Density, refractive index, and derived properties of binary mixtures of water + ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate

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Keywords:

Density, Refractive index, Ionic liquid-water mixtures, Excess volume, Thermal expansion coefficient, Mixing rules

Abstract

The density and refractive index were experimentally determined for binary mixtures of water + ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate throughout the ionic liquid mass fraction range, at atmospheric pressure and various temperatures between 293.15 K and 323.15 K. The refractive index was measured at five wavelengths between 589.2 nm and 935 nm. From the experimental data on density, volumetric properties such as the excess molar volume and thermal expansion coefficient were calculated. The excess molar volume was negative throughout the ionic liquid mass fraction range and its magnitude decreased with temperature. From the experimental data on the refractive index, the deviation in the refractive index and its coefficients of concentration, temperature and chromatic dispersion were obtained. The values of the deviation in the refractive index were positive and decreased with temperature. In order to simultaneously investigate the dependence of the refractive index on concentration, temperature and wavelength, we correlated the experimental data with a two-term Cauchy equation. Furthermore, a comparative study of 11 refractive index mixing rules was performed to assess their prediction ability. More advanced mixing rules do not lead to any improvement in comparison with the simple linear mixing rule (Arago-Biot) for estimating refractive index and the concentration contrast factor of the mixture studied. The results are expected to be useful for tuning the properties of an ionic liquid by adding water or selecting the temperature or optical region.

1. Introduction

Ionic liquids (ILs) have received increasing attention because of such unique properties as negligible vapor pressure, good solubility to many organic and inorganic chemicals, and a wide range of temperatures in the liquid state [1,2]. Because of these features, ILs appeared as environmentally friendly alternatives for conventional volatile solvents [3–5]. However, to assess the potential use of ILs as “greener” alternatives, other properties such as their toxicity and thermal/chemical stability should be fully characterized [6]. Another outstanding feature is that ILs can be synthesized in numerous anion-cation combinations, which gives them the tunability to meet the specific requirements of a given application [7–9]. Consequently, ILs are regarded as emergent materials in various technological fields such as absorption refrigeration systems [10,11], electrolyte and electrode materials for batteries [12], optical media in photonic devices [13,14], etc.

Hydroxyl functionalized ILs endow conventional ILs with useful polarity/solvation properties and have shown great potential in the reversible absorption of gases, including carbon dioxide (CO_2) and ammonia (NH_3) [11,15,16]. Also, hydroxyl ILs exhibit better solubility of inorganic salts and enhanced hydrophilicity and enzyme activity, which means they can be used in a huge variety of applications [17]. For example, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([EtOHmim][BF_4]), as the target IL in the present study, has been used in the synthesis of silver nanoparticles [17]; as a catalyst in the production of liquid fuel from renewable sources [18]; and in the absorption of hydrogen sulfide (H_2S), CO_2 [19], and NH_3 [11]. To further expand the applications of hydroxyl ILs, and in particular of [EtOHmim][BF_4], more detailed knowledge of their thermophysical properties is required. More specifically, given the potential use of [EtOHmim][BF_4] as a solvent, it is essential to understand the thermodynamic behavior of its binary mixtures with water. However, despite its importance, there is little experimental data on pure IL, and very few researchers have reported the thermophysical properties of its binary mixtures with water or other compounds.

In an early experimental work, Kim et al. [20] used the boiling point method to measure the vapor pressure of binary mixtures of water + [EtOHmim][BF_4] in the temperature range between 304.8 K and 475.2 K, and with the IL mole fraction between 0.2 and 0.8. They

correlated the results with an Antoine-type equation with very good fitting quality. Subsequently, Shokouhi et al. [19] determined the solubility and diffusivity of H_2S and CO_2 in [EtOHmim][BF_4]. They found that H_2S and CO_2 are more soluble in the conventional IL 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) and attributed this to a lower molar free volume in [EtOHmim][BF_4]. Finally, they concluded that [EtOHmim][BF_4] can be used to separate these two gases from each other. Our research group at Universitat Rovira i Virgili has also measured some of the thermophysical properties of the IL [EtOHmim][BF_4], such as density (in the temperature range 293.15 K-373.15 K), viscosity (293.15 K-373.15 K), thermal conductivity (293.15 K -313.15 K), and heat capacity (273.15 K -373.15 K) [21]. All these properties were correlated as a function of temperature, and the maximum relative deviation between experimental and calculated values does not exceed 1.16% in any case. Furthermore, the density and viscosity of binary mixtures NH_3 + [EtOHmim][BF_4] were also determined. Cera-Manjarres et al. [11] reported the vapor pressure measurements of NH_3 + protic ILs (HOILs) mixtures as potential working fluids for absorption refrigeration systems. Of all the HOILs investigated, [EtOHmim][BF_4] was selected as the most suitable absorbent for NH_3. More recently, the authors [22] used an advanced optical technique to determine the mutual diffusion coefficients in binary mixtures of water + [EtOHmim][BF_4] throughout the IL mass fraction range between 298.15 K and 313.15 K. We also tested the prediction ability of four thermodynamic models and analyzed the influence of using different excess Gibbs energy (g^E) models to calculate the relevant thermodynamics. The present study is effort further attempt by the authors to characterize the thermodynamic behavior of binary mixtures of water + [EtOHmim][BF_4].

All previous studies show the limited experimental information available on the thermophysical properties of [EtOHmim][BF_4], and especially on its aqueous binary mixtures. Such basic properties as density and refractive index need to be determined and understood so that equipment for commercial applications that use aqueous IL mixtures can be designed, scaled up and sized [23]. Of all the thermophysical properties of aqueous mixtures of ILs, density is probably the most widely studied because of its importance and experimental accessibility [24]. Also, several volumetric properties can be obtained from density measurements. Volumetric properties of binary mixtures depend

on the size, shape, and chemical nature of the components, and structural effects arising from interstitial accommodation due to differences in molar volume and free volume between solution components [25]. These properties provide useful information about the structure and solute-solute, solvent-solvent and solute-solvent interactions in a binary mixture. In comparison with density, the refractive index of aqueous IL mixtures has received considerably less attention. The refractive index of ILs is related to properties like structuredness, polarity, and relative hydrogen bonding donating and accepting ability, which are useful for determining solubilities, partition constants, and reaction rates [26]. Most techniques for determining refractive indices are highly expeditious and accurate, and usually require very small amounts of sample [27]. The refractive index is a fundamental optical property of matter and correlates with the composition, temperature, pressure, and light source wavelength of a liquid mixture [28]. In this regard, the variation of the refractive index with temperature and concentration is the basis of several optical methods that study heat and mass transfer and determine diffusion coefficients in transparent media [29–31]. Furthermore, understanding the temperature, concentration and dispersion coefficients of the refractive index is essential for real-time monitoring of processes of industrial and scientific interest.

The refractive index of liquid mixtures can be estimated from the refractive indices of the pure components and the density data of the mixture using mixing rule equations. Correlations such as Lorentz-Lorenz, Gladstone-Dale or Newton have been extensively tested and validated in the literature [24,28,31]. However, despite the close relationship between the two properties, few studies address the determination of density and refractive index in aqueous mixtures of ILs [4,23,24,27,32,33]. And most of the ones that do provide experimental data of the density and refractive index at only one temperature. Refractive index values are reported in the literature at a single wavelength, most commonly the yellow sodium D-line (wavelength, λ, 589.2 nm). Nevertheless, the potential application of ILs, for instance in variable focus lenses, requires an accurate characterization of the refractive index dispersion to ensure optimal performance [13]. Furthermore, once the density and refractive index of a pure compound or a mixture are known, such related properties as electronic polarizability or molar refraction can be estimated. Therefore, a joint analysis of density and refractive index can provide highly

valuable information about the volumetric and optical behavior of pure ILs and aqueous IL mixtures.

The main aim of this study was to experimentally determine the density and refractive index of the binary mixture water + [EtOHmim][BF_4] throughout the ionic liquid mass fraction range at several temperatures between 293.15 K and 323.15 K. All refractive index measurements were performed at five wavelengths in the visible-near infrared spectral range, from 589.2 nm to 935 nm. From the experimental data of density, the excess molar volume and the thermal expansion coefficient were obtained in the temperature range studied. Similarly, the refractive index data was used to obtain the coefficients of concentration, temperature and chromatic dispersion, and the deviation in the refractive index. Finally, a total of eleven refractive index mixing rules were quantitatively compared in terms of their performance for the studied mixture. To the best of our knowledge, this is the first time that wavelength-dependent refractive index data have been reported for binary aqueous IL mixtures. This study provides a wide variety of new experimental data, such as the concentration, temperature, and chromatic dispersion coefficients of the refractive index of an aqueous mixture of IL.

2. Experimental section

Table 1 shows the specifications of the chemical used in the present study. Extra pure deionized water supplied by Acros Organics was used without further purification. Ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([EtOHmim][BF_4], initial mass fraction purity: >98%, CAS Number: 374564-83-7, Molecular Weight: 213.97 g/mol) was supplied by Iolitec. To remove traces of water from [EtOHmim][BF_4], it was kept under vacuum (0.03 mbar) with heating and stirring at 333.15 K for at least 48 h. The water content (<150 ppm) was determined using a Karl Fisher coulometer (Mettler Toledo, model C20). Mixtures of water + [EtOHmim][BF_4] were prepared gravimetrically using an electronic balance manufactured by Sartorius with a resolution of 10^{-2} mg/30 g. A total of 11 samples (including pure components) were prepared at 0.1 intervals throughout the ionic liquid mass fraction. The estimated uncertainty in the mass fraction is in the range of ±0.0008 to ±0.0029. All the measurements were conducted in a small room with well controlled air temperature at atmospheric pressure.

Table 1. Specifications of chemical used in the present study.

Chemical name	CAS	Purity[1] (mass-fraction, %)	Purification Method	Water content	Supplier
[EtOHmim][BF_4][2]	374564-83-7	>98	Vacuum desiccation	<150 ppm (Karl-Fischer)	Iolitec
Water	7732-18-5	99.998	-	-	Acros Organics

[1] Provided by the supplier.
[2] [EtOHmim][BF_4] = 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate.

Density measurements were made with an oscillating U-tube Anton Paar densitometer (DMA 5000M) at temperatures ranging from 293.15 K to 323.15 K. The temperature uncertainty was estimated to be ±0.01 K. The expanded uncertainty (with 0.95 level of confidence (k=2)) in density is in the range of ±0.0010 to ±0.0056 $g \cdot cm^{-3}$. The quantity of sample required to fill the U-tube was about 5 x 10^{-3} L and was introduced into the equipment with a syringe. Care was taken to prevent bubbles from appearing in the tube. Before the beginning of the experiments, the densitometer was verified by measuring the density of Millipore quality water and dry air according to the supplier's instructions and the deviations were found to be within ±1 x 10^{-5} g cm^{-3}. The density measurements for the binary mixture samples were made in triplicate and the average values were reported. The maximum deviation never exceeded the uncertainty of our measurements.

The refractive indices were measured with an Abbe refractometer, model 60/LR, manufactured by Bellingham and Stanley, with a resolution of 5 x 10^{-5}. Five light emitting diodes, with wavelengths of 589.2 nm, 632.8 nm, 670 nm, 780 nm, and 935 nm, and bandwidth around 20 nm, mounted on a home-built wheel were used as a light source. The light beams were alternately directed into the refractometer through the optical window. Since infrared light is invisible (and harmful) to the human eye, the refractometer was equipped with a high sensitivity camera. All the measurements were performed between 293.15 K and 323.15 K. The temperature during the experiments was controlled by a high precision circulating thermal bath (NESLAB RTE-300). The temperature of the measurement prism of the refractometer was monitored using the built-in temperature sensor with an uncertainty of ±0.1 K. The expanded uncertainty (with 0.95 level of confidence (k=2)) in the refractive index is in the range of ±0.0002 to ±0.0058. The quantity of sample required was about 1 x 10^{-3} L. Prior to the beginning of the experiments, the refractometer was calibrated by measuring the refractive index of

deionized water at known temperature. Deviations did not exceed 7 x 10^{-5}. A minimum of three readings were taken for each sample and the average value was reported. The maximum deviation was always within the uncertainty range of our measurements.

All measurements were made immediately after sample preparation and the techniques used to measure both properties (density and refractive index) are highly expeditious. Under these conditions, we can assume that the composition of the analyzed samples has not changed significantly due to the hydrolysis of the BF_4^- anion during the measurement time [34,35].

3. Results and discussion

In this section, the experimental and calculated properties are presented, and the trends discussed.

3.1. Density and volumetric properties

The experimental density results are listed in Table 2. As expected, density increases with the IL mass fraction and decreases with temperature. Density values range from 0.9880 g cm^{-3} for pure water at 323.15 K to 1.3685 g cm^{-3} for pure ionic liquid at 293.15 K. From experimental density data in Table 2, it is observed that the influence of temperature on density is greater as the IL mass fraction increases.

The relative uncertainty of the density measurements was found to be always less than 0.2%. The low uncertainty values observed are possible evidence that the hydrolysis of the BF_4^- anion has not altered our measurements to a significant extent. Moreover, we identified that the most important contribution to uncertainty in our density measurements is due to the purity of the IL, which is generally overlooked in most studies in the literature [36].

In the literature, there are no density data available for the binary mixture H_2O(1) + [EtOHmim][BF_4](2). However, some values reported for the pure compounds are used for purposes of comparison. Figure 1 shows the deviations between the experimental density values obtained and those reported in the literature for water [4,23,24,37,38] and for ionic liquid [EtOHmim][BF_4] [19,39–42]. Figure 1 a) shows the small deviations between the

density values obtained and those reported in the literature for water. In most of the experimental points investigated, the deviations oscillate between -0.005% and 0.005%.

Table 2. Experimental density, ρ, of H_2O + [EtOHmim][BF_4] mixtures as a function of the ionic liquid mass fraction, ω_2, at temperatures, T[1], ranging from 293.15 K to 323.15 K and at pressure, P[2], 0.1 MPa.

$\omega_2 \pm u(\omega_2)$[3]/ IL mass fraction	Density, ρ/ g cm^{-3}							U(ρ)[4] /g cm^{-3}
	T /K							
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	
0.00000 ±0.00002	0.9982	0.9971	0.9957	0.9940	0.9922	0.9902	0.9880	±0.0010
0.0997 ±0.0010	1.0274	1.0258	1.0241	1.0221	1.0200	1.0177	1.0153	±0.0012
0.2000 ±0.0019	1.0588	1.0569	1.0547	1.0524	1.0500	1.0475	1.0449	±0.0018
0.2989 ±0.0024	1.0964	1.0940	1.0915	1.0889	1.0862	1.0834	1.0805	±0.0022
0.3950 ±0.0028	1.1346	1.1319	1.1291	1.1262	1.1232	1.1202	1.1165	±0.0028
0.4996 ±0.0029	1.1703	1.1673	1.1642	1.1610	1.1577	1.1544	1.1510	±0.0032
0.6045 ±0.0028	1.2037	1.2004	1.1970	1.1937	1.1903	1.1869	1.1836	±0.0036
0.6995 ±0.0025	1.2395	1.2360	1.2324	1.2288	1.2252	1.2215	1.2179	±0.0040
0.8010 ±0.0015	1.2767	1.2725	1.2693	1.2655	1.2618	1.2585	1.2544	±0.0044
0.8988 ±0.0011	1.3211	1.3162	1.3130	1.3091	1.3053	1.3020	1.2975	±0.0050
1.0000 ±0.0008	1.3685	1.3633	1.3600	1.3559	1.3518	1.3485	1.3439	±0.0056

[1] Standard uncertainty u(T) = 0.01 K.
[2] Standard uncertainty u(P) = 10 kPa.
[3] Standard uncertainty u(ω_2) is reported for each mass fraction studied.
[4] Expanded uncertainty with 0.95 level of confidence (k=2).

However, relatively large deviations are generally observed for ionic liquid [EtOHmim][BF_4], as shown in Figure 1 b). These deviations can be attributed to different purities of the ILs, handling of the samples, and measurement methods or experimental procedures used. Furthermore, it can be observed that the deviations are positive, except for the values reported by Shokouhi et al. [19] at temperatures slightly different from those investigated in this study. Restolho et al. [41] and Song and Chen [42] reported density values for [EtOHmim][BF_4] at practically the same temperatures investigated in this study. The deviations between our results and theirs are around 4% and 0.35%, respectively. Therefore, there is excellent agreement between our values and Song and Chen's. Also, an analysis of the values indicates that the values reported by Restolho et al. [41] are

somewhat smaller than the other density values reported in the literature for [EtOHmim][BF_4].

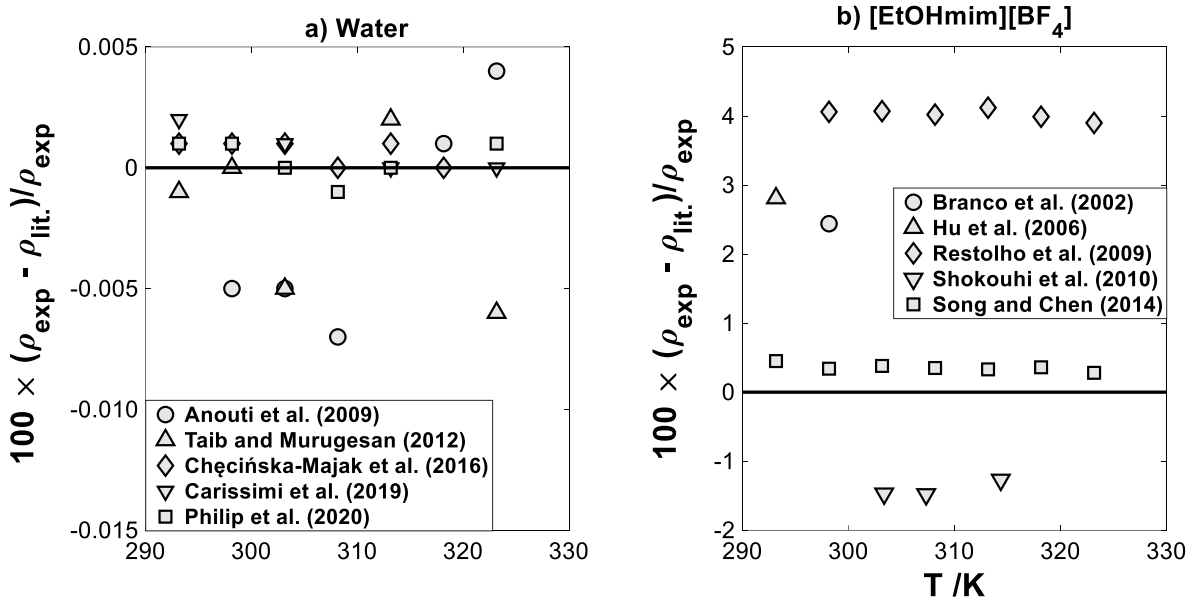

Figure 1. Deviations between the experimental density values obtained in this study and those from the literature for pure compounds at different temperatures: a) for water; and b) for ionic liquid [EtOHmim][BF4].

Furthermore, compared to [emim][BF_4] [26], [EtOHmim][BF_4] has higher density in the temperature range. In this regard, the presence of the hydroxyl group in the cation of [EtOHmim][BF_4] gives rise to a stronger hydrogen bonding attraction, and causes cations and anions to pack more tightly in [EtOHmim][BF_4] than in [emim][BF_4] [19].

The experimental density values were fitted using a second- and first-order polynomial equation on IL mass fraction and temperature, respectively:

$$\rho(\omega,T)/\,\mathrm{g\,cm^3} = \rho_{00} + \omega_2 * (\rho_{10} + \rho_{20} * \omega_2) + (T/K - T_0) * (\rho_{01} + \rho_{11} * \omega_2) \quad (1)$$

where $T_0 = 293.15\ K$ and the coefficients ρ_{ij} are given in Table 3.

Table 3. Coefficients of the fitting Equation (1) and goodness of fit (R^2 and RMSE).

Coefficients	ρ_{00}	ρ_{01}	ρ_{10}	ρ_{11}	ρ_{20}	R^2	RMSE
Value	9.989E-01	-3.802E-04	3.049E-01	-4.522E-04	6.082E-02	0.9992	3.3E-03

In Equation (1), the first term accounts for the density of pure water, the second for the influence of the IL mass fraction on the mixture density, and the third term gives a sense of the variation of the mixture density with temperature in the experimental range studied.

3.1.1. Excess molar volume

The excess molar volume of the H_2O(1) + [EtOHmim][BF_4](2) mixture was calculated from the experimental data of density in Table 2 using Equation (2):

$$V_m^E/\mathrm{cm^3mol^{-1}} = \frac{M_1x_1+M_2x_2}{\rho} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right) \quad (2)$$

The calculated excess molar volumes are tabulated in Table 1s in the supplementary material. The excess molar volume is small, less than 1.4% of the molar volume of the mixture. Furthermore, for the binary system studied, there is a considerable difference between the molecular weights of water (18.0153 g/mol) and ionic liquid (213.97 g/mol). In the molar representation, the measured points are concentrated at low mole fractions and the commonly used fit with the Redlich-Kister polynomial does not work well. Therefore, we used the following equation:

$$V_m^E/\mathrm{cm^3mol^{-1}} = x_2(1-x_2)\frac{\sum_{i=0}^{1} A_i(2x_2-1)^i}{1+\sum_{i=1}^{2} B_i(2x_2-1)^i} \quad (3)$$

which is considered more appropriate than the Redlich-Kister equation if the excess molar volume is sharply asymmetrical [43]. In Equation (3), A_i and B_i are expressed as a linear function on T:

$$A_i = A_{i,0} + A_{i,1}(T/K - 273.15) \quad (4)$$

$$B_i = B_{i,0} + B_{i,1}(T/K - 273.15) \quad (5)$$

and the coefficients are given in Table 4.

Table 4. Coefficients of the fitting Equation (3) and goodness of fit (R^2 and RMSE)

Coefficients	**$A_{0,0}$**	**$A_{0,1}$**	**$A_{1,0}$**	**$A_{1,1}$**
Values	-4.126E-01	7.191E-03	-3.534E-01	7.543E-03
Coefficients	**$B_{1,0}$**	**$B_{1,1}$**	**$B_{2,0}$**	**$B_{2,1}$**
Values	2.146E+00	1.775E-03	1.164E+00	2.065E-03
R^2	0.9763			
RMSE	0.021			

Therefore, we have simultaneously correlated the excess molar volume with temperature (T) and the IL mole fraction (x_2) using Equations (3)-(5). The excess molar volume of the studied mixture and the fitting results using these equations are shown in Figure 2.

A glance at Figure 2 reveals that the excess molar volume is negative. Negative V_m^E values indicate that volume contracts in the mixture with respect to the ideal mixture. This contraction may be due to chemical interactions such as H-bond between the water molecules and the IL ions in the mixture. It may also be due to the geometrical fitting of one component into the other because of the different molar volumes of pure components [25]. V_m^E reaches a minimum value ($V_m^E \approx -0.4\ cm^3 mol^{-1}$) at $x_2 \approx 0.08$. For $x_2 \geq 0.08$, the magnitude of V_m^E gets smaller as the concentration of water decreases in the mixture. This is probably due to the increased intermolecular interaction between the anionic and cationic species of [EtOHmim][BF_4], which is favored over the interaction between water molecules and IL ions [24,25].

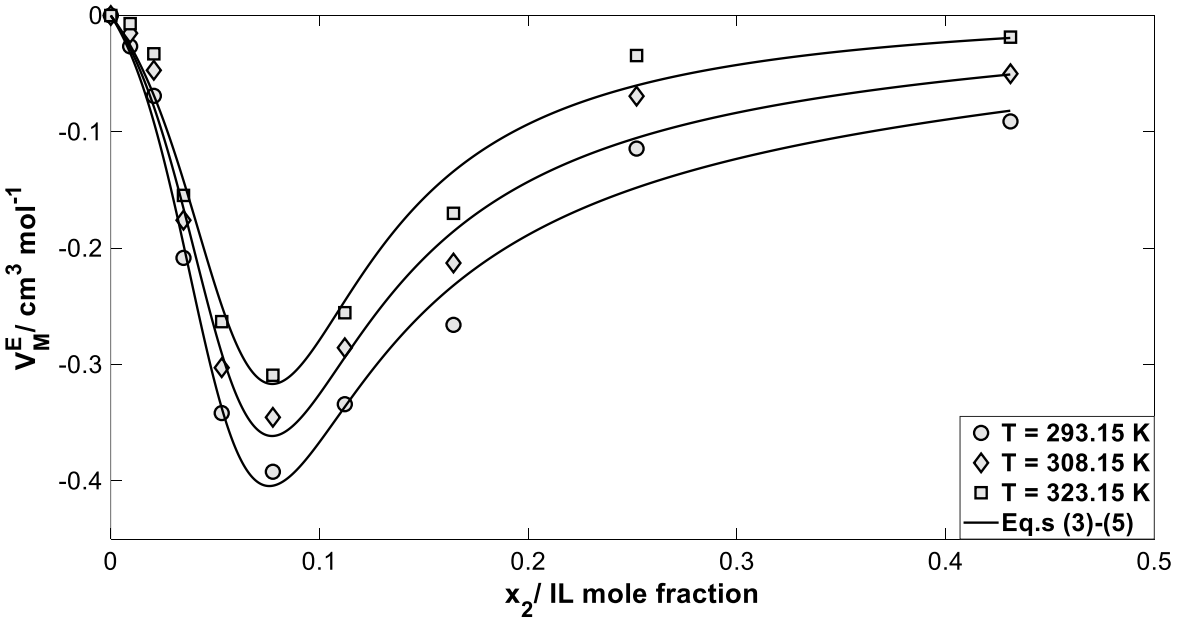

Figure 2. Excess molar volume as a function of the IL mole fraction at 298.15 K, 308.15 K, and 323.15 K.

It is also observed that the magnitude of V_m^E decreases with temperature from 293.15 K to 323.15 K at a given IL mole fraction. This is a common feature of several mixtures of imidazolium-based ILs with water [25]. It may be a consequence of the breaking of specific interactions in the IL-water mixture (usually H-bonds) when the temperature increases [24].

3.1.2. Thermal expansion coefficient

The isobaric thermal expansion coefficient, β, indicates changes in the volume of the mixture with temperature:

$$\beta/\mathrm{K}^{-1} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \quad (6)$$

The thermal expansion coefficient was obtained from the partial derivative of Equation (1) with respect to temperature, and its values are listed in Table 2s in the supplementary material. This table shows that β increases with IL mass fraction and temperature. There are no β data available for the mixture of interest, but we did find β data for the pure IL [EtOHmim][BF_4]. Fakhraee et al.[17] investigated the thermodynamics and structural properties of several 1-(2-hydroxyethyl)-3-methyl imidazolium ionic liquids using molecular dynamics simulations and ab initio calculations. They reported values of β for [EtOHmim][BF_4] at several temperatures. Here, for purposes of comparison we show our experimental values and their calculated values at two temperatures in Table 5. The relative deviation between experimental and calculated values is very small, -0.4% and 0.5% at 298.15 K and 313.15 K, respectively.

Table 5. Comparison between experimental and calculated thermal expansion coefficient, β x 10^{-4}/ K^{-1}, of [EtOHmim][BF_4] at two temperatures, T, 298.15 K and 313.15 K.

	Thermal expansion coefficient, $\beta \times 10^4/\mathrm{K}^{-1}$		
T/ K	**This study**	**Fakhraee et al.** [17]	**Deviation/ %**
298.15	6.11 ± 0.05	6.13 ± 0.06	-0.4
313.15	6.16 ± 0.05	6.06 ± 0.06	0.5

We also calculated the excess thermal expansion coefficient, β^E:

$$\beta^E/\mathrm{K}^{-1} = \beta - \sum_{i=1}^{2} \phi_i \beta_i^0 \quad (7)$$

where β_i^0 is the thermal expansion coefficient of the pure components and ϕ_i is the volume fraction of component i, defined by Equation (8):

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{2} x_i V_i} \quad (8)$$

Here, V_i is the molar volume of component i.

The values of β^E are given in Table 2s in the supplementary material. Figure 3 shows the calculated excess thermal expansion coefficient for the mixture at three experimental temperatures. It can be observed that this magnitude exhibits a positive deviation throughout the IL volume fraction. From this figure, it is also obvious that it depends heavily on the IL volume fraction. β^E increases with the IL volume fraction in the IL-dilute region, reaches a maximum value ($\beta^E \approx 4.3\ x\ 10^{-5}\ K^{-1}$) at $\phi_2 \approx 0.45$, and, from this point onwards, decreases with the IL volume fraction. Figure 3 shows that the influence of temperature on the excess thermal expansion coefficient is almost negligible.

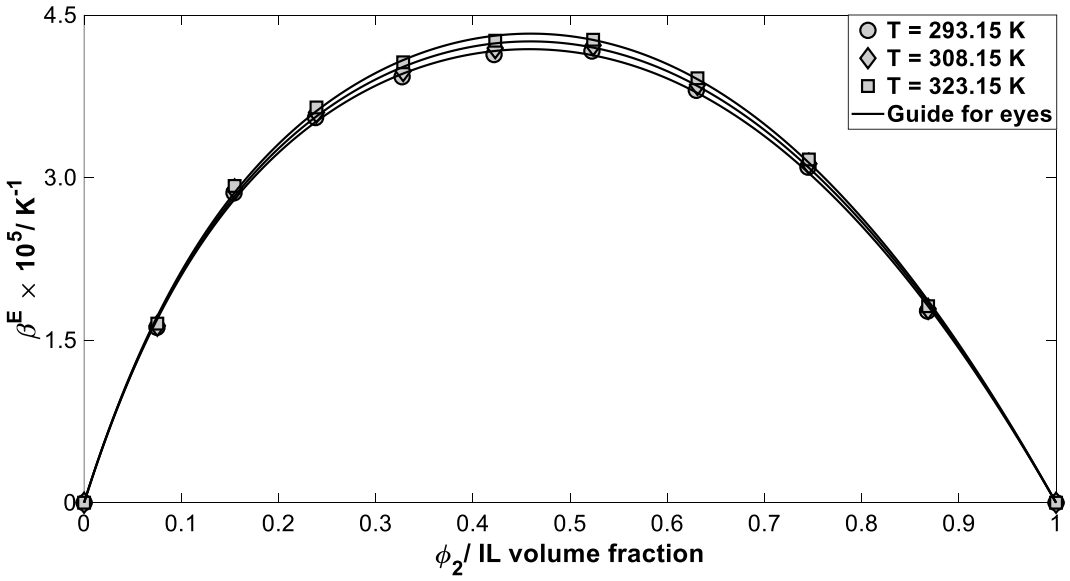

Figure 3. Excess thermal expansion coefficient as a function of the IL volume fraction at 298.15 K, 308.15 K and 323.15 K.

3.2. Refractive index and related properties

Table 6 lists the measured refractive indices of the binary mixture H_2O + [EtOHmim][BF_4] at the temperatures and wavelengths studied. As expected, the refractive index increases with the IL mass fraction, but decreases with temperature and wavelength.

No comparable refractive index data were found in the literature for the pure ionic liquid and the binary mixture studied here. Thus, literature data on refractive index for pure water at the studied temperatures and wavelengths are used for comparison.

Table 6. Experimental refractive index, n, of H_2O + [EtOHmim][BF_4] mixtures with ionic liquid mass fractions, ω_2, from 0 to 1, at temperatures, T[1], ranging from 293.2 K to 323.2 K, at pressure, P[2], 0.1 MPa, and different wavelengths, λ.

$\omega_2 \pm u(\omega_2)$[3]/ IL mass fraction	Refractive index, n							U(n)[4]
	T /K							
	293.2	298.2	303.2	308.2	313.2	318.2	323.2	
				λ = 589.2 nm				
0.00000 ±0.00002	1.3334	1.3328	1.3323	1.3316	1.3309	1.3302	1.3293	0.0002
0.0997 ±0.0010	1.3441	1.3423	1.3415	1.3409	1.3398	1.3391	1.3380	0.0006
0.2000 ±0.0019	1.3527	1.3518	1.3509	1.3501	1.3493	1.3482	1.3473	0.0012
0.2989 ±0.0024	1.3620	1.3604	1.3596	1.3590	1.3580	1.3573	1.3563	0.0016
0.3950 ±0.0028	1.3715	1.3704	1.3692	1.3681	1.3673	1.3662	1.3651	0.0022
0.4996 ±0.0029	1.3809	1.3787	1.3777	1.3769	1.3760	1.3746	1.3738	0.0028
0.6045 ±0.0028	1.3892	1.3883	1.3872	1.3860	1.3849	1.3839	1.3828	0.0034
0.6995 ±0.0025	1.3986	1.3974	1.3966	1.3956	1.3943	1.3934	1.3923	0.0040
0.8010 ±0.0015	1.4081	1.4070	1.4061	1.4050	1.4041	1.4030	1.4020	0.0046
0.8988 ±0.0011	1.4172	1.4161	1.4151	1.4138	1.4132	1.4122	1.4112	0.0050
1.0000 ±0.0008	1.4267	1.4252	1.4243	1.4233	1.4221	1.4211	1.4198	0.0058
				λ = 632.8 nm				
0.00000 ±0.00002	1.3323	1.3316	1.3311	1.3304	1.3297	1.3290	1.3282	0.0002
0.0997 ±0.0010	1.3419	1.3411	1.3398	1.3390	1.3384	1.3374	1.3364	0.0006
0.2000 ±0.0019	1.3510	1.3504	1.3492	1.3485	1.3474	1.3464	1.3456	0.0012
0.2989 ±0.0024	1.3604	1.3596	1.3588	1.3580	1.3565	1.3552	1.3545	0.0016
0.3950 ±0.0028	1.3702	1.3690	1.3681	1.3664	1.3658	1.3650	1.3636	0.0022
0.4996 ±0.0029	1.3791	1.3775	1.3765	1.3751	1.3744	1.3731	1.3722	0.0028
0.6045 ±0.0028	1.3881	1.3870	1.3857	1.3843	1.3833	1.3825	1.3816	0.0034
0.6995 ±0.0025	1.3970	1.3959	1.3948	1.3939	1.3929	1.3914	1.3904	0.0040
0.8010 ±0.0015	1.4063	1.4054	1.4044	1.4034	1.4024	1.4016	1.4003	0.0046
0.8988 ±0.0011	1.4153	1.4142	1.4132	1.4123	1.4115	1.4106	1.4093	0.0050
1.0000 ±0.0008	1.4248	1.4234	1.4224	1.4212	1.4204	1.4196	1.4184	0.0058
				λ = 670 nm				
0.00000 ±0.00002	1.3312	1.3307	1.3301	1.3295	1.3288	1.3281	1.3272	0.0002
0.0997 ±0.0010	1.3408	1.3397	1.3388	1.3377	1.3370	1.3365	1.3350	0.0006
0.2000 ±0.0019	1.3498	1.3487	1.3479	1.3467	1.3460	1.3448	1.3439	0.0012
0.2989 ±0.0024	1.3594	1.3581	1.3575	1.3563	1.3556	1.3542	1.3533	0.0016
0.3950 ±0.0028	1.3681	1.3675	1.3668	1.3656	1.3642	1.3635	1.3625	0.0022
0.4996 ±0.0029	1.3774	1.3762	1.3754	1.3738	1.3732	1.3719	1.3709	0.0028
0.6045 ±0.0028	1.3866	1.3857	1.3848	1.3835	1.3824	1.3818	1.3803	0.0034
0.6995 ±0.0025	1.3957	1.3944	1.3938	1.3927	1.3916	1.3902	1.3894	0.0040
0.8010 ±0.0015	1.4053	1.4042	1.4034	1.4024	1.4013	1.4002	1.3991	0.0046
0.8988 ±0.0011	1.4141	1.4132	1.4125	1.4111	1.4102	1.4093	1.4082	0.0050
1.0000 ±0.0008	1.4235	1.4222	1.4213	1.4204	1.4193	1.4183	1.4174	0.0056
				λ = 780 nm				
0.00000 ±0.00002	1.3290	1.3285	1.3279	1.3273	1.3266	1.3259	1.3251	0.0002
0.0997 ±0.0010	1.3385	1.3370	1.3361	1.3353	1.3343	1.3334	1.3319	0.0006
0.2000 ±0.0019	1.3471	1.3464	1.3457	1.3446	1.3436	1.3426	1.3417	0.0010
0.2989 ±0.0024	1.3565	1.3557	1.3543	1.3534	1.3524	1.3518	1.3509	0.0016
0.3950 ±0.0028	1.3661	1.3651	1.3637	1.3631	1.3620	1.3608	1.3597	0.0022
0.4996 ±0.0029	1.3752	1.3734	1.3722	1.3713	1.3703	1.3694	1.3684	0.0028
0.6045 ±0.0028	1.3843	1.3832	1.3822	1.3810	1.3801	1.3787	1.3775	0.0034
0.6995 ±0.0025	1.3934	1.3920	1.3908	1.3903	1.3887	1.3881	1.3868	0.0040
0.8010 ±0.0015	1.4022	1.4011	1.4002	1.3991	1.3985	1.3972	1.3961	0.0044
0.8988 ±0.0011	1.4119	1.4109	1.4098	1.4084	1.4074	1.4067	1.4059	0.0050

1.0000 ±0.0008	1.4210	1.4199	1.4192	1.4183	1.4171	1.4162	1.4148	0.0056
				λ = 935 nm				
0.00000 ±0.00002	1.3267	1.3260	1.3254	1.3248	1.3241	1.3234	1.3226	0.0002
0.0997 ±0.0010	1.3363	1.3351	1.3337	1.3328	1.3320	1.3311	1.3305	0.0006
0.2000 ±0.0019	1.3448	1.3439	1.3429	1.3420	1.3408	1.3399	1.3390	0.0010
0.2989 ±0.0024	1.3541	1.3530	1.3520	1.3513	1.3504	1.3494	1.3482	0.0016
0.3950 ±0.0028	1.3632	1.3622	1.3617	1.3608	1.3597	1.3590	1.3579	0.0022
0.4996 ±0.0029	1.3728	1.3717	1.3710	1.3696	1.3685	1.3673	1.3669	0.0028
0.6045 ±0.0028	1.3814	1.3806	1.3794	1.3787	1.3777	1.3768	1.3760	0.0034
0.6995 ±0.0025	1.3907	1.3895	1.3884	1.3876	1.3868	1.3859	1.3847	0.0038
0.8010 ±0.0015	1.4001	1.3992	1.3985	1.3972	1.3962	1.3954	1.3941	0.0044
0.8988 ±0.0011	1.4092	1.4079	1.4068	1.4058	1.4048	1.4040	1.4030	0.0050
1.0000 ±0.0008	1.4185	1.4170	1.4162	1.4151	1.4140	1.4132	1.4119	0.0056

[1] Standard uncertainty u(T) = 0.1 K.
[2] Standard uncertainty u(P) = 10 kPa.
[3] Standard uncertainty u(ω_2) is reported for each mass fraction studied.
[4] Expanded uncertainty with 0.95 level of confidence (k=2).

Figure 4 shows the deviations between the refractive index values obtained and those reported in the literature for water [32,38,44–47]. As can be seen, the relative deviations are generally very small and range between -0.12% and 0.07%.

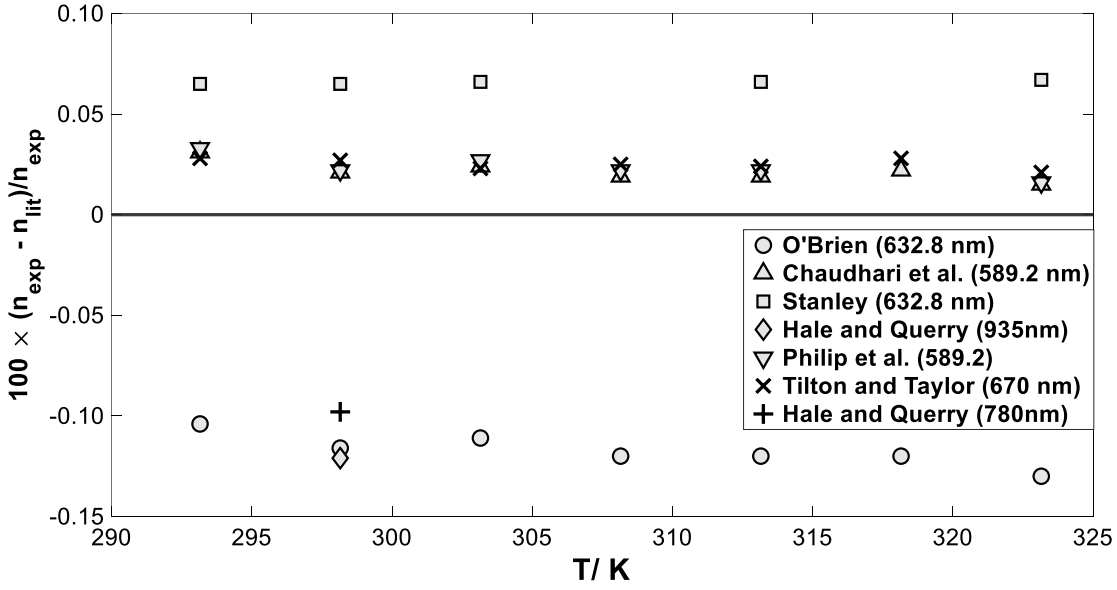

Figure 4. Deviations between the experimental refractive index values obtained in this study and those from the literature for pure water at different temperatures and wavelengths.

In the literature there are few values of the refractive index of water at 780 nm and 935 nm. We have been able to identify a single source from the literature at these

wavelengths (Hale and Querry [47] at 298 K). Therefore, this study also provides new values for the refractive index of water at different temperatures for these wavelengths.

The refractive index of the pure [EtOHmim][BF_4] is in the range from 1.4119 (at λ=935 nm and T = 323.2 K) to 1.4267 (at λ=589.2 nm and T = 293.2 K), which is approximately 1.07 times higher than that of water under the same conditions. Moreover, compared to [emim][BF_4] [26], [EtOHmim][BF_4] exhibits a higher refractive index because of the hydroxyl group in the alkyl chain of its cation, which favors the formation of hydrogen bonds with water.

Here, we have adopted a two-term Cauchy equation [9] to simultaneously investigate the refractive index dependences on temperature, IL mass fraction and wavelength:

$$n(T,\omega_2,\lambda) = A(T,\omega_2) + \frac{B(T,\omega_2)}{\lambda^2} \quad (9)$$

where $A(T,\omega_2) = (a_{00} + a_{10}\cdot\omega_2 + a_{01}\cdot T + a_{11}\cdot\omega_2\cdot T)$ and $B(T,\omega_2) = (b_{00} + b_{10}\cdot\omega_2 + b_{01}\cdot T + b_{11}\cdot\omega_2\cdot T)$. Using an eight-parameter fitting procedure, we determined the values of the coefficients of Equation (9), which are listed in Table 7.

Table 7. Coefficients of Equation (9) and goodness of fit (R^2 and RMSE)

Coefficients	Value
a_{00}	1.3675
a_{10}	1.027E-02
a_{01}	-1.556E-04
a_{11}	-4.086E-05
b_{00}	5.859E-03
b_{10}	4.850E-04
b_{01}	-5.194E-06
b_{11}	-1.025E-07
R^2	0.9999
RMSE	3.5E-04

The relative deviations between the experimental and calculated refractive indices values do not exceed 0.1%. Equation (9) provides excellent estimates of the refractive index, with a coefficient of determination R^2 = 0.9999 and root mean square error RMSE = 3.5E-04.

The analytical expression above enables us to obtain the dispersion relations of the refractive index and interpolate refractive index values between measured points. As an example, Figures 5 and 6 show the refractive index variations with temperature, IL mass fraction and wavelength at selected experimental conditions. In these figures, the fitting results of Equation (9) are also shown. As can be seen in Figure 5, the refractive index decreases linearly with increasing temperature with a slope practically independent of wavelength and IL mass fraction. Moreover, at a given IL mass fraction (ω_2 = 0.5), the refractive index decreases with increasing wavelength. We also observed the refractive index increases linearly with IL mass fraction at a given wavelength. A comparison between Figure 5 a) and b) reveals that dependence of the refractive index on the IL mass fraction is much stronger than on wavelength and temperature within the ranges of values considered.

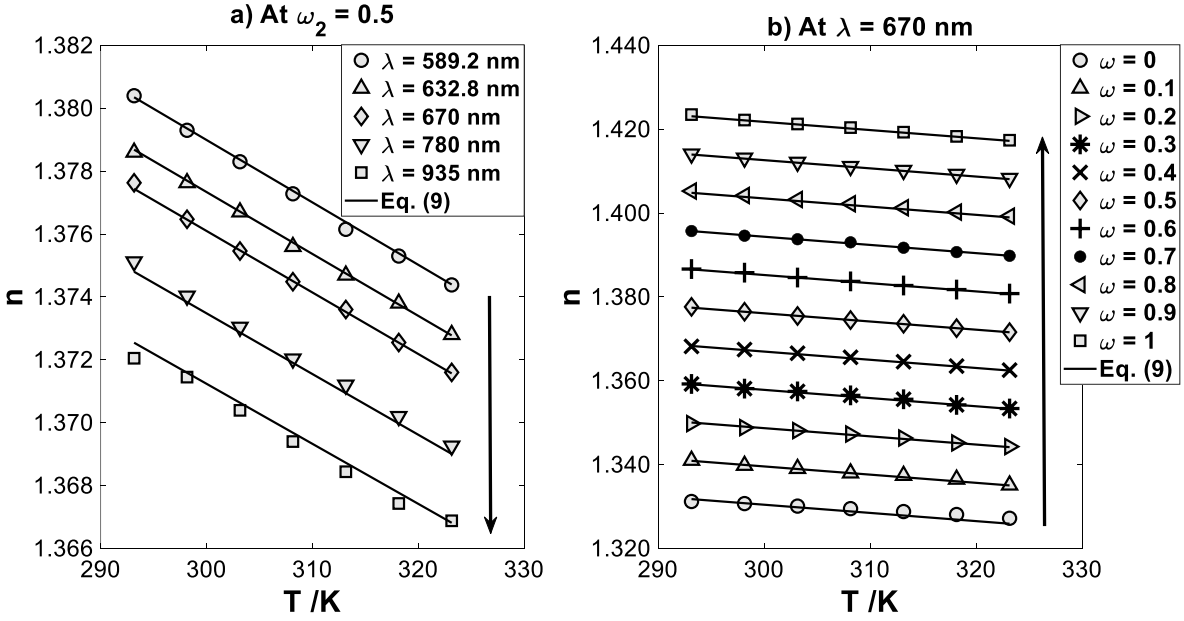

Figure 5. Refractive index (n) variation with temperature (T) for the mixture H_2O + [EtOHmim][BF_4]: a) At several wavelengths for ω_2=0.5; b) At several IL mass fractions for λ=670 nm.

In contrast with the linear relationship between the refractive index and the temperature and IL mass fraction, we observed a nonlinear behavior of the refractive index with variations in wavelength (see Figure 6). The refractive index for the studied mixture presents normal dispersion, which means that as the wavelength increases the refractive

index decreases and the propagation velocity in the material increases [9]. A glance at Figure 6 a) and b) shows that the dependence of the refractive index on the IL mass fraction is much stronger than on the temperature within the ranges of values considered.

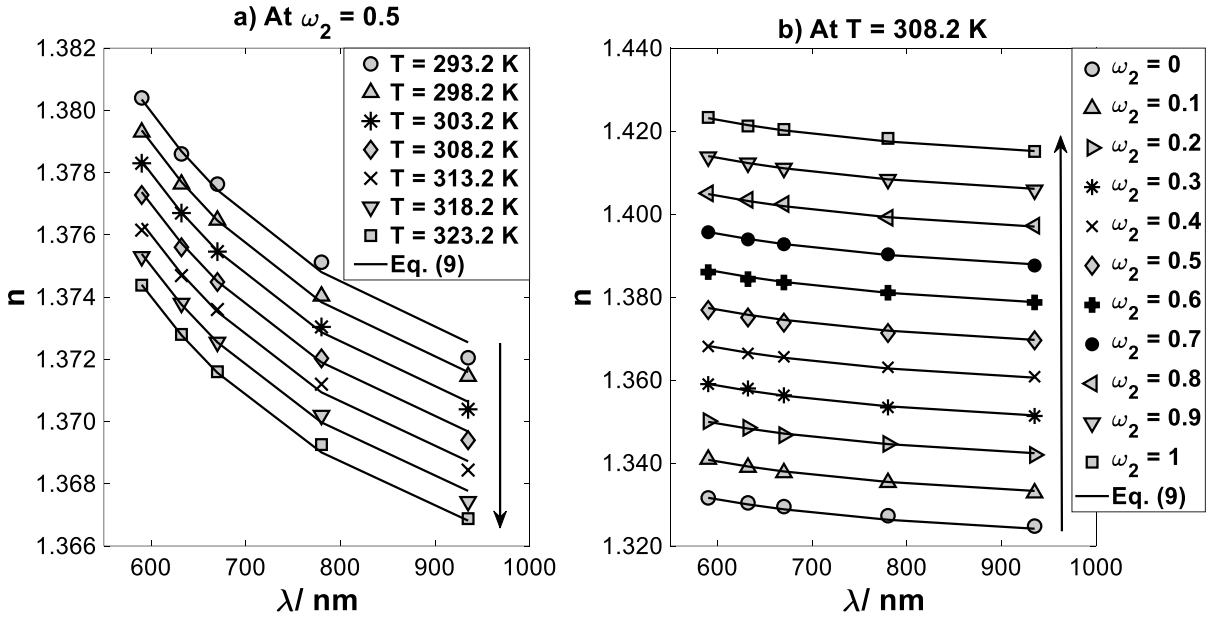

Figure 6. Refractive index (n) variation with wavelength (λ) for the mixture H_2O + [EtOHmim][BF_4]: a) At several temperatures for ω_2=0.5; b) At several IL mass fractions for T=308.2 K.

3.2.1. Concentration, temperature, and dispersion derivatives of the refractive index

The concentration ($\partial n/\partial \omega_2$), and temperature ($\partial n/\partial T$) derivatives of the refractive index (also known as optical contrast factors) can be directly obtained by analytical differentiation of Equation (9). The calculated values of $\partial n/\partial \omega_2$ and $\partial n/\partial T$ are listed in Tables 3s and 4s in the supplementary material, respectively. On one hand, $\partial n/\partial \omega_2$ exhibits a positive sign, which indicates that the refractive index increases with the IL mass fraction. On the other hand, $\partial n/\partial T$ exhibits a negative sign, which indicates that the refractive index decreases with temperature. Moreover, the absolute value of both magnitudes shows a nonlinear decreasing behavior with the wavelength. Thus, the influence of temperature and IL mass fraction on variation in the refractive index decreases as the wavelength increases. Furthermore, $\partial n/\partial T$ and $\partial n/\partial \omega_2$ values are in

the same order as for conventional aqueous liquid mixtures, 10^{-4} K^{-1} and 10^{-2}, respectively.

The chromatic dispersion coefficient, $\partial n/\partial \lambda$, can also be calculated from Equation (9). The negative values at all the experimental temperatures and throughout the IL mass fraction range indicate that the refractive index always decreases with the wavelength. The values of $\partial n/\partial \lambda$ are in the expected order of magnitude (i.e., 10^{-5} nm^{-1}), and are higher at shorter wavelengths. Thus, at shorter wavelengths, the dispersion is more intense, which is also representative of normal dispersion [9].

3.2.2. Deviation in the refractive index

The deviation in the refractive index from ideal behavior Δn is defined as the difference between the refractive index of the mixture and the refractive index of the ideal mixture in the same thermodynamic state. As suggested by some authors [27,43,48], the refractive index for the ideal mixture is calculated in terms of volume fraction not mole fraction. Thus, the deviation in the refractive index was calculated using the following equation:

$$\Delta n = n - \sum_{i=1}^{2} n_i \phi_i \quad (10)$$

where n_i is the refractive index of the pure components, and ϕ_i the volume fraction. The values of Δn are listed in Table 5s in the supplementary material.

Figure 7 shows the deviation in the refractive index of the mixture in different experimental conditions. As can be observed, Δn is positive throughout the IL volume fraction range and approaches a maximum of 7.5 x 10^{-3} at around $\phi_2 \approx 0.42$. In general, positive deviations in refractive index are considered to be associated with significant interactions in the mixtures [49]. Like Brocos et al. [48], we observed that the sign of the values of Δn is opposite to the sign of the excess molar volumes (V_m^E). Moreover, the extrema for both quantities, V_m^E and Δn, are found at the same IL mole fraction (note that $\phi_2 \approx 0.42$ corresponds to an IL mole fraction $x_2 \approx 0.08$). This can be explained by the fact that Δn is intrinsically related to V_m^E via the reduced free volume [27]. As stated by Anouti et al. [50], a negative V_m^E indicates that there is less free volume available than in an ideal solution, so photons will be more likely to interact with the ions or molecules in the mixture. Consequently, light will travel at a lower speed in the medium and its refractive index will

be higher than in an ideal solution. A comparison between Figure 2 and Figure 7 a) reveals opposite trends for V_m^E and Δn with temperature. While the latter decreases, the former increases with increasing temperature. Figure 7 b) shows that Δn also varies with the wavelength, although the variation is quite small. As depicted, Δn slightly decreases with increasing wavelength. A glance at Figure 7 a) and b) shows that the decrease in Δn with temperature and wavelength is more pronounced at low and middle-range IL volume fractions. Furthermore, our results also show that the dependence of Δn on wavelength is much weaker than on temperature.

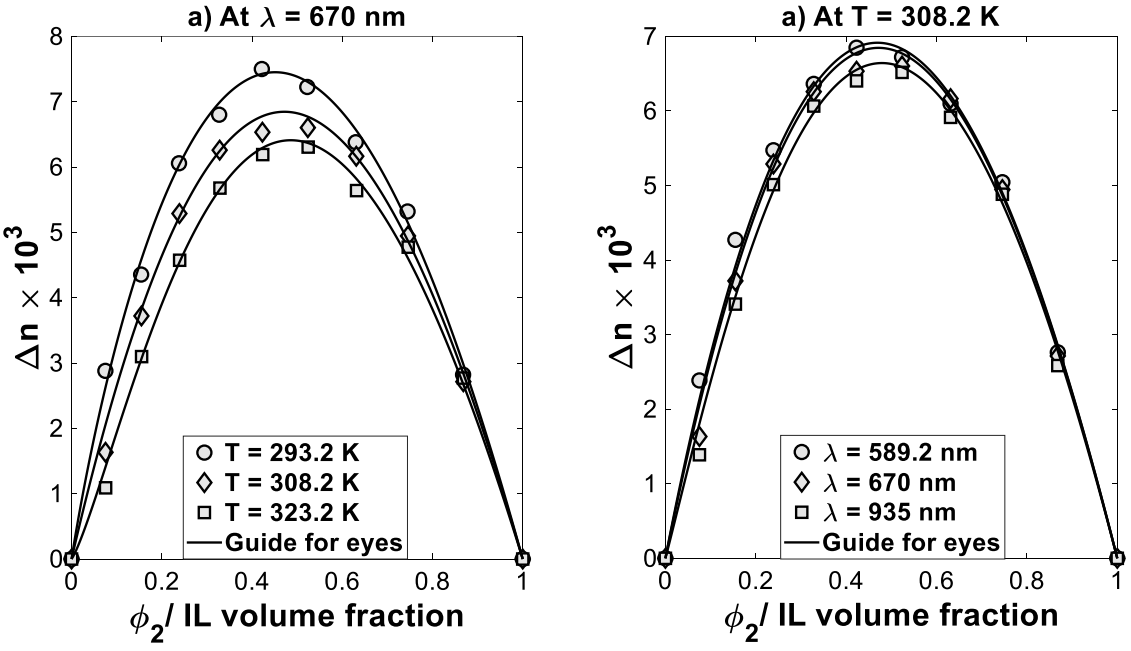

Figure 7. Deviation in refractive index, Δn, as a function of the IL volume fraction, ϕ_2: a) At three temperatures (298.2 K, 308.2 K, 323.2 K) for λ=670 nm. b) At three wavelengths (589.2 nm, 670 nm, 935 nm) for T=308.2 K.

3.2.3. Refractive index mixing rules

The refractive index of a liquid mixture can be estimated from the refractive indices of pure components using mixing rule expressions. We used 11 mixing rules from the literature to estimate the refractive index of the mixture water(1) + [EtOHmim][BF_4](2). Most of the expressions used are based upon the electromagnetic theory of light with the implicit restriction that the molecules (or particles) may be regarded as dipoles or assemblies of dipoles induced by an external field [51]. We made a quantitative

comparison of the refractive indices measured and the values predicted using the mixing rules selected. The average percentage deviation (APD) and maximal deviation (MaxDev) were used as the main criteria to evaluate the prediction ability of the mixing rules investigated.

The values of the APD and MaxDev for all the mixing rules studied are listed in Table 6s in the supplementary material. In general, the estimated values of the refractive index were found to be in good agreement with the experimental values. At all experimental temperatures and wavelengths, APD values do not exceed 0.3%, while MaxDev is about 0.6 %. However, all mixing rules provide comparable results. Therefore, more advanced mixing rules do not lead to any improvement in comparison with the simple linear mixing rule (Arago-Biot). Moreover, deviations between experimental and calculated refractive index refractive values were larger at $\phi_2 \approx 0.42$, lower temperatures, and shorter wavelengths. As discussed above, in these experimental conditions, the non-ideality of the binary system studied is more pronounced.

The concentration contrast factor is an important parameter for several experimental techniques [29–31]. Thus, we also evaluated how the mixing rules calculated the concentration contrast factor of the mixture studied. The results are also listed in Table 6s in the supplementary material. In this case, the deviations were significantly higher than in the case of the refractive index calculations. The APD values were in the range from 18.5% to 19.9%, while the MaxDev values were in the range from 18.9% to 20.3%. Again, a more advanced mixing rule leads to no essential improvement in comparison with the simple linear mixing rule (Arago-Biot).

4. Summary and conclusions

The density and refractive index of binary mixtures of water + ionic liquid [EtOHmim][BF_4] were measured throughout the ionic liquid mass fraction range, at atmospheric pressure and various temperatures between 293.15 K and 323.15 K. The refractive index was measured at five wavelengths between 589.2 nm and 935 nm.

Experimental density values range from 1.3439 g cm^{-3} at 323.15 K to 1.3685 g cm^{-3} at 293.15 K for pure ionic liquid [EtOHmim][BF_4]. Relatively large deviations are observed between the density values reported in different literature sources for this ionic liquid. The

influence of temperature on the density of the binary mixture studied is greater as the IL mass fraction increases. The excess molar volume (V_m^E) is negative throughout the IL mole fraction range studied with a minimum of around $V_m^E = -0.4\ cm\ mol^{-3}$ at an IL mole fraction of around 0.08.

The refractive index of the mixture increases with IL mass fraction but decreases with temperature and wavelength. The results of our investigation show that the refractive index of the mixture exhibit a linear dependence on IL mass fraction and temperature and a nonlinear dependence on wavelength. We successfully correlated the experimental refractive index with a two-term Cauchy equation in order to simultaneously investigate dependences on temperature, IL mass fraction and wavelength. The relative deviation between experimental and calculated refractive indices do not exceed 0.1%. The deviation in the refractive index was found to be positive throughout the composition range. The 11 mixing rules used to estimate the refractive index and concentration contrast factor of the binary mixture studied provide comparable results. Therefore, more advanced mixing rules do not lead to any essential improvement in comparison with the simple linear mixing rule (Arago-Biot).

5. Supporting information

The excess molar volumes, (V_m^E), thermal expansion coefficient, (β), and excess thermal expansion coefficient, (β^E), are included in the supplementary material. Also included are the deviation in the refractive index as a function of the ionic liquid mass fraction, temperature and wavelength, and the performance indicators of the investigated refractive index mixing rules.

6. Acknowledgments

The authors from Universitat Rovira i Virgili acknowledge the financial support under Research project DPI2015-71306-R cofunded by the Ministry of Economy and Competitiveness of Spain and the European Regional Development Fund (FEDER). We also acknowledge the thoughtful comments on the paper of Prof. M. S. Larrechi and Dr. Daniel Salavera of the Universitat Rovira i Virgili. The authors from Université Libre de Bruxelles acknowledge financial support from the PRODEX program of the Belgian Federal Science Policy Office.

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