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Volumetric properties of solutions of choline chloride + glycerol deep eutectic solvent with water, methanol, ethanol, or iso-propanol

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ABSTRACT

Deep eutectic solvents (DESs) are emerging as innovative materials and regarded as cost effective IL replacements. Mixing of DESs with other solvents modifies their properties for specific applications. One of the popular DESs is made of choline chloride and glycerol named as glyceline. Densities of glyceline mixed with water, methanol, ethanol, or iso-propanol were measured in the temperature range of 283.15 to 343.15 or 323.15 K over the entire range of composition at ambient pressure. The temperature dependency was correlated by a quadratic equation for the respective systems. The excess molar volumes were evaluated and correlated by a Redlich-Kister type equation with temperature-dependent parameters. Furthermore, other derived volumetric properties such as the volume expansivity and the apparent molar volume were calculated using the measured data. The H-bond formation is more likely to occur in alcohol solutions than in aqueous solution as inferred by the comparison of the maximum deviations from ideal mixing and the limiting apparent molar volume of glyeline in the solutions.

1. Introduction

The researches on ionic liquids (ILs) as green replacements to volatile organic solvents have increased last two decades in various scientific and engineering fields ever since the potential of application by virtue of their unique physicochemical properties, such as non-volatility, inflammability, and tunability, was recognized [1–4]. The applicability of ILs has been extended to electrochemistry, catalysis, synthesis, biotechnology, and separation process [5–10]. Several researches, however, have revealed unexpected or unusual results associated with ILs [11,12]. In addition, certain types of ILs have been known to show non-biodegradable and toxic behaviors [13,14] and, thus, the impact of ILs on environment became a disputable issue. In addition, as a practical point of view, it should be mentioned that one of major drawbacks associated with the commercialization of processes adopting ILs is the cost of materials. ILs are expensive compared to organic solvents. Commercial scale application of ILs should incorporate an effective IL recovery step after a main process step to enhance economic feasibility. Therefore, at present, ILs have not been widely used for chemical industries [15].

Recently, deep eutectic solvents (DESs) have received attention as IL analogues, which exhibit similar characteristics and properties with ILs [16] such as negligible volatility, high conductivity, inflammability, and superior chemical stability. They are usually formed by complexation of a quaternary ammonium salt with a hydrogen bond donor (HBD). DES is named because the melting point at eutectic composition is 200 to 300 °C lower than those of the respective pure precursors due to large and nonsymmetric ions in a mixture having low lattice energy. DESs have some advantages over ILs because they can be readily prepared with high purity at relatively low cost. Simple mixing of two components at the correct molar ratio under gentle heating is enough to produce DESs. DESs are also tunable by simply selecting appropriate precursors. In principle, ammonium, phosphonium, or sulfonium salt can form a DES when blended with metal halide [17], hydrated metal halide [18], or HBD such as amides, carboxylic acids, and alcohols [19,20]. Currently, some DESs are already commercially available in a bulk or a ton scale [21].

An increasing number of researches for DES application has focused on metal processing and synthesis media. The investigations on DESs have involved with electrochemical processes of metal deposition, metal dissolution, and metal processing by using features of the high solubility of metal salts in DESs and high conductivity of DESs compared to other nonaqueous solvents [22–30]. The uses of DESs as synthesis media are very wide; solvents in enzyme-based biotransformation [31,32], ionothermal synthesis [33,34], gas adsorption [31,32], and biodiesel manufacture [35–39].

To apply DESs in possible engineering processes, their physicochemical properties should be accurately measured and supplied to process and/or product design steps. However, such data are still incomplete

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Table 1
Description of chemical compounds used.

Compounds	Abbreviation	Source	Remark
Choline chloride	ChCl	Sigma-Aldrich	Purity ≥98%
Glycerol	–	Sigma-Aldrich	Purity ≥99.5%
Methanol	MeOH	Sigma-Aldrich	Purity ≥99.9%
Ethanol	EtOH	Sigma-Aldrich	Purity ≥99.8%
Iso-propanol	iPrOH	Sigma-Aldrich	Purity ≥99.9%
Water	–	Produced	Ultrapure

and limited. Density is one of the most basic and critical properties of any materials used in chemical processes. To date, very few data on DES density have been reported in the literature [40–42] and limited to aqueous mixtures [43,44]. The objective of this work was to measure densities of a selected DES mixed with water or alcohol to provide volumetric properties including excess molar volumes to academic and industrial applications.

Most of DES investigations have been based on choline chloride (ChCl) which is also known as (2-hydroxyethyl)-trimethylammonium chloride. It is classified as vitamin B family and commonly used as a nutritional supplement for animal [45]. One of the popular DESs is glyceline which is a named solution of ChCl + glycerol in the mole ratio of 1:2. The melting point of glyceline is −40 °C which is far lower than ChCl (m.p. = 302 °C) and glycerol (m.p. = 18 °C). The solution (hereafter referred to as Gly) is a very viscous substance and addition of a molecular solvent to it could adjust the viscosity. In this work, the mixture densities of Gly + water (H_2O), methanol (MeOH), ethanol (EtOH), or iso-propanol (iPrOH) were measured over the full range of composition at the temperatures of 283.15 to 323.15 or 343.15 K and volumetric properties were calculated based on the experimental results.

2. Experimental

Gly is prepared by measuring ChCl and glycerol at a eutectic mole ratio of 1:2 and mixing them under stirring in a gentle heating (~80 °C) condition [46]. The mixture gradually melts and becomes a homogeneous and colorless liquid phase. Commercially, the DES could be purchased from Scionix Ltd. sold by the name of glyceline 202 (molecular weight 107.95 g/mol) but it had already been found that experimental data obtained from the prepared one were statistically similar with those from the commercial one [44]. ChCl was dried in a vacuum chamber at 90 °C >6 h before mixing. Alcohols of HPLC grade were purchased from chemical suppliers and used without further purification. Deionized water was produced by using Wellix Plus I system of MDM instruments. Details of the chemicals are described in Table 1 with their sources.

Firstly, Gly were prepared by weighing the predetermined amounts of ChCl and glycerol using an analytical balance (Hansung, HS224S) having a precision of 10^{-3} g. Then a molecular solvent (H_2O, MeOH, EtOH, or iPrOH) was added to the prepared Gly under stirring. The uncertainty of mole fraction was estimated to be $<5 \times 10^{-4}$. The solutions were tightly sealed and measurements were carried out immediately.

The densities were measured by means of an oscillating U-tube density meter (Rudolph Research Analytical, DDM2911) of which accuracy and temperature uncertainty are 5×10^{-5} g/cm^3 and 0.03 K, respectively. The instrument was calibrated with ultrapure water and dry air at atmospheric pressure. The controllable built-in thermostat was available to adjust and maintain the temperature at a desired value within the range of 273.15 to 363.15 K. Experimental temperature was gradually increased to a preset value after approximately 1 cm^3 of solution was injected into a U-tube in the instrument. A display screen showing the scanning images of the solution-filled U-tube was monitored to visually detect any bubbles and a measurement was carried out when it was confirmed that there were no bubbles in the tube at the temperature. All measurements were performed in five replicate runs and the average values were obtained. Table 2 presents comparison of densities of pure substances measured by our instrument with those available in literature [42,44,47–49]. The measured data are in good agreement with the literature values.

3. Results and discussion

Density measurements were carried out for four mixture systems. The densities of Gly with water, MeOH, EtOH, or iPrOH were measured from 283.15 K over the entire ranges of composition at atmospheric pressure. The temperature ranges covered up to 343.15 K except for the Gly + MeOH system of which upper temperature value was limited to 323.15 K due to the increased vapor pressure of MeOH. The normal boiling point (b.p.) of MeOH is 337.8 K while those of EtOH and iPrOH are 351.8 and 355.39 K, respectively. As a setting value of temperature gets closer to b.p. of MeOH, the induction time for vapor bubble formation gets shorter and the possibility of vapor bubble formation in the U-tube

Table 2
Measured densities of pure substances (ρ in g/cm^3) and comparison with literature values.

T (K)	Gly			Water			
	Measured	Lit [42]	Lit [44]	Measured	Lit [42]	Lit [44]	
283.15	1.19966	–	1.2001	0.99973	–	0.9997	
293.15	1.19409	–	1.1943	0.99828	–	0.9982	
298.15	1.19125	1.19123	–	–	0.99707	–	
303.15	1.18841	1.18850	1.1885	0.99561	0.99568	0.9957	
308.15	1.18561	1.18574	–	–	0.99407	–	
313.15	1.18277	1.18230	1.1827	0.99229	0.99226	0.9922	
318.15	1.18014	1.18022	–	–	0.99027	–	
323.15	1.17740	1.17746	1.1770	0.98807	0.98808	0.9881	
333.15	1.17201	1.17193	1.1713	0.98324	0.98323	0.9833	
343.15	1.16661	–	1.1648	0.97761	–	0.9778	

T (K)	MeOH			EtOH		iPrOH	
	Measured	Lit [47]	Lit [48]	Measured	Lit [48]	Measured	Lit [49]
283.15	0.80211	–	0.80240	0.79835	0.79813	0.79336	–
293.15	0.79298	0.79130	–	0.78978	–	0.78517	0.78535
298.15	0.78826	0.78658	0.78835	–	0.78530	–	0.78110
303.15	0.78350	0.78186	–	0.78115	–	0.77665	0.77712
308.15	0.77880	0.77711	–	–	–	–	0.77288
313.15	0.77401	0.77233	0.77413	0.77239	0.77222	0.76786	0.76879
318.15	0.76936	0.76752	–	–	–	–	0.76397
323.15	0.76453	–	–	–	–	0.75871	0.75968