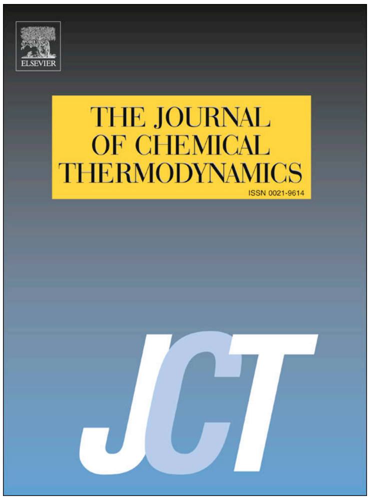

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A molecular interactions study between 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]) and N-methylpyrrolidone

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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][PF$_6$]/ 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 ($V_{\mathrm{m}}^{\mathrm{E}}$)/partial molar volumes ($\overline{V}_m^E$)/ partial molar volumes at infinite dilution ($\overline{V}_m^{E,\infty}$)/isentropic compressibility (κ_s^E)/ free length (L_f^E)/ speeds of sound (u^E) and isobaric thermal expansion coefficient (α_P^E) 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. Furthermore, molecular properties were also evaluated using Sehgal's relation on non-linear parameters of Hartmann-Balizar and Ballou semiempirical relations at all temperatures. Moreover, the activity coefficients were calculated by Margules/Porter/Wilson/NRTL relations at temperature 308.15 K. The results of Prigogine–Flory–Patterson (PFP) theory of excess molar volume and IR spectra were supported the deduced strong interactions.

Key words: [Bmim][PF$_6$]; N-methylpyrrolidone; PFP theory; speed of sound; IR spectra; thermodynamic parameters.

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1. 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 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] [PF_6]) 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 separatión 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] [PF_6] 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][PF_6]) 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][PF_6] 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).

2. Experimental

2.1. Materials and methods

The [Bmim] [PF_6] (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 (starting at room temperature and gradually rising to 333 K). The water content of all samples was further checked, and was found less than 170 ppm, a much lower value than the pre-evacuation analysis, which showed values of around 210 ppm. The NMP solvent was further purified by distillation and [Bmim] [PF_6] was used without further purification (See Table S1, **SI** for other procedures and equipment). Further, the purities were checked by comparing measured density, speed of sound and refractive index with the literature values given in **Table 1**.

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 $5x10^{-3}$ kg.$m^{-3}$and $5x10^{-1}$m.s^{-1}respectively. The standard uncertainties associated with the measurements of temperature, density and speed of sound are estimated to be ±0.01 K, 1.0 kg m^{-3} and ±0.5 m s^{-1} respectively.

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 ±0.01K and $\pm 5x10^{-4}$ 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 instructions. The calibration is checked with pure liquids by known refractive index.

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) cm^{-1} with resolution of 2 cm^{-1} and 100 scans. At least five repeated measurements are performed for each sample.

3. Results and discussion

Experimental density (ρ), speed of sound (u), refractive index (n_D), for binary mixtures of [Bmim] [PF_6] with NMP with respect to the mole fraction (x_1), of [Bmim][PF_6] 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 mention the purity of [Bmim][PF_6]. In this work, we not only used the solvents with high purity but also more sophisticated equipment for accuracy.Both [Bmim][PF_6] and N-methyl pyrrolidine are considered polar, which contributes to the full miscibility of themselves in all proportions and at temperatures. A close look density in **Table 2** clearly demonstrates a linear decrease when temperature rises due to expansiveness of volume. The thermal expansion coefficient (α_p) is a measure of the fluid expansion or contraction with temperature in all directions. The resulting values of [Bmim][PF_6] were smaller than NMP, which means that the IL expands or contracts less than NMP at a predetermined temperature.

From the above experimental data the authors computed the excess properties, molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$), isentropic compressibility (κ_s^E), free length (L_f^E), velocity of sound (u^E) and isobaric thermal expansion coefficient (α_P^E) using thermodynamic equations (**S1-S11; SI**). The Plots of excess molar volume (V_m^E) against mole fraction of IL in the mixture with NMP at studied temperatures **(**303.15 to 323.15) K were shown in **Figure 2**. Excess molar volumes at all investigated temperatures were found negative for the mixtures and the more negative value was found to be $-0.79 \mathrm{x} 10^{-6} \mathrm{m}^3\mathrm{mol}^{-1}$ at x_1 = 0.1894 and T= 303.15 K. At upper temperatures the minimum of V_m^E further decreased (more negative) and changes were marginally to higher mole fraction of IL. Imidazolium ILs can also form hydrogen bonds at suitable conditions, as these act as both donor and acceptor of protons. So, the H-bonds between the [Bmim][PF_6] and NMP can therefore be assumed to be responsible for a significant contraction of the mixture volume. Moreover, the complimentary fitting of smaller NMP solvent molecules (at T=303.15 K, V_m= $96.94 \mathrm{x} 10^{-6}$ $\mathrm{m}^3\mathrm{mol}^{-1}$) into cavities formed by larger [Bmim][PF_6] molecules (at T=303.15 K, V_m= 208.26x10-6 $\mathrm{m}^3\mathrm{mol}^{-1}$) is also considerable for these tough interactions. For other temperatures a similar pattern may also be observed and the effect is more predominant at upper temperature. This is owing to the reason that smaller NMP molecules are more favourably fitted into the cavities produced by larger [Bmim][PF_6] molecules, thus sinking the volume of the mixture to a greater degree, ensuing in more negative values with increasing temperature. In terms of temperature, the order of interaction forces is (323.15>318.15>313.15>308.15>303.15) K. The polynomial coefficients of the Redlich-Kister and the corresponding standard deviations were given in **Table 3**.

The molecular interactions that occur in the system reflect well on the properties of partial molar volumes ($\overline{V}_m^E$). The ($\overline{V}_m^E$) of component 1 ([Bmim][PF$_6$]) and 2 (NMP) in the mixtures were calculated using equations **S12-S17 (**See **SI**) and the values were given in **Table 4**. From this table it can be found that the $\overline{V}_{m,1}$ values for [Bmim][PF$_6$] in the mixtures were almost lower than their individual molar volumes in their pure states, suggesting that the volume contraction occurs by combining [Bmim][PF$_6$] and NMP under any temperature. The **Figures 3** and **4** shows the discrepancy of excess partial molar volumes of ([Bmim][PF$_6$]) and (NMP) in the binary system at T = (303.15, 308.15, 313.15, 318.15 and 323.15) K respectively. The negative pattern of these properties found at all temperatures also supports the resultant negative excess molar volumes. A scrutiny of this data not only shows the presence of strong interactions between the different molecules but also supports conclusions drawn from excess molar volumes.

The partial molar volumes [Bmim][PF$_6$] and NMP denoted as $\overline{V}_{m,1}^{\infty}, \overline{V}_{m,2}^{\infty}$ and excess partial molar volumes at infinite dilution $\overline{V}_{m,1}^{E,\infty}, \overline{V}_{m,2}^{E,\infty}$ were computed from the known equations (**S18** and **S19** of **SI**). The computed values at all investigated temperatures of $\overline{V}_{m,1}^{\infty}, \overline{V}_{m,2}^{\infty}$ and $\overline{V}_{m,1}^{E,\infty}, \overline{V}_{m,2}^{E,\infty}$ were given in **Table 5.** The values of $\overline{V}_{m,1}^{E,\infty}$ were found negative and also become more negative with increased temperatures. This signify that the molecular association effect is larger than the dissociation for [Bmim][PF$_6$] IL system. On the other side the excess partial molar volumes at infinite dilution for NMP ($\overline{V}_{m,2}^{E,\infty}$) are positive at all temperatures determined. This is for the reason that of ion solvation process and extinction of ion-ion interactions in [Bmim][PF$_6$] [48]. This is observed in the case of V_m^E values which reproduce well from the computed parameters of partial molar volumes at infinite dilution at all temperatures calculated.

For [Bmim][PF$_6$] + NMP system, the excess isoentropic compressibility (κ_s^E) behavior is very likely to the $V_{\mathrm{m}}^{\mathrm{E}}$ that was shown in the **Figure 5**. It was also found negative in the entire region of investigated temperatures and composition ratios and becomes more negative with rise in temperature. The negative values of κ_s^E mean that the mixtures are more compressible than the respective ideal mixtures [49]. Therefore, it is assumed that the decrease in free volume is making the mixture more compressible than the ideal mixture, which eventually results in negative values for excess isoentropic compressibility. The disparity of excess free length (L_f^E) against mole fraction of IL is shown in **Figure 6**. The negative values of excess free length suggested the presence of specific interactions between different molecules as well as structural adjustments in the liquid mixture leading to closer molecular packaging.

At all investigated temperatures the clearly **Figure 7** illustrates that the speeds of sound (u^E) values were positive for the current binary system over the whole compositions. The positive deviations are a sign of increase interactions between the component molecules of the binary liquid mixtures [50]. The deviations in refractive index ($\Delta_\phi n_D$) against mole fraction were plotted in **Figure 8** and the values were found positive in the studied composition ratios of the binary mixture. This further supported the existence of strong interaction forces among the component molecules [51]. **Figure 9** indicates negative values of α_P^E for the binary mixture over the entire composition and at all investigated temperatures. This further supported the presence of tough interactions between the component molecules [52].

3.1. Infrared spectral studies

The observed interactions from the above inferences of excess parameters in the system were well supported by the IR spectral data. The unique nature of imidazolium cations is demonstrated well by their electronic structure (**Figure 10**). Because of the less electron density on the C=N bond, the hydrogen in C_2-H has more acidic nature than C_4-H, and C_5-H. These hydrogens' resulting acidity is important for understanding the properties of the current ILs. The 'H' on the C_2 carbon (C_2–H) was shown to be normally associate with solvent molecules [53].

The infrared absorbance was recorded between 650 cm^{-1} to 4000 cm^{-1} wavelength (**Figure 11** and **Table 6**) to know the outcome of molecular interactions. For [Bmim][PF_6], signals can be divided into two different parts, the signals between 3000 cm^{-1} and 3200 cm^{-1} may be endorsed mainly to the C-H vibrational modes of aromatic imidazolium ring [54]. Further, the signals from 2800 cm^{-1} to 3000 cm^{-1} are mainly due to aliphatic C-H stretchings in the methyl and butyl moieties [55–57]. Since for its stronger acidic character, the C_2-H vibrational frequency (3124.3 cm^{-1}) was found to be moved to a lower frequency by around 44.9 cm^{-1} compared to C_4-H and C_5-H stretchings (3169.2 cm^{-1}). The C_2-H and $C_{4,5}$-H stretching frequencies of the IL cation were examined (**Figure 12**) along with C=O stretching area of NMP (**Figure 13**). It was also found that the red shift is very predominant in C_2-H frequencies compared to $C_{4,5}$-H stretching frequencies, implying that more acidic C_2-H plays a most important role in the formation of H-bond with carbonyl oxygen of NMP (**Figure 13**). At the same time, a strong red shift is observed for C=O Sym Stretch frequencies in NMP, as the mole fraction of IL increases. This evidently demonstrated the formation of intermolecular hydrogen bonds between the 'H'-atoms of aromatic imidazolium ring and NMP carbonyl oxygen.

ATR-FTIR studies suggested the key role of hydrogen in miscibility and stability of the binary system. Hence it can be assumed that the hydrogen bonds in the system are also accountable for the existing tough interactions and contractions in the mixtures volumes.

3.2. Prigogine-Flory-Patterson statistical theory for excess molar volume V_m^E

The Prigogine-Flory-Patterson (PFP) theory was used to check and compare experimental excess molar volumes of binary mixtures [58–62]. At *T* = (303.15-323.15) K, we compared 'V_m^E' of the titled binary mixture utilizing the PFP theory over the whole mole fractions range. The calculation of various parameters of this theory is based on relevant equations reported in literature [63–67]. The parameters of pure components for the PFP theory were listed in **Table 7**. In the absence of experimental excess molar enthalpy (H_m^E), the Flory contact interaction parameter χ_{12}, the only adjustable parameter required in the PFP theory, was obtained from experimentally determined values of V_m^E. It was found that for all the investigated temperatures, the Flory contact interaction parameter χ_{12} was found negative. The values of said 3 contributions, V_{int}^E,$V_{fv}^E and V_{P^*}^E$, to V_m^E(PFP) at equimolar composition were given in **Table 8.** The first term V_{int}^E is negative, indicating the tough interactions occur in the mixture. For all measured temperatures the connecting forces contributions were observed negative. The second term V_{fv}^E was also found to be negative as V_{fv}^E is proportional to $-(\tilde{V}_1 - \tilde{V}_2)^2$ [59,68]. The degree of negative values of V_{fv}^E depends on difference in Flory's reduced volumes of the components. Negative values in the magnitude of V_{fv}^E increase further with rise in temperature as more free volume becomes available in [Bmim][PF$_6$] to accommodate the smaller NMP molecules which resulted in more negative V_m^E. The third term, i.e. characteristic pressure $V_{P^*}^E$, was found positive at investigated temperatures, the P* effect which depends on the relative cohesive energy of the expanded and less expanded component. Further, it is proportional to $(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)$ and can have both the negative and positive sign depending upon the magnitude of P_i^* and $\widetilde{V_i^*}$ of unlike components [59,68]. For the system [Bmim][PF$_6$] + NMP, $V_{P^*}^E$ was found positive which was related to the structure-braking consequence of the solvent NMP on the electrostatic interactions between [Bmim][PF$_6$] ions and so the NMP molecules can be placed around the [Bmim]$^+$ and [PF$_6$]$^-$ ions[68]. V_{int}^E and V_{fv}^E were found to be negative in the present system while $V_{P^*}^E$ were found to be positive which indicates that the interaction and free volume contributions are responsible for the strong interactions between solute and solvent particles. We may summarize that the volumetric behavior of the binary mixture of {[Bmim][PF$_6$] + NMP} can be explained very effectively through the application of this PFP theory.

4. Conclusions

Density, speed of sound and refractive index for binary liquid mixtures of [Bmim][PF$_6$] 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, V_m^E, κ_S^E, L_f^E, u^E, α_P^E and $\Delta_\phi n_D$ were calculated. The excess and deviation parameters were fitted to the Redlich-Kister polynomial, and the corresponding standard deviations were also determined. The observed excess values in the current binary liquid system [Bmim][PF$_6$] and NMP clearly indicated the predominance of strong attractive forces. Using Sehgal 's relationship on Hartmann-Balizar and Ballou semiempirical relations, molecular properties were determined at all temperatures. Activity coefficients determined by the NRTL relation showed low standard deviation at 308.15 K compared to other models. The inferences from excess properties were also supported by the IR spectral study. With reasonable success the PFP theory was applied to well explain the volumetric behavior of the studied system.

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Highlights

- The studied binary systems is {**[Bmim][PF$_6$]+1-methylpyrrolidone**}
- Density, speed of sound and refractive index are measured at various temperatures
- The interactions in the system are analyzed in terms of excess parameters
- The existing interactions are well explained with the help of IR spectral studies
- Observed experimental results are correlated with PFP theory

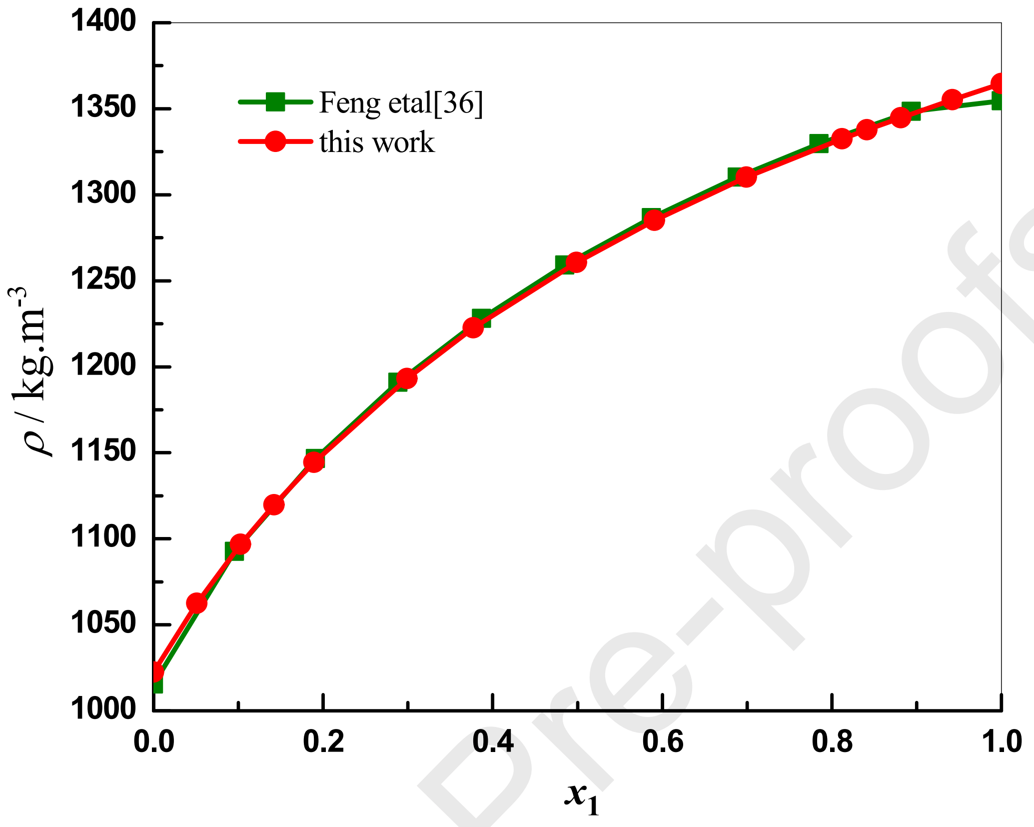


Fig. 1 Plots of experimental densities of Feng etal[36] and this work of the binary mixtures of [Bmim][PF$_6$] with NMP against mole fraction of [Bmim][PF$_6$] at 303.15 K.

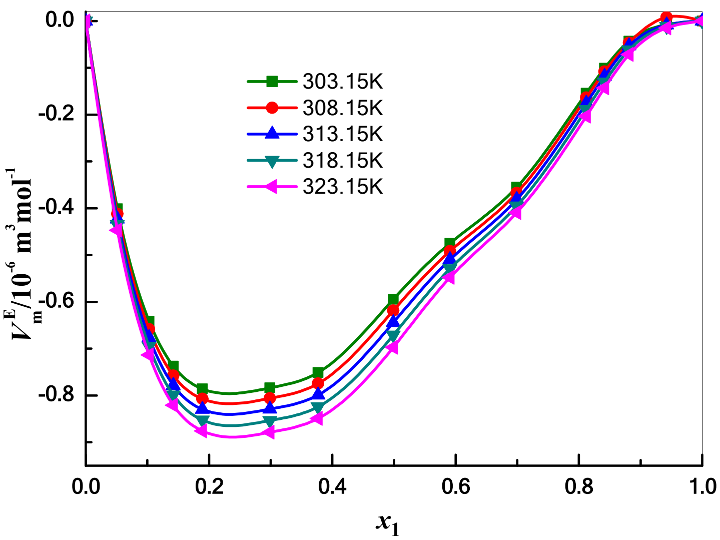


Fig. 2 Plots of excess molar volume (V_m^E) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures**.**

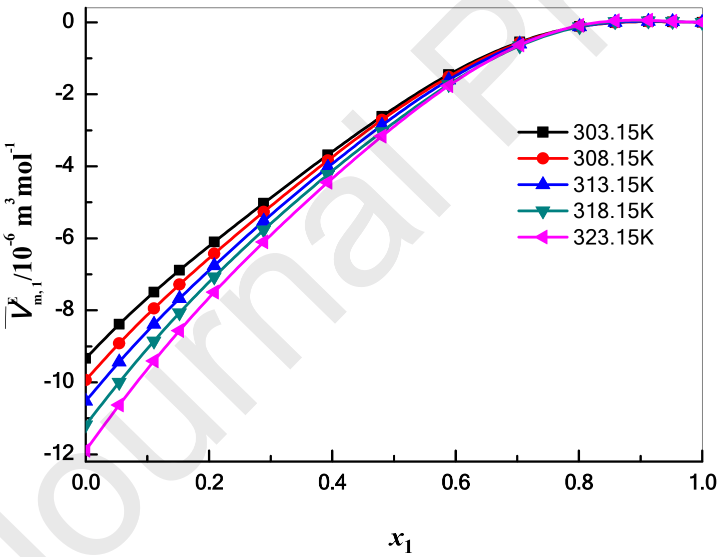


Fig. 3 Plots of excess partial molar volume ($\overline{V}_{m,1}^E$) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures.

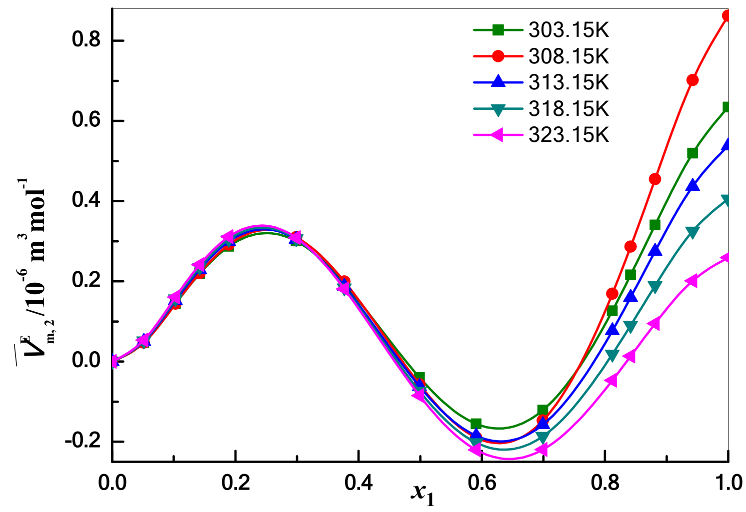


Fig. 4 Plots of excess partial molar volume ($\overline{V}^{E}_{m,2}$) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures.

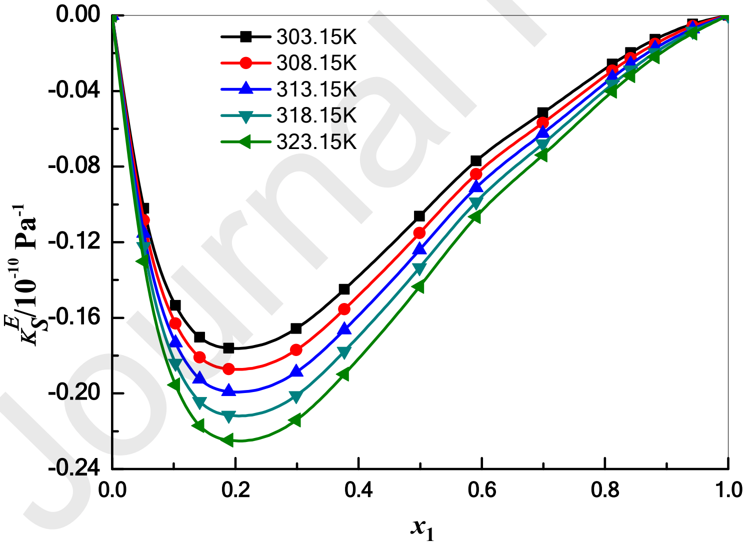


Fig. 5 Plots of excess isentropic compressibility (κ_S^E) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures.

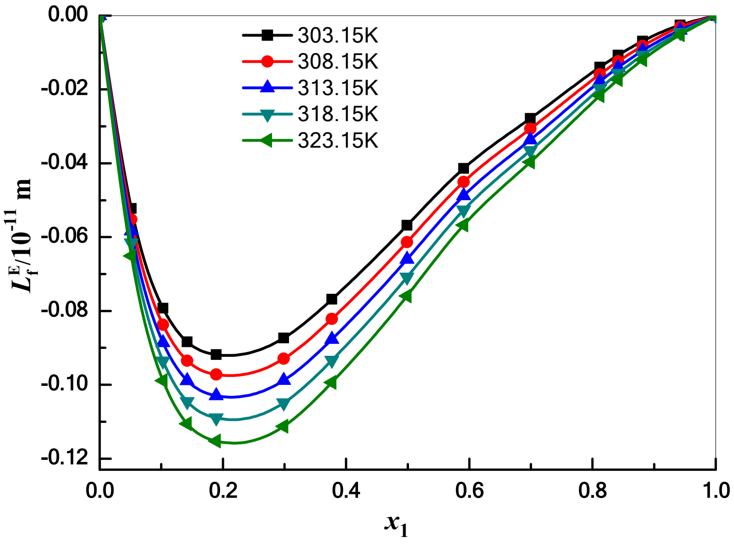


Fig. 6 Plots of excess free length (L_f^E) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures.

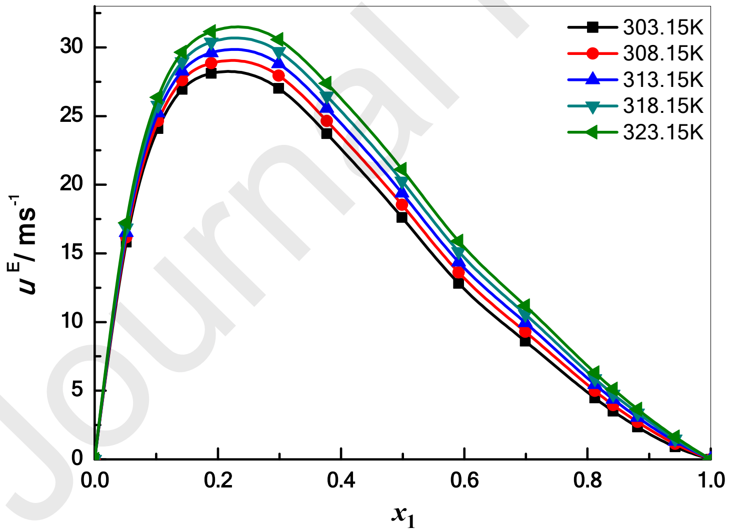


Fig.7 Plots of Excess ultrasonic speed of sounds (u^E) against mole fraction of [Bmim][PF_6] in the mixture with NMP at different temperatures.

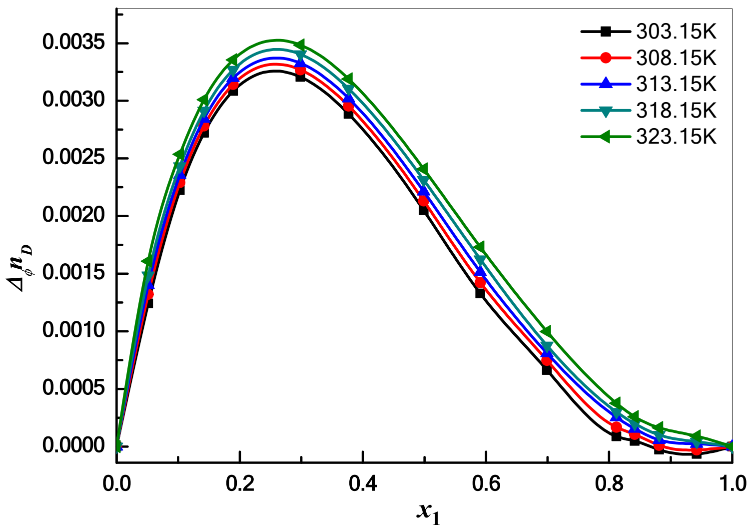


Fig. 8 Plots of deviation in refractive index ($\Delta_{\emptyset} n_D$) against mole fraction of [Bmim][PF$_6$] in the mixture with NMP at different temperatures.

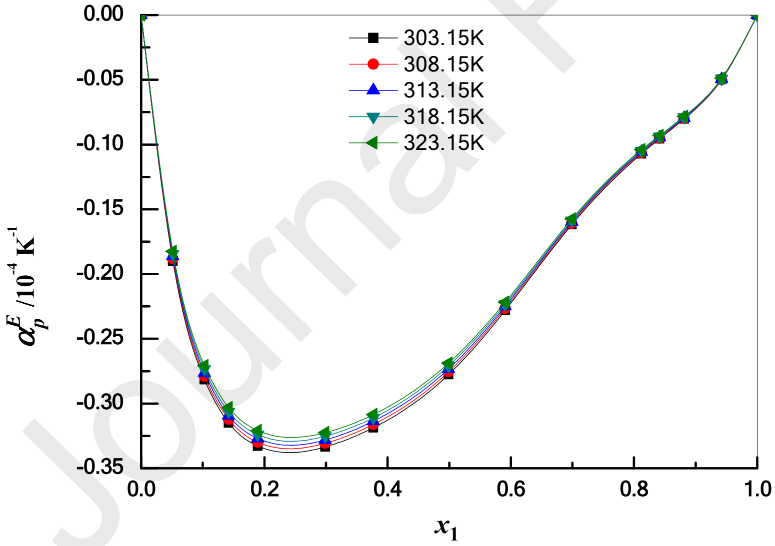
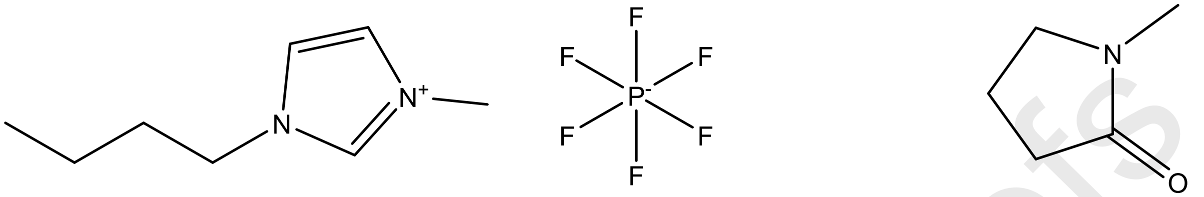


Fig. 9 Plots of Excess isobaric thermal expansion coefficient (α_P^E) against mole fraction of [Bmim][PF$_6$] in the mixture with NMP at different temperatures.



1-butyl-3-methylimidazolium hexafluorophosphate

1-methyl-2-pyrrolidone

Fig.10 Chemical Structures of [Bmim][PF_6] and NMP.

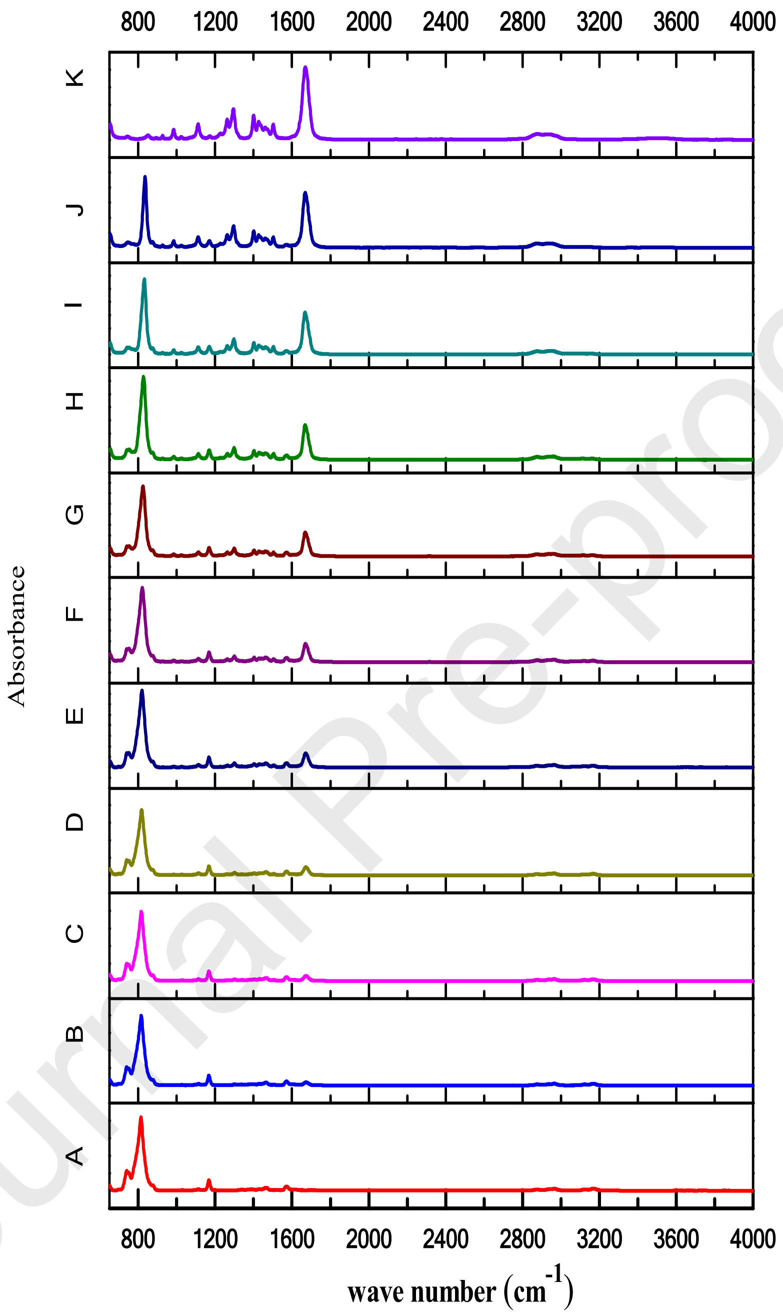


Fig.11 Infrared spectra (650 cm^{-1}-4000 cm^{-1}) of (A) Pure IL [Bmim][PF_6];(B) 0.8812; (C) 0.8120; (D) 0.6991; (E) 0.5910; (F0.4990; (G) 0.3771; (H) 0.2988; (I) 0.1894; (J) 0.1028 and (K) Pure NMP. (B), (C), (D), (E), (F), (G), (H), (I), (J) represents mole fraction of [Bmim][PF_6] in the mixture with NMP.

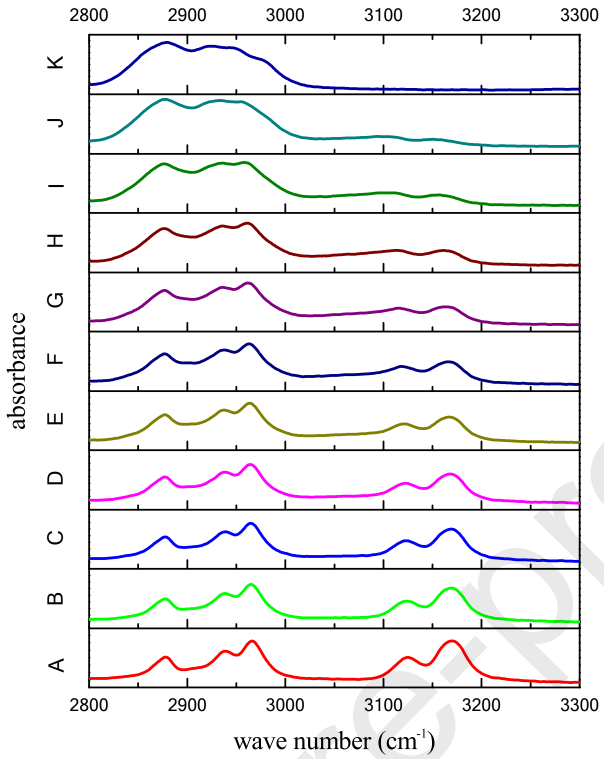


Fig.12 Infrared spectra (2800 cm^{-1}-3300 cm^{-1}) of (A) Pure IL [Bmim][PF$_6$];(B) 0.8812; (C) 0.8120; (D) 0.6991; (E) 0.5910; (F0.4990; (G) 0.3771; (H) 0.2988; (I) 0.1894; (J) 0.1028 and (K) Pure NMP. (B), (C), (D), (E), (F), (G), (H), (I), (J) represents mole fraction of [Bmim][PF$_6$] in the mixture with NMP.

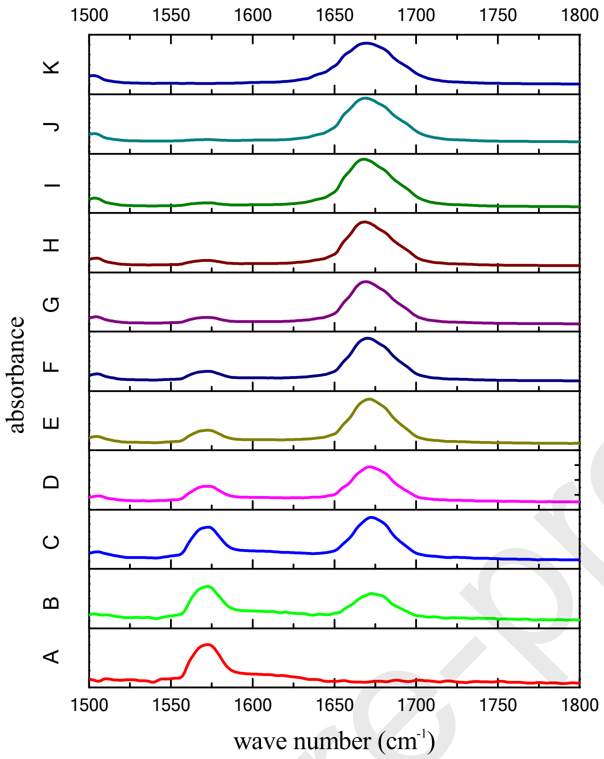


Fig.13 Infrared spectra (1500 cm^{-1}-1800 cm^{-1}) of (A) Pure IL [Bmim][PF$_6$];(B) 0.8812; (C) 0.8120; (D) 0.6991; (E) 0.5910; (F0.4990; (G) 0.3771; (H) 0.2988; (I) 0.1894; (J) 0.1028 and (K) Pure NMP. (B), (C), (D), (E), (F), (G), (H), (I), (J) represents mole fraction of [Bmim][PF$_6$] in the mixture with NMP.

Table 1 Comparison of experimental values of density, *ρ*, speed of sound, *u*, refractive index, n_D, and specific heat, C_p, of pure liquids with the corresponding literature values at different temperatures and at atmospheric pressure P = 101.3 kPa.

Liquid	Temp / (K)	ρ /(kg m^{-3})		u/(m s^{-1})		n_D		C_p/(J K^{-1} mol^{-1})
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Lit.
[Bmim][PF$_6$]	303.15	1364.6	1363.277 [25] 1363.08[26]	1431.7	1430.6 [29] 1431.9[2	1.40823	1.40746 [30] 1.40812[2	410.33 [31]

			1363.2[27] 1362.36[28]		6]		7] 1.4080[28]	
	308.15	1360.4	1359.191[25] 1358.91[26] 1359.0[27]	1419.8	1419.0[29] 1420.1[26]	1.40691	1.40585[30] 1.40679[27]	413.14 [31]
	313.15	1356.2	1355.087[25] 1354.74[26] 1354.9[27] 1353.99[28]	1408.2	1406.4[29] 1408.5[26]	1.40556	1.40468[30] 1.40546[27] 1.4055[28]	415.98 [31]
	318.15	1352.1	1350.980[25] 1350.58[26] 1350.8[27]	1396.8	1395.0[29] 1397.1[26]	1.40414	1.40352[30] 1.40413[27]	418.91 [31]
	323.15	1348.0	1346.874[25] 1346.41[26] 1346.8[27] 1345.70[28]	1385.6	1385.15[29] 1385.9[26]	1.40276	1.40243[30] 1.4030[28]	421.88 [31]
1-Methyl-2-pyrrolidinone	303.15	1022.6	1022.64[32] 1023.95[33] 1023.925[34] 1023.70[35]	1524.3	1524.32[32] 1526.5[33]	1.46638	1.46626[32] 1.4664[33] 1.46520[34]	166 [36]
	308.15	1018.2	1018.18[32] 1019.462[34]	1505.0	1504.96[32]	1.46428	1.46412[32] 1.46306[34]	167 [36]
	313.15	1013.7	1013.72[32] 1015.03[33] 1015.000[34] 1014.78[35]	1485.7	1485.74[32] 1487.8[33]	1.46219	1.46199[32] 1.4621[33] 1.46095[34]	168 [36]
	318.15	1009.3	1009.25[32] 1010.533[34]	1466.7	1466.67[32]	1.46008	1.45983[32] 1.45891[34]	169 [36]
	323.15	1004.8	1004.78[32] 1006.10[33]	1447.8	1447.76[32] 1450.2[3	1.45796	1.45571[32] 1.4576[33]	170 [36]

	1006.061[34] 1005.85[35]	3]	1.45680[34]

Standard uncertainties *u* are: *u* (ρ) = 1.0 kg ·m^{-3},*u* (*u*) = 0.5 ms^{-1}, *u* (n_D) = 0.0005,*u* (I) = 0.01 K and *u*(*P*)=0.5kPa

Table 2 Experimental density (ρ), speed of sound (u), refractive index (n_D), molar volume (V_m),Isentropic compressibility(κ_S),free length (L_f)and isobaric thermal expansion coefficient (α_p) with mole fraction (x_1) of [Bmim][PF$_6$] in the binary liquid mixture of {[Bmim][PF$_6$]+ 1-Methyl-2-pyrrolidinone} from T/K = 303.15 to 323.15 at pressure P = 101.3 kPa.

x_1	ρ / (kg m^{-3})	u / (m s^{-1})	n_D	V_m/ (10^{-6}m^3 mol^{-1})	κ_S / (10^{-10}Pa^{-1})	L_f /(10^{-11}m)	α_p /10^{-4} K^{-1}
303.15 K							
0.0000	1022.6	1524.3	1.46638	96.94	4.21	4.258	8.73
0.0513	1062.4	1522.2	1.46171	102.24	4.06	4.183	8.27

0.1028	1096.7	1516.1	1.45724	107.74	3.97	4.134	7.93
0.1422	1119.8	1510.0	1.45396	112.03	3.92	4.108	7.72
0.1894	1144.5	1502.2	1.45018	117.23	3.87	4.084	7.52
0.2988	1193.2	1485.8	1.44196	129.41	3.80	4.044	7.14
0.3771	1222.6	1474.9	1.43656	138.17	3.76	4.025	6.92
0.4990	1260.6	1460.7	1.42898	151.89	3.72	4.002	6.66
0.5910	1285.0	1451.8	1.42391	162.25	3.69	3.988	6.51
0.6991	1310.2	1444.3	1.41867	174.41	3.66	3.970	6.37
0.8120	1332.4	1437.9	1.41403	187.18	3.63	3.954	6.25
0.8415	1337.7	1436.6	1.41296	190.51	3.62	3.950	6.21
0.8812	1344.7	1434.9	1.41161	194.99	3.61	3.945	6.17
0.9423	1355.2	1432.9	1.40974	201.83	3.59	3.935	6.12
1.0000	1364.6	1431.7	1.40823	208.26	3.58	3.925	6.10
308.15 K							
0.0000	1018.2	1505.0	1.46428	97.36	4.34	4.361	8.77
0.0513	1058.0	1503.9	1.45966	102.67	4.18	4.281	8.31
0.1028	1092.3	1498.8	1.45526	108.17	4.08	4.228	7.97
0.1422	1115.4	1493.2	1.45203	112.46	4.02	4.199	7.76
0.1894	1140.2	1486.0	1.44830	117.67	3.97	4.174	7.55
0.2988	1189.0	1470.9	1.44020	129.88	3.89	4.129	7.17
0.3771	1218.3	1460.6	1.43488	138.65	3.85	4.108	6.95
0.4990	1256.4	1447.2	1.42741	152.40	3.80	4.083	6.69
0.5910	1280.8	1438.8	1.42241	162.78	3.77	4.067	6.54
0.6991	1306.0	1431.7	1.41723	174.97	3.74	4.048	6.40
0.8120	1328.2	1425.8	1.41265	187.77	3.70	4.030	6.27
0.8415	1333.5	1424.5	1.41159	191.11	3.70	4.026	6.23
0.8812	1340.5	1423.0	1.41025	195.60	3.68	4.020	6.19
0.9423	1350.9	1421.1	1.40840	202.47	3.67	4.010	6.14
1.0000	1360.4	1419.8	1.40691	208.90	3.65	3.999	6.11
313.15 K							
0.0000	1013.7	1485.7	1.46219	97.79	4.47	4.467	8.81
0.0513	1053.6	1485.8	1.45764	103.10	4.30	4.381	8.34
0.1028	1088.0	1481.6	1.45329	108.60	4.19	4.324	8.01
0.1422	1111.1	1476.6	1.45011	112.90	4.13	4.293	7.80
0.1894	1135.9	1470.0	1.44643	118.12	4.07	4.265	7.59
0.2988	1184.7	1456.0	1.43845	130.35	3.98	4.216	7.20
0.3771	1214.1	1446.4	1.43320	139.14	3.94	4.193	6.98
0.4990	1252.2	1433.9	1.42582	152.91	3.88	4.165	6.71
0.5910	1276.6	1425.9	1.42088	163.32	3.85	4.148	6.56

0.6991	1301.8	1419.4	1.41577	175.54	3.81	4.126	6.42
0.8120	1324.1	1413.8	1.41123	188.36	3.78	4.107	6.29
0.8415	1329.4	1412.6	1.41018	191.71	3.77	4.103	6.26
0.8812	1336.3	1411.2	1.40886	196.21	3.76	4.096	6.21
0.9423	1346.8	1409.4	1.40703	203.09	3.74	4.085	6.16
1.0000	1356.2	1408.2	1.40556	209.54	3.72	4.074	6.13
318.15 K							
0.0000	1009.3	1466.7	1.46008	98.22	4.61	4.575	8.85
0.0513	1049.2	1467.8	1.45559	103.53	4.42	4.484	8.38
0.1028	1083.6	1464.5	1.45130	109.04	4.30	4.422	8.04
0.1422	1106.8	1460.1	1.44816	113.34	4.24	4.389	7.84
0.1894	1131.6	1454.1	1.44453	118.57	4.18	4.358	7.63
0.2988	1180.4	1441.3	1.43666	130.82	4.08	4.305	7.24
0.3771	1209.8	1432.4	1.43148	139.62	4.03	4.279	7.02
0.4990	1248.0	1420.7	1.42419	153.42	3.97	4.248	6.74
0.5910	1272.4	1413.2	1.41931	163.86	3.94	4.229	6.59
0.6991	1297.6	1407.1	1.41426	176.10	3.89	4.206	6.45
0.8120	1319.9	1402.0	1.40977	188.95	3.85	4.185	6.31
0.8415	1325.2	1400.9	1.40873	192.31	3.85	4.180	6.28
0.8812	1332.2	1399.6	1.40742	196.82	3.83	4.173	6.23
0.9423	1342.6	1398.0	1.40561	203.71	3.81	4.162	6.18
1.0000	1352.1	1396.8	1.40414	210.19	3.79	4.150	6.15
323.15 K							
0.0000	1004.8	1447.8	1.45796	98.66	4.75	4.686	8.89
0.0513	1044.8	1450.1	1.45353	103.97	4.55	4.588	8.42
0.1028	1079.3	1447.6	1.44930	109.48	4.42	4.522	8.08
0.1422	1102.5	1443.8	1.44620	113.79	4.35	4.486	7.87
0.1894	1127.3	1438.4	1.44261	119.02	4.29	4.453	7.66
0.2988	1176.1	1426.7	1.43483	131.29	4.18	4.395	7.27
0.3771	1205.6	1418.5	1.42972	140.11	4.12	4.366	7.05
0.4990	1243.9	1407.6	1.42253	153.93	4.06	4.332	6.77
0.5910	1268.2	1400.6	1.41772	164.40	4.02	4.312	6.61
0.6991	1293.4	1395.1	1.41274	176.67	3.97	4.286	6.47
0.8120	1315.8	1390.3	1.40831	189.54	3.93	4.264	6.33
0.8415	1321.1	1389.3	1.40729	192.91	3.92	4.259	6.30
0.8812	1328.1	1388.1	1.40600	197.43	3.91	4.251	6.25
0.9423	1338.5	1386.6	1.40421	204.34	3.89	4.239	6.20
1.0000	1348.0	1385.6	1.40276	210.83	3.86	4.227	6.17

T/K	A_0	A_1	A_2	A_3	A_4	σ
303.15	-2.4072	2.2409	-1.5853	2.9412	-0.5551	0.0132

Standard uncertainties u are: u (x_1) = 0.0005, u (ρ) = 1 kg·m^{-3},u (u) = 0.5 m s^{-1}, u (n_D) = 0.0005, u (T) = 0.01 K and u(P)= 0.5 kPa Combined uncertainties (Confidence level, 95%).: U_c (V_m) = ± 0.1 x 10^{-6} m^3 mol^{-1},U_c(κ_S) = ± 0.05 x10^{-10} Pa^{-1},U_c (L_f) = ± 0.05 x10^{-11} m, U_c(α_p) = ± 0.06 x10^{-4} K^{-1}. All the experiments were carried out at atmospheric pressure.

Table 3 Redlich-Kister coefficients of deviation/excess properties and corresponding standard deviations (σ) for the system at different temperatures

$V_m^E/(10^{-6}\text{m}^3\text{mol}^{-1})$	308.15	-2.4870	2.2507	-1.7358	3.1317	-0.2971	0.0128
	313.15	-2.5847	2.3292	-1.5966	3.0718	-0.6820	0.0132
	318.15	-2.6796	2.3766	-1.6045	3.1027	-0.7898	0.0133
	323.15	-2.7732	2.4264	-1.6244	3.1294	-0.8987	0.0135
$\kappa_s^E/(10^{-10}\ \text{Pa}^{-1})$	303.15	-0.4256	0.5814	-0.4516	0.6023	-0.4404	0.0023
	308.15	-0.4604	0.6102	-0.4731	0.6364	-0.4763	0.0025
	313.15	-0.4963	0.6419	-0.4948	0.6713	-0.5205	0.0027
	318.15	-0.5338	0.6758	-0.5187	0.7098	-0.5617	0.0028
	323.15	-0.5733	0.7108	-0.5426	0.7545	-0.6087	0.0031
$u^{\text{E}}/\ (\text{ms}^{-1})$	303.15	69.39	-94.57	71.93	-84.42	61.72	0.35
	308.15	73.50	-96.18	72.33	-84.78	64.61	0.36
	313.15	77.42	-97.80	73.48	-85.73	66.46	0.38
	318.15	81.30	-99.62	74.30	-86.60	68.17	0.38
	323.15	85.21	-101.29	74.89	-88.13	70.31	0.39
$L_f^E/(10^{-11}\ \text{m})$	303.15	-0.2246	0.3037	-0.2329	0.2979	-0.2098	0.0012
	308.15	-0.2439	0.3184	-0.2434	0.3126	-0.2254	0.0013
	313.15	-0.2439	0.3184	-0.2434	0.3126	-0.2254	0.0013
	318.15	-0.2844	0.3518	-0.2651	0.3436	-0.2628	0.0014
	323.15	-0.3061	0.3694	-0.2764	0.3627	-0.2829	0.0015
$\alpha_P^E\ (10^{-4}\ \text{K}^{-1})$	303.15	-1.1080	0.8704	-0.1379	0.8614	-1.8421	0.0024
	308.15	-1.1001	0.8638	-0.1304	0.8454	-1.8364	0.0022
	313.15	-1.0915	0.8551	-0.1325	0.8371	-1.8095	0.0022
	318.15	-1.0830	0.8472	-0.1295	0.8260	-1.7919	0.0022
	323.15	-1.0745	0.8393	-0.1256	0.8142	-1.7745	0.0021
$\Delta_\phi n_D$	303.15	0.00812	-0.01538	0.00680	-0.00016	-0.00190	0.00002
	308.15	0.00812	-0.01538	0.00680	-0.00016	-0.00190	0.00002
	313.15	0.00883	-0.01487	0.00575	-0.00143	0.00144	0.00001
	318.15	0.00925	-0.01472	0.00492	-0.00215	0.00331	0.00001
	323.15	0.00968	-0.01430	0.00443	-0.00344	0.00536	0.00002

Table 4 Partial molar volumes of component-1 ($\overline{V}_{m,1}$) ([Bmim][PF_6])and component-2($\overline{V}_{m,2}$) (1-Methyl-2-pyrrolidinone) with mole fraction (x_1) of [Bmim][PF_6] in the binary liquid mixture from T/K =303.15 to 323.15 at pressure P = 101.3 kPa.

x_1	303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	$\overline{V}_{m,1}$	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	$\overline{V}_{m,2}$
	/ 10^{-6} m^3 mol^{-1}		/ 10^{-6} m^3 mol^{-1}		/ 10^{-6} m^3 mol^{-1}		/ 10^{-6} m^3 mol^{-1}		/ 10^{-6} m^3 mol^{-1}	
0.0000	198.53	96.94	199.00	97.36	199.28	97.79	199.63	98.22	199.98	98.66
0.0513	199.62	96.98	200.10	97.41	200.43	97.84	200.82	98.27	201.21	98.71
0.1028	200.83	97.08	201.31	97.50	201.71	97.94	202.14	98.38	202.56	98.82
0.1422	201.75	97.15	202.24	97.58	202.69	98.02	203.15	98.46	203.61	98.90
0.1894	202.82	97.22	203.31	97.65	203.82	98.09	204.31	98.53	204.80	98.97
0.2988	204.91	97.24	205.45	97.67	206.02	98.09	206.58	98.53	207.13	98.97
0.3771	206.01	97.13	206.58	97.56	207.18	97.98	207.76	98.41	208.34	98.84
0.4990	207.09	96.90	207.71	97.30	208.31	97.73	208.92	98.15	209.52	98.57
0.5910	207.54	96.78	208.17	97.17	208.77	97.60	209.39	98.02	210.01	98.44
0.6991	207.83	96.81	208.46	97.21	209.09	97.63	209.72	98.03	210.36	98.44
0.8120	208.04	97.06	208.67	97.53	209.32	97.87	209.96	98.24	210.60	98.61
0.8415	208.09	97.15	208.72	97.65	209.37	97.95	210.01	98.31	210.66	98.67
0.8812	208.15	97.28	208.78	97.81	209.43	98.06	210.08	98.41	210.72	98.75
0.9423	208.23	97.45	208.87	98.06	209.51	98.23	210.16	98.55	210.80	98.86
1.0000	208.26	97.57	208.90	98.22	209.54	98.33	210.19	98.63	210.83	98.92

Combined uncertainties (Confidence level, 95%):$U(\overline{V}_{m,1}) = \pm 0.1 \times 10^{-6}$ m^3 mol^{-1}, $U(\overline{V}_{m,2}) = \pm 0.1 \times 10^{-6}$ m^3 mol^{-1}

Table 5 Partial molar volumes at infinite dilution ($\overline{V}_{m,1}^{\infty}, \overline{V}_{m,2}^{\infty}$) and excess partial molar volumes at infinite dilution ($\overline{V}_{m,1}^{E,\infty}, \overline{V}_{m,2}^{E,\infty}$) of [Bmim][PF_6] and 1-Methyl-2-pyrrolidinone T = (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/ K	$\overline{V}_{m,1}^{\infty}$	$\overline{V}_{m,1}^{E,\infty}$	$\overline{V}_{m,2}^{\infty}$	$\overline{V}_{m,2}^{E,\infty}$
	/(10^{-6} m^3mol^{-1})		/(10^{-6} m^3mol^{-1})	
303.15	198.53	-9.73	97.57	0.63
308.15	199.00	-9.90	98.22	0.86
313.15	199.28	-10.26	98.33	0.54
318.15	199.63	-10.55	98.63	0.41
323.15	199.98	-10.85	98.92	0.26

Standard uncertainties u are: u (x_1) = 0.0002, u (T) = 0.01 K and u(P)=0.5 kPa

Combined uncertainties (Confidence level, 95%):$U(\overline{V}_{m,1}^{E,\infty}) = \pm 0.1 \times 10^{-6}$ m^3 mol^{-1}, $U(\overline{V}_{m,2}^{E,\infty}) = \pm 0.1 \times 10^{-6}$ m^3 mol^{-1}

Table 6 Infrared absorbance wave numbers (cm^{-1}) between 2800 to 3200 of [Bmim][PF$_6$] in NMP at room temperature and atmospheric pressure P = 101.3 kPa.

		Infrared absorbance wave numbers /(cm^{-1})		
Mole fraction of [Bmim][PF$_6$]	Mole fraction of NMP	C$_2$-H stretching	C$_{4,5}$-H stretching	C=O Stretch
1.0000	0.0000	3124.3	3169.2	-
0.8812	0.1188	3123.3	3168.3	1672.7
0.8120	0.1880	3122.2	3168.2	1672.7
0.6991	0.3009	3121.2	3168.2	1671.7
0.5910	0.4090	3120.2	3167.2	1671.7
0.4990	0.5024	3119.2	3166.2	1670.7
0.3771	0.6229	3116.1	3164.1	1669.7
0.2988	0.7012	3113.3	3161.8	1668.5
0.1894	0.8106	-	-	1667.8
0.1028	0.8972	-	-	1668.9
0.0000	1.0000	-	-	1669.3

Table 7 Characteristic and reduced parameters for the pure components used in PFP theory at various temperatures.

T/(K)	$\tilde{V}$	V_1^* /(10^{-6}m^3.mol^{-1})	P_1^* /(10^6 J.mol^{-1})
[Bmim][PF$_6$]			
303.15	1.1642	178.88	604.01
308.15	1.1671	178.99	606.90
313.15	1.1699	179.11	609.77
318.15	1.1728	179.22	612.62
323.15	1.1757	179.33	615.42
NMP			
303.15	1.2242	79.18	713.79
308.15	1.2282	79.27	712.94
313.15	1.2322	79.36	711.85
318.15	1.2361	79.46	710.53
323.15	1.2401	79.56	708.99

Table 8 PFP interaction parameter, χ_{12}, and calculated values of the three contributions from the PFP theory at equimolar composition for ([Bmim][PF$_6$] + NMP) system at *T*=(303.15-323.15) K

T	χ_{12}	$V_m^E(int)$	$V_m^E(fv)$	$V_m^E(ip)$
/K	/(10^6 J m^{-3})	/(10^{-6} m^3 mol^{-1})		
303.15	-56.5832	-0.7253	-0.1598	0.2833
308.15	-56.1203	-0.7346	-0.1654	0.2782
313.15	-55.9229	-0.7474	-0.1711	0.2722
318.15	-55.5898	-0.7584	-0.1768	0.2654
323.15	-55.1682	-0.7684	-0.1827	0.2578