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Temperature dependent study of thermophysical and optical properties of binary mixtures of imidazolium based ionic liquids

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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 α,ω-propanediols have been used to calculate the internal pressure (π_i), free volume (V_f), excess internal pressure (π_i^E), excess free volume (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, 303.15, 308.15, 313,15, 318.15 and 323.15 K). The refractive indices (n_D) of these mixtures have been measured at above-mentioned temperatures and the deviations in refractive index ($\Delta_\phi n_D$) have been calculated. 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 α,ω-propanediols in these mixtures follows the order: 1,2-propanediol > 1,3-propanediol.

Keywords: Thermodynamic properties, Excess thermodynamic properties, Refractive index, Molecular interactions, Alkanediols, 1-Butyl-3-methylimidazolium tetrafluoroborate

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 1,2-propanediol and 1,3-propanediol 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, etc.[9,10]. 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. Glycols find widespread application in automotive, aviation, explosive, textile, surface coating, and food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries[14–16]. The α,ω-propanediols contain both proton donor as well as proton acceptor groups, therefore, there exists a significant degree self-association through inter- and intra-molecular hydrogen bonding in pure state. The thermophysical behavior of α,ω-propanediols both as a pure compound or in binary mixtures were studied in recent years[17–20]. 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[21–25], 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$_4$] +1,2-propanediol or 1,3-propanediol binary mixtures have been measured over entire composition range, expressed by mole fraction (x_1) of [Bmim][BF$_4$] at temperatures 298.15, 303.15, 308.15, 313,15, 318.15 and 323.15 K and at atmospheric pressure. The calculate the internal pressure (π_i), free volume (V_f), excess internal pressure (π_i^E), excess free volume (V_f^E), excess free energy (G^E), excess enthalpy (H^E) and excess entropy (TS^E) and deviations in refractive index ($\Delta_\phi n_D$) of mixing of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]) with 1,2-propanediol or 1,3-propanediol binary mixtures have been calculated from experimental values ultrasonic speeds (u) and densities (ρ) and refractive index (n_D). The experimental data of u and ρ of these binary mixtures has been taken from our previous study[26]. The variations of these excess parameters with composition and temperature of the mixtures are discussed in terms of intermolecular interactions in these mixtures.

Materials and Methods

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; 1,2-propanediol (Sigma Aldrich, CAS No. 57-55-6, purity > 0.99 mass fraction) and 1,3- propanediol (Sigma Aldrich, CAS No. 504-63-2, purities > 0.99 mass fraction) were purified by fractional distillation under low pressure. The water content in the ionic liquid and alkanediols was determined using a Karl Fischer Titrator (Metrohm, 890 Titrando)[27]. The water content was found to be less than 40 ppm. The mass fraction purities of the purified chemicals as determined by gas chromatography were: [Bmim][BF$_4$] > 0.995, 1,2-propanediol > 0.996 and 1,3-propanediol > 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 $\pm 1\times 10^{-4}$.

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.

Results and Discussion

Excess properties

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,

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

where α_p is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of 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 Eq.(1) in the present calculations. Thus, the internal pressure can be shown to be equal to the following relationship[28,29].

$$\pi_i = \frac{\alpha_p T}{k_T} \quad \dots (2)$$

The free volume, V_f of the mixtures are calculated from the relation[21,22,28,29]

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

since P is very small as compared to π_i, it has been neglected in the Eq.(3) in the present calculations. k_T, is calculated using the well-known thermodynamic relationship[31,32],

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

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[33–35] and the C_p values for the mixtures have been calculated by using the following relationship.

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

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 S1 (Supplementary Data). The π_i^E and V_f^E of binary mixtures have been calculated using the relationship,

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

where Y is π_i or V_f and subscripts 1 and 2 refers to pure [Bmim][BF$_4$] and alkanediol, 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[21,22,35].

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

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

The excess free energy (G^E) of mixtures is given by the relationship,

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

The values of u, ρ, π_i and V_f for the binary mixtures of [Bmim][BF$_4$]+1,2-propanediol/1,3-propanediol as functions of mole fraction, x_1 of [Bmim][BF$_4$] at various temperatures are listed in Table 1.

The experimental refractive indices (n_D) of [Bmim][BF$_4$]+1,2-propanediol/1,3-propanediol binary mixtures at investigated temperatures are included in Table 1. The deviations in refractive index, ($\Delta_\phi n_D$) and deviations in molar refractions (ΔR_M) are calculated using the following relationship,

$$\Delta_\phi n_D = n_D - n_D^{id} \qquad \ldots (10)$$

where

$$n_D^{id} = \phi_1 n_{D,1} + \phi_2 n_{D,2} \qquad \ldots (11)$$

Table 1—The values of ρ, u, n, π_i and V_f, for the binary mixtures of [Bmim][BF$_4$]+1,2-propanediol/1,3-propaqnediol as a function of mole fraction, x_1, of [Bmim][BF$_4$] at temperatures T = (298.15 – 318.15) K

[Bmim][BF$_4$]+1,2-propanediol						*[Bmim][BF$_4$]+1,3-propanediol*					
x_1	ρ (kg m^{-3})	u (m s^{-1})	n_D	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})	x_1	ρ (kg m^{-3})	u (m s^{-1})	n_D	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})
298.15 K											
0.0000	1032.64	1510.97	1.43123	4.482	5.531	0.0000	1049.69	1628.79	1.43774	4.454	5.566
0.1034	1064.92	1518.52	1.42844	4.550	5.449	0.1021	1079.28	1612.75	1.43332	4.463	5.555
0.2030	1089.63	1524.65	1.42632	4.586	5.405	0.1994	1101.45	1601.09	1.43010	4.467	5.549
0.3050	1111.80	1530.55	1.42468	4.612	5.375	0.2991	1119.45	1589.97	1.42760	4.459	5.559
0.3835	1127.72	1535.09	1.42375	4.629	5.355	0.3989	1137.28	1580.80	1.42584	4.462	5.555
0.4936	1147.05	1541.08	1.42294	4.639	5.343	0.4970	1151.38	1574.21	1.42475	4.465	5.552
0.5811	1160.41	1545.77	1.42268	4.640	5.342	0.6057	1163.63	1569.19	1.42406	4.468	5.548
0.6878	1172.96	1550.74	1.42248	4.622	5.363	0.6828	1176.10	1565.19	1.42366	4.484	5.528
0.7997	1183.83	1555.93	1.42200	4.595	5.395	0.7928	1185.80	1563.54	1.42293	4.496	5.513
0.8818	1190.44	1559.96	1.42146	4.570	5.424	0.8974	1192.75	1564.24	1.42184	4.512	5.494
1.0000	1198.79	1564.92	1.42059	4.525	5.478	1.0000	1198.79	1565.09	1.42059	4.526	5.477
303.15 K											
0.0000	1028.95	1497.17	1.42951	4.478	5.629	0.0000	1046.55	1617.58	1.43631	4.468	5.641
0.1034	1061.15	1505.26	1.42674	4.548	5.542	0.1021	1075.88	1601.13	1.43184	4.473	5.635
0.2030	1085.54	1511.79	1.42464	4.586	5.496	0.1994	1097.92	1589.41	1.42859	4.476	5.631
0.3050	1107.80	1518.02	1.42303	4.614	5.463	0.2991	1115.83	1578.24	1.42607	4.467	5.642
0.3835	1123.53	1522.78	1.42213	4.631	5.443	0.3989	1133.59	1569.03	1.42430	4.469	5.640

(*Contd.*)

Table 1—The values of ρ, u, n_D, π_i and V_f, for the binary mixtures of [Bmim][BF$_4$]+1,2-propanediol/1,3-propaqnediol as a function of mole fraction, x_1, of [Bmim][BF$_4$] at temperatures T = (298.15 – 318.15) K—*Contd.*

[Bmim][BF$_4$]+1,2-propanediol						*[Bmim][BF$_4$]+1,3-propanediol*					
x_1	ρ (kg m^{-3})	u (m s^{-1})	n_D	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})	x_1	ρ (kg m^{-3})	u (m s^{-1})	n_D	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})
303.15 K											
0.4936	1142.88	1529.00	1.42133	4.643	5.429	0.4970	1147.66	1562.41	1.42319	4.471	5.637
0.5811	1156.26	1533.82	1.42108	4.644	5.427	0.6057	1159.89	1557.38	1.42251	4.474	5.633
0.6878	1169.03	1538.89	1.42092	4.628	5.446	0.6828	1172.38	1553.39	1.42212	4.490	5.614
0.7997	1180.06	1544.10	1.42048	4.601	5.478	0.7928	1182.13	1551.77	1.42140	4.502	5.598
0.8818	1186.82	1548.10	1.41996	4.576	5.508	0.8974	1189.17	1552.52	1.42033	4.519	5.578
1.0000	1195.19	1552.93	1.41914	4.530	5.563	1.0000	1195.19	1553.15	1.41914	4.531	5.562
308.15 K											
0.0000	1025.20	1483.12	1.42762	4.471	5.731	0.0000	1043.41	1606.18	1.43489	4.480	5.719
0.1034	1057.16	1491.81	1.42490	4.543	5.639	0.1021	1072.51	1589.64	1.43034	4.483	5.715
0.2030	1081.55	1498.77	1.42285	4.583	5.590	0.1994	1094.44	1577.80	1.42706	4.484	5.713
0.3050	1103.82	1505.35	1.42130	4.613	5.554	0.2991	1112.27	1566.52	1.42452	4.474	5.727
0.3835	1119.46	1510.36	1.42043	4.631	5.532	0.3989	1129.96	1557.23	1.42276	4.475	5.726
0.4936	1138.72	1516.86	1.41965	4.644	5.517	0.4970	1143.99	1550.57	1.42162	4.476	5.723
0.5811	1152.12	1521.85	1.41942	4.646	5.514	0.6057	1156.21	1545.51	1.42093	4.479	5.720
0.6878	1165.24	1527.05	1.41930	4.632	5.531	0.6828	1168.70	1541.52	1.42055	4.494	5.701
0.7997	1176.31	1532.34	1.41891	4.605	5.563	0.7928	1178.49	1539.93	1.41984	4.507	5.685
0.8818	1183.22	1536.34	1.41842	4.581	5.592	0.8974	1185.59	1540.75	1.41881	4.523	5.664
1.0000	1191.61	1541.18	1.41765	4.535	5.649	1.0000	1191.61	1541.35	1.41765	4.536	5.648
313.15 K											
0.0000	1021.43	1469.03	1.42594	4.461	5.836	0.0000	1040.24	1594.83	1.43337	4.491	5.798
0.1034	1053.35	1478.35	1.42322	4.537	5.738	0.1021	1069.14	1578.11	1.42877	4.491	5.797
0.2030	1077.48	1485.70	1.42120	4.578	5.687	0.1994	1090.96	1566.18	1.42547	4.491	5.797
0.3050	1099.83	1492.64	1.41968	4.610	5.647	0.2991	1108.71	1554.83	1.42294	4.479	5.813
0.3835	1115.37	1497.88	1.41883	4.629	5.624	0.3989	1126.35	1545.49	1.42118	4.479	5.813
0.4936	1134.49	1504.66	1.41808	4.643	5.607	0.4970	1140.34	1538.80	1.42006	4.480	5.811
0.5811	1147.90	1509.83	1.41785	4.646	5.603	0.6057	1152.54	1533.74	1.41936	4.482	5.809
0.6878	1161.36	1515.18	1.41776	4.634	5.618	0.6828	1165.04	1529.76	1.41901	4.497	5.789
0.7997	1172.68	1520.58	1.41741	4.609	5.649	0.7928	1174.87	1528.21	1.41833	4.510	5.773
0.8818	1179.64	1524.63	1.41694	4.585	5.679	0.8974	1182.04	1529.09	1.41732	4.527	5.751
1.0000	1188.05	1529.52	1.41622	4.539	5.736	1.0000	1188.05	1529.69	1.41622	4.540	5.735
318.15 K											
0.0000	1017.63	1454.91	1.42420	4.445	5.951	0.0000	1037.06	1583.48	1.43190	4.500	5.878
0.1034	1049.42	1464.89	1.42148	4.525	5.846	0.1021	1065.77	1566.64	1.42723	4.498	5.880
0.2030	1073.43	1472.67	1.41950	4.568	5.790	0.1994	1087.49	1554.63	1.42389	4.497	5.882
0.3050	1095.70	1479.97	1.41800	4.603	5.747	0.2991	1105.17	1543.21	1.42135	4.484	5.899
0.3835	1111.20	1485.48	1.41717	4.623	5.721	0.3989	1122.75	1533.83	1.41960	4.483	5.901
0.4936	1130.34	1492.55	1.41644	4.639	5.701	0.4970	1136.71	1527.12	1.41845	4.483	5.900
0.5811	1143.50	1497.92	1.41620	4.643	5.697	0.6057	1148.90	1522.06	1.41776	4.485	5.898
0.6878	1157.40	1503.43	1.41616	4.634	5.709	0.6828	1161.40	1518.11	1.41741	4.500	5.878
0.7997	1168.97	1508.95	1.41585	4.610	5.738	0.7928	1171.27	1516.62	1.41678	4.513	5.861
0.8818	1176.07	1513.05	1.41541	4.587	5.766	0.8974	1178.50	1517.59	1.41578	4.531	5.838
1.0000	1184.51	1518.02	1.41473	4.542	5.823	1.0000	1184.51	1518.19	1.41473	4.543	5.822
323.15 K											
0.0000	1013.79	1440.73	1.42248	4.427	6.069	0.0000	1033.87	1572.11	1.43044	4.508	5.960
0.1034	1044.98	1451.40	1.41978	4.509	5.958	0.1021	1062.39	1555.15	1.42570	4.504	5.965
0.2030	1069.42	1459.63	1.41783	4.557	5.895	0.1994	1084.01	1543.09	1.42234	4.501	5.969
0.3050	1091.56	1467.33	1.41637	4.594	5.848	0.2991	1101.63	1531.63	1.41980	4.487	5.988
0.3835	1107.05	1473.11	1.41556	4.617	5.820	0.3989	1119.16	1522.22	1.41805	4.485	5.990
0.4936	1126.22	1480.50	1.41485	4.635	5.797	0.4970	1133.09	1515.51	1.41690	4.485	5.990
0.5811	1139.42	1486.07	1.41462	4.640	5.790	0.6057	1145.27	1510.46	1.41620	4.486	5.989
0.6878	1153.56	1491.76	1.41461	4.633	5.799	0.6828	1157.79	1506.55	1.41588	4.501	5.969
0.7997	1165.28	1497.42	1.41435	4.611	5.827	0.7928	1167.69	1505.13	1.41528	4.515	5.951
0.8818	1172.53	1501.56	1.41395	4.589	5.854	0.8974	1174.98	1506.18	1.41431	4.533	5.927
1.0000	1180.98	1506.62	1.41331	4.544	5.912	1.0000	1180.98	1506.80	1.41331	4.545	5.911

Here ϕ is the volume fraction and V_m is the molar volume of the mixture and are calculated using the relationship.

$$\phi_i = x_i V_{\mathrm{m},i} / \sum_{i=1}^{2} x_i V_{\mathrm{m},i} \qquad \ldots (12)$$

The values of ϕ_i, π_i^E, V_f^E, H^E, TS^E, G^E and $\Delta_\phi n_\mathrm{D}$ for the mixtures are listed in Tables S2 and S3 (Supplementary Data). The values of π_i^E, V_f^E, H^E, TS^E, G^E and $\Delta_\phi n_\mathrm{D}$ were fitted to a Redlich-Kister[36] type polynomial equation

$$Y^\mathrm{E} = x_1(1-x_1)\sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \qquad \ldots (13)$$

where Y^E is π_i^E or V_f^E or H^E or TS^E or G^E or $\Delta_\phi n_\mathrm{D}$. The volume fraction, ϕ, was used instead of x for fitting of $\Delta_\phi n_\mathrm{D}$. The values of coefficients, A_i in Eq. (13) were evaluated by using least-squares method with all points weighted equally. The values of coefficients, A_i of Eq.(13) for the excess functions and the corresponding standard deviations, σ are listed in Table 2. The variation of π_i^E, V_f^E, H^E, TS^E, G^E and $\Delta_\phi n_\mathrm{D}$ with composition and temperature of the mixtures are presented graphically in Figs 1–6, respectively.

Mixing rules for predicting refractive index

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[37–39].

Table 2—Coefficients (A_i) of Eq. (13) for π_i^E, V_f^E, H^E, TS^E, G^E and $\Delta_\phi n_\mathrm{D}$ along with standard deviations (σ) for [Bmim][BF$_4$]+1,2-propandiol/1,3-propanediol binary mixtures at different temperatures

Property	T (K)	A_1	A_2	A_3	A_4	A_5	σ
[Bmim][BF$_4$]+1,2-Propanediol							
π_i^E (10^8 N m^{-2})	298.15	0.5488	-0.0215	-0.1328	-0.1705	0.2941	0.0008
	303.15	0.5597	-0.0195	-0.1264	-0.1717	0.3022	0.0007
	308.15	0.5701	-0.0204	-0.1049	-0.1675	0.2731	0.0006
	313.15	0.5785	-0.0220	-0.0852	-0.1669	0.2642	0.0007
	318.15	0.5889	-0.0258	-0.0704	-0.1615	0.2617	0.0006
	323.15	0.6015	-0.0286	-0.0460	-0.1441	0.2128	0.0004
V_f^E (10^{-6} m^3 mol^{-1})	298.15	-0.6369	0.0457	0.1370	0.2095	-0.3563	0.0009
	303.15	-0.6621	0.0459	0.1295	0.2134	-0.3693	0.0008
	308.15	-0.7036	0.0341	0.1046	0.2100	-0.3359	0.0007
	313.15	-0.7270	0.0308	0.0832	0.2135	-0.3318	0.0009
	318.15	-0.7566	0.0389	0.0701	0.2100	-0.3446	0.0008
	323.15	-0.7684	0.0398	0.0694	0.2132	-0.3464	0.0008
H^E (kJ mol^{-1})	298.15	-6.7214	-0.3516	0.4567	0.1446	-1.2916	0.0066
	303.15	-6.8917	-0.4287	0.4605	0.1538	-1.3247	0.0067
	308.15	-7.0269	-0.4981	0.4778	0.2204	-1.3378	0.0066
	313.15	-7.1368	-0.5478	0.5087	0.2792	-1.4067	0.0067
	318.15	-7.2174	-0.6228	0.5440	0.3590	-1.4555	0.0068
	323.15	-7.3070	-0.6992	0.5660	0.4395	-1.4772	0.0065
TS^E (10^{-2} J mol^{-1})	298.15	-2.9766	0.1267	0.6734	0.9338	-1.5986	0.0043
	303.15	-3.0859	0.1208	0.6479	0.9547	-1.6722	0.0036
	308.15	-3.1962	0.1323	0.5335	0.9485	-1.5290	0.0035
	313.15	-3.2978	0.1482	0.4337	0.9665	-1.5184	0.0040
	318.15	-3.4183	0.1804	0.3673	0.9497	-1.5567	0.0036
	323.15	-3.5534	0.2086	0.2059	0.8639	-1.2570	0.0024
G^E (kJ mol^{-1})	298.15	-3.7448	-0.4778	-0.2172	-0.7914	0.3096	0.0044
	303.15	-3.8057	-0.5496	-0.1870	-0.8013	0.3453	0.0048
	308.15	-3.8356	-0.6267	0.0435	-0.7382	-	0.0044
	313.15	-3.8418	-0.6942	0.1329	-0.6919	-	0.0059
	318.15	-3.8020	-0.8012	0.2299	-0.5963	-	0.0074
	323.15	-3.7477	-0.9127	0.2456	-0.4107	-	0.0061

(*Contd.*)

Table 2—Coefficients (A_i) of Eq. (13) for π_i^{E}, $V_{\mathrm{f}}^{\mathrm{E}}$, H^{E}, TS^{E}, G^{E} and $\Delta_{\phi}n_{\mathrm{D}}$ along with standard deviations (σ) for [Bmim][BF$_4$]+1,2-propandiol/1,3-propanediol binary mixtures at different temperatures—*Contd.*

Property	T (K)	A_1	A_2	A_3	A_4	A_5	σ
$\Delta_{\phi}n_D$ (10^{-2})	298.15	-0.4580	-0.2732	0.7142	1.2375	-	0.0054
	303.15	-0.4849	-0.2866	0.6903	1.2234	-	0.0057
	308.15	-0.5046	-0.3011	0.6513	1.2238	-	0.0059
	313.15	-0.5317	-0.3044	0.6177	1.2054	-	0.0059
	318.15	-0.5573	-0.3291	0.5696	1.2400	-	0.0060
	323.15	-0.5841	-0.3467	0.5339	1.2417	-	0.0060
[Bmim][BF$_4$]+1,2-Propanediol							
π_i^{E} (10^8 N m^{-2})	298.15	-0.1042	-0.0377	0.1343	-0.0397	-	0.0024
	303.15	-0.1181	-0.0326	0.1343	-0.0151	-	0.0025
	308.15	-0.1320	-0.0312	0.1394	-0.0091	-	0.0025
	313.15	-0.1457	-0.0298	0.1403	0.0006	-	0.0025
	318.15	-0.1591	-0.0285	0.1430	0.0098	-	0.0025
	323.15	-0.1719	-0.0270	0.1449	0.0181	-	0.0025
$V_{\mathrm{f}}^{\mathrm{E}}$ (10^{-6} m^3 mol^{-1})	298.15	0.1276	0.0449	-0.1681	0.0500	-	0.0030
	303.15	0.1468	0.0392	-0.1698	0.0204	-	0.0031
	308.15	0.1666	0.0381	-0.1782	0.0119	-	0.0032
	313.15	0.1869	0.0367	-0.1821	-0.0013	-	0.0032
	318.15	0.2072	0.0353	-0.1889	-0.0116	-	0.0033
	323.15	0.2272	0.0340	-0.1944	-0.0234	-	0.0034
H^{E} (kJ mol^{-1})	298.15	1.2732	2.5313	0.6317	-0.8625	-1.7366	0.0310
	303.15	1.3017	2.5407	0.6245	-1.0942	-1.8482	0.0321
	308.15	1.3526	2.6025	0.6242	-1.1598	-1.9749	0.0327
	313.15	1.4138	2.6545	0.6262	-1.2420	-2.0448	0.0333
	318.15	1.4801	2.7113	0.6241	-1.3187	-2.1295	0.0338
	323.15	1.5488	2.7635	0.6196	-1.3985	-2.2074	0.0343
TS^{E} (10^{-2} J mol^{-1})	298.15	0.5741	0.2047	-0.7469	0.2227	-	0.0136
	303.15	0.6605	0.1787	-0.7564	0.0898	-	0.0139
	308.15	0.7502	0.1752	-0.7971	0.0525	-	0.0141
	313.15	0.8420	0.1682	-0.8169	-0.0049	-	0.0144
	318.15	0.9337	0.1621	-0.8452	-0.0520	-	0.0147
	323.15	1.0249	0.1564	-0.8711	-0.1065	-	0.0150
G^{E} (kJ mol^{-1})	298.15	0.7501	2.3271	0.4493	-1.0899	-	0.0394
	303.15	0.6956	2.3618	0.3921	-1.1872	-	0.0403
	308.15	0.6604	2.4271	0.3658	-1.2159	-	0.0411
	313.15	0.5647	2.4862	1.5739	-1.2367	-2.2887	0.0416
	318.15	0.5398	2.5483	1.5879	-1.2641	-2.3512	0.0421
	323.15	0.5176	2.6078	1.6058	-1.2929	-2.4225	0.0425
$\Delta_{\phi}n_D$ (10^{-2})	298.15	-0.5895	-0.2533	0.9709	1.6578	-	0.0043
	303.15	-0.6250	-0.2718	0.9409	1.6127	-	0.0047
	308.15	-0.6598	-0.2769	0.8992	1.5771	-	0.0046
	313.15	-0.7033	-0.2814	0.8710	1.5274	-	0.0050
	318.15	-0.7464	-0.2941	0.8386	1.4952	-	0.0057
	323.15	-0.7909	-0.3066	0.7952	1.4734	-	0.0061

Arago-Biot (A-B)

$$n = n_1\phi_1 + n_2\phi_2 \quad \dots (14)$$

Gladstone-Dale (G-D)

$$n - 1 = (n_1 - 1)\varphi_1 + (n_2 - 1)\varphi_2 \quad \dots (15)$$

Newton's (N) relationship

$$n^2 - 1 = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2 \quad \dots (16)$$

Eyring and John (E-J)

$$n = n_1\phi_1^2 + 2(n_1 n_2)^{1/2}\phi_1\phi_2 + n_2\phi_2^2 \quad \dots (17)$$

Table 3—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) relationships for [Bmim][BF$_4$]+1,2-propandiol/ 1,3-propanediol binary mixtures at different temperatures

T (K)	A–B	G–D	N	E–J	L–L	H	EK	OS	W
[Bmin][BF$_4$]+1,2-propanediol									
298.15	0.0427	0.0427	0.0430	0.0425	0.0423	0.0424	0.0419	0.0417	0.0426
303.15	0.0448	0.0448	0.0451	0.0446	0.0445	0.0445	0.0441	0.0439	0.0447
308.15	0.0464	0.0464	0.0467	0.0463	0.0461	0.0462	0.0458	0.0456	0.0463
313.15	0.0488	0.0488	0.0491	0.0486	0.0484	0.0485	0.0480	0.0478	0.0486
318.15	0.0522	0.0522	0.0525	0.0521	0.0519	0.0520	0.0515	0.0513	0.0521
323.15	0.0557	0.0557	0.0560	0.0555	0.0554	0.0555	0.0550	0.0548	0.0556
[Bmin][BF$_4$]+1,3-propanediol									
298.15	0.0555	0.0555	0.0563	0.0551	0.0546	0.0548	0.0536	0.0531	0.0552
303.15	0.0578	0.0578	0.0586	0.0574	0.0570	0.0571	0.0559	0.0554	0.0575
308.15	0.0604	0.0604	0.0612	0.0600	0.0595	0.0597	0.0585	0.0579	0.0601
313.15	0.0635	0.0635	0.0643	0.0631	0.0627	0.0628	0.0616	0.0611	0.0632
318.15	0.0679	0.0679	0.0689	0.0674	0.0668	0.0671	0.0655	0.0648	0.0675
323.15	0.0730	0.0730	0.0740	0.0724	0.0719	0.0722	0.0706	0.0699	0.0726

Lorentz-Lorentz (L-L)

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

Heller (H):

$$\frac{n-n_1}{n_1}=\frac{3}{2}\left[\frac{(n_2/n_1)^2-1}{(n_2/n_1)^2+2}\right]\phi_2 \qquad \ldots (19)$$

Eykman (EK)

$$\frac{n^2-1}{n+0.4}=\left(\frac{n_1^2-1}{n_1+0.4}\right)\phi_1+\left(\frac{n_2^2-1}{n_2+0.4}\right)\phi_2 \qquad \ldots (20)$$

Oster (OS):

$$\frac{\left(n^2-1\right)\left(2n^2+1\right)}{n^2}=\frac{\left(n_1^2-1\right)\left(2n_1^2+1\right)}{n_1^2}\phi_1+\frac{\left(n_2^2-1\right)\left(2n_2^2+1\right)}{n_2^2}\phi_2 \qquad \ldots (21)$$

Weiner (W)

$$\frac{n^2-n_1^2}{n^2+2n_2^2}=\left(\frac{n^2-n_1^2}{n_2^2+2n_1^2}\right)\phi_2 \qquad \ldots (22)$$

where n represents the refractive index (n_D) in the relations (14)-(22) The refractive indices obtained from Eqs.(17)-(22) have been compared with the experimental values and the results are presented in terms of average percentage deviations (APD) calculated using the relationship,

$$APD=\frac{1}{m}\left[\sum\frac{(n_{Expt}-n_{Calc})}{n_{Expt.}}\times 100\right] \qquad \ldots (23)$$

where m is number of data points. The APDs for the binary systems at investigated temperatures are listed in Table 3.

Excess internal pressure

The results shown in Fig. 1 indicate that the π_i^E values are positive for [Bmim][BF$_4$]+1,2-propanediol and negative for [Bmim][BF$_4$]+1,3-propanediol over entire mole fraction range and at all investigated temperatures. As stated earlier, the molecules of alkanediols are associated through inter- and intra-molecular hydrogen bonding in pure state[40]. Mixing of [Bmim][BF$_4$] with alkanediols would induce mutual dissociation of the hydrogen-bonded structures present in pure alkanediols with subsequent formation of hydrogen bonding and ion-dipole interactions between unlike molecules. The observed positive π_i^E values for [Bmim][BF$_4$]+1,2-propanediol (Fig. 1) can be considered due to the formation of hydrogen bonding between [Bmim]$^+$/[BF$_4$]$^-$ ions and 1,2-propanediol molecules that leads to 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 negative π_i^E values for [Bmim][BF$_4$]+1,3-propanediol mixtures indicate weaker interactions between [Bmim][BF$_4$] and 1,3-propanediol molecules. The magnitude of π_i^E values for [Bmim][BF$_4$]+

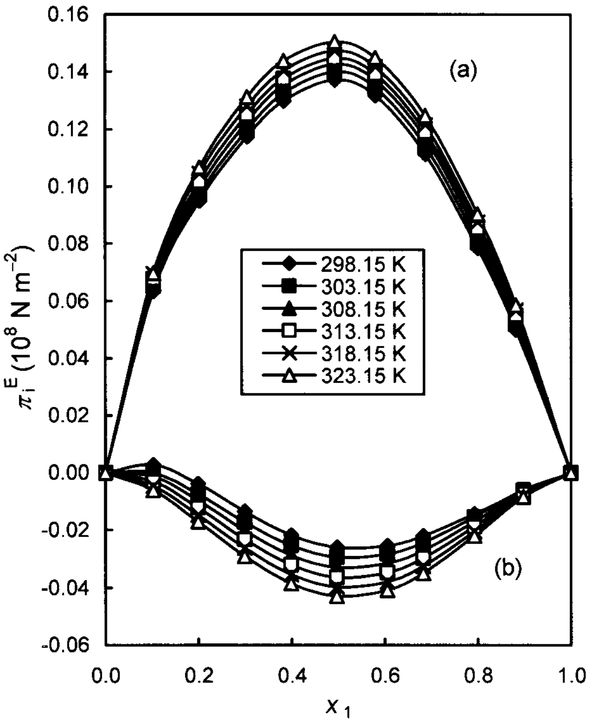

Fig. 1—Variation of excess internal pressure, π_i^E with mole fraction, x_1 of [Bmim][BF$_4$] for the (a) [Bmim][BF$_4$]+ 1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

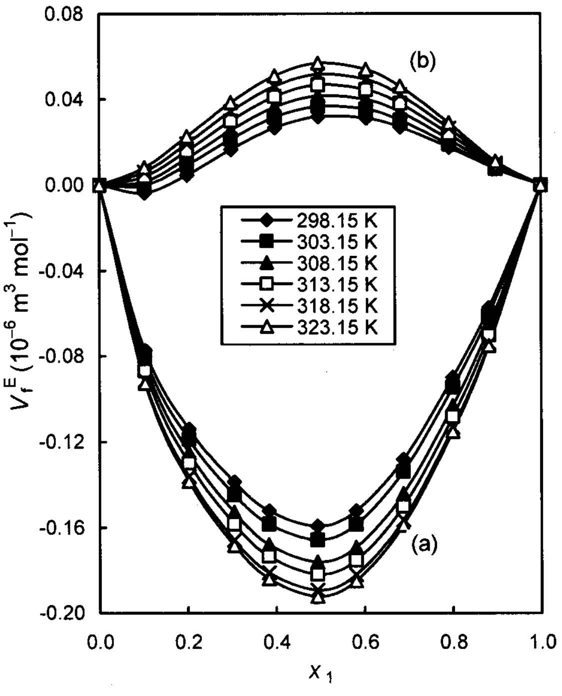

Fig. 2—Variation of excess free volume, V_f^E with mole fraction, x_1 of [Bmim][BF$_4$] for (a) [Bmim][BF$_4$]+1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

1,2-propanediol and 1,3-propanediol mixtures follows the sequence: 1,2-propanediol > 1,3-propanediol, which indicates the order of interactions in these systems.

Excess free volume

The perusal of Fig. 2 indicates that the V_f^E values are positive for [Bmim][BF$_4$]+1,3-propanediol and negative for [Bmim][BF$_4$]+1,2-propanediol mixtures over the entire composition range and at all temperatures. The observed trends in V_f^E value indicate specific interactions in [Bmim][BF$_4$]+ 1,2-propanediol, and weak interactions in [Bmim][BF$_4$]+1,3-propanediol mixtures. But opposite to our expectation, the positive trends are observed in V_f^E values for [Bmim][BF$_4$]+1,3-propanediol (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[41]. 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[42,43].

Excess enthalpy of mixing

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.

It can be observed that the negative value of H^E indicate exothermic process, and positive value of H^E indicates endothermic process in the mixing of the [Bmim][BF$_4$] with α,ω-propanediols systems. Figure 3 shows that the excess molar enthalpies are exothermic for [Bmim][BF$_4$]+1,2-propanediol mixtures with the maxima being exhibited in the equimolar region; while it is endothermic for [Bmim][BF$_4$]+1,2-propanediol mixtures over the entire composition and at each investigated temperature[44]. 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[45]. The negative H^E values may be attributed 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, the dissociation of hydrogen bonding in the alkanediols molecules dominates over the formation of intermolecular bonding between the ionic liquid and alkanediols, and the dissociation of the ionic liquid ion pairs[46]. The magnitude of H^E follows the sequence: 1, 2-proanediol < 1, 3-proanediol.

Excess entropy of mixing

The TS^E values for [Bmim][BF$_4$]+1,2-propanediol are negative while the values for [Bmim][BF$_4$]+ 1,3-propanediol are positive over the entire composition range at each investigated temperature (Fig. 4). The negative TS^E values for [Bmim][BF4]+1,2-propanediol

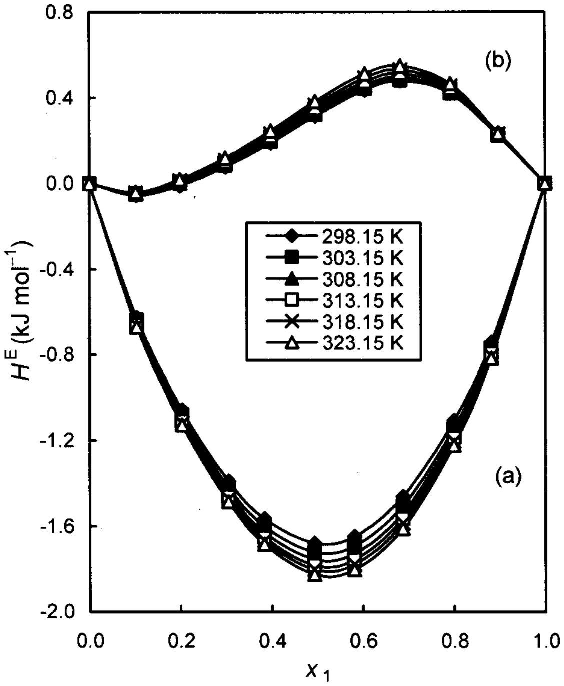

Fig. 3—Variation of excess enthalpy, H^E with mole fraction, x_1, of [Bmim][BF$_4$] for (a) [Bmim][BF$_4$]+1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

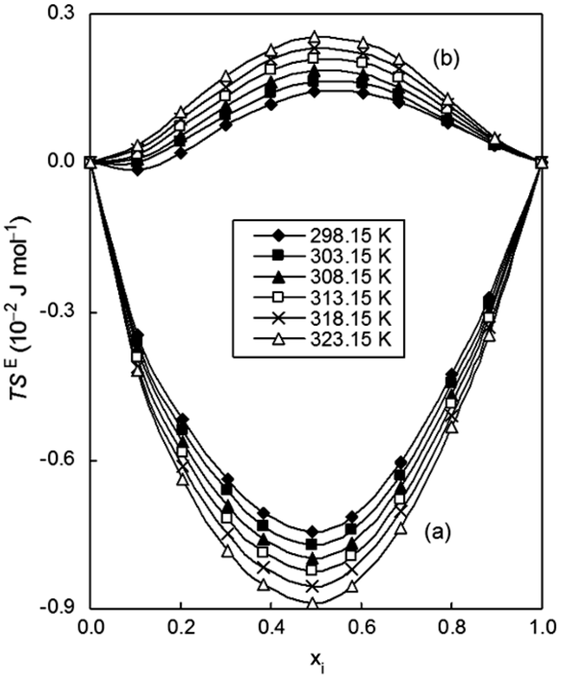

Fig. 4—Variation of excess entropy, TS^E with mole fraction, x_1 of [Bmim][BF$_4$] for (a) [Bmim][BF$_4$]+1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

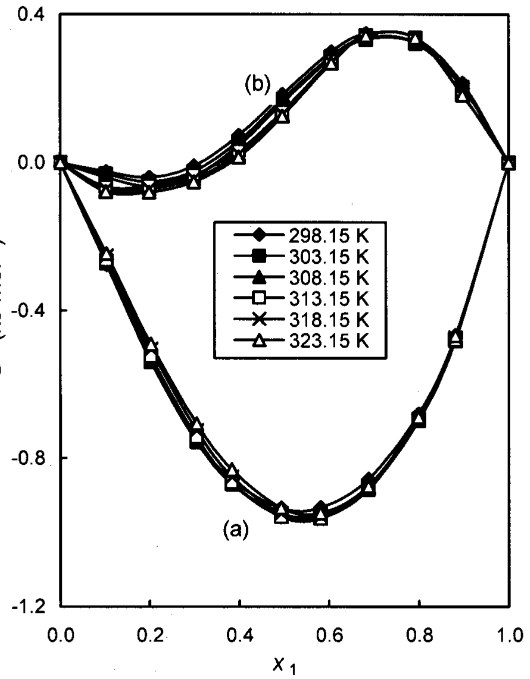

Fig. 5—Variation of excess free energy, G^E with mole fraction, x_1 of [Bmim][BF$_4$] for (a) [Bmim][BF$_4$]+1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

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 1,2-propanediol 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 TS^E values. The positive values of TS^E may be attributed to the disruption of hydrogen bonded associates of propanediols that dominate the hydrogen bonding between unlike molecules.

Excess free energy of mixing

The G^E values for [Bmim][BF$_4$]+1,2-propanediol are negative, while the values for [Bmim][BF$_4$]+ 1,3-propanediol are positive over the entire composition range at each investigated temperature (Fig. 5). The positive values G^E suggest the existence of weak ion-dipole interactions between [Bmim][BF$_4$] and 1,3-propanediol molecules while 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 1,2-propanediol molecules in the mixtures.

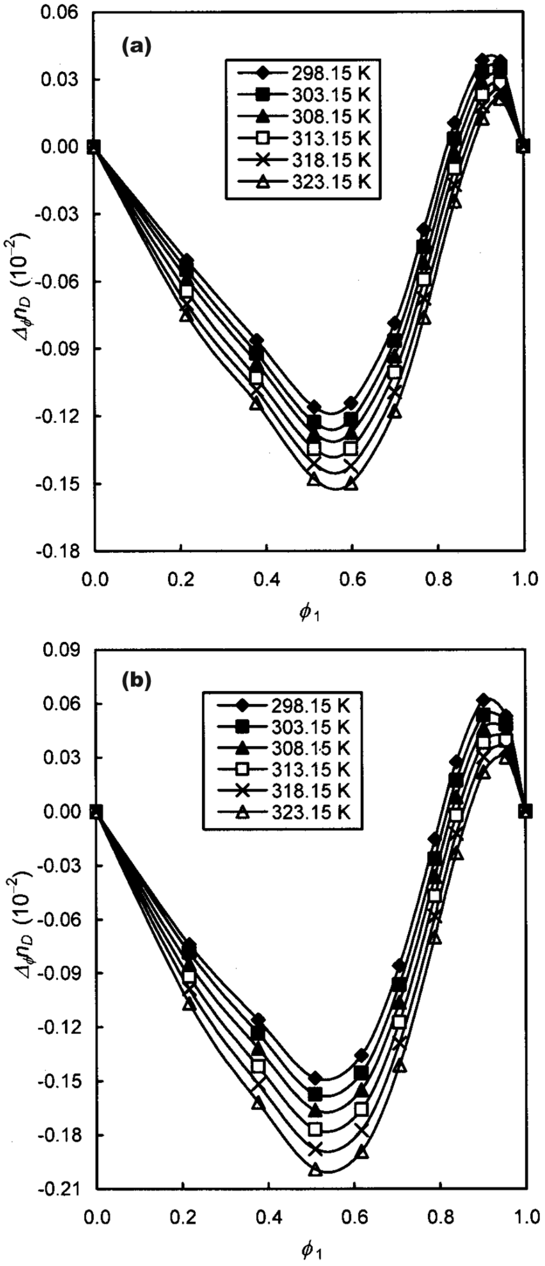

Fig. 6—Variation of deviations in refractive index, $\Delta_\phi n_D$ with volume fraction, ϕ_1 of [Bmim][BF$_4$] for (a) [Bmim][BF$_4$]+ 1,2-propandiol and (b) [Bmim][BF$_4$]+1,3-propanediol binary mixtures at different temperatures.

Deviations in refractive index

The refractive index n_D can be used as a measure of the electronic polarizability of a molecule and can provide useful information when studying the interaction between molecules. In general, the positive deviations in $\Delta_\phi n_D$ values are considered due to the presence of significant interactions in the mixtures, whereas the negative deviations in $\Delta_{\phi}n_{D}$ values indicate weak interactions between the components of the mixture[47]. A perusal of Fig. 6 shows that the $\Delta_{\phi}n_{D}$ values are negative in the mole fraction region of [Bmim][BF$_4$] ($x_1 < 0.8$) and are positive at the higher mole fractions ($x_1 > 0.8$) at all investigated temperatures. The mixing of [Bmim][BF$_4$] with alkanediols leads to mutual dissociation of the hydrogen-bonded structures present in pure alkanediols with subsequent formation of new hydrogen bonding and ion-dipole interactions between unlike molecules. The negative $\Delta_{\phi}n_{D}$ values in the mole fraction region of [Bmim][BF$_4$] ($x_1 < 0.8$) may be attributed to the dominance of disruption of hydrogen bonded associates between propanediol molecules over ion-dipole interactions between [Bmim][BF$_4$] and propanediol molecules in the mixtures. The $\Delta_{\phi}n_{D}$ values decrease with increase in temperature for each binary mixture, indicating that the interactions decrease due to breaking of hydrogen bonds in propanediol. Also, the $\Delta_{\phi}n_{D}$ values are found opposite to the sign of excess molar volumes V_{m}^{E} for all these binary mixtures[26], which is in agreement with the view proposed by Brocos et al.[48,49]. This further reinforces the conclusions drawn regarding intermolecular interactions from the variations of V_{m}^{E} values in our earlier study[26] on these mixtures.

A perusal of Table 3 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$_4$]+1,2-propanediol and 0.053 to 0.074 for [Bmim][BF$_4$]+1,3-propanediol. 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 α,ω-propanediols have been measured over the entire composition range at temperatures from 298.15 to 323.15 K. Using the experimental values of ρ, u and n_D, the internal pressure (π_i), free volume (V_f) and the excess functions; excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess entropy (TS^E), excess Gibbs free energy (G^E) and deviations in refractive index ($\Delta_{\phi}n_D$) have been calculated. The variations of these excess properties with composition indicate that the interactions between [Bmim][BF$_4$] and α,ω-propanediols in these mixtures follows the order: 1,2-propanediol > 1,3-propanediol. The refractive index data are well correlated by various mixing rules.

Supplementary Data

Supplementary data associated with this article, viz., Tables S1–S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(06)664-675_SupplData.pdf.

References

1 Welton T, Chem Rev, 99 (1999) 2071.
2 *Ionic Liquids in Synthesis, edited by* P Wasserscheid & T Welton, (Wiley-VCH, Mannheim) 2003.
3 Risager A, Fehrmann R, Berg R W, Hal R V & Wasserscheid P, *Phys Chem Chem Phys*, 7 (2005) 3052.
4 Leitner W, *Nature*, 423 (2003) 930.
5 Cooper, E R, Andrews C D, Wheatley P S, Webb P B, Wormald P & Morris R E, *Nature*, 430 (2004) 1012.
6 Nain A K, Chand D, Chandra P & Pandey J D, *Phys Chem Liq*, 47 (2009) 195.
7 Renuncio J A R, Breedveld G J F & Prausnitz J M, *J Phys Chem*, 81 (1997) 324.
8 Ali A & Tariq M, *J Chem Res (s)*, 4 (2006) 261.
9 Hapiot P & Lagrost C, *Chem Rev*, 108 (2008) 2238.
10 Bonhote P, Dias A P, Papageorgiou N, Kalyansundaram K & Gratzel M, *Inorg Chem*, 35 (1996) 1168.
11 Earle M J, Mc Cormac P B & Seddon K R, *Green Chem*, 1 (1999) 23.
12 Chauvin Y, Mussmann L & Olivier H, *Angew Chem*, 34 (1995) 2698.
13 Simon L C, Dupont J & de Souza R F, *Appl Catal A*, 175 (1998) 215.
14 Yang C, Ma P, Jing F & Tang D, *J. Chem. Eng. Data*, 48 (2003) 836.
15 Curme G O & Young C O, *Ind. Eng. Chem.*, 17 (1925) 1117.
16 Mohammadi A H, Waheed A & Dominique R, *J Chem Eng Data*, 53 (2008) 683.
17 Origlia-Luster M L, Patterson B A & Wooley E M, *J Chem Thermodyn*, 34 (2002) 511.
18 Sun T & Teja A S, *J Chem Eng Data*, 49 (2004) 1311.
19 Romero C M & Paez M, *J Therm Anal Cal*, 70 (2002) 263.
20 Nagamachi M Y & Francesconi A Z, *J Chem Thermodyn*, 38 (2006) 461.
21 Hildebrand J H & Scott R L, *Solubility of Non-Electrolytes*, 3rd Edn, (Reinhold, New York) 1950.
22 Hildebrand J H & Scott R L, *Regular Solutions*, (Prentice-Hall, Englewood Cliffs, New Jersey) 1962.
23 Barton A F M, *Chem Rev*, 75 (1975) 731.
24 Dack M R J, *Chem Soc Rev*, 4 (1975) 211.
25 Verdier S, Andersen S I, *Fluid Phase Equlib*, 231 (2005) 125.
26 Krishna T S, Sankar M G, Raju K T S S, Rao S G & Munibhadrayya B, *J Mol Liq*, 206 (2015) 350.

27 Scholz E, *Karl Fischer Titration*, (Springer-Verlag, Berlin) 1984.

28 Pandey J D, Shukla R K, Shukla A K & Rai R D, *J Chem. Soc, Faraday Trans I*, 84 (1988) 1853.

29 Pandey J D, Dubey G P, Shukla B P & Dubey S N, *J Am Chem Soc*, 104 (1982) 3299.

30 Hildebrand J H, *J Chem Phys*, 15 (1947) 225.

31 Douheret G, Khadir A & Pal A, *Thermochim Acta*, 142 (1989) 219.

32 Douheret G, Davis M I, Reis J C & Blandamer M J, *Chem Phys Chem*, 2 (2001) 148.

33 Zorebski E, Dzida M & Piotrowska M, *J Chem Eng Data*, 53 (2008) 136.

34 Zafarani-Moattar M T & Shekaari H, *J Chem Thermodyn*, 38 (2006) 1377.

35 Nain A K, *J Mol Liq*, 140 (2008) 108.

36 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.

37 Ali A, Ansari S & Nain A K, *J Mol Liq*, 178 (2013) 178.

38 Eyring H & John M S, *Significant Liquid Structures*, (John Wiley, New York) 1969.

39 Prigogine I, *Molecular Theory of Solutions*, (North-Holland, Amsterdam) 1957.

40 Marcus Y, *Introduction to Liquid State Chemistry*, (Wiley Interscience, New York) 1977.

41 Saleh M A, Akhtar S, Ahmed M S & Uddin M H, *Phys Chem Liq*, 40 (2002) 621.

42 Pikkarainen L, *J Chem Eng Data*, 28 (1983) 381.

43 Assarson P & Eirich F R, *J Phys Chem*, 72 (1968) 2710.

44 Makowska A, Dyoniziak E, Siporska A & Szydłowski J, *J Phys Chem B*, 114 (2010) 2504.

45 Bhujrajh P & Deenadayalu N, *J Chem Thermodyn*, 38 (2006) 278.

46 Gomez E, Gonzalez B, Calvar N, Tojo E & Dominguez A, *J Chem Eng Data*, 51 (2006) 2096.

47 Reis J C R, Lampreia I M S, Santos A F S, Moita M L S J & Douheret G, *ChemPhysChem*, 11 (2010) 3722.

48 Brocos P, Pinerio A, Bravo A & Amigo A, *Phys Chem. Chem Phys,* 5 (2003) 550.

49 Pineiro A, Brocos P, Amigo A, Pintos M & Bravo R, *Phy Chem Liq,* 38 (2000) 251.