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

Nandhibatla V. Sastry *, Nilesh M. Vaghela, Pradip M. Macwan

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar - 388120, Gujarat, India

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ABSTRACT

Experimental densities for seven mixtures of water + 1-butyl-3-methylimidazolium iodide, [C$_4$mim][I], + 1-hexyl-3-methylimidazolium chloride, [C$_6$mim][Cl], + 1-hexyl-3-methylimidazolium bromide, [C$_6$mim][Br], + 1-hexyl-3-methylimidazolium iodide, + [C$_6$mim][I], 1-octyl-3-methylimidazolium chloride, [C$_8$mim][Cl], + 1-octyl-3-methylimidazolium bromide, [C$_8$mim][Br] and + 1-octyl-3-methylimidazolium iodide, [C$_8$mim][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.

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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 electro-chemical 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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* Corresponding author. Fax: +91 2692 236475.
E-mail address: nvsastry17@gmail.com (N.V. Sastry).

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-methylimidazolium 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 $\left(\overline{V}_2\right)$, 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