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New tetrapropylammonium bromide-based deep eutectic solvents: Synthesis and characterizations

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ABSTRACT

Deep eutectic solvents are analogues of ionic liquids that are environmentally benign, have a range of desirable liquid properties and are easy to prepare. In this study, new tetrapropylammonium bromide (TPAB)-based deep eutectic solvents (DESs) are introduced. Different hydrogen bond donors (HBDs) — ethylene glycol, triethylene glycol and glycerol were used at different molar ratios of TPAB:HBD (1:2.5–1:5). Effects of temperature and the TPAB:HBD ratios on the DESs were investigated. Solvents of different physicochemical properties and wide liquid ranges with minimum melting point temperatures of 249.75, 253.95 and 257.05 K were obtained for TPAB:ethylene glycol (1:4), TPAB:triethylene glycol (1:3) and TPAB/glycerol (1:3) respectively. The samples were further characterized in the temperature range of 293.15 to 353.15 K and the property ranges measured were density (1.096–1.218 g/cm^3), viscosity (6.02–1510.0 cP), surface tension (41.9–53.2 mN m^{-1}), conductivity (167.2–11,500.0 μS cm^{-1}), refractive index (1.4466–1.4908) and pH (4.837–7.290). These demonstrate that the samples have excellent potentials for different applications. Relationships between these properties and temperature were explored. Depending on the property, the effect of temperature was modeled using either simple linear or Arrhenius-based models. The properties of these new DESs could be predicted at different temperatures for potential applications. The potential of tunable properties makes it possible to employ DESs as a reaction medium, electrochemical process medium, solvent and absorbent. Therefore, these properties must be measured and modeled for possible use in process simulation package databases.

1. Introduction

There has been an increase in research interest in ionic liquids due to the wide range of possible constituents in their synthesis, their tunable properties and immense potential applications [1]. However, in many cases, the synthesis of ionic liquids (IL) requires the use of organic solvents and supply of heat [2,3]. These and the associated waste disposal raise the cost of IL among other challenges [4]. This led to the recent focus on ionic liquid analogues called deep eutectic solvents (DESs), which were initially demonstrated by Abbott and coworkers in 2003 [5]. DESs consist of a salt and a hydrogen bond donor (HBD). A large number of the possible salts – organic and inorganic (hydrated or anhydrous) – and HBDs make it possible to report many DESs with physicochemical properties similar to those of ILs [4]. In addition, DESs exhibit high thermal and chemical stabilities and are biodegradable. Another advantage is that DESs are generally considered non-toxic, although recent reports have shown that more research is needed to have more categorical conclusions on the toxicity [6,7].

These properties of DESs and their advantage over other ionic liquids indicate their great potential in applications and are therefore considered as advanced ionic liquids [8]. They have been tested in different fields, especially in electrochemical applications such as metal deposition and as electrolytes [9,10]. It was demonstrated that DESs can be effective media for chemical reactions due to their dissolution or catalyst effects [11,12]. Recently, a DES prepared using choline chloride and urea was used as a medium in catalytic reactions and turned out to be more effective than the traditional solvents [13]. Another catalytic effect using choline chloride-based DES was reported in the depolymerization/dehydration of a biopolymer with product yields above 50% [14]. Due to the high viscosity of some reported DESs, there are important questions on understanding the system's hydrodynamics that need to be addressed [4]. There are issues related to possible contamination of reaction products and corrosion by halogen-based DES. This is important due to a recent report of adverse effect of chlorine to enzymes in catalytic biochemical reactions [15] and DES possible degradation at the reaction conditions [16,17]. Such challenges may limit DES potential in catalysis applications [18].

Therefore, there have been attempts to modify reported DESs or introduce new ones. Choline chloride/urea DES showed an eutectic freezing point of 285.15 K. A change from urea to thiourea or chlorine to fluorine led to drastic changes of the freezing point to 342.15 or 274.15 K respectively [5]. In a first pulsed field gradient nuclear

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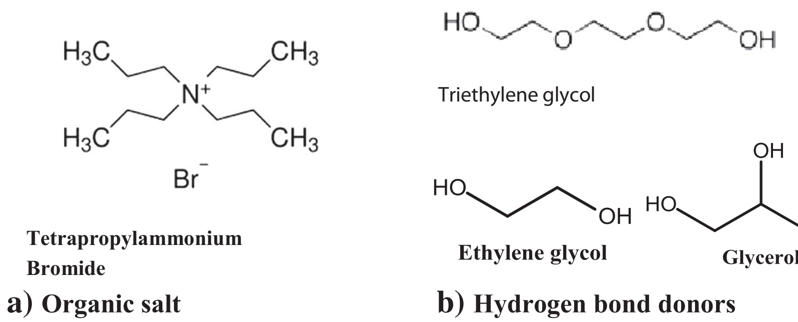

Fig. 1. Chemical structures of the DES constituents used in this work.

magnetic resonance study of choline chloride-based DESs, it has been shown that the molecular structure of the hydrogen bond donor has strong effects on the mobility of the whole DES samples [19]. In a recent study, choline chloride-based DESs were formed with renewable HBDs such as itaconic and tartaric acid with freezing points of 330.15 and 320.15 K respectively. Changing this system to a ternary by addition of glycerol led to a drastic decrease in the freezing point and other properties [20]. Therefore, DES properties such as diffusivity, ionic conductivity and viscosity could be tuned based on the selection of the HBD or co-HBD. In addition, the selection of the salt, HBD and salt/HBD ratios, the salt symmetry and the nature of HBD are important parameters for determining the final properties of the DES.

Based on the foregoing, we found it of interest to study new deep eutectic solvents based on tetrapropylammonium bromide (TPAB) as quaternary ammonium salt and different HBDs. The HBDs considered are ethylene glycol, triethylene glycol and glycerol. These may lead to DESs of different physicochemical properties with potentials for different applications. The study focuses on the synthesis and characterization of the new DESs. The characterization was done by measuring density, viscosity, surface tension, conductivity, reflective index and pH of the synthesized DESs at different TPAB:HBD molar ratios and temperatures. In order to explore possible range of applications, regressions of these properties with temperature were performed using simple mathematical models. This systematic study of the physical properties of ionic liquid-analogue called deep eutectic solvent is important due to potentials of using them in process simulation package databases. Currently, ionic liquid and deep eutectic solvent property data are not available in the database of the commercial process simulators. The new DES characterized could be added to such simulators. The mathematical model may be used to extrapolate the properties. For separation and heat transfer process equipment design; properties such as viscosity, surface tension, density and pH are important. The results reported in this work could be used to estimate the properties for design and/or operation of the process equipment.

2. Experimental

2.1. Chemicals used

For the preparations of the DESs, the chemicals used are tetrapropylammonium bromide (TPAB), ethylene glycol, triethylene glycol and glycerol (with purity >98%) all supplied by Merck Chemicals (Darmstadt, Germany). The chemical structures of these chemicals are shown in Fig. 1.

2.2. Preparation and characterization of TPAB-based deep eutectic solvents

The DESs were prepared with TPAB as the organic salt. The HBD used were ethylene glycol, triethylene glycol and glycerol. The TPAB:HBD of molar ratios 1:3, 1:4, and 1:5 were used. In the case of TPAB:triethylene glycol the ratios were 1:2.5, 1:3, and 1:4. DES samples synthesized in different TPAB/HBD molar ratios are shown in Table 1. An incubator shaker (Brunswick Scientific Model INNOVA 40R) was used to mix the salt and the HBD. Each DES mixture was mixed at 400 rpm and 353.15 K for 2 h until a homogeneous transparent colorless liquid was formed. DES samples were synthesized at atmospheric pressure and under tight control of moisture content. Samples were kept in well-sealed glass vials after preparation and fresh samples were used for analysis to avoid structural change or environmental effects on their physical properties. The properties measured were density, viscosity, surface tension, conductivity, reflective index and pH. The temperature range considered for all measured physical properties was 293.15–353.15 K. A further detail on the preparations and characterizations is given earlier [21].

3. Results and discussion

The deep eutectic solvents were prepared using TPAB as the organic salt. Effects of variations of the HBD, TPAB/HBD ratio and temperature on the physicochemical properties of the samples were studied. Table 1 displays the TPAB/HBD ratios, their abbreviations and freezing points for different ratios. The individual constituents of the DES (and their freezing points) are tetrapropylammonium bromide (543.15 K), ethylene glycol (260.3 K), triethylene glycol (266.2 K) and glycerol (290.5 K). As shown in the table, the DES samples exhibited eutectic points at TPAB/HBD ratio of about 1:4. By adding 4 mol of ethylene glycol to 1 mol of TPAB a freezing point of as low as 249.75 K was observed. Such decrease in freezing; lower than either of the constituents, is associated with sequestration effect of HBD around the bromide ions. Due to hydrogen bonding, the anion is shielded from the quaternary ammonium cation, thereby weakening the electrostatic attractions between the cation and anion. With such weak interactions, the lattice energy decreased, thus leading to lower freezing point. As expected, a HBD with more linear chain shows less decrease in the freezing point [4]. For TPAB–GLY, the lowest freezing point of 257.05 K was obtained. Both results suggest easier packing arrangements of the TPAB–TEG

Table 1
Compositions and abbreviations of the studied DESs.

Molar ratio	Abbreviation	Freezing point, K
TPAB:ethylene glycol		
1:3	DES–EG3	259.85
1:4	DES–EG4	249.75
1:5	DES–EG5	255.65
TPAB:triethylene glycol		
1:2.5	DES–TEG2.5	261.15
1:3	DES–TEG3	253.95
1:4	DES–TEG4	263.55
TPAB:glycerol		
1:2	DES–GLY2	258.15
1:3	DES–GLY3	257.05
1:4	DES–GLY4	268.45

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