ULTRASONIC VELOCITY, DENSITY AND REFRACTIVE INDEX OF BINARY MIXTURES CONTAINING IONIC LIQUID [BMIM][NTF_2] AND DIETHYL CARBONATE FROMT = (298.15 TO 323.15) K

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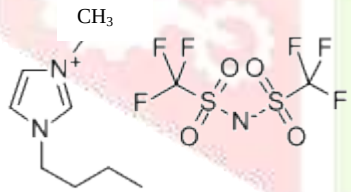
Abstract: The density (ρ), ultrasonic velocity (u) and refractive index (n_D) of the binary mixtures of 1-Butyl 3-Methylimidazoliumbis(Trifluoromethylsulfonyl)Imide (BMIM imide) and diethyl carbonate (DEC) and those of pure liquids were measured using Anton Paar vibrating tube density and sound velocity meter (DSA 5000 M) and Dr. KernchenAbbemat (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), acoustic impedance (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 ofV_m^E,k_S^E, $L_f^E$and positive values for Z^E, u^E, and Δn_D indicate the existence of strong interactions between the components.

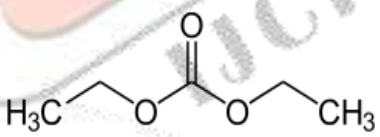
Keywords: BMIM imide, diethyl carbonate, Density, ultrasonic velocity, Refractive index, excess/deviation parameters, Redlich–Kister type equation.

I. INTRODUCTION:

Ionic liquids (ILs) are salts that exist in liquid state at low temperature (<100 ^{0}C). They are non-flammable, thermally stable and have no detectable vapor pressure. They are excellent solvents for a broad range of polar organic compounds and they show partial miscibility with aromatic hydrocarbons. Thus they are intensively investigated especially as replacement solvents for reactions and separations. They are used in synthetic chemistry, sensors, solar cells, photo cells and batteries. They are also used as hydraulic fluids, thermal fluids and lubricants [1-5]. They have applicable electrochemical window [6]. The Imidazoliumcation with varying hetero atom functionality is contained in most commonly studied ILs.



(BMIM imide) $C_{10}H_{15}F_6N_3O_4S_2$



Diethyl carbonate (DEC)$C_5H_{10}O_3$

Diethyl carbonate is a clear liquid with a low flash point. It is used as a solvent such as in Erythromycin intramuscular injection. It can be used as a component of electrolytes in Lithium batteries.

Table 1: Experimental and literature values of density, velocity and refractive index

	ρ kgm^{-3}		u ms^{-1}		n_D	
T/K	**Exp.**	**Lit.**	**Exp.**	**Lit.**	**Exp.**	**Lit.**
[Bmim][imide]						
298.15	1433.721	1433.72[7]	1227.86	1227.86[7]	1.4268	1.4267[7]
303.15	1428.915	1428.95[7]	1216.77	1216.77[7]	1.425	1.42523[7]
308.15	1424.13	1424.18[7]	1205.80	1205.80[7]	1.423	1.42374[7]
313.15	1419.361	1419.41[7]	1194.95	1194.95[7]	1.422	1.42225[7]
318.15	1414.611	1414.64[7]	1184.23	1184.23[7]	1.419	1.42076[7]
323.15	1409.881	1409.87[7]	1173.61	1173.61[7]	1.418	1.41923[7]
diethylcarbonate						
298.15	969.362	969.097[8]	1177.07	1177.46[8]	1.382	1.38252[9]

303.15	963.732	963.468[8]	1156.63	1156.96[8]	1.38	1.3801[10]
308.15	958.08	957.814[8]	1136.29	1136.62[8]	1.377	1.3787[10]
313.15	952.401	952.134[8]	1116.13	1116.45[8]	1.375	1.3775[10]
318.15	946.694	946.428[8]	1096.15	1096.47[8]	1.372	1.3733[11]
323.15	940.96	940.691[8]	1076.35	1076.66[8]	1.37	1.3710[11]

II. THEORY:

The experimentally measured values of ρ, u and $n_D$in comparison with literature values are given in table1. The experimentally measured values and the derived parameter parameters are shown in Table 2. 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 3.

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:

$$V_m = \frac{M_{eff}}{\rho} \qquad (1)$$

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 diethyl 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:

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

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

The excess molar volumes are given by:

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

whereρ is the density of the mixture and M_i , x_i, and $\rho_i$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 ofspeed of sound and density using the Newton–Laplace equation:

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

Excess isentropic compressibility is given by:

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

Where,k_S is the isentropic compressibility

The excess intermolecular free length is given by:

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

The excess speeds of sound,u^E is estimated using thefollowing expression proposed by Douheret et al. [12]:

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

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[13] 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 diethyl 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. Thecorresponding standard deviations σ (Y^E) have been calculated using the followingexpression:

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

where 'm' is the total number of experimental points and n is the number of coefficients in eq.(10). The calculated values of the coefficients A_i along with the standard deviations, σ (Y^E)are given in Table 4.

The partial molar volumes $\bar{V}_{m,1}$ of component1[Bmim][NTf_2]and $\bar{V}_{m,2}$ of component 2 (diethyl carbonate) in the mixtures over the entire composition range have been calculated by using the following relations:

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

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

Where V_1^* and V_2^* are the molar volumes of pure components of [Bmim][NTf_2]and diethyl carbonate respectively. The derivatives in the above equations are obtained by differentiating the Redlich–Kister equation [13], which leads to the following equations for$\bar{V}_{m,1}$, $and\ \bar{V}_{m,2}$:

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

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

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

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

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

The values of $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ are presented in Table 5for 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 indicates contraction of volume take place on mixing [Bmim][NTf_2] with diethyl carbonate at all the temperatures.

Fig.3and 4represent the disparity of excess partial molar volumes of$\bar{V}_{m,1}^E$([Bmim][NTf_2]) and$\bar{V}_{m,2}^E$ (diethyl carbonate) respectively, in the binary mixture at 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:

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

The pertinent data of $\bar{V}_{m,1}^E$ and $\left(\bar{V}_{m,1}^{E,\infty}\right)$are presented in Table 6at 298.15K to 323.15K in steps of 5 K. From this table, the values of$\left(\bar{V}_{m,1}^{E,\infty}\right)$ are found to be negative and to become more negative with increasing temperature. Hence we conclude that strong interactions increase among the unlike molecules of the mixtures with increasing temperature. This argument supports the existing strong molecular interactions that were noticed in the case of $\bar{V}_m^E$ in the binary system that are well reproduced from the evaluated properties of partial molar volumes as well as at all investigated temperatures.

Table 2: The experimentally measured values and the derived parameter parameters

x_1	ρ Kg/m^3	U m/sec	n_D	V_m*10$^-$ m^3	β_s*10$^-$ m^2 N^{-1}	$\bar{M}$ kg	Z*10^5 Kg/m^2.s	Lf *10$^-$	R_m*10$^-$ m^3/mol	r *10$^-$
298.15K										
0.0000	969.36	1177.07	1.3823	121.86	7.4458	0.1181	11.4101	5.6109	28.3769	2.2433
0.1108	1082.79	1184.99	1.3949	139.93	6.5770	0.1515	12.8309	5.2734	33.5364	2.3718
0.2084	1158.54	1197.69	1.4027	156.16	6.0173	0.1809	13.8757	5.0440	38.0846	2.4745
0.2886	1208.82	1206.50	1.4076	169.63	5.6831	0.2050	14.5845	4.9019	41.8065	2.5526
0.3927	1261.73	1213.46	1.4123	187.37	5.3825	0.2364	15.3106	4.7705	46.6571	2.6477
0.4805	1298.48	1217.48	1.4155	202.44	5.1957	0.2629	15.8087	4.6870	50.7479	2.7230
0.5887	1336.32	1220.86	1.4187	221.11	5.0206	0.2955	16.3145	4.6074	55.8003	2.8105
0.7043	1369.91	1223.32	1.4215	241.09	4.8778	0.3303	16.7584	4.5414	61.1997	2.8984
0.8009	1393.90	1224.87	1.4235	257.83	4.7818	0.3594	17.0735	4.4965	65.7195	2.9680
0.9127	1417.88	1226.25	1.4254	277.23	4.6903	0.3931	17.3867	4.4533	70.9511	3.0448
1.0000	1433.72	1227.86	1.4267	292.50	4.6263	0.4194	17.6041	4.4228	75.0546	3.1024
303.15K										
0.0000	963.73	1156.63	1.3799	122.58	7.7563	0.1181	11.1468	5.7824	28.3870	2.2436
0.1108	1077.40	1166.87	1.3930	140.63	6.8168	0.1515	12.5718	5.4209	33.5644	2.3724
0.2084	1153.30	1181.30	1.4012	156.87	6.2135	0.1809	13.6239	5.1755	38.1274	2.4754
0.2886	1203.68	1191.23	1.4062	170.35	5.8546	0.2050	14.3386	5.0238	41.8614	2.5537
0.3927	1256.65	1199.27	1.4111	188.13	5.5329	0.2364	15.0706	4.8838	46.7195	2.6489
0.4805	1293.48	1204.03	1.4142	203.22	5.3329	0.2629	15.5739	4.7947	50.8049	2.7240
0.5887	1331.40	1208.44	1.4173	221.93	5.1433	0.2955	16.0891	4.7087	55.8439	2.8112
0.7043	1365.03	1211.43	1.4200	241.95	4.9918	0.3303	16.5364	4.6388	61.2331	2.8989
0.8009	1389.04	1213.15	1.4220	258.73	4.8917	0.3594	16.8511	4.5921	65.7519	2.9685
0.9127	1413.10	1215.26	1.4239	278.17	4.7917	0.3931	17.1728	4.5449	70.9720	3.0451
1.0000	1428.92	1216.77	1.4252	293.48	4.7269	0.4194	17.3866	4.5141	75.0780	3.1027
308.15K										
0.0000	958.08	1136.29	1.3776	123.30	8.0839	0.1181	10.8866	5.9530	28.3962	2.2438
0.1108	1072.00	1148.87	1.3903	141.34	7.0675	0.1515	12.3158	5.5662	33.5296	2.3716
0.2084	1148.06	1165.00	1.3986	157.58	6.4178	0.1809	13.3749	5.3042	38.0862	2.4745
0.2886	1198.54	1176.03	1.4037	171.08	6.0327	0.2050	14.0951	5.1426	41.8110	2.5527
0.3927	1251.56	1185.15	1.4085	188.90	5.6885	0.2364	14.8329	4.9937	46.6550	2.6477
0.4805	1288.46	1190.66	1.4116	204.02	5.4746	0.2629	15.3412	4.8989	50.7259	2.7226

0.5887	1326.47	1195.83	1.4147	222.75	5.2719	0.2955	15.8623	4.8074	55.7478	2.8096
0.7043	1360.14	1199.42	1.4175	242.82	5.1106	0.3303	16.3137	4.7333	61.1282	2.8972
0.8009	1384.15	1201.53	1.4196	259.65	5.0044	0.3594	16.6309	4.6838	65.6504	2.9670
0.9127	1408.29	1204.05	1.4217	279.11	4.8980	0.3931	16.9565	4.6338	70.8858	3.0438
1.0000	1424.13	1205.80	1.4237	294.47	4.8295	0.4194	17.1722	4.6012	75.0994	3.1030
					313.15K					
0.0000	952.40	1116.13	1.3753	124.03	8.4285	0.1181	10.6300	6.1330	28.4107	2.2442
0.1108	1066.58	1131.03	1.3888	142.06	7.3292	0.1515	12.0634	5.7191	33.5841	2.3729
0.2084	1142.81	1148.82	1.3973	158.31	6.6301	0.1809	13.1289	5.4395	38.1504	2.4759
0.2886	1193.39	1160.94	1.4024	171.82	6.2173	0.2050	13.8545	5.2674	41.8780	2.5541
0.3927	1246.54	1171.10	1.4073	189.66	5.8493	0.2364	14.5983	5.1092	46.7191	2.6489
0.4805	1283.39	1177.41	1.4104	204.82	5.6207	0.2629	15.1107	5.0083	50.7909	2.7237
0.5887	1321.54	1183.32	1.4135	223.58	5.4040	0.2955	15.6380	4.9108	55.8058	2.8106
0.7043	1355.22	1187.51	1.4162	243.71	5.2326	0.3303	16.0933	4.8323	61.1890	2.8982
0.8009	1379.21	1190.02	1.4184	260.58	5.1199	0.3594	16.4129	4.7800	65.7211	2.9680
0.9127	1403.50	1192.96	1.4206	280.07	5.0065	0.3931	16.7432	4.7268	70.9667	3.0450
1.0000	1419.36	1194.95	1.4223	295.46	4.9341	0.4194	16.9607	4.6925	75.1199	3.1033
					318.15K					
0.0000	946.69	1096.15	1.3729	124.78	8.7912	0.1181	10.3772	6.3192	28.4218	2.2445
0.1108	1061.15	1113.34	1.3861	142.79	7.6027	0.1515	11.8142	5.8765	33.5488	2.3721
0.2084	1137.57	1132.78	1.3949	159.04	6.8507	0.1809	12.8861	5.5783	38.1165	2.4752
0.2886	1188.25	1145.98	1.4001	172.57	6.4083	0.2050	13.6171	5.3952	41.8453	2.5534
0.3927	1241.51	1157.26	1.4051	190.43	6.0143	0.2364	14.3675	5.2267	46.6844	2.6482
0.4805	1278.39	1164.28	1.4082	205.62	5.7706	0.2629	14.8840	5.1197	50.7504	2.7230
0.5887	1316.57	1170.94	1.4112	224.43	5.5397	0.2955	15.4162	5.0162	55.7493	2.8096
0.7043	1350.23	1175.72	1.4139	244.61	5.3578	0.3303	15.8749	4.9332	61.1051	2.8969
0.8009	1374.43	1178.66	1.4158	261.48	5.2372	0.3594	16.1999	4.8774	65.5934	2.9661
0.9127	1398.72	1182.01	1.4178	281.03	5.1172	0.3931	16.5330	4.8211	70.7914	3.0425
1.0000	1414.61	1184.23	1.4208	296.45	5.0407	0.4194	16.7522	4.7850	75.1395	3.1035
					323.15K					
0.0000	940.96	1076.35	1.3706	125.54	9.1732	0.1181	10.1280	6.5286	28.4338	2.2448
0.1108	1055.71	1095.81	1.3848	143.52	7.8883	0.1515	11.5686	6.0541	33.6182	2.3737
0.2084	1132.31	1116.88	1.3937	159.78	7.0798	0.1809	12.6465	5.7355	38.1955	2.4769
0.2886	1183.10	1131.15	1.3990	173.32	6.6060	0.2050	13.3827	5.5402	41.9212	2.5549
0.3927	1236.48	1143.52	1.4039	191.20	6.1848	0.2364	14.1394	5.3607	46.7489	2.6495
0.4805	1273.40	1151.26	1.4069	206.43	5.9250	0.2629	14.6602	5.2469	50.8059	2.7240
0.5887	1311.58	1158.64	1.4099	225.28	5.6795	0.2955	15.1965	5.1371	55.8025	2.8105
0.7043	1345.32	1164.04	1.4126	245.50	5.4858	0.3303	15.6600	5.0487	61.1657	2.8978
0.8009	1369.55	1167.39	1.4147	262.42	5.3578	0.3594	15.9880	4.9895	65.6712	2.9673
0.9127	1393.93	1171.15	1.4168	281.99	5.2304	0.3931	16.3250	4.9298	70.8861	3.0438
1.0000	1409.88	1173.61	1.4192	297.44	5.1496	0.4194	16.5465	4.8915	75.1520	3.1037

Table 3: Theexcess parameters ofbinary mixtures of BMIM imide and diethyl carbonate.

x_1	ΔU m/s	$\Delta\beta_{ad}*10^{-10}$ $m^2\ N^{-1}$	Z^E*10^5 $Kg/m^2.s$	L_f^E $*10^{-11}m$	Δn	$\Delta R_{m*}\ 10^{-6}$ m^3/mol	$V^E_m*10^{-6}$ m^3mol^{-1}
			298.15K				
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1108	2.3868	-0.5573	0.7345	-0.2062	0.0081	-0.0129	-0.8419
0.2084	9.9711	-0.8403	1.1760	-0.3191	0.0116	-0.0243	-1.2793
0.2886	14.5644	-0.9470	1.3833	-0.3651	0.0129	-0.0360	-1.4592
0.3927	16.7510	-0.9594	1.4716	-0.3751	0.0131	-0.0502	-1.5004
0.4805	16.0354	-0.8956	1.4230	-0.3531	0.0124	-0.0571	-1.4110
0.5887	13.6533	-0.7628	1.2556	-0.3030	0.0107	-0.0571	-1.2068
0.7043	10.5031	-0.5825	0.9862	-0.2328	0.0082	-0.0501	-0.9397
0.8009	7.2902	-0.4076	0.7041	-0.1635	0.0059	-0.0430	-0.7023
0.9127	2.6898	-0.1807	0.3219	-0.0727	0.0028	-0.0303	-0.3776
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
0.1108	3.7328	-0.6054	0.7346	-0.2216	0.0082	0.0016	-0.8855
0.2084	12.0200	-0.9102	1.1771	-0.3422	0.0118	0.0081	-1.3373
0.2886	16.9777	-1.0247	1.3865	-0.3914	0.0131	0.0059	-1.5222
0.3927	19.3895	-1.0379	1.4780	-0.4023	0.0133	-0.0058	-1.5647
0.4805	18.6522	-0.9690	1.4312	-0.3789	0.0125	-0.0178	-1.4721
0.5887	16.0106	-0.8256	1.2643	-0.3253	0.0108	-0.0288	-1.2592
0.7043	12.3950	-0.6306	0.9941	-0.2501	0.0084	-0.0344	-0.9800
0.8009	8.7233	-0.4419	0.7113	-0.1760	0.0060	-0.0356	-0.7329

0.9127	3.4860	-0.1970	0.3277	-0.0787	0.0028	-0.0290	-0.3967
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
0.1108	5.0527	-0.6576	0.7340	-0.2378	0.0084	-0.0449	-0.9306
0.2084	14.0915	-0.9863	1.1785	-0.3666	0.0121	-0.0442	-1.3982
0.2886	19.3939	-1.1089	1.3897	-0.4190	0.0134	-0.0552	-1.5877
0.3927	21.9504	-1.1218	1.4830	-0.4304	0.0136	-0.0860	-1.6294
0.4805	21.1311	-1.0468	1.4370	-0.4053	0.0128	-0.1141	-1.5319
0.5887	18.2060	-0.8916	1.2702	-0.3479	0.0109	-0.1390	-1.3088
0.7043	14.1260	-0.6809	0.9993	-0.2675	0.0083	-0.1542	-1.0157
0.8009	9.9612	-0.4770	0.7152	-0.1882	0.0059	-0.1613	-0.7571
0.9127	4.0527	-0.2127	0.3296	-0.0842	0.0029	-0.1326	-0.4083
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			313.15K				
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1108	6.3468	-0.7142	0.7333	-0.2552	0.0089	-0.0046	-0.9778
0.2084	16.1196	-1.0684	1.1795	-0.3927	0.0125	0.0032	-1.4629
0.2886	21.7592	-1.1995	1.3924	-0.4484	0.0138	-0.0054	-1.6580
0.3927	24.4583	-1.2119	1.4873	-0.4603	0.0140	-0.0359	-1.6988
0.4805	23.5591	-1.1302	1.4420	-0.4333	0.0132	-0.0677	-1.5940
0.5887	20.3550	-0.9621	1.2752	-0.3720	0.0112	-0.0992	-1.3559
0.7043	15.8181	-0.7345	1.0035	-0.2859	0.0084	-0.1134	-1.0448
0.8009	11.1705	-0.5144	0.7184	-0.2012	0.0059	-0.1076	-0.7746
0.9127	4.6077	-0.2293	0.3311	-0.0900	0.0029	-0.0729	-0.4180
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
0.1108	7.6204	-0.7753	0.7320	-0.2735	0.0098	-0.0558	-1.0236
0.2084	18.1228	-1.1570	1.1802	-0.4204	0.0138	-0.0394	-1.5319
0.2886	24.1041	-1.2972	1.3952	-0.4797	0.0150	-0.0490	-1.7347
0.3927	26.9519	-1.3093	1.4917	-0.4922	0.0147	-0.0899	-1.7723
0.4805	25.9723	-1.2202	1.4469	-0.4631	0.0135	-0.1279	-1.6567
0.5887	22.4831	-1.0379	1.2798	-0.3974	0.0113	-0.1651	-1.4015
0.7043	17.4896	-0.7916	1.0074	-0.3054	0.0086	-0.2102	-1.0758
0.8009	12.3756	-0.5541	0.7218	-0.2149	0.0061	-0.2636	-0.7995
0.9127	5.1838	-0.2473	0.3336	-0.0963	0.0028	-0.2608	-0.4369
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
0.1108	8.8730	-0.8417	0.7307	-0.2940	0.0117	0.0030	-1.0739
0.2084	20.1107	-1.2528	1.1808	-0.4512	0.0157	0.0261	-1.6035
0.2886	26.4307	-1.4022	1.3975	-0.5144	0.0165	0.0134	-1.8133
0.3927	29.4152	-1.4125	1.4957	-0.5273	0.0155	-0.0357	-1.8486
0.4805	28.3476	-1.3147	1.4513	-0.4960	0.0139	-0.0825	-1.7232
0.5887	24.5759	-1.1171	1.2840	-0.4254	0.0117	-0.1271	-1.4501
0.7043	19.1380	-0.8514	1.0108	-0.3268	0.0090	-0.1636	-1.1047
0.8009	13.5627	-0.5957	0.7245	-0.2300	0.0063	-0.1941	-0.8166
0.9127	5.7392	-0.2655	0.3351	-0.1032	0.0028	-0.1812	-0.4463
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: coefficients (A_i) of Redlich–Kister polynomial for excess parameters

T/ ^{0}K	A_0	A_1	A_2	A_3	A_4	σ
V_m^E (*10^{-6} m^3mol^{-1})						
298.15	-5.5205	-3.3305	-1.4901	1.3391	-0.4326	0.00796
303.15	-5.7598	-3.4639	-1.5065	1.3272	-0.6608	0.01001
308.15	-5.9928	-3.6300	-1.5498	1.2699	-0.7759	0.01275
313.15	-6.2322	-3.8766	-1.5135	1.2881	-0.9901	0.01704
318.15	-6.4709	-4.1875	-1.6178	1.5334	-1.0902	0.01330
323.15	-6.7255	-4.4945	-1.6152	1.6165	-1.2449	0.01221
ΔU (m/s)						
298.15	62.73	38.49	4.59	-77.50	-94.58	0.20366
303.15	73.08	41.93	4.15	-78.93	-90.29	0.32487
308.15	82.85	46.16	5.78	-79.40	-91.45	0.34288
313.15	92.41	50.31	7.30	-79.86	-92.44	0.36646
318.15	101.91	54.55	8.50	-80.89	-92.78	0.36998
323.15	111.26	58.84	10.17	-81.98	-94.06	0.37525
Δk_s(*10^{-10} m^2 N^{-1})						
298.15	-3.5006	-2.1852	-1.2040	0.0868	0.6406	0.002103
303.15	-3.7879	-2.3592	-1.2951	0.0744	0.6266	0.003274
308.15	-4.0917	-2.5563	-1.4194	0.0522	0.6627	0.003753
313.15	-4.4170	-2.7718	-1.5546	0.0276	0.6984	0.004149
318.15	-4.7682	-3.0092	-1.6838	0.0054	0.7103	0.004547
323.15	-5.1363	-3.2704	-1.8642	-0.0273	0.7713	0.005938
Z^E*10^5 $Kg/m^2.s$						
298.15	5.6015	2.5073	0.8430	-0.6110	-0.8783	0.002469
303.15	5.6353	2.4869	0.7891	-0.6449	-0.7928	0.004059
308.15	5.6587	2.4791	0.7749	-0.6632	-0.8090	0.004512
313.15	5.6791	2.4743	0.7539	-0.6831	-0.8128	0.004985
318.15	5.6987	2.4764	0.7355	-0.7312	-0.8156	0.004742
323.15	5.7164	2.4764	0.7147	-0.7646	-0.8214	0.004697
L_f^E*10^{-10}m						
298.15	-1.3823	-0.8104	-0.4011	0.1148	0.2994	0.000886
303.15	-1.4834	-0.8650	-0.4248	0.1205	0.2970	0.001395
308.15	-1.5866	-0.9262	-0.4577	0.1218	0.3127	0.001562
313.15	-1.6964	-0.9913	-0.4927	0.1213	0.3266	0.001767
318.15	-1.8130	-1.0635	-0.5300	0.1286	0.3426	0.001822
323.15	-1.9414	-1.1428	-0.5736	0.1327	0.3623	0.001892
Δn						
298.15	0.0485	0.0264	0.0131	0.0060	0.0053	0.0000587
303.15	0.0492	0.0272	0.0144	0.0057	0.0045	0.0001079
308.15	0.0501	0.0298	0.0116	0.0030	0.0087	0.0001079
313.15	0.0515	0.0313	0.0091	0.0054	0.0163	0.0001414
318.15	0.0526	0.0366	0.0251	0.0065	-0.0008	0.0002338
323.15	0.0542	0.0408	0.0422	0.0198	-0.0065	0.0002282
ΔR_m*$10^{-6}$$m^3$/mol						
298.15	-0.2312	0.0524	0.1856	0.1425	-0.3273	0.00195
303.15	-0.0807	0.2389	0.1368	-0.0334	-0.4258	0.00362
308.15	-0.4783	0.5383	0.0737	0.2024	-1.4610	0.00668
313.15	-0.2974	0.6665	0.1656	-0.2460	-0.6878	0.00543
318.15	-0.5413	0.7394	0.0139	1.1754	-3.1695	0.01212
323.15	-0.3672	0.9244	0.3869	0.6073	-2.2967	0.00931

Table 5: Partial molar volumes ($\bar{V}_{m,1}$, and $\bar{V}_{m,2}$ against mole fraction x_1) for [Bmim][NTf_2] and diethyl carbonate mixtures at temperature T and atmospheric pressure:

	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
x	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}$	$V_{m,2}$
	m^3mol^{-1}		m^3mol^{-1}		m^3mol^{-1}		m^3mol^{-1}		m^3mol^{-1}		m^3mol^{-1}	
0.0000	287.05	121.86	287.69	122.58	288.51	123.30	289.31	124.03	289.92	124.78	290.74	125.54
0.1108	289.24	121.77	290.10	122.47	290.97	123.20	291.89	123.93	292.80	124.67	293.73	125.43
0.2084	289.77	121.68	290.65	122.38	291.52	123.11	292.41	123.85	293.34	124.58	294.24	125.35
0.2886	289.87	121.64	290.74	122.35	291.60	123.07	292.46	123.83	293.36	124.57	294.22	125.35
0.3927	289.97	121.58	290.84	122.28	291.71	123.00	292.56	123.76	293.42	124.52	294.26	125.30
0.4805	290.21	121.39	291.10	122.08	291.98	122.79	292.84	123.53	293.69	124.30	294.54	125.08
0.5887	290.71	120.80	291.62	121.46	292.53	122.14	293.42	122.85	294.30	123.59	295.18	124.32
0.7043	291.39	119.52	292.32	120.14	293.25	120.78	294.17	121.41	295.10	122.06	296.02	122.72
0.8009	291.93	117.83	292.88	118.38	293.82	118.94	294.77	119.49	295.73	120.02	296.69	120.57
0.9127	292.38	115.10	293.35	115.48	294.32	115.87	295.30	116.24	296.28	116.61	297.27	116.97
1.0000	292.50	112.43	293.48	112.51	294.47	112.62	295.46	112.71	296.45	112.95	297.44	113.08

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

T/K	$\bar{V}_{m,1}$	$\bar{V}^{E,\infty}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}^{E,\infty}_{m,2}$
	$10^{-6}m^3mol^{-1}$	$10^{-6}m^3mol^{-1}$	$10^{-6}m^3mol^{-1}$	$10^{-6}m^3mol^{-1}$
298.15	287.05	-5.4518	112.43	-9.4346
303.15	287.69	-5.7905	112.51	-10.0637
308.15	288.51	-5.9585	112.62	-10.6786
313.15	289.31	-6.1471	112.71	-11.3243
318.15	289.92	-6.5248	112.95	-11.8331
323.15	290.74	-6.7076	113.08	-12.4636

III. Results and Discussion:

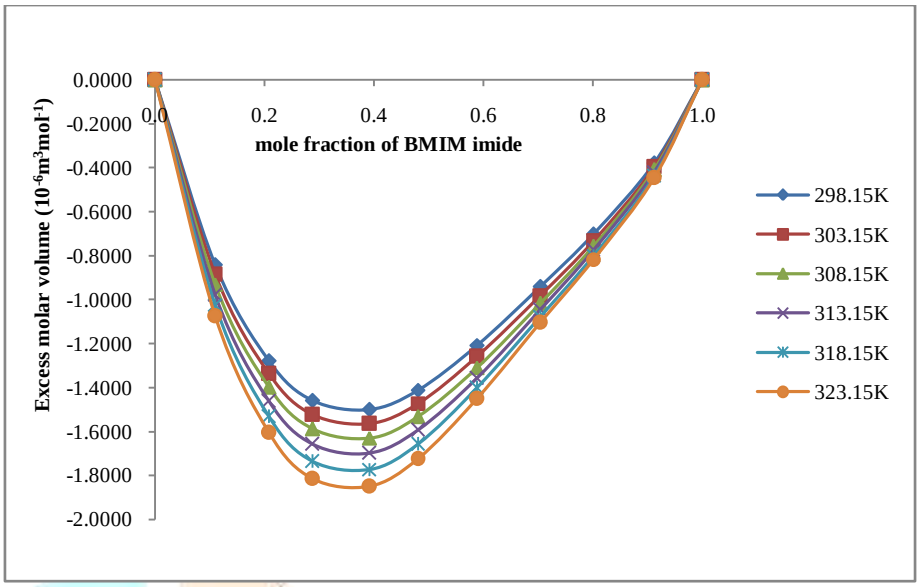


Fig. 4: Plots of excess molar volume (V_m^E) against mole fraction (x_1) for binary mixtures of [Bmim][NTf_2] and Diethyl carbonate at temperature T and atmospheric pressure.

Fig. 4indicates that the V_m^E values are negative over the entire mole fraction range of binary mixtures of [Bmim][NTf_2] and DEC at all temperatures under study. The sign and magnitude of the excess volume is the result of several effects that can operate in the same or in the opposite direction [14,15].

The negative values of V_m^E[16]can be attributed to strong specific interactions such as:

(i) Associationof molecules due to the formation of hydrogen bond (or)dipole-dipole interactions

(ii) Specific interactions like formation of H-bonding, charge transfer (donor–acceptor) complexes, and strong dipole–dipole interactions between the component molecules of the mixture contribute to negative V_m^E values.

(iii) The geometrical fitting of smaller DEC molecules into the available free volume between molecules of ionic liquid takes place on mixing the components.

The variation of excess molar volume in thepresent investigation is negative over the entiremole fractionrange [17].

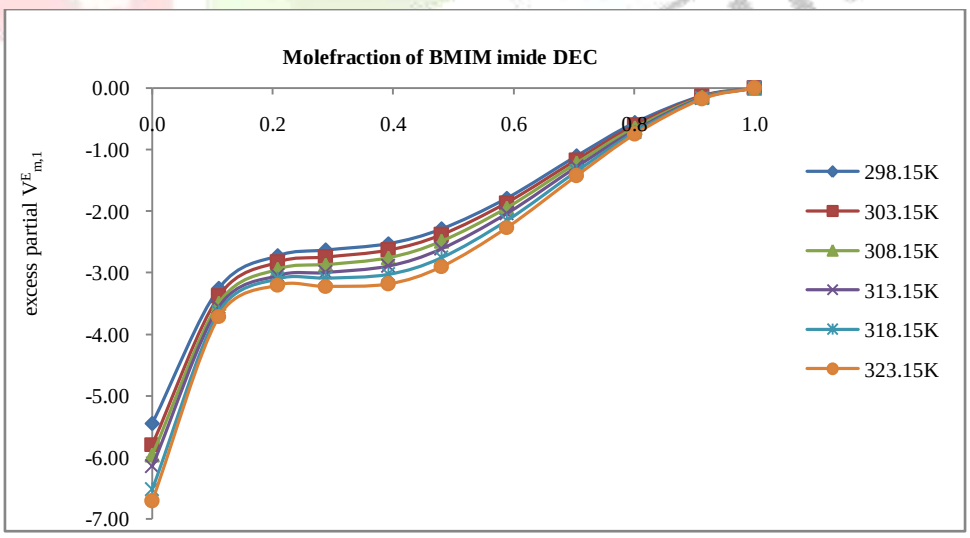


Fig. 5: Plots of partial molar volume ($\overline{V}_{m,1}$) against mole fraction (x_1) for binary mixtures of [Bmim][NTf_2] and Diethyl carbonate at temperature T and atmospheric pressure.

A close perusal of Fig. 5 and 6 indicates thatthe values of $\overline{V}_{m,1}$and $\overline{V}_{m,2}$are negative for the binary mixture overthe whole composition range. This suggests that the molar volumesof each component in the mixture are less than their respectivemolar volume in the pure state, i.e., there is a decrease in thevolume on mixing [Bmim][NTf_2] with DEC. In other words, mixingresults

in volume contraction leading to negative excess volume values. In general, the negative $\bar{V}^{E}_{m,1}$ and $\bar{V}^{E}_{m,2}$ values indicate thepresence of significant solute–solvent interactions between unlike molecules [18], whereas the positive $\bar{V}^{E}_{m,1}$ and $\bar{V}^{E}_{m,2}$ values indicatepresence of solute–solute/solvent–solvent (or weak solute–solvent) interactions between like molecules [20] in the mixture.

The observed negative $\bar{V}^{E}_{m,1}$ and $\bar{V}^{E}_{m,2}$ values indicate that [Bmim][NTf_2]–DEC interactions are stronger than IL–IL or DEC-DECinteractions. A close perusal ofFig.5&6 indicate that the values of $\bar{V}^{E}_{m,1}$ and $\bar{V}^{E}_{m,2}$ are negativefor the binary system at each investigated temperature. Thissuggests that the molar volumes of each component in the mixtureare less than their respective molar volumes in the pure state, i.e.,there is a contraction in volume on mixing [Bmim][NTf_2] withDEC. The decrease in the values of $V^{E}_{m,1}$ and $V^{E}_{m,2}$ with increase intemperature is attributed to the expansion in volume of the mixture,which allows more favourable fitting of smaller DEC molecules into the voids created by larger [Bmim][NTf_2]molecules at higher temperature, thereby, reducing the volumeof the mixture [19].

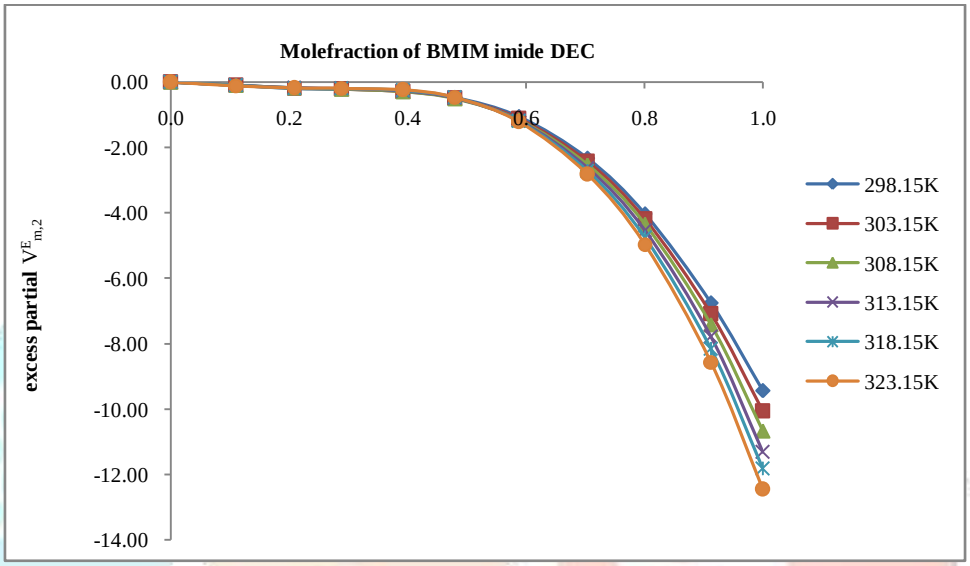


Fig. 6: Plots of partial molar volume ($\bar{V}_{m,2}$) against mole fraction (x_1) for the binary mixtures of [Bmim][NTf_2] and Diethyl carbonate at temperature T and atmospheric pressure.

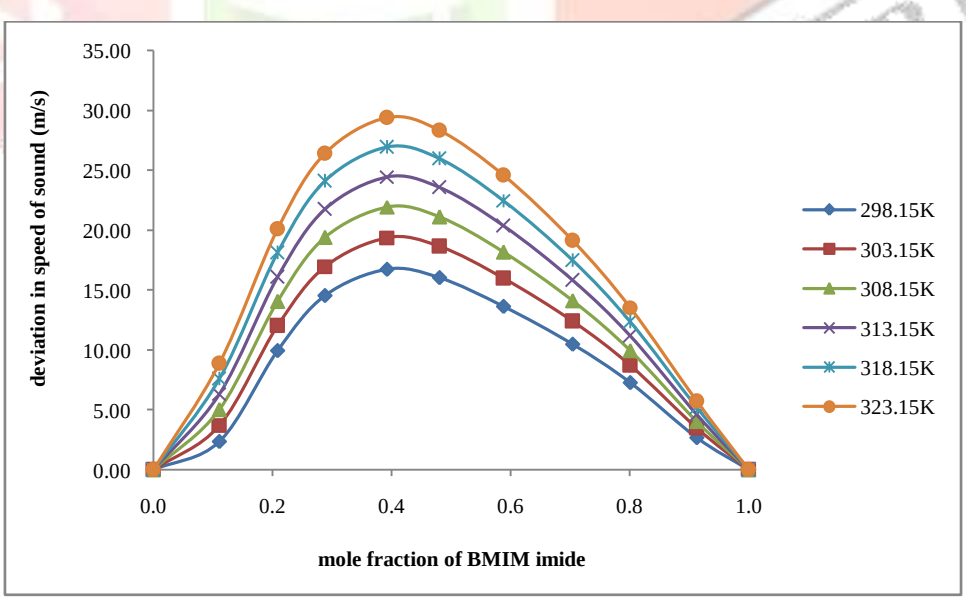


Fig.7: Plots of excess ultrasonic speed of sounds (u^E) against mole fraction (x_1) for the binary mixtures of [Bmim][NTf_2] and Diethyl carbonate at temperature T and atmospheric pressure.

A perusal of Fig.7 reveals that the u^E values are positive for [Bmim][NTf_2] + DEC mixtures over the entire mole fraction range at each investigated temperatures. The sign and magnitude of u^E plays an important role in describing molecular rearrangements as a result of specific interactions occurring in liquid mixture. In general, positive deviations in u^Eindicate the presence of significant interactions and negative deviations in u^E indicate weak interactions between the unlike molecules in the mixtures [20,21]. The observed positive values of u^E for these binary mixtures indicate significant interactions involving the

formation of ion-dipole interactions between the component molecules of the mixture. It is observed that there is an increase in u^E values with increase in temperature, which can be considered due to expansion in free volume of the mixture.

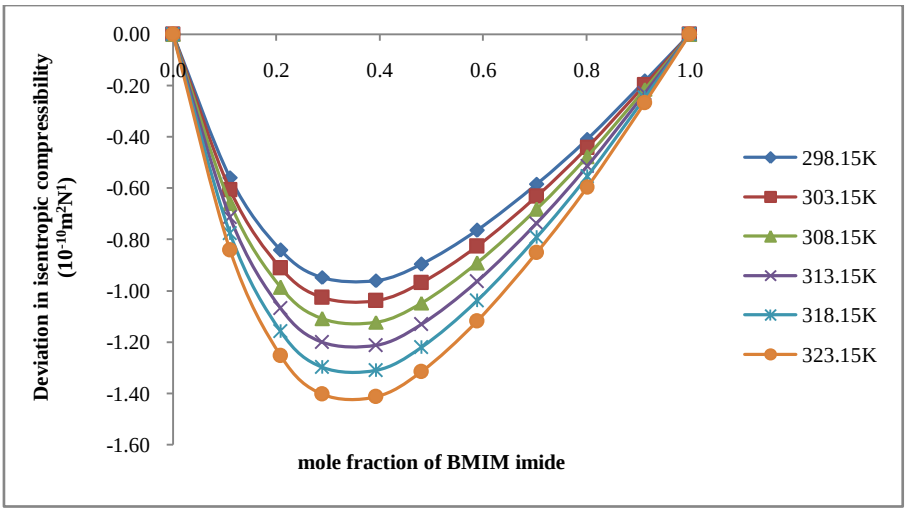


Fig.8: Plots of excess isentropic compressibility (k_s^E) against mole fraction (x_1) for [Bmim][NTf_2] and diethyl carbonate mixtures at temperature T and atmospheric pressure

It canbe seen from the Fig.8 that the deviation inisentropic compressibilityvalues are negative for all the mixtures over the entirerange of composition at all temperatures. The variationof k_s^E with temperature is in a systematic manner. Thenegative values of $k_s^E$are found to increase withincreasing temperature. The more negative value ineach binary system is found to occur atx_1 = 0.4indicating the formation of a stable complex betweenDEC and three benzene derivatives at thiscomposition. The chemical effect includes chargetransfer forces, formation of hydrogen bonds and othercomplex forming interactions making negativecontribution towards k_s^E [22].Generally, the excess properties are considered tobe the reflecting agents of magnitude of polarity at thesite of interactions in the molecules.

In general, the negative values of deviation in isentropic compressibility indicate strong and specific interactions such as H–O and -dipole interactions; on the other hand, the positive values of deviation in isentropic compressibility indicate weak interactions and dispersion forces operating between the molecules of the components of the mixtures [23].

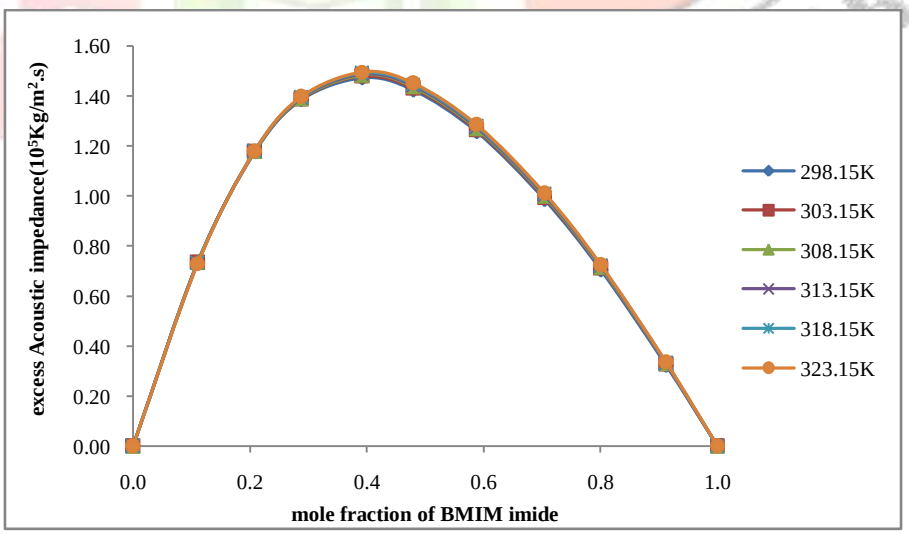


Fig.9: Plots of excess acoustic impedance (Z^E) against mole fraction (x_1) for [Bmim][NTf_2](1) Diethylcarbonate (2) mixtures at temperature T and atmospheric pressure

Fig.9 indicates that the excess acoustic impedance (Z^E) is positive over the entire range of compositions at all the temperatures under study. The positive values of Z^E can be attributed to dispersion forces between the component molecules [24].

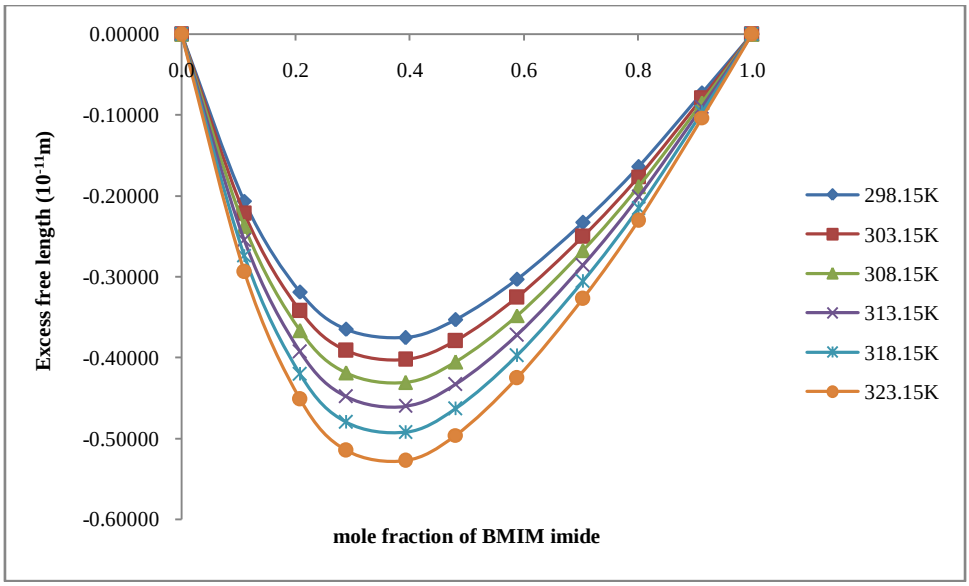


Fig.10: Plots of excess free length (L_f^E) against mole fraction (x_1) for [Bmim][NTf_2] and Diethyl carbonate mixtures at temperature T and atmospheric pressure

The trend of negative L_f^Evalues (Fig.10) is similarto those of k_s^Eat all investigated temperatures. The negativevalues of L_f^E can be attributed to specific interactionsbetween unlike molecules in the mixture. The excess L_f^E values become more negativeindicating the structural readjustments in the liquidmixtures that lead to closer packing of molecules and the liquid mixture becomes less compressible.

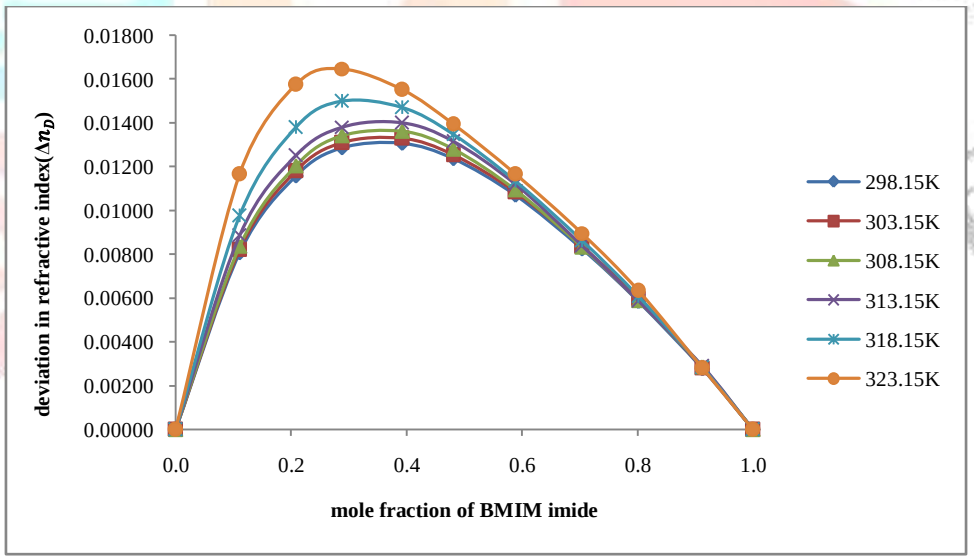


Fig.11: Plots of deviation in refractive index (Δn_D) against mole fraction (x_1) for [Bmim][NTf_2] and Diethyl carbonate mixtures at temperature T and atmospheric pressure

Refractive index (like any other generalized physical property) can provide a selective analysis for a binary system. Refractive index can serve as a control measurement of the split of heavy and light components and thus can provide a single measurement directly useful for process control. The Δn_D values with variation in concentration of [Bmim][NTf_2] can be interpreted as a measure of intermolecular interactions as a consequence of mixing. The Δn_D values represent the electronic perturbation due to mixing of molecules and are a measure of the quantity of interaction. The results presented in Fig.11 indicate that Δn_D values are positive for these mixtures over entire mole fraction range at all investigated temperatures. In general, the positive deviations in Δn_D values are considered due to presence of significant interactions in the mixtures [25], whereas negative deviations in Δn_D values indicate weak interactions between the components of the mixture [26,27]. The positive Δn_D values indicate significant interactions involving ion-dipole interactions between the ions formed by [Bmim][NTf_2] and diethyl carbonate molecules.

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