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Glycerol-based deep eutectic solvents: Physical properties

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ABSTRACT

Deep eutectic solvents (DESs) have been used in many industrial applications. DES is a mixture of a salt and a hydrogen bond donor (HBD). In this study, 70 DESs were synthesized successfully based on glycerol (Gly) as the HBD with different phosphonium and ammonium salts, namely methyl triphenyl phosphonium bromide (MTPB), benzyl triphenyl phosphonium chloride (BTPC), allyl triphenyl phosphonium bromide (ATPB), choline chloride (ChCl), N,N-diethylethanolammonium chloride (DAC), and tetra-n-butylammonium bromide (TBAB). The DESs were prepared using different molar ratios of the HBD to the salts. The freezing point of each DES was determined using Differential Scanning Calorimetry (DSC). The physical properties of these DESs, including density, viscosity, conductivity, and surface tension, were investigated as functions of temperature. In addition, the functional groups were analyzed utilizing Fourier transform infrared (FTIR) spectroscopy. It is worth noting that these systems have a wide variety of physical properties, which implies that these DESs would be suitable for diverse applications.

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1. Introduction

In the last two decades, there has been increasing interest in the applications of ionic liquids (ILs), especially with respect to catalysts, electrochemistry process technology and analytics, biotechnology, and functional liquids. ILs are solvents which consist solely of ions. Mainly, the synthesis of ILs can be split into two distinct categories, those formed from eutectic mixtures of metal halides and organic salts, and those containing discrete anions [1]. Due to the increasing need for organic solvents and the high cost of ILs [2], researchers recently have focused on ionic liquid analogues, i.e., deep eutectic solvents (DESs), which were introduced by Abbot et al. in 2003 [3]. Basically, DESs are mixtures of two or more compounds, and the mixtures have a melting point that is lower than that of the individual compounds [4,5]. Furthermore, DESs are prepared by mixing a salt and a hydrogen bond donor (HBD), hence, the hydrogen bonds with the anion of the salt. DESs can be made from different kinds of salts (organic and inorganic) and different kinds of HBDs [2]. The physicochemical properties of DESs are much like those of conventional ILs [6]. However, DESs have many advantages over conventional ILs, including the simplicity of the synthesis, lower production cost, low or negligible toxicity profiles, and sustainability with respect to environmental and economic benefits [6–8].

Recently, DESs have been reported in many applications, one of which was the use of ChCl-based DESs as functional additives for starch-based plastics [9]. Also, they have been used as catalysts for the production of biodiesel fuel from low grade palm oil [10,11], as an electrolyte in electrochemical processes such as, deposition of specific metals in the electroplating and electroless plating of metals [12,13], and as viable co-solvents for enzyme-catalyzed epoxide hydrolysis [14].

Glycerol is a conventional solvent that is defined simply as a polyol (sugar alcohol), and it is used extensively in many industrial applications, especially in the food and pharmaceutical industries. However, there is a limited use of glycerol in organic transformations due to its low solubility in organic compounds and the intrinsic reactivity of the polyol backbone which leads to the side product formation [15]. Therefore, to overcome these disadvantages, researchers have been working to enhance the physicochemical properties of glycerol by different methods [15,16]. One of these methods is preparing of DESs containing glycerol as HBD.

In the current work, six DES systems were prepared based on glycerol as a HBD and six different salts, i.e., methyl triphenyl phosphonium bromide (MTPB); benzyl triphenyl phosphonium chloride (BTPB); allyl triphenyl phosphonium bromide (ATPB); choline chloride (ChCl); N,N-diethylethanolammonium chloride (DAC); and tetra-n-butylammonium bromide (TBAB). The physical properties of these DESs were investigated,

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including freezing point, density, viscosity, conductivity, and surface tension. Furthermore, the functional groups of these new DESs were analyzed using FTIR.

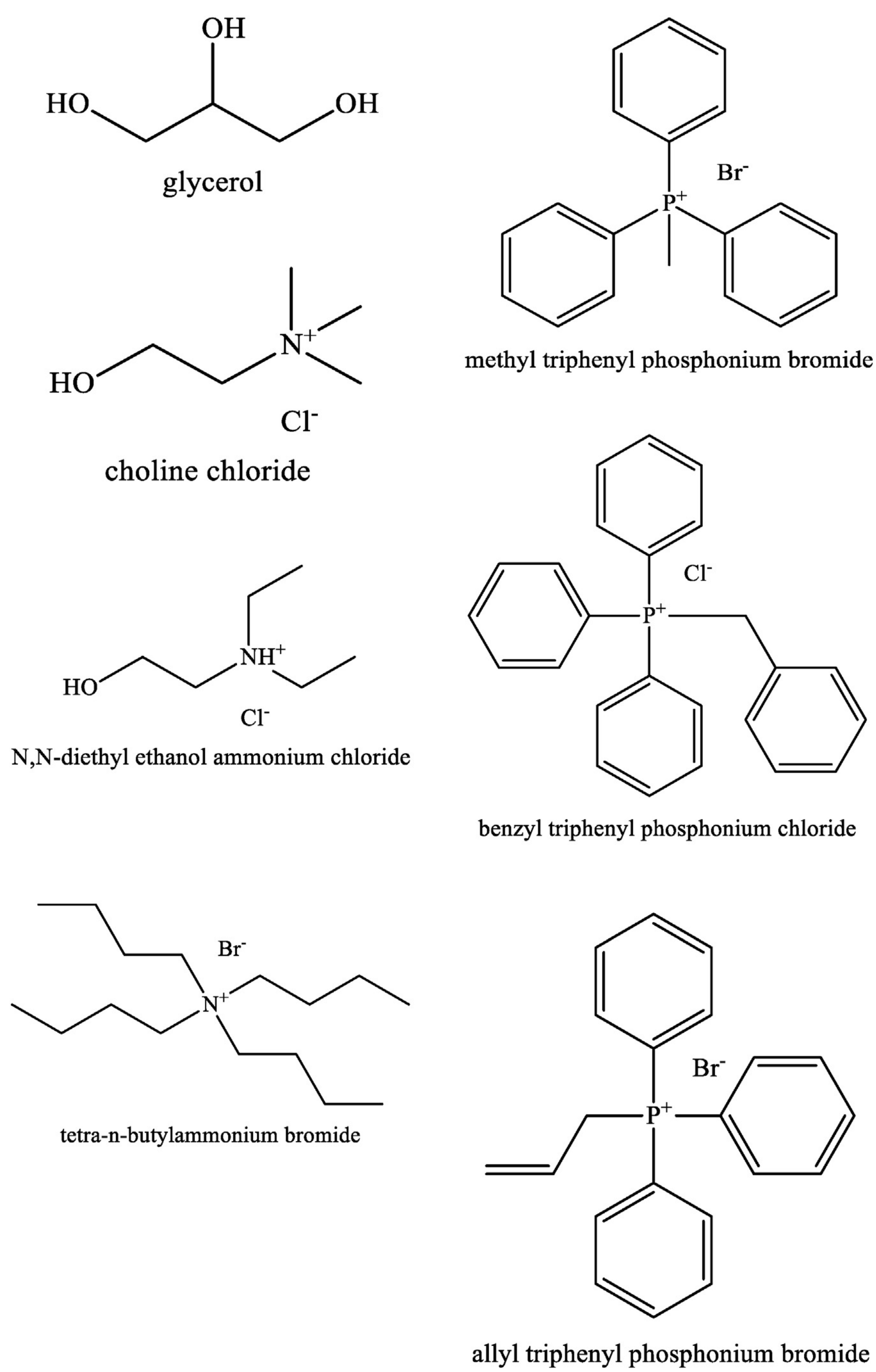
2. Materials and experimental methodology

2.1. Chemicals

All chemicals with purity >99%, except for ChCl, were supplied by Merck, Germany. ChCl was supplied by Sigma-Aldrich. Table 1S shows the salts, HBD, abbreviations, molar ratios, symbols, and phases of the synthesized DESs. Scheme 1 shows the molecular structure of the six salts and the HBD.

2.2. Synthesis and characterization of DESs

In this study, DESs were synthesized with different ratios of salt and HBD. Table 1S (Supplementary information) and Figs. 1S, 2S, 3S, 4S, 5S and 6S show the 70 DESs that are synthesized. Different phases appeared during and after preparing the DESs, such as solid, semi-solid, crystal, and liquid. Only six of the DESs that were synthesized were selected. All chemicals were dried overnight in a vacuum oven and placed in moisture controlled area. Each salt was mixed with HBD using magnetic stirring. The mixtures of the salts and HBD were mixed at 400 rpm and 353 K until a homogeneous mixture without any precipitate was obtained. Differential Scanning Calorimetry (DSC) METTLER TOLEDO® was used to measure the freezing points of the DESs. A rotational viscometer (Anton Paar® Rheolab QC) was used to measure the



Scheme 1. Chemical structure of the six salts and the HBD.

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