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Volumetric Properties of Aqueous Ionic-Liquid Solutions at Different Temperatures

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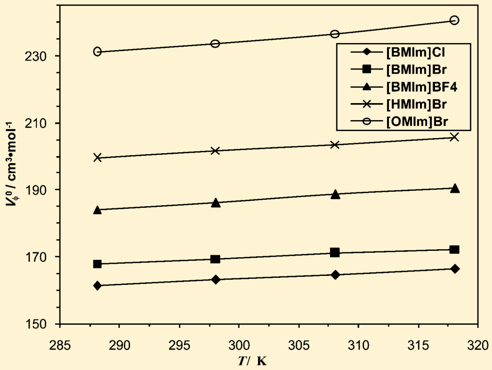
ABSTRACT: Density measurements were carried out for aqueous solutions of the ionic liquids [BMIm]Cl, [BMIm]Br, [BMIm][BF_4], [HMIm]Br, [OMIm]Br, [MMIm][MSO_4], and [EMIm][ESO_4] at T = (288.15−318.15) K. The measured densities were used to compute the standard partial molar volumes (V_ϕ^0) of the ILs using Redlich−Mayer and Pitzer equations. The results show that the V_ϕ^0 values obtained from both equations are fully compatible and that the difference is less than 0.5 $cm^3 \cdot mol^{-1}$ for all the ionic liquids. The first derivative of V_ϕ^0 with respect to temperature give the values of partial molar expansivity (E_ϕ^0), and its second derivative with respect to temperature provided Hepler's constant ($(\partial^2 V_\phi^0/\partial T^2)_P$) an important parameter to discuss the structure-making or -breaking tendency of the ILs in aqueous solutions. The values of $(\partial^2 V_\phi^0/\partial T^2)_P$ for all the ILs except for [OMIm]Br were found to be negative, showing that these ILs behave as structure breakers in aqueous media.



INTRODUCTION

Ionic liquids (ILs) are a class of organic electrolytes which composed of organic cations, such as alkyl-substituted imidazolium, pyridinimum, or phosphonium based and organic or inorganic anions ranging from simple ionic species (e.g., Cl^- and Br^-) up to more bulky and hydrophobic moieties (e.g., BF_4^- and PF_6^-). Ionic liquids have remarkable properties like a large liquid range, nonflammability, negligible vapor pressure, a wide electrochemical window, high thermal stability, and an excellent ability to dissolve many organic and inorganic solutes. These features allow them to be used in a variety of applications, such as catalysis, organic synthesis, extraction, electrochemical processes, and separation technology.[1−4] They are typically used not in their pure state but in the presence of water or organic solvents in mixtures or as additives. Some ILs are considerably soluble in water, and their aqueous solutions therefore became the subject of a variety of potential applications in different areas, such as extraction processes, aqueous biphasic systems and organic and inorganic synthetic reactions .[5−7] The presence of water can dramatically affect the physicochemical and diffusion properties of neat ILs. In most cases, the miscibility of ILs in water is controlled by the corresponding anion. From a microscopic perspective, the structure of aqueous ionic liquid solutions is very complicated. In very low concentrations of water, a general picture is emerging that the water molecules tend to be isolated from each other or exist as small independent clusters dispersed in the continuous IL polar network. As the water concentration increases, continuous water networks start to appear, which dramatically change the properties of the mixture. At this concentration range, IL and water domains coexist and form a nanosegregated biphasic system. For solutions richer in water, the IL networks start to break apart, generating IL clusters dispersed in the continuous water phase.[8,9] For most imidazolium-based ILs, water interacts preferably with the anionic moiety. This means that the anion breaks the structure of water. However, imidazolium based cation was found to enhance the water structure, which was opposite to the effect of ILs.[10,11]

The interactions between water and ILs have recently been a hot topic, and many works have been published to discuss these interactions. The volumetric data of aqueous ILs solutions can be of key role to understand more deeply the behavior of ILs in water. Hence, in this work, densities of aqueous solutions of some commonly used ILs were measured at different temperatures and used to compute their volumetric properties. The obtained results show the effect of cation and anion on the volumetric behavior of ILs in water. The temperature dependency of the volumetric parameters have been investigated.

EXPERIMENTAL SECTION

Synthesis of the Ionic Liquids. 1-Alkyl-3-methylimidazolium halide ([BMIm]Cl, [BMIm]Br, [HMIm]Br, and [OMIm]-Br) was synthesized by direct alkylation of *N*-methylimidazole with an excess amount of 1-haloalkane in a round-bottomed

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Table 1. Description of the Chemicals Used

chemical	molecular formula	molecular mass g·mol^{-1}	purity %	source	purification method	analysis method
N-methylimidazole	$C_4H_6N_2$	82.11	≥ 99	Merck	none	none
diethylsulfate	$C_4H_{10}O_4S$	154.19	> 98	Merck	none	none
dimethylsulfate	$C_2H_6O_4S$	126.13	> 99	Merck	none	none
sodium tetrafluoroborate	$NaBF_4$	109.79	98	Merck	none	none
1-bromohexane	$C_6H_{13}Br$	165.08	≥ 98	Merck	none	none
1-bromooctane	$C_8H_{17}Br$	193.12	> 98	Merck	none	none
1-bromobutane	C_4H_9Br	137.03	> 98	LOBA Chemie	none	none
1-chlorobutane	C_4H_9Cl	92.57	99	Merck	none	none
ethyl acetate	$C_4H_8O_2$	88.10	99.5	Merck	none	none
[BMIm]Cl	$C_8H_{15}ClN_2$	174.67	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[BMIm]Br	$C_8H_{15}BrN_2$	219.13	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[HMIm]Br	$C_{10}H_{19}BrN_2$	247.18	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[OMIm]Br	$C_{12}H_{23}BrN_2$	275.23	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[BMIm][BF$_4$]	$C_8H_{15}BF_4N_2$	226.02	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[MMIm][MSO$_4$]	$C_6H_{12}SO_4N_2$	208.24	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR
[EMIm][ESO$_4$]	$C_8H_{16}SO_4N_2$	236.29	> 98	synthesis	(liquid + liquid) extraction	^{1}H NMR

flask stirred vigorously by a magnetic stirrer under a nitrogen atmosphere. The mixing of the chemicals was done first under ice-cooling, but then the temperature was raised to room temperature. The temperature was then gradually increased over a period of several hours to a final reaction temperature of about 50 °C and kept constant until the end of reaction. The reaction mixture was stirred for 1 week. Finally, the crude product was separated from reagents and then washed three times with fresh ethyl acetate. The removal of residual volatile compounds from the ionic liquid was done under high vacuum at 60 °C using a rotary evaporator for at least 4 h under reduced pressure. The obtained ionic liquid has a purity of about 98 %, verified by ^{1}H NMR spectroscopy. The ionic liquid was used after vacuum desiccation for at least 48 h to remove trace amounts of moisture. Water content in the ionic liquid was less than 0.3 %, as found by the Karl Fischer method.

For synthesis of [BMIm][BF$_4$], 1-chlorobutane was added dropwise into a mixture of *N*-methylimidazole and sodium tetrafluoroborate over 1 h. The mixture was stirred under cooling for 3 h, and then the temperature was raised to 70 °C and stirring continued for 4 h at this temperature. Upon completion of the reaction, the mixture was filtrated to remove the precipitated salt (NaCl). The purification of the IL was done as above method. The purity of ionic liquid was more than 98 %, and water content was found to be 0.2 %.

The ILs [MMIm][MSO$_4$] and [EMIm][ESO$_4$] were prepared by direct alkylation of *N*-methylimidazole with an excess amount of dimethylsulfate and diethylsulfate, respectively, in a round-bottomed flask under vigorous stirring by a magnetic stirrer under a nitrogen atmosphere for 48 h. The purification method was the same as above, and the obtained ILs had purity greater than 98 % with water content of about 0.2 %. All the materials used to synthesize the ILs have been collected in Table 1.

Density Measurement. Solution densities were measured at atmospheric pressure and at T = (288.15 to 318.15) K using a vibrating-tube densimeter (DSA 5000, Anton Paar, Austria) with proportional temperature control that kept the samples at working temperature with stability of $1.0 \cdot 10^{-2}$ K. The densimeter was calibrated using doubly distilled water. The standard uncertainty in density measurements was estimated to be $2.0 \cdot 10^{-5}$ g·cm^{-3}.

The solutions were prepared by completely dissolving the ionic liquid in pure water. The weighings were done on a analytical balance (AND, GR202, Japan) with precision of $1 \cdot 10^{-5}$ g. The standard uncertainty of molalities of the prepared solutions is estimated to be $2.0 \cdot 10^{-5}$ mol·kg^{-1}.

RESULTS AND DISCUSSION

Densities of the studied aqueous ILs solutions at T = (288.15 to 318.15) K are given in Table 2, and their values of two ILs ([BMIm]Cl, [BMIm]Br) are plotted and compared as examples with literature values in Figure 1. These values were used to calculate apparent molar volumes (V_ϕ) of the ILs by the following equation:

$$V_\phi = \frac{M}{d} - \frac{1000(d - d_0)}{mdd_0} \tag{1}$$

where M is the molar mass of the IL, m is the molality of the IL in water, d is the density of the aqueous IL solutions, and d_0 is the density of water. The V_ϕ values are also given in Table 2. Apparent molar volumes can be represented using Redlich–Mayer equation in dilute region[12]

$$V_\phi = V_\phi^0 + A_V m^{1/2} + B_V m \tag{2}$$

where A_V is the Pitzer–Debye–Hückel limiting slope for volume which its values for aqueous 1:1 electrolyte solutions at different temperatures are available in literature.[12] B_V is an adjustable parameter related to the pair interactions and is generally negative. The values of standard partial molar volume (V_ϕ^0) of the ILs and B_V values are included in Table 3. To examine the reliability of Redlich–Mayer equation, the V_ϕ^0 values were also calculated using Pitzer model as follows

$$V_\phi = V_\phi^0 + \nu|z_+z_-|\left(\frac{A_V}{2b}\right)\ln(1 + bI^{1/2}) + 2RT\nu_+\nu_-B_V m + 2RT\nu_+^2\nu_-z_+C_V m^2 \tag{3}$$

in which ν_+ and ν_- are the number of cations and anions such that $\nu = \nu_+ + \nu_-$, z_+ and z_- are respectively the number of

Table 2. Densities (d) and Apparent Molar Volumes (V_ϕ) of Aqueous IL Solutions at Different Temperatures[a]

	T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
m_{IL}	d	V_ϕ	d	V_ϕ	d	V_ϕ	d	V_ϕ
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
[BMIm]Cl								
0.0000	0.999096		0.997040		0.994020		0.990192	
0.0323	0.999529	161.42	0.997423	163.20	0.994372	164.73	0.990507	166.34
0.0586	0.999875	161.43	0.997736	163.13	0.994658	164.65	0.990768	166.24
0.0739	1.000080	161.38	0.997920	163.06	0.994834	164.48	0.990922	166.18
0.0899	1.000289	161.37	0.998113	163.00	0.995007	164.47	0.991091	166.03
0.1048	1.000485	161.35	0.998297	162.92	0.995182	164.33	0.991260	165.81
0.1254	1.000760	161.29	0.998550	162.83	0.995409	164.30	0.991473	165.75
0.1437	1.001007	161.23	0.998776	162.75	0.995622	164.19	0.991680	165.58
0.1687	1.001330	161.22	0.999091	162.62	0.995913	164.07	0.991942	165.52
0.1789	1.001473	161.15	0.999214	162.61	0.996039	163.98	0.992060	165.43
0.1910	1.001631	161.14	0.999373	162.52	0.996185	163.91	0.992216	165.24
0.2204	1.002029	161.04	0.999752	162.37	0.996541	163.74	0.992538	165.14
[BMIm]Br								
0.0317	1.000705	168.21	0.998612	169.66	0.995556	171.14	0.991699	172.55
0.0585	1.002052	168.21	0.999924	169.71	0.996840	171.18	0.992959	172.58
0.0730	1.002780	168.15	1.000633	169.67	0.997535	171.11	0.993641	172.51
0.0916	1.003699	168.21	1.001529	169.73	0.998413	171.15	0.994509	172.48
0.1140	1.004803	168.22	1.002606	169.73	0.999470	171.13	0.995544	172.49
0.1319	1.005688	168.15	1.003472	169.64	1.000321	171.02	0.996382	172.36
0.1508	1.006600	168.21	1.004364	169.68	1.001189	171.10	0.997243	172.38
0.1706	1.007559	168.21	1.005297	169.69	1.002117	171.02	0.998148	172.35
0.1910	1.008546	168.17	1.006259	169.66	1.003068	170.95	0.999080	172.29
[BMIm][BF_4]								
0.0311	1.000384	184.51	0.998274	186.56	0.995194	188.96	0.991332	190.66
0.0527	1.001260	184.70	0.999116	186.69	0.995999	189.01	0.992114	190.70
0.0720	1.002033	184.83	0.999860	186.77	0.996713	189.02	0.992809	190.69
0.0904	1.002760	184.95	1.000559	186.88	0.997385	189.08	0.993467	190.69
0.1103	1.003538	185.07	1.001308	186.98	0.998110	189.08	0.994171	190.71
0.1326	1.004402	185.16	1.002134	187.10	0.998921	189.05	0.994948	190.77
0.1525	1.005166	185.23	1.002864	187.19	0.999635	189.06	0.995643	190.76
0.1788	1.006161	185.34	1.003820	187.28	1.000575	189.04	0.996555	190.75
[HMIm]Br								
0.0314	1.000584	199.69	0.998466	201.93	0.995404	203.83	0.991535	205.72
0.0515	1.001524	199.72	0.999368	201.96	0.996284	203.74	0.992389	205.65
0.0703	1.002398	199.71	1.000205	201.97	0.997097	203.76	0.993185	205.57
0.0881	1.003231	199.57	1.000998	201.91	0.997858	203.80	0.993932	205.54
0.1098	1.004226	199.58	1.001959	201.84	0.998787	203.76	0.994837	205.51
0.1310	1.005184	199.64	1.002880	201.88	0.999688	203.72	0.995704	205.56
0.1505	1.006080	199.52	1.003740	201.76	1.000504	203.74	0.996521	205.41
0.1711	1.007001	199.54	1.004639	201.69	1.001398	203.52	0.997358	205.42
0.1903	1.007870	199.46	1.005466	201.66	1.002201	203.48	0.998139	205.38
[OMIm]Br								
0.0323	1.000510	231.26	0.998383	233.96	0.995284	236.94	0.991366	240.56
0.0501	1.001285	231.16	0.999121	233.80	0.995975	236.89	0.992011	240.44
0.0722	1.002237	231.13	1.000023	233.79	0.996827	236.83	0.992796	240.50
0.0908	1.003035	231.07	1.000773	233.81	0.997539	236.78	0.993460	240.41
0.1112	1.003897	231.08	1.001602	233.70	0.998314	236.74	0.994171	240.45
0.1301	1.004694	231.04	1.002356	233.68	0.999033	236.66	0.994852	240.25
0.1485	1.005467	230.99	1.003082	233.68	0.999725	236.61	0.995483	240.29
0.1707	1.006392	230.93	1.003987	233.46	1.000545	236.61	0.996260	240.19
0.1910	1.007245	230.81	1.004772	233.49	1.001302	236.53	0.996981	240.02
[MMIm][MSO_4]								
0.0333	1.000778	157.38	0.998673	159.27	0.995619	160.73	0.991771	161.71
0.0520	1.001710	157.54	0.999578	159.35	0.996505	160.78	0.992648	161.75
0.0743	1.002810	157.68	1.000649	159.42	0.997553	160.84	0.993684	161.81
0.0945	1.003795	157.81	1.001610	159.48	0.998494	160.89	0.994617	161.83
0.1147	1.004769	157.93	1.002565	159.52	0.999435	160.86	0.995542	161.87

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Table 2. continued

	T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
m_{IL}	d	V_ϕ	d	V_ϕ	d	V_ϕ	d	V_ϕ
$mol\cdot kg^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$
				[MMIm][MSO_4]				
0.1309	1.005548	157.98	1.003325	159.55	1.000180	160.89	0.996280	161.88
0.1517	1.006536	158.08	1.004296	159.58	1.001137	160.88	0.997222	161.90
0.1791	1.007820	158.21	1.005557	159.66	1.002380	160.92	0.998460	161.87
				[EMIm][ESO_4]				
0.0313	1.000546	189.88	0.998448	191.47	0.995398	192.98	0.991566	193.59
0.0499	1.001396	189.93	0.999270	191.61	0.996212	192.89	0.992377	193.54
0.0682	1.002223	190.01	1.000069	191.73	0.996995	193.03	0.993169	193.53
0.0901	1.003210	190.00	1.001037	191.60	0.997930	193.07	0.994105	193.57
0.1095	1.004081	189.97	1.001865	191.74	0.998762	192.99	0.994936	193.52
0.1322	1.005089	189.96	1.002863	191.56	0.999712	193.05	0.995897	193.50

[a] Standard uncertainties of molality, density, and temperature are $2.0\cdot10^{-5}$ $mol\cdot kg^{-1}$, $2.0\cdot10^{-5}$ $g\cdot cm^{-3}$, and $1.0\cdot10^{-2}$ K, respectively. All the measurements were performed at the pressure 0.1 MPa.

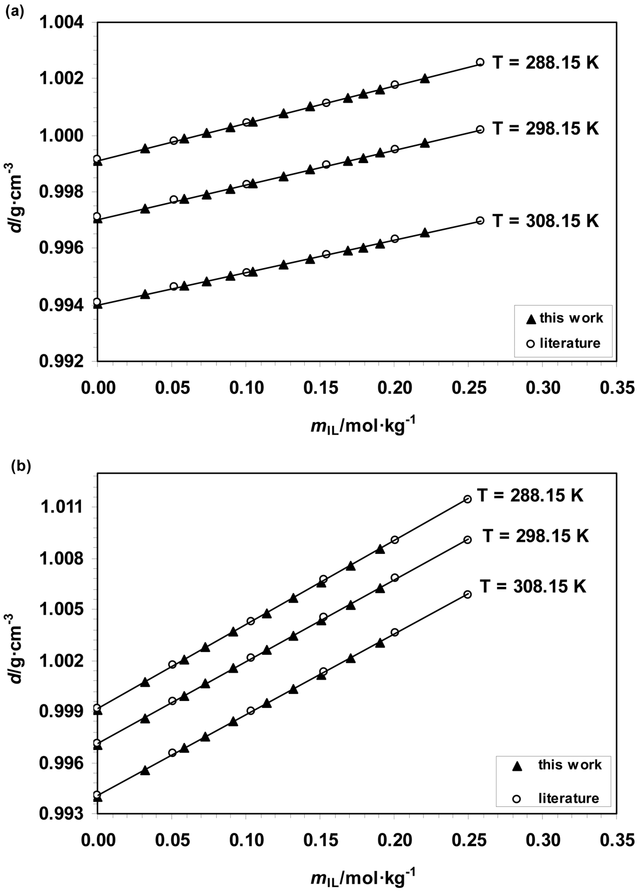

Figure 1. Comparison between the densities of aqueous solutions of the two ILs (a) [BMIm]Cl and (b) [BMIm]Br with literature values.[14]

charges on the cations and anions, I is total ionic strength, R is the gas constant, T is temperature, and B_V is defined by the following equation

$$B_V = \beta_V^0 + \beta_V^1\left(\frac{2}{\alpha^2 I}\right)[1 - (1 + \alpha I^{1/2})\ \exp(-\alpha I^{1/2})] \tag{4}$$

where β_V^0, β_V^1, and C_V are pressure derivatives of Pitzer ion interaction parameters for osmotic coefficient expressions. The parameter b is given the value 1.2 $kg^{1/2}\cdot mol^{-1/2}$ for all electrolytes and $\alpha = 2.0$ for all 1:1 electrolytes. b and α are taken as temperature-independent.[13] The results of fitting V_ϕ values to eq 4 are given in Table 3. Clearly, the difference between the V_ϕ^0 values obtained from the Redlich–Mayer equation and those obtained from Pitzer equation for all the ionic liquids is less than 0.5 $cm^3\cdot mol^{-1}$.

Standard partial molar volume gives important information about ion–water interaction. At infinite dilution, the ions are far from each other; therefore, V_ϕ^0 is unaffected by ion–ion interaction. According to Table 3, the V_ϕ^0 values show the order [BMIm][BF_4] > [BMIm]Br > [BMIm]Cl for their anion dependency, and for a common anion, the V_ϕ^0 values increase with the elongation of alkyl chain of cation in the sequence [OMIm]Br > [HMIm]Br > [BMIm]Br. The standard partial molar volumes also increase when both cation and anion get larger as the order [EMIm][ESO_4] > [MMIm][MSO_4].

The variation of standard partial molar volume with temperature is shown as follows

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{5}$$

in which a_0, a_1, and a_2 have been evaluated by the least-squares fitting of apparent molar volume at different temperatures. Differentiation of eq 5 with respect to temperature at constant pressure gives the partial molar expansibilities (E_ϕ^0) using the following relation

$$E_\phi^0 = \left(\frac{\partial V_\phi^0}{\partial T}\right)_P = a_1 + 2a_2 T \tag{6}$$

The obtained values of E_ϕ^0 are listed in Table 3. Obviously, the E_ϕ^0 values at all temperatures are positive, which indicates that the standard partial molar volumes increase with the increase of temperature (see Figure 2). When the solution is heated, some water molecules may be released from the hydration layers of IL, which results in a rise in the solution volume a little more rapidly than that observed with pure water, so E_ϕ^0 would be positive.

The values of the isobaric thermal expansion coefficient of ILs at infinite dilution (α_{IL}) are determined using the following equation

$$\alpha_{IL} = \frac{E_\phi^0}{V_\phi^0} \tag{7}$$

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Table 3. Coefficients of Redlich−Mayer and Pitzer Equations, Partial Molar Expansibilities (E_ϕ^0), Isobaric Thermal Expansion Coefficients (α_{IL}), and Hepler Constants of Aqueous IL Solutions at Different Temperatures

	Redlich−Mayer					Pitzer			
T	V_ϕ^0	E_ϕ^0	B_V	$10^3 \cdot \alpha_{IL}$	$(\partial^2 V_\phi^0/\partial T^2)_P$	$V_\phi^0/$	$10^{11} \cdot \beta_V^0$	$10^{11} \cdot \beta_V^1$	$10^{14} \cdot C_V$
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-1}$	$cm^3 \cdot kg \cdot mol^{-2}$	K^{-1}	$cm^3 \cdot mol^{-1} \cdot K^{-2}$	$cm^3 \cdot mol^{-1}$	$g \cdot mol^{-1} \cdot Pa^{-1}$	$g \cdot mol^{-1} \cdot Pa^{-1}$	$g^2 \cdot mol^{-2} \cdot Pa^{-1}$
[BMIm]Cl					$-8.50 \cdot 10^{-4}$				
288.15	161.27 ± 0.01	0.177	−4.68 ± 0.11	1.099		161.36 ± 0.04	−0.0006	0.0014	−0.0017
298.15	163.09 ± 0.01	0.168	−7.27 ± 0.07	1.035		163.23 ± 0.04	−0.0019	0.0004	0.0030
308.15	164.60 ± 0.03	0.160	−8.27 ± 0.19	0.974		164.81 ± 0.04	−0.0015	0.0014	−0.0005
318.15	166.25 ± 0.05	0.151	−10.13 ± 0.33	0.913		166.04 ± 0.06	−0.0022	−0.0025	0.0035
[BMIm]Br					$-4.00 \cdot 10^{-4}$				
288.15	167.95 ± 0.03	0.152	−2.79 ± 0.24	0.904		168.00 ± 0.02	−0.0004	0.0005	−0.0002
298.15	169.42 ± 0.02	0.148	−3.05 ± 0.20	0.872		169.24 ± 0.02	−0.0003	−0.0010	−0.0001
308.15	170.92 ± 0.03	0.144	−4.45 ± 0.25	0.841		170.62 ± 0.04	−0.0003	−0.0014	−0.0006
318.15	172.31 ± 0.03	0.140	−5.35 ± 0.22	0.811		171.85 ± 0.03	−0.0009	−0.0032	0.0023
[BMIm][BF_4]					$-1.75 \cdot 10^{-3}$				
288.15	184.16 ± 0.03	0.237	2.72 ± 0.23	1.286		183.88 ± 0.03	−0.0029	0.0037	0.0035
298.15	186.15 ± 0.01	0.219	1.93 ± 0.10	1.178		186.54 ± 0.01	−0.0022	−0.0001	0.0034
308.15	188.69 ± 0.01	0.202	−2.88 ± 0.13	1.069		188.73 ± 0.03	−0.0015	0.0023	0.0030
318.15	190.33 ± 0.03	0.184	−3.04 ± 0.23	0.968		190.84 ± 0.03	−0.0013	−0.0000	0.0027
[HMIm]Br					$-2.35 \cdot 10^{-3}$				
288.15	199.51 ± 0.04	0.231	−4.15 ± 0.30	1.157		199.80 ± 0.04	−0.0010	0.0018	0.0001
298.15	201.79 ± 0.03	0.207	−4.94 ± 0.21	1.027		201.58 ± 0.03	−0.0006	−0.0011	−0.0002
308.15	203.61 ± 0.05	0.184	−5.09 ± 0.41	0.903		203.46 ± 0.04	0.0004	0.0015	−0.0060
318.15	205.42 ± 0.04	0.160	−5.57 ± 0.34	0.780		205.85 ± 0.04	−0.0013	0.0024	0.0010
[OMIm]Br					$4.80 \cdot 10^{-3}$				
288.15	231.06 ± 0.03	0.237	−5.05 ± 0.23	1.027		231.70 ± 0.02	−0.0007	0.0051	−0.0039
298.15	233.73 ± 0.05	0.285	−5.70 ± 0.39	1.216		233.85 ± 0.03	−0.0008	0.0017	−0.0012
308.15	236.71 ± 0.03	0.333	−5.84 ± 0.22	1.403		236.64 ± 0.03	−0.0014	−0.0011	0.0026
318.15	240.34 ± 0.05	0.380	−6.54 ± 0.39	1.582		240.65 ± 0.08	−0.0005	0.0031	−0.0044
[MMIm][MSO_4]					$-5.05 \cdot 10^{-3}$				
288.15	157.00 ± 0.02	0.222	2.79 ± 0.14	1.414		157.32 ± 0.01	0.0010	0.0027	−0.0031
298.15	158.95 ± 0.01	0.172	−0.54 ± 0.07	1.079		159.30 ± 0.01	0.0000	0.0024	−0.0014
308.15	160.44 ± 0.01	0.122	−2.22 ± 0.12	0.754		160.71 ± 0.01	−0.0002	0.0020	−0.0016
318.15	161.38 ± 0.01	0.071	−2.48 ± 0.09	0.437		161.79 ± 0.03	0.0001	0.0033	−0.0037
[EMIm][ESO_4]					$-4.90 \cdot 10^{-3}$				
288.15	189.68 ± 0.03	0.196	−2.44 ± 0.36	1.032		189.44 ± 0.01	−0.0005	−0.0020	0.0021
298.15	191.30 ± 0.10	0.147	−2.49 ± 1.50	0.767		191.12 ± 0.05	0.0007	−0.0003	−0.0064
308.15	192.66 ± 0.06	0.098	−2.79 ± 0.72	0.507		192.57 ± 0.02	−0.0016	−0.0005	0.0065
318.15	193.30 ± 0.03	0.049	−4.81 ± 0.38	0.252		193.54 ± 0.02	−0.0006	0.0021	−0.0010

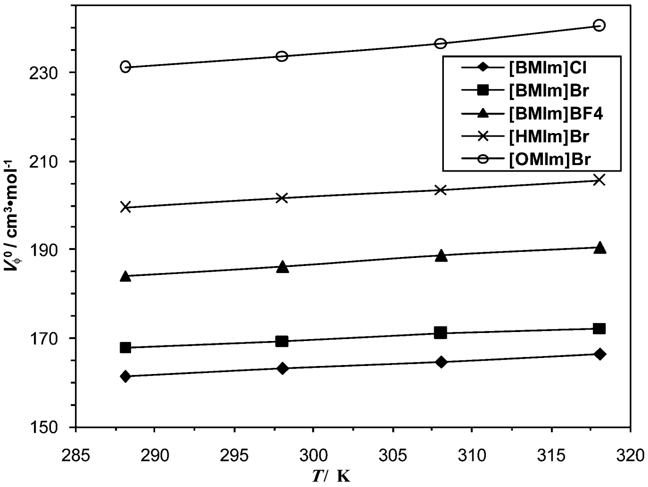

Figure 2. Influence of cation and anion on the standard partial molar volumes of ILs in aqueous solutions.

The coefficient of thermal expansion is a measure for the response of a system's volume to an increase in temperature. The larger α_{IL} value means that the volume of the system is more sensitive versus a change of temperature. Table 3 reveals that among the studied ILs, [OMIm]Br has the largest α_{IL} values at all temperatures except for 288.15 K.

Hepler's constant is another useful thermodynamic parameter that provides qualitative information about the structure-making or -breaking ability of a solute in solution.[15] This parameter is defined as follows

$$\left(\frac{\partial C_P^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 V_\phi^0}{\partial T^2}\right)_P = -T\left(\frac{\partial E_\phi^0}{\partial T}\right)_P \tag{8}$$

where C_P^0 is the heat capacity of solute at infinite dilution. If the sign of $(\partial^2 V_\phi^0/\partial T^2)_P$ is negative, then the solute is a structure breaker; otherwise, it is a structure maker. Table 3 shows that the $(\partial^2 V_\phi^0/\partial T^2)_P$ values of all the ILs with the exception of [OMIm]Br are negative, indicating that the ILs act as a structure breaker in water.

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CONCLUSIONS

The influence of the cation and anion of ILs on their volumetric properties was studied via density measurements of aqueous solutions of the ILs [BMIm]Cl, [BMIm]Br, [BMIm][BF_4], [HMIm]Br, [OMIm]Br, [MMIm][MSO_4], and [EMIm]-[ESO_4] at T = (288.15 to 318.15) K. The standard partial molar volumes of the ILs with the cation $[BMIm]^+$ show the order $BF_4^- > Br^- > Cl^-$, and those of the ILs with the common anion Br^- have the order $[OMIm]^+ > [HMIm]^+ > [BMIm]^+$. The V_ϕ^0 values also increase as both the cation and anion of IL become larger in the sequence [EMIm][ESO_4] > [MMIm]-[MSO_4]. The resulting positive values of partial molar expansibilities (E_ϕ^0) for all the ILs indicate that the standard partial molar volumes increase as temperature increases. Furthermore, the sign of $(\partial^2 V_\phi^0/\partial T^2)_P$ for all the ILs except for [OMIm]Br is negative, showing that these ILs behave as structure maker in aqueous media.

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Notes

The authors declare no competing financial interest.

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