Volumetric properties of binary mixtures of 1-butyl-3-methylimidazolium halides with water, methanol or ethanol at 293.15 to 318.15 K

Byung Heung Park[†]

Department of Chemical and Biological Engineering, Korea National University of Transportation,
50 Daehak-ro, Chungju-si, Chungbuk 27469, Korea
(*Received 5 November 2015 • accepted 18 February 2016*)

Abstract–Densities of nine binary solutions made of one of three 1-butyl-3-methylimidazolium ([bmim]) halides with water, methanol, or ethanol were measured at atmospheric pressure. The compositions of an ionic liquid ([bmim]Cl, [bmim]Br, or [bmim]I) were increased up to 0.4 as a mole fraction at a given temperature within a range of 293.15 to 318.15 K. The measured values were correlated by a quadratic equation to obtain a temperature dependency of the respective systems. Furthermore, the equation was used to obtain the volume expansivity, which would be used for a pressure-volume-temperature behavior of a condensed phase. The apparent molar volumes were also calculated from the experimental data. The remarkable distinction of the volumetric property behavior between aqueous and nonaqueous solutions was found and attributed to strong ion–solvent interactions in the aqueous systems.

Keywords: 1-Butyl-3-methylimidazolium Halides, Ionic Liquid Mixtures, Densities, Volume Expansivity

INTRODUCTION

Ionic liquids (ILs) are materials consisting of only ionic species in a liquid form. They are usually made up of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, and N-alkyl-N-methyl-piperidinium and various anions ranging from simple halides to complex inorganic ones. The tunable feature acquired by combining any of cations with any of anions allows them to be termed "designer solvents" [1]. They have attracted considerable attention as potential alternatives to the conventional organic solvents due to their unique characteristics, such as negligible vapor pressure, thermal and chemical stability, and nonflammability compared to traditional volatile organic solvents used in chemical industry [2,3]. Recently, the applicability of ionic liquids has been widened as novel solvents and the researches have been diversified to electrochemistry, catalysis, synthesis, biotechnology, and separation process [4-9].

Early chemical applications of ILs focused on the improvement of the existing processes by increasing reactivity, easing product separation with reduced downstream processing, stabilizing catalysts and so on. As for development of a chemical process, imidazolium-based ILs have been widely applied since they are readily obtainable and, thus, a number of investigations have focused on the use of N,N-dialkylimidazolium cation derivatives in catalysis, separations, and electrochemistry [10-15]. However, some of them are often extraordinarily viscous or at solid states under a desired temperature condition for a process, which could limit their applications to separation, dissolution, and reaction. One approach to

resolving the problem is to use mixtures of an IL and traditional molecular solvent(s) rather than pure ILs. The addition of solvents could also reduce the viscosity of the imidazolium-based ILs and, thus, increase their applicability related with process operations such as transportation and mixing. In this respect, the solubilities of imidazolium-based ILs in hydrocarbons and alcohols have been measured [16,17] and phase behaviors have been also examined [18,19].

The presence of molecular solvents in IL would have considerable effect in its physical, chemical, and thermodynamic properties. However, there is still limited information on the properties for the mixtures, while pure IL properties are becoming available from both experimental and theoretical studies. One of the fundamental thermophysical data required for the design of relevant industrial process is a liquid density with respect to temperature. Density data would be essential for determining size of equipment, operation time, and process control on industrial applications and for elucidating solute-solvent interactions associated with the unique properties of the solution on academic interests.

The nature of the anion is accounted for many of the physical properties of ILs, such as hydrophobicity and hygroscopicity [20]. It is well known that halide anions promote hydrophilic feature of ILs and secure high solubility in polar substances. Therefore, properties of solutions composed of an imidazolium-based halide IL and a polar solvent could be measured in a relatively wide range of composition. However, experimental studies on the volumetric property measurement of imidazolium-based ILs were focused on the aqueous solution of chloride IL at dilute concentrations. In this work, densities of binary mixtures of hydrophilic 1-butyl-3-methylimidazolium halides and water, methanol, or ethanol were measured up to $x_{IL} \sim 0.4$ with temperature. Also, the volume expansivity and the apparent molar volume values of the respective solutions were calculated with respect to temperature.

[†]To whom correspondence should be addressed.
E-mail: b.h.park@ut.ac.kr

Table 1. Summary of chemical compounds used

Compounds	Abbreviation	Supplier	Remark
1-Butyl-3-methylimidazolium chloride	[bmim]Cl	C-tri	Water content<278.5 ppm
1-Butyl-3-methylimidazolium bromide	[bmim]Br	Sigma-Aldrich	Purity>97%
1-Butyl-3-methylimidazolium iodide	[bmim]I	C-tri	Water content<251.3 ppm
Methanol	MeOH	Sigma-Aldrich	Purity>99.8%
Ethanol	EtOH	Sigma-Aldrich	Purity>99.5%
Water	-		Ultrapure

EXPERIMENTAL

The names, abbreviations, suppliers, and purities of the chemical compounds used in this work are summarized in Table 1. ILs and alcohols were purchased from commercial suppliers and ultrapure water was produced by using Wellix Plus I system of MDM instruments. ILs were dried in a closed vacuum chamber at 80 °C for more than 12 hrs to remove trace amount of moisture while alcohols were used as purchased without further treatment.

Solutions were prepared by measuring the predetermined weight of constituent chemicals using an analytical balance (Hansung, HS224S, precision 10^{-3} g) and dissolving ionic liquid into a solvent. The uncertainty of mole fraction was estimated to be less than 10^{-4}. All the solutions were instantly sealed and tightly kept to mini-mize absorption of atmospheric moisture. Measurements were carried out immediately after the preparation of the solutions.

Densities were automatically measured using an oscillating U-tube density meter (Rudolph Research Analytical, DDM2911, accuracy 5×10^{-5} g·cm^{-3}, temperature uncertainty 0.03 K), which was calibrated with ultrapure water and dry air at atmospheric pressure. A built-in thermostat in the instrument enabled temperature to be maintained at a desired value within the range of 273.15 to 363.15 K. About 1 cm^3 of solution was injected into a U-tube in the instrument and, then, temperature was gradually increased to a preset value. A video viewing screen on the instrument showed the solution-filled U-tube to detect any vapor bubbles and a measurement was performed when it was confirmed by visual inspection that there were no bubbles at the temperature. The density

Table 2. Measured pure solvent densities (ρ in g·cm^{-3}) and comparison with literature values

T/K	Water			MeOH			EtOH	
	Measured	Lit. [21]	Lit. [22]	Measured	Lit. [21]	Lit. [23]	Measured	Lit. [23]
283.15	-	-	-	-	-	0.80240	-	0.79813
288.15	-	-	0.999134	-	-	-	-	-
293.15	0.99815	0.99823	0.998245	0.79111	0.79130	-	0.78941	-
298.15	0.99709	0.99705	0.997089	0.78647	0.78658	0.78835	0.78511	0.78530
303.15	0.99568	0.99566	0.995688	0.78172	0.78186	-	0.78078	-
308.15	0.99405	0.99404	0.994058	0.77696	0.77711	-	0.77642	-
313.15	0.99218	0.99222	-	0.77218	0.77233	0.77413	0.77204	0.77222
318.15	0.99004	0.99022	-	0.76736	0.76752	-	0.76761	-
328.15	-	-	-	-	-	0.75959	-	0.75874

Table 3. Experimental data of binary [bmim]Cl+solvent solution density with ionic liquid compositions at different temperatures

$x_{[bmim]Cl}$	$\rho/(\text{g·cm}^{-3})$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]Cl+Water[a]					
0.0000	0.99815	0.99709	0.99568	0.99405	0.99218	0.99004
0.0474	1.03147	1.02905	1.02642	1.02371	1.02092	1.01803
0.0985	1.05354	1.05053	1.04737	1.04418	1.04096	1.03768
0.1459	1.06586	1.06279	1.05958	1.05639	1.05317	1.04992
0.2015	1.07402	1.07103	1.06788	1.06470	1.06125	1.05825
0.2499	1.07943	1.07656	1.07354	1.07052	1.06748	1.06442
0.3004	1.08167	1.07887	1.07592	1.07297	1.07000	1.06702
0.3498	1.08352	1.08077	1.07787	1.07488	1.07192	1.06903
0.4016	1.08412	1.08138	1.07851	1.07565	1.07276	1.06987

Table 3. Continued

x_{[bmim]Cl}	ρ/(g·cm⁻³)					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]Cl+MeOH[b]					
0.0000	0.79111	0.78647	0.78172	0.77696	0.77218	0.76736
0.0518	0.85607	0.85196	0.84774	0.84353	0.83932	0.83509
0.1030	0.89573	0.89192	0.88800	0.88409	0.88019	0.87629
0.1462	0.92697	0.92332	0.91958	0.91585	0.91213	0.90842
0.1930	0.95967	0.95618	0.95266	0.94917	0.94567	0.94220
0.2367	0.97181	0.96843	0.96498	0.96154	0.95810	0.95468
0.2799	0.98599	0.98269	0.97929	0.97591	0.97256	0.96921
0.3546	1.00496	1.00177	0.99848	0.99521	0.99196	0.98873
0.4067	1.01637	1.01323	1.01000	1.00680	1.00361	1.00044
	[bmim]Cl+EtOH[c]					
0.0000	0.78941	0.78511	0.78078	0.77642	0.77204	0.76761
0.0512	0.83378	0.82992	0.82593	0.82193	0.81793	0.81389
0.0982	0.86534	0.86166	0.85785	0.85405	0.85026	0.84644
0.1464	0.89440	0.89085	0.88720	0.88356	0.87992	0.87628
0.1923	0.91844	0.91502	0.91149	0.90798	0.90447	0.90097
0.2435	0.94521	0.94191	0.93851	0.93513	0.93176	0.92839
0.3031	0.96107	0.95782	0.95449	0.95118	0.94788	0.94459
0.3381	0.97529	0.97211	0.96883	0.96558	0.96235	0.95911
0.4003	0.99238	0.98929	0.98610	0.98294	0.97978	0.97663

[a]SD≤1.63×10⁻⁵ g/cm³
[b]SD≤1.51×10⁻⁵ g/cm³
[c]SD≤1.57×10⁻⁵ g/cm³

was repeatedly measured five times for a data point.

RESULTS AND DISCUSSION

As for pure water, MeOH, and EtOH, the measured densities were compared with literature data in Table 2. The experiment reliably reproduced the literature data, and only little discrepancy of less than $2×10^{-4}$ g·cm⁻³ was found between the measured and the literature data.

Densities of three binary solutions were measured for each ionic liquid with water, MeOH, or EtOH. The data were presented as the averaged values of five measurements at a point. Experimental data of binary solutions for [bmim]Cl and a solvent are presented in Table 3 at a temperature range of 293.15 to 318.15 K with steps of 5 K. As illustrations for data comparison, the measured densities of [bmim]Cl+water and +MeOH at 293.15 and 318.15 K were co-presented with literature data [21] in Fig. 1, and it was observed that the measured data satisfactorily followed the behavior of the literature data with composition. As for the [bmim]Cl+water system, Lal et al. [22] also reported their own density data, but they were not included in the comparison due to the very low composition ($x_{[bmim]Cl}<0.01$) range of their data, which was not covered in the present study. The measured density data for binary [bmim]Br systems and [bmim]I systems are given in Tables 4 and 5, respectively, in the same temperature range. As seen in Tables 3 to 5, the densities of solutions increase with the increase of IL compositions
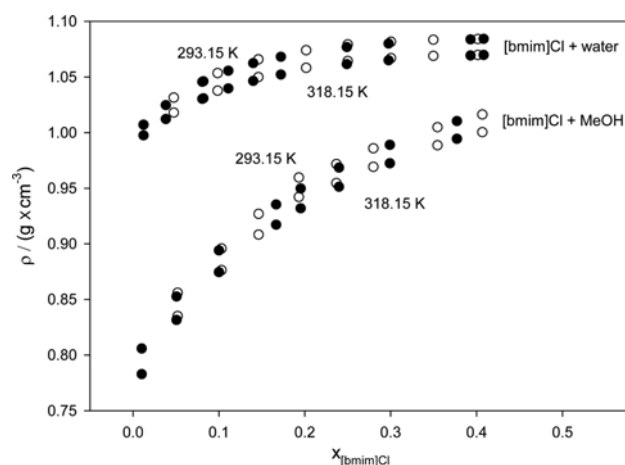
Fig. 1. Comparison of binary solution densities for [bmim]Cl+water and +MeOH: ○ measured data and ● literature data [21].

while decrease with the increase of temperature. The standard deviations (SDs) from the averaged values are reported at the end of the tables for each system as the maximum values from SDs of each data point.

In practice, the effect of temperature on the densities of a binary solution was correlated with an empirical equation. In this work, a quadratic polynomial equation was adopted to describe the non-linear temperature dependence of density at a given composition

Table 4. Experimental data of binary [bmim]Br+solvent solution density with ionic liquid compositions at different temperatures

$x_{[bmim]Br}$	$\rho/(g \cdot cm^{-3})$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
[bmim]Br+Water[a]						
0.0000	0.99815	0.99709	0.99568	0.99405	0.99218	0.99004
0.0477	1.10663	1.10398	1.10113	1.09820	1.09517	1.09207
0.1092	1.18074	1.17735	1.17381	1.17025	1.16666	1.16303
0.1706	1.21908	1.21558	1.21195	1.20832	1.20466	1.20098
0.2274	1.23562	1.23213	1.22851	1.22489	1.22126	1.21761
0.2970	1.25518	1.25174	1.24819	1.24463	1.24106	1.23749
0.3278	1.26205	1.25863	1.25510	1.25159	1.24805	1.24450
0.3463	1.26550	1.26209	1.25858	1.25507	1.25156	1.24804
0.4012	1.27415	1.27080	1.26734	1.26388	1.26042	1.25694
[bmim]Br+MeOH[b]						
0.0000	0.79111	0.78647	0.78172	0.77696	0.77218	0.76736
0.0455	0.89200	0.88764	0.88319	0.87873	0.87428	0.86981
0.0866	0.95823	0.95403	0.94974	0.94547	0.94120	0.93692
0.1387	1.02987	1.02586	1.02174	1.01765	1.01357	1.00950
0.1914	1.07002	1.06612	1.06211	1.05813	1.05416	1.05019
0.2444	1.11666	1.11285	1.10895	1.10508	1.10121	1.09735
0.2763	1.13675	1.13298	1.12912	1.12529	1.12148	1.11770
0.3309	1.16183	1.15814	1.15435	1.15059	1.14685	1.14312
0.3892	1.18285	1.17923	1.17550	1.17178	1.16801	1.16436
[bmim]Br+EtOH[c]						
0.0000	0.78941	0.78511	0.78078	0.77642	0.77204	0.76761
0.0501	0.86607	0.86202	0.85786	0.85369	0.84951	0.84530
0.0901	0.91402	0.91006	0.90598	0.90191	0.89784	0.89374
0.1555	0.98078	0.97686	0.97289	0.96894	0.96499	0.96103
0.1930	1.01535	1.01154	1.00763	1.00373	0.99985	0.99596
0.2464	1.05674	1.05300	1.04916	1.04533	1.04152	1.03772
0.2923	1.08904	1.08536	1.08157	1.07781	1.07406	1.07032
0.3459	1.12926	1.12563	1.12191	1.11822	1.11453	1.11085
0.3969	1.15012	1.14654	1.14286	1.13921	1.13558	1.13196

[a]SD≤1.57×10⁻⁵ g/cm³

[a]$SD \leq 1.57 \times 10^{-5}$ g/cm³
[b]$SD \leq 1.61 \times 10^{-5}$ g/cm³
[c]$SD \leq 1.70 \times 10^{-5}$ g/cm³

Table 5. Experimental data of binary [bmim]I+solvent solution density with ionic liquid compositions at different temperatures

$x_{[bmim]I}$	$\rho/(g \cdot cm^{-3})$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
[bmim]I+Water[a]						
0.0000	0.99815	0.99709	0.99568	0.99405	0.99218	0.99004
0.0449	1.15885	1.15617	1.15325	1.15025	1.14713	1.14390
0.0933	1.24944	1.24599	1.24237	1.23870	1.23497	1.23117
0.1459	1.30714	1.30335	1.29941	1.29546	1.29147	1.28744
0.2012	1.34834	1.34439	1.34032	1.33626	1.33217	1.32805
0.2377	1.36880	1.36483	1.36073	1.35664	1.35253	1.34841
0.3010	1.39505	1.39106	1.38696	1.38287	1.37877	1.37466
0.3412	1.40810	1.40413	1.40005	1.39598	1.39190	1.38781
0.3893	1.42029	1.41633	1.41226	1.40820	1.40415	1.40009

Table 5. Continued

$x_{[bmim]I}$	ρ/(g·cm^{-3})					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]I+MeOH[b]					
0.0000	0.79111	0.78647	0.78172	0.77696	0.77218	0.76736
0.0432	0.91771	0.91302	0.90837	0.90371	0.89905	0.89438
0.0913	1.02250	1.01804	1.01345	1.00889	1.00432	0.99976
0.1402	1.10450	1.10010	1.09560	1.09112	1.08665	1.08218
0.1922	1.17417	1.17002	1.16559	1.16119	1.15681	1.15242
0.2408	1.21480	1.21052	1.20615	1.20181	1.19747	1.19315
0.2876	1.25670	1.25245	1.24813	1.24383	1.23956	1.23529
0.3520	1.30383	1.29964	1.29538	1.29114	1.28694	1.28274
0.3737	1.33909	1.33497	1.33076	1.32657	1.32243	1.31828
	[bmim]I+EtOH[c]					
0.0000	0.78941	0.78511	0.78078	0.77642	0.77204	0.76761
0.0466	0.89163	0.88738	0.88306	0.87874	0.87440	0.87003
0.0981	0.97009	0.96591	0.96161	0.95730	0.95299	0.94866
0.1452	1.04381	1.03965	1.03537	1.03111	1.02682	1.02255
0.1913	1.10253	1.09840	1.09415	1.08992	1.08569	1.08145
0.2381	1.14914	1.14499	1.14077	1.13656	1.13236	1.12815
0.2814	1.18740	1.18328	1.17907	1.17487	1.17070	1.16652
0.3482	1.27845	1.27439	1.27025	1.26614	1.26204	1.25794
0.4172	1.32878	1.32479	1.32069	1.31664	1.31259	1.30855

[a]SD≤1.60×10^{-5} g/cm^3
[b]SD≤1.58×10^{-5} g/cm^3
[c]SD≤1.68×10^{-5} g/cm^3

Table 6. Temperature coefficients for binary [bmim]Cl+solvent solution density and MAPEs

$x_{[bmim]Cl}$	ρ(g·cm^{-3})=k_0+k_1T+k_2T^2			
	k_0/g·cm^{-3}	k_1·10^4/g·cm^{-3}·K^{-1}	k_2·10^7/g·cm^{-3}·K^{-2}	MAPE·10^3/%
	[bmim]Cl+Water			
0.0000	0.6112	28.36100	−51.71400	2.663
0.0474	0.9903	7.66710	−21.35700	3.546
0.0985	1.1339	0.58834	−11.35700	1.425
0.1459	1.1905	−2.28130	−6.71430	4.269
0.2015	1.1774	−0.90596	−8.92860	5.590
0.2499	1.1872	−1.52030	−7.35710	4.172
0.3004	1.1886	−1.59580	−7.00000	2.825
0.3498	1.1918	−1.72360	−6.71430	4.088
0.4016	1.1963	−2.08840	−5.92860	1.334
	[bmim]Cl+MeOH			
0.0000	1.0019	−5.05370	−7.28570	2.542
0.0518	1.0651	−5.95650	−4.00000	3.164
0.1030	1.0994	−6.17300	−2.64290	2.727
0.1462	1.1302	−6.47080	−1.57140	2.368
0.1930	1.1767	−7.77850	1.28570	4.814
0.2367	1.1623	−6.16310	−1.14290	1.801
0.2799	1.1798	−6.50570	−0.35714	1.823
0.3546	1.1930	−6.33110	−0.28571	3.308
0.4067	1.2042	−6.42710	0.07143	2.132

Table 6. Continued

$x_{[bmim]Cl}$	$\rho(g\cdot cm^{-3})=k_0+k_1T+k_2T^2$			
	$k_0/g\cdot cm^{-3}$	$k_1\cdot10^4/g\cdot cm^{-3}\cdot K^{-1}$	$k_2\cdot10^7/g\cdot cm^{-3}\cdot K^{-2}$	$MAPE\cdot10^3/\%$
		[bmim]Cl+EtOH		
0.0000	0.9884	−5.00680	−6.07140	5.271
0.0512	1.0047	−3.86240	−6.71430	3.176
0.0982	1.0460	−4.86420	−4.42860	2.078
0.1464	1.0799	−5.46860	−2.92860	1.701
0.1923	1.1024	−5.60330	−2.28570	4.061
0.2435	1.1275	−5.73460	−1.64290	4.628
0.3031	1.1493	−6.25240	−0.57143	2.040
0.3381	1.1587	−6.04510	−0.71429	4.302
0.4003	1.1654	−5.52490	−1.28570	1.281

by using the following equation.

$$\rho=k_0+k_1T+k_2T^2 \qquad (1)$$

where, ρ is the density in $g\cdot cm^{-3}$ and T is the absolute temperature.

The temperature coefficients k_0, k_1, and k_2 were regressed to fit the experimental data with Eq. (1). The values of temperature coefficients are presented in Tables 6 to 8 with respect to compositions of a binary system. The mean absolute percentage errors (MAPEs)

Table 7. Temperature coefficients for binary [bmim]Br+solvent solution density and MAPEs

$x_{[bmim]Br}$	$\rho(g\cdot cm^{-3})=k_0+k_1T+k_2T^2$			
	$k_0/g\cdot cm^{-3}$	$k_1\cdot10^4/g\cdot cm^{-3}\cdot K^{-1}$	$k_2\cdot10^7/g\cdot cm^{-3}\cdot K^{-2}$	$MAPE\cdot10^3/\%$
		[bmim]Br+Water		
0.0000	0.6112	28.36100	−51.71400	2.663
0.0477	1.0799	7.13060	−21.21400	2.106
0.1092	1.2955	−0.98300	−10.00000	1.409
0.1706	1.3637	−2.79710	−7.28570	1.048
0.2274	1.3912	−3.54820	−6.00000	1.502
0.2970	1.4144	−3.90110	−5.21430	2.503
0.3278	1.4221	−4.01570	−4.92860	3.171
0.3463	1.4339	−4.59280	−3.92680	1.068
0.4012	1.4330	−4.05610	−4.64290	2.362
		[bmim]Br+MeOH		
0.0000	1.0019	−5.05370	−7.28570	2.542
0.0455	1.1158	−6.48360	−3.92860	4.914
0.0866	1.1870	−7.13470	−2.28570	4.280
0.1387	1.2598	−7.54930	−1.00000	1.895
0.1914	1.2902	−7.11380	−1.35710	4.070
0.2444	1.3347	−7.16610	−0.92857	2.725
0.2763	1.3705	−8.28810	1.07140	2.550
0.3309	1.3816	−7.49600	0.00000	1.523
0.3892	1.3797	−6.06530	−2.21430	2.505
		[bmim]Br+EtOH		
0.0000	0.9884	−5.00680	−6.07140	5.271
0.0501	1.0513	−4.47470	−6.28570	2.808
0.0901	1.1082	−5.23990	−4.71430	4.556
0.1555	1.2045	−7.37950	−0.85714	1.727
0.1930	1.2244	−6.54430	−2.00000	1.379
0.2464	1.2682	−6.83520	−1.28570	2.223
0.2923	1.2996	−6.88930	−1.00000	1.538
0.3459	1.3368	−6.80610	−0.92857	2.319
0.3969	1.3634	−7.27600	0.00000	3.150

Table 8. Temperature coefficients for binary [bmim]I+solvent solution density and MAPEs

$x_{[bmim]I}$	$\rho(g \cdot cm^{-3}) = k_0 + k_1T + k_2T^2$			
	$k_0/g \cdot cm^{-3}$	$k_1 \cdot 10^4/g \cdot cm^{-3} \cdot K^{-1}$	$k_2 \cdot 10^7/g \cdot cm^{-3} \cdot K^{-2}$	$MAPE \cdot 10^3/\%$
		[bmim]I+Water		
0.0000	0.6112	28.36100	−51.71400	2.663
0.0449	1.0980	9.50820	−25.35700	4.203
0.0933	1.3181	2.24360	−15.64300	1.479
0.1459	1.4452	−1.77790	−10.00000	1.232
0.2012	1.5246	−4.06320	−6.64290	3.408
0.2377	1.5556	−4.71850	−5.64290	2.637
0.3010	1.5945	−5.54640	−4.28570	1.287
0.3423	1.6064	−5.50640	−4.28570	2.355
0.3893	1.6295	−6.25750	−3.00000	2.052
		[bmim]I+MeOH		
0.0000	1.0019	−5.05370	−7.28570	2.542
0.0432	1.1951	−9.58880	0.42857	1.630
0.0913	1.2616	−7.27580	−3.00000	2.024
0.1402	1.3512	−7.93460	−1.64290	3.627
0.1922	1.3635	−4.36390	−7.14290	3.534
0.2408	1.4637	−8.32150	−0.57143	2.422
0.2876	1.5147	−9.00920	0.71429	1.761
0.3520	1.5641	−9.27480	1.35710	2.092
0.3737	1.5921	−8.90250	0.92857	1.244
		[bmim]I+EtOH		
0.0000	0.9884	−5.00680	−6.07140	5.271
0.0466	1.0997	−5.67430	−4.85710	2.236
0.0981	1.1691	−5.13450	−5.64290	2.175
0.1452	1.2542	−5.94100	−4.21430	1.427
0.1913	1.3188	−6.39120	−3.35710	3.891
0.2381	1.3808	−7.44220	−1.57140	2.133
0.2814	1.4232	−7.75100	−1.00000	2.730
0.3482	1.5165	−8.03730	−0.28571	2.601
0.4172	1.5630	−7.88450	−0.35714	1.134

defined by Eq. (2) were calculated to assess the accuracy of the equation with the regressed temperature coefficients and also given in Table 6 to 8.

$$MAPE(\%) = \frac{100}{n} \sum_i \frac{\left| \rho_i^{cal} - \rho_i^{dat} \right|}{\rho_i^{dat}} \quad (2)$$

where, ρ^{cal} and ρ^{dat} are the density value calculated by Eq. (1) and the measured in this work at a binary system with n number of data, respectively. MAPEs were less than $3.36 \times 10^{-3}\%$ for a binary system, which showed the reliability of the given equation within the composition ranges. Note that the k_2s in Tables 6 to 8 were not negligible in values even within the temperature ranges of 25 K. Therefore, the assumption of linear behavior with temperature would result in escalated errors in properties, which would be derived based on the volumetric property such as the volume expansivity. The selected quadratic polynomial equation is adequate to be used for obtaining some volume-related properties as well as accurately correlating the experimental data.

The volume expansivity, usually denoted as β, is a measure of the volume changes with temperature under a constant pressure. It is used to describe the pressure-volume-temperature relationship on pure or mixed solutions of condensed substances in a single phase region. β is defined by the following equation and readily derived from the volumetric property.

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (3)$$

where, subscript P means that the derivative is carried out at constant pressure. β is evaluated by inserting Eq. (1) into Eq. (3) and, then, introducing the determined temperature coefficients in Tables 6 to 8 for the respective systems. The calculated results are listed in Tables 9 to 11. The volume expansivity of a solution depends on the composition as well as temperature. In the IL+water systems (IL=[bmim]Cl, [bmim]Br, or [bmim]I), the behavior of the volume expansivity exhibits a maximum at around $x_{IL} = 0.1$ after increasing with the IL concentration at low composition (Fig. 2). On the other hand, the IL+MeOH or +EtOH systems show monotonically decreasing behaviors with respect to the corresponding IL concen-

Table 9. Volume expansivity of binary [bmim]Cl+solvent solution with ionic liquid compositions at different temperatures

$x_{[bmim]Cl}$	$\beta \cdot 10^4 / K^{-1}$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
[bmim]Cl+Water						
0.0000	1.9625	2.4833	3.0061	3.5312	4.0591	4.5902
0.0474	4.7061	4.9250	5.1455	5.3677	5.5916	5.8173
0.0985	5.7617	5.8867	6.0126	6.1397	6.2679	6.3972
0.1459	5.8333	5.9137	5.9947	6.0763	6.1587	6.2418
0.2015	5.7171	5.8170	5.9177	6.0192	6.1216	6.2249
0.2499	5.4046	5.4877	5.5714	5.6558	5.7409	5.8266
0.3004	5.2696	5.3485	5.4280	5.5081	5.5888	5.6701
0.3498	5.2236	5.2995	5.3760	5.4530	5.5307	5.6089
0.4016	5.1325	5.2006	5.2692	5.3383	5.4080	5.4781
[bmim]Cl+MeOH						
0.0000	11.787	11.950	12.115	12.283	12.454	12.627
0.0518	9.6970	9.7913	9.8868	9.9834	10.081	10.180
0.1030	8.6215	8.6886	8.7563	8.8248	8.8940	8.9639
0.1462	7.9742	8.0232	8.0726	8.1225	8.1729	8.2238
0.1930	7.3195	7.3329	7.3464	7.3599	7.3735	7.3871
0.2367	7.0314	7.0680	7.1050	7.1422	7.1798	7.2176
0.2799	6.8103	6.8372	6.8643	6.8916	6.9192	6.9469
0.3546	6.4666	6.4904	6.5144	6.5386	6.5629	6.5874
0.4067	6.2822	6.3013	6.3205	6.3398	6.3592	6.3788
[bmim]Cl+EtOH						
0.0000	10.851	10.988	11.127	11.267	11.410	11.555
0.0512	9.3539	9.4789	9.6055	9.7338	9.8637	9.9953
0.0982	8.6216	8.7104	8.8003	8.8911	8.9830	9.0760
0.1464	8.0338	8.0992	8.1652	8.2319	8.2993	8.3673
0.1923	7.5595	7.6132	7.6675	7.7222	7.7774	7.8332
0.2435	7.0856	7.1283	7.1713	7.2147	7.2585	7.3027
0.3031	6.8541	6.8836	6.9134	6.9434	6.9736	7.0041
0.3381	6.6273	6.6566	6.6863	6.7161	6.7462	6.7765
0.4003	6.3269	6.3600	6.3933	6.4269	6.4608	6.4949

Table 10. Volume expansivity of binary [bmim]Br+solvent solution with ionic liquid compositions at different temperatures

$x_{[bmim]Br}$	$\beta \cdot 10^4 / K^{-1}$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
[bmim]Br+Water						
0.0000	1.9625	2.4833	3.0061	3.5312	4.0591	4.5902
0.0477	4.7958	4.9997	5.2052	5.4122	5.6208	5.8312
0.1092	5.7980	5.8999	6.0027	6.1064	6.2109	6.3164
0.1706	5.7983	5.8752	5.9527	6.0309	6.1097	6.1892
0.2274	5.7186	5.7837	5.8494	5.9156	5.9824	6.0497
0.2970	5.5434	5.6005	5.6581	5.7161	5.7745	5.8335
0.3278	5.4716	5.5259	5.5805	5.6355	5.6910	5.7469
0.3463	5.4484	5.4945	5.5409	5.5876	5.6347	5.6821
0.4012	5.3196	5.3704	5.4215	5.4731	5.5250	5.5772

tration over the full range as presented in Figs. 3 and 4. This kind of behavior is also observed in [bmim]Cl+hydrophilic solvents [21]. The effect of temperatures on the volume expansivity seems to diminish with increasing IL composition and the values get closer as x_{IL} increment within the present temperature range.

The apparent molar volume of a solute is defined as the molar

Table 10. Continued

$x_{[bmim]Br}$	$\beta \cdot 10^4/K^{-1}$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
			[bmim]Br+MeOH			
0.0000	11.787	11.950	12.115	12.283	12.454	12.627
0.0455	9.8511	9.9443	10.039	10.134	10.231	10.329
0.0866	8.8445	8.9078	8.9717	9.0364	9.1018	9.1678
0.1387	7.8994	7.9405	7.9820	8.0238	8.0660	8.1086
0.1914	7.3921	7.4322	7.4728	7.5136	7.5549	7.5965
0.2444	6.9051	6.9374	6.9699	7.0027	7.0357	7.0690
0.2763	6.7385	6.7518	6.7652	6.7786	6.7921	6.8056
0.3309	6.4518	6.4726	6.4936	6.5148	6.5361	6.5575
0.3892	6.2252	6.2634	6.3020	6.3408	6.3800	6.4194
			[bmim]Br+EtOH			
0.0000	10.851	10.988	11.127	11.267	11.410	11.555
0.0501	9.4215	9.5392	9.6583	9.7790	9.9012	10.025
0.0901	8.7562	8.8467	8.9381	9.0306	9.1242	9.2189
0.1555	8.0363	8.0775	8.1191	8.1611	8.2034	8.2461
0.1930	7.6001	7.6489	7.6982	7.7479	7.7980	7.8487
0.2464	7.1813	7.2194	7.2578	7.2966	7.3357	7.3751
0.2923	6.8644	6.8972	6.9304	6.9637	6.9974	7.0313
0.3459	6.5089	6.5384	6.5682	6.5981	6.6283	6.6587
0.3969	6.3264	6.3465	6.3667	6.3870	6.4075	6.4280

Table 11. Volume expansivity of binary [bmim]I+solvent solution with ionic liquid compositions at different temperatures

$x_{[bmim]I}$	$\beta \cdot 10^4/K^{-1}$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
			[bmim]I+Water			
0.0000	1.9625	2.4833	3.0061	3.5312	4.0591	4.5902
0.0449	4.6242	4.8545	5.0865	5.3202	5.5557	5.7932
0.0933	5.5448	5.6859	5.8282	5.9717	6.1165	6.2625
0.1459	5.8455	5.9395	6.0342	6.1298	6.2262	6.3234
0.2012	5.9018	5.9687	6.0362	6.1043	6.1729	6.2421
0.2377	5.8643	5.9229	5.9821	6.0417	6.1018	6.1623
0.3010	5.7768	5.8244	5.8724	5.9207	5.9694	6.0185
0.3412	5.6948	5.7416	5.7888	5.8363	5.8843	5.9325
0.3893	5.6442	5.6814	5.7189	5.7566	5.7946	5.8329
			[bmim]I+MeOH			
0.0000	11.787	11.950	12.115	12.283	12.454	12.627
0.0432	10.175	10.222	10.270	10.318	10.367	10.416
0.0913	8.8356	8.9044	8.9739	9.0441	9.1151	9.1870
0.1402	8.0561	8.1037	8.1517	8.2001	8.2490	8.2984
0.1922	7.2831	7.3709	7.4596	7.5491	7.6396	7.7310
0.2408	7.1256	7.1558	7.1863	7.2170	7.2479	7.2790
0.2876	6.8355	6.8532	6.8711	6.8890	6.9070	6.9252
0.3520	6.5030	6.5138	6.5246	6.5354	6.5463	6.5572
0.3737	6.2416	6.2541	6.2668	6.2794	6.2922	6.3050

volume of solute in a solution assuming that the effective volume of a solvent is equal to the pure solvent volume, while all of the volume changes in the solution are accounted for the molar volume of the solute. It is closely related to a partial molar volume of the solute and often more useful in conjunction with other experimental data than the partial molar volume. The apparent molar volume

Table 11. Continued

| $x_{[bmim]I}$	$\beta \cdot 10^4/K^{-1}$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
			[bmim]I+EtOH			
0.0000	10.851	10.988	11.127	11.267	11.410	11.555
0.0466	9.5579	9.6587	9.7607	9.8640	9.9686	10.0745
0.0981	8.7033	8.7998	8.8976	8.9964	9.0964	9.1976
0.1452	8.0587	8.1319	8.2059	8.2807	8.3562	8.4326
0.1913	7.5817	7.6411	7.7012	7.7618	7.8230	7.8848
0.2381	7.2781	7.3185	7.3592	7.4002	7.4416	7.4833
0.2814	7.0216	7.0548	7.0882	7.1220	7.1560	7.1903
0.3482	6.4179	6.4408	6.4638	6.4871	6.5104	6.5340
0.4172	6.0911	6.1125	6.1339	6.1555	6.1772	6.1991
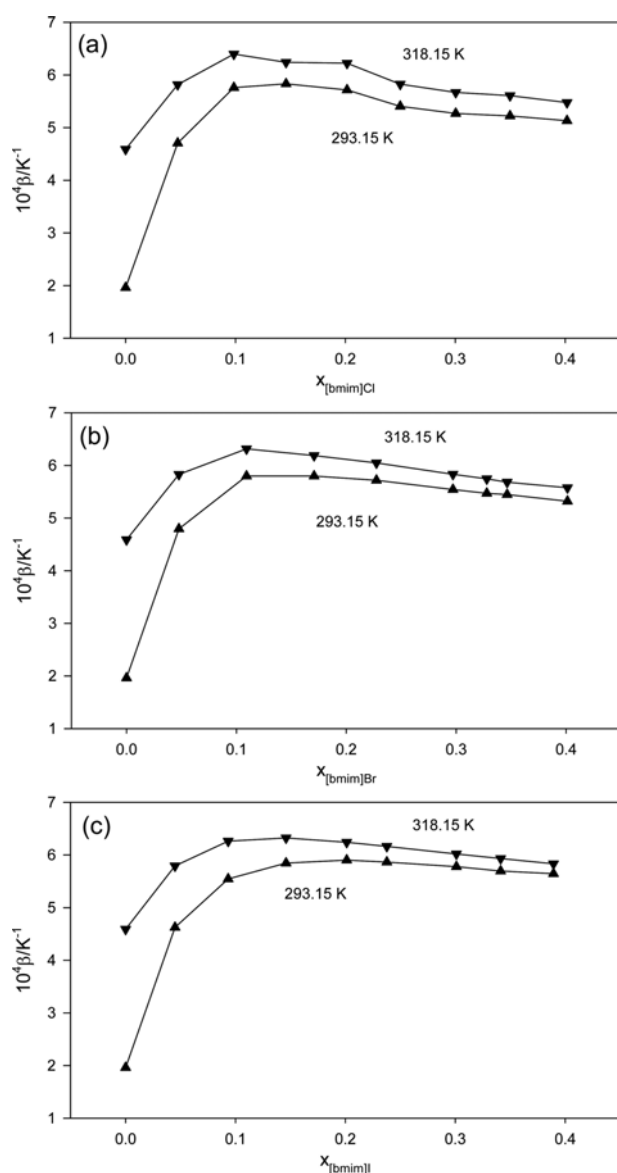
Fig. 2. Volume expansivity of IL (IL=(a) [bmim]Cl, (b) [bmim]Br, or (c) [bmim]I)+water systems with IL composition at different temperatures: from 293.15 and 318.15 K.
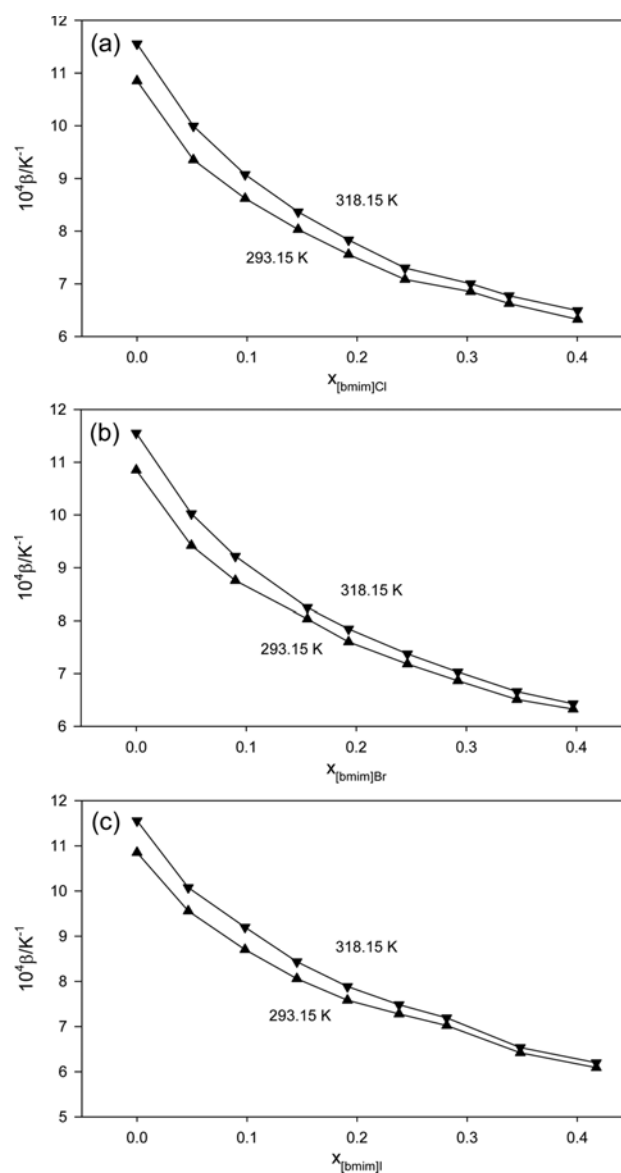
Fig. 3. Volume expansivity of IL (IL=(a) [bmim]Cl, (b) [bmim]Br, or (c) [bmim]I)+MeOH systems with IL composition at different temperatures: from 293.15 and 318.15 K.
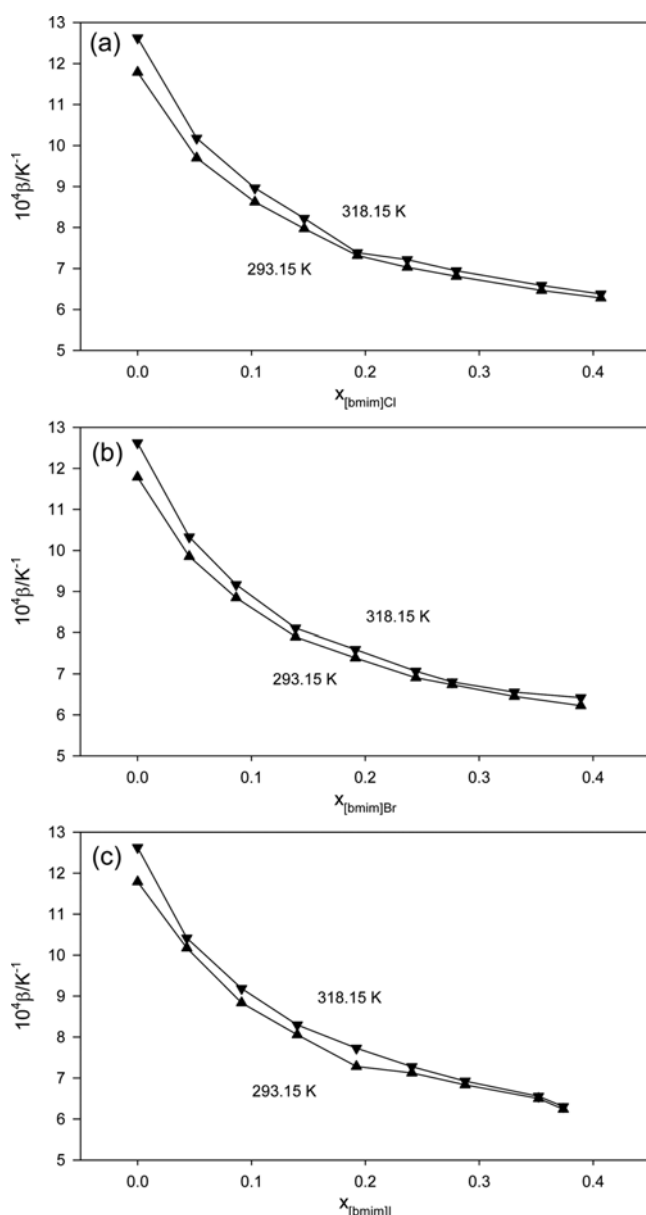
Fig. 4. Volume expansivity of IL (IL=(a) [bmim]Cl, (b) [bmim]Br, or (c) [bmim]I)+EtOH systems with IL composition at different temperatures: from 293.15 and 318.15 K.

can be calculated from the density data using the following relation.

$$V_\phi = \frac{M_1}{\rho} - 1000\frac{(\rho - \rho_0)}{\rho\rho_0 m} \tag{4}$$

where, M_1 is the molecular weight of solute, ρ and ρ_0 are densities of solution and pure solvent, respectively, and m is the molality of a solution (mol·kg^{-1}). The calculated values are listed in Tables 12 to 14. It has been found that there are minimum points of the apparent molar volumes with the molality in [bmim] halides+water systems at a low molality range [21,24]. We also observed for [bmim]Cl or [bmim]Br+water systems. As for [bmim]I+water system, the minimum point was not found in the present range of [bmim]I and, thus, the point would be observed at $m_{[bmim]Br} < 2.61$ if it exists. The changes of the apparent molar volume of ILs in IL+MeOH or EtOH systems were characterized by a sigmoidal shape with the molality. This kind of behavior was examined in partial molar volumes of water + imidazolium-based halides room temperature ILs [25] and attributed to a complex mix of interactions which requires further investigation.

For IL+water mixtures, two types of interactions induced by the significant cation-cation aggregation and the strong Columbic attractions between cation and anion lead to the supra-molecular organization among IL molecules, as pointed out by Sastry et al. [25], and the resulting complexes affect the distinctive volumetric behavior with the composition, unlike the other systems of the present investigation. The interaction between ions of IL and water was stronger than ion-alcohol interaction [26]. Moreover, a clathrate-like structural arrangement in the aqueous IL solution [27] would result in the different behavior of the volume expansivity and the apparent molar volume.

CONCLUSIONS

ILs are considered as alternative chemical media replacing organic solvents used in various applications; their properties are of significance for developing chemical processes using them. In this study, the volumetric properties of binary liquid mixtures made of a [bmim] halide and a commonly acceptable solvent were measured at different composition and temperature. Nine binary systems ([bmim][Cl], [bmim][Br], or [bmim][I]+water, MeOH, or EtOH) were prepared up to $x_{IL} \sim 0.4$ and the densities were measured from 293.15 to

Table 12. Apparent molar volume of [bmim]Cl with ionic liquid compositions at different temperatures

$m_{[bmim]Cl}$	$V_\phi/(cm^3 \cdot mol^{-1})$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]Cl+Water					
2.7627	157.63	158.46	159.29	160.07	160.82	161.52
6.0630	157.11	157.85	158.59	159.31	160.01	160.68
9.4823	157.17	157.81	158.46	159.09	159.70	160.29
14.011	157.58	158.14	158.72	159.29	159.91	160.41
18.493	157.74	158.24	158.77	159.28	159.78	160.28
23.835	158.24	158.71	159.20	159.69	160.17	160.64
29.863	158.56	159.02	159.49	159.97	160.44	160.89
37.254	158.98	159.43	159.88	160.34	160.79	161.24

Table 12. Continued

m$_{[bmim]Cl}$	V$_\phi$/(cm^3·mol^{-1})					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]Cl+MeOH					
1.7054	147.79	147.71	147.63	147.51	147.36	147.19
3.5838	153.81	153.89	153.98	154.05	154.10	154.13
5.3443	153.77	153.91	154.06	154.20	154.32	154.41
7.4641	152.27	152.44	152.60	152.74	152.87	152.99
9.6808	155.46	155.69	155.91	156.13	156.35	156.55
12.132	156.56	156.82	157.09	157.35	157.60	157.85
17.148	158.12	158.42	158.74	159.05	159.35	159.65
21.394	158.76	159.09	159.43	159.76	160.08	160.40
	[bmim]Cl+EtOH					
1.1714	151.94	151.76	151.71	151.63	151.51	151.37
2.3638	154.83	154.84	154.93	154.99	155.02	155.03
3.7230	155.35	155.46	155.61	155.74	155.85	155.94
5.1681	155.75	155.90	156.09	156.26	156.42	156.56
6.9870	154.91	155.10	155.31	155.50	155.68	155.85
9.4410	157.78	158.04	158.31	158.57	158.82	159.06
11.088	157.32	157.58	157.87	158.14	158.40	158.66
14.489	158.13	158.42	158.73	159.03	159.32	159.61

Table 13. Apparent molar volume of [bmim]Br with ionic liquid compositions at different temperatures

m$_{[bmim]Br}$	V$_\phi$/(cm^3·mol^{-1})					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]Br+Water					
2.7804	162.67	163.56	164.41	165.22	166.02	166.79
6.8047	162.80	163.55	164.28	164.99	165.68	166.36
11.418	163.84	164.47	165.10	165.72	166.33	166.93
16.338	165.55	166.13	166.71	167.29	167.85	168.42
23.451	165.82	166.35	166.89	167.42	167.94	168.47
27.069	165.88	166.40	166.92	167.43	167.94	168.45
29.406	165.95	166.46	166.97	167.47	167.98	168.48
37.192	166.14	166.62	167.11	167.60	168.08	168.57
	[bmim]Br+MeOH					
1.4877	152.06	151.96	151.89	151.80	151.66	151.49
2.9590	155.43	155.47	155.53	155.56	155.57	155.55
5.0259	155.20	155.30	155.43	155.53	155.61	155.68
7.3876	160.69	160.89	161.11	161.32	161.51	161.69
10.095	160.09	160.33	160.58	160.82	161.05	161.27
11.916	160.82	161.08	161.35	161.62	161.87	162.11
15.435	162.71	163.01	163.32	163.62	163.91	164.20
19.887	164.38	164.71	165.05	165.39	165.73	166.05
	[bmim]Br+EtOH					
1.1449	155.05	154.91	154.87	154.82	154.72	154.60
2.1495	159.38	159.40	159.49	159.56	159.60	159.62
3.9970	161.57	161.75	161.94	162.11	162.26	162.39
5.1914	161.51	161.69	161.91	162.11	162.30	162.46
7.0974	162.20	162.43	162.68	162.93	163.16	163.37
8.9656	162.33	162.58	162.86	163.13	163.38	163.62
11.479	160.83	161.09	161.38	161.66	161.92	162.18
14.285	162.71	163.01	163.32	163.63	163.93	164.22

Table 14. Apparent molar volume of [bmim]I with ionic liquid compositions at different temperatures

$m_{[bmim]I}$	$V_\phi/(cm^3 \cdot mol^{-1})$					
	T/K=293.15	298.15	303.15	308.15	313.15	318.15
	[bmim]I+Water					
2.6095	176.39	177.29	178.17	179.01	179.84	180.66
5.7119	177.71	178.51	179.29	180.06	180.81	181.56
9.4823	178.61	179.33	180.04	180.74	181.43	182.12
13.982	178.76	179.42	180.08	180.73	181.37	182.01
17.309	178.74	179.37	180.00	180.63	181.25	181.86
23.903	178.83	179.42	180.02	180.61	181.19	181.78
28.749	178.85	179.41	179.99	180.56	181.13	181.69
35.385	178.95	179.50	180.06	180.62	181.17	181.72
	[bmim]I+MeOH					
1.4091	166.24	166.41	166.39	166.37	166.31	166.21
3.1358	169.04	169.17	169.31	169.42	169.52	169.58
5.0891	170.47	170.68	170.89	171.08	171.26	171.42
7.4258	171.11	171.32	171.58	171.83	172.06	172.29
9.8991	174.53	174.84	175.16	175.47	175.77	176.06
12.600	174.59	174.93	175.27	175.61	175.93	176.25
16.954	174.79	175.15	175.52	175.88	176.23	176.58
18.622	170.96	171.29	171.63	171.97	172.30	172.62
	[bmim]I+EtOH					
1.0610	161.57	161.65	161.64	161.62	161.51	161.40
2.3611	174.39	174.58	174.78	174.98	175.12	175.25
3.6873	171.21	171.43	171.64	171.85	172.03	172.18
5.1349	171.31	171.55	171.80	172.04	172.26	172.46
6.7836	173.12	173.42	173.72	174.00	174.27	174.53
8.5004	174.17	174.49	174.82	175.14	175.44	175.73
11.596	166.37	166.66	166.95	167.23	167.50	167.77
15.539	167.18	167.49	167.81	168.12	168.42	168.72

318.15 K at atmosphere pressure. The temperature dependence was correlated by a quadratic polynomial equation. The volume expansivity values were calculated using the regressed temperature coefficients of the equation. Also, the apparent molar volumes were determined based on the measured solution densities. The measured and derived density-related properties were discussed and compared to those of similar binary systems presenting consistent agreements with the reported systems.

REFERENCES

1. B. Kirchner Ed., *Ionic Liquids*, Springer, New York (2010).
2. J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, **105**, 10942 (2001).
3. J. Dupoint, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002).
4. M. Hayyan, F. S. Mjalli, M. A. Hashim, I. M. AlNashef and T. X. Mei, *J. Ind. Eng. Chem.*, **19**, 106 (2013).
5. D. Betz, P. Altmann, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Coordin. Chem. Rev.*, **255**, 1518 (2011).
6. D. Tian, Y. Han, C. Lu, X. Zhang and G. Yuan, *Carbohydr. Polym.*, **113**, 83 (2014).
7. W.-J. Chen, W.-T. Lou, C.-Y. Yu, H. Wu, M.-H. Zong and T. J. Smith, *J. Biotechnol.*, **162**, 183 (2012).
8. K.-S. Kim, S.-Y. Park, S. Choi and H. Lee, *J. Power Sources*, **155**, 385 (2006).
9. B. S. Shin, E. S. Kim, S. K. Kwak, J. S. Lim, K.-S. Kim and J. W. Kang, *Fluid Phase Equilib.*, **382**, 270 (2014).
10. M. Jayakumar, K. A. Venkatesan and T. G. Srinivasan, *Electrochim. Acta*, **53**, 2794 (2008).
11. S. Baj, T. Krawczyk, A. Dabrowska, A. Siewniak and A. Sobolewski, *Korean J. Chem. Eng.*, **32**, 2295 (2015).
12. K.-S. Kim, B.-K. Shin, H. Lee and F. Ziegler, *Fluid Phase Equilib.*, **218**, 215 (2004).
13. G. Fan, C. Liao, T. Fang, M. Wang and G. Song, *Fuel Process. Technol.*, **116**, 142 (2013).
14. X. He, B. Hou, C. Li, Q. Zhu, Y. Jiang and L. Wu, *Electrochim. Acta*, **130**, 245 (2014).
15. P. Bonhte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, **35**, 1168 (1996).
16. U. Domanska and A. Marciniak, *J. Chem. Eng. Data*, **48**, 451 (2003).
17. U. Domanska, E. Bogel-Lukasik and R. Bogel-Lukasik, *J. Phys. Chem. B*, **107**, 1858 (2003).
18. R. P. Swatloski, A. E. Visser, W. M. Reichert, G. A. Broker, L. M.

Farina, J. D. Holbrey and R. D. Rogers, *Green Chem.*, **4**, 81 (2002).

19. T. M. Letcher, N. Deenadayalu, B. Soko, D. Ramjugernath and P. K. Naicker, *J. Chem. Eng. Data*, **48**, 904 (2003).

20. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, **3**, 156 (2001).

21. Q. Yang, H. Zhang, B. Su, Y. Yang, Q. Ren and H. Xing, *J. Chem. Eng. Data*, **55**, 1750 (2010).

22. B. Lal, M. Sahin and E. Ayranci, *J. Chem. Thermodyn.*, **54**, 142 (2012).

23. D. Matkowska and T. Hofman, *J. Mol. Liq.*, **177**, 301 (2013).

24. R. Sadeghi, H. Shekaari and R. Hosseini, *J. Chem. Thermodyn.*, **41**, 273 (2009).

25. N. V. Sastry, N. M. Vaghela and P. M. Macwan, *J. Mol. Liq.*, **180**, 12 (2013).

26. M. T. Zafarani-Moattar and H. Shekaari, *J. Chem. Thermodyn.*, **37**, 1029 (2005).

27. W. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).