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Volumetric Properties of the Ionic Liquid, 1-Butyl-3-methylimidazolium Tetrafluoroborate, in Organic Solvents at $T = 298.15\,\mathrm{K}$

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Abstract Apparent molar volumes, V_ϕ, and compressibilities, κ_ϕ, of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) have been determined from precise density and speed-of-sound measurements in organic solvents, methanol (MeOH), acetonitrile (MeCN), tetrahydrofuran (THF), *N*,*N*-dimethylacetamide (DMA), and dimethylsulfoxide (DMSO) in the dilute region of the ionic liquid. Corresponding values at infinite dilution are estimated by the Redlich–Mayer and Pitzer equations. The results have been interpreted by the interaction of the [BMIm][BF_4] in the organic solvents. Results show that the structure and dielectric constant of the organic solvents play an important role for the ion–solvent interactions in these mixtures. It was found that the strength of interaction between [BMIm][BF_4] with the studied organic solvents has the order DMSO > DMA > MeOH > MeCN > THF.

Keywords Apparent molar volume · 1-Butyl-3-methylimidazolium tetrafluoroborate · Ionic liquids · Ion–solvent interactions · Isentropic compressibility

1 Introduction

In recent years, ionic liquids (ILs) have been considered attractive compounds due to their unique intrinsic properties, such as negligible vapor pressure, large liquid range, ability of dissolving a variety of chemicals, high thermal stability, large

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electrochemical window, and their potential as "designer solvents" and "green" replacements for volatile organic solvents [1–4].

To exploit the tremendous potential of ionic liquids and also design newer ones for specific purposes, it is essential to have a thorough grasp on their physicochemical and thermodynamic properties, especially on the nature of the interactions between cations and anions of ionic liquids with an added co-solvent. However, in spite of successful efforts on phase equilibria and thermophysical properties of ionic liquid + co-solvent mixtures, a detailed understanding of how ionic liquids behave in the presence of a co-solvent for their applications and further development is needed.

As a continuation of our study of thermodynamic properties of the binary mixtures of ionic liquids with conventional organic solvents [5–9], 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIm][BF_4]$) was selected for this study. It is one of the most commonly used ionic liquids for which some physicochemical properties with other organic solvents have been studied. Its volumetric properties, viscosity and speed of sound in water [10–13], vapor–liquid equilibria in binary and ternary mixtures [14], liquid–liquid equilibria [15–17], vapor pressures of binary $[BMIm][BF_4] +$ water mixture [18], activity coefficients at infinite dilution with some organic solvents [19,20], mutual solubilities of this ionic liquid in organic solvents [21,22], volumetric and viscosity study in organic solvents [23], excess thermodynamic functions of $[BMIm][BF_4] + H_2O$ systems at 298.15 K [24], aggregation behavior in aqueous solutions [25], thermophysical properties in organic solvents [26,27], and dipolarity/polarizability and hydrogen-bond donating (HBD) acidity of aqueous $[BMIm][BF_4]$ [28] have been reported.

Volumetric properties of binary liquid mixtures have been extensively studied to understand the nature and extent of various intermolecular interactions existing between different species present in mixtures [29]. In this work, the density and speed of sound were measured for binary mixtures of the ionic liquid, $[BMIm][BF_4]$, and organic solvents, methanol (MeOH), acetonitrile (MeCN), tetrahydrofuran (THF), *N*,*N*-dimethylacetamide (DMA), and dimethylsulfoxide (DMSO), and then using these data, apparent molar volume and apparent molar isentropic compressibility values were calculated at $T = 298.15$ K. The Redlich–Mayer [30] equation was used to fit the apparent molar volumes and apparent molar isentropic compressibility values from which the limiting apparent molar volumes and limiting apparent molar isentropic compressibilities were determined. Apparent molar volume and apparent molar isentropic compressibility data have also been correlated using the Pitzer equation [31] for the investigated systems. The results are discussed in terms of ion–solvent interactions between the ions of the ionic liquid and organic solvents, and their effect on the ion association of the studied ionic liquid.

2 Experimental

Methanol (>99.9 mol%), acetonitrile (>99.9 mol%), *N*,*N*-dimethylacetamide (>99.5 mol%), dimethylsulfoxide (>99.8 mol%), and tetrahydrofuran (>99.5 mol%) were obtained from Merck and used without further purification. $[BMIm][BF_4]$ was obtained from Solvent Innovation Co. (Köln, Germany) (>98 mol%) and was used

Table 1 Densities and speed-of-sound and A_ϕ, A_v, and A_κ values for pure components at $T = 298.15\,K$

Component	d ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	$10^6 A_v$ ($m^3 \cdot kg^{1/2} \cdot mol^{-3/2}$)	$10^{14} A_\kappa$ ($m^3 \cdot kg^{1/2} \cdot mol^{-3/2} \cdot Pa^{-1}$)
THF	0.881996 (Exp.)	1278.49 (Exp.)	107.52	−113.36
	0.88072 [32]	1277.9 [35]		
	0.88201 [33]			
	0.88198 [34]			
MeCN	0.776533 (Exp.)	1278.62 (Exp.)	12.62	−12.93
	0.776532 [36]	1280 [38]	11.81 [40]	−12.2 [41]
	0.77667 [37]	1283 [39]		
MeOH	0.786531 (Exp.)	1102.68 (Exp.)	15.94	−19.69
	0.78656 [42]	1101.9 [42]	16.47 [40][a]	−18.2 [41]
	0.78645 [36]			
	0.77669 [33]			
DMA	0.936274 (Exp.)	1456.52 (Exp.)	7.23	−5.17
	0.936304 [43]	1456.48 [42]		
	0.935287 [44]			
	0.93240 [45]			
DMSO	1.095271 (Exp.)	1485.12 (Exp.)	4.83	−2.40
	1.0972 [46]	1489.2 [46]	5.05 [40]	−2.25 [47]
	1.09533 [39]		7.55 [47]	
$[BMIm][BF_4]$	1.366657 (Exp.)	1442.41 (Exp.)		
	1.36595 [48]	1431.59 [12][b]		
	1.36600 [12]			

[a] The values of A_v in Ref. [40] were expressed in terms of $cm^3 \cdot dm^{3/2} \cdot mol^{-3/2}$, and to obtain their values for concentrations expressed on a molality basis, the entries are multiplied by $d^{1/2}$, where d is the density of the solvent in $kg \cdot dm^{-3}$

[b] This speed-of-sound value is at $T = 294.16\,K$

after vacuum desiccation for at least 24 h to remove trace amounts of water. The sample density and speed-of-sound were measured using a vibrating tube densimeter and a speed-of-sound analyzer (Anton Paar, DSA 5000). Details of the experimental setup and measuring procedure have been given in a previous paper [7]. The temperature was automatically kept constant within $\pm 1.0 \times 10^{-3}$ K. In each measurement, the precision of the density and speed-of-sound measurements were $\pm 3.0 \times 10^{-6} g \cdot cm^{-3}$ and $\pm 0.5\,m \cdot s^{-1}$, respectively. This apparatus was calibrated at each temperature with double-distilled, deionized water and dry air at atmospheric pressure. During the course of the experiments, the purity of the solvents was checked by comparing density and speed-of-sound results with literature values at 298.15 K as given in Table 1.

3 Results and Discussion

3.1 Apparent Molar Volumes

The measured density and speed-of-sound values at $T = 298.15\,K$ for the binary mixtures of the ionic liquid, $[BMIm][BF_4]$, in the investigated organic solvents as a function of the $[BMIm][BF_4]$ concentration are presented in Table 2.

Table 2 Experimental density, d, and speed-of-sound, u, data for (organic solvent + [BMIm][BF_4]) systems at $T = 298.15\,\mathrm{K}$ as a function of ionic liquid molality, m

m ($\mathrm{mol \cdot kg^{-1}}$)	$10^3 d$ ($\mathrm{kg \cdot m^{-3}}$)	u ($\mathrm{m \cdot s^{-1}}$)	$10^6 V_\phi$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$10^{12} \kappa_s$ ($\mathrm{Pa^{-1}}$)	$10^{14} \kappa_\phi$ ($\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}}$)
MeOH					
0.0203	0.788033	1104.41	167.40	1040.39	−15.41
0.0390	0.789368	1105.90	169.06	1035.83	−14.45
0.0564	0.790567	1107.17	170.81	1031.89	−13.35
0.0724	0.791666	1108.20	171.57	1028.54	−12.36
0.1104	0.794278	1110.84	172.19	1020.29	−11.62
0.1461	0.796670	1113.12	172.95	1013.07	−10.82
0.2322	0.802285	1118.83	174.23	995.73	−9.97
0.2495	0.803376	1119.29	174.47	993.56	−9.20
0.3051	0.806868	1122.34	175.10	983.89	−8.50
0.4201	0.813915	1130.32	175.88	961.65	−8.50
0.5784	0.823136	1143.71	176.84	928.75	−9.27
0.6438	0.826790	1146.43	177.21	920.26	−8.45
MeCN					
0.0269	0.778582	1280.40	166.54	783.44	−5.31
0.0578	0.780850	1281.84	167.19	779.41	−4.51
0.0851	0.782806	1282.97	168.05	776.09	−3.89
0.1274	0.785804	1284.71	168.85	771.04	−3.39
0.1488	0.787297	1285.61	169.13	768.50	−3.26
0.2335	0.793124	1289.28	169.87	758.52	−2.97
0.2616	0.794982	1289.81	170.30	756.12	−2.46
0.2819	0.796334	1290.52	170.45	754.01	−2.34
0.3755	0.802412	1293.74	171.22	744.58	−1.90
0.5204	0.811448	1298.45	172.18	730.95	−1.35
0.6652	0.819953	1302.92	173.23	718.42	−0.88
DMSO					
0.0162	1.095695	1485.68	184.07	413.49	4.94
0.0289	1.096029	1486.09	184.14	413.13	4.99
0.0523	1.096640	1486.83	184.16	412.49	5.03
0.0685	1.097059	1487.31	184.20	412.07	5.07
0.0982	1.097818	1488.18	184.24	411.30	5.10
0.1164	1.098270	1488.73	184.31	410.83	5.11
0.1628	1.099414	1490.04	184.41	409.68	5.15
0.2046	1.100409	1491.15	184.53	408.70	5.19
0.2621	1.101750	1492.90	184.64	407.24	5.18
DMA					
0.0172	0.937286	1457.32	173.53	502.36	1.20
0.0222	0.937582	1457.65	173.50	501.98	1.02
0.0370	0.938456	1458.45	173.53	500.96	1.15
0.0672	0.940182	1459.98	174.21	498.99	1.41
0.0870	0.941300	1460.88	174.50	497.79	1.58
0.1353	0.943917	1462.95	175.46	495.00	1.92
0.1650	0.945493	1464.10	175.90	493.40	2.09
0.2144	0.948055	1465.93	176.48	490.84	2.32
0.2521	0.949998	1467.28	176.69	488.94	2.44
0.3439	0.954527	1470.26	177.37	484.64	2.72
0.4517	0.959626	1473.47	177.99	479.97	2.96
0.5318	0.963257	1475.75	178.37	476.69	3.10
THF					
0.0095	0.882621	1278.6	173.25	693.04	4.70
0.0200	0.883210	1278.9	178.80	692.25	4.45
0.0317	0.883326	1278.98	202.65	692.07	8.40

Table 2 Continued

m (mol · kg^{-1})	$10^3 d$ (kg · m^{-3})	u (m · s^{-1})	$10^6 V_\phi$ (m^3 · mol^{-1})	$10^{12} \kappa_s$ (Pa^{-1})	$10^{14} \kappa_\phi$ (m^3 · mol^{-1} · Pa^{-1})
0.0827	0.883900	1279.07	226.40	691.53	12.75
0.1562	0.884926	1279.13	231.51	690.66	13.82
0.1967	0.885110	1279.10	235.18	690.55	14.45
0.2644	0.885264	1279.13	239.56	690.40	15.14

Apparent molar volumes, $V_\phi(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$, of the ionic liquid [BMIm][BF$_4$] were calculated using

$$V_\phi = \frac{M}{d} - \frac{(d - d_0)}{mdd_0} \tag{1}$$

where m (mol · kg^{-1}) is the molality of [BMIm][BF$_4$] in an organic solvent and d and d_0 are the densities (kg · m^{-3}) of the mixture and pure organic solvent, respectively; M is the molar mass of [BMIm][BF$_4$] (kg · mol^{-1}). The calculated apparent molar volume (V_ϕ) values in different organic solvents are also given in Table 2.

The concentration dependences of the calculated V_ϕ values were correlated using the Redlich-Mayer equation in the dilute region of the ionic liquid [30]:

$$V_\phi = V_\phi^0 + S_V m^{1/2} + b_V m \tag{2}$$

where V_ϕ^0 is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution, V_2^0), b_V is an empirical parameter, and S_V is defined as

$$S_V = A_V \left[\frac{1}{2} \left(\sum_i \nu_i z_i^2 \right) \right]^{3/2} \tag{3}$$

where ν_i and z_i are the stoichiometric number and absolute charge of ion i in [BMIm][BF$_4$], respectively. The Debye–Hückel limiting slope for the apparent molar volume is identified as A_V. The values of A_V for each investigated organic solvent have been reported [7] as given in Table 1 and compared with literature values where available. The results of fitting V_ϕ values to Eq. 2 are presented in Table 3.

We have also used the Pitzer equation in the correlation of V_ϕ values for the investigated binary ionic liquid + organic solvent mixtures due to its importance in the correlation of thermodynamic properties of aqueous and nonaqueous electrolyte solutions [31]. The Pitzer equation for the correlation of V_ϕ values in 1:1 electrolytes has the form,

$$V_\phi = V_\phi^0 + \nu \left| z_\mathrm{c} z_\mathrm{a} \right| \left(\frac{A_V}{2b} \right) \ln(1 + bI^{1/2}) + 2RT \nu_\mathrm{c} \nu_\mathrm{a} m [B_V + m \nu_\mathrm{c} z_\mathrm{c} C_V] \tag{4}$$

where ν_c and ν_a are the number of cations and anions and $\nu = \nu_\mathrm{c} + \nu_\mathrm{a}$; the subscripts c and a are used for cation and anion, respectively, z_c and z_a are the number of charges on the cations and anions, I is the ionic strength, and b is the parameter for which the value of $3.2\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ is usually used in nonaqueous solvents. The coefficient, B_V, is defined as

$$B_V = \beta_V^0 + \beta_V^1 \left(\frac{2}{\alpha^2 I}\right) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \tag{5}$$

where β_V^0, β_V^1, and C_V are pressure derivative parameters of Pitzer ion interaction parameters for an osmotic coefficient expression and α is a constant equal to two. The results of fitting V_ϕ values to Eq. 4 are given in Table 3. This table shows that the difference between V_ϕ^0 values obtained from Eq. 2 and those obtained from the Pitzer's equation, in most cases, is less than $1\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. Furthermore, small standard deviations of the fit reported in this table demonstrate that the Pitzer model is a powerful tool for correlation of volumetric properties of binary mixtures of [BMIm][BF$_4$] with organic solvents.

The limiting apparent molar volumes, V_ϕ^0, reflect the extent of ion–solvent interactions [29]. A perusal of Table 3 shows that V_ϕ^0 values are all large and positive. This is due to the large intrinsic volumes of the cation [BMIm]$^+$ and anion [BF$_4$]$^-$ and strong ion–solvent interactions at infinite dilution (as ion–ion interactions vanish at infinite dilution). The smallest value of V_ϕ^0 corresponds to the [BMIm][BF$_4$] + THF system and the largest value of V_ϕ^0, is observed for DMSO, i.e., for the solvent displaying the highest value of the dielectric constant ($\varepsilon = 46.61$ [7]). Similar results have been reported for other organic electrolytes in DMA, MeCN, and DMSO [38]. However, as shown in Table 3, V_ϕ^0 values in MeOH are greater than for MeCN while the dielectric constant of MeCN is greater than that of MeOH. This result means that the ion–solvent interactions in MeOH mixtures of [BMIm][BF$_4$] are stronger than for MeCN mixtures. It was found that the hydrogen bonding polar solvents such as MeOH interact much more strongly with the anion of the ionic liquid by forming a hydrogen bond with MeOH [49].

3.2 Apparent Molar Isentropic Compressibilities

Speed-of-sound measurements in aqueous and nonaqueous electrolyte solutions provide some information about ion–ion and ion–solvent interactions [32]. Based on the speed-of-sound and density values reported in Table 2, the isentropic compressibilities, κ_s, (Pa^{-1}) were calculated from Laplace–Newton's equation:

$$\kappa_s = \frac{1}{du^2} \tag{6}$$

where u ($\mathrm{m} \cdot \mathrm{s}^{-1}$) is the speed of sound of the investigated mixtures.

Table 3 Coefficients of the Redlich–Mayer and Pitzer equations and standard deviations $\sigma(V_\phi)$ of the organic solvent + [BMIm][BF$_4$] mixtures for the apparent molar volume

Solvent	$10^6 V_\phi^0$ (Redlich) ($m^3 \cdot mol^{-1}$)	$10^6 S_V$	$10^6 b_V$	$10^6 \sigma(V_\phi)$	$10^6 V_\phi^0$ (Pitzer) ($m^3 \cdot mol^{-1}$)	$10^3 \beta_V^0$	$10^3 \beta_V^1$	$10^3 C_V$	$10^6 \sigma(V_\phi)$
[BMIm][BF$_4$] +									
THF	150.94	107.52	936.38	4.23(3)	150.65	−74.65	119.30	64.22	3.95
MeCN	164.29	12.62	0.20	0.08(5)	164.35	−0.29	0.77	0.18	0.09
MeOH	165.25	15.94	20.38	0.52(5)	166.16	−0.65	1.64	0.30	0.47
DMA	171.78	7.23	6.34	0.08(8)	171.50	−0.41	1.15	0.20	0.28
DMSO	183.34	4.83	−4.95	0.09(9)	183.83	0.68	−1.14	−0.53	0.02

[a] $\sigma(V_\phi) = \left[\sum_i (V_\phi(\text{exp}) - V_\phi(\text{cal}))^2/n\right]^{1/2}$; numbers in parentheses show the number of experimental data used in calculation of Redlich–Mayer parameters from the dilute region

The apparent molar isentropic compressibilities, κ_ϕ, were computed from the following relation:

$$\kappa_\phi = \frac{(\kappa_s d_0 - \kappa_{s0} d)}{m d d_0} + \frac{\kappa_s M}{d} \tag{7}$$

where κ_{s0} and κ_s are the isentropic compressibilities of the pure organic solvent and the binary mixture of [BMIm][BF$_4$] + organic solvent, respectively. An equation of the form [50],

$$\kappa_\phi = \kappa_\phi^0 + S_\kappa m^{1/2} + b_\kappa m \tag{8}$$

was used for correlating the κ_ϕ values. Here κ_ϕ^0 is the limiting apparent molar isentropic compressibility, b_κ is an empirical parameter, and S_κ is defined as

$$S_\kappa = -A_\kappa \left[\frac{1}{2} \left(\sum_i \nu_i z_i^2 \right) \right]^{3/2} \tag{9}$$

The values of κ_ϕ^0 and b_κ obtained for each mixture at 298.15 K are listed in Table 4. A_κ is the Debye–Hückel slope for the apparent molar isentropic compressibility, taken from Ref. [7]. The calculated A_κ values are also reported in Table 1.

The apparent molar isentropic compressibilities, κ_ϕ, were also calculated by Pitzer's equation [51] as follows:

$$\kappa_\phi = \kappa_\phi^0 - \nu z_\mathrm{c} z_\mathrm{a} \frac{A_k}{2b} \ln(1 + b I^{1/2}) - 2\nu_\mathrm{c}\nu_\mathrm{a} RTm(B_\kappa + m\nu_\mathrm{c} z_\mathrm{c} C_\kappa) \tag{10}$$

where B_κ is the binary interaction parameter which is defined as

$$B_\kappa = \beta_\kappa^{(0)} + \beta_\kappa^{(1)} \frac{2}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} \right) \exp(-\alpha I^{1/2}) \right] \tag{11}$$

The values of Pitzer's parameters, $\beta_\kappa^{(0)}$, $\beta_\kappa^{(1)}$, and C_κ, together with the standard deviations of the fit, $\sigma(\kappa_\phi)$, are also listed in Table 4. On the basis of the $\sigma(\kappa_\phi)$ obtained, we conclude that the Pitzer model represents satisfactorily the apparent molar isentropic compressibility values of the investigated systems.

The κ_ϕ^0 values are interpreted in terms of the compressibility of [BMIm][BF$_4$] due to solute–solvent interactions. These values are negative for [BMIm][BF$_4$] in the organic THF, MeOH, and MeCN solvents and positive for the remaining systems. It is well established that ionic solutes causing electrostriction lead to a decreased compressibility of the solution. This is reflected by the negative values of κ_ϕ^0 of [BMIm][BF$_4$] in THF, MeOH, and MeCN solutions. However, positive κ_ϕ^0 values indicate an increase in the compressibility of the solutions of [BMIm][BF$_4$] in DMA and DMSO compared to the pure organic solvents. Two main factors could contribute to κ_ϕ^0 values: the intrinsic compressibility of ions (positive contribution) and the penetration of the solvent

Table 4 Coefficients of the Redlich–Mayer and Pitzer equations and the standard deviations $\sigma(\kappa_\phi)$ of the organic solvent + [BMIm][BF$_4$] mixtures for the apparent isentropic compressibility

Solvent	$10^{14}\kappa_\phi^0$ (Redlich) ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$)	$10^{14}S_\kappa$	$10^{14}b_\kappa$	$10^{14}\sigma(\kappa_\phi)$	$10^{14}\kappa_\phi^0$ (Pitzer) ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$)	$10^{16}\beta_\kappa^0$	$10^{16}\beta_\kappa^1$	$10^{16}C_\kappa$	$10^{14}\sigma(\kappa_\phi)$
[BMIm][BF$_4$] +									
THF	−6.68	113.36	−157.11	1.15(5)	−3.09	−1.11	−0.29	−0.769	2.25
MeOH	−17.63	19.69	−6.58	0.29(7)	−19.31	0.68	0.14	0.77	1.13
MeCN	−6.82	12.93	−10.12	0.23(7)	−6.38	−0.200	−0.025	−0.066	0.63
DMA	0.3	5.17	−1.83	0.09	0.81	−0.336	−0.038	−0.035	0.21
DMSO	5.74	2.40	−7.71	0.37	4.82	−0.095	−0.014	0.001	0.02

[a] $\sigma(\kappa^\phi) = \left[\sum_i \left(\kappa^\phi(\text{exp}) - \kappa^\phi(\text{cal})\right)^2/n\right]^{1/2}$; numbers in parentheses show the number of experimental data used in calculation of Redlich–Mayer parameters from the dilute region

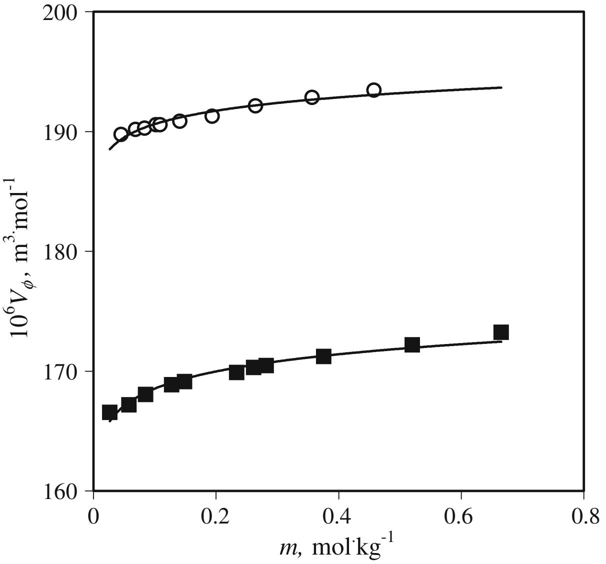

Fig. 1 Comparison of apparent molar volumes V_ϕ of [BMIm][PF_6] (○) [7] and [BMIm][BF_4] (■) in MeCN mixtures at 298.15 K

molecules into the intra-ionic free space of the ionic solute (negative contribution) [52]. The negative κ_ϕ^0 values for [BMIm][BF_4] in THF, MeOH, and MeCN could be attributed to the predominance of the penetration of organic solvents compared to the effect of the intrinsic compressibility on ions. It is known that dilute solutions of ionic liquids can form oligomeric cation–anion aggregates with their free volume depending on the concentration of the solution [33], and this causes penetration of small organic solvents such as MeOH and MeCN in the free volume of the ionic liquid.

3.3 Comparison of [BMIm][BF_4] and [BMIm][PF_6] Behavior

Figure 1 shows that the apparent molar volume values for mixtures of [BMIm][PF_6] in MeCN are greater than the corresponding values for [BMIm][BF_4] + MeCN mixtures. This result shows the small intrinsic volume of the [BF_4]$^-$ anion compared to the large intrinsic volume of the [PF_6]$^-$ anion. This trend was observed for the other studied ionic liquid + organic solvent systems. The comparison of these results with our previously studied system ([BMIm][PF_6] + organic solvents) shows that the limiting apparent molar volumes for the mixtures of [BMIm][PF_6] in organic solvents are greater than the corresponding values in [BMIm][BF_4] mixtures. This result has been interpreted in terms of the stronger ion association in [BMIm][BF_4] via hydrogen bonding of its aromatic hydrogen atoms than the hydrogen atoms of the imidazolium cation in [BMIm][PF_6]. Finally, it is also noted from Fig. 2 that the apparent molar isentropic compressibility, κ_ϕ, values for the [BMIm][PF_6] + MeCN mixture are greater than the corresponding values for the [BMIm][BF_4] + MeCN mixture. This means that the mixtures of [BMIm][PF_6] in MeCN are more compressible than the corresponding

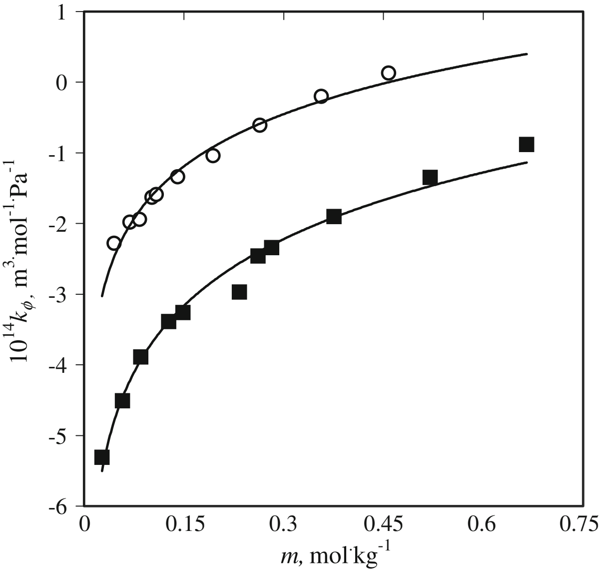

Fig. 2 Comparison of apparent molar isentropic compressibilities κ_ϕ of [BMIm][PF$_6$] (○) [7] and [BMIm][BF$_4$] (■) in MeCN mixtures at 298.15 K

[BMIm][BF$_4$] + MeCN mixtures. The strong ion association in [BMIm][BF$_4$] causes a loss of compressibility for the [BMIm][BF$_4$] + MeCN mixture compared to the mixture of [BMIm][PF$_6$] in MeCN. Similar behavior has been shown for the other studied mixtures.

4 Conclusions

From the measured density and speed-of-sound data at $T = 298.15$ K for mixtures of the ionic liquid, 1-butyl-3-methyimidazolium tetrafluoroborate, with some of the organic solvents (methanol, acetonitrile, tetrahydrofuran, N,N-dimethylacetamide, dimethylsulfoxide), the apparent molar volumes and compressibilities were calculated and fitted satisfactorily to the Redlich–Mayer and Pitzer equations. The obtained values for the limiting apparent molar volume and compressibility values were used to acquire some information with respect to ion–solvent interactions in the 1-butyl-3-methyimidazolium tetrafluoroborate + organic solvent mixtures. It was found that the strength of interaction between the ionic liquid 1-butyl-3-methyimidazolium tetrafluoroborate with the studied organic solvents have the order: DMSO > DMA > MeOH > MeCN > THF.

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