



A molecular interactions study between 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) and N-methylpyrrolidone

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Abstract

The work entitled results from initial determination of physical parameters, density (ρ), speed of sound (u), refractive index of [Bmim][PF₆]/ N-methylpyrrolidone and their binaries at all compositions at atmospheric pressure and at task temperatures ranging from (303.15 - 323.15) K. The experimental results were utilized for computation of molar volumes ()/partial molar volumes ()/ partial molar volumes at infinite dilution ()/isentropic compressibility ()/ free length ()/ speeds of sound () and isobaric thermal expansion coefficient () of the binary system. Further, the binary coefficients and the standard deviations were deduced by fitting the excess properties in Redlich-Kister equation. A fortitude of these parameters indicated strong intermolecular interactions and likewise increases with increase of temperature. The results of Prigogine–Flory–Patterson (PFP) theory of excess molar volume and IR spectra were supported the deduced strong interactions.

Introduction

Today Ionic Liquids (ILs) have attracted significant consideration for the reason of their distinctive properties, *viz.* thermal stability, non-volatility and reuse [1], [2]. ILs can be selected to have various cations and anions, in order to shape Ionic Liquids with preferred properties. Besides, ILs have been recognized for quite a while, yet their wide utility as solvents in catalysis and processes design for chemical synthesis in recent times happen to be noteworthy. ILs have potential applications in many areas but real applications must be investigated further. However, the much cost of the ILs and more viscous nature than conventional organic solvents restricted their use in multiple applications.

Researchers are becoming more interested in IL mixtures with molecular organic solvents, as the resulting liquid mixtures provide many advantages than individual IL and organic solvent. The properties of such mixtures are dependent on the proportion of mixing. Mixing of IL with organic molecular solvents is one of the alternatives for reducing the use of costly ILs and also save the time in preparing new ILs of wanted properties [3], fortunately the mixtures also have reduced viscosity without loss in their advantages as green solvents. Meticulously, the mixing of co-solvents with polar nature may have a significant effect on physical and chemical properties of the IL's[4]. Recently it has been shown that specific (IL + molecular organic solvent) binary systems have better performance than pure ILs. These were also found to be useful in various advanced applications, *viz.* in super capacitors, bio-catalysed processes, as a medium for the solvation of biopolymers, *etc.* [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17]. In recent years, therefore, the thermo-physical study of IL + molecular solvents has received increased attention. In view of the fact that these data are important

for industrial applications, the prospective of the new systems can be exploited by examining their physicochemical properties.

The selection of the studied IL 1-butyl-3-methylimidazolium hexafluorophosphate, ([Bmim] [PF₆]) is based on its ability as a green plasticizer for poly (L-lactide) [18], in Tussah silk dyeing [19], RP HPLC [20], in organic synthesis [21], in separation technology [22] and also used in enzymatic catalysis [23]. On the other hand, NMP (N-methylpyrrolidone) solvent is unique in its properties with low volatility compared to most of the organic liquids, and high polarity. Its commercial uses are in petrochemical and plastic industries, taking advantage of its non-volatility and their capability to dissolve various materials[24]. Further, NMP is also used in drugs formulation and in the manufacture of lithium ion batteries.

Physico-chemical properties between [Bmim] [PF₆] with organic solvents such as dimethyl formamide [37], methyl methacrylate [25], butanol, acetone [38], THF, DMSO, methanol, acetonitrile [39], ethanol, benzene [40], 2-propoxyethanol [30], 2, 2, 2-trifluoroethanol [41], 2-Pyrrolidone [42], N-vinyl-2-pyrrolidinone [43], N-Methylaniline [26] and ethyl acetate [44] were found so far in literature. Feng *etal* [45] has reported density only at (298.15 - 313.15) K for the binary mixture under study. So, in this article, the authors made an attempt to fortitude the molecular interactions between ([Bmim][PF₆]) and N-methylpyrrolidone binary system using a comprehensive study on volumetric, acoustic, optical and their derived parameters at temperatures (303.15 - 323.15) K along with spectral studies.

On the basis of our initial experiments, the selected IL in all proportions completely miscible with NMP. Therefore, in this analysis, we propose to calculate the density, speed of sound and refractive index of [Bmim][PF₆] binary mixtures with NMP between 303.15 K - 323.15 K temperatures across all compositions and at atmospheric pressure. We calculated the deviation / excess properties based on the measured values, and these properties were fitted using Redlich-Kister polynomial equation for their possible application in industrial processes. Additionally, IR spectroscopy sought to understand the contact behavior between the two liquids in the mixture. Finally, the experimental excess molar volume data was contrasted with the theory of Prigogine-Flory-Patterson (PFP).

Section snippets

Materials and methods

The [Bmim] [PF₆] (CAS 174501-64-5) with a mass fraction purity of 0.99 was bought from Iolitec GmbH (Germany); Sigma Aldrich supplied the NMP (CAS 872-50-4), with a mass fraction purity of 0.995. The chemicals used in this work were well purified using known methods [46], [47]. Karl Fisher titrator was used to determine the water content in IL and NMP (Metrohm, 890 Titrando). All samples were dried under reduced pressure (0.1 bar) at moderate temperature for at least 72 h before taking each

Measurement of density and speed of sound

Densities and speed of sound are measured with an Anton Paar DSA-5000M vibrating tube density and sound velocity meter. The density meter is calibrated with doubly distilled degassed water, and with dry air at atmospheric pressure. The temperature of the apparatus is controlled to within ± 0.01 K by a built-in Peltier device. Measured density and speed of sound values (at frequency approximately 3 MHz) are precise to 5×10^{-3} kg.m⁻³ and 5×10^{-1} m.s⁻¹ respectively. The standard uncertainties associated

Measurement of refractive index

The refractive indices are determined using an automatic refractometer (Anton Paar Dr Krenchen Abbemat (WR-HT)) which has also a temperature controller that keeps the samples at working temperature. The uncertainties in the temperature and refractive index values are $\pm 0.01\text{K}$ and $\pm 5 \times 10^{-4}$ respectively. The apparatus is calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (supplied by the company) before each series of measurements according to manual

Measurement of infrared spectra

Infrared transmittance is measured by using Shimadzu Fourier transform infrared (FT-IR) spectrometer (IRAffinity-1S) equipped with attenuated total reflectance (ATR) accessories. The spectral region is $(650-4000)\text{ cm}^{-1}$ with resolution of 2 cm^{-1} and 100 scans. At least five repeated measurements are performed for each sample.

Results and discussion

Experimental density (ρ), speed of sound (u), refractive index (n_D), for binary mixtures of [Bmim][PF₆] with NMP with respect to the mole fraction (x_1), of [Bmim][PF₆] at scrutinizing temperatures were given in Table 2. The densities of the mixtures of this work have been graphically compared (Figure 1) with those of Feng *et al.* [45]. There are clear deviations of densities of pure solvents. This might be due to that Feng *et al.* [45] used NMP with mass fraction purity of 0.99 and didn't

Conclusions

Density, speed of sound and refractive index for binary liquid mixtures of [Bmim][PF₆] with NMP were experimentally determined at atmospheric pressure and at temperatures 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K over the whole compositions. From the experimental results the excess properties, ρ^E , u^E , n_D^E and Δn_D were calculated. The excess and deviation parameters were fitted to the Redlich-Kister polynomial, and the corresponding standard deviations were also determined.