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Densities, excess molar and partial molar volumes for water + 1-butyl- or, 1-hexyl- or, 1-octyl-3-methylimidazolium halide room temperature ionic liquids at T = (298.15 and 308.15) K

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Experimental densities for seven mixtures of water + 1-butyl-3-methylimidazolium iodide, [C_4mim][I], + 1-hexyl-3-methylimidazolium chloride, [C_6mim][Cl], + 1-hexyl-3-methylimidazolium bromide, [C_6mim][Br], + 1-hexyl-3-methylimidazolium iodide, + [C_6mim][I], 1-octyl-3-methylimidazolium chloride, [C_8mim][Cl], + 1-octyl-3-methylimidazolium bromide, [C_8mim][Br] and + 1-octyl-3-methylimidazolium iodide, [C_8mim][I]) were measured across the composition at T = (298.15 and 308.15) K and atmospheric pressure. The excess molar volumes, V_m^E, were calculated and their compositional variation was mathematically represented by Redlich–Kister type equation. The partial excess molar volumes of water as well as the corresponding RTIL were calculated across the composition. The partial molar volumes at infinite dilution for the respective components and the corresponding standard transfer volumes for different combinations of water + RTIL mixtures were also calculated.

1. Introduction

Room temperature ionic liquids (RTILs) are salts that are in liquid form at the room temperature. RTILs consist of bulky and asymmetric organic cations like 1-alkyl-3-methylimidazolium, or 1-alkylpyridinium, or N-methyl-N-alkylpyrrolidinium, or alkyl-ammonium or -sulfonium or -phopshonium etc. and any one of the negative ions from a wide range of species namely simple halides to inorganic anions such as tetrafluoroborate or hexfluorophosphate, or large organic anions like bistriflimide, triflate, tosylate, formate, alkylsulfate, or alkylphosphate etc. RTILs have unique and extraordinary properties such as non-volatility, non-inflammability, reasonable thermal stability, wide liquid range up to 573 K, high viscosity and also conductivity and wide electrochemical window etc. [1–3]. These novel properties distinguish RTILs from the traditional organic molecular solvents. RTILs have high solvation power and can dissolve a wide variety of solutes that include inorganic, organic and polymeric materials. RTILs have also been successfully employed either as solvents or as solvents cum catalysts for carrying out several organic reactions [4–6]. The unique combination of physical properties namely low volatility (or near zero vapor pressure) and wide liquidus range project RTILs as best suitable green solvents i.e. as suitable alternates to the damaging and volatile organic molecular solvents [7]. RTILs are also known as designer solvents because their physical properties can be drastically altered just by replacing either of the ring cation or counter anion [8].

RTILs are usually highly viscous and their viscosities can drastically be decreased by the addition of small amount of water. Most of the industrial requirements also desire simple means of altering the volumetric and transport properties of RTILs. Moreover, the volumetric properties are excellent tools to clearly understand the nature and predominance of a given type of interactions present among the ions of RTILs, RTIL and water and water……water in the aqueous solutions. Therefore, water + RTIL systems as binary liquid mixtures are interesting both from fundamental as well as applied aspects. The knowledge of the thermophysical properties of the binary mixtures of water + hydrophilic RTILs is not only very useful for designing the chemical processes involving ILs in aqueous media but also aids in inventing their novel and still unexplored new practical applications. For example, the processes involving homogenous mixtures of water and volatile organic solvents that are currently in use needs to be improved by substituting the given organic solvent with a RTIL. The accurate data on various thermophysical properties such as heat capacities, phase equilibria, excess molar enthalpies and excess molar volumes etc. are highly desired for the simulation and the design of industrial processes.

In view of the above, attempt was made to analyze the limiting apparent molar volumetric and compressibility properties (as derived from the experimental densities and speeds of sound) of either dilute solutions of 1-butyl-3-methylimidazolium bromide (bmimBr) in aqueous or alcoholic (methanol, ethanol) media [9], or for 1-hexyl-3-methylimidazolium bromide and water mixtures [10], or of aqueous or alcoholic mixtures of 1-propyl-, 1-hexyl-, 1-heptyl, 1-octyl-3-methylimidazolium bromides [11] in terms of RTIL–water interactions. It has been suggested that in the dilute solution region,

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RTIL–water interactions are stronger than IL–methanol or IL–ethanol interactions because of poorer hydrogen bonding capacity of the latter [9,11]. However at high concentrations of RTILs, the hydration around the IL molecules increases and this leads to so called hydrophobic or cage association in which the alkyl chains occupy the intermolecular cavities of an ice-like water structures [10,11]. Gomez et al. [12] have reported the excess molar volumes, V_m^E and viscosity deviations for water + 1-hexyl-3-methylimidazolium chloride or + 1-octyl-3-methylimidazolium chloride binary mixtures across the composition and at different temperatures. The V_m^E values were negative with a minimum around a water mole fraction of ~0.55 and become positive in water rich mole fractions. The authors had attributed these trends in terms of strong hydrogen bonding between the RTIL and water and dissociation of the ions of the ionic liquids at higher concentrations. Even though the strong hydrogen bonding interactions between the ionic liquid molecules and water quite obviously and predominately contribute to the interaction between the two components, the nature of the ring cation as well as hydration characteristics of counter anion are also expected to play a very important role in the overall RTIL–water interactions. Systematic thermophysical and thermodynamic studies on water + RTIL systems (in which the cation of RTILs is fixed and while the hydrophilic character of anion is varied) are very scarce in the literature. Only one such study on excess molar volumes and excess molar enthalpies for water + RTILs based on 1-ethyl- or 1-butyl–3-methylmidazolium cation with different anions namely methylsulfate or ethylsulfate, trifluoromethanesulfonate, or tetrafluoroborate has been reported [13]. It was suggested that the relative affinity of different anions towards water is crucial in deciding the type and magnitude of RTIL–water interactions in the bulk state.

Therefore it is thought that the systematic measurements on the thermophysical properties of water + ionic liquid systems consisting of RTILs prepared from the same cation but different anion of varying hydrophilic character would be very useful and help understand the nature and type of interactions in such systems. The availability of different RTILs with variation in the chemical structure of the cations for binary liquid mixture studies always poses a limitation because the methylimidazolium halides with alkyl chains (higher than C_8 atoms) and most of the pyridine based ILs are solids at room temperature. In the present study, we report the volumetric properties (derived from experimental densities) for seven binary mixtures of water + 1-butyl-3-methylimidazolium iodide, [C_4mim][I], + 1-hexyl-3-methylimidazolium iodide, [C_6mim][I], + 1-octyl-3-methylimidazolium iodide, [C_8mim][I], + 1-hexyl-3-methylimidazolium bromide, [C_6mim][Br], + 1-octyl-3-methylimidazolium bromide, [C_8mim][Br], + 1-hexyl-3-methylimidazolium chloride, [C_6mim][Cl], + 1-octyl-3-methylimidazolium chloride, [C_8mim][Cl], across the composition and at T = (298.15 and 308.15) K. The excess molar volumes, (V_m^E), partial molar volumes of water ($\overline{V}_1$), partial excess molar volumes of water $\left(\overline{V}_1^E\right)$, partial molar volumes of water at infinite dilution $\left(\overline{V}_1^\infty\right)$, partial molar volumes of ionic liquids ($\overline{V}_2$), partial excess molar volumes of ionic liquids $\left(\overline{V}_2^E\right)$ and partial molar volumes of ionic liquids at infinite dilution, $\left(\overline{V}_2^\infty\right)$ were calculated. The standard transfer volumes were also calculated for different combinations of water + RTILs. The analysis of the volumetric functions was done to adjudge the effect of anion environment on the overall volumetric changes at infinite dilution. The chemical structures of the RTILs are particularly chosen so that effects for example, of the chain length of the alkyl branch and hydrophilic character of simple non-hydrolyzable anions namely Cl^- or Br^- or I^- on the bulk interactions can be assessed in aqueous RTIL systems.

2. Experimental

1-Methylimidazole (Alfa Aesar, 99%) was freshly distilled over potassium hydroxide. Chlorohexane (Merck, ≥98%), bromohexane (analytical reagent grade of local make, 98%), chlorooctane (Merck, ≥98%), bromooctane (Spectrochem, India, 98%) were dried over fused calcium chloride and freshly distilled prior to use. Butyl iodide (analytical reagent grade) was purchased locally and was twice recrystallized before use.

2.1. Synthesis of ionic liquids

The general procedure of the synthesis involved a direct reaction between 1-methylimidazole and excess amount of respective haloalkane (iodobutane, chlorohexane, bromohexane, chlorooctane or bromooctane) in acetonitrile at 473.15 K for 1.5 to 3 h. The reactions were conducted under nitrogen blanket in a round bottom flask equipped with reflux condenser and magnetic stirrer. The resulting products were cooled to room temperature by adding 100 cm^3 of analytical reagent grade ethyl acetate under thorough mixing. The excess ethyl acetate was then decanted and the procedure was repeated four times.

2.2. [C_6mim][I] and [C_8mim][I]

These ionic liquids were synthesized from their respective chloride counter parts by an ion exchange reaction. Equimolar solutions of chloride based IL and sodium iodide solutions were mixed in acetone by adding the sodium iodide solution drop wise under stirring at room temperature over a period of three hours. The sodium chloride formed was then slowly got precipitated out during the reaction and the same was removed by filtration. The supernatant liquid was dried in an oven at 343.15 K to evaporate most of the acetone. The product thus obtained was further purified by two cycles of dissolving it first in dichloromethane followed by an extraction of the final product into triple distilled water. Through this process, the organic impurities present (if any) were removed. The ionic liquid samples were characterized by ^{1}H NMR. The chemical shifts and assigned protons for individual RTILs are:

[C_4mim][I]. ^{1}H NMR (400 MHz, D_2O,δ ppm), 0.936 (3H,t, J = 7.0 Hz, N-$(CH_2)_3$-*CH_3*), 1.333 (6H, m, N -CH_2 -CH_2-*CH_2*-CH_3), 1.865 (2H, m, N-CH_2-*CH_2*-CH_2-CH_3), 3.916 (3H, S, N-*CH_3*), 4.218 (2H, t, J = 7 Hz, N-*CH_2*-CH_2-CH_2-CH_3), 7.456 (H, d, *H5*), 7.519 (H, d, *H4*), 8.769 (H, s, *H2*).
[C_6mim][Cl]. 0.790 (3H,t, J = 7.2 Hz, N-$(CH_2)_7$-*CH_3*), 1.225 (6H, m, N -CH_2 -CH_2-*$(CH_2)_3$*-CH_3), 1.807 (2H, m, N-CH_2-*CH_2*-$(CH_2)_3$-CH_3), 3.840 (3H, S, N-CH_3), 4.137 (2H, t, J = 7 Hz, N-*CH_2*-CH_2-$(CH_2)_3$-CH_3), 7.382 (H, d, *H5*), 7.427 (H, d, *H4*), 8.664 (H, s, *H2*).
[C_6mim][Br]. 0.808 (3H,t, J = 7.0 Hz, N-$(CH_2)_7$-*CH_3*), 1.256 (6H, m, N -CH_2 -CH_2-*$(CH_2)_3$*-CH_3), 1.843 (2H, m, N-CH_2-*CH_2*-$(CH_2)_3$-CH_3), 3.899 (3H, S, N-CH_3), 4.192 (2H, t, J = 7 Hz, N-*CH_2*-CH_2-$(CH_2)_3$-CH_3), 7.462 (H, d, *H5*), 7.501 (H, d, *H4*), 8.767 (H, s, *H2*).
[C_6mim][I]. 0.891 (3H,t, J = 7.0 Hz, N-$(CH_2)_7$-*CH_3*), 1.349 (6H, m, N -CH_2 -CH_2-*$(CH_2)_3$*-CH_3), 1.928 (2H, m, N-CH_2-*CH_2*-$(CH_2)_3$-CH_3), 3.966 (3H, S, N-*CH_3*), 4.264 (2H, t, J = 6.8 Hz, N-*CH_2*-CH_2-$(CH_2)_3$-CH_3), 7.517 (H, d, *H5*), 7.568 (H, d, *H4*), 8.818 (H, s, *H2*).
[C_8mim][Cl]. 0.783 (3H,t, J = 7.0 Hz, N-$(CH_2)_7$-*CH_3*), 1.205 (10H, m, N CH_2-CH_2-*$(CH_2)_5$*-CH_3), 1.802 (2H, m, N-CH_2-*CH_2*-$(CH_2)_5$-CH_3), 3.816 (3H, S, N-CH_3), 4.113 (2H, t, J = 7 Hz, N-*CH_2*-CH_2-$(CH_2)_5$-CH_3), 7.351 (H, d, *H5*), 7.395 (H, d, *H4*), 8.627 (H, s, *H2*)
[C_8mim][Br]. 0.824 (3H,t, J = 7.0 Hz, N-$(CH_2)_7$-*CH_3*), 1.245 (10H, m, N CH_2-CH_2-*$(CH_2)_5$*-CH_3), 1.906 (2H, m, N-CH_2-*CH_2*-$(CH_2)_5$-CH_3), 3.965 (3H, S, N-CH_3), 4.277 (2H, t, J = 7.2 Hz, N-*CH_2*-CH_2-$(CH_2)_5$-CH_3), 7.562 (H, d, *H5*), 7.586 (H, d, *H4*), 8.995 (H, s, *H2*)
[C_8mim][I]. 0.828 (3H,t, J = 7.0 Hz, N-$(CH_2)_7$-*CH_3*), 1.287 (10H, m, N CH_2-CH_2-*$(CH_2)_5$*-CH_3), 1.901 (2H, m, N-CH_2-*CH_2*-$(CH_2)_5$-CH_3), 3.984 (3H, S, N-CH_3), 4.299 (2H, t, J = 7.4 Hz, N-*CH_2*-CH_2-$(CH_2)_5$-CH_3), 7.589 (H, d, *H5*), 7.607 (H, d, *H4*), 8.995 (H, s, *H2*).

The water content of the RTILs was determined by using Karl Fischer titrator and water mass fractions were found to range from

5.5×10^{-4} to 7.8×10^{-6} depending upon the length of the alkyl chain. The purity of ionic liquids was estimated by potentiometric titration by argentometric method in which 10 cm^3 of aliquot solution was titrated with $AgNO_3$ solution standardized against a 0.015 mol dm^{-3} of NaCl using $AgCrO_4$ as indicator. The estimated purity of the ionic liquids is ≥97% (on mole basis). Ionic liquids were stored in glass bottles under inert atmosphere and were dried for 24 h at T = 343.15 K under vacuum before use.

2.3. Methods

The binary solutions were prepared by mass in hermetically sealed glass vials. The solutions of each composition were prepared fresh and the densities were measured the same day. The mass measurements, accurate to ±0.01 mg, were made on a single pan analytical balance (Dhona 100 DS, (India)). The estimated uncertainty in the mole fraction was ±0.0001.

Densities, ρ of the pure liquids and their mixtures were measured with a high precision vibrating tube digital density meter (Anton Paar, DMA 5000). The instrument has a built-in thermostat for maintaining the desired temperatures in the range of (273 to 363) K. The repeatability of the temperature has been found to be (±0.002 and ±0.003) K within a given session and/or for two successive sessions respectively. The uncertainty in the temperature during the measurements, however is ±0.01 K because Pt 100 measuring sensors were used. The instrument was calibrated with air, four times distilled and freshly degassed water. The repeatability in the densities for the distilled water, pure ionic liquids and as prepared binary mixture solutions was found to be better than 3×10^{-6} g · cm^{-3}. We have estimated the uncertainty in our measured densities of the pure liquids by comparing our data with the literature values, as listed in Table 1. This comparison gave a mean absolute deviation of 9.0×10^{-4} g · cm^{-3}. It may be mentioned here that the availability of densities of pure RTILs is still very limited in the literature. Even among the available data, the values need to be taken with caution as they are dependent highly on the purity levels. Our measured densities for distilled water match excellently well with literature but the experimental densities of the RTILs deviated by 1.0×10^{-5} to 4.5×10^{-3} g · cm^{-3} with the literature values. Hence the precision and accuracy for the densities reported in the present work are 3.0×10^{-6} and 9.0×10^{-4} g · cm^{-3} respectively.

3. Results and discussion

The experimental data of ρ at T = (298.15 and 308.15) K for the seven binary mixtures are listed in Table 2. Excess molar volumes, V_m^E are calculated using the equation:

$$V_m^E = V - x_1 V_{1.m}{}^{*} + x_2 V_{2.m}{}^{*} \quad (1)$$

Table 1
Densities, ρ for pure water and RTILs at T (298.15 and 308.15) K along with the literature values.

	ρ/(gm.cm^{-3})			
	T = 298.15 K		T = 308.15 K	
	Exp.	Lit.	Exp.	Lit.
[C_4mim][I]	1.484210		1.480731	
[C_6mim][Cl]	1.044202	1.039670 [12]	1.038401	1.033960 [12]
[C_6mim][Br]	1.229168		1.222396	
[C_6mim][I]	1.340202		1.332801	
[C_8mim][Cl]	1.008810	1.008882 [12]	1.003049	1.003060 [12]
[C_8mim][Br]	1.173207		1.166677	
[C_8mim][I]	1.233638		1.225420	
Water	0.997045	0.997043 [11]	0.994029	0.994029 [11]

where V is the volume of a mixture containing 1 mole of IL + water, x_1 and x_2 are the mole fractions of water and IL, respectively. $V_{1.m}^*$ and $V_{2.m}^*$ are the molar volumes of the pure components.

Eq. (1) can be re-casted as:

$$V_m^E/\left(cm^3 \cdot mol^{-1}\right) = \{(x_1 M_1 + x_2 M_2)/\rho_{12}\} - \{(x_1 M_1/\rho_1) + (x_2 M_2/\rho_2)\} \quad (2)$$

where M_1, M_2, ρ_1 and ρ_2 are the molar mass and density of respective pure components and ρ_{12} is the density of mixture of a specified mole fraction for water and IL, respectively.

The V_m^E values were fitted through Redlich–Kister equation of type,

$$Y^E = x_1\,(1-x_1)\sum_{i=0} a_i\,(1-2x_1)^i \quad (3)$$

where $Y^E = V_m^E$ and a_i are the fitting coefficients. a_i were estimated by multiple regression analysis based on a least squares method. The summary of a_i along with the standard deviation, σ between calculated and fitted values is given in Table 3. The graphical variation of V_m^E as a function of water mole fraction for water + RTIL mixtures at T (298.15 to 308.15) K is shown in parts a and b of Fig. 1. An examination of the trends in V_m^E curves gave an interesting insight into the bulk interactions among different halide based RTILs and water mixtures. It can be seen that the volumetric behavior is highly dependent on the nature of the halide ion. In the present study, Cl^-, Br^- and I^- ions are particularly selected because their relative hydration and water binding capacity are not only inversely related but are also different in that order. The features of V_m^E curves for the binary mixtures of water + ILs are as described below:

Cl^- based RTILs: The water + 1-hexyl-, and + 1-octyl-3-methylimidazolium chlorides mixtures were characterized predominantly by negative lobes followed by near zero or slight positive values in the water rich region. The increase in the temperature from (298.15 to 308.15) K increased the positive or negative values (as the case may be). The V_m^E values for the water + [C_6mim][Cl] and + [C_8mim][Cl] mixtures at T = 298.15 K have also been reported by Gomez et al. [12]. The V_m^E values for the same mixtures and at the same temperature but calculated for the mole fractions of the present study, using the fitting coefficients reported by the authors are also shown in part a of Fig. 1. It can be seen that our values match excellently with the literature reported data.

Br^- based RTILs: The nature of the V_m^E curves is similar to that in water + Cl^- based RTIL mixtures i.e. sigmoidal with a negative lobe covering most of the mole fractions of water followed by slight positive values in the water rich region. The mole fraction corresponding to the crossover from negative to positive region was however higher in [C_8mim][Br] + water mixtures.

I^- based RTILs: The binary mixtures of water + 1-butyl-, or 1-hexyl-, or 1-octyl-3-methylimidazolium iodides are characterized by exclusive positive values across the composition. The values increased with the increase in the carbon chain length of alkyl branch from butyl to octyl chains.

The magnitude of equimolar $(V_m^E)x_{1=0.5}$ at T = 298.15 K, for a given alkylmethylimidazolium cation but with different halide anions followed the order:

[C_6mim][Cl] < [C_6mim][Br] < [C_6mim][I] and [C_8mim][Br] < [C_8mim][Cl] < [C_8mim][I],

Table 2
Experimental densities, ρ for water (1) + RTILs (2) at T = (298.15 and 308.15) K.

ρ/(gm.cm^{-3})								
Water (1) + [C_4mim][I] (2)			Water (1) + [C_6mim][Cl] (2)			Water (1) + [C_6mim][Br] (2)		
x_1			x_1			x_1		
T in K	298.15	308.15		298.15	308.15		298.15	308.15
0.0191	1.482978	1.479342	0.0300	1.044459	1.038356	0.0447	1.228661	1.221820
0.0497	1.481008	1.477180	0.0362	1.044499	1.038351	0.0630	1.228448	1.221586
0.0615	1.480236	1.476362	0.0609	1.044648	1.038327	0.0631	1.228446	1.221583
0.1004	1.477632	1.473683	0.1146	1.044848	1.038325	0.1473	1.227241	1.220308
0.1512	1.474021	1.470107	0.1842	1.044976	1.038435	0.1892	1.226420	1.219481
0.2014	1.470124	1.466319	0.3345	1.045186	1.038998	0.2770	1.224007	1.217076
0.2503	1.465916	1.462244	0.3545	1.045218	1.039089	0.3453	1.221287	1.214400
0.3009	1.461032	1.457484	0.4119	1.045330	1.039313	0.3982	1.218594	1.211754
0.3488	1.455831	1.452352	0.4617	1.045394	1.039434	0.4844	1.212867	1.206143
0.3990	1.449677	1.446202	0.4847	1.045393	1.039446	0.4979	1.211808	1.205096
0.4988	1.434728	1.431058	0.5568	1.045236	1.039220	0.5595	1.206294	1.199696
0.5506	1.425163	1.421276	0.5999	1.044920	1.038817	0.6011	1.201856	1.195339
0.5992	1.414678	1.410555	0.6597	1.044036	1.037749	0.6629	1.193922	1.187554
0.6596	1.398909	1.394482	0.7034	1.042930	1.036497	0.7065	1.187046	1.180805
0.7007	1.385806	1.381191	0.8031	1.037997	1.031313	0.7993	1.166674	1.160804
0.7507	1.366108	1.361353	0.9035	1.026547	1.020317	0.8970	1.126504	1.121346
0.8034	1.338642	1.333861	0.9098	1.025445	1.019305	0.9109	1.117412	1.112456
0.8793	1.276920	1.272480	0.9299	1.021405	1.015609	0.9299	1.102586	1.097859
0.9041	1.246647	1.242425	0.9512	1.016126	1.010841	0.9367	1.096388	1.091791
0.9133	1.233396	1.229308	0.9810	1.006059	1.001921	0.9774	1.044647	1.040860
0.9323	1.201613	1.197701						
0.9518	1.160835	1.157183						
0.9684	1.117125	1.113690						
0.9811	1.075942	1.072701						
Water (1) + [C_6mim][I] (2)			Water (1) + [C_8mim][Cl] (2)			Water (1) + [C_8mim][Br] (2)		
0.0211	1.339252	1.331384	0.0278	1.008917	1.003118	0.0250	1.173259	1.166702
0.0488	1.337846	1.329526	0.0441	1.008987	1.003166	0.0507	1.173257	1.166672
0.0667	1.336852	1.328331	0.0769	1.009147	1.003295	0.0692	1.173224	1.166621
0.0888	1.335557	1.326852	0.0975	1.009260	1.003395	0.1059	1.173100	1.166457
0.1888	1.328933	1.320219	0.1389	1.009516	1.003626	0.1986	1.172466	1.165702
0.2501	1.324517	1.316124	0.2395	1.010295	1.004399	0.2226	1.172229	1.165429
0.3026	1.320630	1.312542	0.3045	1.010883	1.004995	0.2975	1.171304	1.164360
0.3488	1.317124	1.309263	0.3388	1.011205	1.005323	0.3262	1.170852	1.163846
0.3976	1.313306	1.305595	0.3812	1.011598	1.005724	0.3886	1.169619	1.162474
0.4439	1.309511	1.301839	0.4527	1.012201	1.006324	0.4441	1.168152	1.160872
0.4989	1.304616	1.296837	0.5098	1.012567	1.006681	0.4840	1.166785	1.159417
0.5898	1.294832	1.286606	0.5508	1.012728	1.006812	0.6138	1.159571	1.151992
0.6438	1.287275	1.278683	0.6015	1.012761	1.006811	0.6499	1.156456	1.148854
0.6898	1.279150	1.270296	0.6510	1.012564	1.006550	0.7004	1.150865	1.143312
0.8079	1.245132	1.236262	0.7212	1.011774	1.005677	0.7928	1.135183	1.127973
0.9004	1.187748	1.180393	0.7833	1.010423	1.004249	0.8975	1.100287	1.094162
0.9111	1.177317	1.170282	0.8989	1.005598	0.999688	0.9115	1.092844	1.086984
0.9305	1.154887	1.148514	0.9100	1.004923	0.999105	0.9297	1.081424	1.075904
0.9504	1.125577	1.119948	0.9322	1.003426	0.997900	0.9494	1.066006	1.060995
0.9808	1.060505	1.056363	0.9502	1.002043	0.996869	0.9797	1.032185	1.028195
			0.9799	0.999326	0.995138			
Water (1) + [C_8mim][I] (2)								
0.0190	1.232937	1.224690						
0.0510	1.231702	1.223404						
0.0904	1.230099	1.221735						
0.1558	1.227281	1.218816						
0.1930	1.225606	1.217086						
0.2071	1.224960	1.216422						
0.3000	1.220544	1.211919						
0.3570	1.217654	1.209013						
0.3858	1.216129	1.207491						
0.4450	1.212787	1.204177						
0.5290	1.207339	1.198822						
0.6197	1.199793	1.191451						
0.6530	1.196331	1.188076						
0.7373	1.184790	1.176793						
0.8540	1.155282	1.147960						
0.9047	1.130561	1.123840						
0.9390	1.103808	1.097796						
0.9500	1.092227	1.086520						
0.9724	1.060996	1.056211						
0.9790	1.049060	1.044588						
0.9810	1.045111	1.040760						

Table 3
Coefficients, a_i (in $cm^3\ mol^{-1}$) of Eq. (3) and root mean square deviation, σ (in $cm^3\ mol^{-1}$) for the mathematical representation of excess molar volumes for water (1) + RTIL (2) mixtures at T = (298.15 and 308.15) K.

Water +	T/K	a_0	a_1	a_2	a_3	σ
[C_4mim][I]	298.15	1.397	0.265	−0.984	−1.695	0.001
	308.15	1.466	0.718	−0.423	−2.702	0.001
[C_6mim][Cl]	298.15	−2.112	−1.052	0.372	1.971	0.001
	308.15	−1.972	−0.934	1.717	1.144	0.001
[C_6mim][Br]	298.15	−0.582	2.438	−0.306	−1.780	0.001
	308.15	−0.484	2.320	−0.201	−1.792	0.001
[C_6mim][I]	298.15	3.493	−3.200	−0.890	3.503	0.001
	308.15	3.816	−2.609	1.077	0.979	0.001
[C_8mim][Cl]	298.15	−2.226	−0.233	1.924	0.943	0.001
	308.15	−2.088	−0.099	2.362	0.997	0.001
[C_8mim][Br]	298.15	−2.413	0.840	2.067	2.144	0.001
	308.15	−1.937	1.122	1.877	1.896	0.001
[C_8mim][I]	298.15	4.151	−1.334	0.147	1.442	0.001
	308.15	4.547	−1.589	0.215	1.693	0.001

*

and similarly for a fixed halide anion but with different alkylimidazolium cations followed:

[C_4mim][I]<[C_6mim][I]<[C_8mim][I]; [C_8mim][Br]<[C_6mim][Br] and [C_8mim][Cl]<[C_6mim][Cl].

Unlike non-electrolyte + water mixtures, the ionic liquid + water systems contain ions and hence the interactions in such mixtures are quite complex. The strong Columbic interactions between the cation and anion on the one hand and the significant cation–cation aggregation on the other hand lead to a kind of supra-molecular organization among IL molecules [14–17]. RTIL + water binary mixtures are expected to be characterized mainly by two types of interactions namely structure making and/or structure breaking. The net interactions get reflected in the sign and the magnitude of the excess molar volumes. Negative V_m^E values in general indicate that the molecular state in the bulk state is characterized by the presence of compact structures. Specific interactions between the RTIL and water would favor the formation of such compact structures. Free volume effect, interstitial accommodation of one of the components into the structure of the other and condensation of negative ions on the positive cationic surface would also contribute to the negative V_m^E values. The predominance of structure breaking effects on the other hand would result in positive V_m^E values [14–17]. Therefore, the observed negative V_m^E values for chloride or bromide based RTIL + water mixtures are attributable to the predominance of structure making interactions over RTIL–RTIL repulsive interactions in the bulk state. On similar lines, it is not unreasonable to state that structure making interactions in water + I^- based RTILs are probably responsible for the observed positive excess molar volumes in these mixtures. Moreover I^- ions being least hydrating and would occupy most of the outer shell around the cation and therefore suppress the RTIL–water structure making interactions considerably.

3.1. Partial molar volumes and transfer functions

The partial molar volume for a given component in a mixture ($\overline{V}_i$) is generally defined by

$$\overline{V}_i = (\partial V/\partial n_i)_{T,P,ni} \tag{4}$$

The following equations can be obtained by differentiation of Eq. (1) followed by its combination with Eq. (4):

$$\overline{V}_1 = V_m^E + V_{1.m}{}^* - x_2\left(\partial V_m{}^E/\partial x_2\right)_{P,T} \tag{5}$$

and

$$\overline{V}_2 = V_m^E + V_{2.m}{}^* + (1-x_2)\left(\partial V_m{}^E/\partial x_2\right)_{P,T} \tag{6}$$

where $\overline{V}_1$ and $\overline{V}_2$ are the partial molar volumes of water and RTIL respectively.

Differentiation of Redlich–Kister equation (Eq. (3)) with respect to x_2 and substitution of the result into Eqs. (5) and (6) give the following relations for the partial molar volumes of water $\overline{V}_1$ and RTIL, $\overline{V}_2$ [18]:

$$\overline{V}_1 = V_{1.m}{}^* + x_2^2 \sum_{i=0} a_i\ (1-2x_2)^i + 2x_2^2\ (1-x_2) \sum_{i=0} i a_i\ (1-2x_2)^{i-1} \tag{7}$$

$$\overline{V}_2 = V_{2.m}{}^* + x_1^2 \sum_{i=0} a_i\ (1-2x_2)^i - 2x_2\ (1-x_2)^2 \sum_{i=0} i a_i\ (1-2x_2)^{i-1} \tag{8}$$

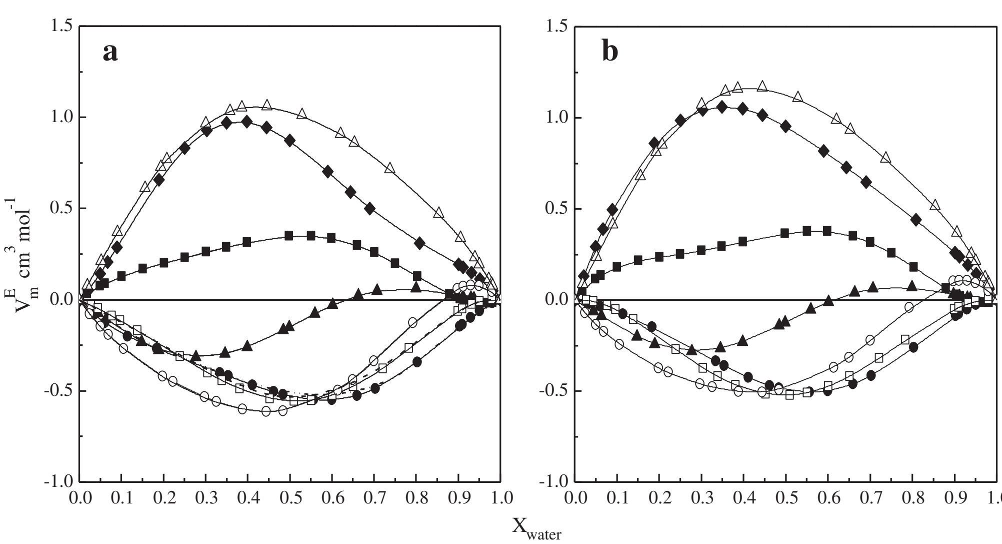

Fig. 1. Excess molar volume, V_m^E for water (1) + RTIL (2) binary mixtures at (a) T = 298.15 K and (b) T = 308.15 K: water + (■) [C_4mim][I], + (●) [C_6mim][Cl], + (▲) [C_6mim][Br], + (◆) [C_6mim][I], + (□) [C_8mim][Cl], + (○) [C_8mim][Br] and + (Δ) [C_8mim][I]. The symbols are experimental points and the solid lines correspond to the correlations by the Redlich–Kister equation (Eq. (3)), —————— are the literature data from ref [12].

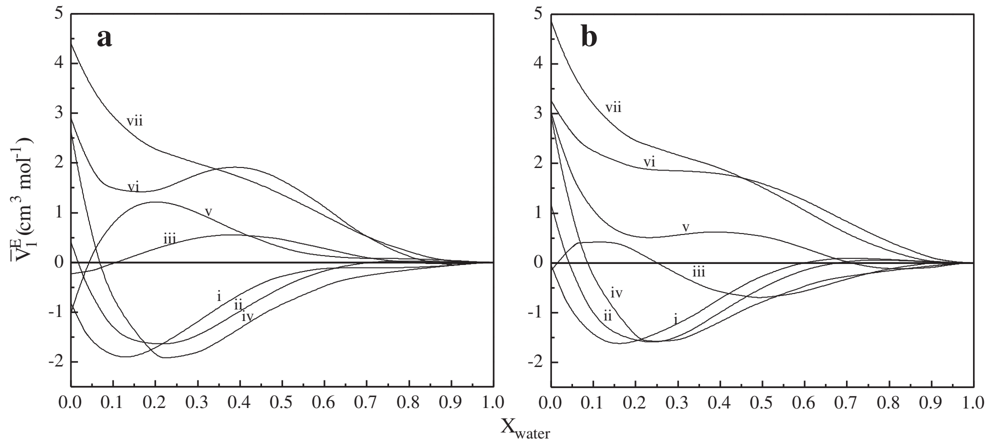

Fig. 2. Partial excess molar volume of water, $\overline{V}_1^E$ plotted against the mole fraction of water in water + RTIL binary mixtures at (a) T = 298.15 K and (b) T = 308.15 K: Water + (i) [C_6mim][Cl], + (ii) [C_8mim][Cl], + (iii) [C_6mim][Br], + (iv) [C_8mim][Br], + (v) [C_4mim][I], + (vi) [C_6mim][I], + (vii) ([C_8mim][I]. Lines are the guide to the eye.

The partial molar excess volumes of the ith component, $\overline{V}_1^E$ can then be defined by

$$\overline{V}_i^{\,E} = \overline{V}_i - V_{i.m}^{\;*} \tag{9}$$

By inserting $x_2 = 1$ (i.e. $x_1 = 0$) in Eq. (7), one gets

$$\overline{V}_1^{\infty} = V_{1.m}^{\;*} + \sum_{i=0} a_i\,(-1)^i \tag{10}$$

and similarly, putting $x_2 = 0$ (i.e. $x_1 = 1$) in Eq. (8), one obtains:

$$\overline{V}_2^{\infty} = V_{2.m}^{\;*} + \sum_{i=0} a_i \tag{11}$$

where $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$ are the partial molar volume of water at infinite dilution in RTIL and the partial molar volume of RTIL at infinite dilution in water. Eqs. (10) & (11) were used to calculate the partial molar volumes of the respective components at infinite dilution across the composition.

The profiles depicting the variation of $\overline{V}_1^E$ and $\overline{V}_2^E$ as a function of mole fractions of water or RTIL are shown in Figs. 2 and 3. It can be seen from Fig. 2 that the V_1^E values at high water mole fractions (≥0.8) are close to zero while the values in the rest of the mole fraction range displayed positive or negative curvatures depending on the given RTIL. For example, water + [C_6mim] [Cl] or + [C_8mim] [Cl] mixtures were mostly characterized by negative values. The curve for water + [C_6mim] [Br] was sigmoidal with initial negative values followed by a positive lobe. While the same for water + [C_8mim] [Br] was characterized by initial positive values which decreased and become negative with the increase in the water mole fraction. The curves for water + [$C_n$mim] [I] mixtures in general are characterized by positive values (only exception being the curve for water + [C_4mim] [I] mixture, which displayed an initial negative region). The increase in temperature from (298.15 to 308.15) K in general resulted in the increase of values in the respective region. These described trends indicate that the liquid mixtures of water + halide based alkylimidazolium RTILs are characterized by a complex mix of interactions. To specify which type of interactions occurs at the molecular level is out of scope of the present investigation. Otherwise, the negative $\overline{V}_1^E$ values in general indicate the predominance of water–water structure making interactions and while positive $\overline{V}_1^E$ values as recorded for water + [$C_n$mim] [I] (where n = 4, or 6, or 8) mixtures suggest that the disruption of water–water interactions (i.e. the hydrogen bonding net work within the water molecules gets weakened in presence of the RTIL). The polarizability of the halide ions follows the order: $I^- > Br^- > Cl^-$ and in fact the detailed Raman and IR spectral studies indeed confirmed that the hydrogen bonding among the tetrahedrally coordinated water structures gets

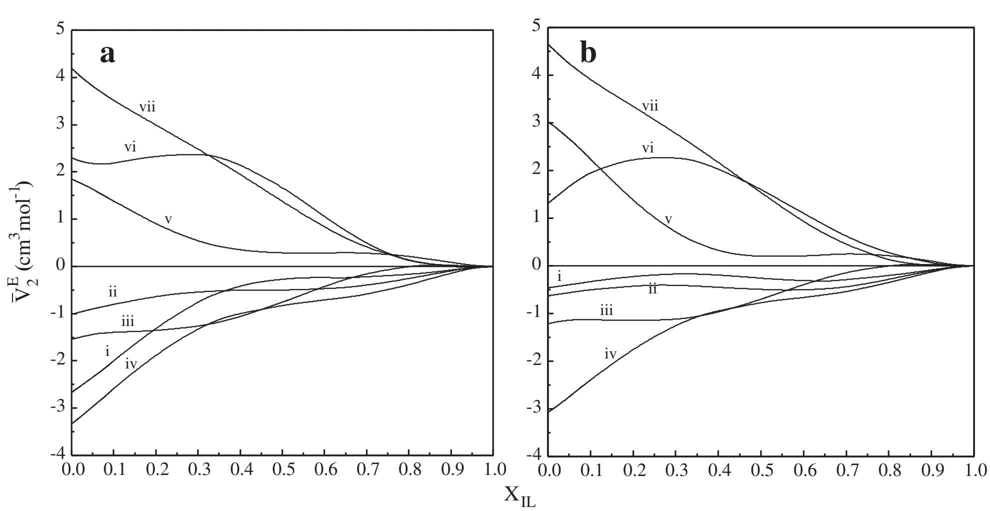

Fig. 3. Partial excess molar volumes of IL, $\overline{V}_1^E$ plotted against the mole fraction of ionic liquids in water + IL binary mixtures at (a) T = 298.15 K and (b) T = 308.15 K: Water + (i) [C_6mim][Cl], + (ii) [C_8mim][Cl], + (iii) [C_6mim][Br], + (iv) [C_8mim][Br], + (v) [C_4mim][I], + (vi) [C_6mim][I], + (vii) ([C_8mim][I]. Lines are guide to the eye.

Table 4
Partial molar volumes at infinite dilution, $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$ and standard transfer volumes, $\overline{V}_{1\,tr}^{\infty}$ and $\overline{V}_{2\,tr}^{\infty}$ in water (1) + RTIL (2) mixtures at T = (298.15 and 308.15) K.

T/K	V_1^{∞} (cm^3 mol^{-1})			$V_1{}^{\infty}{}_{tr}$ (cm^3 mol^{-1})		
	Water + [C_6mim][Cl]	Water + [C_6mim][Br]	Water + [C_6mim][I]	[C_6mim][Cl] → [C_6mim][Br]	[C_6mim][Br] → [C_6mim][I]	[C_6mim][Cl] → [C_6mim][I]
298.15	17.248	17.839	20.975	0.591	3.136	3.727
308.15	18.078	17.966	21.386	−0.112	3.420	3.308
	Water + [C_8mim][Cl]	Water + [C_8mim][Br]	Water + [C_8mim][I]	[C_8mim][Cl] → [C_8mim][Br]	[C_8mim][Br] → [C_6mim][I]	[C_8mim][Cl] → [C_8mim][I]
298.15	18.477	20.707	22.475	2.230	1.768	3.998
308.15	19.295	21.081	22.989	1.786	1.908	3.694
	V_2^{∞} (cm^3 mol^{-1})			$V_2{}^{\infty}{}_{tr}$ (cm^3 mol^{-1})		
	Water + [C_6mim][Cl]	Water + [C_6mim][Br]	Water + [C_6mim][I]	[C_6mim][Cl] → [C_6mim][Br]	[C_6mim][Br] → [C_6mim][I]	[C_6mim][Cl] → [C_6mim][I]
298.15	198.902	197.765	223.604	−1.137	25.839	24.702
308.15	197.556	198.782	219.481	1.226	20.699	21.925
	Water + [C_8mim][Cl]	Water + [C_8mim][Br]	Water + [C_8mim][I]	[C_8mim][Cl] → [C_8mim][Br]	[C_8mim][Br] → [C_6mim][I]	[C_8mim][Cl] → [C_8mim][I]
298.15	230.243	236.246	259.681	6.003	23.435	29.438
308.15	230.900	236.743	261.475	5.843	24.732	30.575

systematically weakened in the presence of large and highly polarizable halide anions for aqueous sodium halide solutions [19].

The $\overline{V}_2^E$ vs X_{IL} profiles (Fig. 3) have also presented interesting trends. Except at very high RTIL mole fractions, the profiles displayed significant and notable changes in the sign and magnitude of $\overline{V}_2^E$ values. The $\overline{V}_2^E$ vs X_{IL} curves for water + ($C_n$mim][I] (where n = 4, or 6, or 8)) mixtures were characterized by positive values which decreased smoothly with the increase in the mole fraction of RTIL in water + [C_4mim][I], or + [C_8mim][I] mixtures. The large and positive $\overline{V}_2^E$ values indicate that water addition significantly weakens the RTIL cation–cation interactions that are otherwise predominantly present in the supra molecular structures of pure RTILs [13–16]. The $\overline{V}_2^E$ values for water + chloride or bromide based RTILs are negative and become less negative with the increase in the IL mole fraction. The negative $\overline{V}_2^E$ values may arise due to the contributions from either RTIL–RTIL interactions and/or minimum structural disruptions in the supra-molecular state of RTILs.

A comparison of the water or RTIL component behavior in water + RTIL mixtures can be made by defining the standard transfer volumes (partial molar volumes at infinite dilution, $\overline{V}_{1\,tr}^{\infty}$ and $\overline{V}_{2\,tr}^{\infty}$) and the same is defined by the following relation:

$$Y_s^{m\rightarrow n} = Y_s^{\infty(n)} - Y_s^{\infty(m)} \tag{12}$$

where $Y_s^{\infty(n)}$ and $Y_s^{\infty(m)}$ are the partial molar volumes of water or RTIL in water + RTIL mixtures, n and m correspond to the ionic liquids as shown to the right and left hand part of the arrow marks shown in the minor headings of column nos. 5–7 of Table 4. It can be seen from the data given in columns 5–7 of Table 4 that $\overline{V}_{1\,tr}^{\infty}$ values for a given RTIL are positive when Cl^- ion is replaced by Br^- and become more positive upon the replacement of Cl^- by I^- as counter anion. Similarly, successive replacement of Br^- with I^- also resulted into positive transfer volumes. These trends clearly indicate that the larger the counter anion and the higher its polarization, the stronger would be its interaction with cation and such interactions induce water–water structure breaking interactions. The replacement of Cl^- with Br^- or I^- resulted into positive $V_2^{\infty}{}_{tr}$ values for a given RTIL (an exception was found for [C_6mim][Cl] → [C_6mim][Br] at 298.15 K). Interestingly, the replacement of Br^- with I^- ion also resulted in large and positive transfer values. As mentioned earlier, I^- ions are closely bound to the RTIL cation and can thus affectively neutralize the positive charge and therefore weaken the supra-molecular organization of pure RTILs and contribute positively to $V_2^{\infty}{}_{tr}$.

4. Conclusions

The binary mixtures of water + ($C_n$mim][X], where n = 4, or 6, or 8 and X = Cl^- or Br^- and I^- are characterized by complex mix of structure breaking and making interactions. The analysis of excess molar volumes, partial molar volumes and related functions of these mixtures revealed that in water + Cl^- or Br^- based RTIL mixtures, structure making interactions are more prevalent and while water + I^- based RTIL mixtures are characterized predominantly by structure breaking interactions. The relative polarizability of halide anions plays a key role on the nature of interactions in such mixtures.

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