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Experimental and theoretical excess molar properties of imidazolium based ionic liquids with molecular organic solvents – I. 1-Hexyl-3-methylimidazlouim tetraflouroborate and 1-octyl-3-methylimidazlouim tetraflouroborate with cyclic ethers

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ABSTRACT

Experimental densities, ρ, speeds of sound, u, and refractive indices, n_D for pure 1-hexyl-3-methylimidazolium tetrafluoroborate ([C_6mim][BF_4]), 1-octyl-3-methylimidazolium tetrafluoroborate ([C_8mim][BF_4]), 1,4 Dioxane (DO) and (THF) between the temperature (293.15 to 323.15 K) at 5 K interval and their binary mixtures at T = (298.15, 308.15 and 318.15) K at entire range of composition have been measured using an Anton-Paar DSA 5000 and Abemmete refractometer. Experimental measurements were used to estimate Rao's molar sound functions, R, excess molar volumes, V_m^E, excess molar isentropic compressibilities, $\kappa_{s,m}^E$, refractive indices deviations $\Delta_\phi n_D$ and deviation in molar refraction, ΔR_m. Excess properties have been fitted to the Redlich–Kister polynomial equation and binary coefficients were obtained. V_m^E and $\kappa_{s,m}^E$ were observed to be negative and decrease with increasing temperature, whereas $\Delta_\phi n_D$ was found to be positive and increases with temperature over the entire composition range. Equations of state and several mixing rules were used to predict refractive indices of the binary mixtures and compared with the experimental values by means of the standard deviation and found to be in excellent agreement. Intermolecular interactions between the unlike molecules of the mixtures have been discussed by well known arguments. Excess molar volumes of the binary mixtures have been analyzed by Prigogine–Flory–Patterson (PFP) theory and results were compared with the experimental results.

1. Introduction

The unique physicochemical properties of room-temperature ionic liquids (RTILs), also named as the 'Designer Solvents', such as low melting point, higher thermal stability, large liquidious range, wide range electrochemical windows, high conductivity, solubility in many organic and inorganic compounds and negligible vapor pressure makes them the most permissive in the scientific community [1–4]. The properties of ILs, which can be tailor made either by changing the cations and/or anions are density, viscosity, surface tension, melting point, polarity, conductivity, and miscibility with water or molecular solvents [5–11]. Various advantages of using ILs in the industrial and academic research include: applicability in catalytic and biocatalytic reactions, in W/IL micro and nanoemulsions, in various synthetic reactions as solvents, in designing the process in chemical industries, in polymerization, electrochemical industry, fuel and solar cell technology, thermal fluids, chromatography as the stationary phase, synthesis of liquid crystals and nano-materials, *etc.* [12–15]. Many technological processes involving ILs require the knowledge of thermophysical properties of mixing them with organic molecular solvents. To understand the interactions of their constituting cations and anions with the molecular solvents, the behavior of ILs when mixed with molecular organic solvents is of utmost importance.

Systematic investigation of the physicochemical properties of ILs with molecular organic solvents including water [16–19], alkanols [20–32], acetonitrile [30–34], alkoxyalkanol [35,36], hydrocarbons [31,32,36], and nitromethane [26,37] have been reported but the data with cyclic ether solvents are scanty [38]. Cyclic ethers are industrially important solvents in many chemical reactions such as in synthetic and natural resins, in extraction of animal and vegetable oils, an important precursor in bio-systems, in adhesives, organic synthesis, as a cosolvent in printing inks, synthesis of PVC to name a few [39–42]. In continuation to our previous work on thermodynamic, acoustic and optical properties of the binary

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mixtures of various organic solvents including ILs at several temperatures [43–47], here we report the effect of the chain length of the ILs on the physicochemical properties of mixing with molecular organic solvents (cyclic ethers). The thermo-physical properties of the most popular hydrophilic ionic liquids, 1-hexyl-3-methylimidazolium tetrafluoroborate ([C_6mim][BF_4]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([C_8mim][BF_4]) with cyclic ethers, tetrahydrofuran (THF) and 1,4 Dioxane (DO) had been investigated.

Physical properties such as densities, ρ speeds of sound, u, and optical property such as refractive index, n_D, and various derived thermodynamic properties, Rao's molar sound function, R, excess molar volumes, V_m^E, excess molar isentropic compressibility, $\kappa_{s,m}^E$, refractive indices deviations, $\Delta_\phi n_D$ and molar refraction deviation, ΔR_M for [C_6mim][BF_4] and [C_8mim][BF_4] with THF and DO over the entire range of composition and at temperature (298.15, 308.15 and 318.15) K at atmospheric pressure had been investigated here. Several mixing rules were applied to predict the refractive index and viscosity of the mixtures from the pure data and the results were in very good agreement with the experimental results. The Prigogine–Flory–Patterson (PFP) theory [48–51] has also been examined to estimate V_m^E for the investigated mixtures and the results were compared with the experimental data.

2. Experimental

2.1. Synthesis of ILs

The synthetic procedure adopted here comprises of two steps [52,53], first step include the formation of the halide intermediate which follows the anion exchange by the tetrafluoroborate anion. The brief procedure is discussed here with the characterization:

Reaction between the excess molar amount of alkyl bromide (1-bromohexane for [C_6mim][BF_4] and 1-bromooctane for [C_8mim][BF_4]) and 1-methylimidazole in 1,1,1-trichloroethane was carried out under reflux conditions and at ca. 343 K for 48 h. Solvent was removed under reduced pressure and bromide intermediate was purified from the unreacted reagent by repeated recrystallization (ethyl acetate/acetonitrile, 3:2 by volume). The aqueous solution of pure bromide intermediate was further reacted with aqueous excess sodium tetraflouroborate to form the desired IL. The purification procedure comprise of extraction by dichloromethane. The unreacted bromide was removed by repeated washing with water [52]. Rotary evaporator was used to remove dichloromethane used in the extraction. All of the ILs were dried under vacuum at 343 K for (2 to 3) days in the presence of P_2O_5. The water content measured using a Karl Fisher titration (Metrohm, 890 Titrando) of the synthesized ILs was lower than 100 ppm. The ILs were also analyzed by ^{1}H NMR and ^{13}C NMR (Advance DPX 200 Bruker, CSMCRI) to confirm the absence of any major impurities.

[C_6mim][BF_4]: The ^{1}H NMR (200 MHz, DMSO-d6, δ ppm): 0.86 (3H, t, N—$(CH_2)_5$—CH_3), 1.27 (br. S, 6H, N—CH_2—CH_2—**$(CH_2)_3$**—CH_3), 1.78 (2H, quintet, N—CH_2—**CH_2**—$(CH_2)_3$—CH_3), 3.85 (3H, singlet, N—CH_3), 4.15 (t, 2H, N—**CH_2**—CH_2—$(CH_2)_3$—CH_3), 7.70 (s, 1H), 7.77 (s, 1H), 9.10 (s, 1H). ^{13}C—NMR (200 MHz, 16.14, 24.18, 27.43, 31.69, 38.10, 41.85, 51.02, 124.56, 125.86, 136.82).

[C_8mim][BF_4]: (200 MHz, DMSO-d6): 0.86 (3H, t, N—$(CH_2)_5$—**CH_3**), 1.25 (br. S, 10H, N—CH_2—CH_2—**$(CH_2)_5$**—CH_3), 1.78 (2H, quintet, N—CH_2—**CH_2**—$(CH_2)_5$—CH_3), 3.85 (3H, singlet, N—**CH_3**), 4.15 (t, 2H, N—**CH_2**—CH_2—$(CH_2)_5$—CH_3), 7.70 (s, 1H), 7.77 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (200 MHz, 16.13, 24.14, 27.83, 30.59, 33.27, 38.37, 51.57, 79.13, 121.21, 123.82, 125.65, 138.13).

2.2. Materials

1-Methylimidazole (>0.99), sodium tetrafluoroborate, 1-bromohexane (>0.98), and 1-bromooctane (>0.98) were purchased from spectrochem and the molecular organic solvents ethyl acetate (>0.995), acetonitrile (>0.995), and 1,1,1-trichloroethane (>0.995) were from Merck. DO (>0.995) and THF (>0.990) obtained from Merck and were stored over KOH [54] and fractionally distilled. Gas chromatography with semi capillary methyl silicone column (OD: 530 μm) and a flame-ionization detector was used to check the purities of the chemicals. Purity of DO and THF were better than 0.996 and 0.993, respectively. The details of the chemicals used in the present work with their purity and method used for purification are also given in table 1. Experimental densities, speeds of sound and refractive index of the synthesized ILs and molecular organic solvents used in the current study were compared with the reported literature [20–24,37,55–89] and are summarized in table 2.

Analytical balance (B 204-S, Mettler Toledo, Switzerland) operated in the dry box to protect the samples from the atmospheric moisture with an uncertainty of $\pm 1 \cdot 10^{-7}$ kg was used to prepare the mixtures by mass such that the estimated uncertainty in the mole fraction must be less than $\pm 1 \cdot 10^{-4}$.

2.3. Apparatus and procedure

2.3.1. Densities and speeds of sound

Density and speeds of sound were automatically and simultaneously measured by Anton-Paar DSA 5000 digital vibrating tube densimeter. The instrument controls the temperature by ±0.001 K with built in solid-state thermostat. The instrument was calibrated by the air free double distilled water. Cyclohexane + benzene was used as the test system to check the performance of the instrument by comparing V_m^E and κ_S^E with the literature values [90–94]. The estimated uncertainty for density and speeds of sound were lower than ± 0.001 kg $\cdot$ m^{-3} and ± 0.01 m $\cdot$ s^{-1} respectively and for excess molar volume to be less than $\pm 0.0002 \cdot 10^{-6}$ m^3 $\cdot$ mol^{-1}.

TABLE 1
CAS number, supplier and purity of components at $T = 298.15$ K.

Component	CAS number	Supplier	Initial Purity in mass fraction	Final	Purification Method
1,4 Dioxane	123-91-1	Merck	0.995	0.996	F.D.[a]
THF	109-99-9	Merck	0.990	0.993	F.D.[a]
1-Methylimidazole	616-47-7	Spectrochem	0.99		None
1-Bromohexane	111-25-1	Spectrochem	>0.98		None
1-Bromooctane	111-83-1	Spectrochem	>0.98		None
Ethyl acetate	141-78-6	Merck	0.995		None
Acetonitrile	75-05-8	Merck	0.995		None
Dichloromethane	75-09-2	Merck	0.995		None

[a] F.D. = fractional distillation.