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Excess Thermodynamic Properties in Mixtures of a Representative Room-Temperature Ionic Liquid and Acetonitrile

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The nature of the interactions between a representative room-temperature ionic liquid, namely 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF₄]) and a common organic solvent, acetonitrile (CH₃CN) has been investigated by means of Brillouin light scattering, over the whole concentration range and in the temperature range from −20 to 45 °C. Negative deviations from the ideal behavior of both molar volumes and adiabatic compressibility have been observed. This result has been interpreted within the framework of a well-established theoretical model, namely a nonadditive hard-sphere mixture. Despite that similar findings were rationalized in terms of enhanced interactions between molecules, a more detailed analysis of excess thermodynamic functions indicates that they are mainly due to excluded volume effects and that the differences in local intermolecular interactions act as higher order contributions: we have found that this can be a general feature of liquid mixtures. On this basis we present a reconsideration for excess thermodynamic data and for their role in providing direct information on intermolecular interactions.

Introduction

Room-temperature ionic liquids (RTIL)^{1–4} are presently attracting a great attention as a consequence of their peculiar chemical physical properties. They are typically built up by a bulky asymmetric cation (e.g., 1-methyl-3-butyl imidazolium (hereinafter [BMIM]) and a fluorinated anion, such as [BF₄][−] or [PF₆][−].⁵ This chemical architecture leads to a low tendency toward crystallization (most of these salts have crystallization temperatures below 25 °C, if any) and to a wide stability range for the liquid state (most RTIL are stable up to 200–300 °C).^{6,7} Their negligible vapor pressure,⁸ high thermal stability,^{7,8} good solvating performances, and high flexibility in chemical design^{4,9–11} make these materials environmentally benign candidates to progressively replace the noxious volatile organic solvents for a wide range of chemical, biocatalytic, and electrochemical applications.^{12–21}

To enlarge the range of application and versatility of these materials, the number of studies on binary mixtures of RTILs is rapidly increasing and many efforts are presently devoted to the investigation of phase behavior and thermodynamic properties of their mixtures with other organic liquids, such as alkanes, alcohols, water, and organic solvents.^{22–26}

The mixtures of 1-methyl-3-butyl imidazolium tetrafluoroborate, [BMIM][BF₄] and acetonitrile (as well as other organic solvents) have been recently investigated by Wang et al.,²⁷ who reported on volumetric and viscosity properties over the whole composition range at 25 °C. This study ascribes the observed large negative excess molar volume of the mixtures to the ion-dipole interactions between components.

[BMIM][PF₆]/CH₃CN and [BMIM][BF₄]/CH₃CN systems have also been investigated by means of volumetric and speed of sound measurements over the temperature range from 25 to 35 °C.^{28,29} These studies accessed the phase diagram of [BMIM]-based ionic liquid/acetonitrile mixtures over the entire concen-

tration range and highlighted the existence of distinct excess molar volume, viscosity, and isoentropic compressibility at a RTIL mole fraction of ca. 0.3. These findings have got a preliminary rationalization in terms of ion–dipole interactions and of an enhancing of cation/anion and CH₃CN/ CH₃CN interactions upon mixing.

The system [BMIM][BF₄]/CH₃CN has been recently investigated by means of molecular dynamics simulations by Wu et al.³⁰ Using a fully atomistic potential, the authors reproduced the experimental densities and viscosities of the binary mixtures at 25 °C. Their numerical simulation results also describe the composition dependence of the excess molar volume and viscosity experimentally observed.²⁷ The authors find that, upon mixing, the self-interactions between cations and anions and between acetonitrile molecules are enhanced; a direct consequence of this effect are deviations from the ideal solution behavior.

In this paper we report the results of a Brillouin spectroscopy experiment on [BMIM][BF₄]/CH₃CN mixtures. The system has been explored over the entire composition range between −20 and 45 °C. In principle, the technique should allow accessing relaxation processes on a time scale of nanoseconds, probing the propagation of density fluctuations and their time decay through different loss channels. However, in the present study the attention is focused on the analysis and interpretation of the concentration dependence of excess compressibility and on the comparison of our results with recent literature data.^{27,29,30}

Together with a description of the nature of interactions between RTILs and an important organic solvent, a goal of this work is to critically discuss the actual details of solute–solvent interaction that can be gained from the knowledge of macroscopic quantities such as compressibility.

Experimental Procedures and Results

[BMIM][BF₄] is a Solvent Innovation product. The as-received sample (purity > 99%) was maintained under vacuum

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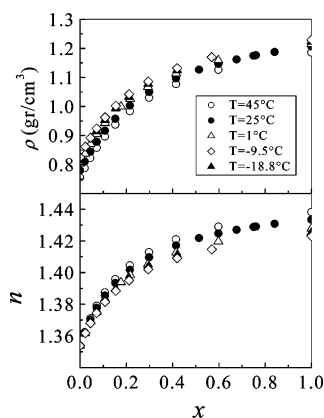


Figure 1. Density and refractive index as a function of [BMIM][BF₄] mole fraction.

(10⁻³ bar) at 40 °C overnight. The sample was then filtered through a 2 μm Teflon filter. After this treatment, the water content (that was reported to be 1500 ppm by the provider) amounts to 800 ppm, as estimated using infrared spectroscopy by comparison of the OH-stretching band amplitude with the corresponding amplitude from a set of measurements with calibrated samples [Triolo, A.; Fazio, B.; Di Marco, G. Unpublished data]. Fluorine content was reported from the provider to be 260 ppm, while no chloride was detected.

Acetonitrile is a Carlo Erba product (purity: 99.8%) and was used without further purification.

Sample handling and mixtures preparation were conducted in a glovebox, using dry N₂ as inert atmosphere. Sealed samples were maintained in a drybox for all the time prior to measurements.

Acetonitrile and [BMIM][BF₄] form homogeneous mixtures over the whole composition range between -20 and 45 °C. Once prepared, the solutions provided reproducible density, refraction index, and light scattering data, as long as care was taken in preventing acetonitrile leakage from the cells.

Mixtures were prepared by weight, spanning the whole concentration range from pure acetonitrile to pure [BMIM][BF₄]. Care was taken to minimize the exposure time to moisture. Once prepared the mixtures were kept at -20 °C to reduce acetonitrile evaporation.

At 1°, 25°, and 45 °C density measurements were collected on an Anton Paar DMA 5000 density meter, while refraction index measurements were carried out, at the same temperatures, by means of an Abbe refractometer. For both properties, estimates at -10 and -18 °C were extrapolated from the data at higher temperature assuming a linear temperature dependence both for density and refractive index.

In the case of the mixture 50 wt %, a more detailed study was conducted measuring density and refraction index between -5 and 45 °C in steps of 5 °C. This measurement set confirmed the linear temperature dependence for both quantities.

The obtained results are summarized in Figure 1. The density data at 25 °C are in good agreement with the corresponding results presented by Wang²⁷ and Zafarani-Moattar.²⁹

Brillouin scattering spectra were collected on a double pass Fabry-Perot interferometer made by SOPRA. The instrument, has been modified to obtain dynamical self-alignment and high stability over long times³¹ and is fully controlled by a PC. The cavity length of the interferometer was set to 15 mm, corresponding to a free spectral range of 20 GHz, and the measurements have been performed in a 90° scattering angle geometry. The 532 nm linearly polarized single-mode line of a Coherent Verdi laser, working at a mean power of 100 mW, was used as

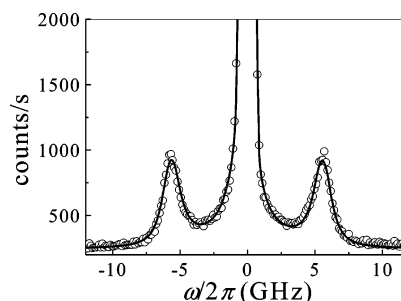


Figure 2. Experimental Brillouin spectrum at 25 °C for [BMIM][BF₄]/CH₃CN mixture at $x = 0.5$. Continuous line represents the best fitting result with eq 1.

the probe. The working finesse, determined by the experimental apparent full-width at half-maximum of the scattering profile from a static scatterer (LATEX), turned out to be about 50.

During the experiment, the sample was contained in an especially built optical thermostat and the temperature was set and controlled within 0.1 °C. Measurements were performed at four different temperatures, namely $T = -18.8$, 1.0, 25.0, and 45.0 °C.

The recorded spectra were fitted with the convolution of the following expression^{32,33} with the experimental elastic scattering profile

$$I_{VV}(\omega) = \delta_R + A_B \left[\frac{\Gamma_B}{\left[\omega - \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2} + \frac{\Gamma_B}{\left[\omega + \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2} \right] + \frac{A_B \Gamma_B}{\sqrt{\omega_B^2 - \Gamma_B^2}} \times \left[\frac{\omega + \sqrt{\omega_B^2 - \Gamma_B^2}}{\left[\omega + \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2} - \frac{\omega - \sqrt{\omega_B^2 - \Gamma_B^2}}{\left[\omega - \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2} \right] \quad (1)$$

where the symbols have the usual meaning.³⁴⁻³⁶ In Figure 2 we report, as an example, the experimental Brillouin spectrum obtained for [BMIM][BF₄]/CH₃CN mixture, at $x = 0.5$ and at a temperature of 25 °C. The continuous line in the same figure represents the fitting of the experimental data with eq 1.

The studied mixture is completely miscible and homogeneous at least in the thermodynamic regimes investigated in this set of measurements. From the fitting procedure the frequency values have been determined with an accuracy of ±1.5%, while the error estimated on the Brillouin HWHM was ±5%.

The fitting parameters, together with the measured refractive indices and densities, were used to calculate the values of the hypersonic velocity, v_h , and the normalized sound absorption, α/f^2 , according to the relations

$$v_h = \omega_B/q \quad (2)$$

$$\alpha/f^2 = 2\pi\Gamma_B/(v_h\omega_B^2) \quad (3)$$

where $q = (4\pi n/\lambda_0) \sin(\theta/2)$ is the amplitude of the exchanged wave-vector, λ_0 is the incident wavelength, and θ is the scattering angle.

Discussion

In Figure 3 the hyperacoustic parameters are reported as a function of the concentration. Given the value of hypersonic

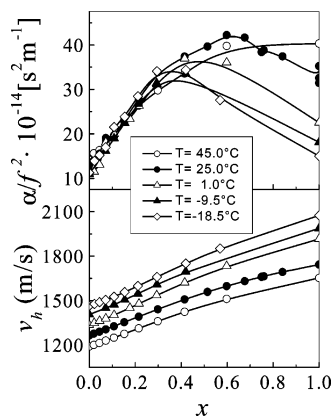


Figure 3. Normalized absorption and hypersound velocity as a function of [BMIM][BF₄] mole fraction at different temperatures.

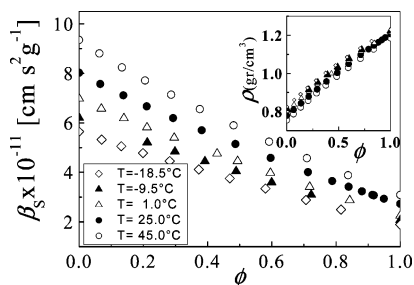


Figure 4. Adiabatic compressibility as a function of [BMIM][BF₄] volume fraction at different temperatures. The inset shows densities of the mixtures as a function of [BMIM][BF₄] volume fraction.

velocity v_h , and density, ρ , the adiabatic compressibility, β_s , can be calculated as $\beta_s = 1/(\rho v_h^2)$. This quantity is shown in Figure 4. We note that the whole set of data agrees well with low-frequency results.²⁹ This makes us confident that no relaxation process is taking place on a time scale down to a few ps.

On this basis the concentration dependence of the normalized absorption is simply due to changes occurring in some related thermodynamic quantities (e.g., density) while the α/f^2 apparent temperature dependence should be mainly ascribed to the larger temperature effects in pure [BMIM][BF₄] with respect to pure CH₃CN.

As a consequence one can try to extract information on the nature of the interactions between the mixture components by analyzing excess thermodynamic quantities. The volume of a mixture, V , is written as

$$V = V_{id} + V_E \quad (4)$$

where

$$V_{id} = n_A V_{mA} + n_B V_{mB} \quad (5)$$

n_A and n_B represent the mole numbers of solvent and solute respectively, V_{mA} and V_{mB} are the corresponding molar volumes and V_E is the excess molar volume.

V_E , calculated according to a formalism currently adopted in literature^{27–29} is reported in Figure 5. The results of Wang and co-workers²⁷ are in good agreement with ours at mole fraction values lower than 0.3 but turn out to be significantly different at higher [BMIM][BF₄] concentrations. A better agreement is observed with the findings by Zafarani-Moattar and co-workers²⁹ for the same system and for a similar one, [BMIM][PF₆]/CH₃CN, investigated between 25 and 45 °C.²⁸

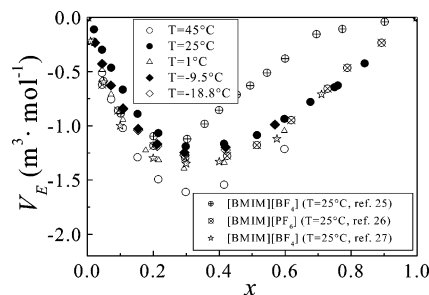


Figure 5. Excess molar volume as a function of [BMIM][BF₄] mole fraction at different temperatures.

Such negative deviations have been generally related to more efficient packing and attractive interactions in the mixtures than in the pure liquids.^{27–29} As a matter of fact, ion–dipole interaction between CH₃CN molecules and [BMIM][BF₄] can give rise to local packing effects. The weight of such effects depends on the probability that a CH₃CN molecule interacts with [BMIM][BF₄] that is higher at intermediate concentrations. As a consequence, the concentration dependence of the excess molar volume can be merely driven by geometrical effects, in agreement with the results of a recent application of the Prigogine–Flory–Patterson theory (PFP)^{37,38} to [BMIM][BF₄]-based mixtures.²⁹ Such statistical behavior is responsible for both the maximum observed in the α/f^2 curves and the recently observed maximum in the viscosity.²⁷

While the calculation of the excess molar volume is a trivial task, the situation becomes more complicated for other excess thermodynamic quantities. As an example, ideal mixing implies that the density behaves linearly with the solute volume fraction, ϕ . The nonideality leads to an implicit difficulty in determining the correct values of ϕ . For this reason experimental results are often reported as a function of the mole fraction, x , that is a safely computable quantity (as in Figure 1). However, the representation of density as a function of x does not allow us to point out the correct concentration dependence of its excess quantity.

To estimate the correct solute volume fractions, the solution molar volume, V_M (which is an experimentally determined quantity) is given by^{39,40}

$$V_M = \frac{M_M}{\rho} = (1-x)V_A^0 + xV_{app} \quad (6)$$

where x is solute mole fraction, $M_M = (1-x)M_A + xM_B$ is the solution molar mass, M_A and M_B being the molar masses of the two components (in our case acetonitrile and [BMIM][BF₄], respectively), V_A^0 is the molar volume of pure acetonitrile and V_{app} is the apparent molar volume of [BMIM][BF₄]. The latter quantity does not correspond to an actual solute property; however, it can be considered as a quantity accounting for all the contributions to the excess volume of the mixture.

Then, the apparent [BMIM][BF₄] volume fraction can be calculated as

$$\phi = \frac{xV_{app}}{(1-x)V_A^0 + xV_{app}} \quad (7)$$

In the inset of Figure 4 the densities data from Figure 1 are alternatively plotted as a function of ϕ , calculated according to eq 7. The deviation from linearity, observed in the ϕ -representation, although less pronounced than in the x -representation,

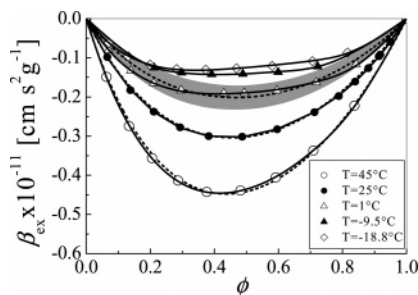


Figure 6. Excess adiabatic compressibility as a function of [BMIM]-[BF₄] volume fraction at different temperatures. The shadowed area represents the typical error bar: continuous lines, fitting with eq 9; dashed lines, fitting with eq 12.

indicates the existence of some *interference* between the local structures of the pure components that leads to nonadditive volumes.

Another quantity that is usually investigated as a function of concentration to deduce the existence of interspecies interactions is the compressibility. The ideal adiabatic compressibility is obtained by differentiating eq 5³⁹

$$\beta_{S,id} = \frac{1}{V_{id}} \left(\frac{\partial V_{id}}{\partial p} \right)_S = \beta_A + (\beta_B - \beta_A)\phi \quad (8)$$

where β_A and β_B are the adiabatic compressibility of pure solvent and solute, respectively.

Any observed deviation from eq 8 is an indication of interspecies interaction. In Figure 6 we report the excess adiabatic compressibility of our mixtures. We note that, although our data set and the one presented in ref 29 agree numerically, the excess compressibility calculated assuming eq 8 as the ideal behavior is definitely smaller than that obtained in ref 29. This mismatch is the consequence of the different definition of the ideal behavior used to calculate the excess compressibility. In a liquid mixture the local structure will depend on forces between molecules, on their shape and volume, and on system composition. As a consequence, the thermodynamic properties of the mixture will be altered by the mixing process in a complicated manner. In general, the adoption of a representation which corrects to null volume change upon mixing does not imply the simultaneous correction of other thermodynamic quantities to their corresponding *ideal* behavior. On this perspective, the choice of assuming the null volume change state as the *ideal* one is rather arbitrary.³⁷ Moreover, it is observed that also in mixtures for which the null volume change condition is experimentally fulfilled (or closely fulfilled), some thermodynamic quantities exhibit clear deviations from the linear behavior as obtained by interpolating between the values of the pure components.^{36,37} This means that these quantities explicitly depend on the system composition. As an example, when the concentration dependence of the compressibility is reported as a function of the volume fraction, we can assume that volume effects are accounted for and, accordingly, any observed deviation from linearity is originated by a concentration dependence of the average intermolecular interaction.

The assumption of a linear dependence of compressibility on mole fraction²⁸ introduces some apparent excess contributions merely because of the different molar volumes of the components. In other words, such an assumption for ideality leads to larger apparent excess compressibility.

The situation is well depicted in Figure 7 where excess compressibility data are calculated in agreement with eq 4 of ref 28. The large increment of the amplitude of the apparent

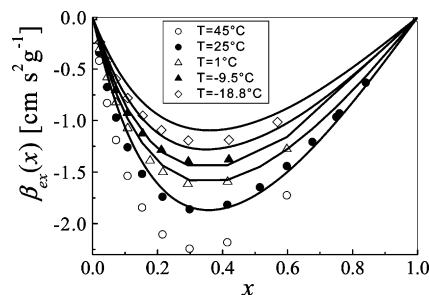


Figure 7. Apparent excess compressibilities as a function of [BMIM]-[BF₄] mole fraction, calculated under the assumption of an ideal compressibility behaving linearly with mole fraction. Continuous lines represent the apparent excess compressibility observed when ϕ -ideal behaviors are plotted as function of x .

excess quantity with respect to Figure 6 is quite evident. The continuous lines in the same figure represent the apparent compressibility that is observed reporting eq 7 as a function of x (a straight line in a ϕ -plot becomes a curve in an x -plot).

In general, an usual empirical approach to describe excess quantities as a function of the concentration makes use of polynomial expansions (Redlich–Kister polynomials⁴²). In the case of compressibility,

$$\beta_{ex}(\phi) = \phi(1 - \phi) \sum_{i=0}^n A_i (1 - 2\phi)^i \quad (9)$$

where A_i are phenomenological expansion coefficients. The continuous lines in Figure 6 represent the result of fitting experimental data with second-order polynomial expansions.

In a recent article³⁶ we have pointed out that eq 8 cannot be taken as a valid reference for liquid mixtures for which excluded volume interactions (for example between like and unlike molecules) are responsible for deviations of the adiabatic compressibility from the ideal behavior. Accordingly, a reliable reference has to take into account local configurations where unlike molecules are occupying contiguous sites. The probability of such configurations, given by $\phi(1 - \phi)$, corresponds, apart from a factor, to the 0th order term of eq 9. This implies that in the case of liquids an excess compressibility behaving like the 0th order does not allow inferring any interspecies interaction apart from excluded volume ones. Indeed, even in the case of binary hard-sphere mixtures excess quantities are observed.⁴¹

As a first approximation, we model our excess data using a hard-sphere potential.^{36,41} Within this framework, the particle interaction is described in terms of two like collision diameters (d_A , d_B) and by an interspecies diameter $d_{AB} = \frac{1}{2}(d_A + d_B)(1 + \Delta)$ where the dimensionless parameter Δ accounts for deviations of unlike excluded-volume interactions from additivity.⁴¹ As is well-known, in a real system such repulsive effects are associated with the overlap between the electron clouds of colliding molecules. Even in a rare-gas mixture, the Lorentz rule ($\Delta = 0$) is not systematically satisfied.⁴³ For instance, deviations from additivity may be expected to occur at high pressures. They also become manifest in the “effective” interactions that characterize some complex polydisperse fluids such as colloid-polymer mixtures.⁴⁴ In general, the thermodynamic and structural properties of a system turn out to be rather sensitively affected by even a modest degree of nonadditivity.

The choice to deal with the ionic liquid as a nonelectrolyte representing the pair cation/anion as a single component with a single collision diameter d_A could appear too crude. On one hand, clear experimental evidence exists that at least partially the [BMIM] cation and the BF₄ anion tend to strongly interact

leading to stable ion pairs (for example in the case of [EMIM]-[Tf₂N] up to 30% of the available ions form pairs at 270 K, and this amount enhances with increasing temperature and dilution of the RTIL).⁴⁵ Moreover the charged portions of both neat and diluted ILs have been found to organize in a rather homogeneous matrix where the nanoscale segregated alkyl tails are embedded. Both theoretical⁴⁶ and experimental⁴⁷ evidence are now available describing this peculiar behavior of ILs. In such a framework, acetonitrile has been proposed⁴⁶ to distribute rather homogeneously both in the charged and in the apolar domains, thus indicating that although strong interaction exists between CH₃CN and the charged portions, good affinity exists between CH₃CN and the alkyl chains as well. Such a morphological scenario in mind and the consideration that the presently employed experimental techniques access a mesoscopic spatial scale (that is not fully adequate to appreciate the microscopic details of interactions) legitimate the choice of an explicitly declared crude modeling for the description of the interaction in the binary mixture [BMIM][BF₄]/CH₃CN in terms of hard-sphere interactions. Finally, we also wish to remark that the aim of this study is to show how the behavior of some thermodynamic quantities, for example, the adiabatic compressibility, can be well modeled just through steric effects.

As in ref 36 the isothermal compressibility can be evaluated starting from the virial equation of state (whose second and third virial coefficients are known analytically):

$$\frac{p}{k_B T} = \sum_{i=1}^{\infty} b_i \rho^i \quad (10)$$

where p is the pressure, T is the absolute temperature, k_B is the Boltzmann constant, $\rho = \rho_A + \rho_B$ is the total number density (ρ_A and ρ_B being the number densities of the species A and B, respectively) and b_i are the virial coefficients ($b_1 = 1$). Differentiating eq 10 with respect to the number density, we obtain the following expression for isothermal susceptibility

$$\chi_T^{-1} = \frac{1}{k_B T} \left(\frac{\partial p}{\partial \rho} \right)_T = \sum_{i=2}^{\infty} (i-1) B_{i-1} \rho^{i-2} \quad (11)$$

and adiabatic compressibility

$$\beta_S = \beta_T \frac{c_v}{c_p} = \rho k_B T \frac{c_v}{c_p} \chi_T \quad (12)$$

where c_p and c_v are the specific heats at constant pressure and volume respectively.^{41,43} The number density depends on the packing fraction, η , through the following relation:

$$\rho = \frac{6}{\pi [x d_A^3 + (1-x) d_B^3]} \eta \quad (13)$$

The dashed lines in Figure 6 represent the results of the fitting with the nonadditive diameters hard-sphere model for the mixtures at $T = 45, 25$, and 1 °C. The results for lower temperatures are not reported since the error bars on the calculated differences become larger than the fitting confidence. The value of Δ has been fixed through all the fittings to the same, temperature independent, realistically small value⁴³ $\Delta = 0.045$. In such a way the only free-fitting parameters were η and the ratio d_B/d_A . The best fitting results reported in Figure 6 have been obtained for values of d_B/d_A of about 0.70, 0.77, and 0.79, while the obtained values of the η parameter were 0.09, 0.17, and 0.22 for the data at $T = 45, 25$, and 1 °C, respectively.

To this purpose, we want to stress that a hard-sphere mixture with $d_B/d_A \approx 0.79$ and $\Delta \approx 0.045$ exhibits a fluid–fluid phase separation only for values of $\eta \approx 0.40$, assuring us that the system is far from demixed states.^{48,49}

As already anticipated, the hard-sphere model is quite a crude approximation for the present liquid mixtures, as a consequence the actual values of these parameters are not to be taken as fully meaningful; still, we note that the observed temperature trend for η is in agreement with the usual thermal expansion. Moreover the observed temperature dependence for the ratio d_B/d_A might reflect the temperature dependence of the ion pairing. On the other hand it is noteworthy that such a crude model can phenomenologically account for the observed excess thermodynamic quantities. In particular, we stress that the main contribution to the excess quantities simply originates from purely mixing contributions, thus indicating that no preferential interactions need to be considered to account for the experimental data.

Summing up, the simultaneous occurrence of negative excess values both for the molar volume and the adiabatic compressibility suggests that the main source of nonideality in [BMIM][BF₄]/CH₃CN mixture is originated by a non-negligible attractive component to the interaction potential between unlike molecules. These findings provide strong experimental basis for a numerical simulation study,³⁰ where microscopic structural data have been interpreted in terms of a concentration-dependent local coordination. More specifically, the molecular dynamics result reproduces the experimental negative excess volumes as originated by an attractive, hydrogen-bond-like interaction between the negative N atom in CH₃CN and the positive H atoms in the imidazolium ring.

The excess properties of aqueous mixture of methanol have been recently described⁵⁰ in terms of a primitive model. The latter represents the system as a fluid of pseudohard bodies consisting of hard-body cores with additional embedded interaction sites;⁵¹ the intermolecular potential is described in terms of an hard-body component plus an additional term to mimic repulsive and attractive contributions. Their approach turns out to be in good qualitative agreement with experimental results.

Despite the similarity of the interaction potentials used to model liquid mixtures in the present work and in ref 50 we stress that our results show that the main role to determine excess adiabatic compressibility is played by pure mixing terms. As a consequence neither occurrence of dimers nor effects of volume changes induced by interactions are required to observe nonzero excess compressibility.

As a last point, the fact that we are not observing significant formation of structural coordination in the [BMIM][BF₄]/acetonitrile mixtures might imply that such effects are not occurring at the time scale accessible in the present study ($\sim 10^{-9}$ s). In addition, the Brillouin scattering technique probes collective adiabatic pressure fluctuations averaged over a spatial scale of about 2500 Å.

Concluding Remarks

In this paper we have discussed excess volume and compressibility properties in [BMIM][BF₄]/acetonitrile mixtures over the whole concentration range and in a wide temperature interval.

This study has a twofold scope: On one side, we investigate the role played by the mutual interaction between different species in determining the concentration dependence of the measured quantities. On the other side we carry out a critical

revisiting about the information that can be extracted from excess quantities in liquid mixtures.

When mixing a representative room-temperature ionic liquid, such as [BMIM][BF₄], with acetonitrile we observe that the interaction between unlike species shows an excess (with respect to the pure hard-sphere excluded volume) attractive term which leads to negative excess contribution both in molar volume and compressibility. Such conclusions agree with previous experimental studies²⁷ performed on a narrower temperature range and numerical simulation investigations³⁰ suggesting the existence of an hydrogen-bond like interaction between ions and acetonitrile.

From a more general point of view, such an investigation can be framed into a recently proposed perspective to interpret excess thermodynamic quantities in liquid mixtures.³⁶ The present study provides further evidence that the role played by excluded volume effects on excess quantities represents a major contribution whose only meaning is the trivial statement that the mixture is a liquid rather than an ideal (gaseous) one. Although this point is well theoretically established^{52,53} it is often nonadequately accounted for when dealing with experimentally determined excess quantities.^{27,29,34}

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