J. Chem. Thermodynamics 98 (2016) 298–308

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

The study of molecular interactions in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate + 1-pentanol from density, speed of sound and refractive index measurements

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ARTICLE INFO

Article history:
Received 5 January 2016
Received in revised form 27 February 2016
Accepted 8 March 2016
Available online 11 March 2016

Keywords:
[Emim][Triflate]
1-Pentanol
Density
Speed of sound
Refractive index
Excess/deviation properties

ABSTRACT

A molecular interaction study is carried out between the ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-pentanol using the experimental values of density, speed of sound and refractive index measurements over the whole composition range as a function of temperature between (298.15 and 328.15) K at atmospheric pressure. The excess/deviation properties, such as molar volumes (V_m^E), partial molar volumes ($\overline{V}_m^E$), partial molar volumes at infinite dilution ($\overline{V}_m^{E,\infty}$), isentropic compressibility (κ_s^E), free length (L_f^E), speeds of sound (u^E), refractive index ($\Delta_\phi n_D$) and isobaric thermal expansion coefficient (α_P^E) obtained from the experimental values are fitted into the Redlich–Kister type equation to obtain the binary coefficients and the standard deviations. The negative values of excess properties such as V_m^E, κ_S^E, L_f^E, α_P^E and the positive values of u^E, $\Delta_\phi n_D$ clearly indicated the existence of strong molecular interactions between the studied components. The values of $\left(\frac{\partial V_m^E}{\partial T}\right)_P$ and $\left(\frac{\partial H_m^E}{\partial P}\right)_T$ are also calculated to support the existing interactions. A quantitative analysis of these parameters is further supported by IR spectroscopic analysis.

1. Introduction

It is well known that Ionic liquids (ILs) are a class of ionic, non-molecular solvents which are exists as liquids at temperatures below 100 °C. These contains variety of properties such as low to negligible vapor pressure [1], high thermal stability, broad liquid temperature ranges [2,3], non-flammability [4,5] and good solvation capacity with water or various organic solvents [6]. Further, IL's also often considered as designer solvents just because of flexibility of varying cation and anion for specific application [7]. The application of ILs are not limited but varies in the broad field of separations [8–10], heat transfer fluids [11–13], processing biomass [14] and electrochemical applications [15], catalysis for clean technology and polymerization processes [9,14,16,17], catalysis [18], CO_2 capture [19,20] and cellulose dissolution [21,22].

However, the present day industry needs for new development which in turn demands for the accurate description of the thermophysical properties which are essential to understand thermophysical behavior of ILs which are not clearly understood so far. So, to exploit the potential of pure component and its mixtures, it would be of great value to have correlation, prediction, simulation and optimization of theoretical model and for such as thermophysical properties like density, speed of sound and refractive index are the basic requirements. In addition, by knowing the excess properties we can better understand the structure-property relation, making it easier choosing an appropriate IL. Therefore, IL + solvent mixtures have received growing attention in the past years [2,23,24].

Systematic investigation of the physicochemical properties of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][Triflate]) with molecular organic solvents including water have been reported by various authors [25–33]. Rodriguez and Brennecke [25] reported the density data of binary mixtures of [Emim][Triflate] with water. Vercher et al. [26,27] studied

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http://dx.doi.org/10.1016/j.jct.2016.03.014
0021-9614/

volumetric and ultrasonic studies with water, methanol, ethanol, 1-propanol, 2-propanol and THF. On the other hand, Miaja et al. [28–30] studied excess volumetric, heat capacities and enthalpies with nitromethane, ethanol and water. Wong et al. [31] studied density of aqueous solutions. Vercher et al. [32,33] reported refractive indices with methanol, ethanol, 1-propanol, 2-propanol, water, acetone, methyl acetate, and ethyl acetate. As per the knowledge of authors, no study have been reported for the binary mixture of [Emim][Triflate] with 1-pentanol.

The choice of the investigated IL, [Emim][Triflate] is done on the basis of its capability to act as solvent for extractive distillation [34]. It is also widely used in electropolymerization [35,36], in electrophoresis [37] and as corrosion inhibitors for CO_2 capture applications [38]. On the other hand, 1-pentanol, which is an industrially important organic solvent has been used in many chemical processes. The mixtures containing 1-pentanol are very important from theoretical point of view, not only because of their self-association, but also due to the strong intermolecular effects produced due to the presence of –OH. Besides its use as a good industrial solvent, 1-pentanol is also used as an intermediate in the production of many organic compounds, pharmaceuticals, lubricants, lubricant additives, production of liquid crystals, flavourings, special catalysts and as an extracting agent [39]. So, because of this wide range of industrial applications of [Emim][Triflate] and 1-pentanol individually, encouraged us to measure the thermophysical properties and understand its interaction behavior.

The IL [Emim][Triflate] is found to be totally miscible with 1-pentanol in all proportions, therefore initially we wished-for measurement of the physical properties like densities, ρ, speeds of sound, u and refractive index, n_D of the binary mixtures of [Emim][Triflate] with 1-pentanol at $T = (298.15–328.15)$ K in the entire composition range and at atmospheric pressure. Later, on the basis of the measured values, we have calculated the excess/deviation properties for their potential application in industrial processes. Here, we reported the properties such as excess molar volume, V_m^E, excess isentropic compressibility, κ_S^E, free length (L_f^E), speed of sound (u^E), isobaric thermal expansion coefficient (α_P^E). Also, the deviation of refractive index on volume fraction basis, $\Delta_\phi n_D$ for binary mixtures and fitted using Redlich–Kister type polynomial equation. Further, an attempt is made to understand the interaction behavior in the studied binary mixture using IR spectral data.

2. Experimental

2.1. Material

The IL 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][Triflate]) (CAS 145022-44-2) with purity of 0.99 mass fraction is acquired from IoLiTec (Germany), while the 1-pentanol (CAS 71-41-0) is supplied by Sigma Aldrich. The chemicals used in the study are purified by the methods described in literature [47]. The details of suppliers and the purity for pure compounds are reported in Table 1. The water content of investigated IL and 1-pentanol are determined using a Karl Fischer titrator (Metrohm, 890 Titrando). [Emim][Triflate] is dried in vacuum of 0.1 Pa for about 72 h at moderate temperature (beginning at room temperature and increasing it gradually over a 6 h period up to 333 K) and 1-pentanol is purified by distillation technique. The water content of all the samples is further checked and found to be in the range of less than 50 ppm, a value much lower than the original pre-evacuation analysis, which typically showed values in the range of less than 200×10^{-6}. The purities of IL and solvent are verified by comparing the measured density, speed of sound and refractive index of the pure liquids with the literature at atmospheric pressure which are presented in Table 2.

2.2. Apparatus and procedure

2.2.1. Sample preparation

All samples are freshly prepared in Amber glass vials with screw caps having PFE septa, and sealed with parafilm to prevent absorption of moisture from the atmosphere, and are then stirred for more than 30 min to ensure total dissolution of the mixtures. Samples are taken from the vials with a syringe through the PFE septum. The mass of the dry bottle is first determined. The less volatile component (RTIL) of the mixture is then introduced in to the bottle and mass is recorded. The other component (organic liquid) is added and the mass of bottle including two components is determined. Samples are weighed using Mettler Toledo AB 135 balance with a precision of ±0.01 mg. The uncertainty of the resulting mole fractions of the mixtures is estimated as being $\pm 2 \times 10^{-4}$.

2.2.2. Measurement of density and speed of sound

Densities and speed of sound are measured with an Anton Paar DSA-5000M vibrating tube density and sound velocity meter. The density meter is calibrated with doubly distilled degassed water, and with dry air at atmospheric pressure. The temperature of the apparatus is controlled to within ±0.01 K by a built-in Peltier device that corresponds to an uncertainty in density of ±0.0002%. Measured density and speed of sound values (at a frequency approximately 3 MHz) are precise to $5 \times 10^{-3}\ \mathrm{kg \cdot m^{-3}}$ and $5 \times 10^{-1}\ \mathrm{m \cdot s^{-1}}$ respectively. The standard uncertainties associated with the measurements of temperature, density and speed of sound are estimated to be ±0.01 K, $\pm 1\ \mathrm{kg \cdot m^{-3}}$ and $\pm 0.5\ \mathrm{m \cdot s^{-1}}$ respectively.

2.2.3. Measurement of refractive index

The refractive indices are determined using an automatic refractometer (Anton Paar Dr KrenchenAbbemat (WR-HT)) that also has a temperature controller that keeps the samples at working temperature. The uncertainties in the temperature and refractive index values are ±0.01 K and $\pm 5 \times 10^{-5}$, respectively. The apparatus is calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (supplied by the company) before each series of measurements according to manual instructions. The calibration is checked with pure liquids with known refractive index.

Table 1
List of chemicals with details of provenance, CAS number, and mass fraction purity.

Chemical	Provenance	CAS number	Purification method	Mass fraction purity	Final water mass fraction	Analysis method
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	Io-Li-Tec, Germany	145022-44-2	Vacuum treatment	0.99	$<5 \times 10^{-5}$	NA
1-Pentanol	Sigma Aldrich	71-41-0	Distillation	0.99	$<5 \times 10^{-5}$	Gas liquid chromatography