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Temperature dependent study of thermophysical properties of binary mixtures of imidazolium based ionic liquids with cyclic amides

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The experimental values of densities (ρ) and speeds of sound (u) of the binary mixtures of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] with cyclic amides 2-Pyrrolidinone(2-PY) and N-Vinyl-2-pyrrolidone (NVP) have been used to calculate the internal pressures (π_i), free volumes (V_f), excess internal pressures (π_i^E), excess free volumes (V_f^E), excess free energy (G^E), excess enthalpy (H^E) and excess entropy (TS^E) covering the entire composition range expressed by mole fractions of ionic liquid at temperatures (298.15-323.15 K). The results have been interpreted in terms of intermolecular interactions between the component molecules in the mixture. The variations of these excess properties with composition indicate that the interactions between [Bmim][BF_4] and cyclic amides in these mixtures follows the order: NVP > 2-PY.

Keywords: 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4], Cyclic amides, Excess thermodynamic properties, Molecular interactions

The present investigation comprises a part of our ongoing research program on the properties of binary mixtures containing ionic liquids involved in separation units for recovering industrial solvents, food engineering, or pharmacological applications[1–5]. The study of propagation of ultrasonic waves in liquids and liquid mixtures is of immense significance for examining the nature of intermolecular and intramolecular interactions in these systems. The ultrasonic speed measurements coupled with other experimental data such as density and refractive index have been used to calculate various thermophysical parameters such as compressibility, internal pressure, free volume, free energy, enthalpy, entropy and their excess values[6–8]. These parameters play a vital role in understanding of the molecular interactions in binary mixtures.

In the present study, the binary mixtures of the imidazolium based ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] with 2-Pyrrolidinone(2-PY) and N-Vinyl-2-pyrrolidone (NVP) have been investigated. The interest in ionic liquids was initiated because of advantageous physicochemical properties such as negligible vapour pressure, high thermal and electrochemical stability, high solvating power[9,10] etc. In the recent years ionic liquids have been used in various applications such as organic synthesis, catalysis, electrochemical devices and solvent extraction for different compounds[1], separation technology[2,3], homogeneous catalysis[4], and templates for zeolites[5]. Ionic liquids have also been used as an effective material to evaluate the reaction rate in hydrogenation[11], hydroformylation[12] and carbonylation[13] processes. There are some critical evaluation criteria for selecting novel working pairs such as to ensure high efficiency of absorption hydrodesulfurization (HDS) to be noncorrosive, to be nontoxic and to ensure secure operation and so on. The determination of the fitting ionic fluid and its capacity to extricate aromatic sulphur compounds is troublesome in these sorts of process. 2-Pyrrolidinone, N-vinyl-2-pyrrolidinone is one of particular advantage in decolorizing crude oil free

from asphaltic constituents and as an adsorbent for sour gases from crude natural gas. Over the years, thermodynamic functions such as internal pressure, free volume have garnered significant interest from chemists, physicists and chemical engineers, as they provide a measure of explaining molecular interactions, internal structure, clustering phenomenon, ionic interactions and dipolar interactions[14–18], and hence have been employed subsequently to investigate the intermolecular interactions in binary mixtures.

In the present article, the refractive indices (n_D) of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] + cyclic amides binary mixtures have been measured over whole composition range, expressed by mole fraction (x_1) of [Bmim][BF_4] at temperatures 298.15–323.15 K and at atmospheric pressure. The internal pressures (π_i), free volumes (V_f), excess internal pressures (π_i^E), excess free volumes (V_f^E), excess free energy (G^E), excess enthalpy (H^E) and excess entropy ($T_S{}^E$) of mixing of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) with 2-Pyrrolidinone(2-PY) and N-Vinyl-2-pyrrolidone (NVP) binary mixtures have been calculated from experimental values ultrasonic speeds (u) and densities (ρ). The experimental data of u, ρ and n_D of these binary mixtures has been taken from our previous study[19,20] and literature comparison was given in Supplementary Table S1. The variations of these excess parameters with composition and temperature of the mixtures are discussed in terms of intermolecular interactions in these mixtures.

Experimental

The ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] (Iolitec GmbH, Germany; CAS 174899-83-3, purity > 0.99 mass fraction) was purified by vacuum distillation, NVP (Sigma Aldrich, CAS No. 57-55-6, purity > 0.99 mass fraction) and 2-PY (Sigma Aldrich, CAS No. 616-45-5, purities > 0.97 mass fraction) were purified by fractional distillation under low pressure. The water content in the ionic liquid and cyclic amides was determined using Karl Fischer Titrator (Metrohm, 890 Titrando)[21]. The water content was found to be 40 ppm. The mass fraction purities of the purified chemicals as determined by gas chromatography were: [Bmim][BF_4] > 0.995, NVP> 0.996 and 2-PY> 0.996. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done by using an electronic balance (Model: CPA-225D, Sartorious, Germany) with a precision of ±0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1\times10^{-4}$.

The refractive indices of the samples were measured using an automatic refractometer (Abbemat-HP Dr. Kernchen, Anton Paar, Austria). The refractometer was calibrated by measuring the refractive index of millipore quality water and tetrachloroethylene before each series of measurements. The calibration was further checked with pure liquids of known refractive index values. The uncertainty in the refractive index measurements was within ±0.00005 and for temperature it was less than ±0.03 K. *Cp, α_p,κ_s and K_T* were given in Table 1.

Theory

The internal pressure of a fluid is related to the thermal pressure coefficient $(\partial P/\partial T)_V$ by the following well-known thermodynamic equation of state

$$\pi_i = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\alpha_p}{k_T}\right) - P \qquad \ldots(1)$$

where α_p is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of

Table 1 — The values of various parameters of pure liquids used in the calculations

Liquid	C_p (J mol^{-1} K^{-1})	α_p (10^{-3} K^{-1})	k_s (10^{-10} m^2 N^{-1})	k_T (10^{-10} m^2 N^{-1})
[Bmim]	364.80	0.601	3.406	3.925
[BF_4]	367.20	0.602	3.468	3.997
	369.50	0.595	3.532	4.055
	371.90	0.598	3.597	4.132
	374.30	0.599	3.663	4.206
	390.35	0.593	3.733	4.254
2-PY	169.37	0.739	3.381	4.120
	171.33	0.741	3.463	4.213
	172.57	0.743	3.547	4.311
	173.91	0.746	3.634	4.412
	175.10	0.748	3.717	4.510
	176.31	0.750	3.813	4.621
NVP	207.73	0.848	4.156	5.260
	208.61	0.851	4.280	5.411
	209.51	0.855	4.408	5.568
	210.40	0.859	4.541	5.730
	211.31	0.863	4.678	5.896
	212.23	0.866	4.820	6.068

the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_p/k_T)$ is very high so that the external pressure (P) becomes negligible in comparison[25,28,29], therefore it may be neglected in the Eqn 1 in the present calculations. Thus, the internal pressure can be shown to be equal to the following relation[22,23].

$$\pi_{nt} = \alpha_p T/k_T \quad \ldots(2)$$

The free volume, V_f of the mixtures are calculated from the relation[14,15,22-24]

$$V_f = \frac{RT}{(P+\pi_i)} \quad \ldots(3)$$

since P is very small as compared to π_i, it has been neglected in the Eqn 3 in the present calculations. k_T, is calculated using the well-known thermodynamic relation[25,26]

$$k_T = k_s + \frac{TV\alpha_p^2}{C_p} \quad \ldots(4)$$

where k_s [$= 1/(u^2\rho)$] is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data[26]. The C_p values of pure liquids have been taken from the literature [27–29] and the C_p values for the mixtures have been calculated by using the following relation

$$C_p = x_1 C_{p,1} + x_2 C_{p,2} \quad \ldots(5)$$

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids used in the calculations are listed in Table 1. The π_i^E and V_f^E of binary mixtures have been calculated using the relation

$$Y^E = Y - \left(x_1 Y_1 + x_2 Y_2\right) \quad \ldots(6)$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure [Bmim][BF_4] and cyclic amide, respectively. The excess enthalpies (H^E) and excess entropies (S^E) are calculated from π_i and V_f by using the following relations based on regular solution theory[14,15,29].

$$-H^E = \pi_i V - \left[x_1 \pi_{i,1} V_1 + x_2 \pi_{i,2} V_2\right] \quad \ldots(7)$$

$$S^E = R\left[x_1 \ln V_{f,1} + x_2 \ln V_{f,2} - \ln V_f\right] \quad \ldots(8)$$

The excess free energy (G^E) of mixtures is given by the relation.

$$G^E = H^E - TS^E \quad \ldots(9)$$

The values of u, ρ, π_i, V_f, π_i^E, V_f^E, H^E, $T_S{}^E$ and G^E for the binary mixtures of [Bmim][BF_4] + NVP or 2-PYas functions of mole fraction, x_1 of [Bmim][BF_4] at various temperatures are listed in Tables 2 and 3.

Table 2 — The values of ρ, u, π_i, V_f, π_i^E, V_f^E, H^E, TS^E, G^E for the binary mixtures of [Bmim][BF_4] and 2-PY as a function of mole fraction, x_1 of [Bmim][BF_4] at temperatures T = (298.15 – 318.15) K

x_1	ρ (kg m^{-3})	u (m s^{-1})	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})	π_i^E (10^8 N m^{-2})	V_f^E (10^{-8} m^3 mol^{-1})	H^E (kJ mol^{-1})	TS^E (10^{-2} J mol^{-1})	G^E (kJ mol^{-1})
298.15 K									
0.0000	1107.16	1634.4	5.347	4.636					
0.1020	1128.93	1625.5	5.240	4.731	0.048	0.014	-0.358	0.010	-0.368
0.1951	1143.99	1618.0	5.148	4.815	0.071	0.024	-0.591	0.018	-0.609
0.3046	1155.01	1608.3	5.028	4.930	0.063	0.052	-0.686	0.033	-0.719
0.3886	1163.44	1601.0	4.950	5.008	0.057	0.063	-0.670	0.039	-0.709
0.5262	1173.25	1590.7	4.834	5.128	0.040	0.074	-0.602	0.044	-0.646
0.6185	1179.38	1584.4	4.767	5.199	0.030	0.072	-0.501	0.042	-0.543
0.6900	1183.57	1579.5	4.718	5.254	0.020	0.070	-0.373	0.040	-0.412
0.7844	1188.69	1574.3	4.664	5.315	0.012	0.056	-0.252	0.031	-0.283
0.8861	1193.47	1569.3	4.611	5.376	0.003	0.036	-0.102	0.020	-0.121
1.0000	1198.78	1565.1	4.565	5.430					

(*Contd.*)

Table 2 — The values of ρ, u, π_i, V_f, π_i^E, V_f^E, H^E, TS^E, G^E for the binary mixtures of [Bmim][BF_4] and 2-PY as a function of mole fraction, x_1 of [Bmim][BF_4] at temperatures T = (298.15 – 318.15) K (*Contd.*)

x_1	ρ (kg m^{-3})	u (m s^{-1})	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})	π_i^E (10^8 N m^{-2})	V_f^E (10^{-8} m^3 mol^{-1})	H^E (kJ mol^{-1})	TS^E (10^{-2} J mol^{-1})	G^E (kJ mol^{-1})
303.15 K									
0.0000	1103.07	1618.0	5.333	4.726					
0.1020	1124.98	1610.2	5.231	4.818	0.050	0.011	-0.373	0.009	-0.382
0.1951	1139.00	1604.1	5.140	4.904	0.072	0.023	-0.645	0.017	-0.662
0.3046	1151.24	1594.5	5.025	5.016	0.066	0.048	-0.715	0.031	-0.746
0.3886	1159.65	1587.5	4.947	5.094	0.059	0.060	-0.698	0.037	-0.735
0.5262	1169.51	1578.1	4.834	5.214	0.043	0.070	-0.646	0.042	-0.688
0.6185	1175.68	1572.5	4.771	5.283	0.035	0.066	-0.582	0.039	-0.620
0.6900	1179.91	1567.2	4.719	5.341	0.022	0.067	-0.405	0.038	-0.444
0.7844	1185.05	1562.2	4.665	5.402	0.013	0.054	-0.279	0.030	-0.309
0.8861	1189.85	1557.3	4.613	5.464	0.004	0.034	-0.126	0.019	-0.145
1.0000	1195.18	1553.2	4.566	5.520					
308.15 K									
0.0000	1098.99	1601.6	5.313	4.822					
0.1020	1121.03	1595.5	5.212	4.915	0.054	0.007	-0.424	0.007	-0.431
0.1951	1135.12	1589.2	5.114	5.010	0.072	0.023	-0.667	0.017	-0.684
0.3046	1147.43	1580.2	4.994	5.130	0.065	0.051	-0.733	0.033	-0.766
0.3886	1155.87	1573.9	4.916	5.212	0.060	0.062	-0.731	0.039	-0.770
0.5262	1165.80	1565.4	4.801	5.336	0.046	0.070	-0.705	0.042	-0.747
0.6185	1172.01	1560.1	4.735	5.410	0.038	0.066	-0.631	0.039	-0.671
0.6900	1176.26	1554.7	4.681	5.473	0.023	0.069	-0.438	0.039	-0.477
0.7844	1181.42	1550.0	4.625	5.540	0.014	0.055	-0.303	0.031	-0.334
0.8861	1186.26	1545.4	4.570	5.605	0.004	0.035	-0.141	0.019	-0.161
1.0000	1191.60	1541.4	4.521	5.666					
313.15 K									
0.0000	1094.90	1585.4	5.293	4.919					
0.1020	1117.09	1580.5	5.200	5.007	0.056	0.004	-0.439	0.005	-0.444
0.1951	1131.25	1575.0	5.107	5.098	0.074	0.018	-0.692	0.014	-0.706
0.3046	1143.62	1566.5	4.992	5.216	0.067	0.045	-0.756	0.030	-0.785
0.3886	1152.11	1560.7	4.916	5.296	0.062	0.056	-0.760	0.035	-0.795
0.5262	1162.12	1552.7	4.805	5.419	0.048	0.065	-0.727	0.039	-0.766
0.6185	1168.35	1547.9	4.742	5.490	0.040	0.061	-0.669	0.036	-0.705
0.6900	1172.63	1542.5	4.687	5.554	0.024	0.066	-0.452	0.037	-0.489
0.7844	1177.81	1537.9	4.633	5.620	0.014	0.053	-0.314	0.030	-0.343
0.8861	1182.68	1533.5	4.580	5.685	0.005	0.034	-0.146	0.019	-0.165
1.0000	1188.04	1529.7	4.532	5.745					
318.15 K									
0.0000	1090.82	1570.4	5.276	5.013					
0.1020	1113.15	1566.0	5.186	5.100	0.056	0.003	-0.436	0.004	-0.441
0.1951	1127.38	1560.9	5.095	5.191	0.073	0.017	-0.687	0.014	-0.701
0.3046	1139.83	1553.8	4.987	5.304	0.071	0.040	-0.800	0.027	-0.826
0.3886	1148.36	1547.8	4.910	5.387	0.063	0.053	-0.777	0.034	-0.811
0.5262	1158.47	1541.2	4.805	5.504	0.054	0.057	-0.809	0.035	-0.844
0.6185	1164.72	1536.4	4.743	5.577	0.045	0.054	-0.736	0.033	-0.769
0.6900	1169.02	1530.7	4.686	5.645	0.025	0.063	-0.482	0.036	-0.518
0.7844	1174.23	1526.2	4.631	5.712	0.015	0.051	-0.328	0.029	-0.357
0.8861	1179.12	1521.9	4.578	5.777	0.005	0.033	-0.156	0.018	-0.174
1.0000	1184.50	1518.2	4.531	5.838					

(*Contd.*)

Table 2 — The values of ρ, u, π_i, V_f, π_i^E, V_f^E, H^E, TS^E, G^E for the binary mixtures of [Bmim][BF_4] and 2-PY as a function of mole fraction, x_1 of [Bmim][BF_4] at temperatures T = (298.15 – 318.15) K (*Contd.*)

x_1	ρ	u	π_i	V_f	π_i^E	V_f^E	H^E	TS^E	G^E
	(kg m^{-3})	(m s^{-1})	(10^8 N m^{-2})	(10^{-6} m^3 mol^{-1})	(10^8 N m^{-2})	(10^{-8} m^3 mol^{-1})	(kJ mol^{-1})	(10^{-2} J mol^{-1})	(kJ mol^{-1})
323.15 K									
0.0000	1086.75	1553.5	5.247	5.120					
0.1020	1109.21	1550.0	5.161	5.205	0.057	0.000	-0.459	0.003	-0.462
0.1951	1123.52	1545.8	5.073	5.296	0.076	0.012	-0.729	0.011	-0.740
0.3046	1136.08	1539.4	4.967	5.409	0.074	0.034	-0.856	0.024	-0.879
0.3886	1144.62	1534.4	4.893	5.491	0.068	0.046	-0.858	0.030	-0.888
0.5262	1154.82	1528.0	4.786	5.613	0.056	0.052	-0.865	0.033	-0.898
0.6185	1161.11	1524.0	4.725	5.686	0.048	0.048	-0.809	0.030	-0.839
0.6900	1165.45	1519.2	4.671	5.752	0.032	0.053	-0.596	0.032	-0.628
0.7844	1170.66	1514.2	4.611	5.827	0.017	0.049	-0.364	0.028	-0.392
0.8861	1175.58	1510.2	4.558	5.895	0.006	0.032	-0.175	0.018	-0.193
1.0000	1180.98	1506.8	4.509	5.958					

Table 3 — The values of ρ, u, π_i, V_f, π_i^E, V_f^E, H^E, TS^E, G^E for the binary mixtures of [Bmim][BF_4] and NVP as a function of mole fraction, x_1 of [Bmim][BF_4] at temperatures T = (298.15 – 318.15) K

x_1	ρ	u	π_i	V_f	π_i^E	V_f^E	H^E	TS^E	G^E
	(kg m^{-3})	(m s^{-1})	(10^8 N m^{-2})	(10^{-6} m^3 mol^{-1})	(10^8 N m^{-2})	(10^{-8} m^3 mol^{-1})	(kJ mol^{-1})	(10^{-2} J mol^{-1})	(kJ mol^{-1})
298.15 K									
0.0000	1039.36	1521.5	4.806	5.157					
0.1046	1069.96	1537.3	4.875	5.084	0.099	-0.102	-0.979	-0.049	-0.930
0.2035	1093.11	1546.0	4.889	5.071	0.140	-0.142	-1.504	-0.068	-1.436
0.3042	1113.53	1552.7	4.882	5.077	0.160	-0.163	-1.844	-0.078	-1.766
0.4060	1131.03	1557.8	4.858	5.102	0.162	-0.166	-2.006	-0.079	-1.927
0.4945	1144.21	1560.6	4.826	5.136	0.151	-0.156	-1.988	-0.073	-1.915
0.6070	1159.22	1563.2	4.777	5.189	0.129	-0.134	-1.811	-0.062	-1.748
0.6970	1170.10	1564.4	4.734	5.236	0.106	-0.111	-1.543	-0.051	-1.492
0.7828	1179.78	1565.8	4.694	5.281	0.085	-0.090	-1.261	-0.041	-1.219
0.9104	1191.59	1566.1	4.622	5.363	0.039	-0.043	-0.618	-0.019	-0.598
1.0000	1198.78	1565.1	4.565	5.430					
303.15 K									
0.0000	1034.95	1502.5	4.770	5.284					
0.1046	1065.76	1519.9	4.849	5.198	0.104	-0.110	-1.015	-0.053	-0.963
0.2035	1089.01	1529.6	4.867	5.178	0.146	-0.154	-1.554	-0.073	-1.480
0.3042	1109.53	1537.2	4.866	5.179	0.167	-0.176	-1.902	-0.084	-1.818
0.4060	1127.12	1543.0	4.847	5.200	0.169	-0.179	-2.067	-0.085	-1.982
0.4945	1140.37	1546.2	4.816	5.234	0.157	-0.167	-2.032	-0.079	-1.953
0.6070	1155.45	1549.5	4.771	5.283	0.134	-0.144	-1.855	-0.067	-1.788
0.6970	1166.39	1551.4	4.731	5.328	0.111	-0.121	-1.601	-0.056	-1.545
0.7828	1176.14	1553.0	4.692	5.372	0.088	-0.097	-1.293	-0.045	-1.249
0.9104	1187.99	1553.9	4.622	5.452	0.041	-0.046	-0.639	-0.021	-0.618
1.0000	1195.18	1553.2	4.566	5.520					
308.15 K									
0.0000	1030.55	1483.7	4.733	5.413					
0.1046	1061.54	1502.4	4.814	5.322	0.108	-0.118	-1.068	-0.056	-1.012
0.2035	1084.92	1513.0	4.834	5.299	0.151	-0.166	-1.635	-0.078	-1.557

(*Contd.*)

Table 3 — The values of ρ, u, π_i, V_f, π_i^E, V_f^E, H^E, TS^E, G^E for the binary mixtures of [Bmim][BF_4] and NVP as a function of mole fraction, x_1 of [Bmim][BF_4] at temperatures T = (298.15 – 318.15) K (*Contd.*)

x_1	ρ	u	π_i	V_f	π_i^E	V_f^E	H^E	TS^E	G^E
	(kg m^{-3})	(m s^{-1})	(10^8 N m^{-2})	(10^{-6} m^3 mol^{-1})	(10^8 N m^{-2})	(10^{-8} m^3 mol^{-1})	(kJ mol^{-1})	(10^{-2} J mol^{-1})	(kJ mol^{-1})
0.3042	1105.54	1521.5	4.833	5.301	0.173	-0.190	-2.004	-0.090	-1.914
0.4060	1123.22	1528.0	4.813	5.323	0.176	-0.193	-2.178	-0.091	-2.087
0.4945	1136.54	1532.1	4.783	5.356	0.164	-0.182	-2.164	-0.085	-2.079
0.6070	1151.70	1535.9	4.735	5.411	0.140	-0.156	-1.960	-0.072	-1.888
0.6970	1162.69	1538.3	4.694	5.458	0.116	-0.131	-1.695	-0.060	-1.635
0.7828	1172.50	1540.6	4.654	5.504	0.093	-0.107	-1.393	-0.049	-1.344
0.9104	1184.40	1542.1	4.582	5.592	0.044	-0.052	-0.702	-0.024	-0.678
1.0000	1191.60	1541.4	4.521	5.666					
313.15 K									
0.0000	1026.14	1465.0	4.694	5.547					
0.1046	1057.33	1485.0	4.785	5.441	0.111	-0.126	-1.083	-0.060	-1.023
0.2035	1080.83	1496.6	4.812	5.411	0.156	-0.176	-1.653	-0.083	-1.570
0.3042	1101.56	1505.9	4.817	5.405	0.179	-0.202	-2.026	-0.095	-1.931
0.4060	1119.32	1513.2	4.803	5.421	0.181	-0.206	-2.204	-0.097	-2.107
0.4945	1132.74	1517.9	4.777	5.450	0.170	-0.194	-2.192	-0.091	-2.101
0.6070	1147.96	1522.3	4.734	5.500	0.144	-0.167	-1.986	-0.077	-1.909
0.6970	1159.01	1525.3	4.696	5.545	0.120	-0.140	-1.720	-0.065	-1.655
0.7828	1168.89	1528.1	4.660	5.587	0.097	-0.115	-1.419	-0.053	-1.366
0.9104	1180.83	1530.1	4.591	5.671	0.046	-0.056	-0.718	-0.025	-0.693
1.0000	1188.04	1529.7	4.532	5.745					
318.15 K									
0.0000	1021.73	1446.5	4.654	5.683					
0.1046	1053.13	1467.7	4.753	5.565	0.114	-0.135	-1.104	-0.063	-1.041
0.2035	1076.75	1480.3	4.786	5.527	0.160	-0.188	-1.684	-0.088	-1.595
0.3042	1097.59	1490.4	4.796	5.515	0.184	-0.215	-2.063	-0.101	-1.962
0.4060	1115.44	1498.5	4.786	5.527	0.187	-0.219	-2.243	-0.103	-2.140
0.4945	1128.96	1503.9	4.764	5.552	0.176	-0.208	-2.236	-0.097	-2.139
0.6070	1144.25	1509.0	4.724	5.599	0.150	-0.178	-2.026	-0.083	-1.943
0.6970	1155.36	1512.5	4.689	5.641	0.125	-0.150	-1.759	-0.069	-1.690
0.7828	1165.30	1515.7	4.656	5.682	0.101	-0.123	-1.456	-0.056	-1.399
0.9104	1177.29	1518.4	4.589	5.764	0.048	-0.060	-0.739	-0.027	-0.712
1.0000	1184.50	1518.2	4.531	5.838					
323.15 K									
0.0000	1017.33	1428.1	4.613	5.824					
0.1046	1048.93	1450.6	4.722	5.689	0.122	-0.149	-1.193	-0.069	-1.123
0.2035	1072.68	1464.1	4.761	5.643	0.172	-0.209	-1.825	-0.098	-1.727
0.3042	1093.63	1475.1	4.776	5.626	0.199	-0.241	-2.245	-0.112	-2.133
0.4060	1111.58	1483.9	4.768	5.634	0.203	-0.246	-2.451	-0.115	-2.336
0.4945	1125.20	1489.9	4.747	5.659	0.191	-0.234	-2.447	-0.109	-2.339
0.6070	1140.57	1495.7	4.708	5.706	0.164	-0.202	-2.236	-0.093	-2.142
0.6970	1151.73	1499.8	4.673	5.750	0.138	-0.172	-1.957	-0.079	-1.878
0.7828	1161.76	1503.5	4.639	5.792	0.113	-0.142	-1.635	-0.065	-1.571
0.9104	1173.77	1506.7	4.570	5.879	0.056	-0.072	-0.869	-0.033	-0.836
1.0000	1180.98	1506.0	4.505	5.964					

The values of π_i^E, V_f^E, H^E, $T_S{}^E$ and G^E were fitted to a Redlich-Kister[30] type polynomial equation:

$$Y^E = x_1(1-x_1)\sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \quad \ldots(10)$$

where Y^E is π_i^E or V_f^E or H^E or $T_S{}^E$ and G^E. The values of coefficients, A_i in Eqn 10 were evaluated by using least-squares method with all points weighted equally. The values of coefficients, A_i of Eqn 10 for the excess functions and the corresponding standard deviations, σ are listed in Table 4. The variation of π_i^E, V_f^E, H^E, $T_S{}^E$ and G^E with composition and temperature of the mixtures are presented graphically in Figs. 1–5, respectively.

The refractive indices of the binary mixtures have been theoretically calculated from the refractive index data of pure components of the mixtures using various mixing rules[31–33]

Table 4 — Coefficients (A_i) of Eq.(13) for π_i^E, V_f^E, H^E, TS^E and G^E along with standard deviations (σ) for [Bmim][BF_4] + 2-PY/NVP binary mixtures at different temperatures

Property	T/K	A_1	A_2	σ
[Bmim][BF4]+2-PY				
π_i^E (10^8 N m^{-2})	298.15	0.2019	-0.2989	0.0063
	303.15	0.2136	-0.2937	0.0061
	308.15	0.2206	-0.2948	0.0069
	313.15	0.2286	-0.3020	0.0072
	318.15	0.2402	-0.2963	0.0064
	323.15	0.2556	-0.2946	0.0061
V_f^E (10^{-6} m^3 mol^{-1})	298.15	0.2792	0.1256	0.0035
	303.15	0.2616	0.1246	0.0036
	308.15	0.2666	0.1289	0.0044
	313.15	0.2441	0.1437	0.0049
	318.15	0.2241	0.1434	0.0048
	323.15	0.1968	0.1504	0.0047
H^E (kJ mol^{-1})	298.15	-2.5016	1.8622	0.0126
	303.15	-2.6993	1.8464	0.0271
	308.15	-2.8742	1.8549	0.0325
	313.15	-2.9829	1.9069	0.0369
	318.15	-3.1560	1.8167	0.0469
	323.15	-3.4618	1.7672	0.0438
TS^E (10^{-2} J mol^{-1})	298.15	0.1670	0.0497	0.0018
	303.15	0.1578	0.0502	0.0019
	308.15	0.1622	0.0513	0.0023
	313.15	0.1492	0.0600	0.0026
	318.15	0.1388	0.0603	0.0024
	323.15	0.1259	0.0630	0.0024
G^E (kJ mol^{-1})	298.15	-2.6685	1.8125	0.0117
	303.15	-2.8571	1.7962	0.0258
	308.15	-3.0364	1.8036	0.0307
	313.15	-3.1322	1.8467	0.0349
	318.15	-3.2948	1.7562	0.0451
	323.15	-3.5870	1.7027	0.0422
[Bmim][BF4]+NVP				
π_i^E (10^8 N m^{-2})	298.15	0.6321	-0.3338	0.0079
	303.15	0.6582	-0.3464	0.0085
	308.15	0.6877	-0.3518	0.0090
	313.15	0.7100	-0.3568	0.0093
	318.15	0.7338	-0.3617	0.0096
	323.15	0.8004	-0.3669	0.0107

(*Contd.*)

Table 4 — Coefficients (A_i) of Eq.(13) for π_i^E, V_f^E, H^E, TS^E and G^E along with standard deviations (σ) for [Bmim][BF_4] + 2-PY/NVP binary mixtures at different temperatures (*Contd.*)

Property	*T*/K	A_1	A_2	σ
[Bmim][BF4]+2-PY				
V_f^E (10^{-6} m^3 mol^{-1})	298.15	-0.6521	0.3199	0.0086
	303.15	-0.7035	0.3461	0.0095
	308.15	-0.7635	0.3603	0.0105
	313.15	-0.8141	0.3820	0.0113
	318.15	-0.8693	0.4038	0.0121
	323.15	-0.9803	0.4209	0.0140
H^E (kJ mol^{-1})	298.15	-8.0837	1.7459	0.0483
	303.15	-8.3198	1.8193	0.0533
	308.15	-8.8128	1.7891	0.0615
	313.15	-8.9301	1.7693	0.0646
	318.15	-9.1097	1.7503	0.0682
	323.15	-10.0152	1.5797	0.0846
TS^E (10^{-2} J mol^{-1})	298.15	-0.3068	0.1620	0.0041
	303.15	-0.3310	0.1730	0.0045
	308.15	-0.3563	0.1798	0.0049
	313.15	-0.3802	0.1882	0.0052
	318.15	-0.4052	0.1963	0.0056
	323.15	-0.4547	0.2040	0.0062
G^E (kJ mol^{-1})	298.15	-7.7768	1.5840	0.0443
	303.15	-7.9888	1.6463	0.0488
	308.15	-8.4564	1.6095	0.0567
	313.15	-8.5498	1.5810	0.0595
	318.15	-8.7045	1.5538	0.0628
	323.15	-9.5606	1.3763	0.0784

The refractive indices of the binary mixtures have been theoretically calculated from the refractive index data of pure components of the mixtures using various mixing rules[31–33]

Arago-Biot (A-B):

$$n = n_1\varphi_1 + n_2\varphi_2 \quad \ldots(11)$$

Gladstone-Dale (G-D):

$$n - 1 = (n_1 - 1)\phi_1 + (n_2 - 1)\phi_2 \quad \ldots(12)$$

Newton's (N) relation:

$$n^2 - 1 = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2 \quad \ldots(13)$$

Eyring and John (E-J):

$$n = n_1\phi_1^2 + 2(n_1 n_2)^{1/2}\phi_1\phi_2 + n_2\phi_2^2 \quad \ldots(14)$$

Lorentz-Lorentz (L-L):

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\phi_2 \quad \ldots(15)$$

Heller (H):

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2 \quad \ldots(16)$$

Eykman (EK):

$$\frac{n^2 - 1}{n + 0.4} = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right)\phi_2 \quad \ldots(17)$$

Oster (OS):

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\phi_1 + \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\phi_2 \quad \ldots(18)$$

Weiner (W)

$$\frac{n^2-n_1^2}{n^2+2n_2^2}=\left(\frac{n^2-n_1^2}{n_2^2+2n_1^2}\right)\phi_2 \qquad \ldots(19)$$

where n represents the refractive index (n_D) in the relations (11)-(19). The refractive indices obtained from Eqns. 11–19 have been compared with the experimental values and the results are presented in terms of average percentage deviations (APD) calculated using the relation

$$APD=\frac{1}{m}\left[\sum\frac{(n_{Expt}-n_{Calc})}{n_{Expt.}}\times 100\right] \qquad \ldots(20)$$

where m is number of data points. The APDs for the binary systems at investigated temperatures are listed in Table 5.

Results and Discussion

The π_i^E values are positive for [Bmim][BF_4] + NVP and [Bmim][BF_4] + 2-PY over entire mole fraction range and at all investigated temperatures are shown in Fig. 1. The internal pressure (also known as the cohesion pressure or energy–volume coefficient) is an interesting and valuable quantity that describes the macroscopic result of molecular interactions.

In condensed phases (solids, liquids, solutions) strong attractive forces exist between molecules, and as a result each molecule has a considerable (negative) potential energy (in contrast with vapor phase molecules which have negligible potential energy). This potential energy is called the molar cohesive energy, -E. It is customary to distinguish three modes of interaction between molecules which collectively produce the cohesive energy characteristic of the liquid state: (i) dispersion or London forces arising from the fluctuating atomic

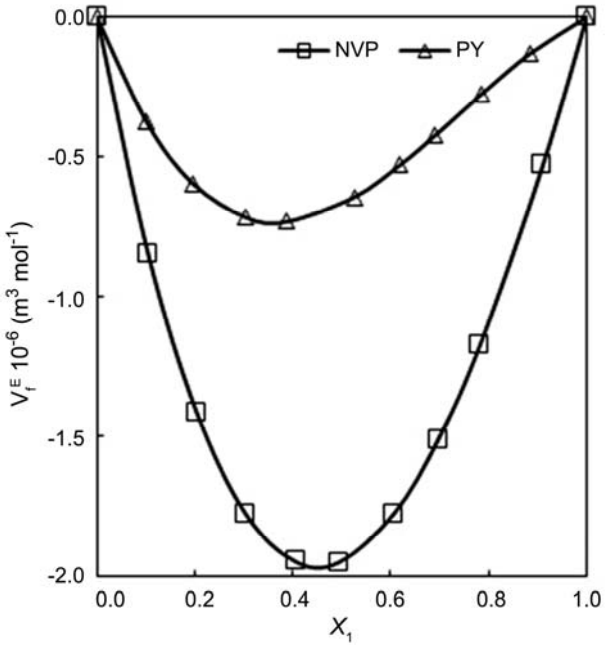

Fig. 1 — Curves of excess internal pressure, π_i^E with mole fraction, x_1 of [Bmim][BF_4] for the [Bmim][BF_4] + 2-PY/NVP binary mixtures at temperature 298.15K. *Symbols* refer to the experimental values and the *solid lines* have been drawn from Eq. (10) using the coefficients given in Table 4.

Table 5 — Average percentage deviations (APD) in Arago-Biot (A–B), Gladstone-Dale (G–D), Newton (N), Eyring-John (E–J), Lorentz-Lorentz (L–L), Heller (H), Eykman (EK), Oster (OS) and Weiner (W) relations for [Bmim][BF_4] + 2-PY/NVP binary mixtures at different temperatures

T/K	A–B	G–D	N	E–J	L–L	H	EK	OS	W
[Bmin][BF_4] + 2-PY									
298.15	0.0848	0.0848	0.0674	0.0935	0.1030	0.0976	0.1255	0.1364	0.0912
303.15	0.0907	0.0907	0.0735	0.0993	0.1087	0.1034	0.1310	0.1418	0.0971
308.15	0.1014	0.1014	0.0843	0.1099	0.1191	0.1139	0.1412	0.1520	0.1077
313.15	0.1050	0.1050	0.0882	0.1134	0.1225	0.1174	0.1444	0.1551	0.1113
318.15	0.1151	0.1151	0.0984	0.1234	0.1324	0.1274	0.1541	0.1646	0.1213
323.15	0.1073	0.1073	0.0908	0.1155	0.1243	0.1194	0.1457	0.1561	0.1134
[Bmin][BF_4] + NVP									
298.15	0.1700	0.1700	0.1409	0.1845	0.2029	0.1964	0.2474	0.2688	0.1812
303.15	0.1656	0.1656	0.1370	0.1807	0.1998	0.1920	0.2435	0.2646	0.1768
308.15	0.1736	0.1736	0.1430	0.1902	0.2089	0.2014	0.2520	0.2727	0.1864
313.15	0.1818	0.1818	0.1491	0.1981	0.2164	0.2091	0.2587	0.2792	0.1944
318.15	0.1925	0.1925	0.1603	0.2085	0.2264	0.2193	0.2681	0.2882	0.2048
323.15	0.2642	0.2642	0.2328	0.2798	0.2972	0.2898	0.3378	0.3574	0.2762

dipole which results from a positive nucleus and an electron cloud (this type of interaction occurs in all molecules); (ii) polar interactions, which can be further divided into dipole-dipole (Keesom) and dipole induced dipole (Debye) interactions, resulting from non-uniform charge distribution; (iii) specific "chemical" interactions, notably hydrogen bonding.

Mixing of [Bmim][BF_4] with cyclic amides would induce mutual dissociation of the hydrogen-bonded structures present in pure cyclic amides with subsequent formation of hydrogen bonding and ion-dipole interactions between unlike molecules. The observed positive π_i^E values for [Bmim][BF_4] + 2PY/NVP (Fig. 1) can be considered due to formation of hydrogen bonding between $[Bmim]^+/[BF_4]^-$ ions and 2-PY/NVP molecules that leads to more closer packing of molecules resulting in a contraction in volume of the mixture, leading to an increase in the internal pressure of the mixture, hence, positive π_i^E values. The magnitude of π_i^E values for [Bmim][BF_4] + NVP and 2-PY mixtures follows the sequence: NVP> 2-PY, which indicates the order of interactions in these systems.

The V_f^E values are negative for [Bmim][BF_4] + 2-PY and for [Bmim][BF_4] + NVP over the entire composition range and at all temperatures are shown in Fig. 2. The observed trends in V_f^E value indicate specific interactions in [Bmim][BF_4]+NVP, and weak interactions in [Bmim][BF_4]+2-PY mixtures. But opposite to our expectation, the positive trends are observed in V_f^E values for [Bmim][BF_4]+2-PY (Fig. 2) over the entire composition range. The results can be explained in terms of molecular interactions, structural effects and interstitial accommodation along with the changes in free volume. The sign of the V_f^E depends on the relative strength between the contractive and expansive forces. The factors responsible for volume contraction are: (i) specific interactions between the component molecules and (ii) weak physical forces, such as ion-dipole or dipole-dipole interactions or van der Waals forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion. The negative values of excess free volume in binary system assert that the combined effects of the factors are responsible for volume contraction and vice-versa[34]. According to these investigations, the positive values of excess free volume (Fig. 2) may be arising from the formation of weaker IL-solvent than IL-IL and solvent-solvent interactions in the liquid mixtures and the negative (Fig. 2) values of excess free volume may be attributed to the packing effect and ion-dipole interaction of solvent molecules with the IL in these mixtures[35,36].

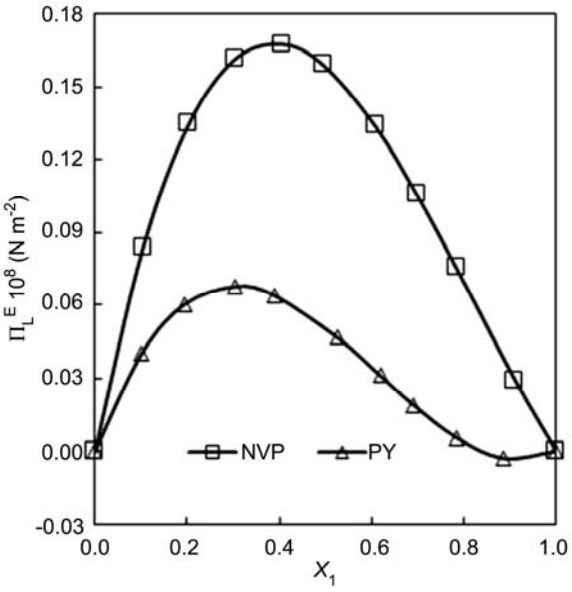

Fig. 2 — Curves of excess free volume, V_f^E with mole fraction, x_1 of [Bmim][BF_4] for the [Bmim][BF_4] + 2-PY/NVP binary mixtures at temperature 298.15K. *Symbols* refer to the experimental values and the *solid lines* have been drawn from Eq. (10) using the coefficients given in Table 4.

In general, H^E values of mixing depend upon the relative enthalpies of endothermic and exothermic effects that arise on mixing of the components. The factors that cause endothermic effect on mixing are:

a) strong specific interactions, usually some type of chemical interactions
b) favourable geometrical fitting of component molecules due to occupation of void spaces of one component by the other when the molecular sizes of the unlike molecules differ by a large magnitude, and
c) ion-dipole interactions of solvent molecules with the ionic liquid molecules.

The factors that cause exothermic effect on mixing of the components are:

a) breakdown of the solvent self-associated molecules from each other
b) breakdown of the ionic liquid ion pairs, and

c) formation of weaker ionic liquid-solvent bonds than ionic liquid-ionic liquid and solvent-solvent bonds.

Generally negative values of H^{E} indicate exothermic process, and positive value of H^{E} indicates endothermic process. In the mixing of the [Bmim][BF_4] with 2-PY and NVP systems observed negative values. The excess molar enthalpies are exothermic for [Bmim][BF_4] + 2-PY/NVP mixtures with the maxima being exhibited in the equimolar region over the entire composition and at each investigated temperature[37] is shown in Fig. 3. The positive H^{E} values may be attributed due to the packing effect and ion-dipole interaction of solvent molecules with the ionic liquid in liquid mixture[38] and negative H^{E} values may be attributed due to dipole-dipole or ion-ion interactions between the solvent molecules and ionic liquids and are dominant over the ion-dipole interaction between unlike molecules, also dissociation of the hydrogen bonding in the cyclic amides being greater than intermolecular bond formation between the ionic liquid and the cyclic amides or due to the dissociation of the ion pairs forming the ionic liquid[39]. The magnitude of H^{E} follows the sequence: 2-PY < NVP.

The $T_S{}^{E}$ values for [Bmim][BF4] + NVP and [Bmim][BF4]+2-PY are negative over the entire composition range at each investigated temperature (Fig. 4). The negative $T_S{}^{E}$ values for [Bmim][BF4]+NVP mixtures further support the conclusions drawn from the π_i^{E} and V_f^{E} values, that the formation of hydrogen bonding between [Bmim]+/[BF4]− ions and NVP molecules leads to closer packing of molecules, resulting in a contraction in volume. This leads to a decrease in the entropy of the mixture resulting in negative $T_S{}^{E}$ values. The positive values of $T_S{}^{E}$ may be attributed to the disruption of hydrogen bonded associates of propanediols that dominate the hydrogen bonding between unlike molecules.

The G^{E} values (Fig. 5) for [Bmim][BF_4] + 2-PY/NVP are negative over the entire composition range at each investigated temperature. The negative values of G^{E} may be attributed to effective geometrical packing effect and formation of hydrogen bonding between $[Bmim]^{+}/[BF_4]^{-}$ ions and 2-PY or NVP molecules in the mixtures.

The refractive index n_D can be used as a measure of the electronic polarizability of a molecule and can

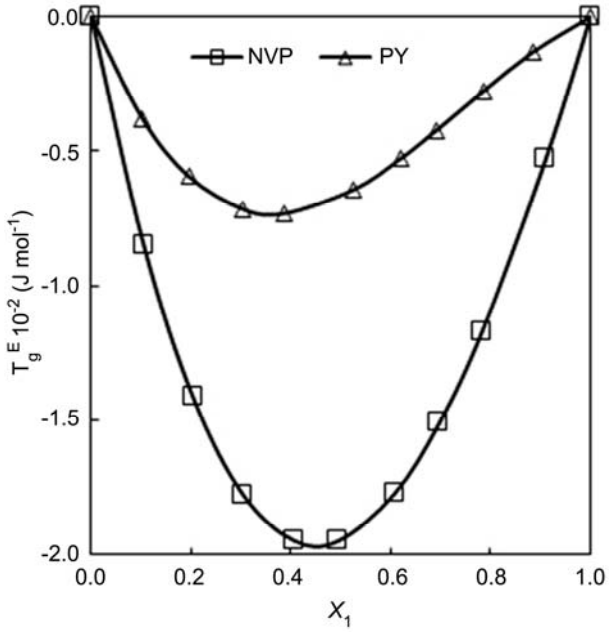

Fig. 3 — Curves of excess free volume, H^{E} with mole fraction, x_1 of [Bmim][BF_4] for the [Bmim][BF_4] + 2-PY/NVP binary mixtures at temperature 298.15K. *Symbols* refer to the experimental values and the *solid lines* have been drawn from Eq. (10) using the coefficients given in Table 4.

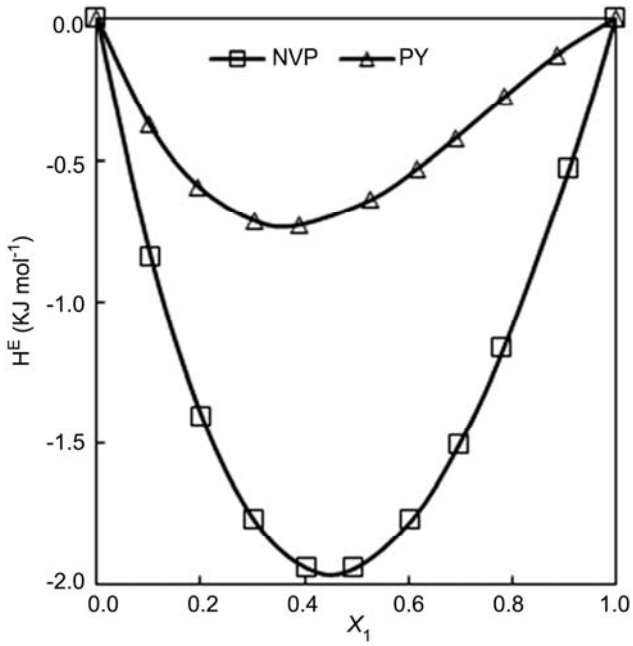

Fig. 4 — Curves of excess free volume, $T_S{}^{E}$ with mole fraction, x_1 of [Bmim][BF_4] for the [Bmim][BF_4] + 2-PY/NVP binary mixtures at temperature 298.15K. *Symbols* refer to the experimental values and the *solid lines* have been drawn from Eq. (10) using the coefficients given in Table 4.

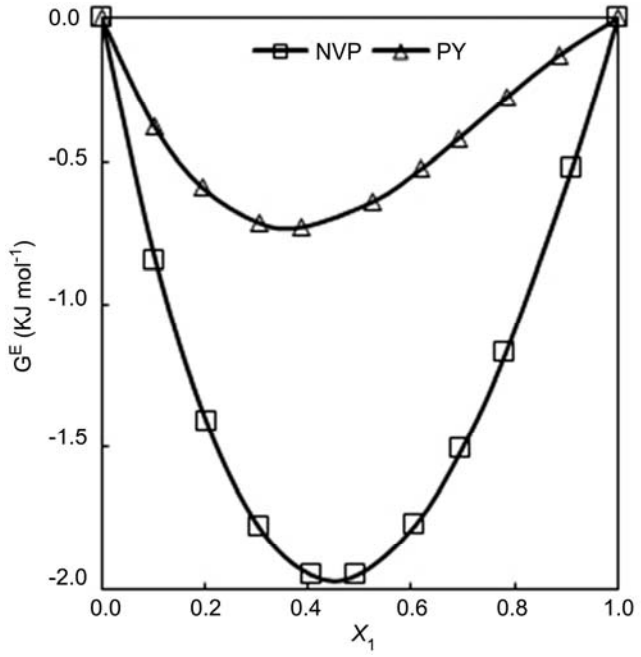

Fig. 5 — Curves of excess free volume, G^E with mole fraction, x_1 of [Bmim][BF_4] for the [Bmim][BF_4] + 2-PY/NVP binary mixtures at temperature 298.15K. *Symbols* refer to the experimental values and the *solid lines* have been drawn from Eq. (10) using the coefficients given in Table 4.

provide useful information when studying the interaction between molecules. A perusal of Table 5 indicates that the APDs between the experimental values of refractive indices of these mixtures and theoretically calculated values from various mixing rules are low in the range of 0.042 to 0.056 for [Bmim][BF_4] + NVP and 0.053 to 0.074 for [Bmim][BF_4] + 2-PY. The low values of APDs clearly indicate the applicability of various mixing rules for the binary mixtures under study.

Conclusions

The refractive indices (n_D) of the binary mixtures of [Bmim][BF_4] with cyclic amides have been measured over whole composition range at temperatures from 298.15 to 323.15 K. Using the experimental values of ρ and u and n_D, the internal pressure (π_i), free volume (V_f) and their excess functions; excess enthalpy (H^E), excess entropy ($T_S{}^E$) and excess Gibbs free energy (G^E) have been calculated. The variations of these excess properties with composition indicate that the interactions between [Bmim][BF_4] and cyclic amides in these mixtures follows the order: NVP> 2-PY.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(09)972-984_SupplData.pdf.

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