



Densities and refractive indices of the deep eutectic solvents (choline chloride + ethylene glycol or glycerol) and their aqueous mixtures at the temperature ranging from 298.15 to 333.15 K

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ABSTRACT

Deep eutectic solvents (DES) are new emerging alternatives to conventional ionic liquids that may find a number of interesting applications in industrial and chemical processes. In this study, the densities, ρ , and refractive indices, n_D , of the DESs (choline chloride + ethylene glycol) and (choline chloride + glycerol) and their aqueous mixtures were investigated at atmospheric pressure over the temperature range 298.15–333.15 K and across a complete composition range. The excess molar volumes, V^E , and refractive index deviations, Δn_D , were also calculated from experimental results. The calculated excess molar volumes were negative at all temperatures over the entire range of composition considered, suggesting the presence of strong interactions between water and the DES in the mixtures. The refractive index deviations, on the other hand, were found positive in the entire concentration range. The calculated properties were fitted to a Redlich–Kister type equation to correlate them to the temperature and composition. The correlations used satisfactorily represent the densities and refractive indices of the pure DESs and their aqueous binary mixtures as functions of temperature and composition as indicated by the low overall average absolute deviations obtained in the calculations.

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1. Introduction

Room temperature ionic liquids (RTILs) have attracted significant research interest over the last decades owing to their unique physical and chemical properties *i.e.* extremely low vapor pressures, high thermal stability, high solvation capacity, non-flammability, high thermal conductivity and wide liquid range [1–3]. RTILs, being designer solvents, have huge number of possible applications in electrochemical, analytical, synthetic and engineering processes [4,5]. They have been used as gas absorption media (*i.e.* CO₂ removal), heat transfer fluids, solvents in electroplating and catalysts in organic and chemical synthesis [6–8]. However, most RTILs work at the disadvantage of high cost for bulk applications. They are relatively expensive and some of them even have very low tolerance to moisture [6]. Furthermore, their toxicology has yet to be examined and some studies suggest for further assessment of their applicability as green media [9].

Recently emerging alternatives to conventional RTILs are deep eutectic solvents (DESs). They belong to a new class of ionic liquids that are made by mixing a substituted quaternary ammonium salt

(*i.e.* 2-hydroxy-*N,N,N*-trimethylethanaminium [choline] chloride) and a hydrogen bond donor (*i.e.* amide, carboxylic acid or alcohol), both of which having high melting points, to form a eutectic mixture with a substantially lower melting point [4,10]. They were found to have solvent properties similar to those of RTILs while possessing several advantages over the latter. DESs are easier to prepare in high purity and at a relatively cheaper cost. Many of them are biodegradable and the toxicology of their components is well characterized [9–11]. It is due to these unique features of DESs that they are considered as potential green solvents for a number of industrial applications. Recent researches reported the applicability of DESs as solvents in the bulk processing of metals [12–14], biodiesel purification [15,16], polymer synthesis [17,18], drug solubilization [11], biological transformations [19,20], carbon-carbon nanotube composite preparation [21], and even CO₂ absorption [3,5]. DESs were also found to be viable solvents for the fabrication of novel metal surfaces and coatings (*i.e.* super-hydrophobic Ni films) [22,23] and thermochromic PVDF composite films [24].

In order to establish the possible use of deep eutectic solvents in industrial and chemical processes, it is necessary to know their physical properties including the density and refractive index. These could also provide important information on the purity of the samples and the molecular interaction in the liquid [25,26].

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To date most of these properties of DES have not yet been investigated extensively. Thus, in this work, the density, ρ , and the refractive index, n_D , of the deep eutectic solvents ethaline (1 mol choline chloride: 2 mol ethylene glycol) and glyceline (1 mol choline chloride: 2 mol glycerol) were determined at atmospheric pressure within the temperature range 298.15–333.15 K. In addition, since the properties of the DESs maybe affected by the presence of water [19–21,27] the ρ and n_D of their corresponding aqueous binary mixtures over the entire range of mole fraction ($x_1 = 0.1$ – 0.9) were also determined. Furthermore, the excess molar volume, V^E , and refractive index deviations, Δn_D , were calculated and correlated to the system's temperature and composition by fitting the experimental data into a Redlich–Kister type equation. Consequently, the resulting correlations were used to predict the density and refractive index of the binary mixtures as functions of temperature and composition. Lastly, the refractive indices of the binary mixtures were predicted using the most important mixing rules such as the Arago–Biot, Gladstone–Dale, Lorentz–Lorenz, Eykman, Weiner, Heller, Newton and Eyring–John correlations which were then compared with the experimental data.

2. Experimental

2.1. Chemicals

The pure deep eutectic solvents ethaline and glyceline (purity >98%) were obtained from Scionix Ltd[®]. They are mixtures of (choline chloride + ethylene glycol) and (choline chloride + glycerol) at 1:2 mol ratios. Each pure sample was dried under vacuum at 333 K for at least 48 h to remove any volatile impurities and stored in a dry box for further use. The water contents of the samples after drying were measured using a Mettler Toledo Karl-Fischer (model DL31) titrator and were ≤ 0.002 (mass fraction). The deionized water (Type I reagent-grade; resistivity = 18.3 M/cm; total organic carbon content (TOC) <15 ppb) used in all the experiments was processed in a Barnstead Thermolyne (model Easy Pure 1052) water purification system and degassed under vacuum prior to use. Aqueous solutions were prepared using a Mettler Toledo (model AL204) digital balance with an accuracy of $\pm 1 \times 10^{-4}$ g.

2.2. Measurement of specific density

The densities of the investigated systems were measured using an Anton Paar (model DMA 5000 M) vibrating tube density meter. It has a measurement cell that is made of a U-shaped borosilicate glass tube and that is equipped with two integrated Pt 100 platinum thermometers together with Peltier elements which controls and measures the temperature. To obtain maximum accuracy for the measurements done at higher temperatures, a temperature range adjustment was done using air and degassed deionized water at 20, 40 and 60 °C. The accuracy of the temperature measurement was ± 0.01 K. The instrument is also equipped with an integrated reference oscillator that provides long-term stability. As for viscosity-related errors, automatic correction was done using the instrument by measuring the damping effect of the sample followed by a mathematical correction of the density. Prior to the measurements, the instrument was calibrated using air and degassed deionized water as standard fluids. The estimated overall experimental uncertainty in the density measurements was $\pm 5 \times 10^{-5}$ g/cm³.

2.3. Measurement of refractive index

The refractive indices of the investigated systems were measured using an Anton Parr (model Abbemat WR) automatic refractometer utilizing a yellow light beam of 589.3 nm sodium D

line wavelength. The temperature was controlled by a built-in internal solid state Peltier thermostat fitted with two internal Pt-100 Platinum resistance temperature sensors that allowed temperature measurement to an accuracy of ± 0.03 K. For each measurement, at least 1.0 mL sample was placed on the measuring prism to minimize vaporization of the water at high temperatures. A cone-shaped yellow light beam illuminated the sample from its bottom side under different angles of reflection and then a microprocessor automatically calculates the refractive index of the sample from the obtained data. The refractometer was calibrated using deionized water and calibration was checked after every few measurements. The estimated overall uncertainty in the refractive index measurement was $\pm 5 \times 10^{-5}$.

All measurements were carried out in three to five replicate runs and the average values were reported. Prior to the analysis of the DES samples, the accuracy of the equipment and procedure used were validated first by measuring the density and refractive index of water and comparing the measurements obtained with the reference data reported by Spieweck and Bettin [28] and Schiebener et al. [29]. The average deviations found were 0.004% and 0.0003% for ρ and n_D , respectively.

3. Results and discussion

The densities and refractive indices of pure ethaline and glyceline and their aqueous binary mixtures were measured over the temperature range 293.15–323.15 K at atmospheric pressure. The experimental values are tabulated in Tables 1 and 2 for ethaline and glyceline systems, respectively. For the pure DESs, both the ρ and n_D were found to decrease linearly with temperature. Such results are expected since generally, as temperature increases substances become less dense due to thermal expansion which also results in decreased refractive index. The experimental ρ values were also compared with those reported by Shahbaz et al. [30,31] and were found to be in good agreement with those data having a maximum relative deviation of -0.01% and a minimum of -0.18% . To the best of our knowledge, no data has been reported for the n_D of the investigated DESs that no comparison was made here.

To obtain correlations for the ρ and n_D of the pure DESs as functions of temperature, the experimental values were fitted by least-squares method using a linear equation of the form

$$Y = a_0 + a_1(T/K) \quad (1)$$

where Y represents ρ , in g/cm³ or n_D ; a_0 and a_1 are empirical constants; and T is the absolute temperature in K. The determined empirical constants together with the corresponding AAD% are presented in Table 3. Based on the AAD% of 0.001 and 0.003 for ρ and n_D , respectively, it can be said that, with only two fitting parameters the proposed linear equation successfully represents the measured properties as a function of temperature.

For the binary aqueous mixtures, results showed that both the ρ and n_D of the investigated systems increased with increasing DES mole fraction. This is expected since densities and refractive indices of the pure DESs are higher than those of water. A decreasing trend in ρ and n_D with temperature was also observed which is similar to that of the corresponding pure DESs. This behavior is consistent with those observed in other aqueous ionic liquid (IL) mixtures reported in literature [32–35].

The excess molar volumes, V^E , were calculated from the experimental molar volumes of the binary mixtures using the following equation

$$V^E = \sum_{i=1}^N x_i M_i (\rho_i^{-1} - \rho^{-1}) \quad (2)$$

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