uncertainty.⁵⁸ A comparison of the pure IL viscosities with literature data was provided in a previous paper.² The viscosity of pure tetraglyme was taken from the literature.⁵⁹ The viscosity of the mixture of [hmim][Tf₂N] with tetraglyme follows the same trend as observed for this mixture previously at higher temperatures.⁶⁰

Density. The density of mixtures of $[P_{66614}]$ [3-Triz] and tetraglyme was measured with an oscillating u-tube Anton Paar 4500 densitometer. The instrument requires about 1.7 mL of sample. Even though the densitometer has a reported uncertainty of ±0.00005 g cm⁻³, we estimate that based on the purity of $[P_{66614}]$ [3-Triz] the uncertainty in the density measurements is ±0.002 g cm⁻³ with a repeatability (for the same sample of IL) of ±0.0001 g cm⁻³. The densities of the particular batches of pure $[P_{66614}]$ [3-Triz] and tetraglyme used to make the mixtures were

Table 3g. Viscosity of [P₆₆₆₁₄][BrBnIm] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		$\mu/mPa \cdot s$									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
157			4346		1903	1319	936		491		278
1	0.0071/0.1897	7870	4760	2960	1910	1270	872	613	441	325	246
0.898	0.0322/0.1791	4400	2780	1780	1190	813	572	413	304	230	177
0.862	0.0291/0.1351	3390	2190	1440	972	675	481	351	261	199	155
0.782	0.0382/0.1366	2070	1360	913	631	449	326	243	185	143	114
0.654	0.0414/0.0897	954	597	420	301	222	167	129	101	81	66
0.522	0.0255/0.1771	426	304	220	164	125	98	77	63	51	
0.362	0.0414/0.1571	138	103	80	62						

^aStandard uncertainties *u* are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3h. Viscosity of [P₆₆₆₁₄][Acetate] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

			μ/mPa·s								
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0705/0.3100	1820	1200	814	566	406	298	224	172	135	107
0.897	0.0729/0.1361	1160	789	549	392	287	216	166	130	103	84
0.793	0.0658/0.1500	651	462	332	244	184	142	112	89	73	60
0.701	0.0671/0.1326	401	291	215	162	125	99	79	64	53	
0.600	0.0681/0.1478	257	191	145	111	88	70	57			
0.501	0.0659/0.2437	176	121	92	73	58					
^a Standard u	ncertainties u are $u(T) = 0.1$ H	X and u(p)	= 0.005 M	Pa, and rel	ative stand	ard uncerta	ainty <i>u_r</i> is <i>u</i>	$u_{\rm r}(\mu) = 0.00$	6 for new v	alues repo	rted here.

Table 3i. Viscosity of [hmmim][Tf₂N] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		µ/mPa·s									
IL mole fraction	water content before/after (weight fraction ×10 ²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 323.15		
1	0.0011/0.0170	485	335	236	172	129	99	78	63		
0.898	0.0189/0.0198	370	258	184	135	103	80	64	52		
0.795	0.0175/0.0266	251	177	129	96	74	58				
0.694	0.0204/0.0421	161	116	86	66	51					
0.601	0.0250/0.0418	109	81	61							
0.501	0.0285/0.0556	70	53								
0.401	0.0349/0.0703	48									

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3j. Viscosity of $[P_{66614}]$ [4-Triz] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures⁴

		μ/mPa ·s									
IL mole fraction	water content before/after (weight fraction ×10 ²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
157			3338		1390	1024	664		367		224
1	0.0091/0.0830	4640	2980	1960	1320	918	654	477	354	269	209
0.954	0.0245/0.2750	3290	2150	1440	994	706	512	382	289	223	176
0.874	0.0170/0.1139	2080	1400	961	679	491	364	275	212	166	133
0.804	0.0134/0.1600	1470	1010	708	508	374	281	217	169	135	109
0.751	0.0145/0.1181	989	691	493	360	269	205	160	126	102	83
0.694	0.0330/0.1586	709	504	366	272	208	162	129	104	86	71
0.610	0.0346/0.1823	415	299	220	167	128	101	81	66	54	
0.516	0.0340/0.2183	259	191	145	111	88	70	57			
0.418	0.0346/0.2328	163	110	85	66	53					
^{<i>a</i>} Standard u	ncertainties u are $u(T) = 0.1$	K and $u(p)$	= 0.005 N	/IPa, and re	lative expa	nded stand	lard <i>u</i> . is u	$L(\mu) = 0.00$	6 for new v	alues repo	rted here

measured here in order to obtain as accurate values as possible with which to calculate the excess molar volumes of the mixtures.

CO₂ Solubility. The measurement of CO_2 solubility is done using a custom built high pressure and temperature apparatus

(HPTA). Five mL of sample is required, which is mixed with a PPI DYNA/MAG mixer that runs continuously, breaking the gas/liquid interface, and rotates at 2500 rpm. The HPTA uses a DKN 600 mechanical convention oven that controls the

temperature between 313.15 and 353.15 K with an uncertainty of ± 0.15 K. The HPTA has a pressure range from vacuum (Welch Chem Star 1400N vacuum pump capable of 0.013 Pa) to 5.0 MPa. Once the system is evacuated and the temperature is equilibrated, a small amount of CO₂ (Praxair, 99.995% purity) is transferred from a reservoir to the sample cell. Equilibrium is determined by steady pressure and temperature in both the reservoir and the sample cell. From the pressure and temperature of CO₂, the molar density is calculated with the Span Wagner equation of state (EOS).⁶¹ This assumes that the vapor phase in both the reservoir and the sample cell is pure CO₂, which is reasonable since the vapor pressure of the IL and the TG (tetraglyme) are both extremely small. The molar density times the volume gives the moles of CO₂ present in each of the vessels, both before and after addition of CO₂ to the sample cell. The amount of moles of CO₂ in the liquid is simply the total moles added from the reservoir minus the moles of vapor CO_2 in the sample cell. From this, the mole ratio and mole fraction can be determined based on the amount of liquid sample used. The volume expansion of the liquid can be measured based on the increase in height of the liquid when exposed to CO2. The overall standard uncertainty for the measurements is $u(x_{CO2}) = 0.02$. However, this overstates the uncertainty at lower pressures. For mole fractions of CO₂ less than 0.1, the standard uncertainty is closer to $u(x_{CO2}) = 0.01$.

The solubility of CO_2 was measured in pure $[P_{66614}][4-Triz]$ using a Hiden Intelligent Gravimetric Analyzer. The details of these measurements are provided elsewhere.¹¹

3. RESULT AND DISCUSSION

Viscosity. Each of the 18 ILs was mixed with tetraglyme and the viscosities measured as a function of temperature and composition. The results are shown in Tables 3a-3r. The water content of the samples was measured both before and after the viscosity measurements and these values are shown in the tables. Despite efforts to exclude water vapor, all of the samples increase somewhat in water content over the course of the measurements. Also shown in the tables are previously published measurements of the viscosities of the pure ILs, when available.^{2,57,58} All of the pure IL viscosities match previously published values within experimental uncertainties except $[P_{2228}][4-NO_2pyra]$. The sample of $[P_{2228}][4-NO_2pyra]$ used here was part of a 2 L bulk synthesis that was of lower purity (97%) than the sample used in a previous publication,² which can account for the 20% higher viscosity reported here.

Table 3l. Viscosity of $[P_{44412}][3$ -Triz] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^{*a*}

				μ/m	Pa∙s		
IL mole fraction	water content before/ after (Weight fraction $\times 10^2$)	T/K = 278.15	<i>T</i> /K = 283.15	<i>T/</i> K = 288.15	<i>T</i> /K = 293.15	<i>T/</i> K = 298.15	T/K = 303.15
1 ²	0.0220/ 0.0420	2660	1660	1060	706	484	343
0.938	0.0300/ 0.2600	1980	1260	824	557	389	280
0.877	0.0280/ 0.2145	1230	809	549	383	276	203
0.845	0.0236/ 0.3170	907	608	419	297	218	164
0.786	0.0226/ 0.1946	671	458	320	231	171	130
0.695	0.0202/ 0.1597	361	256	186	139	107	84
0.605	0.0330/ 0.1860	226	165	124	95	74	59
0.505	0.0272/ 0.2168	131	98	75	59		
0.404	0.0280/	73	57				

^{*a*}Standard uncertainties *u* are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

As expected, the viscosities of all 18 ILs decrease with increasing temperature and increasing tetraglyme composition. The IL/tetraglyme binary mixture viscosity data was fit using eq 3, obtaining different values of the empirical parameter, G, for each temperature (Table 4). Note that if G = 0, this reduces to eq 2, which is entirely predictive, as long as one has the pure component viscosities, and indicates that the logarithm of the viscosity is a linear function of composition (in mole fraction). The motivation of this study was the addition of small amounts of tetraglyme to the ILs in order to reduce their viscosities to values that could be more easily handled in flow equipment. Therefore, the emphasis in fitting the data was placed on the mixtures with small amounts of added tetraglyme. In addition, we chose to use the same number of data points to fit the G values at each temperature. Therefore, some of the lower viscosity data points (higher tetraglyme concentrations) were

Гable 3k. Viscosity of [Р ₆	₆₆₁₄][3-Triz]	Mixed with '	Tetraglyme at 0.1	l MPa and Various	Compositions and	Temperatures
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		μ/mPa·s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
157			1221		595	433	321		186		115
1 ²	0.0294/0.1516	1970	1300	878	611	438	321	242	185	145	116
0.917	0.0313/0.2263	1180	803	562	400	294	221	170	133	106	86
0.878	0.0172/0.1473	1030	707	497	358	266	201	156	123	99	81
0.793	0.0205/0.1400	665	469	339	250	190	147	116	93	76	63
0.690	0.0168/0.1210	420	306	226	172	134	106	85	69	57	
0.602	0.0230/0.2400	271	201	152	118	93	74	62	51		
0.499	0.0244/0.1505	173	132	102	80	65	53				
0.300	0.0250/0.2200	53									

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3m. Viscosity of [P₂₂₂₈][4-NO₂pyra] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		µ/mPa·s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0380/0.1525	1100	716	480	333	238	175	133	103	81	65
1	0.0080/0.0872	1340	868	578	398	282	207	155	119	94	75
0.949	0.0192/0.0742	1010	666	452	317	229	170	130	101	80	65
0.898	0.0180/0.1062	693	471	327	234	172	130	101	80	64	52
0.801	0.0152/0.1039	395	277	199	147	112	87	69	55		
0.700	0.0169/0.1110	229	166	123	94	73	58				
0.596	0.0181/0.0869	129	97	74	59						
0.497	0.0215/0.0904	78	60								
^a Standard u	ncertainties u are $u(T) = 0.1$ I	X and u(p)	= 0.005 M	Pa, and rel	ative stand	ard uncerta	ainty u_r is ι	$u_{\rm r}(\mu) = 0.00$	6 for new v	alues repo	rted here.

Table 3n. Viscosity of [P₂₂₂₈][4-NO₂imid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		μ/mPa·s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0104/0.1600	1220	804	547	382	276	204	155	120	95	76
1	0.0075/0.1058	1270	838	569	398	286	212	160	124	98	78
0.900	0.0377/0.1291	700	481	337	243	180	137	107	85	69	56
0.800	0.0305/0.1769	385	274	198	148	113	88	70	57		
0.699	0.0281/0.1581	210	153	114	87	69	55				
0.599	0.0326/0.2385	125	93	72	56						
0.499	0.0357/0.2562	77	60								

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 30. Viscosity of $[P_{2228}]$ [2-CH₃,5-NO₂imid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^{*a*}

			μ/mPa ·s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	
1 ²	0.0084/0.1628	3720	2280	1440	940	637	446	321	237	179	138	
1	0.0149/0.1880	3660	2240	1410	920	623	435	313	231	174	135	
0.964	0.0457/0.2299	2730	1700	1090	722	495	350	255	189	145	113	
0.933	0.0372/0.1897	1990	1270	829	559	390	280	206	155	120	95	
0.885	0.0307/0.1429	1470	955	636	438	310	227	170	130	101	81	
0.767	0.0280/0.1539	651	446	311	223	166	126	98	78	62		
0.700	0.0313/0.1332	375	262	187	137	103	80	64	51			
0.601	0.0297/0.1502	200	145	107	81	64	50					
0.500	0.0320/0.1503	113	86	66	51							
0.402	0.0335/0.1900	62										
^a Standard u	ncertainties u are $u(T) = 0.1$ H	X and u(p)	= 0.005 M	Pa, and rel	ative stand	ard uncerta	ainty u_r is ι	$u_{\rm r}(\mu) = 0.0$	6 for new v	alues repo	rted here.	

Table 3p. Viscosity of [mm(butene)im][4-NO₂pyra] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		µ/mPa·s									
IL mole fraction	water content before/after (weight fraction ×10 ²)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.1073/0.1717	6650	3260	1720	973	590	380	255	179	131	99
0.952	0.0768/0.3045	4300	2200	1210	706	439	289	204	140	104	81
0.900	0.0750/0.2522	2810	1510	864	525	338	228	161	117	89	70
0.801	0.0713/0.2234	1280	737	447	288	195	138	101	77	60	
0.701	0.0724/0.1838	622	385	249	169	121	89	69	53		
0.601	0.1171/0.3747	267	176	121	87	65					
0.500	0.0781/0.4037	139	97	70	53						
0.400	0.0690/0.3300	70	51								

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3q. Viscosity of $[P_{2224}]$ [2-CH₃,5-NO₂imid] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^{*a*}

		µ/mPa·s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0292/0.1871	2180	1350	858	569	391	277	202	150	115	90
0.952	0.0497/0.2417	1540	975	634	428	299	215	159	121	94	74
0.898	0.0388/0.1875	972	631	421	291	208	153	116	90	71	57
0.799	0.0437/0.2207	516	350	243	175	130	99	77	62		
0.701	0.0510/0.3567	258	183	134	100	76	60				
0.599	0.0499/0.3198	134	99	74	57						
0.499	0.0409/0.3416	74	57								

^aStandard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 3r. Viscosity of [pmmim][4-NO₂pyra] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures^a

		$\mu/\min a$ s									
IL mole fraction	water content before/after (weight fraction $\times 10^2$)	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
1 ²	0.0390/0.2128	9610	4500	2270	1240	722	447	294	200	143	106
0.950	0.1110/0.3000	5420	2660	1400	798	487	314	213	150	111	84
0.900	0.1120/0.3012	3220	1670	929	552	350	234	163	118	90	70
0.799	0.0854/0.3091	1300	743	449	287	194	137	100	76	59	
0.698	0.0324/0.2263	546	338	218	149	106	79	61			
0.601	0.0758/0.3245	252	167	115	83	62					
0.501	0.0661/0.2276	125	88	64							
0.400	0.0617/0.2696	65									
<i>ac.</i> 1 1	(77) 0.1.7	7 1 ()	0.007.10			1 .		()	10	1	. 11

³Standard uncertainties u are u(T) = 0.1 K and u(p) = 0.005 MPa, and relative standard uncertainty u_r is $u_r(\mu) = 0.06$ for new values reported here.

Table 4. Value G, from eq 3, of Various IL + Tetraglyme Mixtures As a Function of Temperature. The ILs Are Ordered from Highest to Lowest Values of G at 278.15 K

					G				
	T/K = 278.15	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
[P ₆₆₆₁₄][4-NO ₂ imid]	1.02	1.01	1.00	0.98	0.93	0.94	0.91	0.93	0.93
[P ₆₆₆₁₄][4,5-CNimid]	1.00	0.99	0.98	0.96	0.95	0.95	0.93	0.95	
$[P_{66614}][Tf_2N]$	0.95	0.90	0.88	0.86					
[P ₆₆₆₁₄][2-CH ₃ ,5-NO ₂ imid]	0.78	0.78	0.78	0.76	0.76	0.77	0.74	0.75	0.75
[P ₆₆₆₁₄][DCA]	0.76	0.75	0.74	0.73	0.73				
$[hmim][Tf_2N]$	0.73	0.65	0.61						
[P ₆₆₆₁₄][BrBnIm]	0.73	0.70	0.70	0.71	0.71	0.72	0.72	0.74	0.75
[P ₆₆₆₁₄][Acetate]	0.61	0.60	0.61	0.63	0.64				
[hmmim][Tf ₂ N]	0.57	0.53	0.50						
[P ₆₆₆₁₄][4-Triz]	0.49	0.52	0.55	0.58	0.61	0.65			
[P ₆₆₆₁₄][3-Triz]	0.42	0.46	0.50	0.53	0.56	0.60			
[P ₄₄₄₁₂][3-Triz]	-0.12	-0.06	0.01	0.06					
[P ₂₂₂₈][4-NO ₂ pyra]	-0.31	-0.25	-0.19	-0.12					
[P ₂₂₂₈][4-NO ₂ imid]	-0.32	-0.28	-0.23	-0.19					
[P ₂₂₂₈][2-CH ₃ ,5-NO ₂ imid]	-0.64	-0.56	-0.49	-0.43					
[mm(butene)im][4-NO ₂ pyra]	-0.68	-0.54	-0.41	-0.30					
[P ₂₂₂₄][2-CH ₃ ,5-NO ₂ imid]	-0.76	-0.68	-0.60	-0.53					
[pmmim][4-NO ₂ pyra]	-1.40	-1.20	-1.01	-0.84	-0.68				

not used in the data fitting. Also please note that the viscosities of the pure ILs and the IL/tetraglyme mixtures were measured in a viscometer whose uncertainty increases greatly for viscosities less than 50 mPa·s. Therefore, measurements are only reported for mixtures with viscosities greater than 50 mPa·s. The pure tetraglyme viscosities are taken from the literature.⁵⁹ This means that fit G values are not reported for all temperatures. For instance, for $[P_{66614}][3-Triz]$, the highest temperature for which a G value is reported is 303.15 K, where the

lowest mole fraction of $[P_{66614}]$ [3-Triz] is 0.499. The *G* values are given for temperatures between 278.15 and 303.15 K, always using the IL compositions between 0.499 and pure IL. The *G* values were determined based on reducing the percent error between experimental data and the fit. It is not recommended to use eq 3 with the *G* values in Table 4 for compositions between pure tetraglyme and lowest mole fraction of IL measured because the mixture may not be single phase in that region.



Figure 1. (a) Viscosities of $[pmmim][4-NO_2pyra] + tetraglyme mixtures as a function of temperature at the following <math>[pmmim]$ [4-NO₂pyra] mole fractions: 1.000, blue circle; 0.950, red square; 0.900, yellow triangel; 0.799, blue X; 0.698, purple asterisk; 0.601, green diamond; 0.501, open square; and 0.000, red dash. (b) Viscosities of $[pmmim][4-NO_2pyra] + tetraglyme mixtures as a function of composition at 278.15 K, purple asterisk; 283.15 K, blue circle; 288.15 K, green diamond; 293.15 K, yellow triangle; and 298.15 K, red square. The lines are the fits to eq 3, with the$ *G*values for the fits given in Table 4.

As an example, Figure 1a shows the viscosity of [pmmim] $[4-NO_2pyra] +$ tetraglyme mixtures as a function of temperature. The solid lines are the VFT fits, with both the pure IL² and the mixtures with tetraglyme showing a slight curvature. Figure 1b shows the same data, plotted as a function of composition at



Figure 2. Value of G (eq 3) at 278.15 K as a function of IL molecular weight (MW).



Figure 3. Value of *G* (eq 3) at 278.15 K as a function of log(Δ MW/ 1000)/ ρ , where Δ MW is MW_{IL} – MW_{TG} and ρ is the density of the IL at 293.15 K.

Table 6. Slope and Intercept of the Linear Correlation Shown in Figure 3 for 278.15 K, as Well As the Equivalent Correlations at Other Temperatures

T/K	slope	intercept
278.15	2.36	1.77
283.15	2.15	1.65
288.15	1.96	1.57
293.15	1.84	1.53

various temperatures. The *G* values are fit to the data at constant temperature and various composition. The *G* values for $[pmmim][4-NO_2pyra] +$ tetraglyme are negative, which is obvious from Figure 1b, where the mixture viscosities are values are less than a straight line between the two pure component viscosities.

Table 5. Properties of Various Ionic Liquids, Including the Molecular Weight, *G* Value for Mixing with Tetraglyme at 278.15 K, the Density at 293.15 K, the Viscosity at 278.15 K, and the Slope and Intercept of the Lines Shown in Figure 1

MW	G at 278.15 K	$ ho/{ m g~cm^{-3}}$ at 293.15 K	$\mu/\mathrm{mPa}\cdot\mathrm{s}$ at 278.15 K	slope	intercept
595.9	1.02	0.943 ²	3376 ²	-0.0026	1.74
600.9	1.00	0.923^{2}	2489 ²	-0.0018	1.51
764	0.95	1.069 ²	1210 ²	-0.0055	2.47
610.0	0.78	0.942^{2}	5887 ²	-0.0009	1.04
549.9	0.76	0.902 ⁵⁸	1750	-0.0011	1.06
447.4	0.73	1.378^{2}	204	-0.0127	4.27
683.9	0.73	1.020 ⁵⁷	7870	0.0009	0.45
542.9	0.61	0.889^{2}	1820 ²	0.0019	0.06
461.4	0.57	1.364	485	-0.0068	2.46
551.9	0.49	0.904 ⁵⁷	4640	0.0063	-1.25
551.9	0.42	0.901 ²	1970 ²	0.0071	-1.54
439.7	-0.12	0.915 ²	2660 ²	0.0124	-3.58
343.5	-0.31	1.034^{2}	1340	0.0125	-3.78
345.5	-0.32	1.032^{2}	1220^{2}	0.0087	-2.73
357.5	-0.64	1.032^{2}	3720 ²	0.0140	-4.54
263.3	-0.68	1.184^{2}	6650 ²	0.0250	-7.63
301.4	-0.76	1.068^{2}	2180 ²	0.0153	-5.02
251.3	-1.40	1.186 ²	9610 ²	0.0358	-11.35
	MW 595.9 600.9 764 610.0 549.9 447.4 683.9 542.9 461.4 551.9 439.7 343.5 345.5 357.5 263.3 301.4 251.3	MWG at 278.15 K 595.9 1.02 600.9 1.00 764 0.95 610.0 0.78 549.9 0.76 447.4 0.73 683.9 0.73 542.9 0.61 461.4 0.57 551.9 0.49 551.9 0.42 439.7 -0.12 343.5 -0.31 345.5 -0.32 357.5 -0.64 263.3 -0.68 301.4 -0.76 251.3 -1.40	MWG at 278.15 K $\rho/g \text{ cm}^{-3}$ at 293.15 K595.91.020.943²600.91.000.923²7640.951.069²610.00.780.942²549.90.760.902⁵8447.40.731.378²683.90.731.020⁵7542.90.610.889²461.40.571.364551.90.420.901²343.5-0.311.034²345.5-0.321.032²263.3-0.681.184²301.4-0.761.068²251.3-1.401.186²	MWG at 278.15 K ρ/g cm ⁻³ at 293.15 K $\mu/mPa \cdot s$ at 278.15 K595.91.020.943²3376²600.91.000.923²2489²7640.951.069²1210²610.00.780.942²5887²549.90.760.902 ⁵⁸ 1750447.40.731.378²204683.90.731.020 ⁵⁷ 7870542.90.610.889²1820²461.40.571.364485551.90.490.904 ⁵⁷ 4640551.90.420.901²1970²439.7-0.120.915²2660²343.5-0.311.034²1340345.5-0.321.032²3720²263.3-0.681.184²6650²301.4-0.761.068²2180²251.3-1.401.186²9610²	MWG at 278.15 K ρ/g cm ⁻³ at 293.15 K $\mu/mPa \cdot s$ at 278.15 Kslope595.91.020.943²3376²-0.0026600.91.000.923²2489²-0.00187640.951.069²1210²-0.0055610.00.780.942²5887²-0.0009549.90.760.902 ⁵⁸ 1750-0.0011447.40.731.378²204-0.0127683.90.731.020 ⁵⁷ 78700.0009542.90.610.889²1820²0.0019461.40.571.364485-0.0068551.90.420.901²1970²0.0071439.7-0.120.915²2660²0.0124343.5-0.311.034²13400.0125345.5-0.321.032²3720²0.0087357.5-0.641.032²3720²0.0140263.3-0.681.184²6650²0.0250301.4-0.761.068²2180²0.0153251.3-1.401.186²9610²0.0358

Table 7. Density of [P₆₆₆₁₄][3-Triz] Mixed with Tetraglyme at 0.1 MPa and Various Compositions and Temperatures⁴

		$ ho/{ m g~cm^{-3}}$									
IL mole fraction	water content (weight fraction ×10 ²)	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 295.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15		
1	0.0090	0.9066	0.9035	0.9005	0.8993	0.8975	0.8945	0.8915	0.8885		
0.850	0.0203	0.9128	0.9097	0.9066	0.9053	0.9035	0.9004	0.8973	0.8943		
0.775	0.0234	0.9166	0.9134	0.9103	0.9090	0.9071	0.9040	0.9009	0.8978		
0.700	0.0193	0.9206	0.9174	0.9141	0.9129	0.9110	0.9078	0.9047	0.9016		
0.600	0.0204	0.9268	0.9235	0.9203	0.9190	0.9170	0.9138	0.9106	0.9075		
0.500	0.0301	0.9348	0.9315	0.9281	0.9268	0.9248	0.9214	0.9180	0.9147		
0.399	0.0312	0.9448	0.9412	0.9377	0.9363	0.9342	0.9307	0.9272	0.9237		
0.330	0.0182	0.9528	0.9491	0.9454	0.9440	0.9417	0.9381	0.9345	0.9309		
0.300	0.0244	0.9565	0.9528	0.9492	0.9477	0.9455					
0.263	0.0307	0.9620	0.9581	0.9543	0.9528						
0.050	0.0192		1.0008	0.9964	0.9946						
0.040	0.0171	1.0082	1.0037	0.9992	0.9975						
0.019	0.0180	1.0142	1.0096	1.0051	1.0033	1.0006	0.9961	0.9916	0.9871		
0	0.0126	1.0203	1.0156	1.0110	1.0092	1.0064	1.0018	0.9972	0.9926		
					$ ho/{ m g}$ c	m^{-3}					
IL mole fraction	water content (weight fraction $\times 10^2$)	<i>T</i> /K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15	T/K = 343.15	T/K = 348.15	T/K = 353.15		
1	0.0090	0.8855	0.8826	0.8796	0.8767	0.8738	0.8708	0.8679	0.8650		
0.850	0.0203	0.8913	0.8882	0.8852	0.8822	0.8792	0.8762	0.8731	0.8701		
0.775	0.0234	0.8948	0.8917	0.8886	0.8855	0.8824	0.8794	0.8763	0.8733		
0.700	0.0193	0.8984	0.8953	0.8922	0.8890	0.8859	0.8828	0.8797	0.8765		
0.600	0.0204	0.9043	0.9011	0.8978	0.8946	0.8914	0.8882	0.8850	0.8818		
0.500	0.0301	0.9114	0.9080	0.9047	0.9014	0.8981	0.8947	0.8914	0.8881		
0.399	0.0312	0.9202	0.9168	0.9133	0.9098	0.9064	0.9029	0.8995	0.8960		
0.330	0.0182	0.9274	0.9238	0.9202	0.9167	0.9131	0.9095	0.9060	0.9024		
0.019	0.0180	0.9826	0.9781	0.9736	0.9691	0.9646	0.9601	0.9556	0.9511		
0	0.0126	0.9880	0.9834	0.9788	0.9742	0.9696	0.9650	0.9604	0.9558		
² Standard unce	ertainties u are $u(T) = 0.01$	$K_{u}(n) = 0.00$	05 MPa and	u(a) = 0.002	$2 \rm{g} \rm{cm}^{-3}$						



Figure 4. Excess molar volume of $[P_{66614}]$ [3-Triz] mixed with tetraglyme at various compositions and at 293.15 K, blue circle; 313.15 K, red square; 333.15 K, green diamond; and 353.15 K, yellow triangle.

The viscosities of all 18 ILs mixed with tetraglyme are roughly linear functions of composition on a logarithmic scale for viscosity (i.e., G = 0). Some of the IL + tetraglyme mixtures are a bit more viscous (G > 0) and some are less viscous (G < 0). Table 4 shows that the highest to lowest G values at 278.15 K are [P₆₆₆₁₄][4-NO₂imid], [P₆₆₆₁₄][4,5-CNimid] < [P₆₆₆₁₄][Tf₂N] < [P₆₆₆₁₄][2-CH₃,5-NO₂imid], [P₆₆₆₁₄][DCA], [hmim][Tf₂N], [P₆₆₆₁₄][BrBnIm] < [P₆₆₆₁₄][acetate] < [hmmim][Tf₂N] < [P₆₆₆₁₄][4-NO₂pyra], [P₂₂₂₈][4-NO₂imid] < [P₂₂₂₈][2-CH₃,5-NO₂imid], [mm(butene)im][4-NO₂pyra] < [P₂₂₂₄][2-CH₃,5-NO₂imid] < [pmimim][4-NO₂pyra], with the G value of [P₄₄₄₁₂][3-Triz] being near 0. Table 4 and Figure S1 (in the Supporting Information) shows how the G values change with increasing

temperature. All of the negative *G* values increase with increasing temperature. ILs with positive *G* values do not show any clear trend with temperature. The slopes and intercepts of linear fits of the *G* values as a function of temperature can be found in Table 5 ($G = \text{slope} \times T(K) + \text{intercept}$).

The G values are positive for all the $[P_{66614}]^+$ ILs. By contrast, the G values are negative for all the shorter chain tetraalkylphosphonium ILs. The $[P_{nnnm}]$ [2-CH₃,5-NO₂imid] ILs provide an excellent comparison. The G values for $[P_{66614}]$ $[2-CH_3,5-NO_2imid]$, $[P_{2228}][2-CH_3,5-NO_2imid]$, and $[P_{2224}]$ [2-CH₃,5-NO₂imid] are 0.8, -0.64, and -0.76 at 273.15 K, respectively. The G values for the imidazolium ILs are more varied, with the $[Tf_2N]^-$ ILs having positive G values but the mixtures of tetraglyme with imidazolium AHA ILs being less viscous than the "ideal" mixing model (eq 2). Some understanding can be drawn from recent molecular simulation results for $[hmim][Tf_2N]$ + tetraglyme mixtures.⁶⁰ The simulations show that the tetraglyme effectively breaks up the interactions between the cation and the anion, with the oxygen atoms of the tetraglyme interacting with the acidic hydrogens of the imidazolium cation. The positive G values for this system can be interpreted as the cation being a larger specie since it is associated with tetraglyme. If one assumes that tetraglyme can also weaken cation-anion interactions for tetra-alkylphosphonium cations, then one can envision screening of the cation short chains from the anion, but the longer alkyl chains extending out and the viscosity being dominated by van der Waals interactions between these long alkyl chains. This effect would be dominant for the largest cations (positive G values for $[P_{66614}]^+$) but less

Table 8. Solubility of CO ₂ (Mole Fraction) In Tetraglyme	P_{66614} [[3-Triz], and [P_{66614}][4-Triz] at 313.15, 333.15, and
353.15 K ^a	

	tetraglyme (TG)			[P ₆₆₆₁₄][3-Triz]			[P ₆₆₆₁₄][4-Triz]	
T/K	P/MPa	x _{CO2}	T/K	P/MPa	x _{CO2}	T/K	P/MPa	x _{CO2}
313.15	0.305	0.06	312.25	0.055	0.11	313.15	0.005	0.16
	0.344	0.08		0.123	0.15		0.015	0.25
	0.726	0.15		0.260	0.20		0.031	0.31
	0.735	0.16		0.576	0.28		0.061	0.35
	1.130	0.22		0.846	0.34		0.123	0.40
	1.269	0.25		1.275	0.41		0.243	0.44
	1.612	0.29		1.718	0.45		0.369	0.47
	1.771	0.32		2.036	0.49		0.504	0.48
	2.190	0.37		2.768	0.56		0.695	0.51
	2.238	0.38		3.377	0.60		1.003	0.53
	2.775	0.44					1.509	0.57
	3.210	0.48						
333.3	0.433	0.08	333.15	0.086	0.07	333.15	0.006	0.10
	0.979	0.15		0.230	0.12		0.016	0.17
	1.512	0.22		0.412	0.17		0.031	0.22
	2.106	0.28		0.640	0.24		0.061	0.28
	2.730	0.34		0.974	0.30		0.094	0.31
	3.365	0.40		1.371	0.34		0.121	0.33
				1.908	0.40		0.243	0.38
				2.326	0.46		0.502	0.44
				3.134	0.52		0.696	0.47
							1.008	0.50
							1.516	0.54
353.6	0.449	0.05	353.3	0.132	0.06			
	0.931	0.10		0.375	0.12			
	1.419	0.15		0.749	0.18			
	1.908	0.20		1.404	0.27			
	2.548	0.25		2.120	0.36			
	3.093	0.30		2.827	0.42			
				3.358	0.47			

^{*a*}Standard uncertainties *u* are u(T) = 0.15 K, u(p) = 0.001 MPa, and $u(x_{CO2}) = 0.02$ for tetraglyme and $[P_{66614}][3-Triz]$ data. Standard uncertainty *u* is u(T) = 0.01 K and relative standard uncertainties u_r are $u_r(p) = 0.00025$ and $u_r(x_{CO2}) = 0.0015$ for the $[P_{66614}][4-Triz]$ data.

important for short chains (e.g., $[P_{2224}]^+$), where the reduced cation–anion interactions dominate and yield a negative *G* value. The explanation for the negative *G* values for the imidazolium AHA ILs is not obvious. Other researchers⁵⁵ have suggested that diluents can both act to solvate the ions, reducing electrostatic forces between the ions (as has been discussed above), and by increasing free volume. While we anticipate that excess molar volumes for all of the IL + tetraglyme mixtures will be small (see next section), it is possible that is not the case for the imidazolium AHA systems, for which no mixture density data are yet available.

In an effort to develop a correlation so that one might be able to "predict" the viscosity of mixtures of other ILs with tetraglyme, we start with the observation that *G* is dependent on the molecular weight, as shown in Figure 2. Moreover, Table 5 shows the *G* values at 278.15 K, the viscosities at 278.15 K, and the densities at 293.15 K of the IL + tetraglyme mixtures, as well as the molecular weight of the IL. The molecular weight of tetraglyme is 222.28 g/mol and the density of pure tetraglyme at 293.15 K is 1.011 g cm⁻³. Figure 3 shows a linear fit of *G* versus log($\Delta MW \times 10^{-3}$) ρ^{-1} at 278.15 K. ΔMW is the difference between the molecular weight of the IL and tetraglyme and the 10^{-3} term is simply a scaling factor. The density was included to account for the much higher densities of the imidazolium [Tf₂N]⁻ ILs. The graphs of *G* versus

 $\log(\Delta MW \times 10^{-3})\rho^{-1}$ are relatively linear at temperatures between 278.15 and 293.15 K and the slopes and intercepts are reported in Table 6. The density used at all four temperatures is the density of the IL at 293.15 K. This is because the pure IL density changes very little over this temperature range. Since the slopes and intercepts shown in Table 6 vary systematically with temperature, they can be further fit as linear functions of temperature to yield eq 5, which gives an entirely empirical estimate of the viscosity of IL + tetraglyme mixtures. Obviously, the molecular weight of the IL must be greater than the molecular weight of tetraglyme and the correlation was fit for temperatures from just 278.15 to 293.15 K. Moreover, a limited number of imidazolium and tetra-alkylphosphonium ILs were used in the development of this correlation.

$$G = (-0.0350T(K) + 12.08) \times \log(\Delta MW/1000)$$

/ $\rho(293.15K) + (-0.0160T(K) + 6.20)$ (5)

Nonetheless, eq 5 gives an equation for G, allowing one to estimate the viscosity of other ILs mixed with tetraglyme. Of course, eq 5 should be used with great caution, as a very rough estimate of mixture viscosity.

Density. Previously it has been shown that the excess molar volumes of $[hmim][Tf_2N]$ + tetraglyme mixtures are very small.⁶⁰ Here we confirm this observation with one of the $[P_{66614}]^+$ ILs.

Table 9. Solubility of CO₂ (Mole Fraction) In an Initial Mixture of 70 mol % $[P_{66614}][3-Triz] + 30$ mol % Tetraglyme and in an Initial Mixture of 70 mol % $[P_{66614}][4-Triz] + 30$ mol % Tetraglyme at 313.15, 333.3, and 353.6 K.^{*a*}

[P ₆₆₆₁₄]	[P ₆₆₆₁₄][3-Triz] 0.700/TG		[P ₆₆₆₁₄][4-Triz] 0.700/TG			[P ₆₆₆₁₄][3-Triz] 0.700/TG			[P ₆₆₆₁₄	₄][4-Triz] 0.700/TG	
T/K	P/MPa	x _{CO2}	T/K	P/MPa	x _{CO2}	T/K	P/MPa	x _{CO2}	T/K	P/MPa	x _{CO2}
313.15	0.037	0.04	313.15	0.007	0.13		2.003	0.38		0.423	0.33
	0.079	0.06		0.030	0.20		2.360	0.41		0.568	0.35
	0.120	0.09		0.049	0.24		2.747	0.45		0.727	0.38
	0.200	0.15		0.072	0.26					0.923	0.41
	0.379	0.20		0.092	0.29					1.131	0.43
	0.534	0.24		0.136	0.31					1.389	0.45
	0.795	0.30		0.200	0.33					1.715	0.47
	1.231	0.38		0.288	0.36					2.064	0.50
	1.625	0.41		0.411	0.38					2.540	0.53
	2.005	0.45		0.558	0.40					3.008	0.56
	2.353	0.49		0.716	0.42	353.6	0.072	0.05	353.6	0.016	0.05
	2.682	0.52		0.920	0.45		0.128	0.06		0.036	0.09
				1.120	0.47		0.211	0.08		0.059	0.12
				1.372	0.49		0.389	0.12		0.088	0.15
				1.702	0.52		0.551	0.15		0.115	0.18
				2.063	0.55		0.806	0.18		0.145	0.19
				2.533	0.58		1.244	0.24		0.206	0.22
				3.031	0.61		1.491	0.28		0.293	0.24
333.3	0.040	0.05	333.3	0.008	0.06					0.427	0.28
	0.082	0.06		0.018	0.10					0.571	0.30
	0.123	0.08		0.036	0.14					0.731	0.33
	0.200	0.12		0.055	0.17					0.920	0.35
	0.383	0.16		0.077	0.20					1.138	0.37
	0.538	0.20		0.094	0.21					1.393	0.40
	0.800	0.25		0.137	0.24					1.708	0.42
	1.258	0.31		0.203	0.27					2.065	0.44
	1.639	0.34		0.289	0.30					2.535	0.47
										3.004	0.49

^aStandard uncertainties u are u(T) = 0.15 K, u(p) = 0.001 MPa, and $u(x_{CO2}) = 0.02$.



Figure 5. Solubility of CO_2 in tetraglyme at 313.15 K, blue circle; 333.3 K, yellow triangle; and 353.6 K, red square.



Figure 6. Solubility of CO_2 in [P₆₆₆₁₄][3-Triz] at 312.25 K, blue circle; 333.15 K, yellow triangle; and 353.3 K, red square.



Figure 7. Solubility of CO_2 in $[P_{66614}]$ [4-Triz] at 313.15 K, blue circle; and 333.15 K, yellow triangle.

Specifically, we have measured the density of $[P_{66614}][3-Triz]$ mixed with tetraglyme, and the results are shown in Table 7. There is a two phase region between IL mole fractions of roughly 0.072 and 0.263. The phase separation kinetics are sluggish so there is some uncertainty in these liquid–liquid phase split composition estimates. Mole fractions near the two-phase region were measured only at low temperatures because there is some indication of lower critical solution temperature behavior. Tetraglyme is more dense than $[P_{66614}][3-Triz]$ and all of the mixtures have densities between the two pure components. The excess molar volumes were calculated at each temperature and mole fraction, and these values are shown in tabular form in the Supporting Information. The excess molar

volumes are all positive, as shown in Figure 4. The greatest excess molar volume value is near a mole fraction of 0.5 of $[P_{66614}][3$ -Triz] and the values tend to decrease with increasing temperature. All of the excess molar volumes are quite small, less than 0.8 cm³ mol⁻¹, consistent with the previously reported values for [hmim][Tf₂N] + TG mixtures.⁶⁰ These small values are within the experimental uncertainty of the density measurements, when taking the sample purities into account. Therefore, no other IL + tetraglyme excess molar volume measurements were undertaken. This is also why the curves in Figure 4 do not fit the data perfectly.

CO₂ Solubility. The solubility of CO₂ in tetraglyme, [P₆₆₆₁₄][3-Triz], [P₆₆₆₁₄][4-Triz], a mixture of 70 mol % [P₆₆₆₁₄][3-Triz] + 30 mol % tetraglyme, and 70 mol % [P₆₆₆₁₄][4-Triz] + 30 mol % tetraglyme was measured at 313.15, 333.3, and 353.6 K. The solubility data, expressed as mole fractions, are shown in Tables 8 and 9 and Figures 5–9,



Figure 8. Solubility of CO_2 in [P₆₆₆₁₄][3-Triz] mixed with 30% mole fraction of tetraglyme at 313.15 K, blue circle; 333.3 K, yellow triangle; and 353.6 K, red square.



Figure 9. Solubility of CO_2 in $[P_{66614}]$ [4-Triz] mixed with 30% mole fraction of tetraglyme at 313.15 K, blue circle; 333.3 K, yellow triangle; and 353.6 K, red square.

where the CO₂ solubility increases with increasing pressure and decreases with increasing temperature. Both $[P_{66614}][3$ -Triz] and $[P_{66614}][4$ -Triz] can react with CO₂, with reported experimental enthalpies of reaction of -37 and -42 kJ/mol, respectively.⁵⁷ This is consistent with density functional theory calculations that show $[P_{66614}][3$ -Triz] having a smaller enthalpy of reaction with CO₂ than $[P_{66614}][4$ -Triz]. This is because the negative charge on the anion is more evenly spread over the anion for $[P_{66614}][3$ -Triz] than $[P_{66614}][4$ -Triz], which leads to $[P_{66614}][3$ -Triz] being less nucleophilic than $[P_{66614}][4$ -Triz]. Therefore, $[P_{66614}][3$ -Triz] has a lower CO₂ capacity and lower enthalpy of reaction than $[P_{66614}][4$ -Triz].⁵⁷ The solubility of CO₂ in tetraglyme is significantly less because tetraglyme does not chemically react with CO₂—the mechanism is simply physical dissolution. The solubility of CO₂ in

the IL + tetraglyme mixtures is between that of the pure IL and pure tetraglyme. As expected, the CO₂ uptake by the mixtures of $[P_{66614}][4$ -Triz] + tetraglyme is higher than $[P_{66614}][3$ -Triz] + tetraglyme because $[P_{66614}][4$ -Triz] has a larger magnitude of enthalpy of reaction with CO₂ than $[P_{66614}][3$ -Triz]. As shown in the Supporting Information, the solubility of CO₂ in the IL + tetraglyme mixtures can be represented reasonably well by the following equation:

$$Z_{\text{mixture}} = x_{\text{IL}} Z_{\text{IL}}(T, P) + x_{\text{TG}} Z_{\text{TG}}(T, P)$$
(6)

where Z_{mixture} , Z_{IL} , and Z_{TG} are the solubility of CO₂ in the mixture, the pure IL, and pure tetraglyme, respectively, expressed as a mole ratio (i.e., moles of CO₂/(moles IL + moles TG), moles of CO₂/mols of IL and moles of CO₂/mols of TG). x_{IL} and x_{TG} are the mole fractions of IL and tetraglyme in the initial IL + tetraglyme mixture. This indicates that tetraglyme does not affect the chemical CO₂ uptake by the IL.

CONCLUSIONS

Although ionic liquids with aprotic heterocyclic anions (AHA ILs) show promise for postcombustion and precombustion CO₂ capture applications, as well as in cofluid vapor-compression refrigeration systems, their relatively high viscosities (i.e., higher than the equivalent $[Tf_2N]^-$ ILs) present a challenge for mass and momentum transfer. Here we show that tetraglyme, which has a relatively low vapor pressure at temperatures of interest for these applications, is an effective additive in reducing viscosity. Tetraglyme is most effective in reducing viscosity for short alkyl chain tetra-alkylphosphonium AHA ILs. Only at very high tetraglyme compositions for some of the ILs whose cations have very long alkyl chains (i.e., $[P_{66614}]^+$) are any liquid–liquid phase splits observed. Excess molar volumes were determined for one [P₆₆₆₁₄][AHA] + tetraglyme mixture and the values were very small. Therefore, it is anticipated that the density of IL + tetraglyme mixtures can be estimated assuming an ideal solution. Moreover, the solubility of CO_2 in two $[P_{66614}][AHA] +$ tetraglyme mixtures suggests that it can be safely estimated from the solubility of CO_2 in the two pure liquids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00596.

Details on the NMR characterization of [hmmim]- $[Tf_2N]$, data of excess molar volumes of $[P_{66614}][3-Triz]$ + tetraglyme mixtures and CO₂ solubility data analysis (PDF)

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REFERENCES

(1) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

(2) Fillion, J. J.; Xia, H.; Desilva, M. A.; Quiroz-Guzman, M.; Brennecke, J. F. Phase Transitions, Decomposition Temperatures, Viscosities, and Densities of Phosphonium, Ammonium, and Imidazolium Ionic Liquids with Aprotic Heterocyclic Anions. J. Chem. Eng. Data 2016, 61, 2897–2914.

(3) Bonhôte, P.; Dias, A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(4) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. J. Chem. Eng. Data **2004**, *49*, 954–964.

(5) Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F. High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 20355–20365.

(6) Gurkan, B.; Goodrich, B. F.; Mindrup, E. M.; Ficke, L. E.; Massel, M.; Seo, S.; Senftle, T. P.; Wu, H.; Glaser, M. F.; Shah, J. K.; Maginn, E. J.; Brennecke, J. F.; Schneider, W. F. Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO₂ Capture. J. Phys. Chem. Lett. **2010**, *1*, 3494–3499.

(7) Seo, S.; DeSilva, M. A.; Xia, H.; Brennecke, J. F. Effect of Cation on Physical Properties and CO_2 Solubility for Phosphonium-Based Ionic Liquids with 2-Cyanopyrrolide Anions. *J. Phys. Chem. B* **2015**, 119, 11807–11814.

(8) Wujek, S. S.; McCready, M. J.; Mozurkewich, G.; Schneider, W. F.; Elbel, S. Experimental and Modeling Improvements to a Co-Fluid Utilizing Ionic Liquids and Carbon Dioxide. 15th International Refrigeration and Air Conditioning Conference, Purdue, 2014, 2501.

(9) Yang, P.; Lau, C.; Liu, X.; Lu, J. Direct Solid-Support Sample Loading for Fast Cataluminescence Determination of Acetone in Human Plasma. *Anal. Chem.* **2007**, *79*, 8476–8485.

(10) 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.

(11) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. J. Phys. Chem. B 2001, 105, 10942–10949.

(12) Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J. Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality. *Inorg. Chem.* **2004**, *43*, 2197–2205.

(13) Xu, H.; Zhao, D.; Xu, P.; Liu, F.; Gao, G. Conductivity and Viscosity of 1-Allyl-3-methyl-imidazolium Chloride + Water and + Ethanol from 293.15 to 333.15 K. *J. Chem. Eng. Data* **2005**, *50*, 133–135.

(14) Fu, D.; Sun, X.; Pu, J.; Zhao, S. Effect of Water Content on the Solubility of CO_2 in the Ionic Liquid [bmim][PF₆]. *J. Chem. Eng. Data* **2006**, *51*, 371–375.

(15) Rodriguez, H.; Brennecke, J. F. Temperature and composition dependence of the density and viscosity of binary mixtures of water + Ionic liquids. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.

(16) Chapeaux, A.; Simoni, L. D.; Stadtherr, M. A.; Brennecke, J. F. Liquid Phase Behavior of Ionic Liquids with Water and 1-Octanol and Modeling of 1-Octanol/Water Partition Coefficients. *J. Chem. Eng. Data* **2007**, *52*, 2462–2467.

(17) Ficke, L. E.; Rodriguez, H.; Brennecke, J. F. Heat Capacities and Excess Enthalpies of 1-Ethyl-3-methylimidazolium-Based Ionic Liquids and Water. *J. Chem. Eng. Data* **2008**, *53*, 2112–2119.

(18) Carvalho, P. J.; Regueira, T.; Santos, L. M. N. B. F.; Fernandez, J.; Coutinho, J. A. P. Effect of water on the viscosites and densites of 1butyl-3-methylimidazolim dicyanamide and 1-butyl-3-methylimidazolium tricyanomethane at atmospheric pressure. *J. Chem. Eng. Data* **2010**, 55, 645–652.

(19) Papaiconomou, N.; Estager, J.; Traore, Y.; Bauduin, P.; Bas, C.; Legeai, S.; Viboud, S.; Draye, M. Synthesis, Physicochemical Properties, and Toxicity Data of New Hydrophobic Ionic Liquids Containing Dimethylpyridinium and Trimethylpyridinium Cations. *J. Chem. Eng. Data* **2010**, *55*, 1971–1979.

(20) Ficke, L. E.; Novak, R. R.; Brennecke, J. F. Thermodynamic and thermophysical properties of ionic liquid + water systems. *J. Chem. Eng. Data* **2010**, *55*, 4946–4950.

(21) Kunze, M.; Jeong, S.; Paillard, E.; Winter, M.; Passerini, S. Melting Behavior of Pyrrolidinium-Based Ionic Liquids and Their Binary Mixtures. J. Phys. Chem. C 2010, 114, 12364–12369.

(22) Jarosik, A.; Krajewski, S. R.; Lewandowski, A.; Radzimski, P. Conductivity of ionic liquids in mixtures. *J. Mol. Liq.* **2006**, *123*, 43–50.

(23) Domanska, U.; Bogel-Lukasik, E.; Bogel-Lukasik, R. 1-Octanol/ Water Partition Coefficients of 1-Alkyl-3-methylimidazolium Chloride. *Chem. - Eur. J.* **2003**, *9*, 3033–3041.

(24) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction. *Chem. Commun.* **1998**, 1765–1766.

(25) Eike, D. M.; Brennecke, J. F.; Maginn, E. J. Predicting Infinitedilution Activity coefficients of organic solutes in ionic liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 1039–1048.

(26) Liu, Z.; Wu, W.; Han, B.; Dong, Z.; Zhao, G.; Wang, J.; Jiang, T.; Yang, G. Study on the Phase Behaviors, Viscosities, and Thermodynamic Properties of $CO_2/[C_4mim][PF_6]/Methanol System at Elevated Pressures.$ *Chem. - Eur. J.***2003**,*9*, 3897–3903.

(27) Blanchard, L. A.; Brennecke, J. F. Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292.

(28) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid phase behavior of imidazolium-based ionic liquids with alcohols. *J. Phys. Chem. B* **2004**, *108*, 5113–5119.

(29) Crosthwaite, J. M.; Muldoon, M. J.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid phase behavior of ionic liquids with alcohols: experimental studies and modeling. *J. Phys. Chem. B* **2006**, *110*, 9354–9361.

(30) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. Influence of Structural Variation in Room-Temperature Ionic Liquids on the Selectivity and Efficiency of Competitive Alkali Metal Salt Extraction by a Crown Ether. *Anal. Chem.* **2001**, *73* (15), 3737–3741.

(31) Dai, S.; Ju, Y. H.; Barnes, C. E. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J. Chem. Soc., Dalton Trans.* **1999**, 1201–1202.

(32) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal. Bioanal. Chem.* **2003**, *375*, 191–199.

(33) Gurkan, B. E.; Gohndrone, T. R.; McCready, M. J.; Brennecke, J. F. Reaction kinetics of CO_2 absorption in to phosphonium based anion-functionalized ionic liquids. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7796–7811.

(34) Aschenbrenner, O.; Supasitmongkol, S.; Taylor, M.; Styring, P. Measurement of vapour pressures of ionic liquids and other low vapour pressure solvents. *Green Chem.* **2009**, *11*, 1217–1221.

(35) Kodama, D.; Kanakubo, M.; Kokubo, M.; Hashimoto, S.; Nanjo, H.; Kato, M. Density; viscosity; and solubility of carbon dioxide in glymes. *Fluid Phase Equilib.* **2011**, *302*, 103–108.

(36) McGee, R. L.; Wallace, W. J.; Rataiczak, R. D. Densities, Viscosities, Refractive Indices, and Molar Refractions of the Binary System Tetraethylene Glycol Dimethyl Ether-Water at 25°C. J. Chem. Eng. Data **1983**, 28, 305–307.

(37) Fulcher, G. S. Analysis of Recent Measurements of the Viscosity of Glasses. J. Am. Ceram. Soc. **1925**, *8*, 339–355.

(39) Vogel, H. Das temperature-abhängigketsgesetz der viskosität vonflüssigkeiten. *Phys. Zeit.* **1921**, *22*, 645–646.

(40) Cohen, M. H.; Turnbull, D. Molecular Transport in Liquids and Glasses. J. Chem. Phys. **1959**, 31, 1164–1169.

(41) Gibbs, J. H.; DiMarzio, E. A. Nature of the Glass Transition and the Glassy State. *J. Chem. Phys.* **1958**, *28*, 373–383.

(42) Adam, G.; Gibbs, J. H. On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids. *J. Chem. Phys.* **1965**, 43, 139–146.

(43) Rault, J. Origin of the Vogel-Fulcher-Tammann law in glass-forming materials: the α - β bifurcation. J. Non-Cryst. Solids 2000, 271, 177–217.

(44) Eyring, H. Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates. J. Chem. Phys. **1936**, *4*, 283–291.

(45) Gong, Y.-h.; Shen, C.; Lu, Y.-z.; Meng, H.; Li, C.-x. Viscosity and density measurements for six binary mixtures of water (methanol or ethanol) with an Ionic liquid ([bmim][DMP] or [emim][DMP] at atmospheric pressure in the temperature range of (293.15 to 333.15) K. J. Chem. Eng. Data **2012**, *57*, 33–39.

(46) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, 40, 345–348.

(47) Ghatee, M. H.; Zare, M.; Moosavi, F.; Zolghadr, A. R. Temperature-Dependent Density and Viscosity of the Ionic Liquids 1-Alkyl-3-methylimidazolium Iodides: Experiment and Molecular Dynamics Simulation. *J. Chem. Eng. Data* **2010**, *55*, 3084–3088.

(48) Seoane, R. G.; Corderi, S.; Gomez, E.; Calvar, N.; Gonzalez, E. J.; Macedo, E. A.; Dominguez, A. Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 2492–2504.

(49) Navia, P.; Troncoso, J.; Romani, L. Viscosities for Ionic Liquid Binary Mixtures with a Common Ion. *J. Solution Chem.* **2008**, *37*, 677–688.

(50) Arrhenius, S. Z. Phys. Chem. 1887, 1, 285.

(51) Grunberg, L.; Nissan, A. H. Mixture Law for Viscosity. *Nature* **1949**, *164*, 799–800.

(52) Katti, P. K.; Chaudhri, M. M. Viscosities of Binary Mixtures of Benzyl Acetate with Dioxane, Aniline, and m-Cresol. *J. Chem. Eng. Data* **1964**, *9*, 442–443.

(53) Domanska, U.; Krolikowska, M.; Walczak, K. Effect of temperature and composition on the density, viscosity surface tension and excess quantities of binary mixtures of 1-ethyl-3-methylimidazolium tricyanomethanide with thiophene. *Colloids Surf., A* **2013**, 436, 504–511.

(54) Comminges, C.; Barhdadi, R.; Laurent, M.; Troupel, M. Determination of viscosity, ionic conductivity, and diffusion coefficients in binary system: ionic liquids + molecular solvents. *J. Chem. Eng. Data* **2006**, *51*, 680–685.

(55) Lopes, J. N. C.; Gomes, M. F. C.; Husson, P.; Padua, A. A. H.; Rebelo, L. P. N.; Sarraute, S.; Tariq, M. Polarity, Viscosity, and Ionic Conductivity of Liquid Mixtures Containing $[C_4C_1im][Ntf2]$ and a Molecular Component. J. Phys. Chem. B **2011**, 115, 6088–6099.

(56) Anouti, M.; Jacquemin, J.; Porion, P. Transport Properties Investigation of Aqueous Protic Ionic Liquid Solutions through Conductivity, Viscosity, and NMR Self-Diffusion Measurements. J. Phys. Chem. B 2012, 116, 4228–4238.

(57) Seo, S.; Quiroz-Guzman, M.; DeSilva, M. A.; Lee, T. B.; Huang, Y.; Goodrich, B. F.; Schneider, W. F.; Brennecke, J. F. Chemically Tunable Ionic Liquids with Aprotic Heterocyclic Anion (AHA) for CO_2 Capture. J. Phys. Chem. B 2014, 118, 5740–5751.

(58) Neves, C. M. S. S.; Carvalho, P. J.; Freire, M. G.; Coutinho, J. A. P. Thermophysical properties of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids. *J. Chem. Thermodyn.* **2011**, 43, 948–957. (60) Sharma, A.; Zhang, Y.; Gohndrone, T.; Oh, S.; Brennecke, J. F.; McCready, M. J.; Maginn, E. J. How Mixing Tetraglyme with the Ionic Liquid 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide Changes Volumetric and Transport Properties: An Experimental and Computational Study. *Chem. Eng. Sci.* **2016**, *159*, 43.

(61) Span, R.; Wagner, W. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509–1596.