Volumetric and Speed of Sound of Ionic Liquid, 1-Butyl-3-methylimidazolium Hexafluorophosphate with Acetonitrile and Methanol at T = (298.15 to 318.15) K

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We report the density (ρ) and speed of sound (u) data for 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) + methanol and ([BMIM][PF_6]) + acetonitrile binary mixtures over the entire range of their compositions at T = (298.15 to 318.15) K. From these data, excess molar volume and isentropic compressibility deviation values have been calculated and fitted to the fourth-order Redlich−Kister equation. The excess molar volume values (V^E) for acetonitrile mixtures are more negative than methanol mixtures. Isentropic compressibility deviation values ($\Delta\kappa_S$) in methanol mixtures are more than acetonitrile mixtures. The results have been interpreted in terms of ion−dipole interactions and structural factors of the ionic liquid and these organic solvents.

Introduction

Room-temperature ionic liquids (RTILs) are a class of organic salts that are liquids at or near room temperature in their pure state. They exhibit many interesting properties such as negligible vapor pressure, low melting point (<373 K), a wide liquid range, suitable viscosity, stability up to high temperature, and high solubility for both polar and nonpolar organic and inorganic substances.[1−3] Due to their nonvolatile nature and favorable solvation properties, RTILs have been suggested as green and benign replacements for traditional volatile organic solvents. These ionic liquids have been recently used as solvents in catalysis, chemical processing, liquid−liquid separations, vapor−liquid equilibria, batteries, and fuel cells investigations.[4−7] Despite their importance and interest, detailed knowledge on the thermodynamic behavior of the mixtures of ionic liquids with organic molecular solvents, which is important for the design of any technological processes, is very limited. The 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) is historically the most important and the most commonly investigated ionic liquid. Thermodynamic functions such as heat capacities, enthalpy changes, and densities for [BMIM][PF_6] have been reported at different temperatures.[8,9] Solid−liquid and liquid−liquid equilibria of this ionic liquid in water and 1-butanol have been studied.[10−12] Its solubilities in aromatic hydrocarbons and alkanes have been performed by dynamic method.[13] Computational method such as Monte Carlo simulation for investigation of this ionic liquid has been performed, and volumetric properties such as isothermal compressibility and volume expansibility values have been computed.[14] The volume expansibility and isothermal compressibility properties of this ionic liquid in pure state have also been obtained.[15] However, there are no reports on the volumetric properties of this ionic liquid in nonaqueous ordinary solvents. There are reports on the volumetric properties of other ionic liquids in aqueous and nonaqueous solvents. Heintz et al.[16] determined the excess molar volumes and viscosities for mixtures of methanol with 4-methyl-*N*-butylpyridinium tetrafluoroborate at different temperatures. Wang et al.[17] have determined densities and viscosities for mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone, and *N*,*N*-dimethylformamide. Recently, experimental data of densities and viscosities have been presented for 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O binary systems over the entire range of compositions at different temperatures by Zhang et al.[18] Also, Rebelo et al.[19] reported the excess molar volumes for 1-butyl-3-methylimidazolium tetrafluoroborate + H_2O. Aki et al.[20] reported that the solvent strength and polarity of [BMIM][PF_6], as measured using two different fluorescent probes, is more polar than MeCN and less polar than MeOH.

In the present work, we report the density and speed of sound measurements on mixtures of [BMIM][PF_6] with methanol (MeOH) and acetonitrile (MeCN) over the entire composition range at T = (298.15 to 318.15) K, from which the excess molar volume (V^E) and isentropic compressibility deviation ($\Delta\kappa_S$) values have been calculated. The chosen solvents MeOH and MeCN are versatile compounds, especially in their wide range of applicability as solvents in chemical and technological processes. These solvents are also the most commonly used for background electrolytes in nonaqueous capillary electrophoresis.[21] These solvents are inexpensive and easily available at high purity. The calculated quantities can be used in a qualitatively or quantitatively way to provide information about molecular structure and nature of intermolecular forces in these kind of liquid mixtures.[22,23]

Experimental Section

Materials. [BMIM][PF_6] was obtained from Solvent Innovation Co. (Köln, Germany) with mass fraction of >0.98, and it was used after being vacuum desiccated for at least 4 h to remove trace amounts of water. MeOH and MeCN were supplied from Merck, with purity gradient grade (mass fraction >0.999), and were used without further purification. During the course of the experiments, the purity of the solvents was monitored by density measurements.

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Table 1. Physical Properties of Pure Components at T = 298.15 K: Density (ρ) and Speed of Sound (u) Data

	ρ/g·cm^{-3}		u/m·s^{-1}	
component	exp.	lit.	exp.	lit.
MeOH	0.786531	0.78656,[32] 0.78654[30]	1102.68	1101.9[32]
MeCN	0.776533	0.776532,[33] 0.77658 [34]	1278.62	1280.8[35]
[BMIM][PF$_6$]	1.366657	1.36603,[34] 1.3603[14,15]	1442.41	

Apparatus and Procedure. Density and speed of sound data were continuously measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000 densimeter and speed of sound analyzer). Details of the experimental setup and measuring procedure have been given elsewhere.[24] The temperature was automatically kept constant within uncertainty ± 0.001 K. In each measurement, the uncertainty of density and speed of sound were $\pm$ 3.0·10^{-6} g·cm^{-3} and $\pm$ 0.1 m·s^{-1}, respectively. Density and speed of sound values of the pure components are given in Table 1 at 298.15 K and compared with the literature values.

Results and Discussion

The experimental density (ρ) and speed of sound (u) data for the MeCN (1) + [BMIM][PF$_6$] (2) and MeOH (1) + [BMIM][PF$_6$] (2) mixtures, as a function of [BMIM][PF$_6$] mole fraction (x_2) at the temperature range from T = (298.15 to 318.15) K are presented respectively in Tables 2 and 3.

Values of the excess molar volume (V^E) were calculated using the relation:

$$V^{E} = \sum_{j=1}^{2} x_j M_j (\rho^{-1} - \rho_j^{-1}) \qquad (1)$$

where M_j, x_j, ρ_j, and ρ are molar mass of the components, mole fractions, densities of pure liquids, and densities of mixtures, respectively, and subscript j=1 is for the MeCN or MeOH and j=2 is for the [BMIM][PF$_6$].

The V^E values have been fitted to the Redlich−Kister equation[25]:

$$V^{E}/\text{m}^3\cdot\text{mol}^{-1} = x_2(1 - x_2)\sum_i A_i(1 - 2x_2)^i \qquad (2)$$

It was found that the fourth-order Redlich−Kister equation represents satisfactorily the experimental excess molar volumes for the studied systems. The polynomial coefficients (A_i) of eq 2 for the studied systems along with the corresponding standard deviations (σ(V^E)) are collected in Table 4.

Speed of sound measurements in solutions furnishes knowledge about ion−ion and ion−solvent interactions.[22,23,26] Using the speed of sound and density data, the isentropic compressibilities (κ_s) were calculated from the Laplace-Newton's equation:

$$\kappa_s = \frac{1}{\rho u^2} \qquad (3)$$

where u is the speed of sound for the investigated mixtures. The experimental isentropic compressibility deviations ($\Delta\kappa_s$) are obtained using the relation:

$$\Delta\kappa_s = \kappa_s - (\sum_j^2 x_j \kappa_{sj}) \qquad (4)$$

where κ_{sj} is the value of isentropic compressibility of pure

Table 2. Experimental Density (ρ) and Speed of Sound (u) Data for the MeCN (1) + [BMIM][PF$_6$] (2) System

	T/K														
	298.15			303.15			308.15			313.15			318.15		
	ρ	u	$10^6\,V^E$	ρ	u	$10^6\,V^E$	ρ	u	$10^6\,V^E$	ρ	u	$10^6\,V^E$	ρ	u	$10^6\,V^E$
x_2	kg·m^{-3}	m·s^{-1}	m^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	m^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	m^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	m^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	m^3·mol^{-1}
1	1366.657	1442.41	0	1362.401	1430.58	0	1358.304	1418.95	0	1354.195	1407.53	0	1350.081	1396.27	0
0.8925	1350.778	1436.54	−0.234	1346.331	1424.49	−0.223	1342.199	1412.62	−0.235	1338.047	1401.01	−0.247	1333.888	1389.50	−0.260
0.7886	1332.552	1427.94	−0.466	1328.297	1415.92	−0.497	1324.054	1404.07	−0.512	1319.812	1392.36	−0.530	1315.594	1380.84	−0.555
0.7285	1320.819	1423.93	−0.657	1316.586	1411.85	−0.700	1312.315	1399.90	−0.722	1308.063	1388.01	−0.750	1303.820	1376.25	−0.783
0.6186	1294.947	1413.51	−0.948	1290.953	1401.05	−1.034	1286.592	1388.69	−1.066	1282.249	1376.50	−1.102	1277.921	1364.43	−1.148
0.5140	1263.518	1402.00	−1.178	1258.712	1389.19	−1.190	1254.638	1376.46	−1.270	1250.219	1363.79	−1.317	1245.806	1351.22	−1.373
0.4241	1228.439	1388.99	−1.277	1223.914	1375.61	−1.333	1219.397	1362.34	−1.382	1214.893	1349.24	−1.436	1210.405	1336.27	−1.502
0.2966	1159.895	1366.45	−1.296	1155.226	1352.23	−1.355	1150.557	1338.10	−1.411	1145.899	1324.03	−1.473	1141.242	1310.05	−1.546
0.2007	1085.082	1341.88	−1.185	1080.247	1326.18	−1.242	1075.415	1310.91	−1.298	1070.583	1295.79	−1.358	1065.762	1280.89	−1.433
0.0935	959.103	1308.88	−0.860	954.020	1291.76	−0.903	948.924	1274.60	−0.947	943.817	1257.52	−0.994	938.706	1240.52	−1.056
0.0453	878.471	1293.53	−0.622	873.235	1275.06	−0.650	866.821	1256.66	−0.600	862.713	1238.37	−0.713	857.428	1220.16	−0.759
0	776.533	1278.62	0	771.116	1258.73	0	765.660	1238.66	0	760.162	1218.52	0	754.462	1198.32	0

Table 3. Experimental Density (ρ) and Speed of Sound (u) Data for the MeOH (1) + [BMIM][PF$_6$] (2) System

	T/K														
	298.15			303.15			308.15			313.15			318.15		
x_2	ρ / kg·m^{-3}	u / m·s^{-1}	10^6V^E / m^3·mol^{-1}	ρ / kg·m^{-3}	u / m·s^{-1}	10^6V^E / m^3·mol^{-1}	ρ / kg·m^{-3}	u / m·s^{-1}	10^6V^E / m^3·mol^{-1}	ρ / kg·m^{-3}	u / m·s^{-1}	10^6V^E / m^3·mol^{-1}	ρ / kg·m^{-3}	u / m·s^{-1}	10^6V^E / m^3·mol^{-1}
1	1366.657	1442.41	0	1362.401	1430.58	0	1358.304	1418.95	0	1354.195	1407.53	0	1350.081	1396.27	0
0.9208	1357.705	1435.22	−0.095	1353.548	1423.47	−0.115	1349.387	1411.94	−0.112	1345.226	1400.58	−0.111	1341.078	1389.38	−0.113
0.7736	1337.498	1421.10	−0.292	1333.239	1409.46	−0.308	1328.992	1397.95	−0.307	1324.76	1386.56	−0.310	1320.543	1375.31	−0.316
0.6222	1308.958	1400.51	−0.439	1304.585	1388.86	−0.453	1300.243	1377.38	−0.455	1295.964	1365.94	−0.467	1291.779	1354.65	−0.491
0.4572	1263.599	1366.68	−0.594	1259.044	1355.14	−0.603	1254.805	1343.61	−0.631	1250.504	1332.11	−0.656	1246.033	1320.70	−0.667
0.3573	1223.908	1340.69	−0.691	1219.386	1329.07	−0.711	1214.871	1317.49	−0.724	1210.364	1305.95	−0.741	1205.873	1294.50	−0.760
0.2156	1136.500	1280.66	−0.761	1131.894	1268.92	−0.784	1127.297	1257.18	−0.805	1122.699	1245.49	−0.828	1118.121	1233.85	−0.855
0.1869	1111.366	1261.62	−0.754	1106.761	1249.80	−0.779	1102.148	1237.97	−0.800	1097.528	1226.13	−0.824	1092.914	1214.27	−0.851
0.0786	972.943	1180.74	−0.578	968.272	1167.69	−0.598	963.583	1154.62	−0.618	958.877	1141.58	−0.639	954.071	1128.58	−0.656
0.0484	914.856	1155.52	−0.467	910.156	1141.54	−0.483	905.442	1127.55	−0.498	900.703	1113.58	−0.515	895.952	1099.67	−0.533
0.0223	852.499	1132.08	−0.285	847.778	1116.93	−0.294	843.039	1101.80	−0.303	838.277	1086.69	−0.313	833.490	1071.68	−0.324
0	786.531	1102.68	0	781.808	1086.37	0	777.066	1070.11	0	772.283	1053.96	0	767.474	1037.91	0

component j. The $\Delta\kappa_s$ values were also correlated by the Redlich−Kister equation:[25−27]

$$\Delta\kappa_s/\text{Pa}^{-1} = x_2(1 - x_2)\sum_i A_{\kappa i}(1 - 2x_2)^i \tag{5}$$

The fitting parameters $A_{\kappa i}$ were estimated by the least-squares method, and the obtained values together with the related standard deviations ($\sigma(\Delta\kappa_s)$) are given in Table 5.

The experimental V^E values for the investigated systems together with the curves obtained using eq 2 are represented in Figures 1 and 2. Similarly, the experimental $\Delta\kappa_s$ and obtained curves using eq 5 are shown in Figures 3 and 4. For V^E and $\Delta\kappa_s$, the Redlich−Kister fitting curves are asymmetric. Also, a minimum in V^E and $\Delta\kappa_s$ are reached with mole fraction of this ionic liquid near to 0.3 and 0.2 for MeCN (1) + [BMIM][PF$_6$] (2) and MeOH (1) + [BMIM][PF$_6$] (2) systems, respectively. Similar behavior has been observed for 1-butyl-3-methylimidazolium tetrafluoroborate in nonaqueous organic solvent such as MeCN, dichloromethane, 2-butanone and *N*,*N*-dimethylformamide.[17] The magnitude and sign of V^E values are a reflection of the type of interactions taking place in the mixture, which are the result of different effects containing the breakdown of the MeCN dipolar interactions and MeOH self-associated molecules from each other (a positive volume), the breakdown of the ionic liquid ion-pair (a positive volume), and the negative contribution of volume due to the packing effect and ion−dipole interaction of MeCN or MeOH molecules with the ionic liquid. The molar volume for [BMIM][PF$_6$] is $207.94 \cdot 10^{-6}$ m^3·mol^{-1}, which is greater than the molar volumes of MeOH ($40.74 \cdot 10^{-6}$ m^3·mol^{-1}) and MeCN ($52.86 \cdot 10^{-6}$ m^3·mol^{-1}) at T = 298.15 K. The large difference between molar volumes of these solvents and [BMIM][PF$_6$] imply that the relatively small MeOH or MeCN molecules fit in the available free volume of ionic liquid upon mixing. Also, the negative values of V^E show that the effect due to the ion−dipole interactions between organic solvents (MeOH or MeCN) and [BMIM][PF$_6$] are dominating over the disruption of dipolar orders in MeCN or MeOH.

As can be seen from the Figures 1 and 2, the V^E values for MeCN mixtures are more negative than the MeOH mixtures. Similar behavior is observed for the other isotherms. Then, the larger negative V^E values for the MeCN (1) + [BMIM][PF$_6$] (2) than the MeOH (1) + [BMIM][PF$_6$] (2) imply that in the MeCN solutions there are stronger ion−dipole interactions and packing effects than the MeOH solutions. The higher relative permittivity and dipole moment of MeCN as compared with the corresponding values for methanol[28] and strong hydrogen bonding between MeOH molecules indicate the stronger ion−dipole interactions and packing effects of MeCN in ionic liquid solutions.

Figure 5 shows that the κ_s values for MeCN mixtures are less than the MeOH mixtures at T = 298.15 K, and similar behavior is observed for the other isotherms. It is obvious from Figure 5 that the solution of [BMIM][PF$_6$] in MeOH is more compressible than the solutions of [BMIM][PF$_6$] in MeCN at a particular concentration and temperature. This indicates a different solvation process of [BMIM][PF$_6$] in MeOH in comparison with the MeCN, because of its characteristic structure as compared with the MeCN. X-ray analysis on pure MeCN has revealed that the linear MeCN dipoles are arranged in antiparallel positions,[21,29] leading to a smaller value for κ_s for MeCN than MeOH for which it was found that it is extensively self-associated through hydrogen bonding in the pure

Table 4. Coefficients of the Redlich−Kister Equation (eq 2) for Excess Molar Volumes (V^E) and the Standard Deviations ($\sigma(V^E)$) of the MeCN (1) + [BMIM][PF$_6$] (2) and MeOH (1) + [BMIM][PF$_6$] (2) Mixtures

solvent	T/K	$10^6 A_0$	$10^6 A_1$	$10^6 A_2$	$10^6 A_3$	$10^6 A_4$	$10^6 \sigma(V^E/\text{m}^3\cdot\text{mol}^{-1})^a$
MeCN	298.15	−4.8252	−2.7242	1.4250	−3.4221	−6.2046	0.024
	303.15	−5.0024	−2.5483	0.6903	−4.3954	−5.0195	0.029
	308.15	−5.2218	−2.8504	0.5481	−3.9914	−4.5048	0.010
	313.15	−5.4397	−2.8728	1.0872	−4.6767	−6.2037	0.027
	318.15	−5.6770	−3.0345	1.0321	−4.998	−6.6254	0.029
MeOH	298.15	−2.2895	−1.4392	−0.9797	−3.6861	−3.8364	0.021
	303.15	−2.3350	−1.4879	−1.1601	−3.6384	−4.0424	0.022
	308.15	−2.4076	−1.5835	−0.9273	−3.7417	−4.4814	0.022
	313.15	−2.4888	−1.6311	−0.7823	−3.9311	−4.8176	0.022
	318.15	−2.5558	−1.6167	−0.8983	−4.2095	−4.0886	0.022

$$^a\sigma(V^E) = \left[\frac{\sum_i (V^E_{\text{exp}} - V^E_{\text{cal}})^2}{n}\right]^{1/2}$$; n is number of the experimental data; the units of A_i values are m^3·mol^{-1}.

Table 5. Coefficients of the Redlich−Kister Equation (eq 5) for Isentropic Compressibility Deviations ($\Delta\kappa_s$) and the Standard Deviations ($\sigma(\Delta\kappa_s)$) of the MeCN (1) + [BMIM][PF$_6$] (2) and MeOH (1) + [BMIM][PF$_6$] (2) Mixtures

solvent	T/K	$10^{10} A_\kappa 0$	$10^{10} A_\kappa 1$	$10^{10} A_\kappa 2$	$10^{10} A_\kappa 3$	$10^{10} A_\kappa 4$	$10^{10} \sigma(\Delta\kappa_s/\text{Pa}^{-1})^a$
MeCN	298.15	−6.601	−4.586	−2.700	−4.464	−4.571	0.014
	303.15	−6.996	−4.852	−2.881	−4.824	−4.880	0.016
	308.15	−7.422	−5.171	−3.142	−5.153	−5.093	0.015
	313.15	−7.885	−5.483	−3.278	−5.656	−5.719	0.019
	318.15	−8.384	−5.837	−3.508	−6.177	−6.250	0.021
MeOH	298.15	−11.652	−8.009	−3.457	−12.712	−14.917	0.062
	303.15	−12.231	−8.392	−3.559	−13.687	−16.160	0.066
	308.15	−12.844	−8.796	−3.650	−14.727	−17.498	0.070
	313.15	−13.487	−9.223	−3.754	−15.827	−18.903	0.075
	318.15	−14.167	−9.668	−3.862	−17.001	−20.400	0.080

$$^a\sigma(\Delta\kappa_s) = \left[\frac{\sum_i (\Delta\kappa_{s(\text{exp})} - \Delta\kappa_{s(\text{cal})})^2}{n}\right]^{1/2}$$; the units of $A_{\kappa i}$ values are Pa^{-1}.

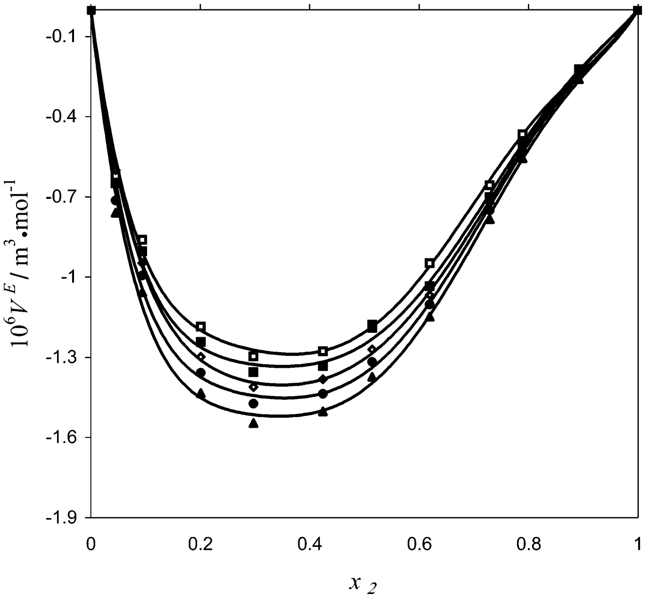

Figure 1. Excess molar volume (V^E) vs mol fraction of [BMIM]-[PF$_6$] for MeCN (1) + [BMIM][PF$_6$] (2) mixture: □, 298.15 K; ■, 303.15 K; ◇, 308.15 K; ●, 313.15 K; ▲, 318.15 K; solid line, Redlich−Kister (eq 2).

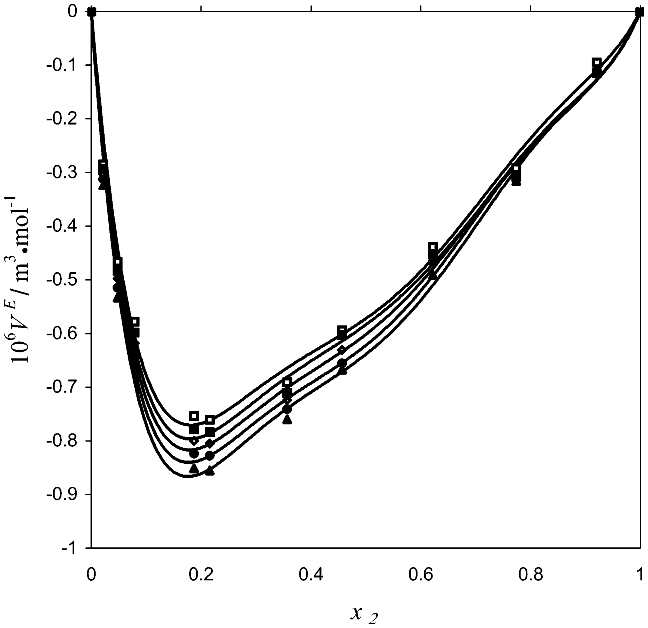

Figure 2. Excess molar volume (V^E) vs mol fraction of [BMIM]-[PF$_6$] for MeOH (1) + [BMIM][PF$_6$] (2) mixture: □, 298.15 K; ■, 303.15 K; ◇, 308.15 K; ●, 313.15 K; ▲, 318.15 K; solid line, Redlich−Kister (eq 2).

state.[29] The results obtained from the κ_s values for the studied mixtures are compatible with those obtained from the excess molar volumes. Recently, similar results have been obtained for tetraalkylammonium tetraphenylborate and tetraalkylammonium bromide in MeOH and MeCN solutions using the association constants determined from conductometric measurements.[36] The association constants for the both studied organic salts in MeOH are higher than that of MeCN. This means that while ion−ion interactions

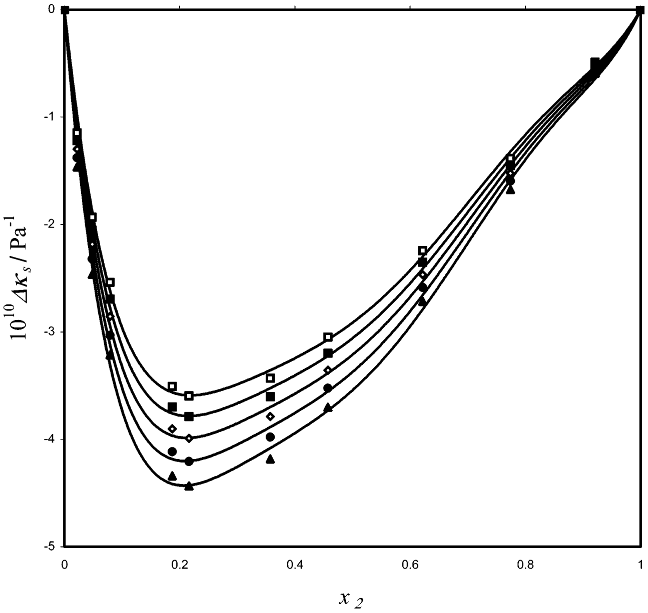

Figure 3. Variation of isentropic compressibility deviations ($\Delta\kappa_S$) vs mol fraction of [BMIM][PF6] for MeOH (1) + [BMIM][PF6] (2) mixture: □, 298.15 K; ■, 303.15 K; ◇, 308.15 K; ●, 313.15 K; ▲, 318.15 K; solid line, Redlich−Kister (eq 5).

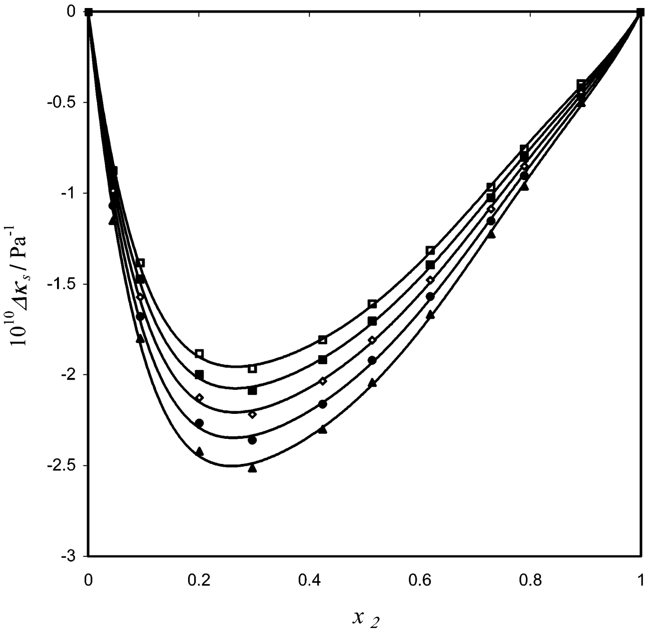

Figure 4. Variation of isentropic compressibility deviations ($\Delta\kappa_S$) vs mol fraction of [BMIM][PF6] for MeCN (1) + [BMIM][PF6] (2) + mixture: □, 298.15 K; ■, 303.15 K; ◇, 308.15 K; ●, 313.15 K; ▲, 318.15 K; solid line, Redlich−Kister (eq 5).

are dominant in MeOH solutions, in the case of MeCN solutions ion−solvent interactions are dominant.

For the both systems the values of $\Delta\kappa_S$ are negative over the entire composition range and at all the temperatures studied. Figures 3 and 4 show that for these systems, the behavior of $\Delta\kappa_S$ versus ionic liquid mole fraction is very similar to those of excess molar volume at the all studied temperatures. The behavior of $\Delta\kappa_S$ implies that these mixtures are less compressible than the ideal mixture. This is due to a closer approach of unlike molecules and stronger interaction between components of mixtures[26,30] that lead to decreasing compressibility.

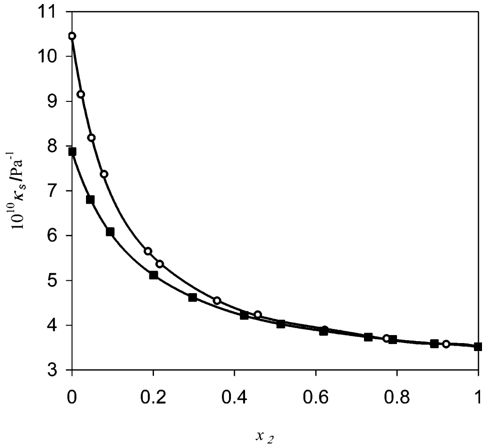

Figure 5. Variation of isentropic compressibility (κ_S) vs mol fraction of [BMIM][PF$_6$]: ○, MeOH (1) + [BMIM][PF$_6$] (2); ■, MeCN (1) + [BMIM][PF$_6$] (2) mixtures at 298.15 K.

Conclusions

Excess molar volume (V^E) and isentropic compressibility deviation ($\Delta\kappa_S$) values of [BMIM][PF$_6$] in MeOH and MeCN mixtures have been calculated from the measured density and speed of sound data at T = (298.15 to 318.15) K. For V^E and $\Delta\kappa_S$, the Redlich−Kister fitting curves are asymmetric. Also, a minimum in V^E and $\Delta\kappa_S$ are reached with a mole fraction of this ionic liquid near 0.3 and 0.2 for the MeCN (1) + [BMIM][PF$_6$] (2) and MeOH (1) + [BMIM][PF$_6$] (2) systems, respectively. The measured negative V^E values for these systems indicate that effect due to the ion−dipole interactions and packing between organic solvents (MeOH or MeCN) and [BMIM][PF$_6$] are dominating over the disruption of dipolar orders in MeCN or MeOH.

The V^E values for MeCN mixtures are more negative than the MeOH mixtures, which imply that in the MeCN solutions there are stronger ion−dipole interactions and packing effects than the MeOH solutions. Similar results are obtained from comparison of the isentropic compressibility values for theses systems.

Literature Cited

(1) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.* **2002**, *102*, 3667−3692.

(2) Earle, M. J.; Seddon, K. R. Ionic liquids: green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391−1398.

(3) Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

(4) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol. Catal. A* **2004**, *214*, 11−17.

(5) Brennecke, J. F.; Maginn, E. J. Ionic liquids: innovative fluids for chemical processing. *AIChE J.* **2001**, *47*, 2384−2389.

(6) Wasserscheid, P.; Keim, W. Ionic liquids new “solution” for transition metal catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773−3789.

(7) Kato, R.; Krummen, M.; Gmehling, J. Measurements and correlation of vapor−liquid equilibria and excess enthalpies of binary systems containing ionic liquids and hydrocarbons. *Fluid Phase Equilib.* **2004**, *224*, 47−54.

(8) Kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the condensed state. *J. Chem. Eng. Data* **2004**, *49*, 453−461.

(9) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−961.

(10) Wong, D. S. H.; Chen, J. P.; Chang, J. M.; Chou, C. H. Phase equilibria of water and ionic liquids [emim][PF6] and [bmim]-[PF6]. *Fluid Phase Equilib.* **2002**, *194−197*, 1089−1095.

(11) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution thermodynamics of imidazolium-based ionic liquids and water. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.

(12) Wu, C. T.; Marsh, K. N.; Deev, A. V.; Boxall, J. A. Liquid−liquid equilibria of room-temperature ionic liquids and 1-butanol. *J. Chem. Eng. Data* **2003**, *48*, 486-491.

(13) Domañska, U.; Marciniak, A. Solubility of 1-alkyl-3-methylimidazolium hexafluorophosphate in hydrocarbons. *J. Chem. Eng. Data* **2003**, *48*, 451−456.

(14) Shah, J. K.; Maginn, E. J. A Monte Carlo simulation study of the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate: liquid structure, volumetric properties and infinite dilution solution thermodynamics of CO_2. *Fluid Phase Equilib.* **2004**, *222−223*, 195−203.

(15) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(16) Heintz, A.; Klasen, D.; Lehmann, J. K. Excess molar volumes and viscosities of binary mixtures of methanol and the ionic liquid 4-methyl-*N*-butylpyridinium tetrafluoroborate at 25, 40, and 50 °C. *J. Solut. Chem.* **2002**, *31*, 467−476.

(17) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and *N*,*N*-dimethylformamide. *Green Chem.* **2003**, *5*, 618−622.

(18) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of physical properties for the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

(19) Rebelo, L. P. N.; Najdavonic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydlowski, J.; Cerdeirina, C. A.; Troncoso, J.; Romani, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A Detailed thermodynamic analysis of $[C_4mimi][BF_4]$ + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369−381.

(20) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. How polar are room-temperature ionic liquids?. *Chem. Commun.* **2001**, 413−414.

(21) Porras, S. P.; Riekkola, M. L.; Kenndler, E. Electrophretic Mobilities of cationic analytes in non-aqueous methanol, acetonitrile and their mixtures influence of ionic strength and ion-pair formation. *J. Chromatogr. A* **2001**, *924*, 31−42.

(22) Das, D.; Das, B.; Hazra, D. K. Ultrasonic velocities and isentropic compressibilities of some symmetrical tetraalkylammonium salts in *N*,*N*-dimethylacetamide at 298.15 K. *J. Mol. Liq.* **2004**, *111*, 15−18.

(23) Nath, J. Speeds of sound in and isentropic compressibilities of (*n*-octanol + *n*-hexane, or *n*-heptane, or *n*-octane) at T = 298.15 K. *Fluid Phase Equilib.* **2002**, *203*, 261−268.

(24) Zafarani-Moattar, M. T.; Shekaari, H. Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* (in press).

(25) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(26) Victor, P. J.; Hazra, D. K. Excess molar volumes, viscosity deviations, and isentropic compressibility changes in binary mixtures of *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water at (308.15, 313.15, and 318.15) K. *J. Chem. Eng. Data* **2002**, *47*, 79−82.

(27) Artigas, H.; Mainar, A. M.; Dominguez, M.; Cea, P.; Lafuente, C. Excess isentropic compressibilities of halohydrocarbon + butanol mixture at 298.15 K. *Thermochim. Acta* **1996**, *287*, 25−34.

(28) Marcus, Y.; Hefter G.; Pang, T. S. Ionic partial molar volumes in non-aqueous solvents. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1899−1903.

(29) Ali, A.; Hyder, S.; Nain, A. K. Studies on molecular interactions in binary liquid mixtures by viscosity and ultrasonic velocity measurements at 303.15 K. *J. Mol. Liq.* **1999**, *79*, 89−99.

(30) Saha, N.; Das, B.; Hazra, D. Viscosities and excess molar volumes for acetonitrile + methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264−1266.

(31) Gill, D. S.; Singh, R.; Anand, H.; Puri, J. K. Compressibility studies of some copper(I) and tetraalkylammonium salts in binary mixtures of triethylphosphite, benzonitrile and pyridine at 298.15 K. *J. Mol. Liq.* **2002**, *98−99*, 15−25.

(32) Resa, J. M.; Gonzalez, C.; Landaluce, S. O.; Lanz, J. (Vapor + liquid) equilibria, densities, excess molar volumes, refractive indices, speed of sound for (methanol + allyl acetate) and (vinyl acetate + allyl acetate). *J. Chem. Thermodyn.* **2002**, *34*, 1013−1027.

(33) Krakowiak, J.; Bobicz, D.; Grzybkowski, W. Partial molar volmues of tetrabutylammonium perchlorate and tetraphenylborate in *N*,*N*-dimethylacetamide, triethylphosphate, acetonitrile and dimethyl sulphoxide. *J. Mol. Liq.* **2000**, *88*, 197−207.

(34) Torres, R. B.; Francesconi, A. Z.; Volpe, P. L. O. Excess molar volumes of binary mixtures of acetonitrile and chloroalkanes at 298.15 K and atmospheric pressure with application of the ERAS-model. *Fluid Phase Equilib.* **2002**, *200*, 1−10.

(35) Jimenez, E.; Casas, H.; Segade, L.; Franjo, C. Surface tensions, refractive indexes and excess molar volumes of hexane + 1-alkanol mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 862−868.

(36) Das, B.; Saha, N.; Hazra, D. Ion association and conductance of symmetrical tetraalkylammonium salts in methanol, acetonitrile, and methanol (1) + acetonitrile (2) mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 353−357.

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