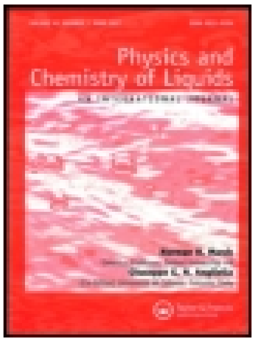

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ARTICLE

Volumetric, acoustic, optical and spectroscopic studies of binary mixtures of the ionic liquid, 1-butyl-3-methyl imidazolium bis (trifluoromethylsulfonyl)imide and diethyl carbonate

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ABSTRACT

The properties, density, speed of sound and refractive index of 'IL' [Bmim][NTf2], diethyl carbonate and their binary mixtures are measured over the whole composition range as a function of temperature between 303.15 and 323.15 K at atm. pressure. These values are used to calculate the excess molar volumes, excess partial molar volumes, partial molar volumes at infinite dilution, excess isentropic compressibility, free length, speeds of sound and isobaric thermal expansion coefficient for the mixture. Various rules were used to predict the refractive indices and the data have been compared with the experimental results. These excess properties are fitted to the Redlich–Kister type equation to obtain the binary coefficients and the standard deviations. A qualitative analysis of these parameters indicates strong intermolecular interactions and the interaction increases with the increase in temperature. This was further supported by IR spectroscopy. In addition, analysis of data of the mixture was done through the Prigogine–Flory–Patterson theory.

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KEYWORDS
Ionic liquid [Bmim][NTf2]; DEC; density; speed of sound; excess thermodynamic parameters; PFP theory

1. Introduction

Substances that are entirely composed of ions and in liquid state are called ionic liquids (ILs). In present days, they attracted considerable attention because of their distinctive properties such as thermal stability, non-volatility and reusability [1–5]. ILs can be selected to have different anions and cations so that one can form IL with the desired properties. ILs with special functional groups have been designed for application in many industrial processes [6,7]. ILs are utilised for different purposes like extraction, separation and alternative solvents in catalytic reactions, synthesis, catalysis, biocatalyst, electro chemical devices, separation technology, reaction media, green solvents and in biodegradable materials.

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 properties of these mixtures are based on the mixing ratio. Mixing of the ILs with molecular solvents is one of the alternative steps not only to minimise the usage of expensive ILs and also to save time for preparing new ILs [8]. From an economic and ecological perspective, the mixtures of ILs and traditional organic solvents may be gaining a

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Supplementary data for this article can be accessed here.

tremendous amount of attention from both the researchers and the industries. ILs are more viscous than conventional organic solvents, which may hamper their application. Fortunately, their mixtures with molecular solvents show reduced viscosity to exploit their potential applications. In particular, the addition of polar co-solvents can strongly influence the physical and chemical properties of ILs such as viscosity, reactivity and electrical conductivity as well as solubility and solvation properties [9]. Recently, several binary IL+ molecular solvent systems have been shown to perform better than the pure ILs, and such systems have been used in numerous applications such as biocatalysed reactions, as super capacitors, as reaction media, medium for dissolution of biopolymers etc. [10–22]. Hence, IL+ molecular solvent mixtures have received growing attention in the past few years. The potential of these new substances can be exploited with experimental methods. Most of these novel media are characterised by their volumetric, acoustic and refractive index properties, since these data are important for industrial applications. To predict molecular interactions between binary liquids, speed of sound and refractive index along with experimental data of density plays vital role.

The choice of the investigated IL, 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 of many organic compounds through liquid–liquid extraction [23,24]. It is also widely used in catalysis [25] and chromatography [26]. The molecular organic liquid, diethyl carbonate (DEC), has been chosen because of its wide range of applications such as fuel additive, as green solvent for the replacement to conventional organic solvents and in organic synthesis [27]. It is also widely used in pesticides, fertiliser, manufacture of dyes and pharmaceutical products. DEC is expansively investigated as an electrolyte for lithium ion batteries [28,29].

Systematic investigation of the physicochemical properties of [Bmim][NTf$_2$] with molecular organic solvents including water has been reported. Alfonsina *et al.*[30] reported the physicochemical properties such as density, refractive index, viscosity of [Bmim][NTf$_2$] binary mixture with ethanol or ethyl acetate. Zarrougui *et al.* [31] reported the density, viscosity and conductivity and thermal expansivities of propylene carbonate with [Bmim][NTf$_2$], whereas Widowati *et al.* [32] reported pressure–volume–temperature properties of binary mixtures of the [Bmim][NTf$_2$] with anisole or acetophenone at elevated pressures. Vranes *et al.* [33] reported density and excess properties of [Bmim][NTf$_2$] + Propylene carbonate binary mixtures, Monika *et al.* [34] reported acoustic and volumetric properties of binary mixtures of [Bmim][NTf$_2$] with acetonitrile or tetrahydrofuran, Vranes *et al.* [35] reported density, electrical conductivity and viscosity of binary liquid mixtures of [Bmim][NTf$_2$], with γ-butyrolactone, Salinas *et al.* [36] reported densities, speed of sound, viscosity and excess properties of binary mixtures formed by ethanol and [Bmim][NTf$_2$], Jacquemin *et al.*[37] reported the density and viscosity of several pure and water-saturated ILs including [Bmim][NTf$_2$], Kassim *et al.* [38] reported the experimental densities and viscosities of binary mixture of [Bmim][NTf$_2$] with glycerol or sulfolane and their molecular interaction by COSMO-RS and Krishna *et al.*[39] reported densities, speeds of sound and refractive indices of the binary mixture of [Bmim][NTf$_2$] with pyrrolidin-2-one. But the thermo-acoustic, volumetric and refractive index data of [Bmim][NTf$_2$] with DEC were not reported.

On the basis our initial experiments, [Bmim][NTf$_2$] is found to be totally miscible with DEC in all proportions. Hence, in the present study, it is proposed to measure the densities, speeds of sound and refractive indices of the binary mixtures of [Bmim][NTf$_2$] with DEC in the temperature range between 303.15 and 323.15 K in the entire composition range and at atmospheric pressure. On the basis of the measured values, we calculated the excess/deviation properties for their potential application in industrial processes. Here, we reported the excess properties such as molar volumes (V_m^E), isentropic compressibilities (κ_s^E), free length (L_f^E), speeds of sound (u^E) and isobaric thermal expansion coefficient (α_P^E) along with $\left(\partial V_m^E/\partial T\right)_P$

and $\left(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial P\right)_T$. Also, the deviation of refractive index on volume fraction basis ($\Delta_{\phi}n_{\mathrm{D}}$) reported for the binary mixture and fitted using Redlich–Kister polynomial equation. Lastly, an attempt has been made to understand the interaction behaviour between the two liquids in the mixture using IR spectroscopy. In addition, analysis of $V_{\mathrm{m}}^{\mathrm{E}}$ data of the present mixture was done through the Prigogine–Flory–Patterson (PFP) theory.

2. Experimental section

2.1. *Materials*

The IL, [Bmim][NTf_2] (CAS 174899-83-3) with purity 0.99 in mass fraction used in this work. It was purchased from Io-Li-Tec GmbH (Germany), while DEC (CAS 105-58-8) 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 [40,41]. The water content in investigated IL and DEC was determined using a Karl Fisher titrator (Mtrohm, 890 Titrando). Before any measurement, all samples were dried for at least 72 h under a vacuum (0.1 Pa) and moderate temperature (beginning at room temperature and increasing it gradually over a 6-h period up to 333 K). The water content of all the samples was 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; DEC is further purified by distillation. List of chemicals with details of provenance, CAS number and mass fraction purity is given in Table 1. The purities were verified by comparing the measured density, speed of sound and refractive index of the pure liquids with the literature at atmospheric pressure are given in Table 2.

Table 1. List of chemicals with details of provenance, CAS number and mass fraction purity.

Chemical	Provenance	CAS number	Purification method	Mass fraction purity	Final water mass fraction	Analysis method
1-Butyl-3-methylimidazoliumbis (trifluoromethylsulfonyl) imide	Io-Li-Tec, Germany	174899-83-3	Vacuum treatment	0.99	$<1.5 \times 10^{-4}$	NA
Diethyl carbonate	Sigma Aldrich	105-58-8	Distillation	0.995	$<1.5 \times 10^{-4}$	Gas liquid chromatography

Table 2. 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.

		ρ (kg m^{-3})		u (m s^{-1})		n_D		C_p (J K^{-1} mol^{-1})
Liquid	Temp (K)	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Lit.
[Bmim][NTf_2]	303.15	1428.9	1429.40 [35]	1216.8	1216.77 [39]	1.42451	1.42523 [39]	569.74 [39]
	308.15	1424.1	1424.57 [35]	1205.8	1205.80 [39]	1.42309	1.42374 [39]	572.82 [39]
	313.15	1419.4	1419.61 [35]	1195.0	1194.95 [39]	1.42104	1.42225 [39]	575.56 [39]
	318.15	1414.6	1414.67 [35]	1184.2	1184.23 [39]	1.41951	1.42076 [39]	578.49 [39]
	323.15	1409.9	1409.65 [35]	1173.6	1173.61 [39]	1.41728	1.41923 [39]	581.68 [39]
Diethyl carbonate	303.15	963.7	963.5 [43]	1156.6	1156.9 [43]	1.37991	1.3802 [43]	213.82 [44]
	308.15	958.1	957.8 [43]	1136.3	1136.6 [43]	1.37755	1.3779 [43]	214.88 [44]
	313.15	952.4	952.1 [43]	1116.1	1116.5 [43]	1.37526	1.3756 [43]	215.82 [44]
	318.15	946.7	946.4 [43]	1096.2	1096.5 [43]	1.37290	1.3733 [43]	218.54 [44]
	323.15	941.0	940.7 [43]	1076.4	1076.7 [43]	1.37055	1.3710 [43]	220.31 [44]

Standard uncertainties u are $u(\rho) = 5 \times 10^{-2}$ kg m^{-3}, $u(u) = 0.5$ m s^{-1}, $u(n_D) = 0.00005$, $u(T) = 0.01$ K and $u(P) = 0.5$ kPa.

2.2. *Apparatus and procedure*

2.2.1. *Sample preparation*

All samples are freshly prepared in amber colour glass vials with screw caps having PFE septa, and a secure seal with parafilm to prevent absorption of moisture from the atmosphere and are then stirred for more than 30 min to ensure total dissolution of the mixtures. Samples are taken from the vials with a syringe through the PFE septum. Samples are prepared by weighing with a precision of ±0.01 mg, using a Sartorius electronic balance (CPA225D). The uncertainty of the resulting mole fractions of the mixtures was estimated as being $\pm 2 \times 10^{-4}$.

2.2.2. *Measurement of density and speed of sound*

Densities and speed of sound are measured with an Anton Paar DSA-5000M-vibrating tube density and sound velocity meter. The density meter is calibrated with doubly distilled degassed water, and with dry air at atmospheric pressure. The temperature of the apparatus is controlled to within ±0.01 K by a built-in Peltier device. Measured density and speed of sound values (at frequency approximately 3 MHz) are precise to 5×10^{-3} kg m^{-3} and 5×10^{-1}m s^{-1}, respectively. The standard uncertainties associated with the measurements of temperature, density and speed of sound are estimated to be ±0.01 K, 5×10^{-2} kg m^{-3} and ±0.5 m s^{-1}, respectively.

2.2.3. *Measurement of refractive index*

The refractive indices are determined using an automatic refractometer (Anton Paar Dr Krenchen Abbemat (WR-HT)) that 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 $\pm 5 \times 10^{-5}$, 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.

2.2.4. *Measurement of infrared spectra*

Infrared transmittance is measured by using Shimadzu Fourier transform infrared spectrometer (IR Affinity-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

The experimentally measured density (ρ), speed of sound (u) and refractive index (n_D) for the binary mixture of [Bmim][NTf_2] with DEC over the region of complete miscibility as a function of temperature between 303.15 and 323.15 K in steps of 5 K under atmospheric pressure are given in Table 3. The changes in values of ρ, u and n_D with respect to temperature and mole fraction are linear and non-linear, respectively. This trend specifies that molecular interactions definitely exist at all temperature between liquids in study. The excess and deviation parameters are calculated from the experimental data according to well-known thermodynamic expressions given below.

The excess molar volume is given by

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \qquad (1)$$

where M_1 and M_2 are the molecular weights, x_1 and x_2 are the mole fractions of [Bmim][NTf_2] and DEC, respectively, while ρ_1, ρ_2 and ρ are the densities of [Bmim][NTf_2], DEC and the mixture, respectively.

Table 3. 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][NTf$_2$] in the binary liquid mixture of {[Bmim][NTF$_2$] + diethyl carbonate} from T (K) = 303.15–323.15 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})	k_s(10^{-10}Pa^{-1})	L_f(10^{-11}m)	a_p(10^{-4} K^{-1})
303.15 K							
0.0000	963.7	1156.6	1.37991	122.58	7.76	5.780	11.81
0.0542	1023.8	1159.2	1.38693	131.33	7.27	5.596	10.81
0.1108	1077.1	1167.9	1.39318	140.66	6.81	5.415	10.02
0.1522	1111.7	1173.8	1.39679	147.51	6.53	5.303	9.57
0.2084	1153.3	1181.1	1.40116	156.85	6.22	5.175	9.08
0.2886	1203.8	1190.0	1.40600	170.35	5.87	5.027	8.54
0.3927	1256.9	1199.0	1.41107	188.10	5.53	4.883	8.06
0.4805	1293.5	1204.5	1.41434	203.23	5.33	4.791	7.79
0.5887	1331.1	1208.9	1.41724	221.96	5.14	4.706	7.54
0.7043	1364.9	1211.5	1.41988	241.99	4.99	4.637	7.29
0.8009	1389.2	1213.0	1.42179	258.70	4.89	4.591	7.05
0.8586	1402.1	1213.9	1.42278	268.71	4.84	4.566	6.89
0.9127	1413.2	1215.1	1.42382	278.15	4.79	4.544	6.76
0.9521	1420.4	1216.3	1.42448	285.08	4.76	4.528	6.69
1.0000	1428.9	1216.8	1.42523	293.48	4.73	4.513	6.66
308.15 K							
0.0000	958.1	1136.3	1.37755	123.30	8.08	5.955	11.88
0.0542	1018.3	1139.3	1.38470	132.04	7.57	5.761	10.88
0.1108	1071.7	1149.6	1.39102	141.36	7.06	5.565	10.09
0.1522	1106.3	1156.5	1.39478	148.22	6.76	5.444	9.64
0.2084	1148.1	1164.9	1.39931	157.57	6.42	5.306	9.14
0.2886	1198.6	1174.9	1.40417	171.09	6.04	5.149	8.60
0.3927	1251.8	1185.0	1.40935	188.86	5.69	4.995	8.11
0.4805	1288.4	1191.1	1.41264	204.02	5.47	4.898	7.83
0.5887	1326.2	1196.2	1.41564	222.80	5.27	4.808	7.58
0.7043	1360.0	1199.5	1.41837	242.87	5.11	4.735	7.32
0.8009	1384.3	1201.4	1.42028	259.61	5.00	4.685	7.08
0.8586	1397.3	1202.6	1.42130	269.64	4.95	4.659	6.92
0.9127	1408.3	1203.9	1.42234	279.10	4.90	4.635	6.78
0.9521	1415.6	1205.2	1.42301	286.04	4.86	4.619	6.71
1.0000	1424.1	1205.8	1.42374	294.47	4.83	4.602	6.68
313.15 K							
0.0000	952.4	1116.1	1.37526	124.03	8.43	6.135	11.96
0.0542	1012.8	1121.1	1.38269	132.76	7.86	5.923	10.95
0.1108	1066.3	1132.1	1.38935	142.08	7.32	5.716	10.16
0.1522	1101.0	1139.5	1.39306	148.93	7.00	5.589	9.70
0.2084	1142.8	1148.6	1.39758	158.29	6.63	5.442	9.20
0.2886	1193.5	1159.7	1.40246	171.82	6.23	5.274	8.66
0.3927	1246.8	1170.9	1.40763	189.63	5.85	5.111	8.16
0.4805	1283.4	1177.9	1.41096	204.82	5.62	5.008	7.88
0.5887	1321.2	1183.7	1.41405	223.64	5.40	4.911	7.62
0.7043	1355.0	1187.6	1.41688	243.75	5.23	4.834	7.36
0.8009	1379.4	1189.9	1.41884	260.54	5.12	4.782	7.11
0.8586	1392.4	1191.2	1.41988	270.58	5.06	4.754	6.95
0.9127	1403.5	1192.8	1.42085	280.05	5.01	4.729	6.81
0.9521	1410.9	1194.2	1.42155	287.01	4.97	4.711	6.74
1.0000	1419.4	1195.0	1.42225	295.46	4.93	4.694	6.71
318.15 K							
0.0000	946.7	1096.2	1.37290	124.78	8.79	6.321	12.03
0.0542	1007.2	1102.3	1.38101	133.49	8.17	6.094	11.02
0.1108	1060.9	1114.4	1.38807	142.81	7.59	5.873	10.23
0.1522	1095.6	1122.5	1.39200	149.66	7.24	5.737	9.77
0.2084	1137.6	1132.5	1.39635	159.03	6.85	5.581	9.27
0.2886	1188.4	1144.7	1.40129	172.56	6.42	5.402	8.71
0.3927	1241.8	1157.1	1.40626	190.39	6.01	5.228	8.21
0.4805	1278.5	1164.8	1.40929	205.62	5.77	5.119	7.92
0.5887	1316.2	1171.3	1.41249	224.49	5.54	5.017	7.66
0.7043	1350.0	1175.8	1.41531	244.66	5.36	4.935	7.39
0.8009	1374.5	1178.5	1.41734	261.46	5.24	4.879	7.13
0.8586	1387.6	1180.1	1.41843	271.53	5.18	4.850	6.97

(*Continued*)

Table 3. (Continued).

x_1	ρ (kg m^{-3})	u (m s^{-1})	n_D	V_m (10^{-6}m^3 mol^{-1})	k_s(10^{-10}Pa^{-1})	L_f(10^{-11}m)	α_p(10^{-4} K^{-1})
0.9127	1398.7	1181.9	1.41940	281.02	5.12	4.823	6.84
0.9521	1406.2	1183.4	1.42008	287.97	5.08	4.804	6.76
1.0000	1414.6	1184.2	1.42076	296.45	5.04	4.786	6.73
323.15 K							
0.0000	941.0	1076.4	1.37055	125.54	9.17	6.513	12.10
0.0542	1001.7	1083.6	1.37982	134.23	8.50	6.271	11.10
0.1108	1055.5	1096.9	1.38670	143.55	7.87	6.035	10.30
0.1522	1090.3	1105.8	1.39066	150.40	7.50	5.890	9.84
0.2084	1132.3	1116.6	1.39515	159.77	7.08	5.724	9.33
0.2886	1183.1	1129.9	1.40046	173.32	6.62	5.534	8.77
0.3927	1236.5	1143.3	1.40501	191.20	6.19	5.349	8.26
0.4805	1273.1	1151.8	1.40778	206.48	5.92	5.233	7.97
0.5887	1311.0	1159.1	1.41101	225.37	5.68	5.124	7.69
0.7043	1345.0	1164.1	1.41379	245.57	5.49	5.037	7.42
0.8009	1369.6	1167.2	1.41582	262.40	5.36	4.979	7.16
0.8586	1382.7	1169.0	1.41692	272.48	5.29	4.947	7.00
0.9127	1394.0	1171.0	1.41787	281.97	5.23	4.919	6.86
0.9521	1401.6	1172.7	1.41855	288.91	5.19	4.899	6.79
1.0000	1409.9	1173.6	1.41924	297.44	5.15	4.880	6.75

Standard uncertainties u are: $u(x_1) = 0.0001$, $u(\rho) = 5 \times 10^{-2}$ kg m^{-3}, $u(u) = 0.5$ m s^{-1}, $u(n_D) = 0.00005$, $u(T) = 0.01$ K and $u(P) = 0.5$ kPa. Combined uncertainties (confidence level, 95%): $U_c(V_m) = \pm 0.05 \times 10^{-6}$ m^3 mol^{-1}, $U_c(\kappa_s) = \pm 0.01 \times 10^{-10}$ Pa^{-1}, $U_c(L_f) = \pm 0.007 \times 10^{-11}$m, $U_c(\alpha_p) = \pm 0.04 \times 10^{-4}$ K^{-1}. All the experiments were carried out at atmospheric pressure.

The isentropic compressibility, κ_S, is computed directly from the measured values of speed of sound and density using the Newton–Laplace equation:

$$\kappa_s = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_s = \left(\frac{1}{\rho u^2}\right) = \left(\frac{V_m}{M u^2}\right) \tag{2}$$

Excess isentropic compressibility is given by

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{3}$$

where κ_S is the isentropic compressibility and κ_S^{id} is the isentropic compressibility of the ideal mixture, which is calculated in the manner as suggested by Benson and Kiyohara [45].

$$\kappa_S^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}}\right] - \left\{ T \frac{\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2}{\left(\sum_{i=1}^{2} x_i C_{p,i}\right)} \right\} \tag{4}$$

where ϕ_i is the volume fraction of the ith component and is given by, $\phi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i$, T is the temperature, $\kappa_{s,i}$ is the isentropic compressibility, V_i is the molar volume, α_i is the isobaric thermal expansion coefficient and $C_{P,i}$ is heat capacity of the ith component.

Free length is given by

$$L_f = \kappa_j (\kappa_S)^{1/2} \tag{5}$$

where κ_j is the temperature-dependent Jacobson's constant which is equal to $\kappa_j = (93.875 + 0.375T) \times 10^{-8}$.

The excess intermolecular free length is given by

$$L_f^E = L_f - L_f^{id} = \kappa_j(\kappa_S)^{1/2} - \kappa_j\left(\kappa_S^{id}\right)^{1/2} \tag{6}$$

The excess speeds of sound, u^E is estimated in binary and ternary mixtures using the following expression [42]:

$$u^E = u - u^{id} = u - \left(\rho^{id}k_S^{id}\right)^{-1/2} \tag{7}$$

where $\rho^{id} = \sum_{i=1}^{2}\phi_i\rho_i$

Isobaric thermal expansion coefficient, α_p, of the pure components is calculated from the measured densities by the relation,

$$\alpha_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right) \tag{8}$$

The values of α_p are derived by taking differentiation linear regression between density and temperature.

Excess isobaric thermal expansion coefficient, α_P^E is calculated from the following equation:

$$\alpha_P^E = \alpha_P - \alpha_P^{id} = \frac{\left(\partial V_m^E/\partial T\right)_P - V_m^E\alpha_P^{id}}{V_m^{id} + V_m^E} \tag{9}$$

where $\alpha_P^{id} = \sum_{i=1}^{2}\phi_i\alpha_{P,i}^*$.

The dependence of the excess molar enthalpy of mixing with pressure at fixed temperature $\left(\partial H_m^E/\partial P\right)_T$ can be derived indirectly from accurate measurement of V_m^E, as a function of the temperature and composition by application of the following exact thermodynamic expression:

$$\left(\frac{\partial H_m^E}{\partial P}\right)_T = V_m^E - T\left(\frac{\partial V_m^E}{\partial T}\right)_P. \tag{10}$$

If the difference between the refractive indices of the two components is small, then deviation in refractive index of binary mixtures containing ILs:

$$\Delta_\phi n_D = n_D - n_D^{id} \tag{11}$$

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

The excess/deviation properties are fitted to a Redlich–Kister polynomial equation given by

$$Y^E = x_1x_2\sum_{i=o}^{j}A_i(x_1 - x_2)^i \tag{12}$$

where $Y^E = V_m^E$, κ_s^E, L_f^E, u^E, α_P^E, $\Delta_\phi n_D$, $\left(\partial V_m^E/\partial T\right)_P$ and $\left(\partial H_m^E/\partial P\right)_T$. x_1 and x_2 are the mole fraction of [Bmim][NTf$_2$] and DEC, respectively. Further, A_i are the adjustable parameters of the function and are determined using the least square method. In the present investigation '*i*' values are taken from 0 to 4. The corresponding standard deviations $\sigma(Y^E)$ are calculated using the following expression and represented in Table S1 of the supplementary material.

$$\sigma\left(Y^E\right) = \left[\frac{\sum\left(Y_{exp}^E - Y_{cal}^E\right)^2}{(m-n)}\right]^{1/2} \tag{13}$$

where m is the total number of experimental points and n is the number of coefficients in Equation (12).

The variations as observed in these excess/deviation parameters indicate the strength of interactions that exist between the component molecules of the binary mixture under study and their further dependence on the composition, molecular size, shape and temperature. The effects which influence these thermodynamic functions may be the resultant contribution from several opposing effects, namely chemical, structural and physical [46,47]. The chemical or specific interactions include the formation of hydrogen bonding between component molecules, charge-transfer complexes. The structural contributions arise from several effects such as interstitial accommodation and geometrical fitting of one component into another. Excess molar volumes for the binary mixture of [Bmim][NTf$_2$] with DEC as a function of composition from T = 303.15 to 323.15 K are shown in Figure 1. The variations of excess molar volumes are found to be negative in the whole composition range at all temperatures which may be credited to the hydrogen bonding between solute and solvent molecules and also favourable fitting of smaller DEC molecules (at T = 303.15 K, V_m = 122.58 × 10^{-6} m^3 mol^{-1}) into the voids created by larger [Bmim][NTf$_2$] molecules (at T = 303.15 K, V_m = 293.48 × 10^{-6} m^3 mol^{-1}) is definitely contributing to interactions. The similar variations in V_m^E values are also observed for the rest of studied temperatures. Moreover, the variation of V_m^E for the present system as a function of temperature becomes more negative with rise in temperature. This is because of the fact that, more favourable fitting of smaller DEC molecules into the voids created by larger IL molecules, thereby, shrinkage of the volume of the mixture to a larger extent, resulting in more negative V_m^E values with rise in temperature. Therefore, order of strength of interaction enhances with rise in temperature.

The existing molecular interactions in the current binary system are properly reflected on the properties of partial molar volumes of the constituent molecules. Partial molar volume is the contribution that a component of a mixture makes to the total volume of the solution. Therefore, the partial molar volume is a function of mixture composition. The partial molar volumes $\bar{V}_{\mathrm{m},1}$ of component **1** ([Bmim][NTf$_2$]) and $\bar{V}_{m,2}$ of component **2** (DEC) in the mixtures over the whole composition range have been computed using the following relationships:

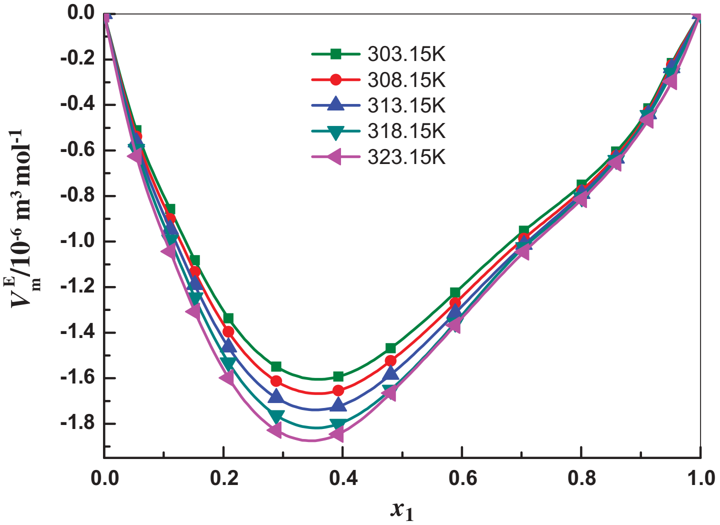

Figure 1. Plots of excess molar volume (V_m^E) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

$$\bar{V}_{\mathrm{m},1} = V_{\mathrm{m}}^{\mathrm{E}} + V_1^* + x_2\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x_1}\right)_{T,P} \tag{14}$$

$$\bar{V}_{\mathrm{m},2} = V_{\mathrm{m}}^{\mathrm{E}} + V_2^* - x_1\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x_1}\right)_{T,P} \tag{15}$$

where V_1^* and V_2^* are the molar volumes of pure components of [Bmim][NTf$_2$] and DEC, respectively. The derivatives in the above equations are obtained by differentiating Redlich–Kister equation (12) which leads to the following equations for $\bar{V}_{\mathrm{m},1}$ and $\bar{V}_{\mathrm{m},2}$.

$$\bar{V}_{m,1} = V_1^* + x_2^2\sum_{i=0}^{4} A_i(x_1 - x_2)^i - 2x_1x_2^2\sum_{i=1}^{4} A_i(i)(x_1 - x_2)^{i-1} \tag{16}$$

$$\bar{V}_{m,2} = V_2^* + x_1^2\sum_{i=0}^{4} A_i(x_1 - x_2)^i + 2x_2x_1^2\sum_{i=1}^{4} A_i(i)(x_1 - x_2)^{i-1} \tag{17}$$

Using the above equations, $\bar{V}_{\mathrm{m},1}^{\mathrm{E}}$ and $\bar{V}_{\mathrm{m},2}^{\mathrm{E}}$ have been calculated using,

$$\bar{V}_{\mathrm{m},1}^{\mathrm{E}} = \bar{V}_{\mathrm{m},1} - V_1^* \tag{18}$$

$$\bar{V}_{\mathrm{m},2}^{\mathrm{E}} = \bar{V}_{\mathrm{m},2} - V_2^* \tag{19}$$

The calculated values of $\bar{V}_{\mathrm{m},1}$ and $\bar{V}_{\mathrm{m},2}$ for the studied binary system are represented in Table 4. On visualising the values of $\bar{V}_{\mathrm{m},1}$ and $\bar{V}_{\mathrm{m},2}$ for the two components in the mixtures (Table 4), it is evident that the values are lower than their individual molar volumes in the pure state, which reveals contraction of volume occurs on mixing [Bmim][NTf$_2$] with DEC at all examined temperatures. Figures 2 and 3 represent the disparity of excess partial molar volumes of $\bar{V}_{\mathrm{m},1}^{\mathrm{E}}$ ([Bmim][NTf$_2$]) and $\bar{V}_{\mathrm{m},2}^{\mathrm{E}}$ (DEC), respectively, in the binary mixture at T = 303.15, 308.15, 313.15, 318.15 and 323.15 K. Figures 2 and 3 not only show the existence of strong forces between the unlike molecules but also support the inferences drawn from excess molar volume.

The excess partial molar volumes at infinite dilution of component **1** ($\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty}$) and component **2** ($\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty}$) have been calculated using:

$$\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty} = A_0 - A_1 + A_2 - A_3 + \ldots = \bar{V}_{\mathrm{m},2}^{\infty} - V_2^* \tag{20}$$

$$\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty} = A_0 + A_1 + A_2 + A_3 + \ldots = \bar{V}_{\mathrm{m},1}^{\infty} - V_1^* \tag{21}$$

The partial molar volumes ($\bar{V}_{\mathrm{m},1}^{\infty}$, $\bar{V}_{\mathrm{m},2}^{\infty}$) and excess partial molar volumes at infinite dilution ($\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty}$, $\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty}$) of [Bmim][NTf$_2$] and DEC are calculated using Equations (18–21). The pertinent data of $\bar{V}_{\mathrm{m},1}^{\infty}$, $\bar{V}_{\mathrm{m},2}^{\infty}$ and $\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty}$, $\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty}$ is presented in Table 5 at T = (303.15, 308.15, 313.15, 318.15 and 323.15) K. The values of $\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty}$ and $\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty}$ are found to be negative and become more negative with increase of temperature. This indicates that the association effect is greater than the dissociation effect for both the components in the present system. The excess partial molar volumes at infinite dilution for [Bmim][NTf$_2$] ($\bar{V}_{\mathrm{m},1}^{\mathrm{E},\infty}$) are more negative than those of DEC ($\bar{V}_{\mathrm{m},2}^{\mathrm{E},\infty}$) at all studied temperatures. This is because for more concentrated DEC solution, no hydrogen bonds exist among DEC molecules. Hence, we conclude that strong interactions increase among the unlike molecules of the mixtures with increase in temperature [48]. These are noticed in the case of $V_{\mathrm{m}}^{\mathrm{E}}$ values in the binary system which are well reproduced from the evaluated properties of partial molar volumes at infinite dilution as well as at all investigated temperatures.

Table 4. Partial molar volumes of component-1 ($\bar{V}_{m,1}$) ([Bmim][NTf$_2$]) and component-2 ($\bar{V}_{m,2}$) (diethyl carbonate) with mole fraction (x_1) of [Bmim][NTF$_2$] in the binary liquid mixture from T (K) = 303.15–323.15 at pressure P = 101.3 kPa.

	303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$
x_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})		(10^{-6} m^3 mol^{-1})	
0.0000	284.14	122.58	284.53	123.30	284.93	124.03	285.27	124.78	285.56	125.54
0.0542	285.09	122.56	285.55	123.29	286.02	124.02	286.45	124.77	286.81	125.54
0.1108	285.98	122.53	286.52	123.26	287.07	124.00	287.60	124.75	288.04	125.52
0.1522	286.59	122.51	287.18	123.24	287.78	123.98	288.38	124.73	288.88	125.51
0.2084	287.38	122.48	288.04	123.22	288.70	123.96	289.38	124.70	289.95	125.49
0.2886	288.45	122.45	289.20	123.18	289.93	123.92	290.68	124.66	291.34	125.47
0.3927	289.80	122.36	290.63	123.08	291.43	123.83	292.22	124.57	293.00	125.41
0.4805	290.87	122.17	291.75	122.88	292.60	123.63	293.41	124.41	294.28	125.24
0.5887	292.03	121.64	292.95	122.34	293.85	123.10	294.72	123.92	295.68	124.72
0.7043	292.94	120.61	293.90	121.28	294.85	122.01	295.80	122.82	296.81	123.51
0.8009	293.36	119.36	294.34	119.98	295.33	120.65	296.33	121.34	297.35	121.88
0.8586	293.47	118.48	294.46	119.07	295.45	119.68	296.46	120.25	297.48	120.69
0.9127	293.50	117.63	294.49	118.18	295.48	118.72	296.49	119.17	297.50	119.51
0.9521	293.49	117.02	294.48	117.55	295.47	118.05	296.47	118.41	297.47	118.68
1.0000	293.48	116.37	294.47	116.87	295.46	117.33	296.45	117.61	297.44	117.82

Standard uncertainties u are $u(x_1) = 0.0001$, $u(\rho) = 5 \times 10^{-2}$ kg m^{-3}, $u(T) = 0.01$ K and $u(P) = 0.5$ kPa.
Combined uncertainties (confidence level, 95%): $U(\bar{V}_{m,1}) = \pm 0.05 \times 10^{-6}$ m^3 mol^{-1} and $U(\bar{V}_{m,2}) = \pm 0.05 \times 10^{-6}$ m^3 mol^{-1}.

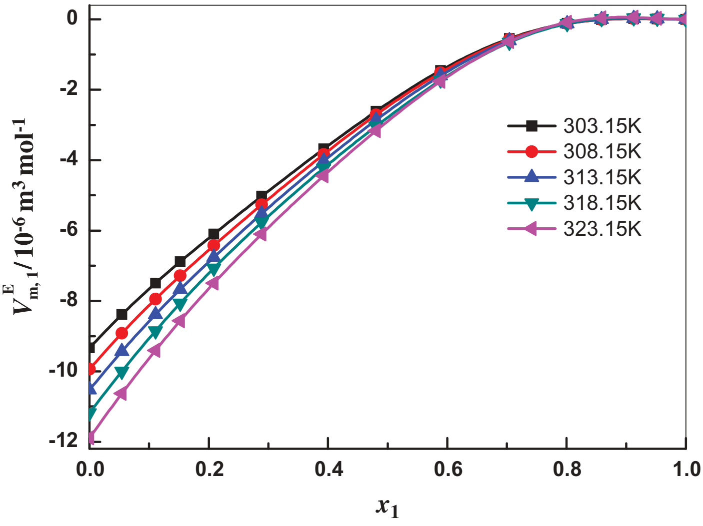

Figure 2. Plots of excess partial molar volume ($V^E_{m,1}$) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

In Figure 4, the κ^E_s values for [Bmim][NTf$_2$] + DEC are negative in the whole composition range at all investigated temperatures. The negative κ^E_s values attributed to the strong attractive interactions between the molecules of the components [49]. This supports the inference drawn from V^E_m. The intermolecular free length indicates closer approach of unlike molecules. The trends of L^E_f values (Figure S1 of the supplementary material) are negative at all investigated temperatures. The negative values of L^E_f are generally observed due to the dominance of specific interactions between unlike molecules in the liquid mixture and also due to the structural readjustments in the liquid mixture towards a less compressible phase of fluid and closer packing of molecules [50]. Figure S2 of the supplementary material shows that the u^E values are positive for the system

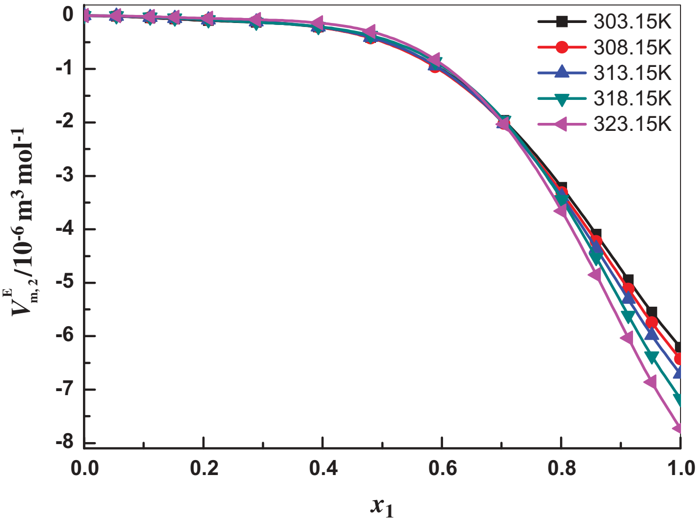

Figure 3. Plots of excess partial molar volume ($V^E_{m,2}$) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

Table 5. Partial molar volumes at infinite dilution ($\bar{V}^{\infty}_{m,1}$,$\bar{V}^{\infty}_{m,2}$) and excess partial molar volumes at infinite dilution ($\bar{V}^{E,\infty}_{m,1}$, $\bar{V}^{E,\infty}_{m,2}$) of [Bmim][NTf$_2$] and diethyl carbonate at T = (303.15, 308.15, 313.15, 318.15 and 323.15) K.

	$\bar{V}^{\infty}_{m,1}$	$\bar{V}^{E,\infty}_{m,1}$	$\bar{V}^{\infty}_{m,2}$	$\bar{V}^{E,\infty}_{m,2}$
Temp (K)	(10^{-6} m^3 mol^{-1})		(10^{-6} m^3 mol^{-1})	
303.15	284.14	−9.34	116.37	−6.21
308.15	284.53	−9.94	116.87	−6.43
313.15	284.93	−10.53	117.32	−6.71
318.15	285.27	−11.18	117.61	−7.17
323.15	285.55	−11.89	117.81	−7.73

Combined uncertainties (confidence level, 95%): $U\left(\bar{V}^{E,\infty}_{m,1}\right) = \pm 0.05 \times 10^{-6}$ m^3 mol^{-1} and $U\left(\bar{V}^{E,\infty}_{m,2}\right) = \pm 0.05 \times 10^{-6}$ m^3 mol^{-1}.

over the entire ranges of composition at all the studied temperatures. Positive deviations indicate the increasing strength of interaction between component molecules of binary liquid mixtures. In general, strong interactions among the components of a mixture lead to the formation of molecular aggregates and more compact structures; then, sound will travel faster through the mixture [51]. According to Ali *et al.* [52], more positive values mean much more strong interactions between the molecules.

The refractive indices (n_D) for the binary mixtures at the studied temperatures over the whole composition range were given in Table 3 which increases with increase in the concentration of the ILs in the mixture and decreases as the temperature increases for a particular concentration of [Bmim][NTf$_2$]. The values of $\Delta_\phi n_D$ are positive over the studied range of composition for the binary mixtures (Figure 5) which may be attributed to the non-availability of the free volume in the mixture in comparison with the ideal mixtures. As the mole fraction of the [Bmim][NTf$_2$] increases, V^E_m becomes more negative because the free space available decreases in the mixtures and speed of the light travel with lesser velocity than that in the ideal mixtures [53,54]. This gives increase in refractive index (n_D) causing $\Delta_\phi n_D$ positive. Further, as temperature increases, V^E_m found to become more negative and consequently $\Delta_\phi n_D$ become more positive. Thus, the inference of $\Delta_\phi n_D$ also supports the increase of strength of strong interactions with increase in temperature. A number of mixing rules of refractive index (n_D) have been proposed for liquid mixtures in terms of the refractive indices of the pure components proposed by different investigators such as Arago–Biot (A–B) [55], Gladstone–Dale

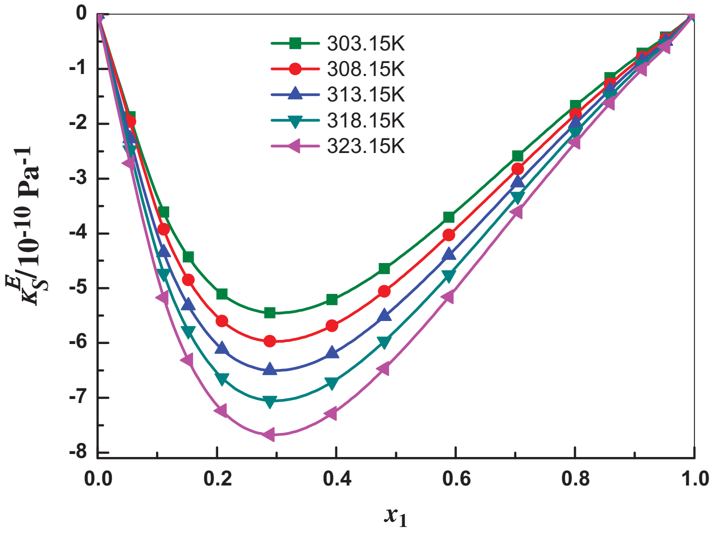

Figure 4. Plots of excess isentropic compressibility (κ_s^E) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

(G–D) [56], Newton (N) [57], Eyring and John (E–J) [58], Lorentz–Lorenz (L–L) [59], Heller (H) [60], Eykman (EK) [61], Oster (Os) [62] and Weiner (W) [63] which were examined for present [Bmim][NTf$_2$] + DEC mixture. The refractive indices values calculated from various theories along with experimental values at different temperatures are represented in Figure 6. The absolute percentage deviation (APD) of experimental refractive index is calculated by Equation (22) and represented in Table 6.

$$\mathrm{APD} = \frac{100}{n}\sum_{i=1}^{n}\left(\left|\frac{n_{\mathrm{cal}}}{n_{\mathrm{exp}}} - 1\right|\right) \tag{22}$$

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 negative values of $\alpha_{\mathrm{P}}^{\mathrm{E}}$ are due to strong interactions between solute and solvent molecules [64]. Figure 7 shows negative values of $\alpha_{\mathrm{P}}^{\mathrm{E}}$ in the whole composition range and at all investigated temperatures for the binary mixture in study. This further supports the existence of strong interactions between the constituent molecules in binary liquid solution. In Table 7, the values of excess functions $\left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T\right)_P$ and $\left(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial P\right)_T$ are represented. The variation of $\left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T\right)_P$ and $\left(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial P\right)_T$ is similar with the mole fraction and temperature but with opposite sign. The negative values of $\left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T\right)_P$ for the studied mixture may be due to strong interactions existing between the unlike molecules of the mixture [65]. The isothermal pressure coefficient of excess molar enthalpy $\left(\partial H_{\mathrm{m}}^{\mathrm{E}}/\partial P\right)_T$ has positive values in the whole composition range. This reflects increase in attraction forces between two components of this mixture by increasing pressure. Hence, contraction in the volume of the mixture is still possible by increasing pressure [48,66].

3.1. *Infrared spectral studies*

The existence of strong interactions in the system which were drawn from the above inferences of derived excess/deviation parameters is well supported by IR spectral studies. The unique properties of imidazoliumcations are found in their electronic structure. The electronic structure of

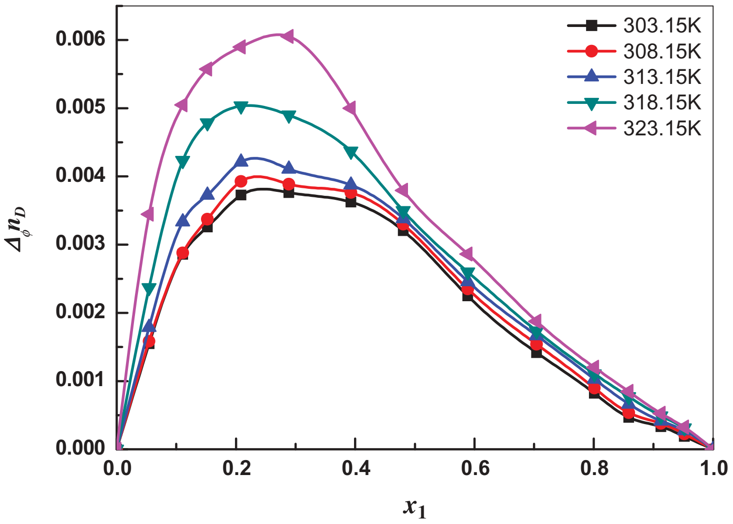

Figure 5. Plots of deviation in refractive index ($\Delta_{\phi} n_D$) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

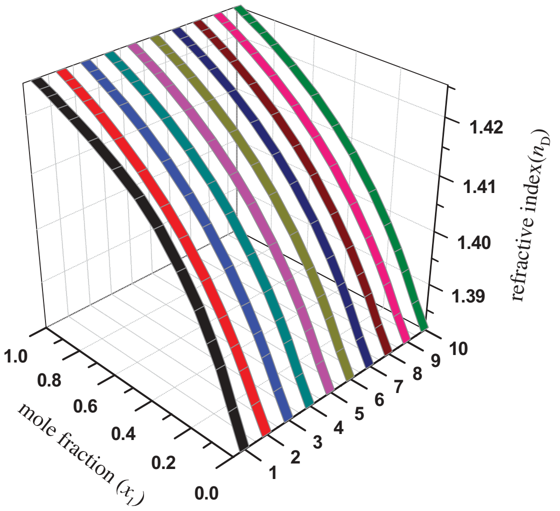

Figure 6. Plots of deviations in refractive index ($\Delta_{\phi_{n_D}}$) calculated from various theories along with experimental values against mole fraction of [Bmim][NTf$_2$] with DEC at 303.15 K.

(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 6. Average percentage deviation of calculated refractive indices compared to experimental values at various temperatures of [Bmim][NTf$_2$] and diethyl 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	0.13	0.13	0.12	0.13	0.14	0.14	0.15	0.15	0.13
308.15	0.14	0.14	0.13	0.14	0.14	0.14	0.15	0.16	0.14
313.15	0.15	0.15	0.14	0.15	0.15	0.15	0.16	0.17	0.15
318.15	0.17	0.17	0.16	0.18	0.18	0.18	0.19	0.20	0.17
323.15	0.20	0.20	0.19	0.21	0.21	0.21	0.22	0.23	0.20
Average	0.16	0.16	0.15	0.16	0.16	0.16	0.17	0.18	0.16

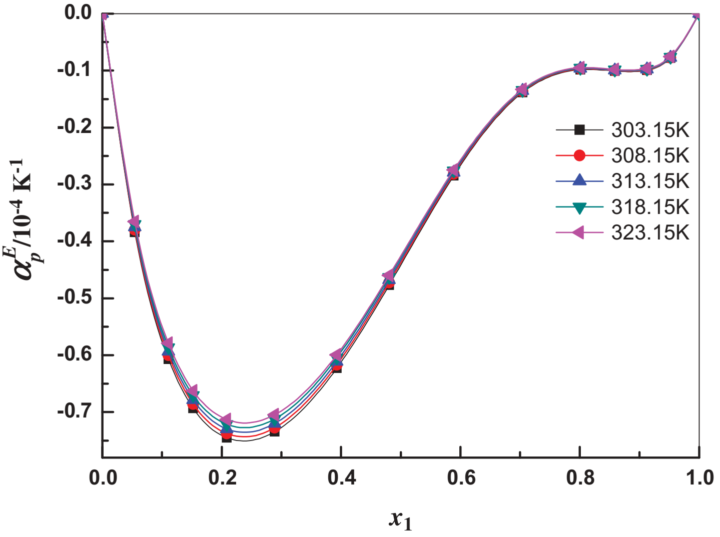

Figure 7. Plots of excess isobaric thermal expansion coefficient (α_P^E) against mole fraction of [Bmim][NTf$_2$] with DEC at different temperatures.

Table 7. The values of excess functions $\left(\partial V_m^E/\partial T\right)_P$ and $\left(\partial H_m^E/\partial P\right)_T$ at 298.15 K against mole fraction of [Bmim][NTf$_2$].

x_1	$\left(\partial V_m^E/\partial T\right)_P$ (10^{-9} m^3 mol^{-1} K^{-1})	$\left(\partial H_m^E/\partial P\right)_T$ (10^{-6} J mol^{-1} Pa^{-1})
0.0000	0.0	0.00
0.0542	−5.62	1.19
0.1108	−9.45	2.01
0.1522	−11.34	2.36
0.2084	−13.00	2.60
0.2886	−13.95	2.68
0.3927	−13.10	2.38
0.4805	−10.90	1.84
0.5887	−7.27	0.98
0.7043	−4.06	0.28
0.8009	−3.08	0.18
0.8586	−3.13	0.35
0.9127	−3.04	0.51
0.9521	−2.37	0.50
1.0000	0.00	0.00

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%): $U\left(\partial V_m^E/\partial T\right)_P = \pm 0.1 \times 10^{-9}$ m^3 mol^{-1} K^{-1} and .

$U\left(\partial H_m^E/\partial P\right)_{T=298.15\,\mathrm{K}} = \pm 0.06 \times 10^{-6}$ J mol^{-1} Pa^{-1}

imidazolium cations (Figure 8) contains delocalised 3-centre-4-electron configuration across the N$_1$–C$_2$–N$_3$ moiety, a double bond between C$_4$ and C$_5$ at the opposite side of the ring, and a weak delocalisation in the central region [67]. 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 key to understand the properties of these ILs. The hydrogen on the C$_2$ carbon (C$_2$–H) has been shown to bind typically with solute molecules [68,69].

In order to study the effects of molecular interactions, infrared absorbance is recorded from 650 to 4000 cm^{-1} (Figure 9 and Table 8). 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

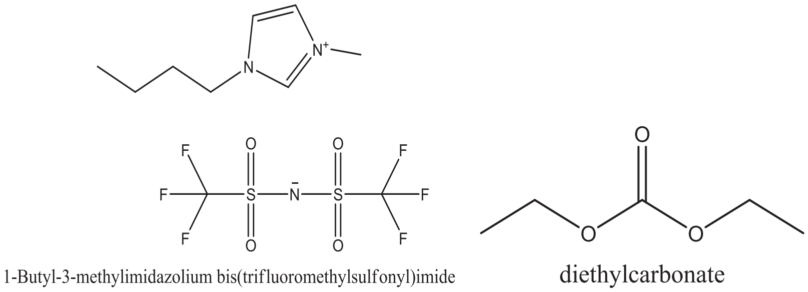

Figure 8. Chemical Structures of ([Bmim][NTf_2]) and DEC.

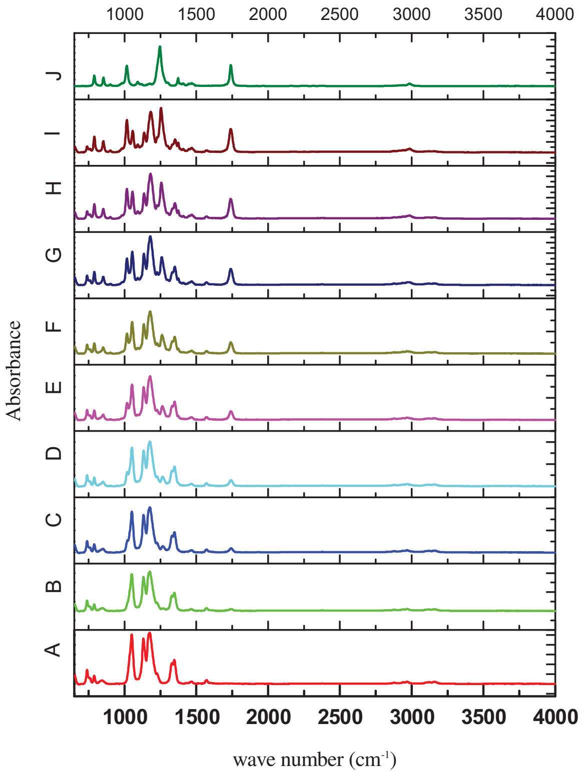

Figure 9. Infrared spectra of (A) pure IL [Bmim][NTf_2], (B) 0.8892, (C) 0.7916, (D) 0.7114, (E) 0.6073, (F) 0.5195, (G) 0.4113, (H) 0.2957, (I) 0.1991, (J) 0.0873 and (K) pure DEC. (B–J) represents mole fraction of [Bmim][NTf_2] in DEC.

two parts: signals between 3000 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 [70]. The signals between 2800 and 3000 cm^{-1} are due to aliphatic C–H groups in the methyl and butyl moieties [71–73]. The C_2–H vibrational frequency (3120.7 cm^{-1}) is shifted to lower frequencies by about 36.5 cm^{-1} when compared to the C_4–H and C_5–H stretches (3157.2 cm^{-1}) because of its stronger acidic character. In [Bmim][NTf_2], there exist hydrogen bond between aromatic C–H hydrogen's of the cation and oxygen, fluorine atoms of the anion [74]. In the present mixtures, C_2–H and $C_{4,5}$–H stretching frequencies of the cation and SO_2 Sym. stretch, CF_3 Sym. stretch of the anion are analysed where there is no overlap from peaks of DEC. As mole fraction of IL (x_1) changes from 1.0000 to 0.7916, not very much change in the frequencies

Table 8. Infrared absorbance wave numbers (cm^{-1}) between 2800 and 3200 of [Bmim][NTf$_2$] in DEC at room temperature and atmospheric pressure P = 101.3 kPa.

Mole fraction of [Bmim][NTf$_2$]	Mole fraction of DEC	C$_2$–H stretching	C$_{4,5}$–H stretching	SO$_2$ Sym. stretch	CF$_3$ Sym. stretch
1.0000	0.0000	3120.7	3157.2	1131.5	1226.1
0.8892	0.1108	3120.7	3157.5	1131.6	1226.6
0.7916	0.2084	3120.7	3157.5	1131.6	1226.6
0.7114	0.2886	3120.2	3156.9	1132.2	1226.6
0.6073	0.3927	3120.2	3156.9	1133.4	1226.6
0.5195	0.4805	3119.6	3156.3	1134.0	1226.6
0.4113	0.5887	3119.3	3156.1	1134.6	1226.6
0.2957	0.7043	3119.0	3156.0	1135.2	1227.2
0.1991	0.8009	3118.8	3155.8	1136.5	1228.4
0.0873	0.9127	–	–	1138.2	1228.8
0.0000	1.0000	–	–	–	–

indicates the existence of ionic clusters. Further, in the region $x_1 < 0.7916$, the significant change in [NTf$_2$]$^-$ ion frequencies indicated the formation of ion pairs from clusters. Furthermore, in DEC-rich region, complete solvation of individual ions takes place. There is a slight red shift in C$_2$–H and C$_{4,5}$–H stretching frequencies indicating the formation of hydrogen bond between [Bmim]$^+$ and carbonyl oxygen atoms of DEC. Simultaneously, a clear blue shift in SO$_2$ Sym. stretching frequencies is observed because of the breakup of hydrogen bond between cation and anion of the IL. The shifts are predominant at DEC-rich region. But, not much variation in CF$_3$ Sym. stretching frequencies is observed.

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$_2$] + DEC 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 the hydrogen bonds between the IL [Bmim][NTf$_2$] and DEC are also responsible to make a remarkable contraction in the volume of the mixture.

3.2. *PFP statistical theory for excess molar volume V_m^E*

The PFP theory may be used to analyse and correlate the experimental excess molar volumes of binary mixtures [75–78]. We have correlated V_m^E of presently studied binary mixture using PFP theory over entire range of mole fractions at T = 303.15–323.15 K. The PFP theory considered V_m^E in three different contributions [79]: (1) interaction contribution V_{int}^E, which is associated with intermolecular-specific interaction with sign of ; H_m^E (2) free volume contribution V_{fv}^E, which is associated with reduced volume to reduced temperature ratio with negative sign and (3) internal pressure contribution, V_{P*}^E, which is associated with breaking of IL structure with introduction of molecular organic solvents and changes in reduced volume of components with positive or negative sign. The calculation of various parameters of the theory based on relevant equations is given elsewhere [80–83].

The pure components parameters for the PFP theory are included in Table S2 of the supplementary material. The Flory contact interaction parameter χ_{12}, the only adjustable parameter, needed in the PFP theory was obtained by experimental V_m^E values in absence of the experimental excess molar enthalpy (H_m^E). The Flory contact interaction parameter χ_{12} was found to be negative for all the investigated temperatures. The values of three contributions V_{int}^E, V_{fv}^E and V_{P*}^E, to V_m^E (PFP) at equimolar composition, are summarised in Table 9. The first term V_{int}^E is negative which suggests that the strong interactions take place in the binary mixture. The interactional contributions are negative at all calculated temperatures. The second term V_{fv}^E was found to be negative for the system studied (Table 9) as V_{fv}^E is proportional to $-\left(\tilde{V}_1 - \tilde{V}_2\right)^2$ [76]. The magnitude of negative values for

Table 9. PFP interaction parameter, χ_{12}, and calculated values of the three contributions from the PFP theory at equimolar composition for ([Bmim][NTf$_2$] + DEC) system at T = (303.15–323.15) K.

		V_m^E(int)	V_m^E(*fv*)	V_m^E(ip)
T (K)	χ_{12} (10^6 J m^{-3})		(10^{-6} m^3 mol^{-1})	
303.15	−51.8174	−1.2439	−0.6509	0.4628
308.15	−50.2984	−1.2387	−0.6724	0.4252
313.15	−48.8677	−1.2349	−0.6942	0.3846
318.15	−44.9035	−1.2392	−0.7170	0.3487
323.15	−44.9035	−1.1939	−0.7398	0.3055

V_{fv}^E depends upon difference in Flory's reduced volumes of involved components. Negative values of V_{fv}^E increase in magnitude as the temperature increases which shows that as the temperature increases, more free volume in the [Bmim][NTf$_2$] becomes available to accommodate the smaller DEC molecules which resulted in more negative V_m^E. The third term, i.e. characteristic pressure $V_{P^*}^E$, the P^* effect which depends on the relative cohesive energy of the expanded and less expanded component, is found to be positive at all investigated temperatures. It is proportional to $\left(\tilde{V}_1 - \tilde{V}_2\right)\left(P_1^* - P_2^*\right)$ and can have both the negative and positive sign depending upon the magnitude of P_i^* and $\tilde{V}_i^*$ of unlike components [76]. For the system [Bmim][NTf$_2$] + DEC, $V_{P^*}^E$ is positive which is related to the structure-braking effect of the DEC on the electrostatic interactions between the ions of [Bmim][NTf$_2$] and so, the DEC molecules can be placed around the [Bmim]$^+$ and [NTf$_2$]$^-$ ions [76,84]. In the present system, V_{int}^E and V_{fv}^E were found to be negative while $V_{P^*}^E$ was found to be positive which shows that the interaction and free volume contributions are responsible for the overall strong interactions between solute and solvent molecules. Figure 10 indicates the composition dependence of V_m^E (PFP) values calculated from PFP theory for [BMIM][NTf$_2$] + DEC mixture compared with experimental V_m^E at 303.15 K. From the Figure, the V_m^E values calculated from PFP theory are in good agreement with the experimental values at whole composition range. We can conclude that it is possible to explain the volumetric behaviour of [Bmim][NTf$_2$] + DEC binary mixture by the application of the PFP theory quite successfully.

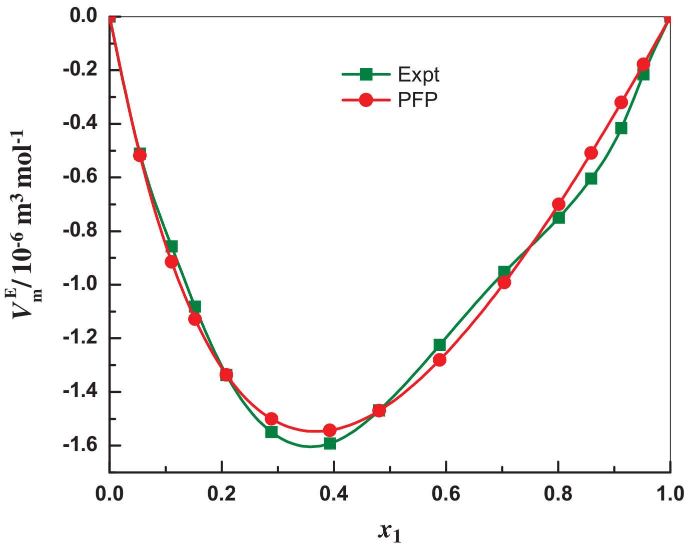

Figure 10. Plots of excess molar volumes (V_m^E) of experimental and calculated from PFP theory against mole fraction of [Bmim][NTf$_2$] with DEC at 303.15 K.

4. Conclusions

Densities, ultrasonic speed of sounds and refractive indices for binary liquids of [Bmim][NTf$_2$] with DEC, have been measured experimentally at atmospheric pressure over the entire composition range at temperature 303.15, 308.15, 313.15, 318.15 and 323.15 K. From the experimental data excess/deviation properties such as V_S^E, κ_S^E, L_f^E, u^E, α_P^E and $\Delta_\phi n_D$ have been evaluated. The excess and deviation parameters have been fitted to Redlich–Kister-type polynomial and also corresponding standard deviations have been computed. In the present binary liquid systems of [Bmim][NTf$_2$] with DEC, the observed excess values clearly reflect the dominance of strong attractive forces. The observed lower partial molar volumes in the liquid mixture when compared to the molar volumes of respective pure components also support the existence of strong interactions in the system. Various mixing rules were used to predict the refractive indices and the data have been compared with the experimental results. The IR spectral studies also supported the presence of strong interaction between molecules in study. PFP theory was able to explain the volumetric behaviour of the system quite successfully.

Disclosure statement

No potential conflict of interest was reported by the authors.

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