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Investigation of intermolecular interactions in binary liquid mixtures of [Bmim][NTf_2] and propylene carbonate at different temperatures using ultrasonic, optical and FT-IR studies

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Abstract

Speeds of sound and refractive indices of [Bmim][NTf_2]+propylene carbonate mixtures have been measured experimentally over the entire composition range at 303.15, 308.15, 313.15, 318.15 and 323.15 K, under 101.3 kPa pressure. Semi empirical relations of speed of sound and refractive index have been applied for the liquid mixtures in terms of the pure components proposed by different investigators. The deviation of refractive index on volume fraction basis ($\Delta_\phi n_D$) reported for the binary mixture and fitted using Redlich-Kister polynomial equation. The measured and computed data have been used to interpret intermolecular interactions between unlike molecules upon mixing. This was further supported by FTIR spectroscopy.
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Keywords: Bmim][NTf_2]; Propylene carbonate; Speed of sound; Refractive index; FTIR spectroscopy

1. Introduction

Recently, Ionic Liquids attracted considerable attention because of their distinctive properties which are desirable for the field of green chemistry such as thermal stability, non-volatility and reusability [1,2]. Ionic liquids can be selected to have different anions and cations, so that one can form ionic liquid with the desired properties. Mixing of the ILs with molecular solvents is one of the alternative steps to minimize the usage of expensive ILs and to save time for preparing new ILs of desired properties [3]. Fortunately, their mixtures with molecular solvents show reduced viscosity without affecting their advantages as green solvents. Mixtures of ILs and molecular organic solvents are gaining interest of researchers as resultant liquid mixtures containing the advantages over both IL and molecular organic solvents. The measurement and interpretation of physical properties of ionic liquids and their mixtures are necessary to develop those applications and to explain the physical and chemical behavior of ILs. The properties of these mixtures are based on the mixing ratio. The importance of these

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new substances can be exploited by studying their properties like acoustic and refractive index which provide vital information about solute–solute and solute–solvent interactions occurring in mixtures.

The choice of the investigated Ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([Bmim][NTf_2]) was on the basis of its ability to act as extracting solvent for the removal many organic compounds through liquid–liquid extraction [4,5]. It is also widely used in catalysis [6] and chromatography [7]. The molecular organic solvent, Propylene carbonate (PC) used in extractions, in the production of many synthetic and natural resins and polymers [8], in the synthesis of pharmaceuticals [9], in agricultural chemistry, and as fuel additive [10]. Particularly, there is high interest in the propylene carbonate applications as storage batteries [11,12], such batteries can be recharged thermally at relatively low temperatures.

Systematic investigation of the physicochemical properties of [Bmim][NTf_2] with molecular organic solvents like ethanol or ethyl acetate [13], anisole or acetophenone [14], acetonitrile or tetrahydrofuran [15], γ-butyrolactone [16], ethanol [17], water [18] and pyrrolidin-2-one [19] have been reported. Vranes et al. [20] reported density and excess properties of [Bmim][NTf_2]+Propylene carbonate binary mixtures. However, the literature review indicates that the systematic acoustic, optical and spectroscopic properties of binary mixtures of [Bmim][NTf_2] with propylene carbonate (PC) have not been reported earlier.

On the basis of our initial experiments, [Bmim][NTf_2] is found to be totally miscible with PC in all proportions. Hence, in the present study, it is proposed to measure the speeds of sound and refractive indices of the binary mixtures of [Bmim][NTf_2] with PC in the temperature range between 303.15 and 323.15 K for the entire composition range and at atmospheric pressure. An attempt has been made to understand the interaction behavior between the two liquids in the mixture using FTIR spectroscopy. On the basis of the measured and calculated properties, molecular interactions in the binary mixtures have been interpreted for their potential application in industrial processes.

2. Experimental section

2.1. Materials

The ionic liquid, [Bmim][NTf_2] (CAS 174899-83-3) with purity 0.99 in mass fraction used in this work. It was purchased from Iolitec GmBH (Germany), while PC (CAS 108-32-7) with purity 0.995 in mass fraction was supplied by Sigma Aldrich. The chemicals used in the present investigation were purified by the methods described in literature [21,22]. The water content in investigated IL and DEC was determined using a Karl Fisher titrator (Metrohm, 890 Titrando). The water content of all the samples were further checked and found to be in the range of less than 150 ppm, a value much lower than the original pre-evacuation analysis, which typically showed values in the range of less than 210 ppm. [Bmim][NTf_2] is used without further purification; PC is further purified by distillation. List of chemicals with details of Provenance, CAS number and mass fraction purity along with the purities verified by comparing the measured speed of sound and refractive index of the pure liquids with the literature at atmospheric pressure are given in Table 1.

2.2. Procedure

Samples are prepared by weighing with a precision of ±0.01 mg, using a Sartorius electronic balance

Table 1
List of chemicals with details of Provenance, Comparison of experimental values of speed of sound, u and refractive index, n_D, of pure liquids with the corresponding literature values including density, ρ, at different temperatures and at atmospheric pressure P = 101.3 kPa.

Liquid	Provenance	Mass fraction purity	Temp/K	ρ/(kg m^{-3})	u/m s^{-1}		n_D	
				Lit.	Lit.	Lit.	Expt.	Lit.
[Bmim][NTf_2]	Io-Li-Tec, Germany	0.99	303.15	1429.40 [20]	1216.8	1216.77 [19]	1.42451	1.42523 [19]
			308.15	1424.57 [20]	1205.8	1205.80 [19]	1.42309	1.42374 [19]
			313.15	1419.61 [20]	1195.0	1194.95 [19]	1.42104	1.42225 [19]
			318.15	1414.67 [20]	1184.2	1184.23 [19]	1.41951	1.42076 [19]
			323.15	1409.65 [20]	1173.6	1173.61 [19]	1.41728	1.41923 [19]
Propylene carbonate	Sigma Aldrich	0.995	303.15	1194.00 [20]	1414.9	–	1.41802	1.4174 [23]
			308.15	1188.57 [20]	1397.9	–	1.41602	1.4155 [23]
			313.15	1183.11 [20]	1381.1	–	1.41402	
			318.15	1177.55 [20]	1364.4	–	1.41198	
			323.15	1171.96 [20]	1347.9	–	1.40995	–

(CPA225D). The uncertainty of the resulting mole fractions of the mixtures was estimated as being $\pm 2 \times 10^{-4}$. Speeds of sound are measured with an Anton Paar DSA-5000 M 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^{-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 and ±0.5 m s^{-1} respectively. The refractive indices are determined using an automatic refractometer (Anton Paar Dr Krenchen Abbemat (WR-HT)). The uncertainties in the temperature and refractive index values are ±0.01 K and $\pm 5 \times 10^{-5}$ respectively. Infrared transmittance is measured by using Shimadzu Fourier transform infrared (FT-IR) spectrometer (IR Affinity-1S) equipped with attenuated total reflectance (ATR) accessories.

3. Theory

3.1. Theoretical calculation of ultrasonic sound velocities

3.1.1. Nomoto's relation

Nomoto [24] derived the following relation for sound velocity based on the assumption of the linearity of the molecular sound velocity and the additivity of molar volume.

$$U_N = \{(\Sigma x_i R_i)/(\Sigma x_i V_i)\}^3, \quad (1)$$

where 'x_i'is mole fraction, 'R_i' is the molar sound speed and V_i is the molar volume of the ith component.

3.1.2. Van Dael and Vangeel's equation

Van Dael and Vangeel [25] obtained the ideal mixture relation

$$\sum \left(x_i M_i / u_i^2\right) = \left\{1 \Big/ \sum x_i M_i\right\}\{1/U_V\}^2, \quad (2)$$

where 'M_i' is molecular weight of ith component in the liquid mixture and U_V is the Van Dael's velocity.

3.1.3. Impedance relation

Impedance dependence relation [26] is given by

$$U_{imp} = \Sigma x_i Z_i / \Sigma x_i \rho_i, \quad (3)$$

where 'Z_i' is the acoustic impedance and 'ρ_i' is the density of the ith component of the mixture.

3.2. Refractive index mixing rules

A number of mixing rules of refractive index have been proposed for liquid mixtures in terms of the refractive indices of the pure components such as Arago–Biot (A–B) [27], Gladstone–Dale (G–D) [28], Newton (N) [29], Eyring and John (E–J) [30], Lorentz–Lorenz (L–L) [31], Heller (H) [32], Eykman (EK) [33], Oster (Os) [34] and Weiner (W) [35] were examined for present [Bmim][NTf_2]+PC mixture.

$$n = \sum_{i=1}^{2} n_i \phi_i \quad \text{Arago} - \text{Biot} \quad (4)$$

$$n - 1 = \sum_{i=1}^{2} (n_i - 1)\phi_i \quad \textit{Gladstone} - \textit{Dale} \quad (5)$$

$$n^2 - 1 = \sum_{i=1}^{2} \left(n_i^2 - 1\right)\phi_i \quad \textit{Newton} \quad (6)$$

$$n = n_1\phi_1^2 + 2(n_1 n_2)^{1/2}\phi_1\phi_2 + n_2\phi_2^2 \quad \textit{Eyring} - \textit{John} \quad (7)$$

$$\frac{n^2 - 1}{n^2 + 2} = \sum_{i=1}^{2} \left(\frac{n_i^2 - 1}{n_i^2 + 2}\right)\phi_i \quad \textit{Lorentz} - \textit{Lorenz equation} \quad (8)$$

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \quad \textit{Heller} \quad (9)$$

$$\frac{n^2 - 1}{n^2 + 0.4} = \sum_{i=1}^{2} \left(\frac{n_i^2 - 1}{n_i^2 + 0.4}\right)\phi_i \quad \textit{Eykman} \quad (10)$$

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \sum_{i=1}^{2} \left(\frac{\left(n_i^2 - 1\right)\left(2n_i^2 + 1\right)}{n_i^2}\right)\phi_i \quad \textit{Oster} \quad (11)$$

$$\frac{n^2 - n_1^2}{n^2 + 2n_1^2} = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \quad \textit{Wiener} \quad (12)$$

where, ϕ_i, is the volume fraction of the ith component and is given by $\phi_i = \frac{x_i V_i}{\sum_{i=1}^{2} x_i V_i} n_i$ and n are the refractive indices of each component and mixture respectively.

The Absolute Percentage Deviation (APD) of experimental refractive index is calculated by the relation

$$AAD = \frac{100}{n} \sum_{i=1}^{n} \left(\left|\frac{n_{cal}}{n_{\exp}} - 1\right|\right) \quad (13)$$

where n_{exp} is experimental refractive index and n_{cal} is the value calculated from various mixing rules and 'n' is the number of data points.

The Maximal deviation (M Dev) is given by

$$MDev = 100*\max\left|\frac{n_{cal}}{n_{\exp}} - 1\right| \quad (14)$$

3.3. Deviations in refractive index

$$n_D^{id} = \phi_1 n_{D,1} + \phi_2 n_{D,2} \quad (15)$$

$$\Delta_\phi n_D = n_D - n_D^{id} \quad (16)$$

The deviation in refractive index is fitted to the following Redlich-Kister polynomial equation and the corresponding values are represented in Table 3.

$$Y^E = x_1 x_2 \sum_{i=o}^{j} A_i (x_1 - x_2)^i \quad (17)$$

4. Results and discussion

The values of the experimental speed of sound, u, and refractive index, n_D for the binary mixtures of [Bmim][NTf_2] with PC as a function of mole fraction, x_1 of [Bmim][NTf_2] at investigated temperatures are given in Table 2. The speeds of sound of [Bmim][NTf_2]+PC binary system is decreasing as the concentration of IL increases and decreases with rise in temperature. The trend indicates that the mixtures become more compressible at IL rich region and also the mixtures become more compressible at higher temperatures. However, theoretical formulations based on Nomoto, Van Dael and Vangeel, Impedance equations are widely used to calculate speeds of sound in binary systems of nonelectrolyte mixtures. Therefore, we in the present work attempt to extend these formulations for calculating the speeds of sound in [Bmim][NTf_2]+PC mixtures. The pertinent relations are summarized in theory section. The calculated ultrasonic speeds along with the experimental speeds are represented in Fig. 1 and deviations in the calculated values from the experimental values are listed in Table 4. The results indicate that Nomato's and Impedance relations provide the best results for ultrasonic speeds of the system under study when compared to Van Deal and Vangeel's relations. The large deviations for Van Deal and Vangeel's relation is expected, as this formulation is applicable for nonassociating binary

Table 2
Experimental speed of sound (u), refractive index (n_D mole fraction (x_1) of [Bmim][NTf_2] in the binary liquid mixture of {[Bmim][NTf_2]+Propylene Carbonate} 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	
	u/m s^{-1}	n_D	u/m s^{-1}	n_D	u/m s^{-1}	n_D	u/m s^{-1}	n_D	u/m s^{-1}	n_D
0.0000	1414.91	1.41802	1397.92	1.41602	1381.10	1.41402	1364.43	1.41198	1347.93	1.40995
0.0522	1392.42	1.41892	1376.13	1.41697	1360.02	1.41502	1344.05	1.41305	1328.24	1.41109
0.0903	1376.93	1.41955	1361.14	1.41762	1345.50	1.41571	1330.02	1.41378	1314.68	1.41187
0.1422	1357.09	1.42034	1341.92	1.41845	1326.90	1.41658	1312.04	1.41471	1297.31	1.41286
0.1963	1337.96	1.42110	1323.39	1.41924	1308.97	1.41742	1294.70	1.41560	1280.55	1.41381
0.3000	1305.68	1.42237	1292.11	1.42057	1278.68	1.41882	1265.41	1.41709	1252.24	1.41540
0.3959	1280.98	1.42332	1268.18	1.42157	1255.51	1.41987	1242.98	1.41820	1230.56	1.41658
0.4993	1259.91	1.42410	1247.75	1.42240	1235.71	1.42074	1223.81	1.41912	1212.02	1.41755
0.6001	1244.92	1.42462	1233.20	1.42297	1221.60	1.42133	1210.14	1.41974	1198.79	1.41819
0.7112	1234.73	1.42492	1223.29	1.42331	1211.97	1.42168	1200.79	1.42010	1189.71	1.41856
0.7826	1231.69	1.42496	1220.31	1.42337	1209.07	1.42174	1197.94	1.42015	1186.93	1.41860
0.8290	1229.69	1.42499	1218.29	1.42337	1207.02	1.42177	1195.88	1.42017	1184.84	1.41860
0.8736	1227.30	1.42504	1215.87	1.42337	1204.58	1.42183	1193.41	1.42022	1182.36	1.41863
0.9432	1222.29	1.42514	1210.96	1.42348	1199.77	1.42200	1188.71	1.42042	1177.75	1.41884
1.0000	1216.77	1.42523	1205.80	1.42374	1194.95	1.42225	1184.23	1.42076	1173.61	1.41924

Table 3
Redlich-Kister coefficients of deviation of refractive indices and corresponding standard deviations (σ) for the systems at different temperatures.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
$(\Delta_\phi n_D)$	303.15	0.00202	0.00227	−0.00479	0.00097	−0.00007	0.00001
	308.15	0.00186	0.00238	−0.00523	0.00089	0.00011	0.00002
	313.15	0.00173	0.00239	−0.00539	0.00089	0.00002	0.00002
	318.15	0.00162	0.00236	−0.00590	0.00098	0.00049	0.00003
	323.15	0.00151	0.00237	−0.00643	0.00120	0.00107	0.00003

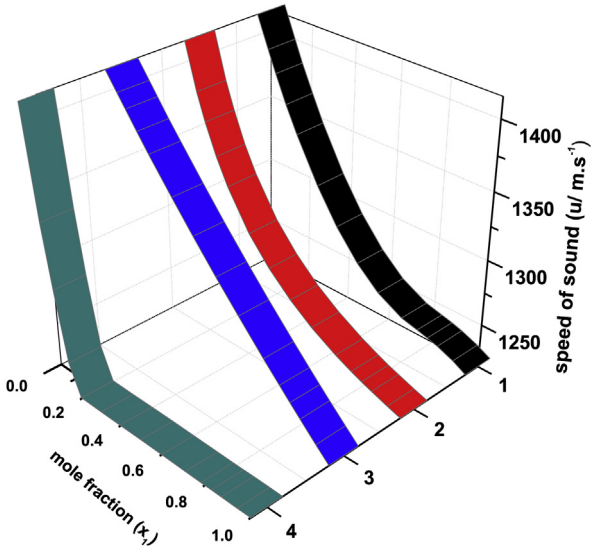

Fig. 1. Plots of speeds of sound (u) calculated from various theories along with experimental values against mole fraction of [Bmim][NTf_2] in the mixture with PC at 303.15 K. 1- Expt. 2- Nomato 3- Imped 4- Vand-Vang.

Table 4
Average percentage deviation of calculated speeds of sound compared to experimental values at various temperatures of [Bmim][NTf_2] and propylene carbonate binary mixture at T = (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/K	Nomato	Imped	Vand-Vang
303.15	0.46	−1.73	8.20
308.15	0.45	−1.69	8.28
313.15	0.44	−1.65	8.35
318.15	0.43	−1.61	8.42
323.15	0.42	−1.57	8.50
Average	0.44	−1.65	8.35

systems, while [Bmim][NTf_2]+PC binary mixture displays strong nonideal deviations.

The refractive indices (n_D) for the binary mixtures at the studied temperatures over the whole composition range were given in Table 2. Refractive index increases as the concentration of the ILs in the mixture increases. For the fixed concentration of [Bmim][NTf_2], as the temperature increases, n_D decreases which may be due to the non availability of free volume which leads to more compressible structure in the mixture as compared to the ideal mixtures [36]. The values of $\Delta_\phi n_D$ are positive at $x_1 > 0.3$ for the binary mixtures (Fig. 2) which may be attributed to the non-availability of the free volume in the mixture in comparison with the ideal mixtures. It is very similar to the V_m^E reported in the literature for the binary mixture [20].

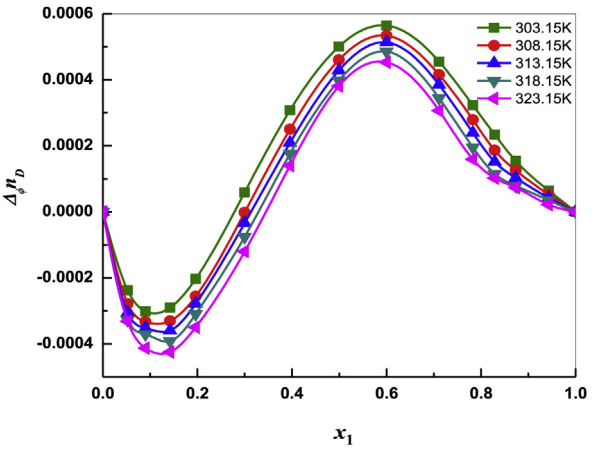

Fig. 2. Plots of deviation in refractive index ($\Delta_\varnothing n_D$) against mole fraction of [Bmim][NTf_2] in the mixture with PC at different temperatures.

A number of mixing rules of refractive index (n_D) have been proposed by different investigators were examined for present [Bmim][NTf_2]+PC mixture. The refractive indices values calculated from various theories along with experimental values at different temperatures are represented in Fig. 3. The absolute percentage deviation is obtained as described in eq (13) are represented at Table 5. From these calculations, we conclude that the Newton equation is the one that best fitted our experimental results.

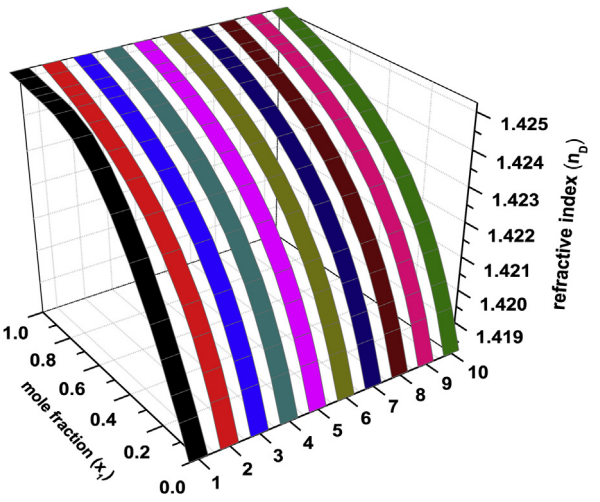

Fig. 3. Plots of refractive indices (n_D) calculated from various theories along with experimental values against mole fraction of [Bmim][NTf_2] in the mixture with PC at 303.15 K. 1- Expt. 2- Ara–Biot 3- Gla–Dale 4- Newton 5- Eyri–John 6- Lor–Lor 7- Heller 8- Eykman 9- Oster 10-Wiener.

Table 5
Average percentage deviation of calculated refractive indices compared to experimental values at various temperatures of [Bmim][NTf_2] and propylene carbonate binary mixture at T = (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/K	A–B	G–D	N	E–J	L–L	H	EK	Os	W
303.15	0.008	0.008	0.007	0.008	0.008	0.008	0.008	0.008	0.008
308.15	0.005	0.005	0.005	0.005	0.005	0.005	0.006	0.006	0.005
313.15	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.004	0.004
318.15	0.002	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002
323.15	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000
Average	0.004	0.004	0.003	0.004	0.004	0.004	0.004	0.004	0.004

4.1. Infrared spectral studies

The existence of interactions in the system which were drawn from the above inferences of derived excess/deviation parameters are well supported by IR spectral studies. The unique properties of imidazolium cations are found in their electronic structure. The hydrogen in C_2-H is more acidic than C_4-H, and C_5-H due to the electron deficiency in the C=N bond. The resultant acidity of the hydrogen atoms is the key to understand the properties of these ionic liquids. The hydrogen on the C_2 carbon (C_2-H) has been shown to bind typically with solute molecules [37].

In order to study the effects of molecular interactions, infrared absorbance is recorded from 650 cm^{-1} to 4000 cm^{-1} (Fig. 4 and Table 6). In $[Bmim]^+$ cation, the C-H stretching region from 2800 to 3200 cm^{-1} is investigated. For [Bmim][NTf_2], the signals in this region can be separated into two parts: signals between 3000 cm^{-1} and 3200 cm^{-1} can be attributed to C-H vibrational modes mainly arising from the aromatic imidazolium ring, from C_2-H and $C_{4,5}$-H stretching frequencies [38]. The signals between 2800 cm^{-1} and 3000 cm^{-1} are due to aliphatic C-H groups in the methyl and butyl moieties [39–41]. The C_2-H vibrational frequency (3121.4 cm^{-1}) is

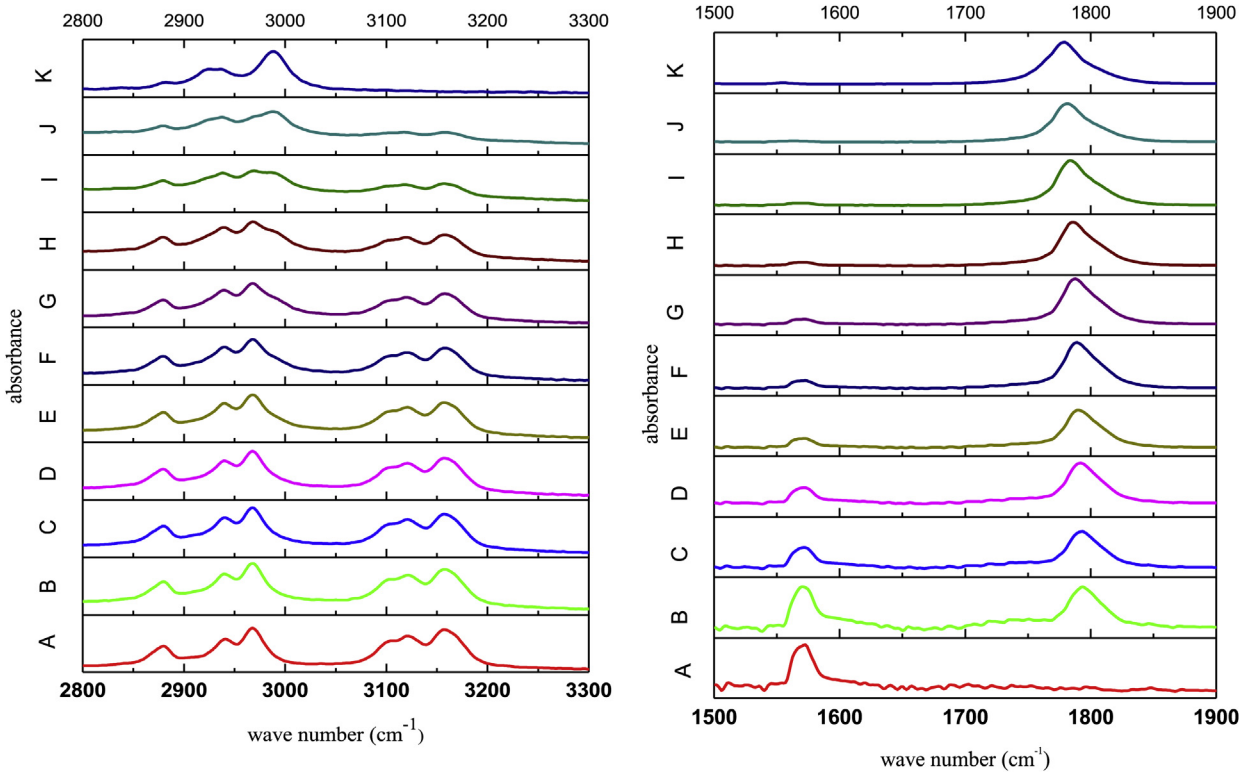

Fig. 4. Infrared spectra (1500 cm^{-1}–1900 cm^{-1} and 2800 cm^{-1}–3300 cm^{-1}) of (A) Pure IL [Bmim][NTf_2]; (B) 0.8736; (C) 0.7826; (D) 0.7112; (E) 0.6001; (F) 0.4993; (G) 0.3959; (H) 0.3000; (I) 0.1963; (J) 0.0903and (K) Pure PC. (B), (C), (D), (E), (F), (G), (H), (I), (J) represents mole fraction of [Bmim][NTf_2] in the mixture with PC.

Table 6
Infrared absorbance wave numbers (cm^{-1}) between 2800 and 3200 of [Bmim][NTf_2] in PC at room temperature and atmospheric pressure P = 101.3 kPa.

Mole fraction of [Bmim][NTf_2]	Mole fraction of PC	C_2-H stretching	$C_{4,5}$-H stretching	C=O sym stretch
0.0000	1.0000	–	–	1778.7
0.0903	0.9097	3118.1	3157.5	1781.4
0.1963	0.8037	3118.6	3157.8	1783.7
0.3000	0.7000	3119.2	3157.8	1785.8
0.3959	0.6041	3119.3	3157.5	1787.5
0.4993	0.5007	3120.2	3157.5	1788.9
0.6001	0.3999	3120.5	3156.5	1790.0
0.7112	0.2888	3120.7	3156.8	1792.1
0.7826	0.2174	3120.9	3157	1793.3
0.8736	0.1264	3121.2	3157.2	1793.6
1.0000	0.0000	3121.4	3157.5	–

shifted to lower frequencies by about 36.1 cm^{-1} when compared to the C_4-H and C_5-H stretches (3157.5 cm^{-1}) because of its stronger acidic character. In the present mixtures, C_2-H and $C_{4,5}$-H stretching frequencies of the cation is analyzed (Fig. 4). The experimental ATR-IR spectra for PC for the C=O stretching (Fig. 4) spectral regions are reported. A peak at 1778.7 cm^{-1} corresponding C=O stretching region of pure PC [42,43]. The band around 1575 cm^{-1} belongs to ring in-plane symmetric/anti-symmetric stretch, CH_2(N) and CH_3(N) CN stretch of pure [Bmim][NTf_2] [44].

As mole fraction of PC increases a blue shift in C_2-H and $C_{4,5}$-H stretching frequencies indicating the formation of hydrogen bond between $[Bmim]^+$ and PC. The blue shift is very predominant in C_2-H frequencies when compared to $C_{4,5}$-H stretching frequencies which indicates that more acidic C_2-H plays major role in the formation of hydrogen bond with carbonyl oxygen of PC (Fig. 4). Simultaneously, as mole fraction of IL increases a clear red shift in C=O Sym Stretch frequencies is observed in PC. This clearly indicates the formation of intermolecular hydrogen bond between hydrogens of aromatic imidazolium ring and carbonyl oxygen of PC.

By examining ATR-FTIR, it can be accomplished that hydrogen bonds exist extensively in such systems which play a key role towards the miscibility and stability of the [Bmim][NTf_2]+PC binary system. Additionally, the hydrogen bonding interactions are also accountable in the present system to get complete miscibility and solvation. Hence, it can be assumed that contraction in volumes of the mixtures are because of hydrogen bonds between the ionic liquid [Bmim][NTf_2] and PC.

5. Conclusions

Ultrasonic speed of sounds and refractive indices for binary liquids of [Bmim][NTf_2] with PC have been measured experimentally at atmospheric pressure over the entire composition range at temperature 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K. In the present binary liquid system, the observed excess values clearly reflecting the dominance of strong attractive forces. The IR spectral studies also supported the inferences drawn from excess properties.

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