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A new correlation between excess viscosity and excess molar volume for 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim][BF₄]) mixtures with water.

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A new correlation between excess viscosity and excess molar volume for 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) mixtures with water.

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ABSTRACT: Densities and viscosities of binary mixtures containing 1-butyl-3-methylimidazolium tetrafluoroborate with water over the salt-rich region concentrations are reported for a temperature range of (283.15 to 373.15) K. The temperature dependence of the mixture densities and dynamic viscosities were accurately described by an empirical, linear relationship and by the Vogel-Fucher-Tammann (VFT) equation, respectively. We identify a new correlation between the excess mixture viscosity and the excess molar volume in the ionic liquid rich regime that is consistent with free volume theory. The broader validity of this correlation is tested against literature data for aqueous mixtures of similar ionic liquids.

Keywords: ionic liquid, water, density, viscosity, temperature, free volume theory

INTRODUCTION

Room temperature ionic liquids (RTILs) are molten salts composed of organic cations and inorganic or organic anions.¹ They have special physicochemical properties, such as negligible vapor pressure, high thermal stability, nonflammability, a wide electrochemical window and a wide liquid range.^{1,2} Consequently, RTILs have received considerable interest for application in fields such as: catalysis,^{1,2,3} separations,^{1,4} heat transfer,⁵ electrolytes,⁶ and drug delivery.⁷ They are also proposed for use a “green” replacement for traditional organic solvents,^{1,2,3} lubricants for space and high vacuum environments,^{8,9} separation media for batteries, fuel cells,¹⁰ dye sensitized solar cells,⁶ as well as candidates for industrial scale carbon capture from flue gases.¹¹

The physicochemical properties of ionic liquids and their mixture with organic/inorganic solvents are of importance for their application.^{12,13} Therefore, thermodynamic properties, such as density, viscosity, surface tension, refractive index, conductivity and the speed of sound of binary mixtures of ionic liquids with molecular solvents are interesting both from practical and theoretical point of view. Recently, systematic studies of the density, viscosity of ionic liquids [C_nmim][BF₄] with water,^{14,15,16,17,18} alcohols,^{19,20} dimethyl sulfoxide (DMSO),²¹ ethylene glycol (EG)²¹ *et al.* over broad composition ranges have been reported. Importantly, Rodriguez and Brennecke²² studied the temperature and composition dependence of the density and viscosity of aqueous solutions of a series of 1-ethyl-3-methylimidazolium with varying anions, whereupon they suggested a trend between excess volume and viscosity.²² In this work, we explore such thermodynamic relationships between transport and state properties in more detail, and in doing so identify a semi-empirical relationship between excess viscosity and excess free volume that is consistent with free volume theory.

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3 1-butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄], is among the most prevalently
4 used and commonly investigated ionic liquids. It is well known that water is a common
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6 contaminant in ionic liquids,²³ especially for hydrophilic ionic liquids, such as [C₄mim][BF₄].
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8 The addition of trace amount of water into ionic liquids significantly changes the thermodynamic
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10 properties by affecting the microstructure.²⁴ Therefore, in addition to the inherent importance of
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12 understanding the density and viscosity of binary mixture of [C₄mim][BF₄] with water,
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14 knowledge of excess properties provides insight into the molecular interactions in these mixtures
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16 and aids in developing structure-property relationships necessary for optimizing the properties of
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18 ionic liquids for specific applications.¹²
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26 In the following, we explore the effects of addition of water on the density, viscosity, and their
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28 correlation for [C₄mim][BF₄] over the salt-rich regime (up to 40% water molar fraction) over the
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30 temperature range 283.15 to 373.15 K. The temperature dependence of density and dynamic
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32 viscosity of aqueous mixtures are described by an empirical, linear relationship and by the
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34 Vogel-Fucher-Tammann (VFT) equation, respectively. The excess molar volumes are calculated
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36 using the measured experimental data and fitted to the Redlich-Kister equation. From this
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38 analysis, we discover a new correlation between the excess mixture viscosity and the excess
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40 molar volume in the ionic liquid rich regime that is consistent with free volume theory. The non-
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42 ideal densities and viscosities are understood in terms of the interactions between cations and
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44 anions of the ionic liquid and the water molecules. Finally, we explore the generality of this
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46 observation by analyzing published data on aqueous solutions of related ionic liquids.
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MATERIALS AND METHODS

Materials. The ionic liquid [C₄mim][BF₄] (>99% pure, Iolitec, 226 g/mol), was dehydrated under vacuum at 70 °C for 24 h prior to use. The final water content was 373 ppm as determined by Karl Fischer titration. Millipore deionized water of 18.3 MΩ was used for the preparation of the aqueous ionic liquid solutions for density and viscosity measurement. Samples were prepared gravimetrically within 2 days of measurement and stored in airtight glass vials sealed with parafilm.

Density. The densities of pure ionic liquid [C₄mim][BF₄] and of its aqueous mixtures were measured with an oscillating U-tube densitometer Anton Paar DMA 4500 M at temperatures from 283.15 K to 363.15 K with Peltier temperature control with an accuracy of ± 0.03 K. The uncertainty of the corresponding density measurement was ± 0.00005 g/cm³. The densitometer was calibrated with dry air and ultra-pure water at atmospheric pressure.

Viscosity. Kinematic viscosities were measured using an Anton Paar AMVn automated microviscometer at temperatures from 293.15 K to 373.15 K. The temperature was controlled by a built-in Peltier thermometer within 0.01 K. Measurements were made with different angles using calibrated capillary of $d = 3.0$ mm and stainless steel balls of $d = 2.5$ mm following standard protocols.²⁵ The repeatability of the viscosity measurement was within 0.35%. Shear viscosities are reported here, which are the product of the measured kinematic viscosities and the density.

RESULTS AND DISCUSSION

Density and viscosity measurements for the pure ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ over the temperature range 283.15 K to 373.15 K are compared with the available literature data in Figure 1. The corresponding comparisons for $[\text{C}_4\text{mim}][\text{BF}_4]$ - water systems with various water contents at 298.15 K are shown in Figure S1. A satisfactory agreement is found. The densities and viscosities results show minor differences (with a few outlier points in the literature data), which may be attributable to differences in sample purity.

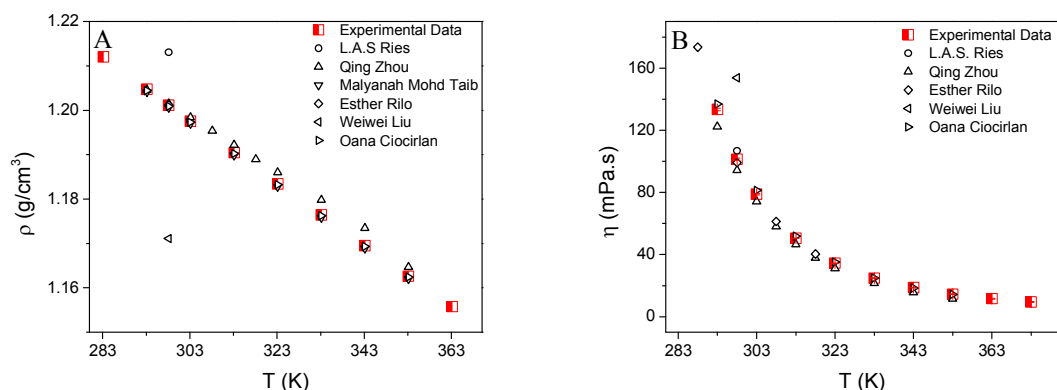


Figure 1. Comparison of measured densities and dynamic viscosities with literature values for pure $[\text{C}_4\text{mim}][\text{BF}_4]$ at temperatures from 283.15 K to 373.15 K. The literature data are from: Ries,¹⁴ Zhou and Wang,¹⁵ Taib and Murugesan,¹⁶ Rilo and Cabeza,¹⁷ Liu and Wang,²⁶ and Ciocirlan.²¹

The densities of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions with respect to water weight fraction and temperature are shown in Figure 2 and in Table S1 (see the Supporting Information). The addition of small amounts of water decreases the mixture density, which also decreases with temperature. Figure 2A shows that the density decreases linearly with the water mass fraction at

each temperature, and the values of the linear fits are given in Table 1. The density decreases with increasing temperature, as shown in Figure 2B, but the relative effect of water addition is nearly insensitive to temperature. A linear correlation between density and temperature is observed for each composition as shown in Figure 2B and the fitting parameters are also given in Table 1. These linear correlations between density and water weight fraction and/or temperature are also be useful for determining water content from density experiments.

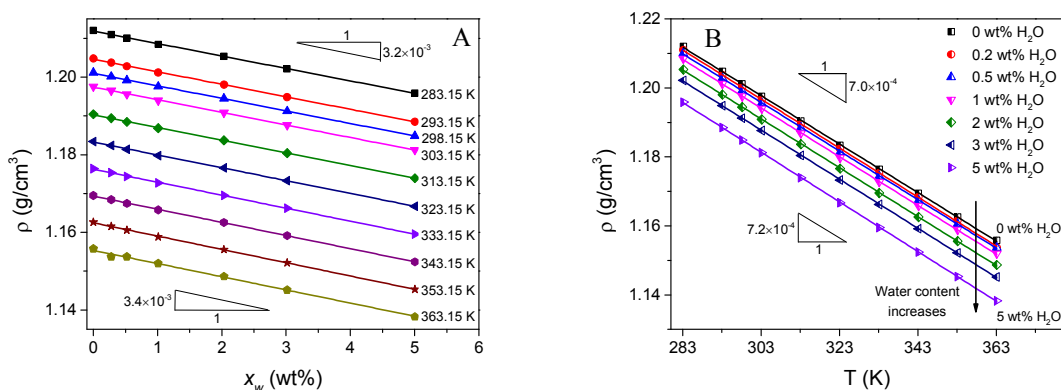


Figure 2. The densities of [C₄mim][BF₄] aqueous solution for varying water content (A) and temperature (B). Solid lines represent the linear correlations, respectively. (The mass fraction of water: 0.28wt%, 0.52wt%, 1.01wt%, 2.03wt%, 3.01wt%, and 5.00wt% corresponding to molar fraction of water: 0.03, 0.06, 0.11, 0.21, 0.28, and 0.40, respectively)

Table 1. Fitting parameters of the linear relation of density - water content (Figure 2A) and density - temperature (Figure 2B) for ionic liquid aqueous solutions.

Density-Water content (Figure 2A)					
T(K)	Slope	Intercept (g/cm ³)	T(K)	Slope	Intercept (g/cm ³)
283.15	3.21×10^{-3}	1.212	323.15	3.30×10^{-3}	1.183
293.15	3.22×10^{-3}	1.205	333.15	3.35×10^{-3}	1.176
298.15	3.23×10^{-3}	1.201	343.15	3.39×10^{-3}	1.169
303.15	3.24×10^{-3}	1.197	353.15	3.43×10^{-3}	1.162
313.15	3.27×10^{-3}	1.190	363.15	3.40×10^{-3}	1.155
Density-Temperature (Figure 2B)					
x_w (wt%)	Slope	Intercept (g/cm ³)	x_w (wt%)	Slope	Intercept (g/cm ³)
0.00	-7.03×10^{-4}	1.412	2.03	-7.08×10^{-4}	1.406
0.28	-7.10×10^{-4}	1.411	3.01	-7.12×10^{-4}	1.403
0.52	-7.04×10^{-4}	1.409	5.00	-7.20×10^{-4}	1.400
1.01	-7.06×10^{-4}	1.408			

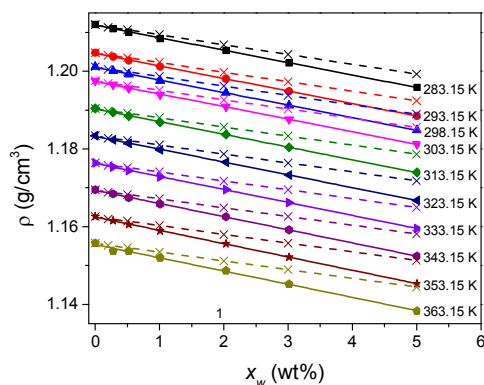


Figure 3. The experimental densities of [C₄mim][BF₄] aqueous solution at different water contents compared with calculated densities based on ideal mixing theory. The solid/dash lines represent the linear correlations between experimental/calculated density and water mass fraction.

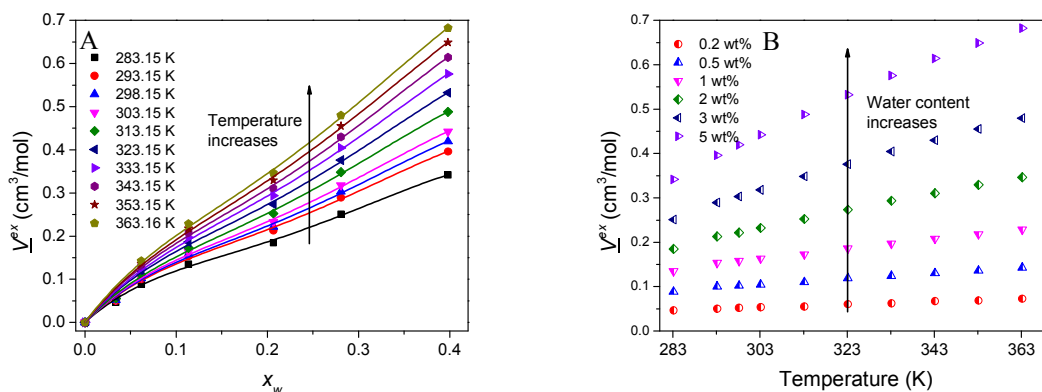


Figure 4. Excess molar volume \underline{V}^{ex} of [C₄mim][BF₄] aqueous solution dependence on water molar fraction x_w (A) and temperature (B). The symbols represent experimental value. The solid lines are fits to the Redlich-Kister equation.

The experimental densities for the binary mixtures are compared with calculated densities based on ideal mixing theory in Figure 3, where negative deviations from ideal mixing are observed for all mixtures. The negative deviations indicate an expansion of the ionic liquid microstructure with the addition of small amounts of water. The excess molar volumes \underline{V}^{ex} are calculated as:

$$\underline{V}^{ex} = \frac{x_{IL}M_{IL} + x_wM_w}{\rho_m} - \frac{x_{IL}M_{IL}}{\rho_{IL}} - \frac{x_wM_w}{\rho_w} \quad (1)$$

where ρ_m is the density of the mixture; x_{IL} and x_w are the molar fraction of ionic liquid and water, respectively; M_{IL} and M_w are the molecular weight of pure ionic liquid and water. The values of \underline{V}^{ex} shown in Figure 4A at several temperatures are fitted to the Redlich-Kister polynomial equation:

$$\underline{V}^{ex} = x_w x_{IL} \sum_{i=0}^m A_i (x_w - x_{IL})^i \quad (2)$$

Where A_i are the fitting coefficients, m is the order of the Redlich-Kister polynomial equation, x_w and x_{IL} are the molar fraction of water and ionic liquid in the aqueous mixtures. Good fits are achieved with $m = 3$ and the fitting parameters are reported in Table S2 (See Supporting Information). Figure 4A shows that the values of excess molar volume are positive at all temperatures and over the solution compositions studied. The values of \underline{V}^{ex} are expected to eventually decrease for compositions $x_w > 0.4$ and reach zero at $x_w = 1$ (pure water) as reported for other ionic liquids mixture systems.^{14, 16, 19}

The measurement of positive excess molar volumes is consistent with the reported structure of isolated water molecules hydrogen bonding to two anions via hydrogen bonds for trace water in ionic liquid as reported by simulation²⁷ and experiments.²⁸ The intercalation of water into the ionic bonds in the ionic liquid is expected to expand the ionic liquid. Further evidence for this can be found in the work of Ries *et al.*¹⁴, whose study of the conductivity and infrared spectra (IR) of [C₄mim]BF₄ water solutions at room temperature shows that the solution conductivities increase due to the weakening of the intermolecular interaction between the anionic and cationic species of [C₄mim][BF₄] upon the addition of water. The magnitude of \underline{V}^{ex} increases with increasing temperature, as shown in Figure 4B. This increase is expected due to the further weakening of the ionic interactions at increasing temperatures. Our data show that the \underline{V}^{ex} of mixture solutions with higher water concentrations are more strongly affected by temperature.

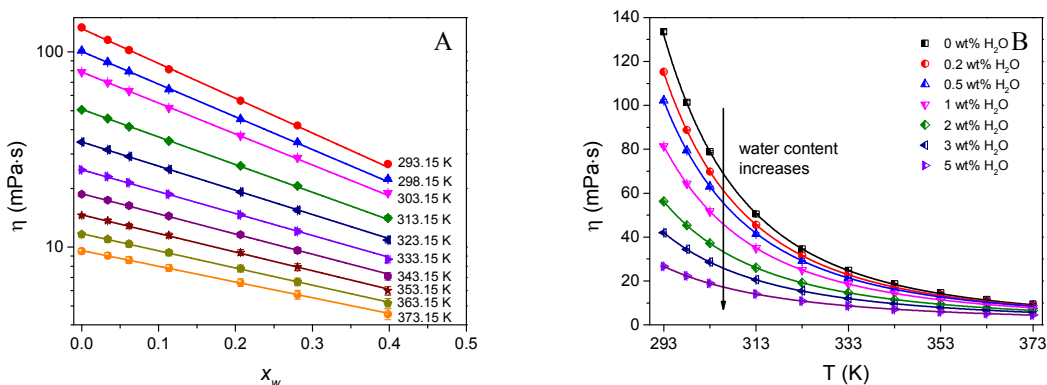


Figure 5. The viscosities of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution at different water molar fraction (A) and temperatures (B). Solid lines represent an empirical correlation (A) and the Vogel-Fulcher-Tamann (VFT) equation correlation, respectively.

Table 2. Fitting parameters (A and B) of the VFT equation for $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions with various compositions.

Water content	A	B
wt %	$\text{mPa}\cdot\text{s}\cdot\text{K}^{-0.5}$	K
0	0.0065	870.6
0.28	0.0072	841.2
0.52	0.0079	815.1
1.01	0.0090	771.2
2.03	0.0106	705.7
3.01	0.0116	659.1
5.00	0.0125	594.1

The viscosities of the ionic liquid aqueous mixtures are observed to decrease strongly with the addition of water and increase in temperature as shown in Figure 5. Importantly, the viscosity

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3 decreases significantly with the addition of small amount of water. The viscosity dependence on
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5 water molar fraction shown in Figure 5A can be correlated by an exponential function:
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$$\eta = \eta_0 \exp(-x_w / a) \quad (3)$$

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12 where η is the viscosity of the aqueous solution at certain temperature, η_0 is the viscosity of pure
13 ionic liquid at the same temperature, x_w is the molar fraction of water and a is a fitting constant
14 reported in Table S3 (See Supporting Information). The sensitivity to water addition increases
15 with temperature, as evident by the values of the fitting constant a , which increases from 0.24 at
16 293.15 K to 0.54 at 373.15 K.
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25 The mixture viscosities decrease with temperature as shown in Figure 5B. This behavior can be
26 accurately described by the Vogel-Fulcher-Tammann (VFT) equation:
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$$\eta = AT^{1/2} \exp[B / (T - T_0)] \quad (4)$$

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35 where A and B are the fitting parameters. T_0 is often associated with the glass transition
36 temperature,²¹ which is reported to be 193.6 K for the pure ionic liquid [C₄mim][BF₄] as
37 determined using differential scanning calorimetry.²⁹ Domanska *et al.*^{30, 31} proposed using the
38 ideal transition temperature for T_0 , for glass-forming ionic liquids and their mixtures with
39 organic solvents. Ciocirlan *et al.*²¹ set the value of T_0 to be 170 K for the [C₄mim][BF₄]/
40 dimethyl sulfoxide (DMSO) and [C₄mim][BF₄]/ ethylene glycol (EG) mixtures to correlate the
41 temperature dependence of the viscosity. We adopt this value for the aqueous [C₄mim][BF₄]
42 mixtures used here. Eqn. (4) provides a successful correlation of the viscosity measurements, as
43 shown in Figure 5B. The fitting parameters are listed in Table 2. These parameters vary
44 smoothly as the water content increases in the mixtures. We note that the VFT equation provides
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a better correlation of the viscosity data than a simple Arrhenius plot (see the Supporting Information - Figure S3), which was suggested by Haghani *et al.*, who modeled an extensive variety of binary ionic liquid mixtures.³²

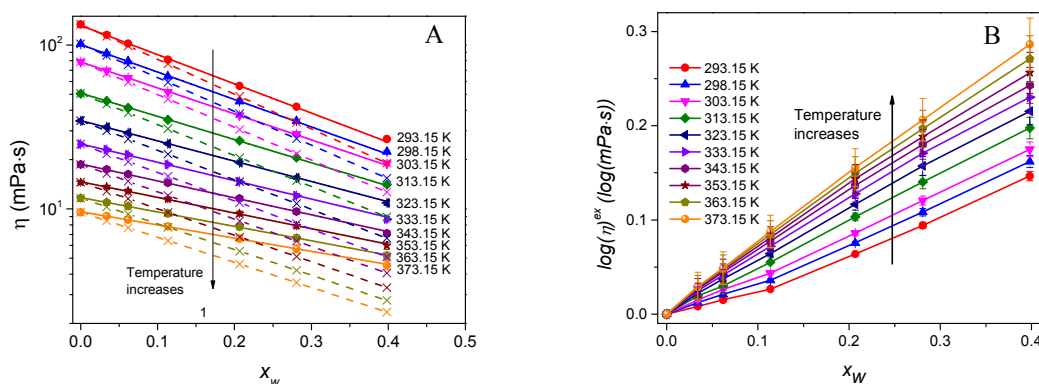


Figure 6. (A) Viscosities of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions as a function of water mole fraction (solid lines and symbols) compared with calculated viscosities based on ideal mixing theory (-x-). (B) Excess log viscosity, $\log(\eta)^{ex}$, vs molar fraction of water x_w for $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous mixtures as a function of temperature.

The viscosity of ideal mixtures can be approached according to the Arrhenius ideal solution model,^{33, 34} which is equivalent to the fluidity additivity rule.

$$\log(\eta_{ideal}) = x_{IL} \log(\eta_{IL}) + x_w \log(\eta_w) \quad (5)$$

where η_{ideal} , η_{IL} and η_w are the viscosities of the ideal mixture, pure ionic liquid and water, respectively. We define the excess log viscosity $\log(\eta)^{ex}$ as the difference between the logarithm of the mixture viscosity and that defined by the Arrhenius ideal mixture viscosity³⁵:

$$\log(\eta)^{ex} = \log(\eta) - \log(\eta_{ideal}) \quad (6)$$

The ideal mixture viscosities calculated from Eq. (5) are compared with experimental results in Figure 6A and the excess viscosities are plotted vs water molar fraction in Figure 6B. Positive deviations from ideal mixing are an indication of strong interactions between the water and the [C4mim][BF₄], such that water does not exhibit its bulk viscosity as anticipated in the Arrhenius ideal mixing theory.

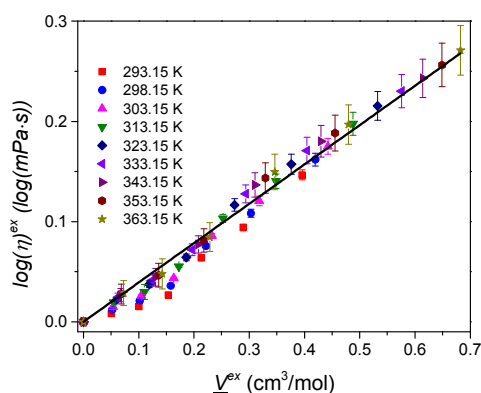


Figure 7. The global linear correlation between excess log viscosity, $\log(\eta)^{ex}$, and excess molar volume, V^{ex} , of [C₄mim][BF₄] aqueous solution at various temperatures.

Doolittle *et al.*³⁶ related the shear viscosity of simple liquids with the free volume in solution V_f , with an empirical equation that has successfully modeled the viscosity of ordinary liquids:

$$\log \eta = \log A + B \frac{V - V_f}{V_f} \quad (7)$$

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3 where A and B are empirical constants, \underline{V} and \underline{V}_f are the molar volume and molar free volume of
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5 the liquid. Based on the Doolittle equation, we propose the following, semi-empirical
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7 relationship between the excess viscosity and the free volume:
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$$\log(\eta)^{\alpha} = C\underline{V}^{\alpha} \quad (8)$$

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15 Where C is an empirical constant, which is taken to be independent of temperature and
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17 composition.
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21 The physical basis for this semi-empirical relationship lies in the expectation that the excess
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23 molar volume arises from the strong interaction between the water and the ionic liquid at lower
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25 water content. Thus, the excess viscosity should be positive as the “fluidity” of the water in this
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27 bound state is dramatically lowered as compared to water in the free-state. Consistently, we
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29 assume that, again to first order, the molar free volume is relatively constant over the range of
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31 conditions explored, and therefore, according to the Doolittle application of free volume theory,
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33 the excess volume acts to increase the viscosity above what would be expected for ideal mixing.
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35 Note that a possible relationship between the excess mixing properties, including the viscosity
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37 and molar volume, and free volume theory has been explored for binary liquid mixtures for over
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39 forty years,³⁵ but a formal relationship of the form of Eqn. (8) has not been derived or validated.
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45 Therefore, we propose it as a semi-empirical relationship to be tested against experimental data.
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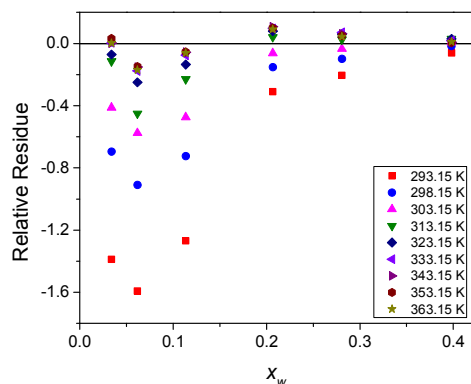


Figure 8. The relative residues of excess log viscosity $\log(\eta)^{ex}$ from correlation Eqn. (8) of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions at various temperatures and compositions.

For the $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions, it is found that excess log viscosity $\log(\eta)^{ex}$ is indeed linearly correlated with the excess molar volume \underline{V}^{ex} ($R^2 = 0.996$) over the range of compositions and temperatures studied. This new correlation provides insight into the significant effect of water on the viscosity of ionic liquids. The relative residues of the excess log viscosity $\log(\eta)^{ex}$ from the correlation fitting for different temperatures and various water compositions are shown in Figure 8. The relative residues in Figure 8 indicate the significant deviations occur at low water content and at lower temperatures, with the maximum relative deviation at water molar fraction $x_w = 0.06$ composition with temperature 293.15 K. Correlation improves with increasing water content and temperature.

Finally, we explore whether this semi-empirical correlation is applicable to aqueous solutions of other ionic liquids. For the imidazolium-based ionic liquids with the same anion $[\text{BF}_4]^-$, such as 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ($[\text{Pdmim}][\text{BF}_4]$),³⁷ the excess molar volumes and excess log viscosity are positive for the entire water compositions, and a good linear correlation ($R^2 = 0.959$) is observed for the salt-rich regime (water molar fraction up to

30%) as shown in Figure 9A. The density and viscosity of pyridinium-based ionic liquid aqueous solutions have been reported by Mokhtarani.³⁸ In contrast to [C₄mim][BF₄], the excess log viscosity of 1-butylpyridinium tetrafluoroborate ([BuPy][BF₄]) aqueous solutions are negative for certain water compositions and temperatures in the salt rich regime and no linear correlation between excess molar volume and excess log viscosity is observed for this system (See Supporting Information - Figure S9). However, for the 1-octylpyridinium tetrafluoroborate ([OcPy][BF₄]), which has a longer alkyl chain, the excess log viscosity is positive for the entire water compositions, and as shown in Figure 9B, a good linear correlation between excess molar volume and excess log viscosity of aqueous solution with water molar fraction up to 35% is observed with $R^2 = 0.955$.

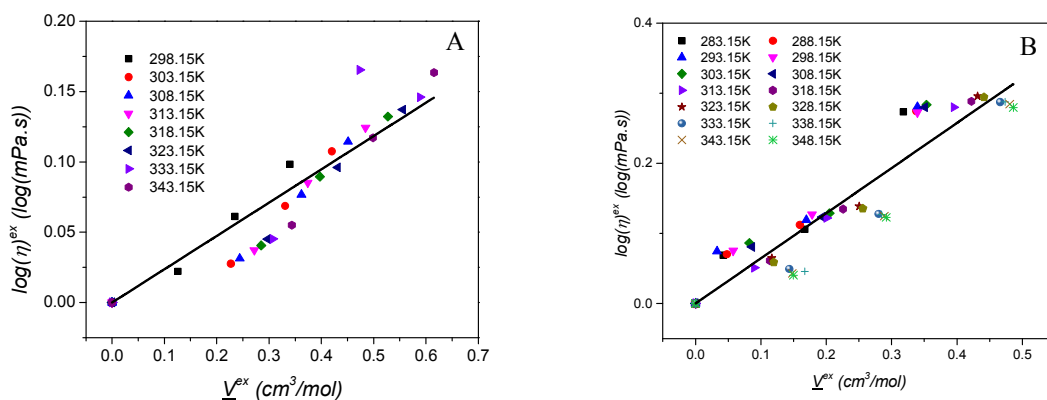
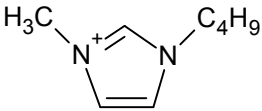
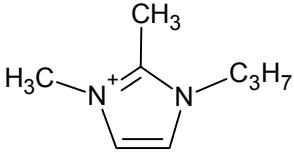
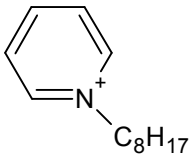


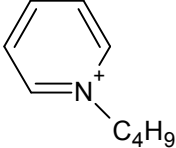
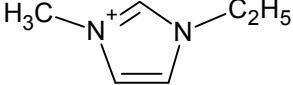
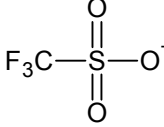
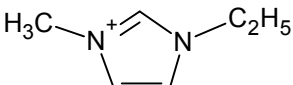
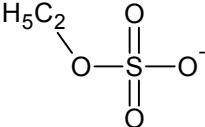
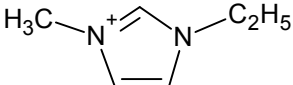
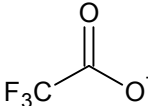
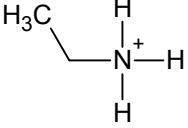
Figure 9. The semi-empirical linear correlation between excess log viscosity, $\log(\eta)^{ex}$, and excess molar volume, V^{ex} , of [Pdmim][BF₄] (A) and [OcPy][BF₄] (B) aqueous solutions in salt-rich regime respectively at various temperatures.

Imidazolium-based ionic liquids aqueous systems with anions other than [BF₄]⁻ have also been studied. The density and viscosity values for mixtures of water and three ionic liquids: 1-ethyl-3-methylimidazolium ethylsulfate ([C₂mim][EtSO₄]), 1-ethyl-3-methylimidazolium

trifluoroacetate ([C₂mim][TFA]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂mim][OTf]) are reported by Rodriguez and Brennecke.²² Their excess molar volumes are negative for the entire compositions (e.g. [C₂mim][TFA] aqueous solutions) or partial compositions (e.g. [C₂mim][EtSO₄] and [C₂mim][OTf]). No obvious linear correlations are observed for these systems (See Supporting Information – Figure S9). The same for the widely used protic ionic liquid ethylammonium nitrate (EAN) water system.³⁹ The excess molar volumes change from positive to negative with increasing water content and the semi-empirical linear correlation between excess molar volume and excess log viscosity cannot be applied to this system.

Table 3. Summary of validation of semi-empirical linear correlation between excess log viscosity and excess molar volume of various ionic liquids.

Ionic liquid	Cation structure	Anion structure	$\log(\eta)^{ex*}$	\underline{V}^{ex*}	Linear correlation	Ref.#
1-butyl-3-methylimidazolium tetrafluoroborate ([C ₄ mim][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	
1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([Pdmim][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	37
1-octylpyridinium tetrafluoroborate ([OcPy][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	38

1-butylpyridinium tetrafluoroborate ([BuPy][BF ₄])		BF ₄ ⁻	Mostly positive	Positive	No	38
1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C ₂ mim][OTf])			Positive	Mostly positive	No	22
1-ethyl-3-methylimidazolium ethylsulfate ([C ₂ mim][EtSO ₄])			Positive	Mostly negative	No	22
1-ethyl-3-methylimidazolium trifluoroacetate ([C ₂ mim][TFA])			Positive	Negative	No	22
ethylammonium nitrate (EAN)		NO ₃ ⁻	Mostly negative	Mostly negative	No	39

* The positive or negative values of excess log viscosity, $\log(\eta)^{ex}$, and excess molar volume, V^{ex} of entire water compositions. “Positive” indicates the values are positive for the entire water compositions, and “Mostly positive” indicates the values are positive for most of the water concentration and only for small part of water compositions are negative, “Negative” and “Mostly negative” can be deduced by analogy.

The survey of the available literature and our research, as summarized in Table 3, shows that this semi-empirical correlation is valid for [C₄mim][BF₄] aqueous solutions and other aqueous solutions of ionic liquids containing the [BF₄]⁻ anion. The cations include another imidazolium ([Pdmim][BF₄]) and a pyridinium ([OcPy][BF₄]). Note this semi-empirical linear correlation applies only for aqueous ionic liquid solutions in the salt-rich regime ($x_w < 50\%$). It is known

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3 that the interactions between ionic liquids and water lead to microphase separation and phase
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5 inversion for higher water concentrations,^{27, 28, 40} which would suggest the model is not
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7 applicable.
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11 As summarized in Table 3, both the excess molar volume and excess log viscosity must be
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13 positive over the entire water composition range of interest for this correlation to apply. The
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15 excess properties are determined by the specific interactions between ions and water molecules.²⁴
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17 It is reported that anions have the dominant effect on the ionic liquid-water interactions, while
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19 water hydrogen bonding with the cations is a secondary effect.²⁴ The anion [OTf]⁻ (i.e., CF₃SO₃⁻)
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21 has a slightly larger water solubility than [BF₄]⁻ group,^{41, 42} and it can form strong acid CF₃SO₃H
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23 with the present of proton and react with water molecules to form ion-ligand complex CF₃SO₃⁻ •
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25 H₂O or CF₃SO₃⁻ • 2H₂O.⁴³ The strength of H-bonding or water solubility increases in the order
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27 [BF₄]⁻ < [OTf]⁻, [EtSO₄]⁻ < [NO₃]⁻ < [TFA]⁻.⁴² The water interactions with [OTf]⁻, [EtSO₄]⁻,
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29 [TFA]⁻ and [NO₃]⁻ differ from that with [BF₄]⁻, which results in different excess properties and
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31 that are not captured by our semi-empirical linear correlation. The specific cation plays a
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33 secondary effect on the ionic liquids and water molecules interactions, and the cations [Pdmim]⁺,
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35 and [OcPy]⁺ have similar hydrophobicity as [C₄mim]⁺, but [BuPy]⁺, and [C₂mim]⁺ are less
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37 hydrophobic.⁴¹ Consequently, this semi-empirical linear correlation is not valid for [BuPy][BF₄]
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39 aqueous solutions due to differing cation-water interactions. This empirical survey of the
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41 available literature provides hints that the development of a molecular thermodynamic theory for
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43 water interactions with ionic liquids in the salt rich regime may be able to predict the broad range
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45 of composition specific nonideal behaviors reported to date.
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CONCLUSIONS

The densities and viscosities of binary mixtures of 1-Butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) with water are reported for the temperature range of (283.15 to 373.15) K over the salt-rich composition regime. Excess molar volumes are and excess viscosities are calculated and can be accurately fit with simple correlation, which are provided for reference. A new semi-empirical correlation between the excess mixture viscosities and the excess molar volumes in the salt-rich regime is identified, which is consistent with free volume theory. This correlation enables predicting the viscosity of ionic liquids with added water directly from density measurements, and is also found to be valid for other ionic liquids aqueous solutions with similar ion structures. A survey of the literature identifies ionic liquids for which this correlation is valid or inapplicable, and provides evidence for the role of specific molecular interactions that govern the observed nonidealities in salt-rich aqueous solutions of ionic liquids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

The SI contains: Tabulated data of density and viscosity of [C₄mim][BF₄] aqueous solutions, comparison of measured densities and dynamic viscosities with literature values at 298.15 K for [C₄mim][BF₄] with various water contents, derivation of equation 8 using free space theory. The values of fitting parameters for density and viscosity temperature/water content correlations.

The relation between viscosity and temperature fitted with Arrhenius equation. Plots of excess log viscosity vs. excess molar volume of different ionic liquid aqueous systems.

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