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Acoustic and Thermodynamic Properties of Binary Mixtures of Ionic Liquid [Bmim][PF_6] and 2-Pyrrolidone from T = (298.15to 323.15)K

N. Bhanu Murthy[1], M. Rangacharyulu[2], J. Siva Rama Krishna[3]

[1, 2, 3]Department of Physics, AcharyaNagarjuna University

Abstract: ***The density (ρ), ultrasonic velocity (u) and refractive index (n_D) of the binary mixtures of 1-Butyl 3-Methylimidazolium Hexafluoropasphate (Bmim [PF_6]) and 2-pyrrolidone 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 between298.15 and 323.15 K in steps of 5K at atmospheric pressure. From the experimental data, the excess values of molar volumes (V_m^E), 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. From the values ofV_m^E,k_s^E, L_f^E, we observe that the inversion in the sign from negative to positive indicates decrease of interaction between [Bmim][PF_6] and 2-Pyrrolidonewith the increase of IL concentration. Negative values of deviation in refractive index suggest that the ion-ion interactionsbetween [Bmim+] and [PF_6^-] ions dominate at higher mole fractions of [Bmim][PF_6] in the mixture.***

Keywords: [Bmim][PF_6], 2-Pyrrolidone, Density, ultrasonic velocity, Refractiveindex, excess/deviation parameters, Redlich–Kister type equation

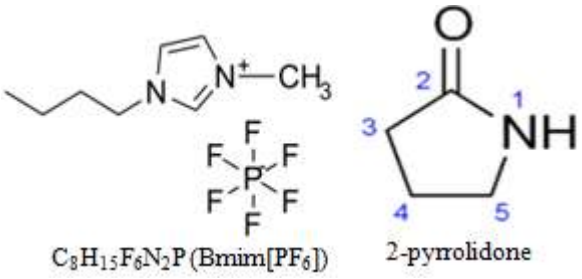
1. Introduction

The measurement of density, velocity, refractive index and related excess propertiesare included in the investigation of the physico-chemical behavior of liquid systems andprovides useful information regarding the intermolecular interactionsin liquids and their mixtures. This experimental data is useful for industrialobjectives, for theoretical and applied thermodynamics.

The nature and strength of molecular interactions can be known by studying the variation of thermo physical properties with several parameterswhich enables to determine the deviation and excess properties of mixtures.

Ionic liquids (ILs) are a group of organic salts formed by thecombination of organic cations and inorganic anions. The imidazoliumcation with varying heteroatom functionality is contained in most commonly studied ILs. Inthis study, we have used the ionic liquid formed by 1-butyl-3-methylimidazolium ion ($BMIM^+$) as cation and 2-pyrrolidone as anion. The properties of ionic liquids can be improved by the addition of a co-solvent which causes them to use effectively in various chemical processes. Bmim [PF_6] is a light yellow colored liquid.

Many scientific investigations [1–7] are focusing on the mixtures of ILswith other organic solvents.Because of its high significanceand experimental accessibility [8–12], density has been widely studied among the various physicochemical properties of ILs. Physicochemical properties of ethylene glycolderivatives in the aqueous or non-aqueous solvents have been widelystudied [13–19]. There has been little focus[20–23] on the refractive index of binary mixtures containingionic liquids.Various researchers [24–30] studied the physicochemical properties of mixtures of [BMIM][PF_6] with someorganic solvents have been by



$C_8H_{15}F_6N_2P$ (Bmim[PF_6]) 2-pyrrolidone

2-pyrrolidone is a colorless liquid which is used as apaint removing agent, solvent for surface treatment for textiles, polymers, and metal coated plastics. It is also used as an intermediate in the production of vinylpyrrolidone and drug piracetam. The structure of2-pyrrolidone is of great interest as it is related to many structural problems in molecular biology. The self-association of 2-pyrrolidone serves as a model for hydrogen bonding in nucleic acid amides.

Pyrrolidin-2-one [31] is aprotic solvent having low volatility, high dipolemoment (3.91 D at 20^0C). It is miscible with water and organic solvents. It has been chosen because it is used in industry,applied chemistry, and participation in biological processes [32,33]. Pyrrolidin-2-one is a five member cyclic amide (lactam) possessing high dipole moment due to which the basic structural peptide bond ANHACOA confers theoretically interesting properties as solvent. It adopts cis conformation (n < 9) [31] and is self-associated through hydrogen bonding in pure state [34].

However, the literature reviewindicates that the systematic volumetric, acoustic, optical and spectroscopic properties of binary mixtures of[BMIM][PF_6] with 2-pyrrolidone have not been reported earlier.

2. Experimental

1-Butyl 3-Methylimidazolium hexafluoropasphateis obtained from "IoLiTec Ionic Liquids Technology GmbH, Germany" >99% and Pyrrolidin-2-one of A.R. grade product is obtained from Merck, Germany. The weighing was done on a Sartorius semi-micro balance CP225-D within ±1 × 10−5 g.All the solutions were kept tightly sealed to minimize absorption of atmospheric moisture. Measurements were performed immediately after preparation of solutions.

Densities and speeds of sound values of the pure liquids and their mixtures were measured using density and sound analyzer apparatus (Anton Paar DSA 5000M). The uncertainties in the density and speed of sound measurements are $1x10^{-3}$ Kg/m^3 and 0.1m/s respectively. Further, uncertainty in the temperature measurement is $\pm 0.001^0$C.

The refractive indices of pure compounds and mixtures are measured using Dr. KrenchenAbbemat RXA170 refractometer of Anton Paar, Germany.

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][PF$_6$]						
298.15	1368.3	1367.88 [35]	1442.58	1442.80[38]	1.409	1.4089 [35]
303.15	1364.2	1362.98 [36]	1430.94	1430.60[38]	1.407	1.4073 [40]
308.15	1360.1	1359.33 [35]	1419.45	1419.00[38]	1.406	1.4057 [40]
313.15	1355.9	1354.58 [36]	1408.04	1407.53[39]	1.405	1.4046 [40]
318.15	1351.8	1350.87 [35]	1396.72	1396.27[39]	1.404	1.4036 [40]
323.15	1347.7	1346.72 [37]	1385.36	1385.15[40]	1.402	1.4025 [40]
2-pyrrolidone						
298.15	1107	1107.12 [41]	1634	1633.95 [45]	1.485	1.4853 [48]
303.15	1103	1103.40 [42]	1618	1617.64 [46]	1.483	1.4839 [49]
308.15	1099	1099.15 [43]	1602	1601.62[47]	1.482	1.4822 [50]
313.15	1095	1095.00 [42]	1586	1585.44[47]	1.480	1.4805 [50]
318.15	1091	1091.05 [42]	1570	1570.39[47]	1.478	1.4790 [50]
323.15	1087	1087.10 [44]	1554	1553.48[47]	1.476	1.4769 [50]

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) and isentropic compressibility (k_S). We calculate thermodynamic parameters such as internal pressure (π_i) and free volume (V_f) assuming the specific heats of the binary mixtures as ideal. The experimentally measured values and the derived parameter values are shown in Table 2. The derived excess/deviation parameter values are shown in Table 3

The molar volume was calculated by using the following equation:

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

Where, M is the effective molecular weight (= x_1M_1 + x_2M_2), and M_1, 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 excess molar volumes are given by:

$$V_m^E = \frac{x_1M_1+x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (3)$$

where, ρ_1, ρ_2 and ρ are the densities of IL, dimethyl carbonate and 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:

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

Excess isentropic compressibility is given by:

$$k_s^E = k_s - (x_1k_{s1} + x_2k_{s2}) \quad (5)$$

Where$k_S$is the isentropic compressibility of the binary mixture andk_{s1}, k_{s2} are that of pure components.

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

$$L_f = \frac{K}{\sqrt{\rho u^2}} \quad (6)$$

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

The excess intermolecular free length is given by:

$$L_f^E = L_f - \left(x_1L_{f1} + x_2L_{f2}\right) \quad (7)$$

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

$$u^E = u - (x_1u_1 + x_2u_2) \quad (8)$$

4. Analysis of Experimental Data

5.

Table 2: The experimentally measured values and the derived parameter parameters binary mixtures of Bmim [PF_6] with 2-pyrrolidinone.

x_1	ρ	u	n_D	V_m*10^{-6}	$\beta_{ad}*10^{-10}$	$\bar{M}$	$Z*10^5$	L_f	R_m*10^{-6}	r
	Kg/m^3	m/sec		$m^3 mol^{-1}$	$m^2 N^{-1}$	$kg\ mol^{-1}$	$Kg/m^2.s$	$*10^{-11}m$	m^3/mol	$*10^{-10}m$
					298.15K					
0.0000	1107.00	1634.00	1.4850	76.87	3.3834	0.0851	18.0884	3.7822	22.0324	2.0618
0.1025	1168.84	1594.39	1.4688	90.26	3.3655	0.1055	18.6360	3.7723	25.1281	2.1542
0.2215	1221.98	1555.98	1.4536	105.72	3.3801	0.1292	19.0137	3.7804	28.6075	2.2494
0.3376	1259.73	1525.52	1.4419	120.91	3.4110	0.1523	19.2174	3.7977	31.9843	2.3346
0.4502	1287.22	1501.82	1.4330	135.73	3.4444	0.1747	19.3318	3.8162	35.2775	2.4121
0.5654	1309.40	1482.66	1.4260	150.95	3.4741	0.1977	19.4140	3.8326	38.6752	2.4872
0.6527	1323.68	1471.08	1.4217	162.46	3.4910	0.2150	19.4723	3.8419	41.2574	2.5414
0.7421	1336.82	1461.43	1.4180	174.18	3.5024	0.2328	19.5367	3.8482	43.8926	2.5944
0.8295	1348.58	1453.79	1.4148	185.56	3.5085	0.2502	19.6055	3.8516	46.4476	2.6438
0.9019	1357.56	1448.53	1.4123	194.95	3.5106	0.2647	19.6647	3.8527	48.5438	2.6830
1.0000	1368.30	1442.58	1.4090	207.69	3.5119	0.2842	19.7388	3.8534	51.3468	2.7336
					303.15K					
0.0000	1103.00	1618.00	1.4830	77.15	3.4631	0.0851	17.8465	3.8266	22.0344	2.0619
0.1025	1164.79	1579.64	1.4669	90.57	3.4406	0.1055	18.3995	3.8141	25.1269	2.1542
0.2215	1217.88	1542.36	1.4517	106.08	3.4516	0.1292	18.7841	3.8202	28.6015	2.2492
0.3376	1255.61	1512.71	1.4400	121.31	3.4804	0.1523	18.9938	3.8361	31.9723	2.3343
0.4502	1283.09	1489.57	1.4312	136.17	3.5125	0.1747	19.1125	3.8538	35.2582	2.4117
0.5654	1305.26	1470.78	1.4241	151.43	3.5416	0.1977	19.1976	3.8697	38.6470	2.4866
0.6527	1319.53	1459.37	1.4198	162.97	3.5584	0.2150	19.2568	3.8788	41.2217	2.5406
0.7421	1332.68	1449.81	1.4160	174.72	3.5699	0.2328	19.3213	3.8851	43.8486	2.5935
0.8295	1344.45	1442.20	1.4128	186.13	3.5761	0.2502	19.3896	3.8885	46.3953	2.6428
0.9019	1353.44	1436.93	1.4103	195.54	3.5784	0.2647	19.4480	3.8897	48.4848	2.6819
1.0000	1364.20	1430.94	1.4070	208.31	3.5800	0.2842	19.5209	3.8906	51.2792	2.7324
					308.15K					
0.0000	1099.00	1602.00	1.4820	77.43	3.5455	0.0851	17.6060	3.8718	22.0756	2.0632
0.1025	1160.75	1564.79	1.4660	90.89	3.5184	0.1055	18.1633	3.8570	25.1722	2.1555
0.2215	1213.82	1528.55	1.4509	106.43	3.5260	0.1292	18.5538	3.8612	28.6518	2.2505
0.3376	1251.53	1499.68	1.4392	121.70	3.5527	0.1523	18.7689	3.8758	32.0273	2.3357
0.4502	1279.00	1477.08	1.4304	136.60	3.5836	0.1747	18.8918	3.8926	35.3169	2.4130
0.5654	1301.17	1458.67	1.4233	151.90	3.6120	0.1977	18.9798	3.9080	38.7082	2.4879
0.6527	1315.44	1447.46	1.4190	163.48	3.6284	0.2150	19.0405	3.9168	41.2832	2.5419
0.7421	1328.58	1438.06	1.4152	175.26	3.6397	0.2328	19.1057	3.9229	43.9089	2.5947
0.8295	1340.34	1430.55	1.4120	186.70	3.6457	0.2502	19.1743	3.9261	46.4522	2.6439
0.9019	1349.33	1425.35	1.4094	196.14	3.6478	0.2647	19.2328	3.9273	48.5372	2.6828
1.0000	1360.10	1419.45	1.4060	208.94	3.6491	0.2842	19.3059	3.9280	51.3224	2.7332
					313.15K					
0.0000	1095.00	1586.00	1.4800	77.72	3.6306	0.0851	17.3667	3.9180	22.0777	2.0633
0.1025	1156.70	1550.00	1.4641	91.21	3.5984	0.1055	17.9289	3.9006	25.1719	2.1555
0.2215	1209.73	1514.84	1.4491	106.79	3.6023	0.1292	18.3255	3.9027	28.6504	2.2505
0.3376	1247.43	1486.72	1.4376	122.10	3.6268	0.1523	18.5457	3.9160	32.0270	2.3356
0.4502	1274.88	1464.63	1.4289	137.05	3.6566	0.1747	18.6723	3.9320	35.3198	2.4131
0.5654	1297.03	1446.58	1.4219	152.39	3.6844	0.1977	18.7625	3.9469	38.7165	2.4881
0.6527	1311.28	1435.55	1.4176	164.00	3.7006	0.2150	18.8241	3.9556	41.2972	2.5422
0.7421	1324.41	1426.28	1.4140	175.81	3.7117	0.2328	18.8897	3.9615	43.9299	2.5951
0.8295	1336.16	1418.89	1.4108	187.28	3.7175	0.2502	18.9586	3.9646	46.4812	2.6444
0.9019	1345.14	1413.79	1.4083	196.75	3.7193	0.2647	19.0174	3.9656	48.5735	2.6835
1.0000	1355.90	1408.04	1.4050	209.59	3.7200	0.2842	19.0916	3.9659	51.3695	2.7340
					318.15K					
0.0000	1091.00	1570.00	1.4780	78.00	3.7186	0.0851	17.1287	3.9652	22.0796	2.0633
0.1025	1152.66	1535.27	1.4622	91.53	3.6807	0.1055	17.6963	3.9450	25.1713	2.1554
0.2215	1205.66	1501.19	1.4473	107.15	3.6805	0.1292	18.0991	3.9448	28.6486	2.2504
0.3376	1243.35	1473.79	1.4359	122.50	3.7028	0.1523	18.3243	3.9568	32.0257	2.3356
0.4502	1270.83	1452.17	1.4273	137.48	3.7315	0.1747	18.4545	3.9721	35.3204	2.4131
0.5654	1293.03	1434.42	1.4205	152.86	3.7587	0.1977	18.5474	3.9865	38.7207	2.4882
0.6527	1307.31	1423.55	1.4163	164.49	3.7746	0.2150	18.6102	3.9950	41.3053	2.5424
0.7421	1320.46	1414.42	1.4127	176.34	3.7855	0.2328	18.6768	4.0007	43.9434	2.5954
0.8295	1332.21	1407.16	1.4096	187.84	3.7909	0.2502	18.7464	4.0035	46.5020	2.6448
0.9019	1341.15	1402.20	1.4072	197.33	3.7923	0.2647	18.8057	4.0043	48.6023	2.6840
1.0000	1351.80	1396.72	1.4040	210.22	3.7920	0.2842	18.8809	4.0042	51.4131	2.7348
					323..15K					
0.0000	1087.00	1554.00	1.4760	78.29	3.8095	0.0851	16.8920	4.0134	22.0815	2.0634
0.1025	1148.60	1520.46	1.4603	91.85	3.7660	0.1055	17.4640	3.9904	25.1704	2.1554
0.2215	1201.62	1487.44	1.4455	107.51	3.7614	0.1292	17.8734	3.9880	28.6430	2.2503

0.3376	1239.36	1460.80	1.4341	122.90	3.7811	0.1523	18.1045	3.9984	32.0148	2.3353
0.4502	1266.86	1439.70	1.4256	137.91	3.8083	0.1747	18.2389	4.0127	35.3041	2.4127
0.5654	1289.03	1422.31	1.4187	153.34	3.8348	0.1977	18.3341	4.0267	38.6985	2.4877
0.6527	1303.28	1411.64	1.4145	165.00	3.8505	0.2150	18.3976	4.0349	41.2781	2.5418
0.7421	1316.37	1402.66	1.4109	176.88	3.8612	0.2328	18.4642	4.0405	43.9099	2.5947
0.8295	1328.08	1395.53	1.4078	188.42	3.8663	0.2502	18.5337	4.0432	46.4604	2.6440
0.9019	1337.00	1390.68	1.4053	197.95	3.8674	0.2647	18.5934	4.0437	48.5514	2.6831
1.0000	1347.70	1385.36	1.4020	210.86	3.8662	0.2842	18.6705	4.0431	51.3440	2.7336

Table 3: The excess parameters of binary mixtures of Bmim [PF_6] with 2-pyrrolidone

x_1	ΔU	$k_S^E * 10^{-10}$	$Z^E * 10^5$	L_f^E	Δn	$\Delta R_{m*} 10^{-6}$	$V^E_{m_6} * 10^{-6}$
	m/s	$m^2 N^{-1}$	$Kg/m^2.s$	$*10^{-11}m$		m^3/mol	m^3mol^{-1}
				298.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	-2.293	-0.0310	0.3785	-0.0173	-0.0034	0.0921	-0.0193
0.2215	-3.298	-0.0317	0.5598	-0.0176	-0.0036	0.0826	-0.1231
0.3376	-8.833	-0.0157	0.5718	-0.0086	-0.0050	0.0545	-0.1298
0.4502	-9.266	0.0032	0.5004	0.0019	-0.0038	0.0492	-0.0293
0.5654	-13.560	0.0181	0.3926	0.0101	-0.0045	0.0693	0.1170
0.6527	-14.197	0.0237	0.3067	0.0132	-0.0043	0.0909	0.2001
0.7421	-13.322	0.0237	0.2234	0.0132	-0.0042	0.1051	0.2219
0.8295	-10.147	0.0185	0.1481	0.0103	-0.0037	0.0988	0.1709
0.9019	-5.412	0.0114	0.0877	0.0063	-0.0020	0.0718	0.0906
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				303.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	-1.017	-0.0345	0.3814	-0.0190	-0.0034	0.0959	-0.0195
0.2215	-1.596	-0.0374	0.5668	-0.0205	-0.0036	0.0900	-0.1231
0.3376	-6.751	-0.0222	0.5819	-0.0121	-0.0051	0.0639	-0.1287
0.4502	-7.339	-0.0032	0.5123	-0.0016	-0.0039	0.0592	-0.0263
0.5654	-11.691	0.0125	0.4044	0.0069	-0.0047	0.0784	0.1219
0.6527	-12.524	0.0190	0.3174	0.0105	-0.0045	0.0986	0.2060
0.7421	-11.902	0.0200	0.2322	0.0110	-0.0044	0.1107	0.2280
0.8295	-9.070	0.0160	0.1542	0.0088	-0.0039	0.1022	0.1762
0.9019	-4.749	0.0099	0.0913	0.0054	-0.0021	0.0736	0.0942
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				308.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	0.167	-0.0377	0.3831	-0.0206	-0.0033	0.0999	-0.0206
0.2215	-0.060	-0.0424	0.5714	-0.0231	-0.0035	0.0988	-0.1255
0.3376	-4.897	-0.0277	0.5890	-0.0150	-0.0050	0.0771	-0.1314
0.4502	-5.668	-0.0085	0.5206	-0.0045	-0.0038	0.0759	-0.0285
0.5654	-10.073	0.0079	0.4127	0.0044	-0.0045	0.0973	0.1209
0.6527	-11.069	0.0153	0.3249	0.0083	-0.0043	0.1177	0.2059
0.7421	-10.637	0.0173	0.2381	0.0094	-0.0042	0.1283	0.2288
0.8295	-8.070	0.0142	0.1582	0.0077	-0.0038	0.1163	0.1773
0.9019	-4.122	0.0089	0.0935	0.0048	-0.0020	0.0830	0.0951
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				313.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	1.352	-0.0413	0.3855	-0.0223	-0.0032	0.0929	-0.0226
0.2215	1.463	-0.0481	0.5768	-0.0259	-0.0034	0.0852	-0.1296
0.3376	-3.078	-0.0340	0.5966	-0.0182	-0.0048	0.0594	-0.1366
0.4502	-4.050	-0.0143	0.5291	-0.0076	-0.0037	0.0564	-0.0335
0.5654	-8.524	0.0033	0.4206	0.0018	-0.0044	0.0781	0.1170
0.6527	-9.688	0.0116	0.3315	0.0063	-0.0043	0.1002	0.2034
0.7421	-9.440	0.0147	0.2429	0.0079	-0.0042	0.1138	0.2275
0.8295	-7.119	0.0127	0.1611	0.0068	-0.0037	0.1059	0.1770
0.9019	-3.531	0.0081	0.0949	0.0044	-0.0020	0.0766	0.0952
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				318.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	2.502	-0.0454	0.3881	-0.0242	-0.0031	0.0860	-0.0234
0.2215	2.934	-0.0543	0.5824	-0.0290	-0.0033	0.0723	-0.1311
0.3376	-1.317	-0.0405	0.6041	-0.0215	-0.0046	0.0421	-0.1396
0.4502	-2.497	-0.0202	0.5371	-0.0107	-0.0035	0.0363	-0.0396

0.5654	-7.046	-0.0014	0.4281	-0.0007	-0.0042	0.0568	0.1057
0.6527	-8.385	0.0081	0.3379	0.0044	-0.0040	0.0791	0.1872
0.7421	-8.327	0.0124	0.2478	0.0066	-0.0040	0.0945	0.2073
0.8295	-6.247	0.0114	0.1643	0.0060	-0.0036	0.0902	0.1559
0.9019	-3.004	0.0075	0.0967	0.0040	-0.0019	0.0659	0.0782
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				323.15K			
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1025	3.636	-0.0493	0.3897	-0.0260	-0.0030	0.0905	-0.0233
0.2215	4.385	-0.0606	0.5875	-0.0320	-0.0031	0.0805	-0.1363
0.3376	0.423	-0.0475	0.6121	-0.0250	-0.0044	0.0533	-0.1510
0.4502	-0.963	-0.0267	0.5463	-0.0140	-0.0032	0.0500	-0.0543
0.5654	-5.585	-0.0067	0.4366	-0.0035	-0.0039	0.0727	0.0927
0.6527	-7.097	0.0040	0.3447	0.0021	-0.0038	0.0963	0.1792
0.7421	-7.228	0.0096	0.2523	0.0050	-0.0038	0.1117	0.2064
0.8295	-5.386	0.0098	0.1665	0.0051	-0.0034	0.1055	0.1615
0.9019	-2.486	0.0067	0.0973	0.0035	-0.0018	0.0771	0.0859
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

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

RKC/Tem	A_0	A_1	A_2	A_3	A_4	σ
V_m^E $(*10^{-6}\ m^3 mol^{-1})$						
298.15	0.1363	-2.6211	0.2902	2.8946	0.2406	0.0004410
303.15	0.1516	-2.6553	0.2958	2.9063	0.2415	0.0004441
308.15	0.1447	-2.6759	0.3043	2.9156	0.2431	0.0004458
313.15	0.1264	-2.6957	0.3160	2.9242	0.2446	0.0004483
318.15	0.0938	-2.6056	0.2098	2.9626	0.2466	0.0004496
323.15	0.0352	-2.6294	0.3677	2.9182	0.2492	0.0004633
ΔU (m/s)						
298.15	-46.80	52.40	-17.70	-38.80	40.30	0.94500
303.15	-39.00	54.30	-14.90	-36.10	42.70	0.88100
308.15	-32.20	56.10	-11.50	-33.90	45.30	0.81800
313.15	-25.70	58.20	-7.90	-31.80	47.50	0.75400
318.15	-19.50	60.40	-4.60	-29.60	49.70	0.69100
323.15	-13.40	62.60	-1.30	-27.30	51.60	0.63100
k_S^E $(*10^{-10}\ m^2\ N^{-1})$						
298.15	0.0420	-0.2688	-0.2205	-0.0379	-0.0165	0.0000497
303.15	0.0176	-0.2817	-0.2245	-0.0383	-0.0179	0.0000574
308.15	-0.0026	-0.2946	-0.2261	-0.0414	-0.0230	0.0000482
313.15	-0.0240	-0.3133	-0.2312	-0.0415	-0.0211	0.0000663
318.15	-0.0457	-0.3345	-0.2350	-0.0455	-0.0256	0.0000503
323.15	-0.0699	-0.3554	-0.2370	-0.0457	-0.0261	0.0000468
$Z^E*10^{-5}\ Kg/m^2.s$						
298.15	1.8236	1.8740	1.1306	0.1412	0.0412	0.0000258
303.15	1.8718	1.8719	1.1137	0.1354	0.0381	0.0000304
308.15	1.9057	1.8706	1.0973	0.1307	0.0337	0.0000187
313.15	1.9393	1.8790	1.0759	0.1270	0.0363	0.0000317
318.15	1.9710	1.8882	1.0667	0.1206	0.0324	0.0000158
323.15	2.0075	1.8986	1.0303	0.1139	0.0298	0.0000337
$L_f^E*10^{-11}m$						
298.15	0.02371	-0.14863	-0.12200	-0.02298	-0.01169	0.0000107
303.15	0.01007	-0.15415	-0.12400	-0.02234	-0.01139	0.0000336
308.15	-0.00097	-0.15966	-0.12500	-0.02417	-0.01137	0.0000192
313.15	-0.01256	-0.16791	-0.12600	-0.02446	-0.01076	0.0000401
318.15	-0.02398	-0.17827	-0.12800	-0.02421	-0.01123	0.0000462
323.15	-0.03658	-0.18699	-0.12800	-0.02452	-0.01048	0.0000135
Δn						
298.15	-0.0169	0.0025	-0.0248	-0.0120	0.0078	0.000491
303.15	-0.0176	0.0031	-0.0246	-0.0119	0.0076	0.000485
308.15	-0.0169	0.0029	-0.0242	-0.0116	0.0075	0.000476
313.15	-0.0166	0.0033	-0.0240	-0.0114	0.0076	0.000468
318.15	-0.0156	0.0030	-0.0241	-0.0111	0.0079	0.000466
323.15	-0.0146	0.0028	-0.0241	-0.0108	0.0081	0.000465
$\Delta R_m*10^{-6}m^3/mol$						
298.15	0.2219	-0.3453	1.0110	0.7377	0.1068	0.000205
303.15	0.2611	-0.3317	0.9972	0.7380	0.1076	0.000207
308.15	0.3325	-0.3721	1.0020	0.7394	0.1082	0.000207

313.15	0.2538	-0.3751	1.0088	0.7395	0.1078	0.000208
318.15	0.1706	-0.3504	0.9870	0.7462	0.1075	0.000208
323.15	0.2296	-0.3914	1.0300	0.7345	0.1085	0.000210

6. Discussion

The comparison of experimental and literature values of ρ, n_D and u for pure [Bmim][PF_6], pure2-Pyrrolidone are given in table 1and the experimental values of binary mixtures are given in table 2 at temperatures from(298.15 to 323.15) K in steps of T = 5 K under atmospheric pressure.In thepresent study, since 2-pyrrolidone(ε = 28.18 at T = 298.15 K) is a highly dielectric and polar solvent [16], [Bmim][PF_6] is completely miscible in 2-pyrrolidone overthe entire range of compositions at all temperatures under study,The values of ρ of the binary mixtures increase gradually with the increase inmole fraction(x_1) of [Bmim][PF_6] in the mixture, at all the investigated temperatures. It can be seen that the values of ρsignificantly decrease with the increase of temperature. It canbe clearly seen that at a given temperature, n_D and u values aredecreasing with increase in mole fraction of [Bmim][PF_6]. Further, it can also be seen that the values of $n_D$and u are decreasing as the temperature is increasing. Thevariations in the values of q, n_D and u with the concentrationand temperature suggest that the physical properties of [Bmim][PF_6] can be adjusted to meet the need of applications of [Bmim][PF_6] by adding 2-pyrrolidone or changing temperature [51].

The molar volume (V_m) values, for the for this system areincreasing with increasing mole fraction of [Bmim][PF_6] concentration and also with temperature(table 2). The increase in the V_m of a system on mixing the components indicates the dissociationof one component or both the components and formation of solute - solvent bonds.

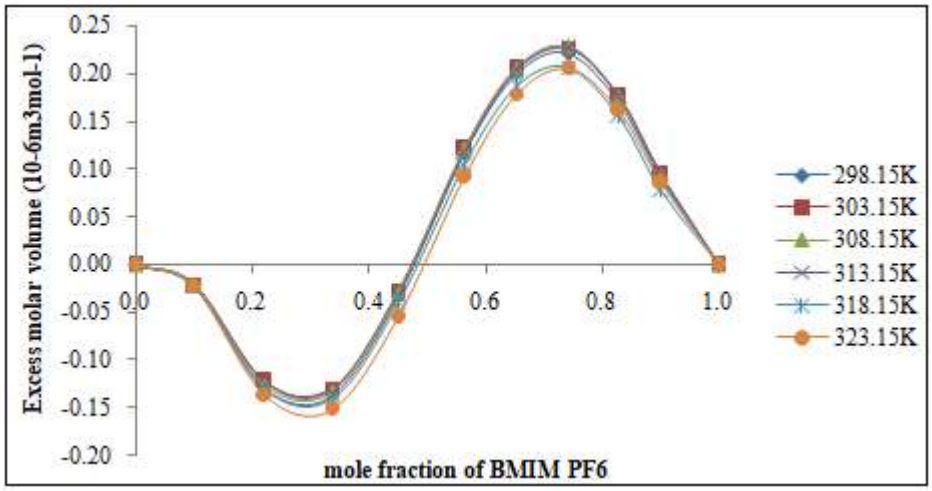


Figure 1: Variation of excess molar volume with mole fraction of BMIM **PF_6**

It can be seen from fig.1that the values of V_m^E for this system exhibit an inversion in the sign from negative to positivedeviation, which indicatesdecrease of interaction between [Bmim][**PF_6**] and 2-Pyrrolidonewith the increase of IL concentration. Moreover,the values of V_m^E are negative for rich compositions of 2-Pyrrolidone and positive for rich compositions of[Bmim][**PF_6**] in themixture, at all temperatures under study. The decrement in themagnitude of the negative V_m^E values with [Bmim][**PF_6**] compositionindicates the decrement in the strength ofion - dipole interactions. Further the positive deviations can be attributed to the decrease in packing efficiency between 2-Pyrrolidone and [Bmim][**PF_6**] with increase in the concentration of [Bmim][**PF_6**]. The values of V_m^E are minimum at lower concentration(x_1 = 0.3376) of [Bmim][**PF_6**] and maximum at higher concentration(x_1 = 0.7421)of [Bmim][**PF_6**], in the mixture, at all temperatures under study.

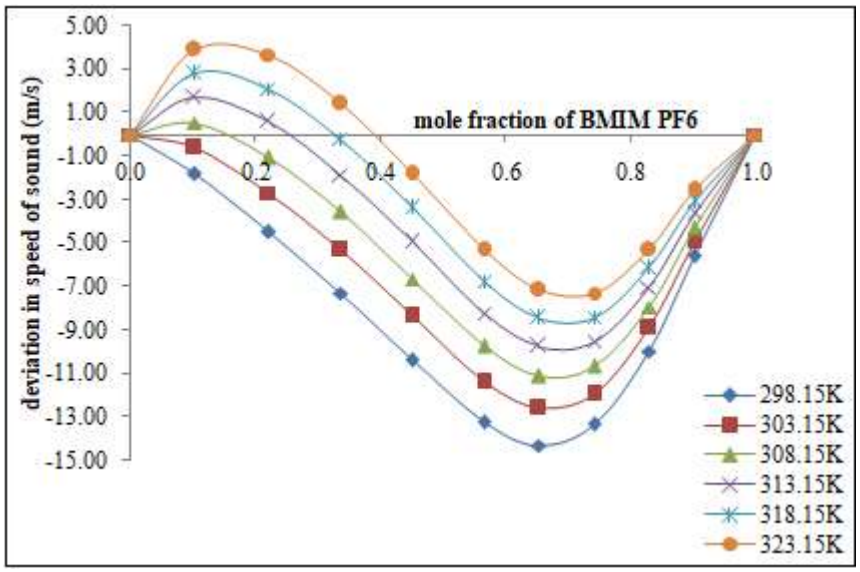


Figure 2: variation of deviation in speed of sound with mole fraction of BMIM $\mathbf{PF_6}$

It can be seen that the u^E values for this system are initially showing a positive trend. This can be attributed to weak ion – dipole interactions in the smaller mole fraction range of BMIM PF_6.But with small increase in the mole fraction of BMIM PF_6 the velocity of the mixture was found to be decreasing leading to negative u^E values. This can be attributed to the decrease in the strength of interaction between the component molecules.

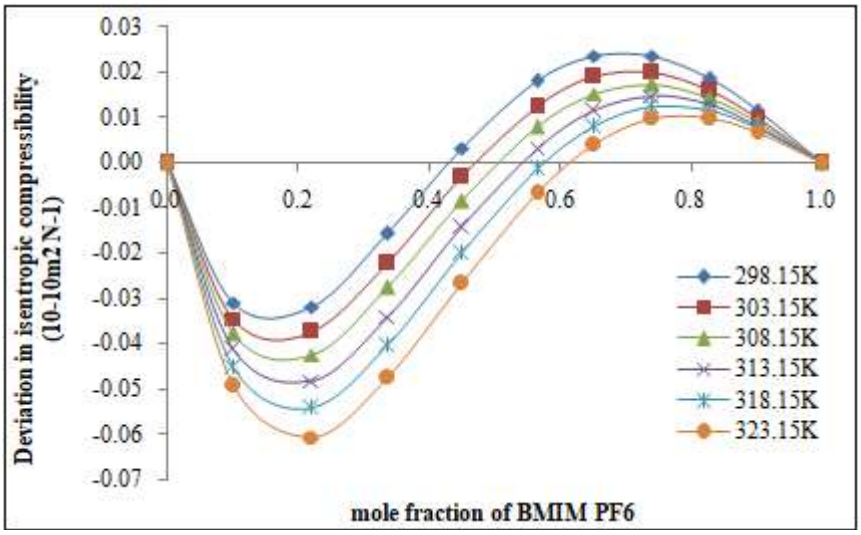


Figure 3: Deviation in isentropic compressibility with mole fraction of BMIM $\mathbf{PF_6}$

In figure 3, the k_S^E values for this system are similar to V_m^E. The negative k_S^E values are attributed to the strong attractiveinteractions due to the solvation of the ions in the mixture. Thenegative values of k_S^E of the [Bmim][$\mathbf{PF_6}$] with 2-pyrrolidone imply thatsolvent molecules around solute are less compressible than thesolvent molecules in the bulk solutions. While on further additionof [Bmim][$\mathbf{PF_6}$], k_S^E show positive trend. ie.Increase in the compressibility graph atall temperature ranges. This might be due to decrease in attractionof [Bmim][$\mathbf{PF_6}$]and2-pyrrolidonemolecules. The inversion of sign from negative to positive is in agreement with variation of V_m^E over the entire range of compositions.

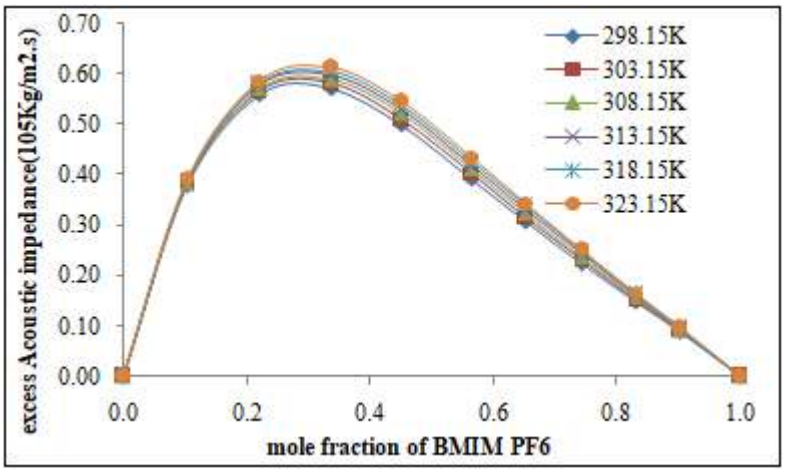


Figure 4: Variation of excess acoustic impedance with mole fraction of BMIM PF_6

The values of Z^E are positive over the entire range of compositions. Prakash et.al [52] in their study represented that more than one type of interaction may be present in the given system. Dispersion forces make the positive contribution for the excess values while dipole induced dipole and dipole-dipole interactions make negative contribution. The magnitude of Z^E being positive suggests the dispersion forces between the component molecules.

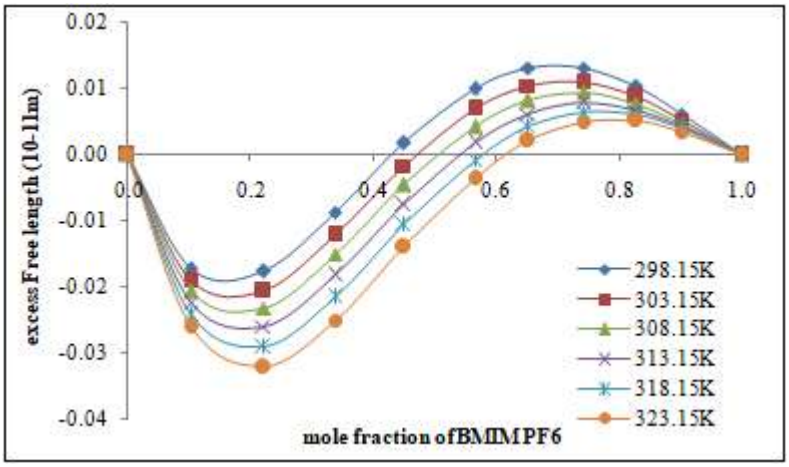


Figure 5: Variation of excess free length with mole fraction of BMIM $\mathbf{PF_6}$

The values of k_S^E and L_f^E can be examined by considering the following factors which influence several contributions arising from physical, chemical and structural effects [53, 54].

The physical contribution consists of dispersion forces or weak dipole-dipole interactions leading to positive values of k_S^E and L_f^E, whereas the geometric fitting of molecules of two different sizes into each other's structure results in negative k_S^E and L_f^E values. Chemical contributions include breaking up of the molecular association present in the pure liquid, resulting in k_S^E and L_f^E values, and specific interactions such as the formation of new hydrogen bonds (including strong dipole-dipole interactions among component molecules) result in negative k_S^E and L_f^E values.

In fig. 5, the inversion of sign from negative to positive indicates that specific interactions, such as formation of new hydrogen bonds, occur among unlike molecules initially at small mole fraction of BMIM [PF6] but as the concentration of the IL increase, the physical contribution consisting of dispersion forces or weak dipole-dipole interactions prevail leading to positive values of k_S^E and L_f^E.

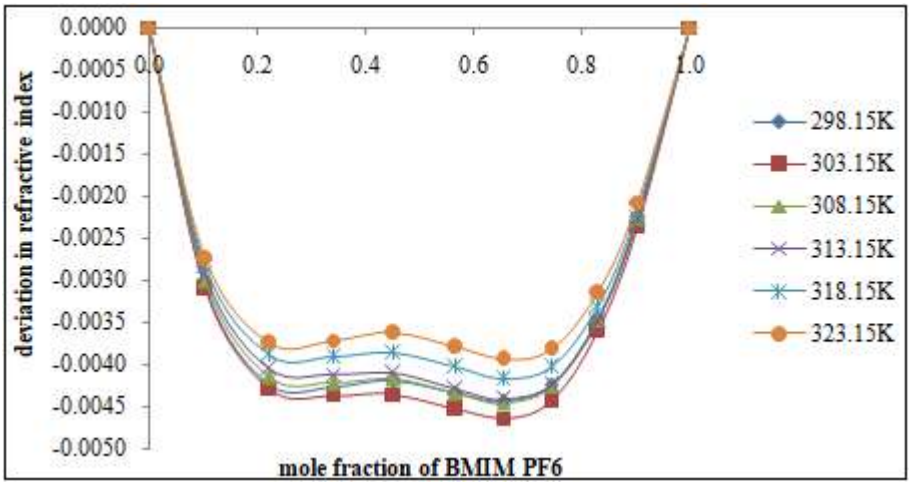


Figure 6: Deviation in refractive index with mole fraction of BMIM $\mathbf{PF_6}$

The D/n_D values represent the electronic perturbation due to mixing ofmolecules and are a measure of the quantity of interaction. Theresults presented in Fig. 6 indicate that D/n_D values are positive for these mixtures over entire mole fraction range at all investigatedtemperatures. In general, the positive deviations in D/n_D values are considered due to presence of significant interactions in themixtures, whereas negative deviations in D/n_D values indicate weak interactions between the components of the mixture[55]. Negative values suggest that the ion-ion interactions between [Bmim+] and [PF_6^-] ions dominate at higher mole fractions of [Bmim][PF_6] in the mixture.

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