

# Densities and Viscosities of Mixtures of Two Ionic Liquids Containing a Common Cation

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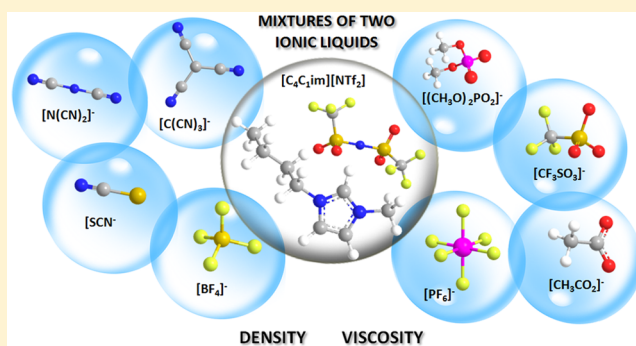
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## Supporting Information

**ABSTRACT:** Density and dynamic viscosity data of binary mixtures of ionic liquids (ILs) were determined in this work, at temperatures from 283.15 to 363.15 K and at 0.1 MPa. The mixtures of two ILs comprise a common cation and different anions, combining 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide with eight other ionic liquids, namely, 1-butyl-3-methylimidazolium thiocyanate, 1-butyl-3-methylimidazolium dicyanamide, 1-butyl-3-methylimidazolium tricyanomethane, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, and 1-butyl-3-methylimidazolium dimethylphosphate. Five mole fractions (0.00, 0.25, 0.50, 0.75, 1.00) of each mixture were prepared and characterized in terms of density and dynamic viscosity. The temperature dependence of density was described using a linear model, while the Vogel–Tammann–Fulcher equation was used to describe the temperature dependence of viscosity. Ideal mixing rules were used to predict the molar volume and viscosity and to infer on the mixtures ideal/nonideal behavior. For the mixtures of ILs investigated almost null or small deviations were observed in the molar volumes, meaning that their mixing is remarkably close to linear ideal behavior when molar volumes of mixtures are considered. For viscosity, larger deviations were observed for some particular systems; yet, and in general, mixtures of ILs do not deviate in a significant extent from ideal behavior. Therefore, ideal mixture models can be used to predict the physical properties of mixtures of ILs and to a priori design mixtures with specific features.



## INTRODUCTION

Ionic liquids (ILs), known as salts with a melting temperature below a conventional temperature of 100 °C,<sup>1</sup> have been largely explored in the past few years and are at last start reaching their place in industry.<sup>2</sup> Ionic liquids are typically composed of an organic cation and an organic or inorganic anion, where a large number of potential fluids can be synthesized by simple chemical structural rearrangements either in the cation or in the anion. In an ideal situation, the combination of different ions allocates the tailoring of their properties and characteristics and allows them to be task specific fluids for particular applications. The ionic nature and the large array of cation–anion combinations of ILs are the main characteristics responsible for some of their outstanding properties, namely, a negligible vapor pressure, a high ionic conductivity, nonflammability, high thermal and chemical stabilities, and an enhanced solvation ability for a large variety of compounds.<sup>2–8</sup> Due to the great interest in ILs from fundamental and applied point of views, and the wide number of ILs that is possible to obtain by the simple combination of the available cations and anions, the study of thermophysical properties

of ILs mixtures is an important task given that the possibility of finding tailored fluids with target properties is largely increased.

Recently, Niedermeyer et al.<sup>9</sup> reported a critical review on the use of mixtures of two and three ILs as a way of further extending the ability to design ILs with tailored properties.<sup>9,10</sup> The authors<sup>9</sup> proposed a nomenclature for such mixtures, and here adopted, where mixtures of two ILs, [A][X] and [A][Y], bearing a common cation [A]<sup>+</sup>, is abbreviated to [A][X]<sub>x</sub>[Y]<sub>1–x</sub>, whereas for the [A][X] + [B][X] mixtures, bearing a common anion [X]<sup>–</sup>, it is abbreviated to [A]<sub>x</sub>[B]<sub>1–x</sub>[X], where *x* and (1 – *x*) are the mole fraction of each IL.<sup>9</sup> Within IL mixtures, Canongia Lopes et al.<sup>10</sup> provided a pioneering work on their excess molar volumes (*V*<sup>E</sup>), namely for the following mixtures: [C<sub>4</sub>C<sub>1</sub>im]–[PF<sub>6</sub>]<sub>x</sub>[NTf<sub>2</sub>]<sub>1–x</sub>, [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>]<sub>x</sub>[NTf<sub>2</sub>]<sub>1–x</sub>, and [C<sub>4</sub>C<sub>1</sub>im]–[BF<sub>4</sub>]<sub>x</sub>[PF<sub>6</sub>]<sub>1–x</sub>. All of these mixtures were found to exhibit

**Special Issue:** In Honor of Kenneth R. Hall

**Received:** February 29, 2016

**Accepted:** July 4, 2016

**Published:** July 14, 2016

almost linear mixing behavior. Excess molar volumes for these mixtures were always found to be small—less than 0.1% of the overall volume and less than 1.5% of the difference in the molar volumes of the pure components. Similar results were presented by Clough et al.,<sup>11</sup> where the  $V^E$  for an extended number of mixtures presents deviations lower than 0.5%. Density measurements by Stoppa et al.<sup>12</sup> and Larriba et al.<sup>13</sup> showed that the excess molar volumes for  $[C_2C_1im][N(CN)_2]_x[BF_4]_{(1-x)}$  and  $[C_4C_1pyrr][BF_4]_x[NTf_2]_{(1-x)}$ , respectively, are small and positive (0.1%), in agreement with the results of Canongia Lopes et al.<sup>10</sup> for  $[C_4C_1im][BF_4]_x[PF_6]_{(1-x)}$ . Larriba et al.<sup>13</sup> also determined refractive indices, densities, and viscosities of a mixture of two pyridinium-based ILs, namely,  $[C_4py][BF_4]_x[NTf_2]_{(1-x)}$ . Gouveia et al.<sup>14</sup> determined the density, viscosity, and refractive index of mixed imidazolium-based ILs, containing a common cation and the tricyanomethane anion, combined with a series of amino acid based fluids, namely,  $[C_2C_1im][C(CN)_3]_x[Gly]_{(1-x)}$ ,  $[C_2C_1im][C(CN)_3]_x[L-Ala]_{(1-x)}$ ,  $[C_2C_1im][C(CN)_3]_x[Tau]_{(1-x)}$ ,  $[C_2C_1im][C(CN)_3]_x[L-Ser]_{(1-x)}$ , and  $[C_2C_1im][C(CN)_3]_x[L-Pro]_{(1-x)}$ .

In addition to the previous studies where mixtures of ILs with a common cation were investigated, further studies appeared on mixtures composed of ILs with the same anion and cation core, yet changing the cation alkyl side chain length.<sup>8,15,16</sup> Navia et al.<sup>8,15</sup> determined densities, excess molar volumes, isobaric thermal expansivities, excess enthalpies, and viscosities of  $[C_6C_1im]_x[C_2C_1im]_{(1-x)}[BF_4]$ ,  $[C_6C_1im]_x[C_4C_1im]_{(1-x)}[BF_4]$ ,  $[C_4C_1im][BF_4]_x[MeSO_4]_{(1-x)}$ , and  $[C_4C_1im][BF_4]_x[PF_6]_{(1-x)}$ . Song and Chen<sup>16</sup> determined viscosities and densities of  $[C_2C_1im]_x[C_3C_1im]_{(1-x)}[BF_4]$ ,  $[C_3C_1im]_x[C_6C_1im]_{(1-x)}[BF_4]$ , and  $[C_2C_1im]_x[C_6C_1im]_{(1-x)}[BF_4]$ . On the other hand, analyses of mixtures of two ILs bearing distinct cation cores, like pyrrolidinium and pyridinium, as well as with different anions, were performed. Viscosity and NMR-based data on ion–ion correlations and diffusion of pyrrolidinium- and imidazolium-based ionic liquids were measured by Castiglione et al.<sup>17</sup> for  $[C_1C_4pyr][NTf_2]_x[BETI]_{(1-x)}$ ,  $[C_1C_4pyr][NTf_2]_x[IM_{14}]_{(1-x)}$ ,  $[C_1C_4pyr][BETI]_x[IM_{14}]_{(1-x)}$ , and  $[C_1C_4pyr][NTf_2]_x[BETI]_y[IM_{14}]_{(1-x-y)}$ .

The aim of this work consists on the determination and analysis of densities and dynamic viscosities of mixtures of two ILs containing the common 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide,  $[C_4C_1im][NTf_2]$ , mixed with an additional IL also based on the 1-butyl-3-methylimidazolium cation, yet with different anions. The  $[C_4C_1im][NTf_2]$  IL was chosen as a starting point of this study since it is a well-studied IL, with accurate density and dynamic viscosity data available.<sup>18–25</sup> Members of three different families of ILs, with different properties regarding density and viscosity, were chosen to prepare

mixtures with  $[C_4C_1im][NTf_2]$ : (i) ILs containing fluorinated anions, such as  $[C_4C_1im][BF_4]$ ,  $[C_4C_1im][PF_6]$ , and  $[C_4C_1im][CF_3SO_3]$ ; (ii) ILs containing cyano-based anions,  $[C_4C_1im][SCN]$ ,  $[C_4C_1im][N(CN)_2]$ , and  $[C_4C_1im][C(CN)_3]$ ; and (iii) ILs containing nonfluorinated organic acids derived anions, such as  $[C_4C_1im][CH_3CO_2]$  and  $[C_4C_1im][(CH_3O)_2PO_2]$ . Densities and dynamic viscosities of eight mixtures of two ILs were studied in this paper, namely,  $[C_4C_1im][NTf_2]_x[SCN]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[N(CN)_2]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[C(CN)_3]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[BF_4]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[PF_6]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[CH_3CO_2]_{(1-x)}$ ,  $[C_4C_1im][NTf_2]_x[CF_3SO_3]_{(1-x)}$ , and  $[C_4C_1im][NTf_2]_x[(CH_3O)_2PO_2]_{(1-x)}$ , at temperatures between 283.15 and 363.15 K and at 0.1 MPa. Five mole fractions of  $[C_4C_1im][NTf_2]$  were investigated for each mixture ( $x = 0.00, 0.25, 0.50, 0.75, \text{ and } 1.00$ ), which include the respective properties for the pure ILs.

## EXPERIMENTAL SECTION

**Materials.** Binary IL mixtures were prepared with 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ( $[C_4C_1im][NTf_2]$ ), combined with 1-butyl-3-methylimidazolium thiocyanate ( $[C_4C_1im][SCN]$ ), 1-butyl-3-methylimidazolium dicyanamide ( $[C_4C_1im][N(CN)_2]$ ), 1-butyl-3-methylimidazolium tricyanomethane ( $[C_4C_1im][C(CN)_3]$ ), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[C_4C_1im][BF_4]$ ), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[C_4C_1im][PF_6]$ ), 1-butyl-3-methylimidazolium acetate ( $[C_4C_1im][CH_3CO_2]$ ), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ( $[C_4C_1im][CF_3SO_3]$ ), and 1-butyl-3-methylimidazolium dimethylphosphate ( $[C_4C_1im][(CH_3O)_2PO_2]$ ). In Table 1 are listed the ILs used in this work, along with the CAS number, purity, and source. Furthermore, the purity of each IL, after the drying step described below, was further checked by  $^1H$  and  $^{13}C$  NMR (and  $^{19}F$  NMR for the fluorinated ILs).

**Preparation of Ionic Liquid Mixtures.** Before the preparation of each mixture, pure ILs were dried at moderate temperature ( $\approx 318$  K) and high vacuum ( $\approx 10^{-5}$  Pa), under constant stirring, for a minimum period of 48 h, to remove traces of water and volatile compounds. Binary mixtures of ILs were then prepared using an analytical balance (model Mettler Toledo XS205 Dual Range) with an accuracy of  $4 \times 10^{-6}$  g. To ensure a proper mixing, magnetic stirring for at least 20 min, in closed glass vials, was carried out. Afterward, the prepared binary mixtures of ILs at 0.25, 0.50, and 0.75 mole fractions of  $[C_4C_1im][NTf_2]$  were dried again at moderate temperature ( $\approx 318$  K) and high vacuum ( $\approx 10^{-5}$  Pa), under constant stirring, for a minimum period of 48 h. After the drying step and immediately before the measurements of density and viscosity, the water content of each pure and mixture of ILs was determined by Karl Fischer titration, making use of a

Table 1. Specifications of the Compounds Used

compound	abbreviation	CAS No.	source	initial mole fraction purity	purification procedures
1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide	$[C_4C_1im][NTf_2]$	174899-83-3	Iolitec	0.99	drying
1-butyl-3-methylimidazolium thiocyanate	$[C_4C_1im][SCN]$	344790-87-0	Iolitec	>0.98	drying
1-butyl-3-methylimidazolium dicyanamide	$[C_4C_1im][N(CN)_2]$	448245-52-1	Iolitec	>0.98	drying
1-butyl-3-methylimidazolium tricyanomethane	$[C_4C_1im][C(CN)_3]$	878027-73-7	Merck	>0.98	drying
1-butyl-3-methylimidazolium tetrafluoroborate	$[C_4C_1im][BF_4]$	174501-65-6	Iolitec	0.99	drying
1-butyl-3-methylimidazolium hexafluorophosphate	$[C_4C_1im][PF_6]$	174501-64-5	Iolitec	0.99	drying
1-butyl-3-methylimidazolium acetate	$[C_4C_1im][CH_3CO_2]$	284049-75-8	Iolitec	0.98	drying
1-butyl-3-methylimidazolium trifluoromethanesulfonate	$[C_4C_1im][CF_3SO_3]$	174899-66-2	Iolitec	0.99	drying
1-butyl-3-methylimidazolium dimethylphosphate	$[C_4C_1im][(CH_3O)_2PO_2]$	891772-94-4	Iolitec	>0.98	drying

Metrohm 831 Karl Fischer coulometer. The reagent employed was Hydranal-Coulomat AG from Riedel-de Haën. The water content of each IL and mixture is presented in Table 2.

**Density and Viscosity Measurements.** Density ( $\rho$ ) and dynamic viscosity ( $\eta$ ) measurements were carried out using an automated SVM 300 Anton Paar rotational Stabinger viscometer–densimeter in the temperature range from 283.15 to 363.15 K, at 0.1 MPa. The absolute uncertainty in density is  $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$ , and the relative uncertainty in dynamic viscosity is  $\pm 0.35\%$  according to the manufacturer. The relative uncertainty in temperature is within  $\pm 0.02 \text{ K}$ . Further details on the use of the same equipment for the determination of viscosities and densities of ILs can be found elsewhere.<sup>26–28</sup> The measured viscosity and density and the calculated molar volume,  $V_m$ , of the pure ILs and their mixture at 298.15 K are presented in Table 2.

## RESULTS AND DISCUSSION

In Table 2, the water content of the pure ILs and studied mixtures of ILs is presented. It can be observed that these values are rather small, ranging from 0.0089% up to 0.0986% in mass, even for the most hydrophilic ILs, such as  $[\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{CO}_2]$ . Also, a summary of the viscosity, density, and molar volume for all the studied mixtures and pure fluids at 298.15 K and 0.1 MPa is

presented in Table 2. ILs from three different families of anions were selected to prepare binary mixtures with  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ . From the results obtained, it is possible to draw general trends for each one of the different families: (i) ILs containing cyano-based anions are generally the most fluid and the least dense, due most likely to the fact that both anion charge density and anion mass density are low;<sup>29</sup> (ii) ILs with fluorine-containing anions have intermediate viscosity (with exception of highly viscous  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ ) and are quite dense (with the exception of  $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$  due to low charge density and low symmetry of the anion),<sup>29</sup> owing to the presence of the fluorine atoms that increase density and their noncoordinating nature resulting in low viscous fluids; and (iii) ILs bearing nonfluorinated and organic acids derived anions are the most viscous, due to the high hydrogen bonding ability of these anions, and have intermediate density.

**Volumetric Properties.** The density values of pure and binary mixtures of ILs were determined at 0.1 MPa in the temperature range from 283.15 to 363.15 K and 0.1 MPa. The results obtained are presented in Table 3. The relative deviations between the data measured in this work and those already reported<sup>18–22,24,26,30–40</sup> for the pure ILs were also determined and are depicted in Figure S1. These relative deviations, between different authors and for different ILs, range from  $-0.65\%$  up

**Table 2. Composition, Water Content, Viscosity ( $\eta$ ), Density ( $\rho$ ), and Calculated Molar Volume ( $V_m$ ) for the Studied Binary Mixtures at 298.15 K and 0.1 MPa<sup>a</sup>**

	composition/mole fraction		water content (% mass)	$M$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$\eta$ (mPa·s)	$\rho$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$V_m$ ( $\text{cm}^3\cdot\text{mol}^{-1}$ )
	$x$ ( $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ )	$(1-x)$ ( $[\text{C}_4\text{C}_1\text{im}][\text{Y}]$ )					
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$	1.0000	0.0000	0.0089	419.37	51.58	1.4372	291.80
$[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$	0.0000	1.0000	0.0220	197.30	62.64	1.0702	184.36
$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$	0.0000	1.0000	0.0243	205.26	30.08	1.0602	193.60
$[\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$	0.0000	1.0000	0.0216	229.28	27.97	1.0476	218.86
$[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$	0.0000	1.0000	0.0780	226.02	108.74	1.2016	188.10
$[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$	0.0000	1.0000	0.0332	287.18	285.02	1.3676	209.99
$[\text{C}_4\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]$	0.0000	1.0000	0.0341	288.29	99.14	1.2963	222.39
$[\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{CO}_2]$	0.0000	1.0000	0.0467	198.26	292.57	1.0528	188.32
$[\text{C}_4\text{C}_1\text{im}][(\text{CH}_3\text{O})_2\text{PO}_2]$	0.0000	1.0000	0.0165	264.03	641.71	1.1579	228.03
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{SCN}]_{0.75}$	0.2501	0.7499	0.0140	252.82	61.69	1.1954	246.34
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{SCN}]_{0.50}$	0.4999	0.5001	0.0275	308.34	58.50	1.2931	281.37
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{SCN}]_{0.25}$	0.7483	0.2517	0.0199	363.85	55.06	1.3717	295.54
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{N}(\text{CN})_2]_{0.75}$	0.2506	0.7494	0.0192	258.79	36.45	1.1830	252.77
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{N}(\text{CN})_2]_{0.50}$	0.4569	0.5431	0.0138	312.32	41.02	1.2685	284.77
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{N}(\text{CN})_2]_{0.25}$	0.7486	0.2514	0.0164	365.84	46.82	1.3681	296.70
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{C}(\text{CN})_3]_{0.75}$	0.2517	0.7483	0.0106	276.80	31.92	1.1672	267.89
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{C}(\text{CN})_3]_{0.50}$	0.5000	0.5000	0.0214	324.33	37.61	1.2688	293.07
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{C}(\text{CN})_3]_{0.25}$	0.7508	0.2492	0.0627	371.85	43.15	1.3581	300.07
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{BF}_4]_{0.75}$	0.2497	0.7503	0.0488	274.36	88.56	1.2791	242.80
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{BF}_4]_{0.50}$	0.4979	0.5021	0.0263	322.70	72.77	1.3428	276.16
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{BF}_4]_{0.25}$	0.7509	0.2491	0.0563	371.03	60.64	1.3951	291.97
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{PF}_6]_{0.75}$	0.2499	0.7501	0.0194	320.23	148.96	1.3894	248.31
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{PF}_6]_{0.25}$	0.7479	0.2521	0.0168	386.32	68.88	1.4237	288.71
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{PF}_6]_{0.50}$	0.4996	0.5004	0.0222	353.28	97.74	1.4080	274.36
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{CF}_3\text{SO}_3]_{0.75}$	0.2503	0.7497	0.0346	321.06	71.42	1.3398	258.00
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{CF}_3\text{SO}_3]_{0.50}$	0.5001	0.4999	0.0405	353.83	66.62	1.3755	281.07
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{CF}_3\text{SO}_3]_{0.25}$	0.7460	0.2540	0.0399	386.60	68.68	1.4078	291.98
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[\text{CH}_3\text{CO}_2]_{0.75}$	0.2498	0.7502	0.0986	253.54	189.58	1.1819	249.57
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[\text{CH}_3\text{CO}_2]_{0.50}$	0.4984	0.5016	0.0863	308.82	119.72	1.2838	283.47
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[\text{CH}_3\text{CO}_2]_{0.25}$	0.7487	0.2513	0.0658	364.09	76.32	1.3678	296.45
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.25}[(\text{CH}_3\text{O})_2\text{PO}_2]_{0.75}$	0.2499	0.7501	0.0475	302.87	432.55	1.2391	267.92
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.50}[(\text{CH}_3\text{O})_2\text{PO}_2]_{0.50}$	0.5005	0.4995	0.0202	341.70	222.26	1.3120	290.07
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_{0.75}[(\text{CH}_3\text{O})_2\text{PO}_2]_{0.25}$	0.7468	0.2532	0.0200	380.54	104.86	1.3770	297.41

<sup>a</sup>Standard uncertainties  $u$  are  $u(x,y) = 0.0001$ ,  $u(T) = 0.02 \text{ K}$ ,  $u(p) = 10 \text{ kPa}$ , the combined expanded uncertainty  $U_c$  is  $U_c(\rho) = 0.5 \text{ kg}\cdot\text{m}^{-3}$ , and expanded uncertainty  $U_i$  is  $U_i(\eta) = 0.05$ , with an expanded uncertainty at the 0.95 confidence level ( $k \approx 2$ ).

Table 3. Experimental Densities ( $\rho$ ) of the Studied Mixtures of Ionic Liquids as a Function of Temperature ( $T$ ) at Pressure  $p = 0.1 \text{ MPa}^a$ 

$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{SCN}]$						$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$					
$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$						$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$					
$x$						$x$					
$T \text{ (K)}$	1.000	0.748	0.500	0.250	0.000	$T \text{ (K)}$	1.000	0.749	0.457	0.251	0.000
283.15	1.4518	1.3853	1.3053	1.2062	1.0792	283.15	1.4518	1.3818	1.2808	1.1943	1.0700
288.15	1.4469	1.3807	1.3012	1.2026	1.0762	288.15	1.4469	1.3772	1.2766	1.1905	1.0667
293.15	1.4421	1.3762	1.2971	1.1990	1.0732	293.15	1.4421	1.3727	1.2725	1.1867	1.0634
298.15	1.4372	1.3717	1.2931	1.1954	1.0702	298.15	1.4372	1.3681	1.2685	1.1830	1.0602
303.15	1.4324	1.3673	1.289	1.1918	1.0672	303.15	1.4324	1.3636	1.2644	1.1793	1.0570
308.15	1.4276	1.3628	1.285	1.1883	1.0642	308.15	1.4276	1.3592	1.2604	1.1757	1.0538
313.15	1.4229	1.3584	1.281	1.1847	1.0613	313.15	1.4228	1.3547	1.2564	1.1720	1.0506
318.15	1.4182	1.3540	1.2771	1.1812	1.0584	318.15	1.4181	1.3503	1.2524	1.1684	1.0475
323.15	1.4135	1.3497	1.2731	1.1777	1.0555	323.15	1.4134	1.3459	1.2485	1.1649	1.0444
328.15	1.4088	1.3453	1.2692	1.1743	1.0526	328.15	1.4087	1.3415	1.2446	1.1613	1.0413
333.15	1.4041	1.3410	1.2653	1.1708	1.0498	333.15	1.4040	1.3372	1.2407	1.1578	1.0382
338.15	1.3994	1.3367	1.2615	1.1674	1.0470	338.15	1.3993	1.3329	1.2368	1.1543	1.0352
343.15	1.3948	1.3324	1.2576	1.1640	1.0441	343.15	1.3947	1.3286	1.233	1.1508	1.0321
348.15	1.3902	1.3281	1.2538	1.1606	1.0414	348.15	1.3901	1.3243	1.2292	1.1473	1.0291
353.15	1.3856	1.3239	1.2500	1.1573	1.0386	353.15	1.3855	1.3200	1.2254	1.1438	1.0261
358.15	1.3811	1.3197	1.2462	1.1540	1.0358	358.15	1.3810	1.3158	1.2216	1.1404	1.0232
363.15	1.3766	1.3155	1.2424	1.1507	1.0331	363.15	1.3764	1.3116	1.2179	1.1370	1.0203
$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{C}(\text{CN})_3]$						$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$					
$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$						$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$					
$x$						$x$					
$T \text{ (K)}$	1.000	0.751	0.501	0.252	0.000	$T \text{ (K)}$	1.000	0.751	0.498	0.250	0.000
283.15	1.4518	1.3719	1.2816	1.1789	1.0581	283.15	1.4518	1.4091	1.3558	1.2912	1.2125
288.15	1.4469	1.3673	1.2773	1.175	1.0546	288.15	1.4469	1.4044	1.3514	1.2871	1.2088
293.15	1.4421	1.3627	1.2730	1.1711	1.0511	293.15	1.4421	1.3998	1.3471	1.2831	1.2052
298.15	1.4372	1.3581	1.2688	1.1672	1.0476	298.15	1.4372	1.3951	1.3428	1.2791	1.2016
303.15	1.4324	1.3536	1.2646	1.1634	1.0442	303.15	1.4324	1.3905	1.3385	1.2751	1.1980
308.15	1.4276	1.3491	1.2604	1.1596	1.0408	308.15	1.4276	1.3860	1.3342	1.2712	1.1945
313.15	1.4228	1.3446	1.2563	1.1558	1.0375	313.15	1.4228	1.3815	1.3299	1.2673	1.1909
318.15	1.4181	1.3402	1.2522	1.1521	1.0341	318.15	1.4181	1.3769	1.3257	1.2634	1.1874
323.15	1.4134	1.3358	1.2481	1.1483	1.0308	323.15	1.4134	1.3724	1.3214	1.2595	1.1840
328.15	1.4087	1.3314	1.2440	1.1446	1.0275	328.15	1.4087	1.3680	1.3172	1.2556	1.1805
333.15	1.4040	1.3270	1.2400	1.1409	1.0242	333.15	1.4040	1.3635	1.3131	1.2518	1.1770
338.15	1.3993	1.3227	1.2359	1.1373	1.0209	338.15	1.3993	1.3591	1.3089	1.248	1.1736
343.15	1.3947	1.3184	1.2320	1.1337	1.0177	343.15	1.3947	1.3548	1.3048	1.2442	1.1702
348.15	1.3901	1.3141	1.228	1.1300	1.0145	348.15	1.3901	1.3504	1.3007	1.2404	1.1668
353.15	1.3855	1.3098	1.2241	1.1265	1.0113	353.15	1.3855	1.346	1.2966	1.2367	1.1634
358.15	1.381	1.3056	1.2202	1.1229	1.0081	358.15	1.381	1.3417	1.2926	1.233	1.1601
363.15	1.3764	1.3014	1.2163	1.1194	1.0050	363.15	1.3764	1.3375	1.2886	1.2293	1.1568
$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$						$x [\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + (1-x) [\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{CO}_2]$					
$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$						$\rho \text{ (g}\cdot\text{cm}^{-3}\text{)}$					
$x$						$x$					
$T \text{ (K)}$	1.000	0.748	0.500	0.250	0.000	$T \text{ (K)}$	1.000	0.749	0.498	0.250	0.000
283.15	1.4518	1.4374	1.4211	1.4025	1.3799	283.15	1.4518	1.3814	1.2965	1.1932	1.0627
288.15	1.4469	1.4331	1.4172	1.3983	1.3765	288.15	1.4469	1.3768	1.2922	1.1894	1.0594
293.15	1.4421	1.4284	1.4126	1.3938	1.3720	293.15	1.4421	1.3723	1.2880	1.1856	1.0560
298.15	1.4372	1.4237	1.4080	1.3894	1.3676	298.15	1.4372	1.3678	1.2838	1.1819	1.0528
303.15	1.4324	1.4190	1.4035	1.3850	1.3634	303.15	1.4324	1.3633	1.2797	1.1783	1.0497
308.15	1.4276	1.4143	1.399	1.3807	1.3592	308.15	1.4276	1.3588	1.2757	1.1747	1.0466
313.15	1.4228	1.4097	1.3945	1.3764	1.3551	313.15	1.4229	1.3543	1.2716	1.1711	1.0435
318.15	1.4181	1.4051	1.3900	1.3721	1.3510	318.15	1.4182	1.3499	1.2675	1.1675	1.0405
323.15	1.4134	1.4005	1.3856	1.3679	1.3470	323.15	1.4135	1.3454	1.2635	1.1639	1.0375
328.15	1.4087	1.3959	1.3812	1.3636	1.3429	328.15	1.4088	1.3410	1.2594	1.1603	1.0345
333.15	1.4040	1.3913	1.3767	1.3594	1.3389	333.15	1.4041	1.3366	1.2554	1.1568	1.0315
338.15	1.3993	1.3868	1.3723	1.3552	1.3349	338.15	1.3994	1.3323	1.2514	1.1532	1.0285
343.15	1.3947	1.3823	1.3680	1.3510	1.3309	343.15	1.3948	1.3279	1.2475	1.1497	1.0256
348.15	1.3901	1.3779	1.3636	1.3469	1.3269	348.15	1.3902	1.3236	1.2435	1.1461	1.0226



Table 3. continued

$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1 - $x$ ) [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1 - $x$ ) [C <sub>4</sub> C <sub>1</sub> im][CH <sub>3</sub> CO <sub>2</sub> ]						
$\rho$ (g·cm <sup>-3</sup> )					$\rho$ (g·cm <sup>-3</sup> )						
$x$					$x$						
T (K)	1.000	0.748	0.500	0.250	0.000	T (K)	1.000	0.749	0.498	0.250	0.000
353.15	1.3855	1.3734	1.3593	1.3427	1.3230	353.15	1.3856	1.3194	1.2396	1.1426	1.0197
358.15	1.3810	1.369	1.3551	1.3386	1.3190	358.15	1.3811	1.3151	1.2357	1.1391	1.0167
363.15	1.3764	1.3646	1.3508	1.3346	1.3152	363.15	1.3766	1.3109	1.2318	1.1356	1.0139
$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1 - $x$ ) [C <sub>4</sub> C <sub>1</sub> im][CF <sub>3</sub> SO <sub>3</sub> ]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1 - $x$ ) [C <sub>4</sub> C <sub>1</sub> im][(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ]						
$\rho$ (g·cm <sup>-3</sup> )					$\rho$ (g·cm <sup>-3</sup> )						
$x$					$x$						
T (K)	1.000	0.746	0.500	0.250	0.000	T (K)	1.000	0.747	0.501	0.250	0.000
283.15	1.4518	1.4218	1.3890	1.3527	1.3084	283.15	1.4518	1.3906	1.3251	1.2510	1.1684
288.15	1.4469	1.4171	1.3844	1.3483	1.3043	288.15	1.4469	1.3860	1.3206	1.2470	1.1649
293.15	1.4421	1.4124	1.3799	1.3440	1.3003	293.15	1.4421	1.3815	1.3162	1.2431	1.1614
298.15	1.4372	1.4078	1.3755	1.3398	1.2963	298.15	1.4372	1.3770	1.3120	1.2391	1.1579
303.15	1.4324	1.4032	1.3710	1.3355	1.2923	303.15	1.4324	1.3725	1.3078	1.2352	1.1543
308.15	1.4276	1.3986	1.3666	1.3313	1.2884	308.15	1.4276	1.3681	1.3037	1.2314	1.1509
313.15	1.4229	1.3940	1.3622	1.3270	1.2845	313.15	1.4229	1.3636	1.2997	1.2277	1.1476
318.15	1.4182	1.3894	1.3578	1.3228	1.2806	318.15	1.4182	1.3592	1.2956	1.2241	1.1443
323.15	1.4135	1.3849	1.3535	1.3187	1.2767	323.15	1.4135	1.3548	1.2916	1.2204	1.1410
328.15	1.4088	1.3804	1.3492	1.3145	1.2728	328.15	1.4088	1.3504	1.2876	1.2168	1.1378
333.15	1.4041	1.3760	1.3449	1.3104	1.2689	333.15	1.4041	1.3460	1.2835	1.2132	1.1346
338.15	1.3994	1.3715	1.3406	1.3062	1.2651	338.15	1.3994	1.3417	1.2795	1.2097	1.1314
343.15	1.3948	1.3671	1.3363	1.3022	1.2613	343.15	1.3948	1.3374	1.2756	1.2061	1.1283
348.15	1.3902	1.3626	1.3320	1.2981	1.2575	348.15	1.3902	1.3331	1.2716	1.2025	1.1251
353.15	1.3856	1.3582	1.3278	1.2940	1.2537	353.15	1.3856	1.3288	1.2677	1.1990	1.1220
358.15	1.3811	1.3538	1.3235	1.2900	1.2499	358.15	1.3811	1.3246	1.2637	1.1955	1.1189
363.15	1.3766	1.3495	1.3193	1.2861	1.2462	363.15	1.3766	1.3204	1.2599	1.192	1.1157

<sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.02$  K,  $u$  are  $u(x,y) = 0.0001$ ,  $u(p) = 10$  kPa, and the combined expanded uncertainty  $U_c$  is  $U_c(\rho) = 0.5$  kg·m<sup>-3</sup>, with expanded uncertainty at the 0.95 confidence level ( $k \approx 2$ ).

to 0.23%. In summary, the absolute average relative deviations (AARD) between the data collected in this work for the density values of pure ILs and those reported in the literature are 0.12%,<sup>18</sup> 0.05%,<sup>19,20</sup> 0.03%,<sup>21</sup> and 0.01%,<sup>22</sup> for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]; 0.07%<sup>40</sup> and 0.04%<sup>30</sup> for [C<sub>4</sub>C<sub>1</sub>im][SCN]; 0.28%,<sup>26</sup> 0.08%,<sup>22</sup> 0.03%,<sup>31</sup> and 0.01%<sup>40</sup> for [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>]; 0.04%<sup>26</sup> and 0.02%<sup>32,40</sup> for [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>]; 0.07%,<sup>21</sup> 0.03%,<sup>33</sup> and 0.01%<sup>34</sup> for [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>]; 0.04%,<sup>21</sup> 0.03%,<sup>20</sup> and 0.02%<sup>35</sup> for [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>]; 0.20%<sup>24</sup> and 0.01%<sup>36,37</sup> for [C<sub>4</sub>C<sub>1</sub>im]-[CH<sub>3</sub>CO<sub>2</sub>]; 0.62%,<sup>34</sup> 0.25%,<sup>31</sup> and 0.18%<sup>38</sup> for [C<sub>4</sub>C<sub>1</sub>im]-[CF<sub>3</sub>SO<sub>3</sub>]; and 0.37%<sup>39</sup> for [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]. In summary, no significant differences exist in the densities values reported for the same set of ILs.

Regarding mixtures of ILs, Clough et al.<sup>11</sup> also determined the density of [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>(1-x)</sub> and [C<sub>4</sub>C<sub>1</sub>im]-[NTf<sub>2</sub>]<sub>x</sub>[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]<sub>(1-x)</sub> at 298.15 K. For the pure fluids, the density deviations are below 0.01%, while for [C<sub>4</sub>C<sub>1</sub>im]-[NTf<sub>2</sub>]<sub>x</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>(1-x)</sub> and [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]<sub>(1-x)</sub> low negative deviations were also obtained.

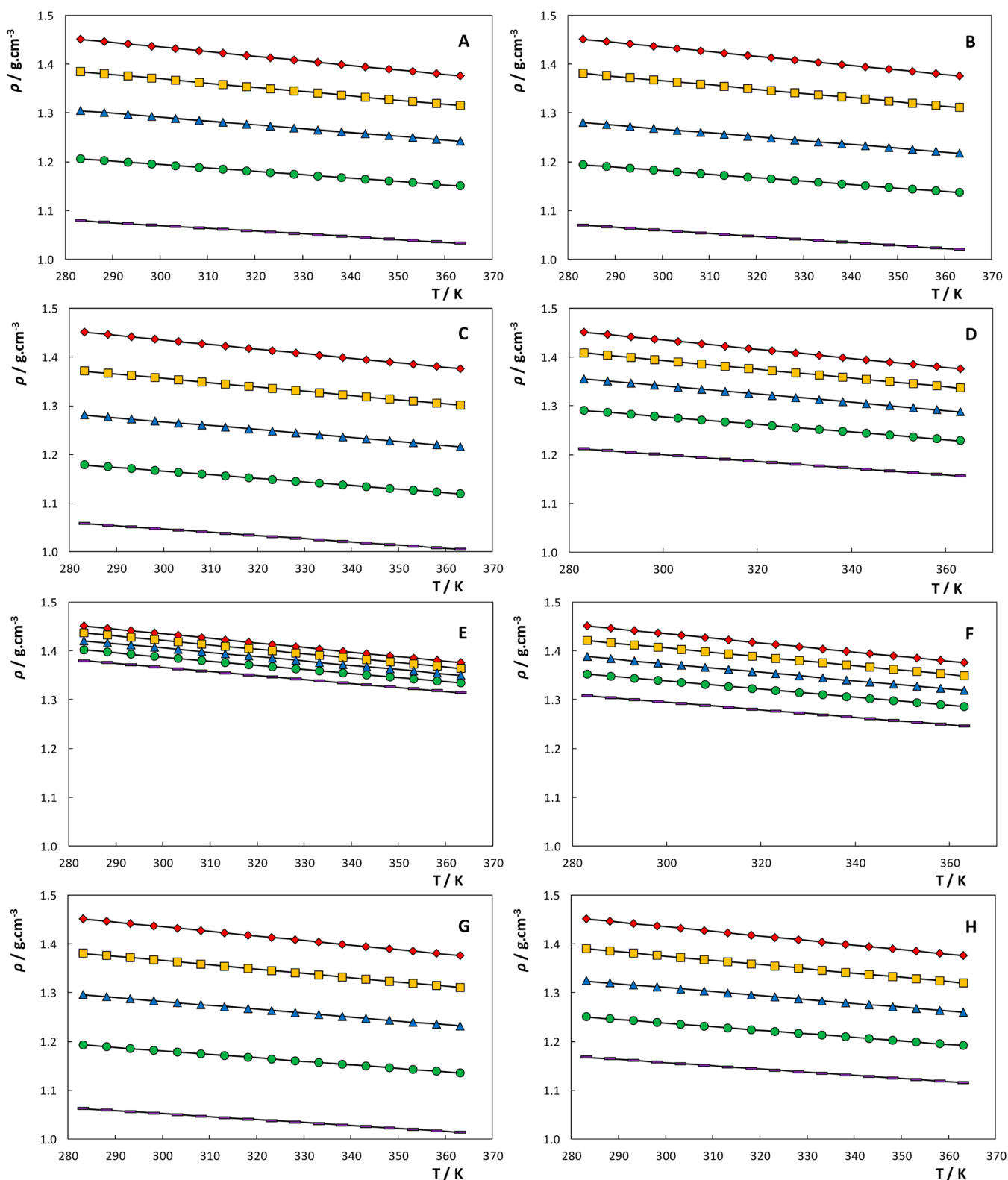
In general, for a given temperature, the densities of the pure ILs at a fixed temperature can be ordered according to the following sequence: [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] > [C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>] > [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] > [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][SCN] > [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>] ≈ [C<sub>4</sub>C<sub>1</sub>im]-[CH<sub>3</sub>CO<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>]. As expected, and with few exceptions, the density data for ILs bearing the same cation can be correlated with the anion size (see  $V_M$  in Table 2, since cation is constant in these mixtures, the effect of the anion size is easily perceived): the smaller the anion size, the smaller the density, according to the following

orders: [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>] > [C<sub>4</sub>C<sub>1</sub>im]-[PF<sub>6</sub>] > [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] > [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im]-[CH<sub>3</sub>CO<sub>2</sub>]. However, the opposite trend is observed for the density of cyano-based ILs; i.e., ILs with smaller anions in terms of volume lead to denser ILs ([C<sub>4</sub>C<sub>1</sub>im][SCN] > [C<sub>4</sub>C<sub>1</sub>im]-[N(CN)<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>]). As previously observed by Neves et al.,<sup>40</sup> the anions in this series are not completely homologous due to the presence of different central atoms.

The temperature dependence of density for the mixtures of ILs measured in this work is depicted in Figure 1 and reported in Table 3. The same scale was used in the density plots for all of the studied systems so that density variations can be better appreciated. It can be seen that all systems show a linear dependence of density with temperature, where the density decreases with the increase of temperature. Since the pure [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] IL is present in all of the studied mixtures, and taking into account that it has the highest density values among the studied ILs, the decrease of the mole fraction of this IL leads to a density decrease for all of the studied mixtures. Also, for the systems where there is a large difference in density between the two ILs constituents of the mixture, such as the case of [C<sub>4</sub>C<sub>1</sub>im]-[NTf<sub>2</sub>]<sub>x</sub>[SCN]<sub>(1-x)</sub>, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[N(CN)<sub>2</sub>]<sub>(1-x)</sub>, [C<sub>4</sub>C<sub>1</sub>im]-[NTf<sub>2</sub>]<sub>x</sub>[C(CN)<sub>3</sub>]<sub>(1-x)</sub>, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[CH<sub>3</sub>CO<sub>2</sub>]<sub>(1-x)</sub>, and [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]<sub>(1-x)</sub>, the variation of density along the mixture composition is thus more evident.

The density values ( $\rho$ ) were fitted as a function of temperature,  $T$  (K), by a least-squares method, using the linear expression given by eq 1,

$$\rho = a + b(T) \quad (1)$$



**Figure 1.** Densities of IL mixtures and their temperature dependence: (A)  $[C_4C_1im][NTf_2]_x[SCN]_{(1-x)}$ , (B)  $[C_4C_1im][NTf_2]_x[N(CN)_2]_{(1-x)}$ , (C)  $[C_4C_1im][NTf_2]_x[C(CN)_3]_{(1-x)}$ , (D)  $[C_4C_1im][NTf_2]_x[BF_4]_{(1-x)}$ , (E)  $[C_4C_1im][NTf_2]_x[PF_6]_{(1-x)}$ , (F)  $[C_4C_1im][NTf_2]_x[CF_3SO_3]_{(1-x)}$ , (G)  $[C_4C_1im][NTf_2]_x[CH_3CO_2]_{(1-x)}$ , and (H)  $[C_4C_1im][NTf_2]_x[(CH_3O)_2PO_2]_{(1-x)}$ ;  $\blacklozenge$ ,  $x = 1.00$ ;  $\blacksquare$ ,  $x = 0.75$ ;  $\blacktriangle$ ,  $x = 0.50$ ;  $\bullet$ ,  $x = 0.25$ ;  $-$ ,  $x = 0.00$ ; and respective correlation using the least-squares method by eq 1 (lines).

where  $a$  and  $b$  are adjustable parameters, presented in Table 4 together with the respective correlation coefficients.

Although the use of a linear correlation or a second-order polynomial equation to correlate experimental density data raises

some controversy,<sup>41,42</sup> the use of a linear function is enough to describe the measured density data in this work, at least within the temperature range studied. The fitting given by eq 1 is also presented in Figure 1.

**Table 4.** Fitted Parameters of eq 1<sup>a</sup> and Respective Correlation Coefficients,  $R^2$ , and Thermal Expansion Coefficients,  $\alpha_p$ , and Respective Standard Deviations ( $\sigma$ ), for the Studied Pure ILs and Their Mixtures at 298.15 K and 0.1 MPa

	$a$ (g·cm <sup>-3</sup> )	$b \times 10^4$ (g·cm <sup>-3</sup> ·K <sup>-1</sup> )	$R^2$	$10^4 (\alpha_p \pm \sigma)$ (K <sup>-1</sup> )
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	1.7168	-9.38	0.9999	6.65 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][SCN]	1.2426	-5.78	0.9998	5.46 ± 0.08
[C <sub>4</sub> C <sub>1</sub> im][N(CN) <sub>2</sub> ]	1.2462	-6.24	0.9997	5.95 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][C(CN) <sub>3</sub> ]	1.2458	-6.65	0.9998	6.44 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	1.4082	-6.94	0.9998	5.88 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	1.6112	-8.17	0.9998	6.04 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][CH <sub>3</sub> CO <sub>2</sub> ]	1.2328	-6.04	0.9998	5.85 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][CF <sub>3</sub> SO <sub>3</sub> ]	1.5280	-7.77	0.9996	6.09 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ]	1.3513	-6.50	0.9999	5.75 ± 0.08
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [SCN] <sub>0.75</sub>	1.4022	-6.94	0.9995	5.90 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [SCN] <sub>0.50</sub>	1.5271	-7.85	0.9995	6.17 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [SCN] <sub>0.25</sub>	1.6322	-8.74	0.9998	6.46 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [N(CN) <sub>2</sub> ] <sub>0.75</sub>	1.3955	-7.13	0.9998	6.14 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [N(CN) <sub>2</sub> ] <sub>0.50</sub>	1.5024	-7.85	0.9998	6.29 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [N(CN) <sub>2</sub> ] <sub>0.25</sub>	1.6298	-8.78	0.9999	6.52 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [C(CN) <sub>3</sub> ] <sub>0.75</sub>	1.3880	-7.41	0.9998	6.48 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [C(CN) <sub>3</sub> ] <sub>0.50</sub>	1.5117	-8.15	0.9998	6.54 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [C(CN) <sub>3</sub> ] <sub>0.25</sub>	1.6203	-8.80	0.9998	6.60 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [BF <sub>4</sub> ] <sub>0.75</sub>	1.5120	-7.81	0.9998	6.14 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [BF <sub>4</sub> ] <sub>0.50</sub>	1.5938	-8.42	0.9998	6.36 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [BF <sub>4</sub> ] <sub>0.25</sub>	1.6648	-9.04	0.9998	6.52 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [PF <sub>6</sub> ] <sub>0.75</sub>	1.6427	-8.50	0.9998	6.22 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [PF <sub>6</sub> ] <sub>0.50</sub>	1.6719	-8.86	0.9999	6.39 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [PF <sub>6</sub> ] <sub>0.25</sub>	1.6943	-9.09	0.9998	6.53 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.75</sub>	1.5877	-8.32	0.9999	6.32 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.50</sub>	1.6337	-8.67	0.9999	6.43 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.25</sub>	1.6777	-9.05	0.9999	6.53 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.75</sub>	1.3955	-7.16	0.9999	6.17 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.50</sub>	1.5220	-8.00	0.9999	6.39 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.25</sub>	1.6308	-8.82	0.9999	6.56 ± 0.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.75</sub>	1.4558	-7.28	0.9999	6.02 ± 0.09
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.50</sub>	1.5520	-8.05	0.9999	6.28 ± 0.10
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.25</sub>	1.6384	-8.77	0.9999	6.48 ± 0.11

<sup>a</sup>Standard uncertainties  $u$  are  $u(a) = 0.002$  and  $u(b) = 4 \times 10^{-6}$ .

The thermal expansion coefficient values at a given pressure were calculated for both the pure and the IL mixtures using the following equation:

$$\alpha_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p = \left( \frac{\partial \ln \rho}{\partial T} \right)_p \quad (2)$$

where  $\rho$  is the density in g·cm<sup>-3</sup>,  $T$  is the temperature in K, and  $P$  is the pressure in kPa.

The thermal expansion coefficient values of all of the studied pure and mixtures of ILs are provided in Table 4. Since the thermal expansion coefficients obtained in this work for the pure ILs and their binary mixture in the temperature range from 283.15 to 363.15 K and 0.1 MPa do not change considerably with temperature, in accordance to what was observed in the literature,<sup>41,43</sup> an average thermal expansion coefficient independent of temperature is here provided.

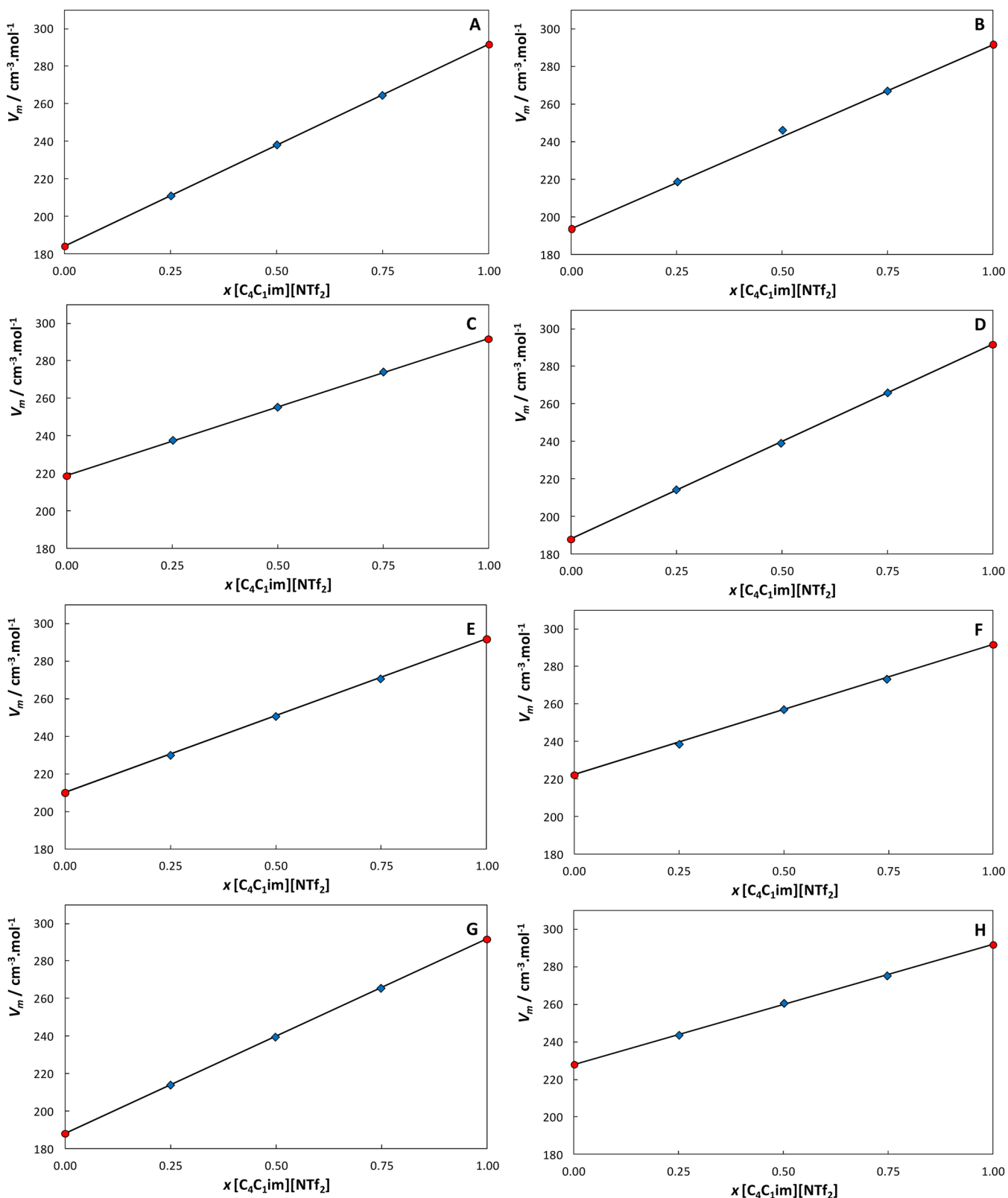
The molar volumes ( $V_m$ ) of the pure ILs and their mixtures were calculated applying eq 3,

$$V_{m,\text{exp}} = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad (3)$$

where  $x$  is the mole fraction and  $M$  is the molecular weight (g·mol<sup>-1</sup>). The subscripts 1 and 2 refer to each pure IL.

The molar volumes of both pure ILs and their mixtures, at 298.15 K, are depicted in Figure 2, and listed in Table S1 in the Supporting Information. Straight lines connecting the pure fluid density values represent the ideal molar volume, which is also listed in Table 5 for each one of the studied compositions. The molar volume of a mixture is directly related to the chemical potentials of the pure compounds present in the mixture and thus displays a linear dependence with the mole fraction when ideal mixing occurs. As expected, very small deviations from the ideal behavior can be generally observed for all of the most of the studied mixtures, with the highest deviation found for the [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>0.5</sub>[N(CN)<sub>2</sub>]<sub>0.5</sub> mixture. It should be noted that the differences between the experimental and the ideal molar volumes for the ILs mixtures are in general very small (tenths of the unit) in comparison to the molar volumes (in order of hundreds of the unit) used in their calculations. In order to better appreciate the very small deviations of the experimental molar volumes from the ideality, the excess molar volumes were also calculated using Equation 4 and are listed in Table 5 and depicted in Figure S2, in Supporting Information.

$$V_m = V_{m,\text{exp}} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (4)$$



**Figure 2.** Molar volumes of the studied mixtures: (A)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{SCN}]_{(1-x)}$ , (B)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{N}(\text{CN})_2]_{(1-x)}$ , (C)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{C}(\text{CN})_3]_{(1-x)}$ , (D)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{BF}_4]_{(1-x)}$ , (E)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{PF}_6]_{(1-x)}$ , (F)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{CF}_3\text{SO}_3]_{(1-x)}$ , (G)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{CH}_3\text{CO}_2]_{(1-x)}$ , and (H)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[(\text{CH}_3\text{O})_2\text{PO}_2]_{(1-x)}$ , at 298.15 K and 0.1 MPa. Blue diamond represents experimental molar volume; straight lines and red circles represent the ideal behavior described by eq 3.

where  $V_{m,\text{exp}}$  corresponds to the molar volume of the mixture and the second term corresponds to the ideal molar volume of the mixture.

The most striking feature of the excess molar volume representation is that the small experimental error in density is directly translated in considerable error in the excess molar volumes, due



**Table 5.** Experimental Molar Volume ( $V_{m,exp}$ ), Ideal Molar Volume ( $V_{m,id}$ ), and Excess Molar Volume ( $V^E$ ) for Pure ILs and Their Mixtures at  $T = 298.15$  K and  $0.1$  MPa

$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][SCN]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][N(CN) <sub>2</sub> ]				
$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
1.0000	1.4372	291.80	291.80	0.00	1.0000	1.4372	291.80	291.80	0.00
0.7483	1.3717	264.75	264.46	0.29	0.7486	1.3681	267.07	266.96	0.11
0.4999	1.2931	238.40	238.03	0.37	0.4569	1.2685	246.21	245.41	0.80
0.2501	1.1954	211.25	210.93	0.32	0.2506	1.183	218.73	218.06	0.67
0.0000	1.0702	184.36	184.36	0.00	0.0000	1.0602	193.60	193.60	0.00
$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][C(CN) <sub>3</sub> ]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]				
$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
1.0000	1.4372	291.80	291.80	0.00	1.0000	1.4372	291.80	291.80	0.00
0.7508	1.3581	274.33	274.17	0.16	0.7509	1.3951	266.18	266.08	0.10
0.4999	1.2688	255.56	255.28	0.28	0.4979	1.3428	239.31	238.94	0.37
0.2517	1.1672	237.92	237.77	0.15	0.2497	1.2791	214.55	214.11	0.44
0.0000	1.0476	218.86	218.86	0.00	0.0000	1.2016	188.10	188.10	0.00
$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][CF <sub>3</sub> SO <sub>3</sub> ]				
$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
1.0000	1.4372	291.80	291.80	0.00	1.0000	1.4372	291.80	291.80	0.00
0.7479	1.4237	270.71	270.71	0.00	0.7460	1.4078	273.48	273.35	0.13
0.4996	1.408	250.70	250.69	0.01	0.5001	1.3755	257.29	257.15	0.14
0.2499	1.3894	230.01	229.97	0.04	0.2503	1.3398	238.87	238.95	-0.08
0.0000	1.3676	209.99	209.99	0.00	0.0000	1.2963	222.39	222.39	0.00
$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][CH <sub>3</sub> CO <sub>2</sub> ]					$x$ [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] + (1-x) [C <sub>4</sub> C <sub>1</sub> im][(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ]				
$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$x$	$\rho$ (g·cm <sup>-3</sup> )	$V_{m,exp}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V_{m,id}$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
1.0000	1.4372	291.80	291.80	0.00	1.0000	1.4372	291.80	291.80	0.00
0.7487	1.3678	265.76	265.51	0.25	0.7468	1.377	275.36	274.90	0.46
0.4984	1.2838	239.78	239.29	0.49	0.5005	1.312	260.70	260.17	0.53
0.2498	1.1819	214.23	213.88	0.35	0.2499	1.2391	243.71	243.21	0.50
0.0000	1.0528	188.32	188.32	0.00	0.0000	1.1579	228.03	228.03	0.00

to their very small values. Thus, the accuracy of density measurements is a crucial factor when discussing excess molar volumes and the information derived from these results.

**Viscosity-Derived Properties.** The viscosity of pure ILs and mixtures of ILs were measured at  $0.1$  MPa in the temperature range from  $283.15$  to  $363.15$  K and are presented in Table 6. Contrarily to density values discussed before, viscosities for pure ILs display considerable discrepancies among different authors.<sup>20,21,23–26,31,33,39–41,44–48</sup> The absolute average relative deviations between the data collected in this work and those reported in the literature are  $2.98\%$ ,<sup>23</sup>  $2.91\%$ ,<sup>24</sup>  $2.57\%$ ,<sup>20</sup>  $0.96\%$ ,<sup>21</sup> and  $0.12\%$ <sup>25</sup> for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>];  $9.52\%$ <sup>40</sup> for [C<sub>4</sub>C<sub>1</sub>im][SCN];  $3.28\%$ ,<sup>26</sup>  $0.84\%$ ,<sup>31</sup> and  $0.60\%$ <sup>40</sup> for [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>];  $3.62\%$ <sup>26</sup> and  $0.54\%$ <sup>40</sup> for [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>];  $3.80\%$ ,<sup>44</sup>  $2.16\%$ ,<sup>21</sup> and  $0.98\%$ <sup>33</sup> for [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>];  $3.17\%$ ,<sup>21</sup>  $2.98\%$ ,<sup>45</sup> and  $0.08\%$ <sup>46</sup> for [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>];  $34.75\%$ ,<sup>36</sup>  $33.49\%$ ,<sup>47</sup> and  $1.17\%$ <sup>41</sup> for [C<sub>4</sub>C<sub>1</sub>im][CH<sub>3</sub>CO<sub>2</sub>];  $16.90\%$ <sup>48</sup> and  $10.59\%$ <sup>31</sup> for [C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>]; and  $8.36\%$ <sup>39</sup> for [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]. The average relative deviations between the data collected in this work and those already reported in literature<sup>20,21,23–26,31,33,39–41,44–48</sup> are depicted in Figure S3. It is well-known that the viscosity of ILs is highly affected by the presence of small amounts of impurities. One of the main reason for the high viscosity variations of [C<sub>4</sub>C<sub>1</sub>im][CH<sub>3</sub>CO<sub>2</sub>] is due to the source where ILs are purchased, where differences of the purity and purification procedures may cause a wide variation between the viscosity results in this work and those previously reported. In addition, the measurement technique, the sample purification steps, and the sample handling are also additional factors that may lead to large divergences in the viscosity values.<sup>49</sup>

Regarding the viscosity of mixtures of ILs, the results obtained in this work show a similar behavior to those presented by Clough et al.<sup>11</sup> for the systems [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>(1-x)</sub> and [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]<sub>(1-x)</sub>. Since Clough et al.<sup>11</sup> prepared mixtures with different mole fractions, it is not possible to calculate direct deviations.

For a given temperature, the viscosity of pure ILs, for instance at  $298.15$  K, decreases according to the following trend: [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][CH<sub>3</sub>CO<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im]-[PF<sub>6</sub>] > [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] > [C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>] > [C<sub>4</sub>C<sub>1</sub>im]-[SCN] > [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] > [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>] ≈ [C<sub>4</sub>C<sub>1</sub>im]-[C(CN)<sub>3</sub>]. Two factors might be playing a major role in this trend: size or entanglement of the ions and/or the establishment of strong interactions between the different ions. The most viscous ILs here studied are those containing nonfluorinated organic acids derived anions, known for their capacity to establish strong hydrogen bonds with other ions,<sup>50</sup> thus explaining their high viscosity. Within this family, [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>] has also a larger molar volume which explains its higher viscosity. The ILs with intermediate viscosity are those bearing fluorine anions, with the exception [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] which displays high viscosity, due to the large cation–anion interactions.<sup>29</sup> The most fluid ILs are those containing cyano groups. However, the less viscous liquids in this family are also the bulkier ones, in contrast to what happens to the previous two families of ILs. This behavior was previously discussed by Neves et al.,<sup>40</sup> and it was related to the intermolecular interactions that occur at the bulk liquid.

The viscosity values for the pure and mixtures of ILs studied in this work are depicted in Figure 3 and reported in Table 6. For all systems, the viscosity decreases with the increase in temperature,

Table 6. Experimental Dynamic Viscosities ( $\eta$ ) of  $[C_4mim][NTf_2]_x[Y]_y$  IL Mixtures on Mole Fraction ( $x_1$ ) as a Function of Temperature ( $T$ ) at Pressure  $p = 0.1$  MPa<sup>a</sup>

$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][SCN]$						$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][N(CN)_2]$					
$\eta$ (mPa·s)						$\eta$ (mPa·s)					
$x$						$x$					
$T$ (K)	1.000	0.748	0.500	0.250	0.000	$T$ (K)	1.000	0.749	0.457	0.251	0.000
283.15	106.78	115.12	124.13	133.49	139.54	283.15	106.77	95.811	82.502	72.335	58.350
288.15	82.142	88.289	94.681	101.08	104.51	288.15	82.163	73.993	64.112	56.465	45.906
293.15	66.356	71.221	76.166	80.920	82.913	293.15	64.531	58.315	50.832	44.977	36.830
298.15	51.580	55.058	58.499	61.694	62.635	298.15	51.601	46.816	41.019	36.451	30.080
303.15	41.940	44.621	47.235	49.547	49.936	303.15	41.933	38.184	33.660	30.024	24.945
308.15	34.601	36.704	38.704	40.423	40.483	308.15	34.585	31.605	28.006	25.081	20.979
313.15	29.479	31.225	32.846	34.219	34.081	313.15	28.907	26.501	23.603	21.219	17.865
318.15	24.472	25.811	27.027	28.045	27.804	318.15	24.456	22.481	20.116	18.156	15.383
323.15	20.928	22.012	22.975	23.786	23.489	323.15	20.908	19.273	17.327	15.700	13.384
328.15	18.071	18.956	19.740	20.387	20.064	328.15	18.052	16.681	15.056	13.693	11.739
333.15	15.947	16.702	17.356	17.910	17.577	333.15	15.719	14.564	13.267	12.047	10.383
338.15	13.828	14.436	14.940	15.384	15.077	338.15	13.797	12.817	11.723	10.676	9.2509
343.15	12.234	12.744	13.160	13.539	13.238	343.15	12.198	11.360	10.432	9.5297	8.2978
348.15	10.898	11.328	11.671	11.998	11.713	348.15	10.856	10.136	9.3349	8.560	7.4878
353.15	9.9850	10.359	10.653	10.916	10.672	353.15	9.7200	9.0975	8.4083	7.7277	6.7943
358.15	8.8060	9.1135	9.3505	9.5766	9.3553	358.15	8.7541	8.2106	7.6155	7.0165	6.1965
363.15	7.9803	8.2417	8.4395	8.6206	8.4365	363.15	7.9257	7.4488	6.9321	6.4030	5.6772
$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][C(CN)_3]$						$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][BF_4]$					
$\eta$ (mPa·s)						$\eta$ (mPa·s)					
$x$						$x$					
$T$ (K)	1.000	0.751	0.501	0.252	0.000	$T$ (K)	1.000	0.751	0.498	0.250	0.000
283.15	106.77	88.875	77.278	65.872	58.153	283.15	106.77	127.96	158.06	200.83	264.99
288.15	82.163	68.485	59.443	50.602	44.500	288.15	82.163	97.869	119.67	149.79	192.43
293.15	64.531	53.860	46.775	39.793	34.896	293.15	64.531	76.327	92.467	114.12	143.08
298.15	51.601	43.148	37.605	31.918	27.974	298.15	51.601	60.641	72.767	88.561	108.74
303.15	41.933	35.156	30.660	26.075	22.854	303.15	41.933	48.975	58.236	69.908	84.284
308.15	34.585	29.072	25.433	21.650	18.979	308.15	34.585	40.138	47.312	56.119	66.520
313.15	28.907	24.374	21.394	18.218	15.995	313.15	28.907	33.348	38.961	45.704	53.372
318.15	24.456	20.684	18.216	15.530	13.657	318.15	24.456	28.045	32.485	37.722	43.471
323.15	20.908	17.745	15.719	13.389	11.796	323.15	20.908	23.853	27.356	31.518	35.894
328.15	18.052	15.384	13.614	11.663	10.291	328.15	18.052	20.484	23.288	26.630	30.014
333.15	15.719	13.437	11.899	10.249	9.0624	333.15	15.719	17.751	20.023	22.707	25.376
338.15	13.797	11.837	10.543	9.0781	8.0449	338.15	13.797	15.514	17.365	19.581	21.683
343.15	12.198	10.504	9.3836	8.0998	7.1942	343.15	12.198	13.660	15.186	17.022	18.696
348.15	10.856	9.387	8.4227	7.2747	6.4748	348.15	10.856	12.112	13.383	14.910	16.263
353.15	9.7200	8.4352	7.5491	6.5736	5.8619	353.15	9.7200	10.807	11.844	13.146	14.256
358.15	8.7541	7.6234	6.8579	5.9737	5.3373	358.15	8.7541	9.6882	10.551	11.663	12.591
363.15	7.9257	6.9255	6.2877	5.4554	4.8837	363.15	7.9257	8.7334	9.4667	10.420	11.196
$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][PF_6]$						$x [C_4C_1im][NTf_2] + (1 - x) [C_4C_1im][CH_3CO_2]$					
$\eta$ (mPa·s)						$\eta$ (mPa·s)					
$x$						$x$					
$T$ (K)	1.000	0.748	0.500	0.250	0.000	$T$ (K)	1.000	0.749	0.498	0.250	0.000
283.15	106.77	148.25	221.31	360.25	794.33	283.15	106.78	175.10	310.72	577.38	1013.40
288.15	82.163	112.57	166.04	264.71	557.27	288.15	82.142	129.87	220.24	385.58	645.60
293.15	64.531	87.233	126.16	196.39	393.86	293.15	66.356	101.85	159.18	265.43	421.35
298.15	51.601	68.875	97.744	148.96	285.02	298.15	51.580	76.324	119.72	189.58	292.57
303.15	41.933	55.303	77.094	115.08	210.93	303.15	41.940	60.267	91.377	138.72	206.68
308.15	34.585	45.077	61.820	90.440	159.46	308.15	34.601	48.439	71.140	104.00	150.08
313.15	28.907	37.247	50.313	72.177	122.78	313.15	29.479	40.339	56.475	79.571	110.79
318.15	24.456	31.165	41.516	58.449	96.281	318.15	24.472	32.702	45.443	62.278	85.027
323.15	20.908	26.376	34.680	47.959	76.721	323.15	20.928	27.359	37.162	49.567	66.071
328.15	18.052	22.556	29.299	39.841	62.044	328.15	18.071	23.178	30.802	40.094	52.293
333.15	15.719	19.471	25.002	33.466	50.855	333.15	15.947	20.113	26.092	33.138	42.287
338.15	13.797	16.955	21.534	28.386	42.201	338.15	13.828	17.145	21.927	27.382	34.385

Table 6. continued

$x [C_4C_1im][NTf_2] + (1-x) [C_4C_1im][PF_6]$						$x [C_4C_1im][NTf_2] + (1-x) [C_4C_1im][CH_3CO_2]$					
$\eta$ (mPa·s)						$\eta$ (mPa·s)					
$x$						$x$					
$T$ (K)	1.000	0.748	0.500	0.250	0.000	$T$ (K)	1.000	0.749	0.498	0.250	0.000
343.15	12.198	14.880	18.705	24.305	35.427	343.15	12.234	14.955	18.788	23.054	28.476
348.15	10.856	13.148	16.376	20.992	30.038	348.15	10.898	13.127	16.247	19.626	23.878
353.15	9.7200	11.698	14.442	18.288	25.722	353.15	9.9850	11.891	14.490	17.208	20.631
358.15	8.7541	10.473	12.824	16.042	22.222	358.15	8.8060	10.347	12.454	14.643	17.348
363.15	7.9257	9.4276	11.455	14.168	19.363	363.15	7.9803	9.2719	11.024	12.813	15.003
$x [C_4C_1im][NTf_2] + (1-x) [C_4C_1im][CF_3SO_3]$						$x [C_4C_1im][NTf_2] + (1-x) [C_4C_1im][(CH_3O)_2PO_2]$					
$\eta$ (mPa·s)						$\eta$ (mPa·s)					
$x$						$x$					
$T$ (K)	1.000	0.746	0.500	0.250	0.000	$T$ (K)	1.000	0.747	0.501	0.250	0.000
283.15	106.78	145.79	145.00	154.70	225.61	283.15	106.78	251.51	630.61	1433.70	2315.60
288.15	82.142	111.50	109.34	117.06	168.05	288.15	82.142	183.60	433.30	930.25	1454.60
293.15	66.356	87.296	84.529	90.691	128.51	293.15	66.356	137.30	301.49	618.01	943.97
298.15	51.580	68.684	66.622	71.417	99.144	298.15	51.580	104.86	222.26	432.55	641.71
303.15	41.940	55.861	53.393	57.294	78.260	303.15	41.940	81.713	165.15	307.85	446.92
308.15	34.601	45.795	43.559	46.662	62.755	308.15	34.601	64.812	125.35	224.53	319.33
313.15	29.479	38.101	35.960	38.523	51.328	313.15	29.479	52.462	96.268	166.25	232.10
318.15	24.472	32.200	30.150	32.190	42.099	318.15	24.472	42.722	76.392	127.53	174.70
323.15	20.928	27.440	25.432	27.212	35.127	323.15	20.928	35.402	61.136	98.918	133.37
328.15	18.071	23.466	21.659	23.236	29.632	328.15	18.071	29.688	49.652	78.040	103.62
333.15	15.947	20.273	18.550	20.057	25.498	333.15	15.947	25.420	41.066	62.705	81.972
338.15	13.828	17.604	16.080	17.397	21.720	338.15	13.828	21.556	34.048	50.834	65.623
343.15	12.234	15.457	14.132	15.234	18.840	343.15	12.234	18.628	28.686	41.865	53.395
348.15	10.898	13.662	12.541	13.429	16.474	348.15	10.898	16.232	24.417	34.896	44.013
353.15	9.9850	12.227	11.183	11.944	14.834	353.15	9.9850	14.572	21.362	29.799	37.081
358.15	8.8060	10.929	9.9806	10.634	12.864	358.15	8.8060	12.605	18.178	25.026	30.935
363.15	7.9803	9.9093	8.9726	9.5407	11.476	363.15	7.9803	11.217	15.879	21.499	26.332

<sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.02$  K,  $u$  are  $u(x,y) = 0.0001$ ,  $u(p) = 10$  kPa, and the combined expanded uncertainty  $U_r$  is  $U_r(\eta) = 0.05$ , with expanded uncertainty at the 0.95 confidence level ( $k \approx 2$ ).

and the viscosity values for the mixtures are between those of the pure ILs. Unlike densities, viscosities do not vary linearly with the IL mole fraction of a mixture, even for the mixtures where linear volumetric behavior occurs. For the systems containing a second IL that is more viscous than  $[C_4C_1im][NTf_2]$ , the viscosities decrease with the addition of  $[C_4C_1im][NTf_2]$ , according to the pure IL viscosity trend (Table 2)  $[C_4C_1im][NTf_2]_x \cdot [(CH_3O)_2PO_2]_{(1-x)} > [C_4C_1im][NTf_2]_x [CH_3CO_2]_{(1-x)} > [C_4C_1im][NTf_2]_x [PF_6]_{(1-x)} > [C_4C_1im][NTf_2]_x [BF_4]_{(1-x)} > [C_4C_1im][NTf_2]_x [SCN]_{(1-x)}$ . For the systems containing a second IL that is less viscous than  $[C_4C_1im][NTf_2]$ , the viscosities increase with the addition of  $[C_4C_1im][NTf_2]$ , according to the pure IL viscosity trend (Table 2):  $[C_4C_1im][NTf_2]_x [N(CN)_2]_{(1-x)} < [C_4C_1im][NTf_2]_x [C(CN)_3]_{(1-x)}$ . However, an odd behavior was observed for the  $[C_4C_1im][NTf_2]_x [CF_3SO_3]_{(1-x)}$  system. Since the viscosity of  $[C_4C_1im][CF_3SO_3]$  is higher than that of  $[C_4C_1im][NTf_2]$ , the addition of this last IL should always decrease the viscosity of the mixture. Nevertheless, the viscosities for this system decrease according to the following mole fraction sequence:  $x = 0.00 > 0.25 > 0.50 \approx 0.75 > 1.00$ . This might be due to the similar molecular structure of the two anions present in the mixture, where it can be assumed that  $[CF_3SO_3]^-$  is "half" of  $[NTf_2]^-$ .

The experimental viscosity values were fitted as a function of temperature, using the Vogel–Fulcher–Tammann (VTF)

model, described in eq 5,

$$\ln \eta = A_\eta + \frac{B_\eta}{(T - C_\eta)} \quad (5)$$

where  $\eta$  is the viscosity in mPa·s,  $T$  is the temperature in K, and  $A_\eta$  (mPa·s),  $B_\eta$  (K), and  $C_\eta$  (K) are adjustable parameters. The adjustable parameters were determined from the fitting of the experimental data and are presented along with the absolute average relative deviation (ARD) in Table 7.

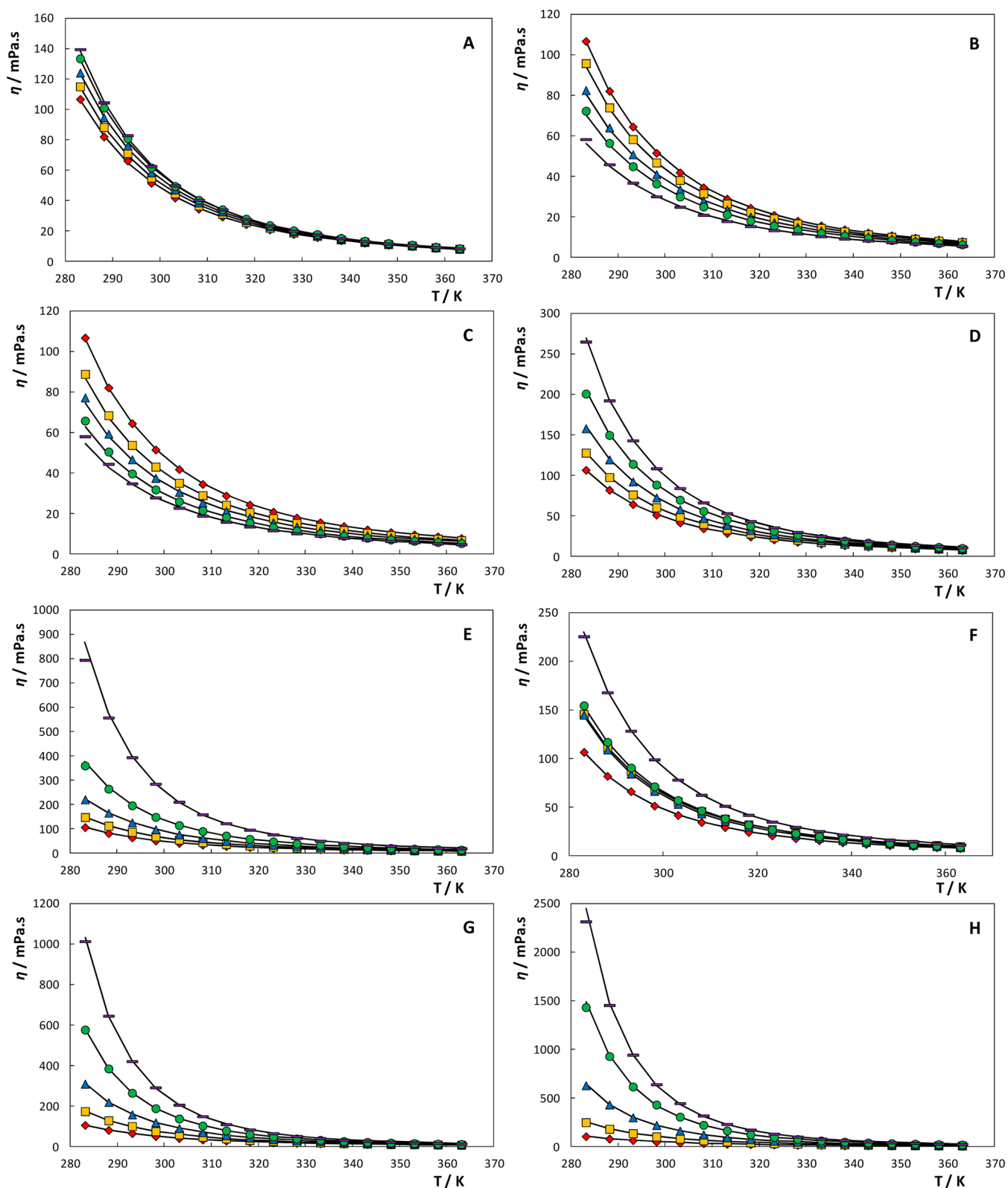
The absolute average relative deviation was calculated according to eq 6

$$ARD(\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{\eta_{calc,i} - \eta_{exp,i}}{\eta_{exp,i}} \right| \times 100 \quad (6)$$

where  $N$  is the total number of experimental points and  $\eta_{exp}$  and  $\eta_{calc}$  are the experimental and calculated viscosity, respectively. The fitting of the viscosity data as a function of temperature is also depicted in Figure 3.

The energy barrier was determined through eq 7, based on the viscosity dependence with temperature,

$$E_\eta = R \times \frac{\partial \ln \eta}{\partial \left(\frac{1}{T}\right)} = R \left( \frac{B_\eta}{\left(\frac{C_\eta^2}{T^2} - \frac{2C_\eta}{T} + 1\right)} \right) \quad (7)$$



**Figure 3.** Viscosities of IL mixtures and their temperature dependence: (A)  $[C_4C_1im][NTf_2]_x[SCN]_{(1-x)}$ , (B)  $[C_4C_1im][NTf_2]_x[N(CN)_2]_{(1-x)}$ , (C)  $[C_4C_1im][NTf_2]_x[C(CN)_3]_{(1-x)}$ , (D)  $[C_4C_1im][NTf_2]_x[BF_4]_{(1-x)}$ , (E)  $[C_4C_1im][NTf_2]_x[PF_6]_{(1-x)}$ , (F)  $[C_4C_1im][NTf_2]_x[CF_3SO_3]_{(1-x)}$ , (G)  $[C_4C_1im][NTf_2]_x[CH_3CO_2]_{(1-x)}$ , and (H)  $[C_4C_1im][NTf_2]_x[(CH_3O)_2PO_2]_{(1-x)}$ ;  $\blacklozenge$ ,  $x = 1.00$ ;  $\blacksquare$ ,  $x = 0.75$ ;  $\blacktriangle$ ,  $x = 0.50$ ;  $\bullet$ ,  $x = 0.25$ ;  $—$ ,  $x = 0.00$ , and respective correlation using eq 4 (lines).

where  $\eta$ ,  $T$ ,  $B_\eta$  and  $C_\eta$  were obtained from eq 5, and  $R$  is the universal gas constant ( $8.3144598 \times 10^{-3} \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). The energy barrier of a fluid to share stress at 298.15 K is listed in

Table 7 and depicted in Figure 4.  $E_\eta$  is the energy barrier that must be overcome to move ions upon the other ions in the IL. Therefore, the higher the  $E_\eta$  value is, the more difficult it is for the

Table 7. Fitted Parameters of eq 4, Respective AARD, and Energy Barriers ( $E_\eta$ ) Values at  $T = 298.15$  K and 0.1 MPa

	$A_\eta$ (mPa·s)	$B_\eta$ (K)	$C_\eta$ (K)	AARD (%)	$E_{\eta(298.15\text{ K})}$ (kJ·mol <sup>-1</sup> )
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-8.8750	823.398	159.006	0.80	31.43
[C <sub>4</sub> C <sub>1</sub> im][SCN]	-8.9508	824.105	165.008	1.00	34.36
[C <sub>4</sub> C <sub>1</sub> im][N(CN) <sub>2</sub> ]	-9.0543	821.843	150.080	1.01	27.70
[C <sub>4</sub> C <sub>1</sub> im][C(CN) <sub>3</sub> ]	-9.3007	822.517	154.458	1.01	27.70
[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-8.8467	825.308	173.596	0.21	39.32
[C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-8.5595	826.324	184.962	1.57	47.67
[C <sub>4</sub> C <sub>1</sub> im][CH <sub>3</sub> CO <sub>2</sub> ]	-9.0081	826.860	191.673	0.70	53.90
[C <sub>4</sub> C <sub>1</sub> im][CF <sub>3</sub> SO <sub>3</sub> ]	-8.7108	825.309	169.189	0.57	36.68
[C <sub>4</sub> C <sub>1</sub> im][(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ]	-8.6896	869.013	192.484	1.71	57.53
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [SCN] <sub>0.75</sub>	-8.8761	823.929	163.014	0.83	33.35
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [SCN] <sub>0.50</sub>	-8.8694	823.810	161.646	0.72	32.68
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [SCN] <sub>0.25</sub>	-8.8652	823.688	160.209	0.75	31.99
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [N(CN) <sub>2</sub> ] <sub>0.75</sub>	-8.9897	823.020	153.200	0.79	28.95
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [N(CN) <sub>2</sub> ] <sub>0.50</sub>	-8.9359	823.168	154.794	0.73	29.60
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [N(CN) <sub>2</sub> ] <sub>0.25</sub>	-8.9155	823.424	157.489	0.48	30.76
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [C(CN) <sub>3</sub> ] <sub>0.75</sub>	-9.2077	823.099	155.328	1.33	28.95
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [C(CN) <sub>3</sub> ] <sub>0.25</sub>	-8.9899	823.393	157.321	0.72	30.69
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [C(CN) <sub>3</sub> ] <sub>0.50</sub>	-9.0721	823.268	155.999	0.97	30.11
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [BF <sub>4</sub> ] <sub>0.75</sub>	-8.8069	824.560	168.958	0.30	36.51
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [BF <sub>4</sub> ] <sub>0.50</sub>	-8.8172	824.215	165.136	0.26	34.43
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [BF <sub>4</sub> ] <sub>0.25</sub>	-8.8278	823.691	161.438	0.19	32.57
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [PF <sub>6</sub> ] <sub>0.75</sub>	-8.7959	870.393	171.856	0.78	40.33
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [PF <sub>6</sub> ] <sub>0.50</sub>	-8.8510	865.923	165.420	0.13	36.33
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [PF <sub>6</sub> ] <sub>0.25</sub>	-8.7944	823.869	163.497	0.09	33.58
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.75</sub>	-8.9314	869.592	159.955	0.14	33.65
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.50</sub>	-8.9942	865.568	160.466	0.33	33.75
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [CF <sub>3</sub> SO <sub>3</sub> ] <sub>0.25</sub>	-8.7078	823.705	161.698	0.29	32.70
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.75</sub>	-9.1858	871.269	182.287	0.37	47.97
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.50</sub>	-9.0904	866.643	173.746	0.34	41.39
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [CH <sub>3</sub> CO <sub>2</sub> ] <sub>0.25</sub>	-8.9149	824.273	168.227	0.66	36.09
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.25</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.75</sub>	-8.7835	868.111	188.586	1.50	53.45
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.50</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.50</sub>	-8.8557	867.343	179.994	0.72	45.92
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] <sub>0.75</sub> [(CH <sub>3</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sub>0.25</sub>	-8.8055	824.751	172.218	0.38	38.44

ions to move past each other. This can be a direct effect of the size or entanglement of the ions and/or by the presence of stronger interactions in the fluid. From the analysis of Figure 4, only the pure [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>] and [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>] ILs and the systems containing these two ILs, [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>]<sub>x</sub>[NTf<sub>2</sub>]<sub>(1-x)</sub> and [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>]<sub>x</sub>[NTf<sub>2</sub>]<sub>(1-x)</sub>, present lower  $E_\eta$  than the pure [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>], while the other pure ILs and their mixtures with [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] present higher  $E_\eta$  values. Also to be noted the almost constant values for the energy barrier for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[CF<sub>3</sub>SO<sub>3</sub>]<sub>(1-x)</sub>, due to the similarity between both ILs as discussed before.

The viscosity of IL mixtures can be calculated from the pure IL viscosities using the ideal Grunberg and Nissan mixing rules,<sup>51</sup> according to the following equation

$$\log_{10}(\eta) = x_1 \log_{10}(\eta_1) + x_2 \log_{10}(\eta_2) \quad (8)$$

The obtained results are compared in Figure 5 to the experimental viscosity data (symbols) measured in this work for all the systems studied, in the temperature range from 283.15 to 363.15 K. Surprisingly, it can be observed that, despite the chemical and size differences (see  $V_M$  in Table 2) between the two ILs, the [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[CH<sub>3</sub>CO<sub>2</sub>]<sub>(1-x)</sub> system exhibits very small deviations from the ideal Grunberg and Nissan mixing rules.<sup>51</sup> For [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[BF<sub>4</sub>]<sub>(1-x)</sub>, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[SCN]<sub>(1-x)</sub>, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[N(CN)<sub>2</sub>]<sub>(1-x)</sub>, and [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[C(CN)<sub>3</sub>]<sub>(1-x)</sub> systems, small deviations are

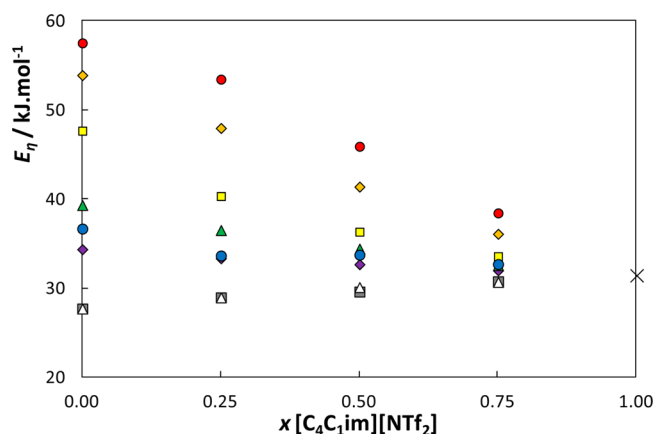
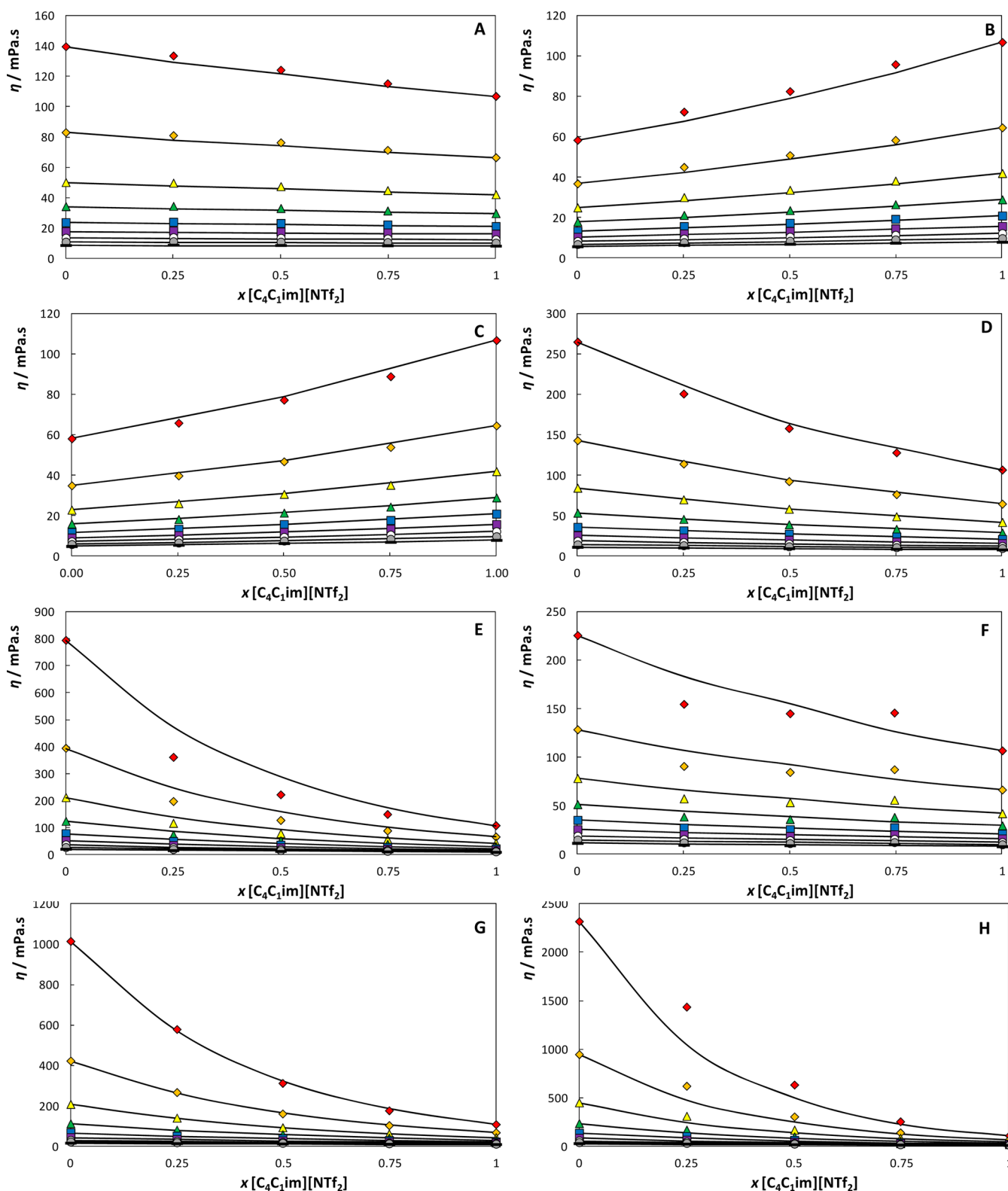


Figure 4. Energy barrier ( $E_\eta$ ) for the mixtures studied at 298.15 K: red ●, [C<sub>4</sub>C<sub>1</sub>im][(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]; orange ◆, [C<sub>4</sub>C<sub>1</sub>im][CH<sub>3</sub>CO<sub>2</sub>]; yellow ■, [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>]; green ▲, [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>]; blue ●, [C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>]; purple ◆, [C<sub>4</sub>C<sub>1</sub>im][SCN]; gray ■, [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>]; △, [C<sub>4</sub>C<sub>1</sub>im][C(CN)<sub>3</sub>]; ×, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>].

observed, especially at lower temperatures. However, for the [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]<sub>(1-x)</sub> and [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>]<sub>x</sub>[PF<sub>6</sub>]<sub>(1-x)</sub> systems, larger deviations are observed at lower temperatures and lower mole fractions of [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] (for instance at  $x = 0.25$ ). Larger deviations from ideality for the





**Figure 5.** Viscosities for all the systems studied in this work: (A)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{SCN}]_y$ , (B)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{N}(\text{CN})_2]_{(1-x)}$ , (C)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{C}(\text{CN})_3]_{(1-x)}$ , (D)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{BF}_4]_{(1-x)}$ , (E)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{PF}_6]_{(1-x)}$ , (F)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{CF}_3\text{SO}_3]_{(1-x)}$ , (G),  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{CH}_3\text{CO}_2]_{(1-x)}$ , and (H)  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[(\text{CH}_3\text{O})_2\text{PO}_2]_{(1-x)}$ ; red  $\blacklozenge$ , 283.15 K; orange  $\blacklozenge$ , 293.15 K; yellow  $\blacktriangle$ , 303.15 K; green  $\blacktriangle$ , 313.15 K; blue  $\blacksquare$ , 323.15 K; purple  $\blacksquare$ , 333.15 K;  $\circ$ , 343.15 K; gray  $\bullet$ , 353.15 K; —, 363.15 K, and description by the Grunberg and Nissan mixing rule<sup>51</sup> (lines).

$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[(\text{CH}_3\text{O})_2\text{PO}_2]_{(1-x)}$  mixture were also observed by Niedermeyer et al.<sup>9</sup> As expected, the ideal Grunberg and Nissan mixing rules<sup>51</sup> fail in describing the viscosity of the

$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]_x[\text{CF}_3\text{SO}_3]_{(1-x)}$  system, due to the almost constant behavior of viscosity with the composition of the second IL. Although Niedermeyer et al.<sup>9</sup> supported the ideal/nonideal

behavior according to the differences in polarity or hydrogen-bonding ability (comprising both the basicity and acidity of the IL ions) of each IL in the mixture, among other factors, our data for  $[C_4C_1im][NTf_2]_x[CH_3CO_2]_{(1-x)}$  follow an opposite trend. Both ILs are almost in the extremes of hydrogen-bond basicity ( $[NTf_2]^-$  versus  $[CH_3CO_2]^-$ )<sup>50</sup> and the mixture  $[C_4C_1im][NTf_2]_x[CH_3CO_2]_{(1-x)}$  follows an almost ideal behavior. Additionally, the two ILs in  $[C_4C_1im][NTf_2]_x[PF_6]_{(1-x)}$  are composed of anions with similar hydrogen-bond basicity,<sup>50</sup> and larger deviations on their ideal mixing behavior were observed. Therefore, even that substantial differences in hydrogen bonding abilities might contribute to the observed deviations from ideality these are not the dominant factor, and other factors do appear to be critical as well as explained by the authors.<sup>9</sup>

## CONCLUSIONS

New experimental data were reported for density and dynamic viscosity of eight mixtures of ILs in the temperature range between 283.15 and 363.15 K and at 0.1 MPa.  $[C_4C_1im][NTf_2]_x[Y]_{(1-x)}$  mixtures were investigated, where [Y] covers eight ILs with different anions and  $x$  covers five different mole fractions, including pure ILs. The second IL was chosen in order to evaluate the effect of distinct anions on the thermophysical properties of IL mixtures and if these mixtures follow an ideal behavior. In general, small deviations from ideality were observed for density, while larger deviations were observed for viscosity for some particular mixtures.

The mixing of ILs could potentially lead to fluids with “tailored” properties within those displayed by the pure components. If mixtures of ILs follow a closely ideal behavior, it will allow the prediction of their properties and their a priori fine-tuning. As shown in this work, and although some additional care should be taken into account with some mixtures of ILs where higher deviations from the ideal behavior were observed, in general, ideal mixture models can be used to predict the physical properties of IL mixtures.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00178.

Calculated molar volumes for the studied mixtures as a function of composition and temperature and the relative deviations between the experimental data and literature data for density and viscosity for pure ILs; the excess molar volumes and their standard deviations for the studied mixtures (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was funded by Fundação para a Ciência e Tecnologia (FCT) through PTDC/EQU-FTT/1686/2012, Research Unit GREEN-it “Bioresources for Sustainability” (UID/Multi/04551/2013), and POCI-01-0145-FEDER-007679 (FCT ref. UID/CTM/S0011/2013), CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC and when

appropriate cofinanced by FEDER under the PT2020 Partnership Agreement. H.F.D.A. acknowledges FCT for the PhD grant SFRH/BD/88369/2012 and I.M.M. for a contract under the program FCT Researcher 2012.

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