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Thermophysical, excess and transport properties of organic solvents with imidazolium based ionic liquids

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Ultrasonic velocity and refractive index have been evaluated for eight binary mixtures comprising imidazolium based ([BMIM][PF_6], [HMIM][PF_6], [OMIM][PF_6] and [MMIM][CH_3SO_4]) ionic liquids with three organic solvents of varying nature, viz., 2-propanol, 2-butanone and ethylacetate, at three different temperatures (293.15, 298.15 and 303.15 K). Evaluation of refractive index has been carried out by eight approaches, whereas five methods have been employed for computation of ultrasonic velocity. Molecular interaction studies have been carried out with the help of intermolecular free length, and interaction parameter. Furthermore, the excess counterpart of the coefficient of thermal expansion has been determined to get a deeper understanding on the behavior in terms of nature and extent of interactions present in these systems.

Keywords: Solution chemistry, Ionic liquids, Imidazolium ionic liquids, Refractive index, Ultrasonic velocity, Molecular interactions, Thermal expansion

In the recent past, significant studies have been carried out to understand the properties of existing and newly developed room temperature ionic liquids (RTILs) owing to their growing importance as a cleaner possible replacement as solvents for the existing volatile, high vapor pressure and toxic organic compounds.[1-4] The unique properties like negligible vapor pressure, low melting point, high thermal stability and a higher degree of solubility with polar and non polar substances offers a viable alternative. As a result of these characteristics they can be employed for various applications like fuel cells,[5] separation processes, catalysis, [6] adsorption of CO_2, etc.[7-8].

Whilst majority of research work is being carried out on organic synthesis and chemical reaction of ionic liquids[9-12], systematic studies involving thermodynamic and transport properties[13-16] of ILs primarily of mixtures containing ILs are rare. Information of these properties is of substantial importance for selecting appropriate ILs and their mixtures in different applications of chemical engineering as mentioned earlier[17]. Literature survey reveals that relatively lesser amount of work has been done on binary or higher order liquid mixtures[18] of ionic liquids with organic solvents as compared to pure ionic liquids[19].

High density values[20] ranging from 1 to 1.6 g cm^{-3} is one of the major disadvantages of commercially used single ionic liquid, which can hinder their application in separation process. Ionic liquids are found to be miscible with variety of organic and inorganic solvents without change in chemical properties. Hence, by mixing them with organic and inorganic solvents their physical properties can be tuned resulting in highly efficient solutions for various chemical processes. Mixtures of ionic liquids with organic solvents have advantages over pure ionic liquid, the unique property of each component can be utilized; also they can be combined in such a way that properties which are anticipated, cannot be fulfilled by a single ionic liquid[21].

It is a well known fact that the shape and structure of component molecules and the various intermolecular forces play a key role in understanding the thermodynamic and transport properties of liquid mixture which is the result of intermolecular interactions taking place thereof. It thus becomes highly imperative to study the thermodynamic, transport and allied properties of binary mixture of ionic liquids with organic solvents to get a better understanding of various intermolecular interactions thus paving the way for better equipment design and various engineering applications like heat and mass transfer, fluid flow, extraction process etc.

Ionic liquids having imidazolium cation and hexaflurophosphate anion result in hydrophobic solvents[22], as they lack hydrogen bond accepting ability. The most recognized and tested ionic liquid in various applications contains PF_6^- as the anion counterpart. ILs based on methylsulphate ($CH_3SO_4^-$) anion does not undergo hydrolysis at high temperature or in contact with water[23]. Thus a comparative study of the properties of IL's involving the two contrasting anions in terms of their industrial application is evidently needed.

In the present work, all the necessary experimental data has been taken from literature[24]. The following systems (at 293.15 K, 298.15 K and 303.15 K and atmospheric pressure) have been taken for the present investigation:

- 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM][PF_6])+2-butanone/ethyl acetate/2-propanol;
- 1,3-dimethyl imidazolium methyl sulfate ([MMIM][CH_3SO_4])+2-butanone/ethyl acetate/ 2-propanol;
- 1-hexyl-3-methyl imidazolium hexafluorophosphate ([HMIM][PF_6])+2-propanol;
- 1-octyl-3-methyl imidazolium hexafluorophosphate ([OMIM][PF_6])$_+$ethyl acetate.

The structures of the ionic liquids are shown in Fig 1.

Refractive index along with density is usually reported as a proof of purity since high precision can be obtained easily for both these quantities[25]. For RTILs the studies related to refractive index have received less attention[26-28]. Measurement of refractive index can be used for providing the information about the forces between the molecules[29] or their behavior when they are in solution[30]. It can also be used as a measure of electronic polarizability of the molecule[31].

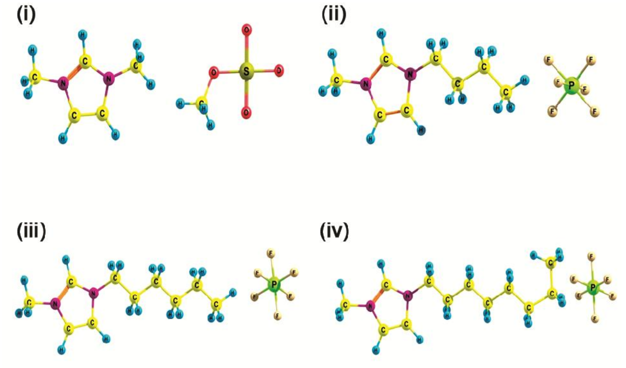

Fig. 1—Structures of (i) [MMIM][CH_3SO_4], (ii) [BMIM][PF_6]$^-$, (iii) [HMIM][PF_6]$^-$ and (iv) OMIM PF_6]$^-$.

Ultrasonic velocity and absorption measurement serve as the versatile tool for the study of intermolecular interactions in liquid and liquid mixtures. This makes the need for theoretical evaluation of sound velocity, a matter of considerable significance due to which various theories have been proposed by several workers over the years[32].

The objective of the investigation is to provide information about the like and the unlike molecular interactions by making use of the experimental and evaluated parameters. The measured values of ultrasonic velocity and density were used to compute various parameters like Intermolecular free-length (L_f), interaction parameter (χ), to get an in-depth picture of the interactions taking place[33-34]. The average absolute percentage deviation from experimental values[24] has also been evaluated and a comparative study has been carried out based on the merits and demerits of various approaches. In order to get a better understanding of the nature and the extent of interactions present in the systems under consideration, coefficient of thermal expansion (α) or thermal expansibility under isobaric conditions, and its excess counterpart have also been determined.

Theory

For estimation of refractive index the following mixing rules have been used in the present study.

Gladstone Dale[35] proposed an important equation for calculating refractive index using volume fraction and refractive index of pure components given by

$$(n_m - 1) = \varphi_1(n_1 - 1) + \varphi_2(n_2 - 1) \qquad \dots (1)$$

where n_m, n_1 and n_2 represent the refractive indices of the mixture and pure components 1 and 2 respectively.

Arago-Biot[35] made use of volume fraction additivity to estimate refractive index for binary solutions:

$$n_m = \varphi_1 n_1 + \varphi_2 n_2 \qquad \dots (2)$$

where as ratio of refractive index of pure component (m) was used in a relation proposed by Heller[35]:

$$\frac{n_m - n_1}{n_1} = \frac{3}{2}\left(\frac{m^2-1}{m^2-2}\right)\varphi_2 \qquad \dots (3)$$

where $m = n_2/n_1$.

The relation proposed by Wiener[35] is given as:

$$\left(\frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2}\right) = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\varphi_2 \qquad \dots (4)$$

Lorentz-Lorentz relation[35] is based on the change in molecular polarizabilty, D = [(n^2-1)/ (n^2+2)] with volume fraction,

$$\left(\frac{n_m^2-1}{n_m^2+2}\right)\frac{1}{\rho_m}=\left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{w_1}{\rho_1}+\left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{w_2}{\rho_2} \qquad \dots (5)$$

Newton's relation[35] may be represented as:

$$(n_m^2-1)=\varphi_1(n_1^2-1)+\varphi_2(n_2^2-1) \qquad \dots (6)$$

Eykman's[35] proposed the following relation:

$$\left(\frac{n_m^2-1}{n_m+0.4}\right)V_m=\left(\frac{n_1^2-1}{n_1+0.4}\right)\frac{M_1x_1}{\rho_1}+\left(\frac{n_2^2-1}{n_2+0.4}\right)\frac{M_2x_2}{\rho_2} \qquad \dots (7)$$

Oster's relation[35] is given as:

$$\left[\frac{(n_m^2-1)(2n_m^2+1)}{n_m^2}\right]V_m=\left[\frac{(n_1^2-1)(2n_1^2+1)}{n_1^2}\right]\frac{M_1x_1}{\rho_1}+\left[\frac{(n_2^2-1)(2n_2^2+1)}{n_2^2}\right]\frac{M_2x_2}{\rho_2} \qquad \dots (8)$$

where all the symbols have their usual meaning.

Velocity of ultrasonic waves according to Danusso[32] model is given by the equation:

$$u_m=\frac{1}{\rho_m}\frac{1}{M_{eff}^{-1/2}}\left[\left(\frac{x_1M_1}{\rho_1^2\,U_1^2}\right)+\left(\frac{x_2M_2}{\rho_2^2\,U_2^2}\right)\right]^{-1/2} \qquad \dots (9)$$

where M_{eff} is the effective molecular weight, ρ_m the density of the mixture and other symbols have their usual meaning.

van Dael and Vangeel[32] proposed the following ideal mixing relation for predicting ultrasonic velocity of a binary liquid mixture:

$$\frac{1}{(x_1M_1+x_2M_2)U_m^2}=\left[\left(\frac{x_1}{M_1U_1^2}\right)+\left(\frac{x_2}{M_2U_2^2}\right)\right] \qquad \dots (10)$$

Assuming the linearity of the molar sound velocity (R) and the additivity of the molar volumes in liquid solutions, Nomoto[32] gave the relation:

$$u_m=\left(\frac{x_1R_1+x_2R_2}{x_1V_1+x_2V_2}\right)^3 \qquad \dots (11)$$

Zhang Junjie[32] gave the following relation for the ultrasonic velocity in a binary mixture:

$$u_m=(x_1V_1+x_2V_2)\left[\frac{(x_1M_1+x_2M_2)}{\times\left[\left(\frac{x_1M_1}{\rho_1U_1^2}\right)+\left(\frac{x_2M_2}{\rho_2U_2^2}\right)\right]}\right]^{-1/2} \qquad \dots (12)$$

Nutsch-Kuhnkies[32] extended the relation proposed by Schaaffs for predicting ultrasonic velocity in pure liquids on the basis of collision factor theory, CFT, for the binary liquid mixtures (Eq. 13).

$$u_m=\frac{U_\infty}{V_m}(x_1S_1+x_2S_2)(x_1B_1+x_2B_2) \qquad \dots (13)$$

In Eq. (13), S and B are collision factor and actual volume of the molecules per mole respectively of the first and second component and are given by the expressions:

$S=\frac{UV}{U_\infty B}$, and $B=\frac{4}{3}\pi r^3N_0$.

where U_∞ = 1600 m/s, N_0 is the Avogadro number and r is the molecular radius.

Furthermore, ultrasonic velocity and density were used to compute various parameters like intermolecular free-length (L_f), and interaction parameter (χ)[34].

$$\text{Intermolecular free length } (L_f)=K\beta_s^{\frac{1}{2}} \qquad \dots (14)$$

$$\text{Jacobson constant, } K=(93.875+0.375\,T)10^{-8} \qquad \dots (15)$$

The interaction parameter was calculated using the relation,

$$\chi=\left(\frac{u}{u_{id}}\right)^2-1 \qquad \dots (16)$$

where u_{id} is given as

$$u_{id}=\sum x_iu_i \qquad \dots (17)$$

Coefficient of thermal expansion (α) has been determined by using density data given in literature[24], using the expression[36],

$$\alpha=\frac{1}{V}\left(\frac{\delta V}{\delta T}\right)=\rho\left(\frac{\delta\rho^{-1}}{\delta T}\right)_P \qquad \dots (18)$$

where V and ρ are volume and density of the mixture respectively. The excess coefficient of thermal expansion (α^E) has been evaluated by method given elsewhere[37].

The average absolute percentage deviations (AAPD)[38] by the different approaches have been computed using the expression:

$$AAPD=\frac{1}{n}\sum\left|\frac{u_{expt}-u_{theoret}}{u_{expt}}\right|\times 100 \qquad \dots (19)$$

Results and Discussion

Ultrasonic velocity, refractive index and interaction parameter of binary systems containing ionic liquids have been evaluated at three different temperatures (293.15, 298.15 and 303.15 K) using various approaches. Furthermore, intermolecular free length and acoustic impedance have also been evaluated.

Table 1—Density, ultrasonic velocity, refractive index and coefficient of thermal expansion of pure components at 298.15 K

Components	Density ρ (g cm^{-3})	Ultrasonic vel. u (m s^{-1})	Ref. index[24] n	Coeff. of thermal exp. α (K^{-1})
[BMIM][PF_6]	1.3673	1443	1.40937	0.000629
[HMIM][PF_6]	1.2937	1424	1.41787	0.000642
[MMIM][CH_3SO_4]	1.3272	1813	1.48270	0.000623
[OMIM][PF_6]	1.2357	1408	1.42302	0.000542
2 Butanone	0.7997	1192	1.37618	0.001336
2 Propanol	0.7810	1139	1.37496	0.001076
Ethylacetate	0.8944	1141	1.36977	0.001375

Table 2—Average absolute percentage deviation for refractive index of investigated systems by various approaches at different temperatures (293.15, 298.15 and 303.15 K)[a]

Systems	Temp. (K)	AB	GD	LL	E	W	H	N	O
[BMIM][PF_6]+2-butanone	293.15	0.530	0.284	0.287	0.285	0.274	0.287	0.255	0.283
	298.15	0.876	0.687	0.689	0.688	0.662	0.689	0.685	0.686
	303.15	0.866	0.654	0.656	0.654	0.635	0.656	0.651	0.652
[BMIM][PF_6]+ethylacetate	293.15	0.558	0.290	0.295	0.292	0.252	0.295	0.285	0.288
	298.15	0.897	0.678	0.682	0.679	0.653	0.682	0.675	0.677
	303.15	0.850	0.619	0.622	0.620	0.595	0.622	0.615	0.617
[BMIM][PF_6]+2-propanol	293.15	0.132	0.027	0.028	0.027	0.052	0.031	0.026	0.027
	298.15	0.505	0.422	0.423	0.422	0.403	0.424	0.422	0.505
	303.15	0.457	0.368	0.368	0.368	0.347	0.370	0.367	0.367
[HMIM][PF_6]+2-propanol	293.15	0.557	0.406	0.407	0.406	0.420	0.409	0.405	0.405
	298.15	0.302	0.067	0.069	0.355	0.327	0.074	0.065	0.353
	303.15	0.249	0.048	0.051	0.049	0.425	0.136	0.046	0.294
[OMIM][PF_6]+ethylacetate	293.15	0.843	0.392	0.399	0.394	0.338	0.399	0.385	0.208
	298.15	0.824	0.212	0.220	0.347	0.999	0.220	0.202	0.188
	303.15	0.239	0.284	0.248	0.242	0.208	0.247	0.230	0.234
[MMIM][CH_3SO_4]+2-butanone	293.15	0.452	0.282	0.292	0.181	0.351	0.419	0.274	0.173
	298.15	0.326	0.151	0.161	0.154	0.370	0.191	0.142	0.146
	303.15	0.158	0.158	0.169	0.161	0.369	0.199	0.148	0.152
[MMIM][CH_3SO_4]+2-propanol	293.15	0.884	0.191	0.227	0.202	0.195	0.224	0.156	0.171
	298.15	0.917	0.213	0.251	0.225	0.187	0.247	0.177	0.174
	303.15	0.219	0.219	0.220	0.231	0.190	0.253	0.182	0.198
[MMIM][CH_3SO_4]+ ethylacetate	293.15	0.324	0.150	0.156	0.147	0.220	0.160	0.132	0.136
	298.15	0.327	0.144	0.158	0.148	0.218	0.162	0.132	0.327
	303.15	0.128	0.128	0.142	0.132	0.126	0.146	0.116	0.121

[a] AB: Arago-Biot; GD: Gladstone-Dale; LL: Lorentz-Lorentz; E: Eykman; W: Wiener; H: Heller; N: Newton; O: Oster.

Table 1 presents some important thermodynamic and transport properties of pure components reported in literature[24]. The variations of the parameters with respect to mole fraction of first component (x_1) have been represented graphically (Figs 2-13) along with experimental data. Interaction parameter have been plotted and shown in Figs 12 and 13. Average absolute percentage deviations were also calculated using Eq. 19, which are given in Table 2 for refractive index and in Table 3 for ultrasonic velocity. The experimental data have also been taken from the literature [24].

[BMIM][PF_6]+(2-butanone, 2-propanol, ethylacetate)

From Fig. 2 it can be seen that the trend shown by the values obtained through various approaches are similar to that shown by the experimentally obtained values. The refractive index obtained by Arago-Biot relation is found to be increasing linearly with mole fraction (x_1) of the first component unlike other approaches. Minimum average absolute percentage deviation (AAPD) is shown by Wiener relation, whereas for Arago-Biot, it is maximum. A look at the plots (Fig. 2) reveal that the predicted values lie close to experimental values for 293.15 K but tend to shift

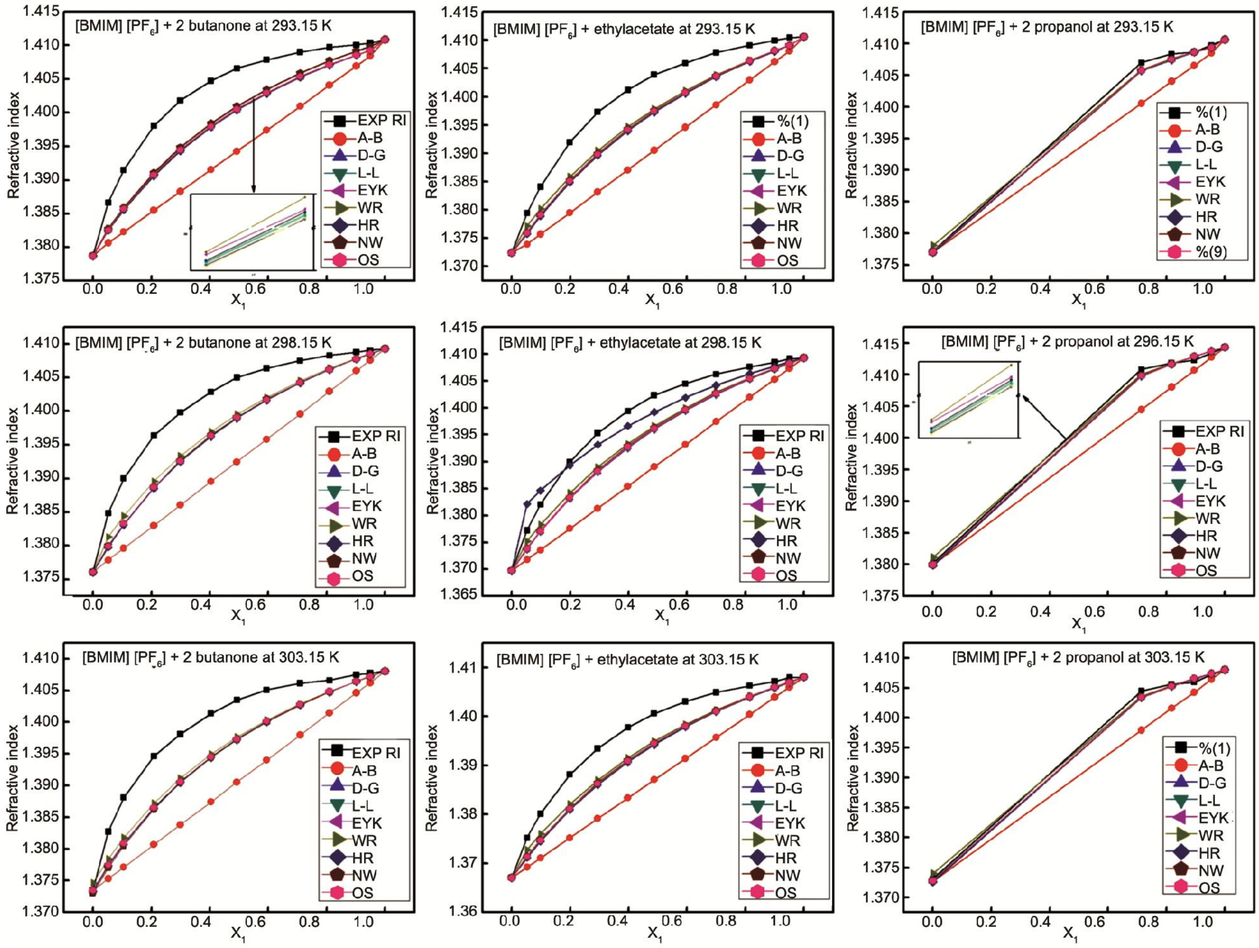

Fig. 2—Plots of refractive index versus mole fraction (x_1) for [BMIM][PF$_6$]+(2 butanone/ 2-propanol/ ethylacetate) at three different temperatures.

with increase in temperature and this behavior is also reflected in the corresponding AAPD values (Table 2).

From the Fig. 3 it is seen that the values of ultrasonic velocity computed by Nomoto and CFT approach follow a trend similar to that of experimental values, while those computed by remaining three approaches, viz., van Deal, Junjie and Danusso shows opposite trends.

One common observation in all the three binary systems at all temperatures is that the best result is given by Nomoto approach (Eq. 11), while the highest AAPD are recorded for van Deal ideal mixing relation (Eq. 10). The deviation computed by Junjie and Danusso approach lie in between maximum and minimum deviations.

[HMIM][PF$_6$]+2-propanol

From Fig. 4 we find that the values of refractive index evaluated by various approaches are in good agreement with the experimental values and gets better as the temperature is increased. The highest deviations are shown by Arago-Biot and least by Newton. The values computed by Weiner and Oster at 303.15 K are less than the experimental values as compared to those obtained from other relations, thereby resulting in positive and negative deviations respectively. Computed values for the ultrasonic velocity as shown in Fig. 5 reveals that Nomoto, CFT, Danusso and Junjie relations show similar trend as that of experimental values. The AAPD values indicate that maximum deviations are shown by the van Deal method and minimum by the Nomoto approach. The computed values of ultrasonic velocity by CFT approach are also found to be in good agreement with experimental values[24].

[MMIM][CH$_3$SO$_4$]+(2-butanone, 2-propanol, ethylacetate)

Figure 6 reveals that all the methods, except Arago-Biot, used for computing refractive index give

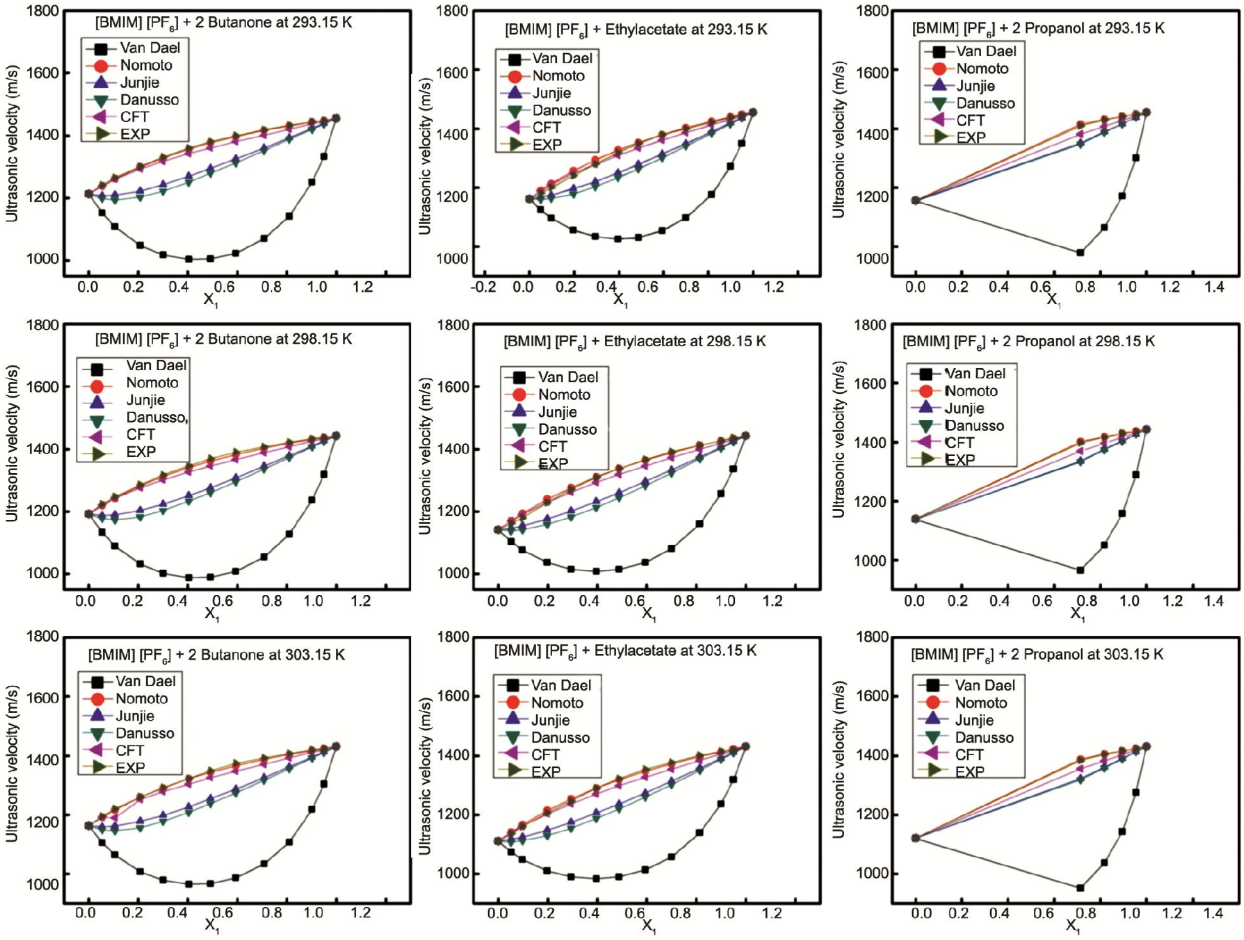

Fig. 3—Plots of ultrasonic velocity versus mole fraction (x_1) for [BMIM][PF$_6$] at three different temperatures.

good result for the system under consideration. Arago-Biot approach continues to show similar trend as seen in previous systems, i.e., it increases linearly. The average absolute percentage deviation (Table 2) by the Oster relation is seen to be lowest and that for Arago-Biot approach the highest for the two temperatures (293.15 and 298.15 K) but the AAPD values show a decrease at 303.15 K for all the systems under consideration. Figure 7 depict the change in values of ultrasonic velocity computed by different approaches with the variation in mole fraction of the ionic liquid. The plots indicate that the values obtained by the Nomoto relation and CFT show very good agreement with experimental findings. The values obtained from van Deal relation show large deviation from the experimental values for all the systems at all temperatures, and those by Danusso and Junjie relation are found to lie close to one another and show reasonably good agreement with the experimental values. A glance at Table 3 reveals that the minimum AAPD values are given by Nomoto relation and CFT whereas maximum deviations are shown by van Deal approach.

[OMIM][PF$_6$]+ethyl acetate

Table 2 shows that the maximum average absolute percentage deviation of 0.843 is given by Arago-Biot approach at 293.15 K, whereas least AAPD value of 0.188 is given by Oster relation at 298.15 K, which performs the best (Fig. 8) amongst all the relations under consideration. In case of ultrasonic velocity (Fig. 9), Nomoto relation gives excellent agreement with experimental values whereas van Deal approaches give highest deviations (Table 3).

Refractive index and ultrasonic velocity

Keeping in view the behavior of the systems under present investigation it can be said that the positive deviation in the value of computed properties may be due to molecular association or complex formation whereas negative deviation may have arisen due to

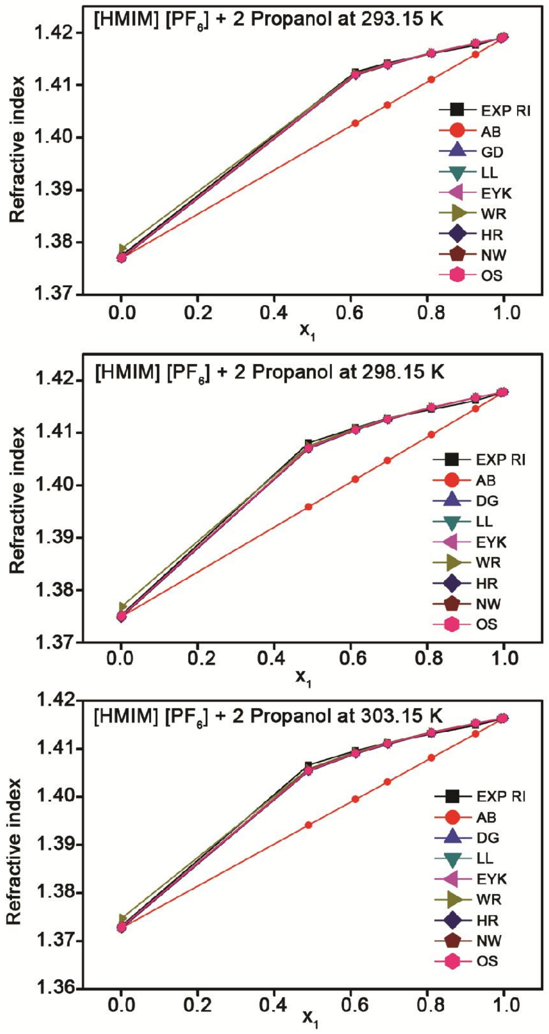

Fig. 4—Plots of refractive index versus mole fraction (x_1) for [HMIM][PF$_6$]+2-propanol at three different temperatures.

molecular dissociation of associated species caused by the addition of organic solvents. The highest deviations given by Arago-Biot relation (Table 2) for all the system under consideration may be attributed to the fact that this approach considers the volume fraction additivity of refractive index thereby leading to ideal mixing relation, the high value of deviations stemming from the fact that the systems are far removed from ideality. Minimum AAPD values are given by the Weiner relation for [BMIM][PF$_6$] and [HMIM][PF$_6$] systems whereas for [MMIM][CH$_3$SO$_4$] and [OMIM][PF$_6$], Oster relation is seen to give the best result. The overall superiority of the Weiner relation may be attributed to the relation being accountable for isotropic body. It also takes into consideration that the molecules are spherically symmetrical and follow volume additivity.

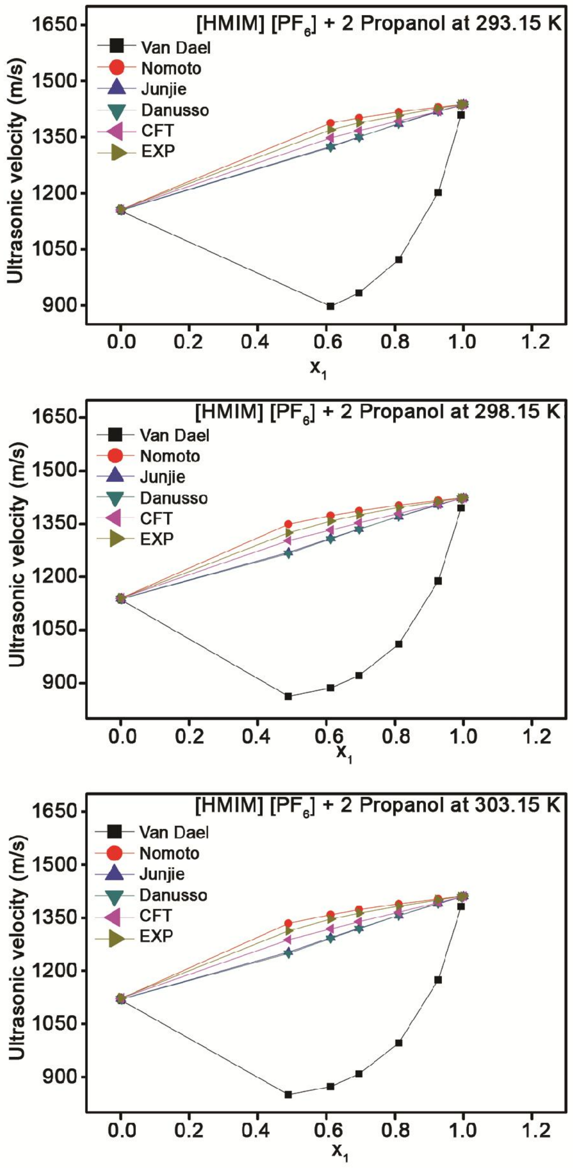

Fig. 5—Plots of ultrasonic velocity versus mole fraction (x_1) for [HMIM][PF$_6$]+2-propanol at three different temperatures.

A perusal of the graphical variation of ultrasonic velocity with mole fraction of the first component clearly indicates that the highest positive deviation is shown by van Deal ideal mixing relation (Table 3). Both Junjie and Danusso relation also shows positive deviations. However the deviations are much less as compared to that shown by van Deal and exhibit a reasonably good agreement with experimental values. A closer inspection reveals that on the whole Junjie relation performs better than the Danusso relation. Nomoto relation employs the use of molar sound velocity of pure component along with

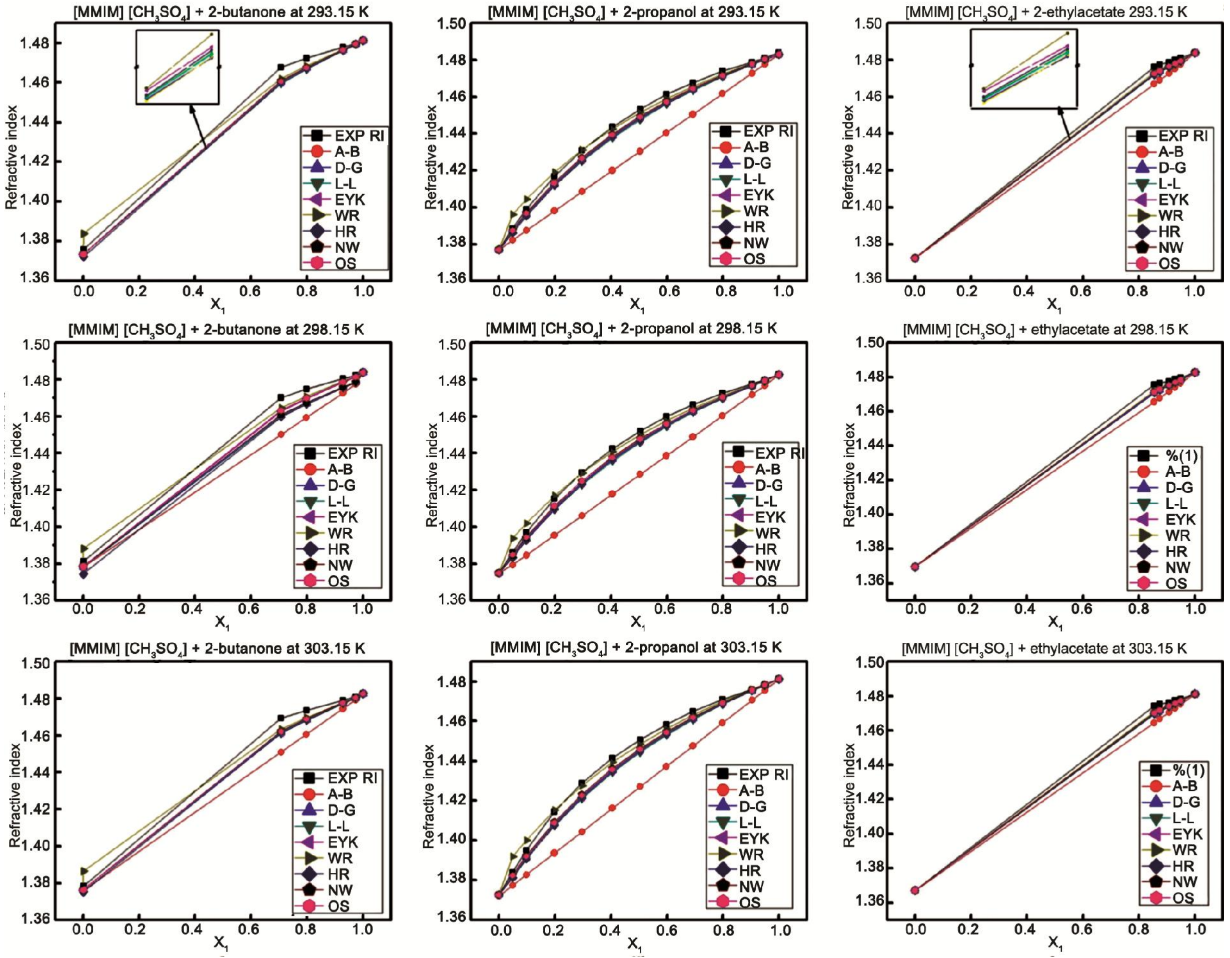

Fig. 6—Plots of refractive index versus mole fraction (x_1) for [MMIM][CH_3SO_4]+(2-butanone/ 2-propanol/ ethylacetate) at three different temperatures.

molar volume giving the minimum values of AAPD. All the systems under consideration seem to be adhering to the linearity of the molar sound velocity and the additivity of molar volume.

Collision factor theory takes into account the interaction present in the binary systems as a result of which the values of ultrasonic velocity obtained by CFT for all the systems are close to experimental finding. The molecules are considered as real non-elastic and the collision between them produces the interaction. There are four adjustable parameter (S_1, S_2, B_1 and B_2) involved in computation. Actual volume 'B' depends upon the molecular radius of the pure components [39]. The ideal mixing relation developed by van Deal and Vangeel takes into consideration the additivity of adiabatic compressibility based on the ideal nature of liquid mixture with the variation arising due to change in composition. The relation involves the computation of ultrasonic velocity by employing the molar masses and ultrasonic velocity of pure component on a mole fraction additive basis and is found to give reasonably good agreement for the systems which tend towards ideality[32]. Literature data[24] pertaining to excess molar volume clearly indicates that with the exception of a certain composition range in the system [HMIM][PF_6]+2-propanol (x_1 = 0.8110 to 0.9933) all the values are negative for all the binary systems under investigation over the entire composition range. Further it is also seen that these excess values show an increase with the increase in temperature for all the systems. The excess negative values indicate towards a decrease in volume on mixing as compared to the unmixed volume. The negative values exhibit volume contraction and since the magnitude is seen to increase with rise in temperature, it points towards the fact that the interactions are found to be more intense with the increase in temperature. The difference

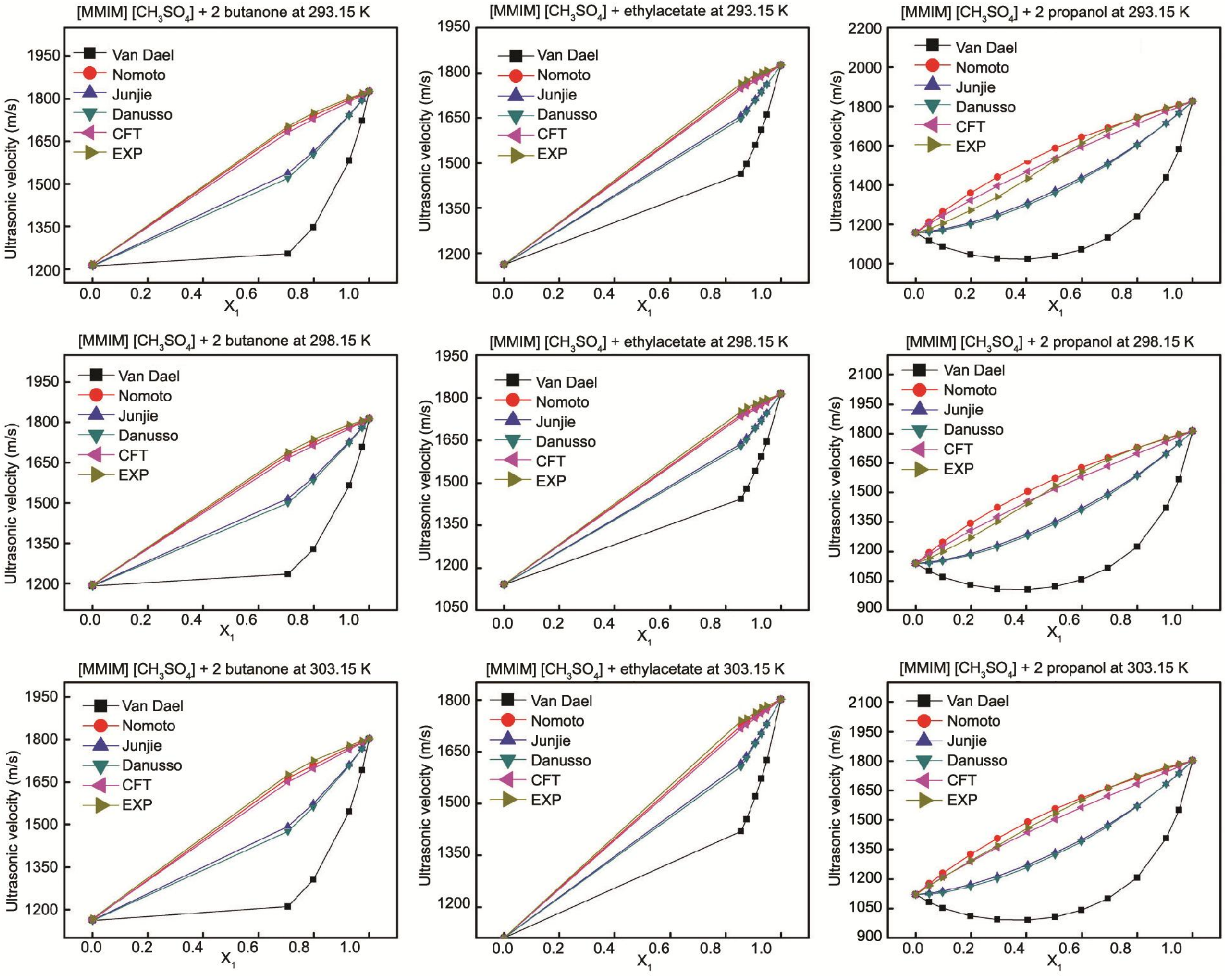

Fig. 7—Plots of ultrasonic velocity versus mole fraction (x_1) for [MMIM][CH_3SO_4]+(2-butanone/ 2-propanol/ ethylacetate) at three different temperatures.

between the unmixed volume of the components and that of the mixture leading to the sign and magnitude of the excess molar volume results from (a) differences between intermolecular forces in the solution and those in the pure components (b) differences between packing of molecules in the mixture and the packing in the pure components (c) due to the differences in sizes and shapes of molecules on mixing. A similar trend is also exhibited by isentropic compressibility values [24], both of which points towards a higher degree of interaction occurring between the constituent components of binary systems under consideration. This clearly indicates that all the systems are far removed from ideality, hence the high average absolute percentage deviations shown by the van Deal ideal mixing relation and Arago-Biot approach stand well justified.

Intermolecular free length (L_f)

Figure 10 shows the decreasing trend of the intermolecular free length values with increase in mole fraction of the first component. Also, the L_f values are least for [MMIM][CH_3SO_4]+2-butanone/ 2-propanol/ethylacetate at all the three temperatures. This may be attributed to the higher value of ultrasonic velocity of ionic liquid. The observation is further strengthened by the fact that the L_f values are much higher for [HMIM][PF_6]+2-propanol and [OMIM][PF_6]+ethylacetate (Fig. 11) system in comparison to all the other systems under investigation. It can also be seen that L_f values increase with increase in temperature as the distance between the molecules increases. The decrease in intermolecular free length with increase in mole fraction of the first component is the result of compression in the volume due to interaction taking place.

Table 3—Average absolute percentage deviation for ultrasonic velocity investigated systems by various approaches at different temperatures

System	Temp. (K)	van Deal	Nomoto	Junjie	Danusso	CFT
[BMIM][PF$_6$]+2-butanone	293.15	16.08	0.12	3.62	4.34	0.7
	298.15	16.42	0.28	3.91	4.68	0.85
	303.15	16.75	0.17	4.04	4.84	1.00
[BMIM][PF$_6$]+ethylacetate	293.15	13.39	0.44	2.65	3.36	0.58
	298.15	13.83	0.27	3.03	3.78	0.88
	303.15	14.41	0.29	3.44	4.22	0.81
[BMIM][PF$_6$]+2-propanol	293.15	10.68	0.07	1.19	1.23	0.66
	298.15	10.81	0.05	1.24	1.29	0.61
	303.15	10.96	0.04	1.30	1.36	0.64
[HMIM][PF$_6$]+2-propanol	293.15	12.54	0.35	0.95	0.95	0.54
	298.15	13.59	0.41	1.24	1.28	0.63
	303.15	13.77	0.38	1.36	1.41	0.71
[OMIM][PF$_6$]+ethylacetate	293.15	12.89	0.63	1.88	3.08	0.35
	298.15	13.14	0.53	2.09	3.31	0.46
	303.15	13.82	0.22	2.61	2.66	0.79
[MMIM][CH$_3$SO$_4$]+2-butanone	293.15	7.57	0.23	2.55	2.78	0.43
	298.15	7.71	0.25	2.66	2.92	0.45
	303.15	7.97	0.29	2.84	3.10	0.49
[MMIM][CH$_3$SO$_4$]+2-propanol	293.15	18.82	2.71	5.35	5.73	1.78
	298.15	19.55	2.01	6.16	6.57	1.33
	303.15	20.59	1.01	7.34	7.76	1.03
[MMIM][CH$_3$SO$_4$]+ethylacetate	293.15	9.24	0.41	3.17	3.36	0.68
	298.15	9.51	0.47	3.36	3.58	0.73
	303.15	9.89	0.46	3.59	3.80	0.73

Table 4—Excess coefficient of thermal expansion, (α^E, 10^{-5} K^{-1}) for all the binary systems at 293.15, 298.15 & 303.15 K

x_1	α^E (10^{-5} K^{-1}) at T (K)			x_1	α^E (10^{-5} K^{-1}) at T (K)			x_1	α^E (10^{-5} K^{-1}) at T (K)			x_1	α^E (10^{-5} K^{-1}) at T (K)		
	293.15	298.15	303.15		293.15	298.15	303.15		293.15	298.15	303.15		293.15	298.15	303.15
[BMIM][PF$_6$]+2-butanone				[BMIM][PF$_6$]+ethylacetate				[OMIM][PF$_6$]+ethylacetate				[MMIM][CH$_3$SO$_4$]+2-propanol			
0.0533	-9.98	-9.79	-9.74	0.052	-6.77	-6.68	-6.61	0.0547	-6.97	-6.89	-6.79	0.049	-5.64	-5.58	-5.56
0.1058	-14.83	-14.60	-14.51	0.0979	-9.99	-9.87	-9.75	0.0964	-8.37	-8.27	-8.17	0.0981	-7.56	-7.51	-7.47
0.2081	-16.07	-15.88	-15.75	0.198	-13.26	-13.13	-12.98	0.1996	-10.29	-10.20	-10.09	0.1987	-9.50	-9.43	-9.41
0.2992	-15.12	-14.98	-14.85	0.2939	-12.74	-12.62	-12.49	0.2941	-10.06	-9.96	-9.87	0.2961	-11.08	-11.01	-11.00
0.4044	-14.06	-13.93	-13.82	0.3968	-15.07	-14.94	-14.81	0.3939	-9.17	-9.09	-9.02	0.4055	-10.78	-10.70	-10.71
0.4926	-13.64	-13.51	-13.42	0.4883	-16.86	-16.71	-16.59	0.4944	-7.12	-7.07	-7.01	0.5043	-7.80	-7.73	-7.76
0.5943	-11.91	-11.80	-11.74	0.5936	-14.86	-14.74	-14.64	0.6046	-6.19	-6.15	-6.10	0.5987	-6.68	-6.64	-6.66
0.7085	-8.55	-8.48	-8.43	0.7	-10.80	-10.71	-10.65	0.7033	-6.17	-6.12	-6.09	0.6937	-5.54	-5.51	-5.53
0.8093	-6.55	-6.50	-6.47	0.8146	-4.61	-4.58	-4.55	0.8019	-3.22	-3.20	-3.18	0.7992	-6.63	-6.60	-6.59
0.9013	-2.15	-2.13	-2.12	0.8997	-2.78	-2.76	-2.75	0.9033	-1.41	-1.40	-1.39	0.9042	-3.88	-3.86	-3.86
0.9491	-1.76	-1.75	-1.74	0.9499	-1.36	-1.35	-1.34	0.9952	-0.10	-0.09	-0.10	0.9502	-1.56	-1.54	-1.55
[BMIM][PF$_6$]+2-propanol				[HMIM][PF$_6$]+2-propanol				[MMIM][CH$_3$SO$_4$]+2-butanone				[MMIM][CH$_3$SO$_4$]+ethylacetate			
0.0008	-1.38	-1.38	-1.35	0.0011	1.17	1.14	1.15	0.0006	-2.61	-2.58	-2.55	0.8549	-5.85	-5.81	-5.82
0.0011	-0.13	-0.13	-0.13	0.0019	-0.21	-0.24	-0.21	0.0012	-1.39	-1.36	-1.35	0.8746	-4.89	-4.86	-4.88
0.7136	-3.03	-3.00	-2.98	0.6123	-3.67	-3.65	-3.62	0.0029	-4.06	-3.98	-3.95	0.9072	-3.34	-3.32	-3.33
0.8175	-2.88	-2.87	-2.85	0.6958	-3.74	-3.72	-3.69	0.7074	-9.10	-9.02	-8.98	0.9294	-3.85	-3.83	-3.83
0.8945	-3.01	-2.99	-2.97	0.811	-3.58	-3.56	-3.53	0.7983	-6.10	-6.05	-6.02	0.9491	-3.72	-3.69	-3.69
0.9542	-1.06	-1.05	-1.04	0.926	-2.75	-2.73	-2.71	0.9284	-3.32	-3.29	-3.28				
				0.9933	-3.13	-3.11	-3.09	0.9743	-0.89	-0.88	-0.88				

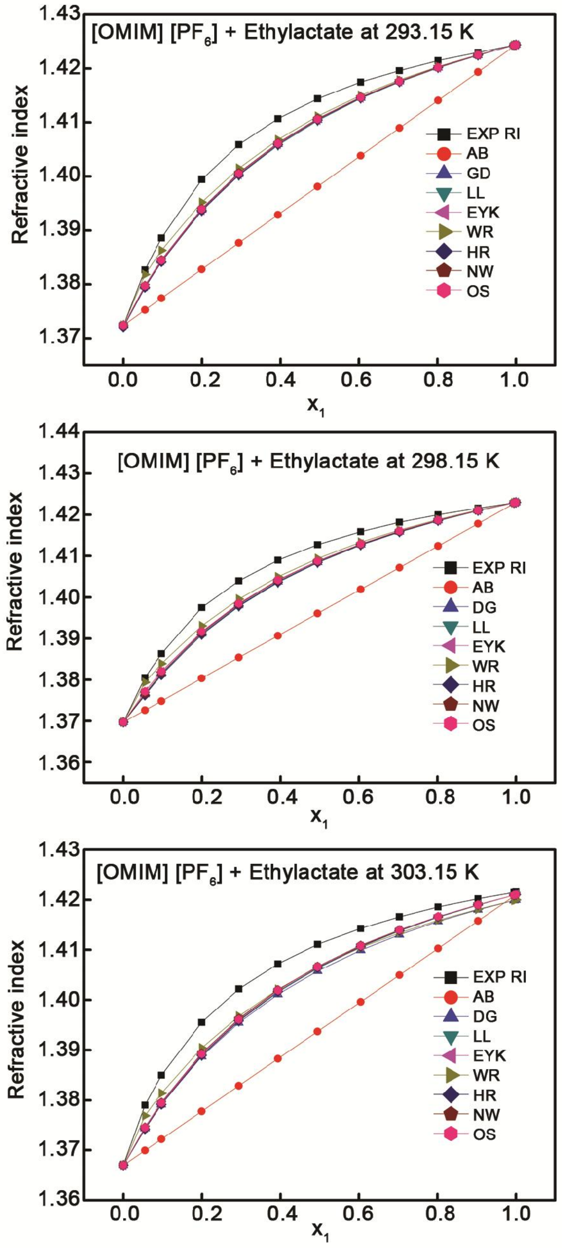

Fig. 8—Plots of refractive index versus mole fraction (x_1) for [OMIM][PF$_6$]+ethylacetate at three different temperatures.

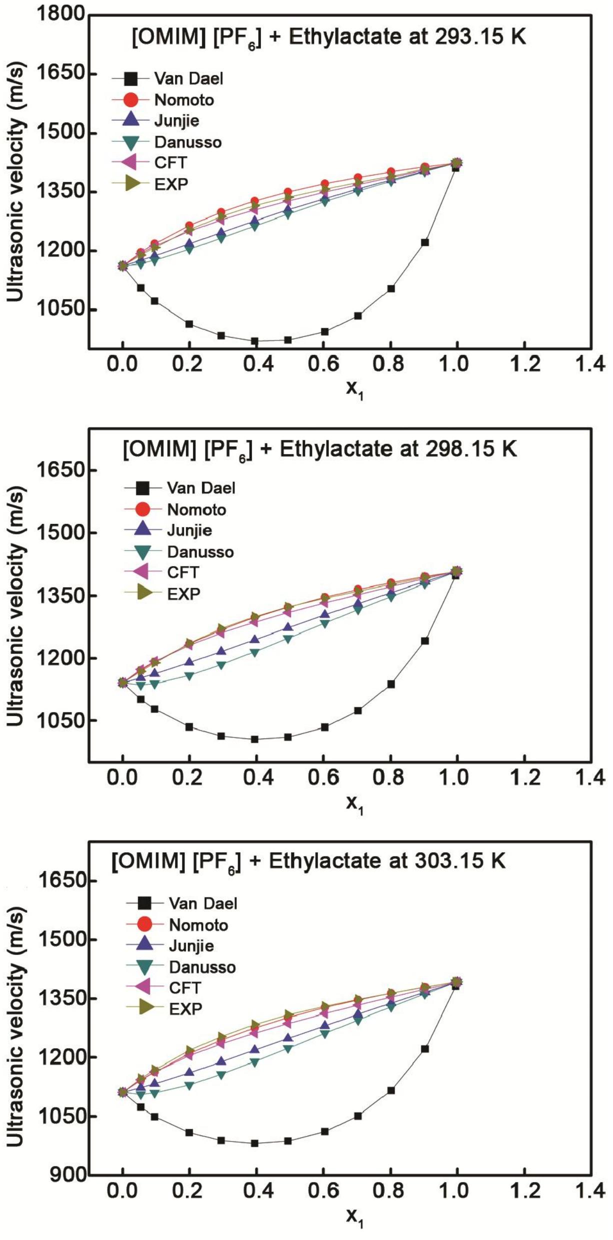

Fig. 9—Plots of ultrasonic velocity versus mole fraction (x_1) for [OMIM][PF$_6$]+ethylacetate at three different temperatures.

Interaction parameter (χ)

Interaction parameter values shows that all the system exhibit an increasing trend with the increase in temperature from 293.15 K to 303.15 K which is seen to be in conjunction with the reported literature[24] values of V_m^E . The value of interaction parameter is positive indicating the presence of strong interactions[34]. A closer look at the Figs 12 and 13 reveals that these values are higher for [MMIM][CH$_3$SO$_4$]+2-propanol and [OMIM][PF$_6$]+ethylacetate as compared to the rest of the binary systems. This behavior may be attributed to the difference in the values of ultrasonic velocity of the two components of binary mixtures being greater than any other system. A perusal of all the parameters reveals that the order of interaction in the case of [BMIM][PF$_6$] systems are [BMIM][PF$_6$]+2-butanone > [BMIM][PF$_6$]+ethylacetate > [BMIM][PF$_6$]+2-propanol, whereas in the case of [MMIM][CH$_3$SO$_4$] the order is [MMIM][CH$_3$SO$_4$]+2-propanol > [MMIM] [CH$_3$SO$_4$]+ 2-butanone > [MMIM][CH$_3$SO$_4$]+ethylacetate. [BMIM]

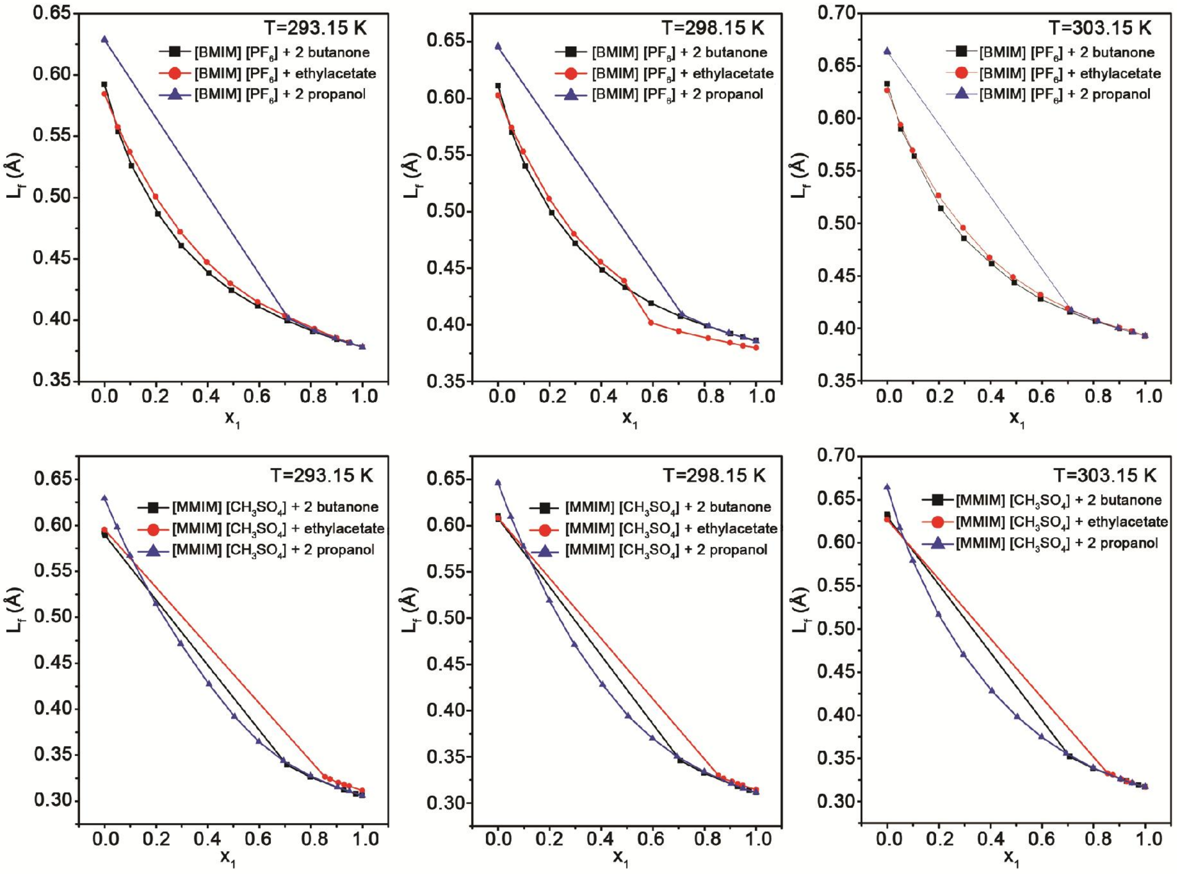

Fig. 10—Plots of intermolecular free length (L_f) versus mole fraction (x_1) for [BMIM][PF$_6$]/ [MMIM][CH$_3$SO$_4$]+2-butanone/ 2-propanol/ ethylacetate at three different temperatures.

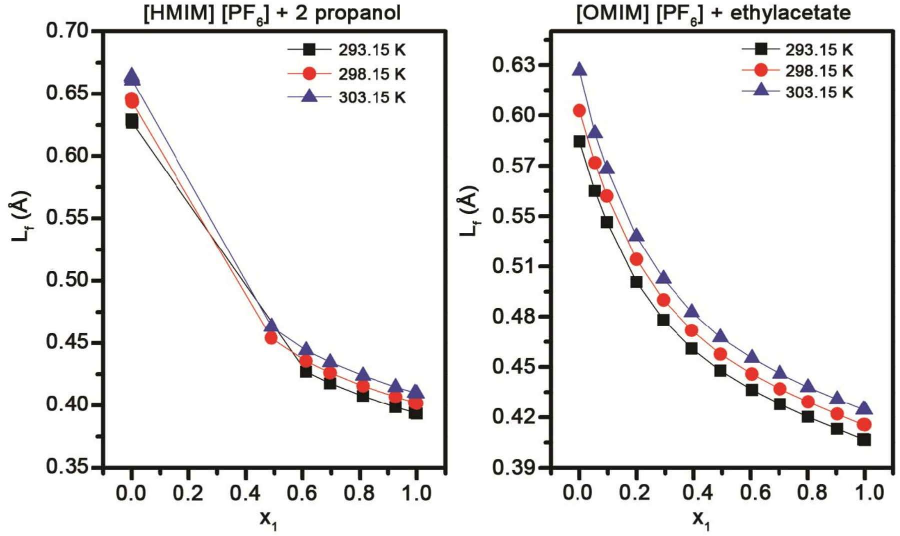

Fig. 11—Plots of intermolecular free length (L_f) versus mole fraction (x_1) for [HMIM][PF$_6$]+2-propanol and [OMIM][PF$_6$]+ethylacetate at three different temperatures.

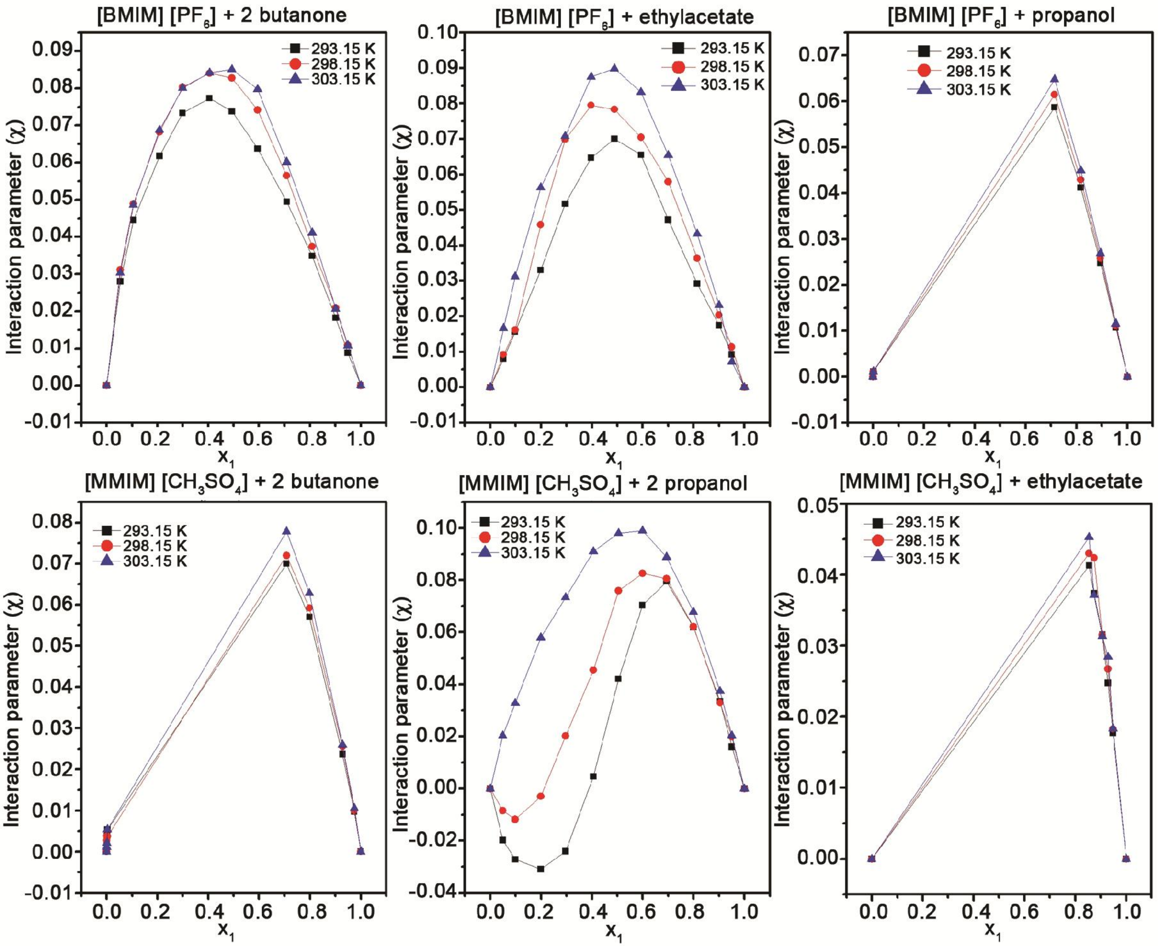

Fig. 12—Plots of interaction parameter (χ) versus mole fraction (x_1) for [BMIM][PF_6]/ [MMIM][CH_3SO_4]+2-butanone/ 2-propanol/ ethylacetate at three different temperatures.

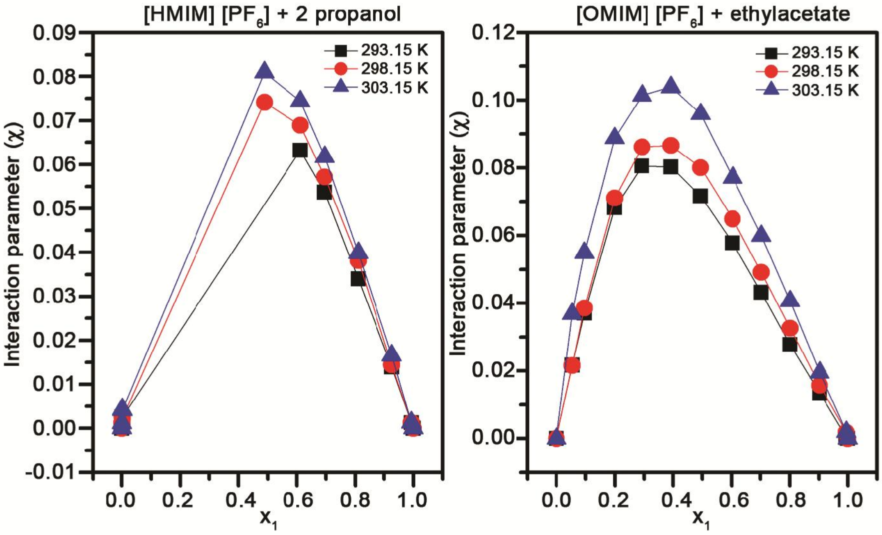

Fig. 13—Plots of interaction parameter (χ) versus mole fraction (x_1) for [HMIM][PF_6]+2-propanol and [OMIM][PF_6]+ethylacetate at three different temperatures.

$[PF_6]$ exhibits strong ion-ion interaction and forms a highly ordered three-dimensional structure which is linked by columbic interaction or H-bond or may be both. Structure of ILs is responsible for the strength of ion–ion interaction which in turn affects the ability of its anion or cation counterpart to interact with dissolved species [41]. When $[BMIM][PF_6]$ and 2-propanol are mixed together, the like-like interaction are stronger as compared to unlike interaction, due to which it exhibits least interaction among others. The solubility of IL increases with increase in the ability of polar anion to form hydrogen bond with alcohol [42]. The interaction of $CH_3SO_4^-$ anion is so strong with alcohol that maximum interaction is observed with 2-propanol. It is also reported that the ionic liquid forms a network with the interstitial spaces available in the fluid and the smaller organic molecule fits into the interstices when mixed with ionic liquid[43]. The organic liquids interact by ion dipole interaction with cation of ionic liquids. Interaction in case of $HMIM][PF_6]$ and $[OMIM][PF_6]$ increases with increase in temperature.

Excess coefficient of thermal expansion (α^E)

Coefficient of thermal expansion helps to understand the changes taking place in the structure of binary solution upon mixing[44]. Excess coefficient of thermal expansion has been calculated for entire composition range at all the temperatures to understand the molecular orientation and packing of mixtures[45]. Molecular orientation of the mixture can be attributed to occurrence of some specific interaction such as hydrogen bond for polar solvent, shape of the molecule for nonpolar solvent and dipole moment[46]. As seen from Table 4, all the excess values are seen to be negative and follow the order as described previously. As the temperature increases, value of α^E decreases for $[BMIM][PF_6]$+2-butanone and $[BMIM][PF_6]$+ethylacetate, but this trend is not so pronounced in $[BMIM][PF_6]$+2-propanol system. An increasing trend is visible till 0.3–0.4 mole fraction of the first component and then decreases for systems with $[BMIM][PF_6]$. Similar trend is also seen in $[OMIM][PF_6]$ and $[MMIM][CH_3SO_4]$ systems. The negative excess values indicate presence of specific interaction between the unlike molecules in the solution throughout the composition range for all the systems. For $[HMIM][PF_6]$ system, values of α^E are very different from those exhibited by any other system at very low mole fraction of IL. Positive α^E value is observed at mole fraction $x_1 = 0.0011$for all the three temperatures, whereas towards the IL rich region it is seen that the values do not follow a trend and these irregularities are seen to be in agreement with the non uniform behavior exhibited by the excess volume data in literature[24].

Conclusions

The present investigation is an attempt to carry out a study on the influence of thermodynamic, excess and transport parameters on the extent and the nature of the molecular interactions in binary liquids mixtures of ionic liquids comprising of imidazolium cations with different anions on their mixing with organic solvents of different molecular shape, mass and size. To the best of our knowledge, the mixing relations for the binary systems of imidazolium based ionic liquids with organic solvents have been put to test for the first time. The main aim of the work was to understand how the intermolecular interactions varied and which amongst them predominated on mixing an organic solvent with imidazolium cation based ionic liquids at different temperatures. Another motivation for carrying out the present work is to determine the feasibility of a suitable, greener alternative IL for industrial application compared to its more hazardous counterpart by studying the impact of the replacement of PF_6^- anion with the $CH_3SO_4^-$ anion. The $CH_3SO_4^-$ anion ILs are hydrolysis stable[47], halogen-free, environmentally benign compounds as compared to the PF_6^- anion based ILs which liberate highly toxic and corrosive HF on hydrolysis in the environment. This may prove to be a critical step for designing extractive processes involving the ionic liquids for azeotropic mixtures on an industrial scale.

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