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# Densities and Viscosities for Binary Mixtures of 1-Butyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid with Molecular Solvents

Oana Ciocirlan,* Oana Croitoru, and Olga Iulian

Department of Applied Physical Chemistry and Electrochemistry, Politehnica University of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania

**ABSTRACT:** The densities and viscosities for the binary systems of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF4], with the molecular solvents: dimethylsulfoxide (DMSO) and ethylene glycol (EG), were measured over the whole concentration range in the temperature range from (293.15 to 353.15) K by using an Anton Paar DMA 4500 densimeter and an Anton Paar AMVn measuring assembly, respectively. The temperature dependence of density and dynamic viscosity both for pure [Bmim][BF4] and its binary mixtures can be described by an empirical linear equation and by the Vogel-Fucher-Tammann (VFT) equation, respectively. The excess molar volumes, $V^E$, were calculated by using the measured experimental data and fitted to a Redlich−Kister equation. These values are negative for the [Bmim][BF4] + DMSO system and positive for the [Bmim][BF4] + EG system over the whole composition range at investigated temperatures. The $V^E$ results have been analyzed using the Prigogine−Flory−Patterson (PFP) theory, which can explain the volumetric behavior of the investigated binary mixtures.

## INTRODUCTION

Room temperature ionic liquids (ILs) are a class of organic salts that are liquids at or near room temperature in their pure state. They exhibit interesting properties, such as negligible vapor pressure, low melting point, a wide liquid range, suitable viscosity, high thermal stability, are good solvents for both polar and nonpolar organic and inorganic substances, have a high electrical conductivity, and have wide electrochemical windows, which suggest many applications as green and possibly benign replacements for traditional volatile organic solvents. The key attraction of ILs is their possibility to be tuned by varying the nature of the cations and anions. The ILs present possible applications in different fields, such as synthesis,[1] catalysis,[1,2] extraction technologies,[3] electrochemistry,[4] biotechnologies,[5] nanomaterials,[6] etc.

Generally, the technological processes use binary mixtures of ILs with organic and inorganic solvents. The physicochemical properties, like viscosity and density, of IL+ molecular solvent binary mixtures are interesting both from practical and theoretical point of view. Moreover, the knowledge of excess properties helps us to understand the structure−property relation, making it easier to search for an optimal ionic liquid for a specific application.

1-Butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF4], is historically one of the most important and commonly investigated ionic liquid.[7−15] The thermophysical properties of the binary mixtures of [Bmim][BF4] with molecular solvents as water, alcohols, ethers, esters, nitroalkanes, and chloroalkanes have been studied in some extent in literature.[16−22] Dimethylsulfoxide (DMSO) and ethylene glycol (EG) are important polar organic solvents with extensive use in many chemical processes, biology and medicine. The mixtures of DMSO with ILs are scarcely examined.[20,23]

In this context, we report here densities and viscosities of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate and its binary mixtures with DMSO and EG over the whole composition range and temperatures between (293.15 and 353.15) K at atmospheric pressure. To our best knowledge, for the [Bmim][BF4] + DMSO binary system experimental density data are reported only at 298.15 K[20] and no viscosity data are available in literature. Moreover, for the binary [Bmim][BF4] +EG system, the density data are limited[18,19] and no viscosity data are available in literature.

## EXPERIMENTAL SECTION

**Materials.** Reagents used were 1-butyl-3-methylimidazolium tetrafluoroborate (mass fraction > 0.99), DMSO (mass fraction > 0.999), and ethylene glycol (mass fraction > 0.995), which were purchased from Merck. The organic solvents were dried and stored over 3A molecular sieves and were used without further purification. Because of the hygroscopic character of the ionic liquid, it was treated for 11 h at 333 K under vacuum. It was then conditioned under a nitrogen atmosphere. To avoid any contact of the sample with atmosphere, a Schlenk tube and a syringe equipped with a Luer Lock valve were used to prepare the samples and to load them into the instruments.

**Apparatus and Procedure.** The binary mixtures were prepared by mass on a HR-120 (A&D Japan) electronic balance with a precision of ± $10^{-4}$ g. The experimental uncertainty in mole fractions was estimated to be less than ± 0.0002.

**Measurement of Density.** The density measurements of the pure ionic liquid and of its binary mixtures were performed by means of an Anton Paar DMA 4500 densimeter with a

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**Table 1. Comparison of Measured Densities and Dynamic Viscosities with Literature Values for Pure Components at $T$ = (293.15 and 353.15) K**

| component | $T$ / K | $\rho$ / g·cm$^{-3}$ exptl | $\rho$ / g·cm$^{-3}$ lit. | $\eta$ / mPa·s exptl | $\eta$ / mPa·s lit. |
|---|---|---|---|---|---|
| [Bmim][BF$_4$] | 293.15 | 1.20444 | 1.2049[11]<br>1.20483[12] | 136.9 | 135.6[12]<br>136.3[14] |
|  | 298.15 | 1.20089 | 1.2011[11]<br>1.20129[12]<br>1.20100[13] |  |  |
|  | 303.15 | 1.19734 | 1.1974[11]<br>1.19755[12]<br>1.19760[13] | 81.40 | 80.6[12,14] |
|  | 313.15 | 1.19027 | 1.1901[11]<br>1.19068[12]<br>1.19080[13] | 51.79 | 51.3[12]<br>51.5[14] |
|  | 323.15 | 1.18324 | 1.1827[11]<br>1.18367[12]<br>1.18400[13] | 35.23 | 34.6[12]<br>34.9[14] |
|  | 333.15 | 1.17625 | 1.1753[11]<br>1.17670[12]<br>1.17720[13] | 24.97 | 24.5[12] |
|  | 343.15 | 1.16932 | 1.1680[11]<br>1.16979[12]<br>1.17040[13] | 18.49 | 18.1[12] |
|  | 353.15 | 1.16244 | 1.16292[12]<br>1.16360[13] | 14.37 | 13.9[12] |
| DMSO | 293.15 | 1.10076 | 1.100424[24]<br>1.10053[25] | 2.210 | 2.210[24]<br>2.244[25] |
|  | 298.15 | 1.09574 | 1.09562[26]<br>1.0957[27] |  |  |
|  | 303.15 | 1.09073 | 1.090467[24]<br>1.09049[25] | 1.843 | 1.810[24]<br>1.830[25] |
|  | 313.15 | 1.08069 | 1.080490[24]<br>1.08032[25] | 1.556 | 1.514[24]<br>1.534[25] |
|  | 323.15 | 1.07066 | 1.07057[28] | 1.337 | 1.313[28] |
| ethylene glycol | 293.15 | 1.11345 | 1.11323[29]<br>1.11347[30] | 21.44 | 20.81[29] |
|  | 298.15 | 1.10996 | 1.11000[31]<br>1.109955[32] |  |  |
|  | 303.15 | 1.10645 | 1.10546[29]<br>1.10663[31] | 14.33 | 13.87[29] |
|  | 313.15 | 1.09938 | 1.09835[29]<br>1.09964[31] | 10.01 | 9.53[29] |

precision of ± 0.05 kg·m$^{-3}$, between 293.15 K and 353.15 K. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The thermostatted sample was controlled to ±0.01 K. The uncertainty in the density determination is ± 5 × 10$^{-5}$ g·cm$^{-3}$ and for $V^E$ is less than ± 10$^{-2}$ cm$^3$·mol$^{-1}$.

**Measurement of Viscosity.** Dynamic viscosities, $\eta$, were obtained using an Anton-Paar AMVn falling ball automated viscometer. The temperature is controlled by means of a built-in Peltier thermostat within ±0.01 K. Various combinations of ball/capillary of different diameters $d$ were selected to allow measurement of viscosities from 1 to 136.9 mPa·s. Measurements were made with different angles using three calibrated capillaries with $d$ = 1.6 mm, $d$ = 1.8 mm, and $d$ = 3 mm. The repeatability in the measurement of the viscosity is ± 0.1%, and its reproducibility is < 0.5%.

The experimental data of pure components and comparison with the literature data are given in Table 1.

## ■ RESULTS AND DISCUSSION

The measured densities, $\rho$, and the dynamic viscosities, $\eta$, for the binary mixtures of [Bmim][BF4] with DMSO and EG at $T$ = (293.15, 303.15, 313.15, 323.15, 333.15, 343.15, and 353.15) K over the whole composition range are listed in Tables 2 and 3. Moreover, we present our measured densities at 298.15 K to compare them with the existing literature data.[18−20] These obtained values for both systems at 298.15 K are also included in Table 2.

As can be seen, the density of all of the mixtures always increases with the IL mole fraction, $x_1$, and decreases with temperature, $T$. The temperature variation of densities for both pure [Bmim][BF4] and its binary mixtures of different composition with DMSO and EG, respectively, are shown in Figures 1 and 2. A very good linear correlation is observed for all compositions ($r =$ 1), this linear behavior with temperature being also reported by other authors for pure ionic liquids.[11−13]

A perusal of Table 3 reveals that viscosities are more influenced by temperature than densities. The Vogel−Fulcher−Tammann (VFT) equation generally gave a better description of temperature dependence of dynamic viscosity for glass forming ionic liquids, than Arrhenius law.[33−35] VFT equation adds an additional adjustable parameter, $T_0$, glass transition temperature, to the exponential term

$$\eta = AT^{0.5}\exp[B/(T - T_0)] \tag{1}$$

$A$ and $B$ are the adjustable parameters, determined empirically. For the glass-forming ILs and their mixtures with organic solvents, Domanska et al.[36] have used a refined value for $T_0$ (called the ideal transition temperature), which is lower than the glass transition temperature. These considerations have been adopted by us in this paper. For [BmimM][BF4] the temperature of glass transition determined by differential scanning calorimetry was 193.6 K.[37] For the best correlation of the experimental curves the value of $T_0$ equal to 170 K was used in all calculations, including binary mixtures. Figures 3 and 4 show the experimental dynamic viscosities for the [Bmim][BF4] + DMSO and the [Bmim][BF4] + EG systems as a function of temperature, for different compositions, with the VFT equation. The adjustable parameters and the standard deviations, which were obtained from the VTF correlation have been listed in Table 4. The obtained parameters $A$ and $B$ change smoothly with composition for binary mixtures.

The viscosities of the mixtures decrease rapidly when organic compounds are added to the ionic liquid, especially at lower temperatures. This decrease is particularly strong in dilute solutions of organic compounds in the ionic liquid. The strong coulomb interactions between the [BF4]$^-$ anion and

Table 2. Experimental Densities, $\rho$, and Molar Excess Volumes, $V^E$ for the Binary Systems [Bmim][BF$_4$] + DMSO and [Bmim][BF$_4$] + EG at Different Temperatures

| $x_1$ | $T$ = 293.15 K | $T$ = 298.15 K | $T$ = 303.15 K | $T$ = 313.15 K | $T$ = 323.15 K | $T$ = 333.15 K | $T$ = 343.15 K | $T$ = 353.15 K |
|---|---|---|---|---|---|---|---|---|
| [Bmim][BF$_4$] (1) + DMSO (2) | | | | | | | | |
| $\rho$/g·cm$^{-3}$ | | | | | | | | |
| 0.0000 | 1.10076 | 1.09574 | 1.09073 | 1.08069 | 1.07066 | 1.06063 | 1.05058 | 1.04051 |
| 0.0722 | 1.12091 | 1.11622 | 1.11154 | 1.10221 | 1.09289 | 1.08358 | 1.07429 | 1.06499 |
| 0.1764 | 1.14223 | 1.13784 | 1.13345 | 1.12471 | 1.11601 | 1.10734 | 1.09870 | 1.09008 |
| 0.2145 | 1.14847 | 1.14416 | 1.13987 | 1.13131 | 1.12279 | 1.11430 | 1.10583 | 1.09739 |
| 0.3225 | 1.16289 | 1.15877 | 1.15466 | 1.14647 | 1.13833 | 1.13022 | 1.12216 | 1.11412 |
| 0.4189 | 1.17283 | 1.16884 | 1.16485 | 1.15691 | 1.14902 | 1.14118 | 1.13338 | 1.12562 |
| 0.6070 | 1.18694 | 1.18257 | 1.17932 | 1.17176 | 1.16425 | 1.15679 | 1.14937 | 1.14199 |
| 0.6557 | 1.18845 | 1.18538 | 1.18100 | 1.17363 | 1.16630 | 1.15897 | 1.15160 | 1.14428 |
| 0.8283 | 1.19744 | 1.19378 | 1.19012 | 1.18284 | 1.17562 | 1.16844 | 1.16132 | 1.15424 |
| 0.9155 | 1.20103 | 1.19743 | 1.19383 | 1.18665 | 1.17953 | 1.17245 | 1.16543 | 1.15844 |
| 1.0000 | 1.20444 | 1.20089 | 1.19734 | 1.19027 | 1.18324 | 1.17625 | 1.16932 | 1.16244 |
| $V^E$/cm$^3$·mol$^{-1}$ | | | | | | | | |
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.0722 | −0.174 | −0.183 | −0.192 | −0.214 | −0.237 | −0.261 | −0.288 | −0.317 |
| 0.1764 | −0.319 | −0.333 | −0.347 | −0.378 | −0.412 | −0.450 | −0.491 | −0.535 |
| 0.2145 | −0.354 | −0.368 | −0.384 | −0.418 | −0.455 | −0.495 | −0.538 | −0.585 |
| 0.3225 | −0.407 | −0.421 | −0.437 | −0.471 | −0.508 | −0.549 | −0.594 | −0.642 |
| 0.4189 | −0.416 | −0.429 | −0.443 | −0.474 | −0.509 | −0.548 | −0.590 | −0.635 |
| 0.6070 | −0.276 | −0.287 | −0.298 | −0.328 | −0.358 | −0.391 | −0.420 | −0.452 |
| 0.6557 | −0.232 | −0.241 | −0.252 | −0.279 | −0.308 | −0.337 | −0.364 | −0.392 |
| 0.8283 | −0.075 | −0.077 | −0.079 | −0.084 | −0.093 | −0.103 | −0.115 | −0.126 |
| 0.9155 | −0.013 | −0.013 | −0.015 | −0.016 | −0.019 | −0.023 | −0.029 | −0.031 |
| 1.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| [Bmim][BF$_4$] (1) + EG (2) | | | | | | | | |
| $\rho$/g·cm$^{-3}$ | | | | | | | | |
| 0.0000 | 1.11345 | 1.10996 | 1.10645 | 1.09938 | 1.09224 | 1.08500 | 1.07765 | 1.07017 |
| 0.0895 | 1.13364 | 1.12995 | 1.12626 | 1.11886 | 1.11143 | 1.10395 | 1.09642 | 1.08883 |
| 0.1758 | 1.14786 | 1.14407 | 1.14028 | 1.13271 | 1.12513 | 1.11755 | 1.10996 | 1.10235 |
| 0.3578 | 1.16780 | 1.16396 | 1.16012 | 1.15249 | 1.14489 | 1.13735 | 1.12984 | 1.12235 |
| 0.4397 | 1.17428 | 1.17046 | 1.16664 | 1.15907 | 1.15154 | 1.14407 | 1.13664 | 1.12925 |
| 0.6482 | 1.18763 | 1.18391 | 1.18021 | 1.17285 | 1.16556 | 1.15832 | 1.15114 | 1.14400 |
| 0.8121 | 1.19619 | 1.19256 | 1.18895 | 1.18174 | 1.17460 | 1.16755 | 1.16056 | 1.15354 |
| 1.0000 | 1.20444 | 1.20089 | 1.19734 | 1.19027 | 1.18324 | 1.17625 | 1.16932 | 1.16244 |
| $V^E$/cm$^3$·mol$^{-1}$ | | | | | | | | |
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.0895 | 0.145 | 0.157 | 0.168 | 0.190 | 0.211 | 0.232 | 0.252 | 0.271 |
| 0.1758 | 0.249 | 0.269 | 0.289 | 0.327 | 0.365 | 0.401 | 0.435 | 0.468 |
| 0.3578 | 0.440 | 0.471 | 0.500 | 0.556 | 0.611 | 0.661 | 0.708 | 0.753 |
| 0.4397 | 0.501 | 0.532 | 0.562 | 0.618 | 0.673 | 0.722 | 0.769 | 0.813 |
| 0.6482 | 0.496 | 0.521 | 0.542 | 0.584 | 0.621 | 0.654 | 0.685 | 0.715 |
| 0.8121 | 0.326 | 0.340 | 0.350 | 0.372 | 0.393 | 0.403 | 0.412 | 0.431 |
| 1.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 |

[Bmim]$^+$ cation are weakened upon mixing with the polar organic compounds, which leads to decreased viscosity of the mixtures.[22]

In Figure 5 are given the relative deviations of density and viscosity reported by different authors[11−14] from our measurements for pure [Bmim][BF4]. The obtained average values for density and viscosity measurements are about 0.04% and 1%, respectively. We can appreciate that the data for pure [Bmim][BF4] ionic liquid correspond well with those reported in literature.[11−14]

**Table 3. Experimental Viscosities, $\eta$, for the Binary Systems [Bmim][$BF_4$] + DMSO and [Bmim][$BF_4$] + EG at Different Temperatures**

| $x_1$ | $T$ = 293.15 K | $T$ = 303.15 K | $T$ = 313.15 K | $T$ = 323.15 K | $T$ = 333.15 K | $T$ = 343.15 K | $T$ = 353.15 K |
|---|---|---|---|---|---|---|---|
| | | | [Bmim][$BF_4$] (1) + DMSO (2) | | | | |
| 0.0000 | 2.210 | 1.843 | 1.556 | 1.337 | 1.165 | 1.028 | 0.917 |
| 0.0722 | 3.514 | 2.827 | 2.324 | 1.951 | 1.668 | 1.447 | 1.272 |
| 0.1764 | 6.283 | 4.839 | 3.845 | 3.137 | 2.615 | 2.222 | 1.918 |
| 0.2145 | 7.911 | 5.968 | 4.668 | 3.767 | 3.118 | 2.638 | 2.278 |
| 0.3225 | 13.46 | 9.732 | 7.347 | 5.742 | 4.618 | 3.801 | 3.195 |
| 0.4189 | 20.76 | 14.46 | 10.58 | 8.052 | 6.327 | 5.104 | 4.210 |
| 0.6070 | 42.17 | 27.68 | 19.29 | 14.12 | 10.69 | 8.359 | 6.702 |
| 0.6557 | 48.88 | 31.52 | 21.66 | 15.79 | 11.78 | 8.977 | 7.182 |
| 0.8283 | 83.33 | 51.43 | 33.94 | 25.01 | 17.38 | 13.21 | 10.34 |
| 0.9155 | 107.2 | 64.87 | 42.14 | 29.99 | 20.96 | 15.78 | 12.24 |
| 1.0000 | 136.9 | 81.40 | 51.79 | 35.23 | 24.97 | 18.49 | 14.37 |
| | | | [Bmim][$BF_4$] (1) + EG (2) | | | | |
| 0.0000 | 21.44 | 14.33 | 10.01 | 7.121 | 5.330 | 4.103 | 3.242 |
| 0.0895 | 19.89 | 12.66 | 8.881 | 6.422 | 4.880 | 3.807 | 2.872 |
| 0.1758 | 19.29 | 12.72 | 8.902 | 6.528 | 4.971 | 3.909 | 3.163 |
| 0.3578 | 23.44 | 15.48 | 10.87 | 8.034 | 6.160 | 4.870 | 3.932 |
| 0.4397 | 23.39 | 17.50 | 12.33 | 9.112 | 7.005 | 5.552 | |
| 0.6482 | 39.69 | 26.17 | 18.29 | 13.41 | 10.20 | 8.019 | 6.479 |
| 0.8121 | 68.29 | 41.88 | 28.17 | 20.62 | 14.84 | 11.41 | 8.692 |
| 1.0000 | 136.9 | 81.40 | 51.79 | 35.23 | 24.97 | 18.49 | 14.37 |

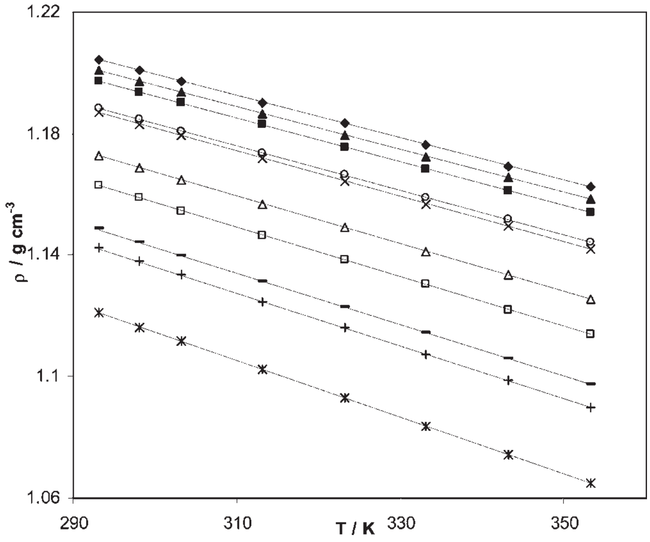

**Figure 1.** Density $\rho$ for the [Bmim][$BF_4$] + DMSO mixtures as a function of temperature at different mole fractions of the IL: ♦, 1.0000; ▲, 0.9155; ■, 0.8283; o, 0.6557; ×, 0.6070; Δ, 0.4189; □, 0.3225; -, 0.2145; +, 0.1764; *, 0.0722. Solid lines represent the linear correlation ($r$ = 1).

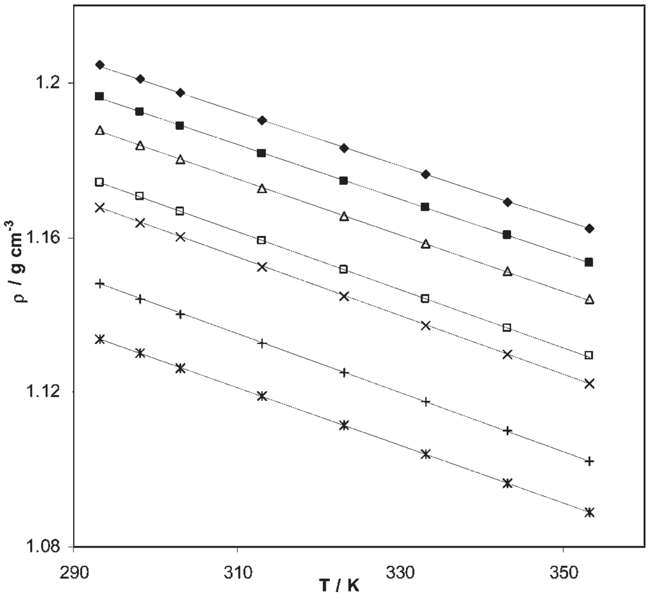

**Figure 2.** Density $\rho$ for the [Bmim][$BF_4$] + EG mixtures as a function of temperature at different mole fractions of the IL: ♦, 1.0000; ■, 0.8121; Δ, 0.6482; □, 0.4397; ×, 0.3578; +, 0.1758; *, 0.0895. Solid lines represent the linear correlation ($r$ = 1).

The experimental excess molar volumes, $V^E$, for the binary mixtures were obtained from the following relation:

$$V^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (2)$$

where $\rho_1$, $\rho_2$, and $\rho$ are the densities of IL, organic compounds, and their mixtures, respectively. $M_1$ and $M_2$ are the molar masses and $x_1$ and $x_2$ are the mole fractions of the IL and organic compounds, respectively. The $V^E$ values determined are indicated also in Table 2.

The experimental values of $V^E$ have been fitted to Redlich–Kister type polynomials:

$$V^E = x_1 x_2 \sum_k A_k (x_1 - x_2)^k \qquad (3)$$

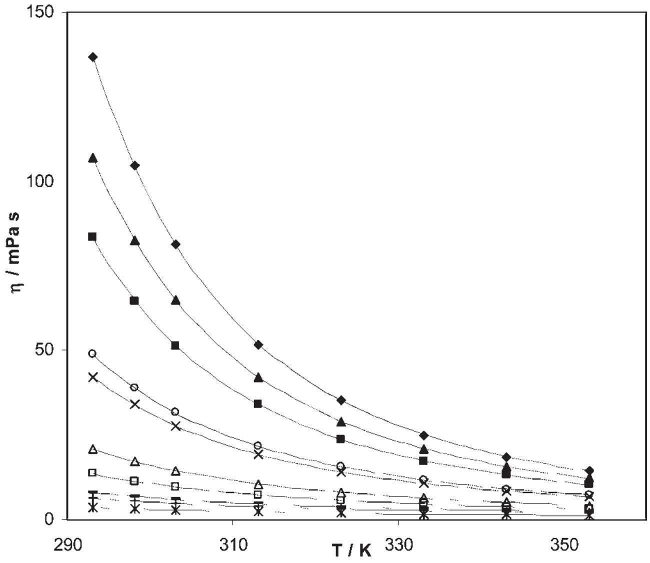

**Figure 3.** Dynamic viscosity $\eta$ for the [Bmim][$BF_4$] + DMSO mixtures as a function of temperature at different mole fractions of the IL: ◆, 1.0000; ▲, 0.9155; ■, 0.8283; ○, 0.6557; ×, 0.6070; Δ, 0.4189; □, 0.3225; -, 0.2145; +, 0.1764; *, 0.0722. Solid lines represent the VFT equation.

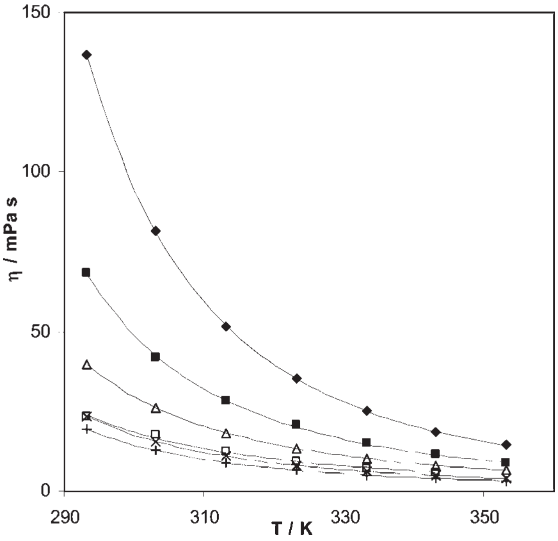

**Figure 4.** Dynamic viscosity $\eta$ for the [Bmim][$BF_4$] + EG mixtures as a function of temperature at different mole fractions of the IL: ◆, 1.0000; ■, 0.8121; Δ, 0.6482; □, 0.4397; ×, 0.3578; +, 0.1758. Solid lines represent the VFT equation.

**Table 4. Adjustable Parameters of the VFT Equation (*A* and *B*) and Standard Deviations, $\sigma$**

| $x_1$ | *A* mPa·s·$K^{-0.5}$ | *B* K | $\sigma$ mPa s |
|---|---|---|---|
| | [Bmim][$BF_4$] (1) + DMSO (2) | | |
| 0.0722 | 0.0074 | 410.7 | 0.027 |
| 0.1764 | 0.0078 | 474.9 | 0.035 |
| 0.2145 | 0.0080 | 500.6 | 0.021 |
| 0.3225 | 0.0077 | 570.3 | 0.043 |
| 0.4189 | 0.0073 | 629.3 | 0.054 |
| 0.6070 | 0.0070 | 721.4 | 0.064 |
| 0.6557 | 0.0065 | 750.2 | 0.098 |
| 0.8283 | 0.0062 | 819.9 | 0.029 |
| 0.9155 | 0.0062 | 852.0 | 0.039 |
| 1.0000 | 0.0061 | 885.0 | 0.135 |
| | [Bmim][$BF_4$] (1) + EG (2) | | |
| 0.1758 | 0.0035 | 712.9 | 0.015 |
| 0.3578 | 0.0045 | 704.6 | 0.019 |
| 0.4397 | 0.0086 | 626.6 | 0.594 |
| 0.6482 | 0.0070 | 714.2 | 0.038 |
| 0.8121 | 0.0060 | 800.3 | 0.423 |
| 1.0000 | 0.0061 | 885.0 | 0.135 |

The adjustable parameters $A_k$ obtained by fitting the equations to the experimental values with a least-squares type algorithm are given in Table 5, along with the standard deviation, $\sigma$, defined as follows

$$\sigma = [\sum_{i=1}^{n}(V^E_{\text{exp},i} - V^E_{\text{calc},i})^2/(n-m)]^{0.5} \qquad (4)$$

where *n* is the number of experimental data and *m* is the number of parameters.

From the experimental results shown in Table 2 and Figures 6 and 7 it can be observed that at all investigated temperatures, the excess molar volume values are negative for the [Bmim][BF4] + DMSO, system and positive for the [Bmim][BF4] + EG system over the whole composition range. The $V^E$ results at 298.15 K for both investigated systems are in accordance with those founded in literature (Figures 6-7).

The $V^E$ behavior of [Bmim][BF4] + solvent systems can be predicted and correlated using the Prigogine−Flory−Patterson (PFP) theory, which has been widely used to analyze the excess thermodynamic properties for different kinds of mixtures, including IL + solvent systems. For the excess molar volumes some authors have already applied the PFP theory to the binary systems with ionic liquids.[38−40] The PFP theory considers the excess molar volume of binary mixtures to be the sum of three contributions: (i) interactional contribution, which is proportional with the interaction parameter, $\chi_{12}$; (ii) free volume contribution, that is, originated in a difference in the degree of thermal expansion between the components involved; (iii) internal pressure contribution, which arises from the differences in the internal pressures and reduced volumes of components.

According to the PFP theory, $V^E$ can be calculated as follows:

$$\frac{V^E_{\text{PFP}}}{X_1V_1^* + X_2V_2^*} = V^E_{\text{int}} + V^E_{fv} + V^E_{ip} = \frac{(\tilde{v}^{1/3}-1)\tilde{v}^{2/3}\psi_1\theta_2\chi_{12}}{[(4/3)\tilde{v}^{-1/3}-1]P_1^*} - \frac{(\tilde{v}_1-\tilde{v}_2)^2((14/9)\tilde{v}^{-1/3}-1)\psi_1\psi_2}{[(4/3)\tilde{v}^{-1/3}-1]\tilde{v}} + \frac{(\tilde{v}_1-\tilde{v}_2)(P_1^*-P_2^*)\psi_1\psi_2}{P_2^*\psi_1+P_1^*\psi_2} \qquad (5)$$

In these equations $\Psi_i$ represent the contact energy fraction, $\theta_i$, surface site fraction, $\tilde{v}_i$, reduced volume for pure substance *i*, and $P_i^*$, characteristic pressure. The reduced volume and the characteristic pressure are calculated from the thermal expansion

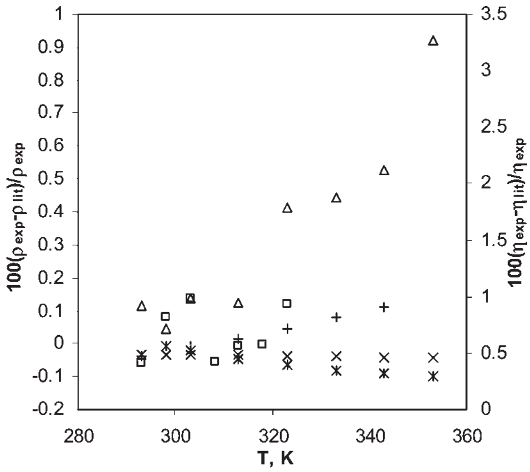

**Figure 5.** Relative deviations of the literature properties for [Bmim][BF$_4$] from our experimental data. For density: +, ref 11; ×, ref 12; *, ref 13. For viscosity: Δ, ref 12; □, ref 14.

**Table 5. Coefficients $A_k$ of the Fitting Equation 2 and Standard Deviations, $\sigma$**

| $T$ / K | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|
| | | [Bmim][BF$_4$] + DMSO | | | |
| 293.15 | −1.4582 | 1.2618 | 0.2149 | 0.131 | 0.007 |
| 298.15 | −1.5104 | 1.3611 | 0.2120 | 0.207 | 0.007 |
| 303.15 | −1.5622 | 1.3226 | 0.1810 | 0.261 | 0.007 |
| 313.15 | −1.6902 | 1.3472 | 0.1531 | 0.511 | 0.006 |
| 323.15 | −1.8275 | 1.3907 | 0.1053 | 0.715 | 0.006 |
| 333.15 | −1.9752 | 1.4555 | 0.0460 | 0.885 | 0.007 |
| 343.15 | −2.1221 | 1.5708 | −0.0531 | 0.981 | 0.008 |
| 353.15 | −2.2812 | 1.6910 | −0.1364 | 1.119 | 0.008 |
| | | [Bmim][BF$_4$] + EG | | | |
| 293.15 | 2.0648 | 0.3322 | −0.2378 | | 0.008 |
| 298.15 | 2.1867 | 0.2929 | −0.2504 | | 0.008 |
| 303.15 | 2.3013 | 0.2341 | −0.2914 | | 0.008 |
| 313.15 | 2.5173 | 0.1413 | −0.3173 | | 0.008 |
| 323.15 | 2.7243 | 0.0273 | −0.3558 | | 0.007 |
| 333.15 | 2.9181 | −0.0291 | −0.4203 | | 0.010 |
| 343.15 | 3.0861 | −0.2453 | −0.4949 | | 0.008 |
| 353.15 | 3.2513 | −0.3339 | −0.4858 | | 0.007 |

coefficient, $\alpha_i$, and the isothermal compressibility coefficient, $k_{Ti.}$ of the pure components.

$$\tilde{v}_i = \left[\frac{1+\alpha_i T}{1+(4/3)\alpha_i T}\right]^3 P_i^* = \frac{T\tilde{v}_i^2\alpha_i}{k_{Ti}} \tag{6}$$

The various characteristic and reduced parameters of pure liquids needed for the $V^E$ estimation were calculated by using the expressions given in literature[41] and are listed in Table 6.

The experimental and calculated $V^E$ values using PFP theory and the three PFP contributions at around $x_1 = 0.4$ and temperature of 298.15 K are summarized in Table 7 and reflected in Figures 8 and 9. For comparison, we have selected a mole fraction of around $x_1 = 0.4$, because the $V^E$ curves of these two binary systems present minimum/maximum values around this composition. The interaction parameter, $\chi_{12}$, was evaluated by fitting the experimental $V^E$results to eq 5 using the least-squares method over the whole mole fraction range at 298.15 K for each system. The obtained $\chi_{12}$ values are also indicated in Table 6, together with standard deviation, $\sigma$, calculated using type (4) equation.

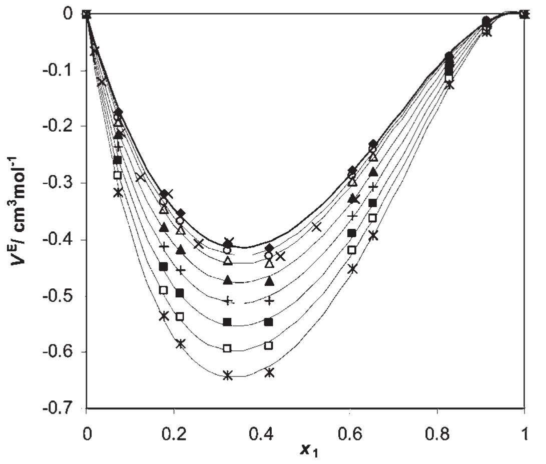

**Figure 6.** Excess molar volumes, $V^E$, for the [Bmim][BF$_4$] (1) + DMSO (2) mixtures at different temperatures: ♦, 293.15 K; ○, 298.15 K; Δ, 303.15 K; ▲, 313.15 K; +, 323.15 K; ■, 333.15 K; □, 343.15 K; *, 353.15 K; solid line, Redlich−Kister correlation; ×, 298.15 K (ref 20).

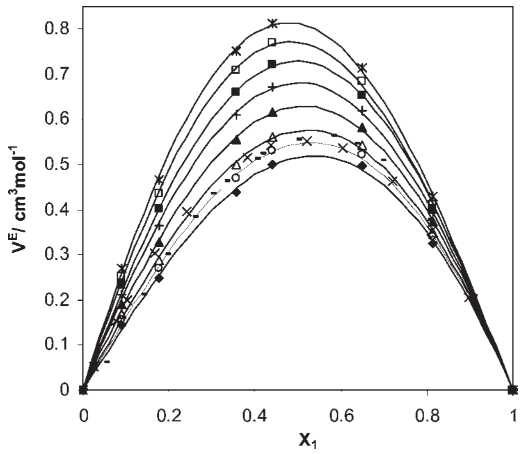

**Figure 7.** Excess molar volumes, $V^E$, for the [Bmim][BF$_4$] (1) + EG (2) mixtures at different temperatures: ♦, 293.15 K; ○, 298.15 K; Δ, 303.15 K; ▲, 313.15 K; +, 323.15 K; ■, 333.15 K; □, 343.15 K; *, 353.15 K; solid line, Redlich−Kister correlation; -, 298.15 K (ref 19); ×, 298.15 K (ref 18).

Study of Table 7 reveals that the interaction parameter, $\chi_{12}$, is positive for [Bmim][BF4] + EG system, which suggests relatively weak intermolecular specific interactions when mixture is created, and negative for the [Bmim][BF4] + DMSO system, suggesting a relative strong intermolecular specific between [Bmim][BF4] and DMSO on mixing. Free volume contributes negatively to the $V_{\mathrm{PFP}}^E$ values for both systems and does not seem to play a dominant role in deciding the sign and magnitude of the excess molar volume. The internal pressure contributions are positive for both systems, being more important for [Bmim][BF4] + DMSO system, where the differences between the

Table 6. Physicochemical Data of Pure Components Used in Prigogine—Flory—Patterson Theory at $T/K = 298.15$

| | $\alpha^*$ | $k_T{}^*$ | $\tilde{V}_i$ | $V$ | $V_i^*$ | $P_i^*$ | $\tilde{T}_i$ | $T_i^*$ |
|---|---|---|---|---|---|---|---|---|
| | $K^{-1}$ | $cm^3 \cdot J^{-1}$ | | $cm^3 \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ | $J \cdot cm^{-3}$ | | K |
| [Bmim][BF4] | 0.000588[a] | 0.000386[b] | 1.1567 | 188.21 | 162.72 | 607.5 | 0.04094 | 7278 |
| EG | 0.000652[a] | 0.000373[c] | 1.1717 | 55.92 | 47.73 | 715.4 | 0.04391 | 6786 |
| DMSO | 0.000916[a] | 0.000522[d] | 1.2303 | 71.30 | 57.96 | 792.1 | 0.05425 | 5493 |

[a] This work. [b] Ref 16. [c] Ref 42. [d] Ref 43.

Table 7. Experimental and Calculated $V^E$ Using PFP Theory and the Three PFP Contributions at Around $x_1 = 0.4$ and $T/K = 298.15$

| mixtures of [Bmim][BF4]+ | $V^E_{exp}$ | $V^E_{PFP}$ | $V^E_{int}$ | $V^E_{fv}$ | $V^E_{ip}$ | $\chi_{12}$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | $cm^3 \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ | $J \cdot cm^{-3}$ | $cm^3 \cdot mol^{-1}$ |
| EG | 0.5322 | 0.4922 | 0.4498 | −0.0073 | 0.0497 | 65.01 | 0.1023 |
| DMSO | −0.4293 | −0.3835 | −0.6405 | −0.2011 | 0.4581 | −75.57 | 0.0377 |

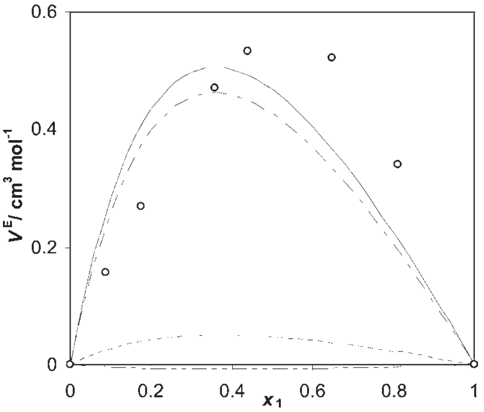

Figure 8. Excess molar volume $V^E$ for the [Bmim][BF$_4$] (1) with EG (2) binary system at $T$ = 298.15 K calculated with the PFP theory: dotted-dashed line, interactional contribution; dotted—dotted-dashed line, free volume contribution; dashed line, internal pressure contribution; solid line, total excess molar volume predicted by PFP theory; ○, experimental results.

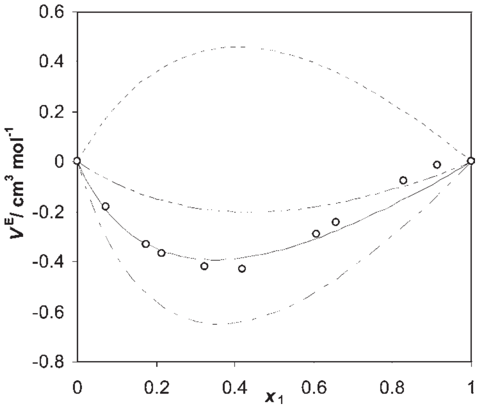

Figure 9. Excess molar volume $V^E$ for the [Bmim][BF$_4$] (1) with DMSO (2) binary system at $T$ = 298.15 K calculated with the PFP theory: dotted-dashed line, interactional contribution; dotted—dotted-dashed line, free volume contribution; dashed line, internal pressure contribution; solid line, total excess molar volume predicted by PFP theory; ○, experimental results.

internal pressures and reduced volumes of components are bigger than for the other system.

From infrared spectroscopic studies it was found that in [Bmim][BF4] + DMSO system hydrogen bond interactions are formed between the hydrogen atom at position 2 of the imidazole ring and the functional group S═O of DMSO.[23] These investigations are in accordance with the negative obtained values of the interaction parameter, $\chi_{12}$. The $V^E_{int}$ contribution is the most significant term in deciding the sign and magnitude of $V^E$ values for this system.

Even though the PFP theory leads to a one-parameter model, the agreement between experimental and calculated values of excess molar volume is satisfactorily, better for the [Bmim][BF4] + DMSO system, with standard deviations in the range of 0.1—0.03$\cdot$cm$^3\cdot$mol$^{-1}$, as is shown in Table 7.

Our results show that $V^E$ values become more negative when temperature increases for the system with DMSO and increase with temperature for the system with EG. The general tendency of $V^E$ is to have bigger deviation from ideality with increasing temperature.

## CONCLUSION

The densities and the dynamic viscosities of selected binary mixtures of the ionic liquid, [Bmim][BF4], with polar solvents, DMSO, and ethylene glycol, in the temperature range from (293.15 to 353.15) K were reported.

The variation of densities with temperature both for pure [Bmim][BF4] and its binary mixtures of different composition with DMSO and EG, respectively, are very good represented by linear equations($r$ = 1). The temperature dependence of viscosity for the investigated systems was described by the Vogel—Fucher—Tammann equation, which give good results both for pure ionic liquid, [Bmim][BF4], and its binary mixture with DMSO and EG, respectively.

The excess molar volumes are negative for the [Bmim][BF4] + DMSO system and positive for the [Bmim][BF4] + EG system over the whole composition range at investigated temperatures. The PFP theory has a good performance in predicting excess molar volumes of the studied binary systems. The analysis of relative contribution suggests that the interactional contribution is the most significant term in excess molar volume. $V^E_{int}$ has positive values for [Bmim][BF4] + EG system, which means relatively weak intermolecular specific interactions on mixing, and negative values for the [Bmim][BF4] + DMSO system, suggesting a relative strong intermolecular specific between [Bmim][BF4] and DMSO.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: ciocirlan_o@yahoo.com. Tel.: +40214023855.

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## REFERENCES

(1) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.

(2) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.* **2002**, *102*, 3667–3692.

(3) Huddleston, J. G.; Willaver, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, D. Room temperature ionic liquids as novel media for ‘clean’ liquid−liquid extraction. *Chem. Commun* **1998**, 1765–1866.

(4) Nishida, T.; Tashiro, Y.; Yamamoto, M. Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *J. Fluorine Chem.* **2003**, *120*, 135–141.

(5) Park, S.; Kazlauskas, R. J. Biocatalysis in ionic liquids—Advantages beyond green technology. *Curr. Opin. Biotechnol.* **2003**, *14*, 432–437.

(6) Wang, L.; Chang, L.; Zhao, B.; Yuan, Z.; Shao, G.; Zheng, W. Systematic investigation on morphologies, forming mechanism, photocatalytic and photoluminescent properties of ZnO nanostructures constructed in ionic liquids. *Inorg. Chem.* **2008**, *47*, 1443–1452.

(7) Seddon, K. R.; Stark, A. S.; Torres, M. J. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids. In *Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities*, Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington DC, 2004.

(8) Tariq, M.; Forte, P. A. S.; Costa Gomes, M. F.; Canongia Lopes, J. N.; Rebelo, L. P. N. Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: Effect of temperature, alkyl chain length, and anion. *J. Chem. Thermodyn.* **2009**, *41*, 790–798.

(9) Wang, J.; Li, C.; Shen, C.; Wang, Z. Towards understanding the effect of electrostatic interactions on the density of ionic liquids. *Fluid Phase Equilib.* **2009**, *279*, 87–91.

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

(11) Jacquemin, J.; Ge, R.; Nancarrow, P.; Rooney, D. W.; Costa Gomes, M. F.; Padua, A. A. H.; Hardacre, C. Prediction of ionic liquid properties. I. Volumetric properties as a function of temperature at 0.1 MPa. *J. Chem. Eng. Data* **2008**, *53*, 716–726.

(12) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate: Viscosity and density relationships in ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 2425–2430.

(13) Soriano, A. N.; Doma, B. T., Jr.; Li, M.-H. Measurements of the density and refractive index for 1-*n*-butyl-3-methylimidazolium-based ionic liquids. *J. Chem. Thermodyn.* **2009**, *41*, 301–307.

(14) Sanmamed, Y. A.; González-Salgado, D.; Troncoso, J.; Cerdeiriña, C. A.; Romaní, L. Viscosity-induced errors in the density determination of room temperature ionic liquids using vibrating tube densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96–102.

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

(16) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydlowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romaní, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A detailed thermodynamic analysis of [C4mim][BF4] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.

(17) Qi, F.; Wang, H. Application of Prigogine−Flory−Patterson theory to excess molar volume of mixtures of 1-butyl-3-methylimidazolium ionic liquids with N-methyl-2-pyrrolidinone. *J. Chem. Thermodyn.* **2009**, *41*, 265–272.

(18) Singh, T.; Kumar, A.; Kaur, M.; Kaur, G.; Kumar, H. Non-ideal behaviour of imidazolium based room temperature ionic liquids in ethylene glycol at $T$ = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 717–723.

(19) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romanı, L. Density and refractive index in mixtures of ionic liquids and organic solvents: Correlations and predictions. *J. Chem. Thermodyn.* **2008**, *40*, 949–956.

(20) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of binary mixtures of ionic liquids with polar solvents. *J. Chem. Eng. Data* **2009**, *54*, 472–479.

(21) Bester-Rogac, M.; Hunger, J.; Stoppa, A.; Buchner, R. Molar conductivities and association constants of 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate in methanol and DMSO. *J. Chem. Eng. Data* **2010**, *55*, 1799–1803.

(22) Tian, Y.; Wang, X.; Wang, J. Densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate + molecular solvent binary mixtures. *J. Chem. Eng. Data* **2008**, *53*, 2056–2059.

(23) Zhang, L.; Wang, Y.; Xu, Z.; Li, H. Comparison of the blue-shifted C-D stretching vibrations for DMSO-$d_6$ in imidazolium-based room temperature ionic liquids and in water. *J. Phys. Chem. B* **2009**, *113*, 5978–5984.

(24) Barthel, J.; Neueder, R. *Electrolyte Data Collection*, Part 1h. In DECHEMA Chemistry Data Series, Vol XII; Eckermann, R., Kreysa, G., Eds.; DECHEMA: Frankfurt, Germany, 2003.

(25) Tsierkezos, N. G.; Kelarakis, A. E.; Palaiologou, M. M. Densities, viscosities, refractive indices, and surface tensions of dimethyl sulfoxide + bytyl acetate mixtures at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **1998**, *453*, 395–398.

(26) Wang, H.; Liu, W.; Huang, J. Densities and volumetric properties of a (xylene + dimethyl sulfoxide) at temperature from (293.15 to 353.15) K. *J. Chem. Thermodyn.* **2004**, *36*, 743–752.

(27) Ali, A.; Nain, A. K.; Chand, D.; Ahmad, R. Volumetric and ultrasonic studies of molecular interactions in binary mixtures of dimethyl sulfoxide with some aromatic hydrocarbons at different temperatures. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 702–710.

(28) Ciocirlan, O.; Iulian, O. Vapor pressure, density, viscosity and refractive index of dimethyl sulfoxide + 1,4-dimethylbenzene system. *J. Serb. Chem. Soc.* **2008**, *73*, 73–85.

(29) Tsierkezos, N. G.; Molinou, I. E. Thermodynamic properties of water + ethylene glycol at 283.15, 293.15, 303.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989–993.

(30) Chiavonefilho, O; Proust, P; Rasmussen, P. Vapor-liquid-equilibria for glycol ether plus water-systems. *J. Chem. Eng. Data* **1993**, *38*, 128–131.

(31) Sastry, N. V.; Patel, M. C. Densities, excess molar volumes, viscosities, speeds of sound, excess isentropic compressibilities, and relative permittivities for alkyl (methyl, ethyl, butyl, and isoamyl) acetates + glycols at different temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1019–1027.

(32) George, J.; Sastry, N. V. Partial excess molar volumes, partial excess isentropic compressibilities and relative permittivities of water + ethane-1,2-diol derivative and water + 1,2-dimethoxyethane at different temperatures. *Fluid Phase Equilib.* **2004**, *216*, 307–321.

(33) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol.Catal. A: Chem.* **2004**, *214*, 11–17.

(34) Okoturo, O. O.; Vandernoot, J. J. Temperature dependence of viscosity for room temperature ionic liquids. *J. Electroanal. Chem.* **2004**, *568*, 167–181.

(35) Gomez, E.; Gonzalez, B.; Calvar, N.; Tojo, E.; Dominguez, A. Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.

(36) Domanska, U.; Krolikowska, M. Density and viscosity of binary mixtures of {1-butyl-3-methylimidazolium thiocyanate + 1-heptanol, 1-octanol, 1-nonanol, or 1-decanol}. *J. Chem. Eng. Data* **2010**, *55*, 2994–3004.

(37) Qi, M.; Wua, G.; Li, Q.; Luo, Y. $\gamma$-Radiation effect on ionic liquid [bmim][BF4]. *Radiat. Phys. Chem.* **2008**, *77*, 877–883.

(38) Singh, T.; Kumar, A. Volumetric behaviour of 1-butyl-3-methyl imidazolium hexafluorophosphate with ethylene glycol derivatives: Application of Prigogine—Flory—Patterson theory. *J. Mol. Liq.* **2010**, *153*, 117–123.

(39) Zafarani-Moattar, M. T.; Shekaari, H. Application of Prigogine—Flory—Patterson theory to excess molar volume and speed of sound of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate or 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in methanol and acetonitrile. *J. Chem. Thermodyn.* **2006**, *38*, 1377–1384.

(40) Qi, F.; Wang, H. Application of Prigogine—Flory—Patterson theory to excess molar volume of mixtures of 1-butyl-3-methylimidazolium ionic liquids with *N*-methyl-2-pyrrolidinone. *J. Chem. Thermodyn.* **2009**, *41*, 265–272.

(41) Torres, R. B.; Francesconi, A. Z.; Volpe, P. L. O. Thermodynamics of binary liquid mixtures: Application of the Prigogine—Flory—Patterson theory to excess molar volumes of acetonitrile + 1-alkanol systems. *J. Mol. Liq.* **2004**, *110*, 81–85.

(42) Zorebski, E. Internal pressure studies of alcohols on the basis of ultrasonic measurements. *Mol. Quant. Acoust.* **2003**, *4*, 261–270.

(43) Ali, A.; Nain, A. K.; Chand, D.; Ahmad, R. Volumetric and ultrasonic studies of molecular interactions in binary mixtures of dimethyl sulfoxide with some aromatic hydrocarbons at different temperatures. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 702–710.