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Excess Thermodynamic and Volumetric Properties of Binary Mixtures containing Ionic Liquid [Bmim][NTf_2]and Dimethyl Carbonate from T = (298.15to 323.15) K

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Abstract **- The density (ρ), ultrasonic velocity (u) and refractive index (n_D) of the binary mixtures of 1-Butyl 3-Methylimidazolium bis (Trifluoromethylsulfonyl)Imide (Bmim [NTf_2]) and dimethyl carbonate (DMC)and those of pure liquids were measured using Anton Paar vibrating tube density and sound velocity meter (DSA 5000 M) and Dr. Kernchen Abbemat (Anton Paar, Austria) refractometer over the whole composition range as a function of temperature between 298.15 and 323.15 K in steps of 5K at atmospheric pressure. From the experimental data, the excess values of molar volumes (V_m^E), partial molar volume($\bar{V}_m^E$), partial molar volume at infinite dilution($\bar{V}_m^{E,\infty}$), isentropic compressibility (k_s^E), acousticimpedance (Z^E), free length (L_f^E), speeds of sound (u^E), and deviations in refractive index (Δn_D) were calculated and fitted to a Redlich–Kister type equation. The negative values of V_m^E,k_s^E, L_f^E and positive values of Z^E, u^E, and Δn_D indicate the existence of strong interactions between the components.**

Keywords: Bmim imide, dimethyl carbonate, Density, ultrasonic velocity, Refractiveindex, excess/deviation parameters, Redlich–Kister type equation.

INTRODUCTION

Since Ionic liquids (ILs) have large variety of new applications, a major focus of study is being carried out both at laboratory and industrial scale. The interesting properties such as negligible volatility or non-flammability make them suitable for the replacement of conventional liquids.

The measurement of physical properties is one of the most important research areas involving ILs for the use of them from laboratory level to industrial applications.

Basing on how they attain the charge, Ionic liquids are divided into three types:

(1) protic; (2) aprotic; and (3) zwitter ionic.

Protic ILs are formed by proton-transfer reaction as acid and base as they donate and accept hydrogen bonds making hydrogen bonded network like water [1]. Aprotic ILs consist of imidazolium and pyrrolidium based cations and form inter molecular hydrogen bonds but not as protic ILs.

Polarity is an important parameter to describe nature of a solvent. Ionic liquids are considered to be highly polar but weak as coordinating solvent [2]. Their polarity is between that of the water and chlorinated organic solvents.

Solvent feature of ionic liquid comes from H-bond donation from cation, H-bond accepting functionality of the anion, and π-π bonding. ILs are immiscible to non polar organic solvents and can be used in two phase system.

They have applicable electrochemical window. For some ILs it is in the range of ~6V [3]. However choice of electrode has some effect on the electrochemical window. Ionic liquids like ammonium, piperidinium, morpholinium with 4 coordinated nitrogen have larger electrochemical window compared to others [3].

In the present work BMIM imide ionic liquid was mixed with well known green solvent dimethyl carbonate in different proportions and the density, sound velocity and refractive index were measured for each mixture at six temperatures in steps of 5K from 298.15K to 323.15K.

[Bmim] [NTf_2] has many applications such as extracting solvent for the removal of many organic compounds through liquid–liquid extraction [4, 5], in chromatography [6] and enzyme catalysis in ionic liquids [7], etc.

Dimethyl carbonate (DMC) can be used as an anti-knocking agent and can possibly (partially) replace MTBE or ethanol as a fuel additive [8]. In addition, DMC can potentially replace dimethyl sulfate and methyl halides in methylation reactions [9]. It may also be suitable to replace phosgene as a carbonylation agent for the production of polycarbonates and urethane polymers [9]. DMC is relatively non toxic, especially in comparison to the mentioned chemicals [10]. It is of great importance to understand the mixing behavior of ILs in dimethyl carbonate and to provide accurate physicochemical data. The thermo acoustic, volumetric and refractive index data of [Bmim][NTf_2] with dimethyl carbonate were not reported earlier.

Basing on our preliminary experiments, [Bmim][NTf_2] was found to be miscible with dimethyl Carbonate at all proportions. Hence, it is proposed to measure the densities (ρ), speeds of sound(u), refractive

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indices (n_D) of the binary mixtures of [Bmim][NTf_2] with dimethyl carbonate in the temperature range from 298.15 to 323.15K and over the whole composition range and to estimate their excess/deviation properties for their potential application in industrial processes. On the basis of the measured values the properties such as excess values of molar volumes($\bar{V}_m^E$), partial molar volumes , partial molar volumes at infinite dilution $\left(\bar{V}_m^{E,\infty}\right)$, isentropic compressibility(k_s^E), acoustic impedance (Z^E), free length (L_f^E), speeds of sound (u^E), and deviations in refractive index Δn_D for binary mixtures were fitted using Redlich–Kister type polynomial equation.

2 EXPERIMENTAL

Chemicals:

The ionic liquid, (BMIM imide) or [Bmim][NTf_2] , with purity 0.99 in mass fraction was used in this work. It was purchased from Iolitec, GmBH (Germany), while the dimethyl carbonate was supplied by Sigma Aldrich. The IL [Bmim][NTf_2] was used without any further purification and dimethyl carbonate was further purified by distillation. The measured density, speed of sound and refractive index of the pure liquids at atmospheric pressure are compared with literature values to verify the purity of liquids under investigation and are presented in table 1. Ever since the concept of hindered internal rotation about single bonds was established, it has been expected that esters of simple carboxylic acids might exist in a conformational equilibrium in their fluid states. Such equilibrium is expected, on theoretical grounds, to involve the two planar conformations for DMC (shown in fig.1d).

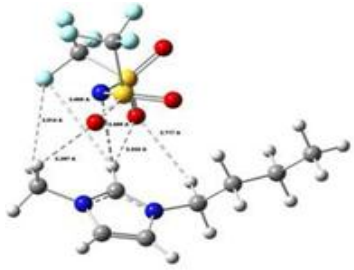

Fig1a: Ball and stick model of Bmim NTf_2

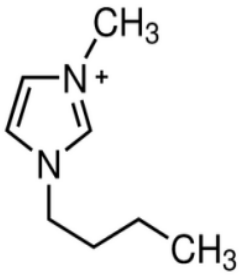

Fig 1b: 1-Butyl 3-Methylimidazolium cation

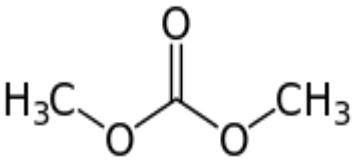

Fig1c: molecular structure of dimethyl carbonate

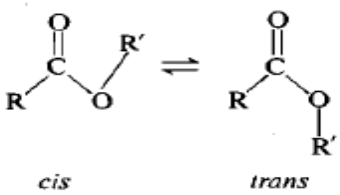

Fig 1d: molecular conformations of dimethyl carbonate

Table 1: Experimental and literature values of density, velocity and refractive index at temperatures 298.15K to 323.15K

	ρ kgm^{-3}		u ms^{-1}		n_D	
T/K	*Exp.*	*Lit.*	*Exp.*	*Lit.*	*Exp.*	*Lit.*
[Bmim][NTf_2]						
298.15	1433.72	1433.72[11]	1227.86	1227.86[11]	1.4268	1.4267[11]
303.15	1428.92	1428.95[11]	1216.77	1216.77[11]	1.4250	1.4252[11]
308.15	1424.13	1424.18[11]	1205.8	1205.80[11]	1.4230	1.4237[11]
313.15	1419.36	1419.41[11]	1194.95	1194.95[11]	1.4220	1.4223[11]
318.15	1414.61	1414.64[11]	1184.23	1184.23[11]	1.4190	1.4208[11]
323.15	1409.88	1409.87[11]	1173.61	1173.61[11]	1.4180	1.4192[11]
Dimethyl carbonate						
298.15	1063.43	1063.39[12]	1198.87	1198[16]	1.3664	1.3664[13]
303.15	1056.82	1056.35[13]	1177.29	1177[16]	1.3641	1.3652[17]
308.15	1050.18	1050.14 [12]	1155.63	1155[16]	1.3618	1.3644[17]
313.15	1043.50	1043.10[14]	1134.23	1134[16]	1.3594	1.3624[17]
318.15	1036.79	1035.60[15]	1113.09	-	1.3570	1.3622[17]
323.15	1030.04	1028.40[15]	1092.16	-	1.3547	1.3590[17]

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3. THEORY:

The experimentally measured values of ρ, u and n_D were used to calculate the values of thermodynamic and acoustical parameters such as molar volume (V_m), intermolecular free length (L_f), isentropic compressibility (k_S). The derived excess/deviation parameter values are shown in Table 2.

The excess/deviation parameters for the above parameters including deviations in refractive index Δn_D, $\left(\frac{\partial V_m^E}{\partial T}\right)_p$ were also calculated by using the following equations:

$$V_m = \frac{M}{\rho} \quad (1)$$

Where M_{eff} is the effective molecular weight (= x_1M_1 + x_2M_2), where M_1 and M_2 are the molar masses and x_1 and x_2 are the mole fractions of IL and dimethyl carbonate, respectively), and ρ is the density of the medium.

The speed of sound (u) and the density of the medium (ρ) using Newton–Laplace equation give the intermolecular free length as:

$$L_f = \frac{K}{\sqrt{\rho u^2}} \quad (2)$$

Where, K is a temperature dependent constant equal to (93.875 + 0.375T) x 10^{-8}.

The excess molar volumes are given by:

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \quad (3)$$

Where ρ is the density of the mixture and M_i, x_i and ρ_i are the molar mass, mole fraction, and density of the i^{th} component in the mixture, respectively.

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

$$k_s = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\right)_s = \left(\frac{1}{\rho u^2}\right) = \left(\frac{V_m}{M u^2}\right) \quad (4)$$

Excess isentropic compressibility is given by:

$$k_S^E = k_S - \sum_{i=1}^{2} x_i k_{Si} \quad (5)$$

Where, k_S is the isentropic compressibility
The excess intermolecular free length is given by:

$$L_f^E = L_f - [x_1 L_{f1} + x_2 L_{f2}] \quad (6)$$

The excess speeds of sound, u^E are estimated in binary mixtures using the following expression proposed by Douheret et al. [18]:

$$u^E = u - [x_1 u_1 + x_2 u_2] \quad (7)$$

Table 2: The excess parameters of binary mixtures of BMIM imide and dimethyl carbonate.

x_1	ΔU m/s	$\Delta k_s * 10^{-10}$ $m^2 N^{-1}$	$Z^E * 10^{-5}$ $Kg/m^2 .s$	$L_f^E * 10^{-10} m$	Δn	$\Delta R_m * 10^{-3}$ m^3/mol	$V_m^E * 10^{-3}$ $m^3 mol^{-1}$
				298.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	12.8047	-0.5778	0.1030	-0.0236	0.0142	0.0461	0.0461
0.1945	20.4161	-0.8050	0.1519	-0.0334	0.0198	0.0512	0.0512
0.2994	22.7964	-0.8617	0.1712	-0.0362	0.0215	0.0429	0.0429
0.3999	20.7558	-0.8132	0.1678	-0.0344	0.0208	0.0339	0.0339
0.4976	17.1026	-0.7195	0.1525	-0.0306	0.0190	0.0272	0.0272
0.5842	13.8382	-0.6168	0.1331	-0.0262	0.0166	0.0222	0.0222
0.6886	10.3700	-0.4775	0.1051	-0.0204	0.0131	0.0153	0.0153
0.8014	6.5662	-0.3122	0.0700	-0.0134	0.0087	0.0064	0.0064
0.8890	3.1392	-0.1757	0.0399	-0.0075	0.0051	0.0005	0.0005
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				303.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	15.0762	-0.6359	0.1043	-0.0257	0.0147	0.0593	0.0593
0.1945	23.7000	-0.8837	0.1539	-0.0363	0.0205	0.0793	0.0793
0.2994	26.5399	-0.9451	0.1737	-0.0394	0.0222	0.0730	0.0730
0.3999	24.5321	-0.8926	0.1705	-0.0375	0.0214	0.0540	0.0540
0.4976	20.6386	-0.7907	0.1552	-0.0333	0.0193	0.0352	0.0352
0.5842	16.9889	-0.6784	0.1356	-0.0286	0.0169	0.0233	0.0233
0.6886	12.9079	-0.5256	0.1071	-0.0223	0.0133	0.0146	0.0146
0.8014	8.3429	-0.3443	0.0715	-0.0146	0.0089	0.0071	0.0071
0.8890	4.2584	-0.1950	0.0409	-0.0083	0.0052	0.0003	0.0003
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				308.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	17.2744	-0.6989	0.1054	-0.0278	0.0152	0.0752	0.0752
0.1945	27.0122	-0.9700	0.1559	-0.0394	0.0212	0.1033	0.1033
0.2994	30.3474	-1.0366	0.1763	-0.0427	0.0229	0.0993	0.0993
0.3999	28.3119	-0.9790	0.1732	-0.0406	0.0220	0.0764	0.0764
0.4976	24.0985	-0.8674	0.1577	-0.0361	0.0198	0.0505	0.0505
0.5842	20.0194	-0.7443	0.1378	-0.0311	0.0172	0.0315	0.0315
0.6886	15.3092	-0.5766	0.1089	-0.0242	0.0135	0.0167	0.0167
0.8014	9.9657	-0.3779	0.0728	-0.0159	0.0090	0.0081	0.0081
0.8890	5.2075	-0.2143	0.0416	-0.0090	0.0053	0.0033	0.0033
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

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				313.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	19.3383	-0.7660	0.1064	-0.0301	0.0159	0.1011	0.1011
0.1945	30.1866	-1.0623	0.1577	-0.0427	0.0220	0.1343	0.1343
0.2994	34.0354	-1.1349	0.1787	-0.0463	0.0236	0.1295	0.1295
0.3999	31.9856	-1.0717	0.1757	-0.0441	0.0226	0.1026	0.1026
0.4976	27.4678	-0.9497	0.1601	-0.0392	0.0203	0.0689	0.0689
0.5842	22.9806	-0.8150	0.1400	-0.0337	0.0176	0.0407	0.0407
0.6886	17.6696	-0.6314	0.1107	-0.0263	0.0137	0.0155	0.0155
0.8014	11.5609	-0.4138	0.0740	-0.0173	0.0091	0.0032	0.0032
0.8890	6.1230	-0.2348	0.0423	-0.0098	0.0053	0.0023	0.0023
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				318.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	21.0881	-0.8355	0.1069	-0.0324	0.0166	0.1249	0.1249
0.1945	33.1742	-1.1605	0.1593	-0.0460	0.0228	0.1669	0.1669
0.2994	37.6602	-1.2406	0.1810	-0.0500	0.0244	0.1633	0.1633
0.3999	35.6027	-1.1714	0.1781	-0.0477	0.0233	0.1324	0.1324
0.4976	30.7489	-1.0376	0.1623	-0.0424	0.0208	0.0917	0.0917
0.5842	25.8536	-0.8904	0.1420	-0.0365	0.0180	0.0556	0.0556
0.6886	19.9882	-0.6902	0.1124	-0.0284	0.0140	0.0200	0.0200
0.8014	13.1508	-0.4527	0.0753	-0.0187	0.0092	-0.0021	-0.0021
0.8890	7.0069	-0.2567	0.0430	-0.0106	0.0054	-0.0060	-0.0060
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				323.15K			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	23.0531	-0.9141	0.1078	-0.0351	0.0174	0.1585	0.1585
0.1945	36.1970	-1.2678	0.1609	-0.0498	0.0237	0.2105	0.2105
0.2994	41.1885	-1.3542	0.1830	-0.0542	0.0253	0.2070	0.2070
0.3999	39.1366	-1.2784	0.1804	-0.0516	0.0240	0.1715	0.1715
0.4976	34.0006	-1.1325	0.1645	-0.0460	0.0215	0.1246	0.1246
0.5842	28.7112	-0.9719	0.1440	-0.0396	0.0185	0.0821	0.0821
0.6886	22.2596	-0.7532	0.1140	-0.0308	0.0143	0.0384	0.0384
0.8014	14.6873	-0.4940	0.0764	-0.0203	0.0094	0.0083	0.0083
0.8890	7.9013	-0.2804	0.0436	-0.0115	0.0055	-0.0008	-0.0008
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 3: coefficients (A_i) of Redlich–Kister polynomial for excess parameters

V_m^E*(*10^{-3} m^{3}mol^{-1})*

RKC/Tem	A_0	A_1	A_2	A_3	A_4	σ
298.15	-0.0036	-0.0026	-0.0028	-0.0009	0.0001	0.0000077
303.15	-0.0038	-0.0028	-0.0026	-0.0009	-0.0006	0.0000098
308.15	-0.004	-0.0029	-0.003	-0.001	-0.0002	0.0000095
313.15	-0.0042	-0.003	-0.003	-0.0012	-0.0005	0.0000067
318.15	-0.0044	-0.0032	-0.0032	-0.0012	-0.0004	0.0000095
323.15	-0.0047	-0.0034	-0.0032	-0.0012	-0.0006	0.0000100
ΔU (m/s)						
298.15	68.03	78.36	74.73	-14.04	-73.94	0.371650
303.15	82.14	85.68	78.21	-12.15	-69.26	0.310580
308.15	95.94	94.37	83.35	-11.4	-69.71	0.320470
313.15	109.38	102.66	88.66	-11.08	-71.84	0.334690
318.15	122.46	111.37	95.81	-14.45	-80.72	0.394440
323.15	135.43	119.26	100.22	-14.41	-81.85	0.409580
*Δk_s(*10^{-10} m^2 N^{-1})*						
298.15	-2.8673	-2.2132	-1.7337	-1.0524	-0.2247	0.001590
303.15	-3.1512	-2.4128	-1.8744	-1.1771	-0.3334	0.001210
308.15	-3.457	-2.6435	-2.0486	-1.3062	-0.4018	0.001320
313.15	-3.7848	-2.8912	-2.2401	-1.4415	-0.4586	0.001510
318.15	-4.1353	-3.1648	-2.4716	-1.5496	-0.4447	0.002090
323.15	-4.5136	-3.4515	-2.6897	-1.7165	-0.5302	0.002250
*Z^E*10^{-5} Kg/m^2.s*						
298.15	0.60805	0.39801	0.26675	0.09804	-0.02633	0.00034
303.15	0.61872	0.40144	0.26571	0.09555	-0.02112	0.00027
308.15	0.62867	0.40664	0.26852	0.09212	-0.02618	0.00027
313.15	0.63825	0.41091	0.27134	0.08990	-0.03208	0.00029
318.15	0.64721	0.41599	0.27637	0.08149	-0.04611	0.00036
323.15	0.65590	0.41967	0.27684	0.07797	-0.04860	0.00039
*L_f^E*10^{-10}m*						
298.15	-0.1218	-0.0923	-0.0708	-0.0362	-0.0017	0.000088
303.15	-0.1327	-0.0997	-0.0758	-0.0400	-0.0043	0.000076
308.15	-0.1440	-0.1079	-0.0833	-0.0432	-0.0022	0.000085
313.15	-0.1562	-0.1167	-0.0910	-0.0463	-0.0013	0.000097
318.15	-0.1690	-0.1263	-0.0969	-0.0485	-0.0018	0.000111
323.15	-0.1832	-0.1366	-0.1036	-0.0525	-0.0043	0.000126

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Δn						
298.15	0.0756	0.0476	0.0328	0.0292	0.0183	0.000050
303.15	0.0772	0.0509	0.0377	0.0285	0.0144	0.000056
308.15	0.0790	0.0537	0.0393	0.0286	0.0158	0.000070
313.15	0.0809	0.0567	0.0401	0.0305	0.0200	0.000070
318.15	0.0831	0.0596	0.0412	0.0328	0.0222	0.000099
323.15	0.0856	0.0624	0.0432	0.0360	0.0256	0.000129
$\Delta R_m * 10^{-3}\ m^3/mol$						
298.15	0.1084	0.119	0.1572	0.3123	0.1111	0.00495
303.15	0.1393	0.3318	0.4637	0.1261	-0.2718	0.00485
308.15	0.1995	0.4968	0.495	0.0044	-0.2107	0.00479
313.15	0.2724	0.6919	0.4106	-0.0173	0.0903	0.00385
318.15	0.3627	0.8606	0.3977	0.0652	0.0984	0.00608
323.15	0.4934	1.0005	0.4812	0.1594	0.1649	0.00827

If the difference between the refractive indices of the two components is small then thedeviation in refractive index of binary mixtures containing ILs is given by:

$$\Delta n_D = n_D - [x_1 n_{D1} + x_2 n_{D1}] \qquad (8)$$

The excess/deviation properties have been fitted to a Redlich–Kister type polynomial equation given by:

$$Y^E = x_1 x_2 \sum_{i=0}^{j} A_i (x_2 - x_1)^i \qquad (9)$$

Where, x_1 and x_2 are the mole fraction of ionic liquid and dimethyl carbonate, respectively and the A_i are adjustable parameters of the function and are determined using the leastsquares method. In the present investigation the 'i' values have been taken from 0 to 4. The corresponding standard deviations σ (Y^E) have been calculated using the followingexpression:

$$\sigma(Y^E) = \left\{\frac{\sum(Y^E_{exp} - Y^E_{cal})}{m-n}\right\} \qquad (10)$$

where 'm' is the total number of experimental points and n is the number of coefficients in eq.(22). The calculated values of the coefficients A_i along with the standard deviations, σ (Y^E)are given in Table 4.

4. RESULTS AND DISCUSSION

In the present study, excess molar volume (V_m^E), excess partial molar excess volume ($\bar{V}_m^E$), partial molar excess volume at infinite dilution ($\bar{V}_m^{E,\infty}$), excess isentropic compressibility (k_s^E), excess free length (L_f^E), excess acoustic impedance (Z^E), excess ultrasonic velocity (u^E), and deviations in refractive index (Δn_D) were calculated. The strength of interactions present between the component molecules of the binary mixture under study is indicated by the variations observed in these excess/deviation parameters. Further these variations are effected by the composition, molecular size, shape and temperature. The physical, chemical, and structural contributions [18, 19] influence these thermodynamic parameters.

Excess molar volumes V_m^E for binary mixture of [Bmim][NTf_2] and dimethyl carbonate as a function of composition from 298.15 to 328.15 K are shown in Fig. 1. The contraction in the volume of the mixture can be attributed to the formation of hydrogen bonds between the ionic liquid [Bmim][NTf_2] and dimethyl carbonate.

The values of V_m^E become more negative with increase in temperature. This is due to the fitting of smaller dimethyl carbonate molecules into the voids created by larger IL molecules leading to decrease in volume of the mixture to a greater extent, which results in more negative V_m^E values with increase in temperature.

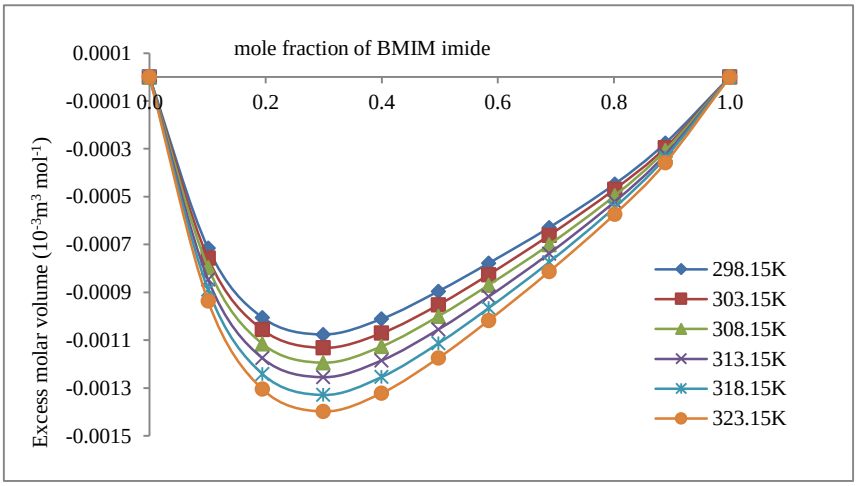

Fig. 2: Plots of excess molar volume (V_m^E) against mole fraction (x_1) for binary mixtures of [Bmim][NTf_2] and Dimethyl carbonate at temperature T and atmospheric pressure.

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The strength of interaction follows the order: (323.15>318.15>313.15>308.15>303.15>298.15) K. The properties of partial molar volumes reflect the existing molecular interactions in the system. The contribution of a component of a mixture to the overall volume of the solution is interpreted in terms of Partial molar volume. Therefore, the partial molar volume is a function of composition of the mixture. The partial molar volumes $\bar{V}_{m,1}$ of component 1[Bmim][NTf$_2$] and $\bar{V}_{m,2}$ of component 2 (dimethyl carbonate) in the mixtures over the entire range of composition have been calculated by using the following equations:

$$V_{m,1} = V_m^E + V_1^* + x_2\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,p} \quad (11)$$

$$\bar{V}_{m,2} = V_m^E + V_2^* - x_1\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,p} \quad (12)$$

Where V_1^* and V_2^* are the molar volumes of pure components of [Bmim][NTf$_2$] and dimethyl carbonate respectively. Differentiating the Redlich–Kister equation for V_m^E, we get the derivatives $\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,p}$ mentioned in the equations (11) and (12) are obtained by, which leads to the following equations for $\bar{V}_{m,1}, and\ \bar{V}_{m,2}$:

$$\bar{V}_{m,1} = V_1^* + x_2^2\sum_{i=0}^{4} A_i\,(x_2 - x_1)^i - 2x_1x_2^2\sum_{i=1}^{4} A_i(i)(x_2 - x_1)^{i-1} \quad (13)$$

Table 5: Partial molar volumes ($V_{m,1}, and V_{m,2}$ against mole fraction x$_1$) for [Bmim][NTf$_2$] and dimethyl carbonate mixtures at temperature T and atmospheric pressure:

	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
x	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$
	$10^{-6}m^3mol^{-1}$		$10^{-6}m^3mol^{-1}$		$10^{-6}m^3mol^{-1}$		$10^{-6}m^3mol^{-1}$		$10^{-6}m^3mol^{-1}$		$10^{-6}m^3mol^{-1}$	
0.0000	289.6753	84.7069	290.2161	85.2368	291.2702	85.7760	291.9740	86.3250	292.8900	86.8837	293.5233	87.4529
0.1010	290.2420	84.6762	291.1750	85.2028	291.9834	85.7437	292.8723	86.2926	293.7347	86.8498	294.6158	87.4143
0.1945	290.6148	84.6124	291.5405	85.1476	292.3743	85.6794	293.2657	86.2320	294.1386	86.7855	295.0418	87.3498
0.2994	290.8308	84.5448	291.6912	85.0939	292.5899	85.6092	293.4643	86.1628	294.3464	86.7156	295.2249	87.2847
0.3999	290.9022	84.5086	291.7564	85.0518	292.6748	85.5623	293.5584	86.1056	294.4357	86.6634	295.3081	87.2316
0.4976	290.9488	84.4698	291.8400	84.9801	292.7461	85.5024	293.6519	86.0263	294.5253	86.5876	295.4128	87.1422
0.5842	291.0535	84.3426	291.9794	84.8107	292.8752	85.3458	293.7956	85.8518	294.6780	86.4023	295.5851	86.9330
0.6886	291.3290	83.8449	292.2725	84.2660	293.1807	84.7881	294.1064	85.2746	295.0197	85.7743	295.9474	86.2606
0.8014	291.8079	82.3974	292.7519	82.7678	293.7003	83.1984	294.6341	83.6283	295.5920	84.0091	296.5409	84.4086
0.8890	292.2160	80.1124	293.1728	80.3718	294.1495	80.6678	295.1071	80.9382	296.0906	81.1889	297.0620	81.4444
1.0000	292.4976	74.8593	293.4814	74.6123	294.4675	74.7296	295.4569	74.3886	296.4490	74.4948	297.4435	74.3206

$$\bar{V}_{m,2} = V_2^* + x_1^2\sum_{i=0}^{4} A_i\,(x_2 - x_1)^i + 2x_2x_1^2\sum_{i=1}^{4} A_i(i)(x_2 - x_1)^{i-1} \quad (14)$$

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

$$\bar{V}_{m,1}^E = \bar{V}_{m,1} - V_1^* \quad (15)$$

$$\bar{V}_{m,2}^E = \bar{V}_{m,2} - V_2^* \quad (16)$$

The values of $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ are presented in Table 5 for all the systems. From this table, we observe that the values of $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ for both the components in the mixtures are lower than their individual molar volumes in the pure state, which represents the contraction of volume on mixing [Bmim][NTf$_2$] with dimethyl carbonate at all the temperatures under study.

The variation of excess partial molar volumes of $\bar{V}_{m,1}^E$ [Bmim][NTf$_2$] and $\bar{V}_{m,2}^E$ (dimethyl carbonate) are represented in Figures 3 and 4 respectively, in the temperature range from 298.15 to 323.15K. Inspection of these figures not only reveals the existence of strong forces between the unlike molecules but also supports the deductions drawn from excess molar volume. The partial molar volumes and excess partial molar volumes of [Bmim][NTf$_2$] at infinite dilution, $\left(\bar{V}_{m,1}^{E\infty}\right)$ and $\left(\bar{V}_{m,2}^{E\infty}\right)$, are given by:

$$\bar{V}_{m,1}^{E,\infty} = A_0 + A_1 + A_2 + A_3 + \cdots = \bar{V}_{m,1}^{\infty} - V_1^* \quad (17)$$

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The data of $\bar{V}_{m,1}^{E}$ and $(\bar{V}_{m,1}^{E,\infty})$ are presented in Table 6 at 298.15K to 323.15K in steps of 5 K. From this table, the values of $(\bar{V}_{m,1}^{E,\infty})$ are found to be negative and become more negative with increasing temperature. Hence we can conclude that with increasing temperature, strong interactions increase among the unlike molecules of the mixtures. This supports the existing strong molecular interactions that were observed with the variation of $\bar{V}_{m}^{E}$.

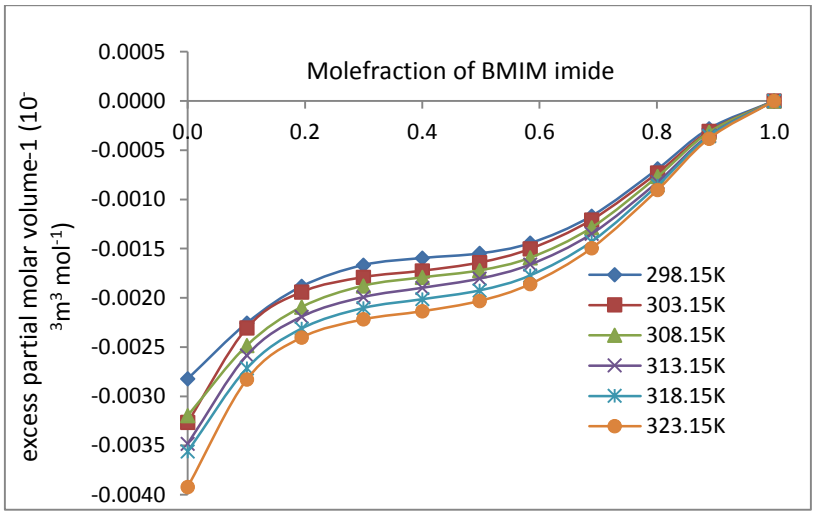

Fig. 3: Plots of excess partial molar volume ($\bar{V}_{m,1}^{E}$) against mole fraction x_1 for [Bmim][NTf_2] and Dimethyl carbonate mixtures at temperature T and atmospheric pressure

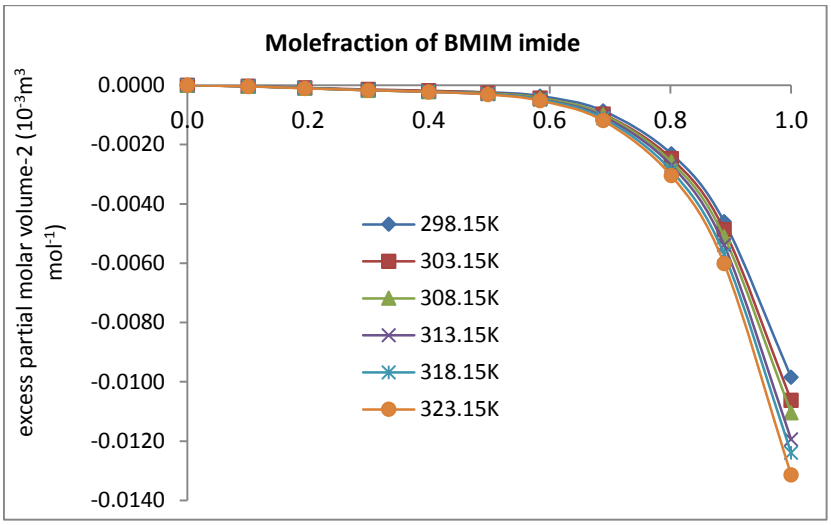

Fig. 4: Plots of excess partial molar volume ($\bar{V}_{m,2}^{E}$) against mole fraction (x1) for [Bmim][NTf_2] and dimethyl carbonate mixtures at temperature T and atmospheric pressure

Table 6: Partial ($\bar{V}_{m,1}^{E}$) and excess partial molar volumes ($(\bar{V}_{m,1}^{E\infty})$) at infinite dilution for [Bmim][NTf_2] (1) Dimethyl carbonate(2) mixtures at temperature T and atmospheric pressure

T/K	$\bar{V}_{m,1}$ $10^{-6}m^3mol^{-1}$	$\bar{V}_{m,1}^{E,\infty}$ $10^{-6}m^3mol^{-1}$	$\bar{V}_{m,2}$ $10^{-6}m^3mol^{-1}$	$\bar{V}_{m,2}^{E,\infty}$ $10^{-6}m^3mol^{-1}$
298.15	289.68	-2.82	74.86	-9.85
303.15	290.22	-3.27	74.61	-10.62
308.15	291.27	-3.2	74.73	-11.05
313.15	291.97	-3.48	74.39	-11.94
318.15	292.89	-3.56	74.49	-12.39
323.15	293.52	-3.92	74.32	-13.13

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In Fig. 4, the k_s^E values for this system are found to be negative in the whole composition range at all investigated temperatures. The negative k_s^E values are attributed to the strong attractive interactions between the molecules of the components [20]. In the present study, the negative k_s^E values can be attributed to a closer approach of unlike molecules and a stronger interaction between components of mixtures at all temperatures. This supports the inference drawn from V_m^E.

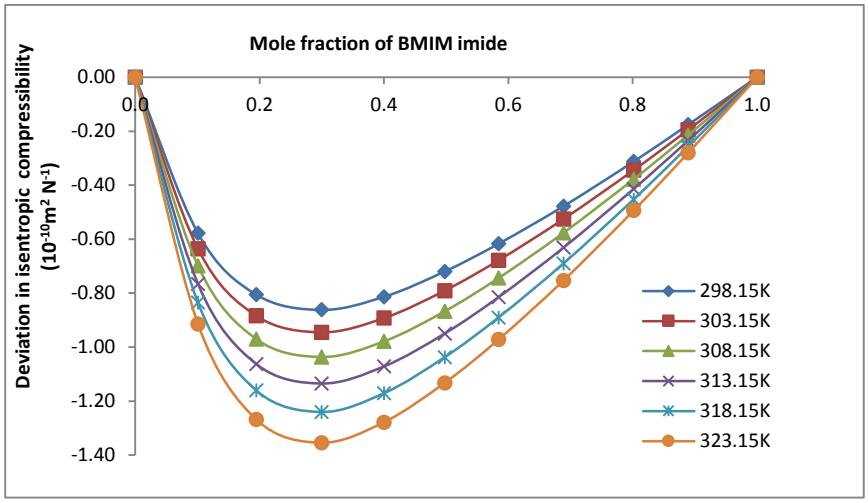

Fig. 4: Plots of excess isentropic compressibility (k_s^E) against mole fraction (x_1) for [Bmim][NTf_2] and dimethyl carbonates mixtures at temperature T and atmospheric pressure

In the present study, the negative L_f^E were observed. The trend of L_f^E values (Fig. 5) is similar to that of k_s^E at all temperatures under study. The specific interactions between unlike molecules in the liquid mixture lead to negative values of L_f^E . The structural readjustments in the liquid mixture towards a less compressible phase of fluid and closer packing of molecules [20] also contribute to negative L_f^E.

Figure 6 shows that Z^E is positive for the systems at all the temperatures under study. Specific acoustic impedance is a parameter that depends on the molecular packing of the mixture. The positive values of Z^E indicate the presence of strong interactions between the component molecules [18].

From the figure 7 the u^E values are found to be positive over the entire range of composition at all investigated temperatures. This indicates the increasing strength of interaction between component molecules of binary liquid mixtures. In general, strong interactions among the components of a mixture cause the formation of molecular aggregates and more compact structures due to which the ultrasonic velocity increases leading to positive u^E. On the other hand, if the structure-breaking factor predominates, it leads to expansion of the liquid mixture, and hence the ultrasonic velocity decreases resulting in negative u^E [20]. The positive values of u^E in the present system indicate much stronger interactions between the molecules [21].

Fig.8 shows that the values of Δn_D are positive over the entire range of compositions at a given temperature. The variation of refractive index deviations Δn_D with the mole fraction of IL shows the reverse trend to k_s^E [22]. This further supports the presence of strong interactions between component molecules in study.

Generally, the cohesive forces (attraction forces) or dispersive forces between the molecules of a mixture cannot be easily assessed by any theory.

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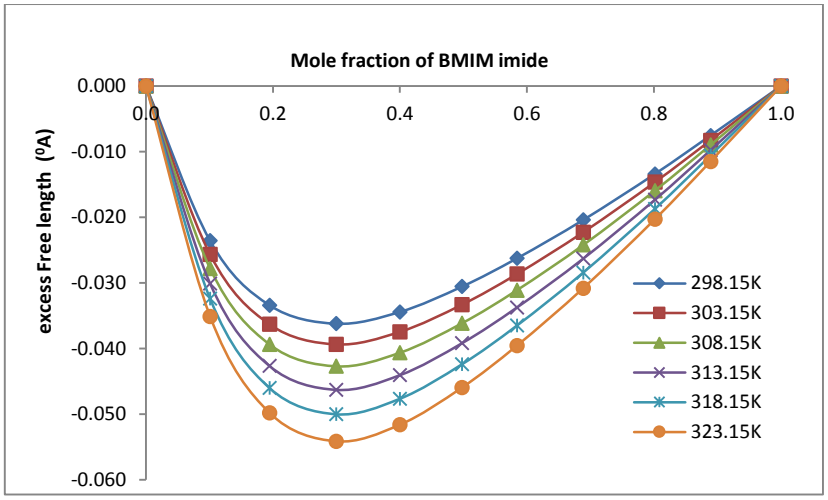

Fig. 5: Plots of excess free length (L^{E}_{f}) against mole fraction (x1) for [Bmim][NTf_2] and Dimethyl carbonate mixtures at temperature T and atmospheric pressure

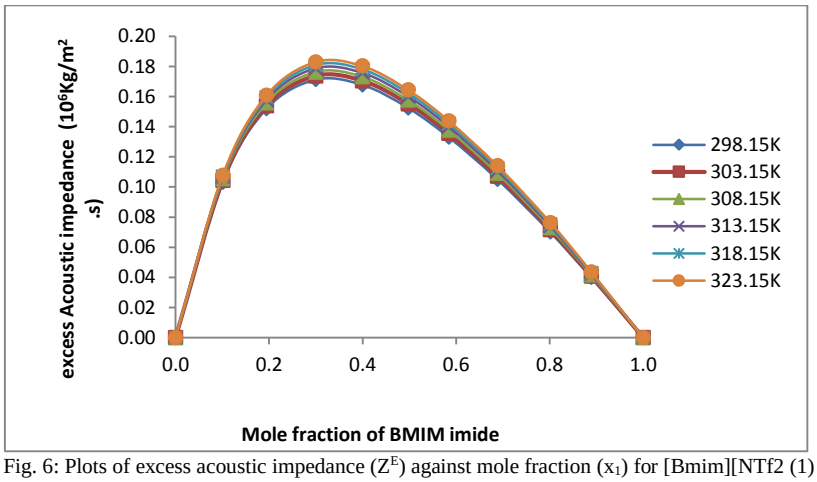

Fig. 6: Plots of excess acoustic impedance (Z^{E}) against mole fraction (x_1) for [Bmim][NTf2 (1) dimethyl carbonate (2) mixtures at temperature T and atmospheric pressure

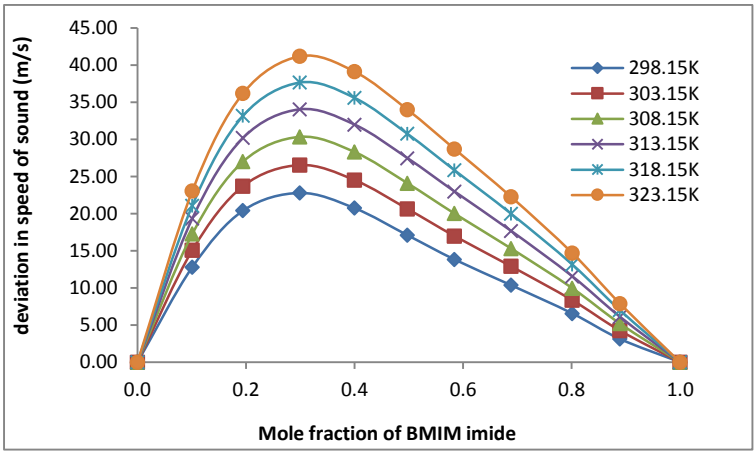

Fig. 7: Plots of excess ultrasonic speed of sounds (u^{E}) against mole fraction (x_1) for [Bmim][NTf_2]

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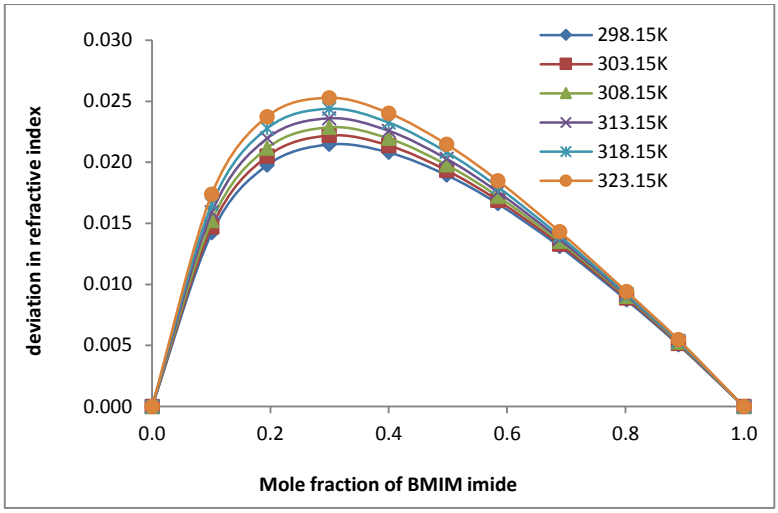

Fig. 8: Plots of deviation in refractive index (Δn_D) against mole fraction (x_1) for [Bmim][NTf_2] and Dimethyl carbonate mixtures at temperature T and atmospheric pressure

The electronic structure of the aromatic cations reflect the unique properties of imidazolium cations. The delocalized 3-center-4-electron configuration are contained in the electronic structure of these salts across the N1–C2–N3 moiety, a double bond between C4 and C5 at the opposite side of the ring, and a weak delocalization in the central region [23]. Almost the same charge is carried by the hydrogen atoms C2–H, C4–H, and C5–H, but carbon C2 is positively charged owing to the electron deficit in the C=N bond. On the other hand C4 and C5 are practically neutral. The properties of these ionic liquids arise from the resulting acidity of the hydrogen atoms. The hydrogen on the C2 carbon (C2–H) has been shown to bind specifically with solute molecules.

The hydrogen bonds play an important role in the stability and miscibility of the binary liquid mixtures of [Bmim][NTf_2] (1) and dimethyl carbonate(2). The nature of interaction of dimethyl carbonate molecules with the cation is different from that of anion. The characteristic groups which interact with dimethyl carbonate molecules are the C–H groups in the imidazolium ring and oxygen atoms in the anion. The complete miscibility and solvation of cations and anions in the ionic liquid is due to sufficient hydrogen bonding interactions of dimethyl carbonate with [Bmim][NTf_2]. Hence, the remarkable contraction in the volume of the mixture can be attributed to the hydrogen bonds between the ionic liquid [Bmim][NTf_2] (1) dimethyl carbonate (2).

5 CONCLUSION

- From the experimental data, parameters such as V_m^E, k_s^E, L_f^E, Z^E, u^E, Δn_D, have been evaluated. The excess and deviation properties have been fitted to Redlich–Kister type polynomial and the corresponding standard deviations were in good agreement with the experimental value.
- The values of V_m^E become more negative with increase in temperature.
- The values of $(\bar{V}_{m,1}^{E,\infty})$ are found to be negative and become more negative with increasing temperature. Hence we can conclude that with increasing temperature, strong interactions increase among the unlike molecules of the mixtures. This supports the existing strong molecular interactions that were observed with the variation of $\bar{V}_m^E$.
- In the present study, the negative k_s^E values can be attributed to a closer approach of unlike molecules and a stronger interaction between components of mixtures over the entire range of composition at all temperatures under study.
- The negative L_f^E were observed. The trend of L_f^E values (Fig. 5) is similar to that of k_s^E at all temperatures under study.
- Z^E is positive for the systems at all the temperatures under study. The positive values of Z^E indicate the presence of strong interactions between the component molecules.
- Similarly the positive values of u^E indicate much stronger interactions between the molecules.
- The positive values of Δn_D at a given temperature over the entire composition range indicate the strong interactions between the component molecules
- Finally it may be concluded that the observed negative values of V_m^E, k_s^E, L_f^E, and positive values of Z^E, u^E, Δn_D clearly indicate the dominance of strong attractive forces.

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