



# Densities of a deep eutectic solvent based on choline chloride and glycerol and its aqueous mixtures at elevated pressures

Rhoda B. Leron<sup>a</sup>, David Shan Hill Wong<sup>b</sup>, Meng-Hui Li<sup>a,\*</sup>

<sup>a</sup> R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chung Li 32023, Taiwan, ROC

<sup>b</sup> Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan, ROC

## ARTICLE INFO

### Article history:

Received 4 May 2012

Received in revised form 9 August 2012

Accepted 20 August 2012

Available online 28 August 2012

### Keywords:

Deep eutectic solvent

Excess molar volume

Glyceline

High-pressure density

Tait-type equation

## ABSTRACT

Deep eutectic solvents are cheap and biodegradable alternatives to conventional ionic liquids and volatile organic solvents. In this work, we present new measurements on the densities of the deep eutectic solvent choline chloride:glycerol (GLY) and its aqueous mixtures in the temperature range (298.15–323.15) K and pressures up to 50 MPa. The density was measured using a vibrating-tube density meter and the experimental uncertainty was estimated to be  $\pm 0.1\%$ . Density data were used to derive other properties such as isothermal compressibility, isobaric expansivity, and excess molar volume. The excess molar volumes of the mixtures of GLY (1) + H<sub>2</sub>O (2) were investigated and an empirical equation was used to represent their dependence on temperature, pressure, and composition. The density data at elevated pressures were correlated with the temperature, pressure, and composition by a Tait-type equation.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to their unique properties, ionic liquids (ILs) are regarded as green replacements to volatile solvents in many electrochemical, synthetic, analytical, and engineering processes [1]. However, the disadvantage is they are costly; thus, they have not yet been widely adapted for industrial applications [2]. Also, certain types of ILs (i.e. imidazolium-based) are non-biodegradable and toxic [3–5]. Thus, researchers continue to search for new and even greener alternatives to ILs that may overcome the said limitations.

An alternative class of ILs called deep eutectic solvents (DESs), which are formed by the complexation of a substituted quaternary ammonium salt with hydrogen-bond-forming compounds, has recently been investigated by Abbott et al. [6,7]. When mixed at the correct molar ratio, these compounds form a mixture with a substantially low melting point [7,8]. For example, the DES formed from choline chloride (m.p. = 302 °C) and glycerol (m.p. = 18 °C) at 1:2 molar ratio (trade name glyceline) has a melting point of  $-40$  °C [9]. DESs have also shown to have solvent properties similar to conventional ILs, including negligible volatility, high conductivity, non-flammability, high thermal and chemical stability, and high solvation capacity. But compared to ILs, DESs are desirable for large-scale applications because they can be prepared with high purity at lower costs [7]. DESs can easily be prepared by simply mixing their

individual components with gentle heating. Some DESs are already being processed in bulk or in ton scale and available for commercial use [10]. They are generally less moisture-sensitive compared to ILs [8] and many of them are made from biodegradable components, which exhibit low or non-toxicity [7,11].

Some DESs are currently being utilized in the electrodeposition, electroplating, and electropolishing of metals while their potential for other applications are also being explored [10]. Certain types of DESs have been reported to be promising solvents in enzyme-based biotransformations [12,13], solubilization of poorly soluble compounds for early drug development [14], fabrication of nanostructured Ni and composite films [15,16], and absorption of CO<sub>2</sub> [17,18]. The use of glycerol-based DES as a promising solvent in the efficient extraction of glycerol from biodiesel has also been demonstrated by several authors [9,19–21].

To assess and design the possible industrial-scale applications of DESs, it is imperative that their thermophysical properties are known. Among them is the density, which is an important physical property of any material. Very few data on the density of DESs have been reported in the literature and measurements are limited at atmospheric condition [22–24]. The objective of this work is to contribute to the database of thermodynamic properties of DESs which could be useful for future applications. Thus, we report new measurements on the densities of the deep eutectic solvent 1 mole choline chloride:2 moles glycerol (GLY) and its aqueous mixtures for pressures from (0.1 to 50) MPa and temperatures (298.15–323.15) K. Ten different compositions ( $x_1 = 0.1–1.0$ ) were considered. A Tait-type equation was used to correlate the

\* Corresponding author. Tel.: +886 3 265 4109; fax: +886 3 265 4199.  
E-mail address: [mhli@cycu.edu.tw](mailto:mhli@cycu.edu.tw) (M.-H. Li).

high-pressure density with temperature, pressure, and composition. The isothermal compressibilities and isobaric expansivities of GLY were derived from experimental density data. The excess molar volumes,  $V^E$ , of the mixtures of GLY (1) + H<sub>2</sub>O (2) were investigated, and an empirical equation proposed by Lugo et al. [25] was used to represent  $V^E$  as a function of temperature, pressure, and composition.

## 2. Materials and methods

### 2.1. Materials

The deep eutectic solvent glyceline 200 (purity >0.98 mass fraction), a mixture of choline chloride + glycerol (1:2 molar ratio), was obtained from Scionix Ltd<sup>®</sup>. The water content of the sample was measured using a Mettler Toledo Karl–Fischer (model DL31) titrator, and was found to be <0.005 (mass fraction). The sodium chloride used in the preparation of calibration solutions was American Chemical Society (ACS)-certified grade and was obtained from J.T. Baker. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF<sub>4</sub>], (purity >0.98 mass fraction) was supplied by Tokyo Chemical Co., Ltd. Prior to use, the pure [Bmim][BF<sub>4</sub>] sample was dried at 343 K for at least 48 h in an evacuated oven in order to remove any volatile impurities and to reduce the water content. The final water content of the sample was 392 ppm. Distilled deionized water (Type I reagent-grade; resistivity = 18.3 MΩ cm), which was processed in a Barnstead Thermolyne (model Easy Pure 1052) water system, was used in all the experiments. All aqueous solutions were prepared from degassed samples and weight measurements were done using a Mettler Toledo (model AL204) digital balance with an accuracy of  $\pm 1 \times 10^{-4}$  g. The description of the chemicals used together with their sources is provided in Table 1.

### 2.2. Density measurements

Density measurements were performed using an Anton Paar (model DMA HP) vibrating-tube density meter connected to a model DMA 5000M master instrument. The DMA HP measured the period of harmonic oscillation of a built-in U-tube containing the sample. The temperature in the measuring cell was controlled by an integrated Peltier thermostat. The accuracy of the temperature measurement was  $\pm 0.05$  K. The pressure was created using a pressure generator from High Pressure Equipment Company (HIP model #62-6-10), and was monitored with a GE Druck pressure gauge (model DPI 104, 0–100 MPa) having an accuracy of 0.05% FS. The period of oscillation, cell temperature, and pressure were recorded using the DMA 5000 M master instrument which was connected to the DMA HP via the DMA HP interface. All high pressure valves and fittings were supplied by High Pressure Equipment Company (USA) and Nova Swiss (Switzerland). A detailed schematic repre-

sentation of the high pressure density installation can be found in our previous work [26].

Before each experiment, the system was rinsed with deionized water and ethanol, dried with nitrogen gas, and slowly evacuated for at least 3 h. Then, the inlet valve was opened to fill the system and the pressure generator cell with the sample, and the valve was closed. To avoid any trapped air in the system, the outlet valve was slightly opened and a few milliliters of the sample was allowed to flow out by moving the pressure generator piston forward. The outlet valve was then closed, and the system was brought to the desired temperature and pressure. The temperature was allowed to stabilize for at least 30 min for a 5-K interval. Upon thermal and mechanical equilibrations, the period of oscillation was recorded using the DMA 5000M master instrument, which was then converted to the density.

The density meter was calibrated using distilled deionized water and NaCl (aq) solutions of molalities (1 and 3) mol kg<sup>-1</sup>. NaCl (aq) solutions were used in this work because they have been recommended by several authors as high-density calibration fluids for high-pressure density meters [27–29]. The calibration was carried out in the temperature range (298.15–323.15) K and over the pressure range (0.1–50) MPa and a total of 198 data points were used. The reference data reported by Wagner and Pruss [30] for water and by Archer [31] for NaCl (aq) were used to correlate the density with the temperature and pressure using the equation

$$\rho = \sum_{j,k,l} a_{jkl} p^j T^k p^l \quad (1)$$

where  $\rho$  is the reference density;  $p$  is the oscillation period;  $T$  is the temperature;  $P$  is the pressure; and  $a_{j,k}$  are fitting parameters, with  $j = 0, 2$ ;  $k = 0, 1, 2$ ; and  $l = 0, 1, 2$ . The average absolute deviation (AAD) between the reference and the calculated data was 0.003%. The AAD is defined as

$$\text{AAD}\% = 100 \times \frac{1}{N} \sum_i \frac{|\rho_{i,ref} - \rho_{i,cal}|}{\rho_{i,ref}} \quad (2)$$

where  $\rho_{i,ref}$  is the  $i$ th reference density data and  $\rho_{i,cal}$  is the density calculated by Eq. (1). The calibration was tested by measuring the densities of NaCl (aq) solutions with concentrations (2 and 4.5) mol kg<sup>-1</sup> within the considered temperature and pressure ranges and by comparing them with the reference data taken from Archer [31]. The AAD between the measured and the reference data is less than 0.02%, which is well within the error of the experiment. The calibration was further tested by measuring the densities of [Bmim][BF<sub>4</sub>] at the considered temperature and pressure ranges. This IL has been extensively studied, and the densities at varied range of temperatures and pressures are well-reported in the literature. Our measured values agree very well with those reported by Zafarani-Moattar and Shekaari [32], Sanmamed et al. [33] and Soriano et al. [34] at 1 atm with AAD not exceeding 0.06%. Our results are also close to the data reported by Gardas et al. [35] (AAD = 0.04%) and the calculated values from the correlation proposed by Matkowska and Hofman [36] (AAD = 0.02%) for different range of temperatures and pressures. The measured densities are in between the values calculated from the correlations proposed by Jacquemin et al. [27] (AAD = 0.16%) and those calculated from Rebelo et al. [37] (AAD = 0.28%). These deviations, which are typical of ILs, may be mainly due to the differences in the purities of the samples used. The results of the validation experiments serve to confirm the correctness of the apparatus calibration, accuracy of the method as well as the operation of the equipment, and the validity of the reported measurements.

Anton Paar DMA HP does not possess a built-in correction system for viscosity effects. Such correction has been recommended

**Table 1**  
Description of the chemicals used in this study.

| Chemical   | Purity (% mass) | Source                            |
|--|-----------------|-----------------------------------|
| 1-Butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF <sub>4</sub> ] | >98             | Tokyo Chemical Industry Co., Ltd. |
| Glyceline 200 (GLY) (1 mole choline chloride + 2 moles glycerol)       | >98             | Scionix Ltd.                      |
| Sodium chloride (ACS reagent Baker analyzed)                           | 100.2 (NaCl)    | J.T. Baker                        |

Download English Version:

<https://daneshyari.com/en/article/203946>

Download Persian Version:

<https://daneshyari.com/article/203946>

[Daneshyari.com](https://daneshyari.com)