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Triethylene glycol based deep eutectic solvents and their physical properties

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ABSTRACT

Deep eutectic solvents (DESs) have been recently emerged as new ionic liquids (ILs) analogues. The low vapor pressure, inflammability, biodegradability and positive effect on the environment make DESs more favorable as neoteric solvents. In this study, triethylene glycol (TEG) was selected as a hydrogen bond donor (HBD) to form DESs with five types of phosphonium and ammonium salts, namely methyltriphenylphosphonium bromide (MTPB), benzyltriphenylphosphonium chloride (BTPC), allyltriphenylphosphonium bromide (ATPB), choline chloride (2-hydroxyethyl-trimethylammonium) (ChCl) and *N*,*N*-diethylenethanolammonium chloride (DAC). The physical properties of the synthesized DESs were measured such as freezing point, viscosity, electrical conductivity, Walden rule, density, pH and water content. In addition, the Fourier transform infrared spectroscopy (FTIR) was employed to study the functional groups. The experiments were conducted at different temperatures, *i.e.* 25–80 °C. It was found that DESs have suitable properties to be used in industrial processes such as separation, extraction, biochemical, petroleum and gas technology.

1. Introduction

In the area of green chemistry, the development of reaction efficiency, avoidance of toxic reagents, reduction of waste, and the responsible utilization of resources have a considerable interest in the laboratory of green media [1].

DESs are widely known as green alternative solvents to the conventional ILs [2,3]. DES is a combination of two or more compounds which has a melting point lower than that of its individual components. They comprise mixtures of organic halide salts, such as ChCl with an organic compound which is a HBD. The HBD can form a hydrogen bonding with the halide ion, such as amides, amines, alcohols, carboxylic acids and many more [4]. They are liquids at temperatures of 100 °C or below and exhibit similar solvent properties to ILs.

DESs are simple to synthesize compared to the conventional ILs. The components salt and HBD/complexing agent can be easily mixed and converted to a total homogenous mixture without any need for further purification. Besides, DESs have low synthesis cost due to the low cost of raw materials. DES is expected to have good biocompatibility when using quaternary ammonium salts such as ChCl that is being used as an additive in chicken food [1,5,6].

DESs share many characteristics with conventional ILs, *e.g.* non-reactive with water and non-volatile [7]. However, DESs cannot be considered as ILs because of the non-ionic chemical structure of some of its species, as it can also be formed from non-ionic species [8]. Abbott and co-workers defined DESs using the general formula $R_1R_2R_3R_4N^+X^-Y^-$ [9].

Type I DES $Y = MCl_x$, M = Zn, Sn, Fe, Al, Ga
Type II DES $Y = MCl_x \bullet yH_2O$, M = Cr, Co, Cu, Ni, Fe
Type III DES $Y = R_5Z$ with Z = −$CONH_2$, −COOH, −OH

Noting that the same group also defined a fourth type of DES which is composed of metal chlorides (*e.g.* $ZnCl_2$) mixed with different HBDs such as urea, ethylene glycol, acetamide or hexanediol (type IV DES) [8,9].

The conventional solvent TEG causes some industrial problems such as [10]:

1. TEG solutions may be contaminated by dirt, scale, and iron oxide.
2. Overheating of TEG solution may lead to decomposed products and cause some loss of efficiency.

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3. TEG can be lost due to foaming, degradation, inadequate mist extraction and many other reasons.

The aforementioned industrial problems encouraged researchers to develop and improve new or alternative solvents to replace TEG. As compared to traditional organic solvents, DESs are not considered as volatile organic solvents and not flammable, making their storage is convenient. From the viewpoint of green chemistry, these DESs are even more attractive since some of them have been proven to be biodegradable and compatible with enzymes. Additionally, synthesis of DESs is economically more viable compared to ILs, easy to handle and no purification is required; and thus, their large-scale up use is feasible [8].

Recently, researchers devote their efforts to implement DESs in the industrial applications. Rimsza and Corrales (2010) used ChCl-based DESs as agents for surface contaminant cleaning to selectively remove CuO from a silicon dioxide surface [11]. ChCl-based DES was also used as functional additives for starch based plastics [12]. Also, DESs were employed as catalysts for biodiesel production from industrial low-grade crude palm oil [13,14]. DESs play multiple roles in the synthesis of polymers and related materials [7]. DESs are viable co-solvents for enzyme-catalyzed epoxide hydrolysis [15]. Gore et al. (2011) reported the multicomponent synthesis of valuable biologically active dihydropyrimidinone (DHPM) in acidic DESs [16]. DESs have been employed as electrolytes for electrodeposition of metals, for electropolishing and for dye sensitized solar cells [8].

Owing to their promising applications, many efforts have been devoted to the physicochemical characterization of DESs such as freezing point, viscosity, conductivity, and pH [8]. Recently, Hayyan et al. have reported the physical properties of fructose and glucose-based DESs synthesized from mixing of ChCl with the monosaccharide sugar D-glucose anhydrous [6,17]. Previous studies have measured the physical properties of ChCl, DAC, MTPB and BTPC based DESs with glycerol (GL) and ethylene glycol (EG) as HBD [18,19]. Densities and refractive indices of DESs (choline chloride + ethylene glycol or glycerol) and their aqueous mixtures were studied by Leron et al. [18]. It is observed that the above researchers have arrived to the potentiality of DESs to be used in the industry with higher performance comaring to the conventional solvents.

In this study, TEG was used as a HBD to mix with different salts forming new DESs. TEG was selected as one of the recommended glycols that widely used in the industry. It is the most popularly glycol used as it provides superior dew point depression. Furthermore, it is easier to regenerate up to ~99%, has a high decomposition temperature with relatively high reliability, low performing cost, and low vaporization losses [10]. It is also used as heat transfer fluids [20].

As DESs are new mixtures, different types of salts and HBDs were used to form DESs. This work is a further effort to contribute in the green engineering. In this study, new types of DESs have been synthesized and introduced based on TEG as the HBD with five types of phosphonium and ammonium salts. It was measured physical properties including freezing point, viscosity, electrical conductivity, Walden rule, density, and water content as a function of temperature. In addition, the functional groups were identified using FTIR.

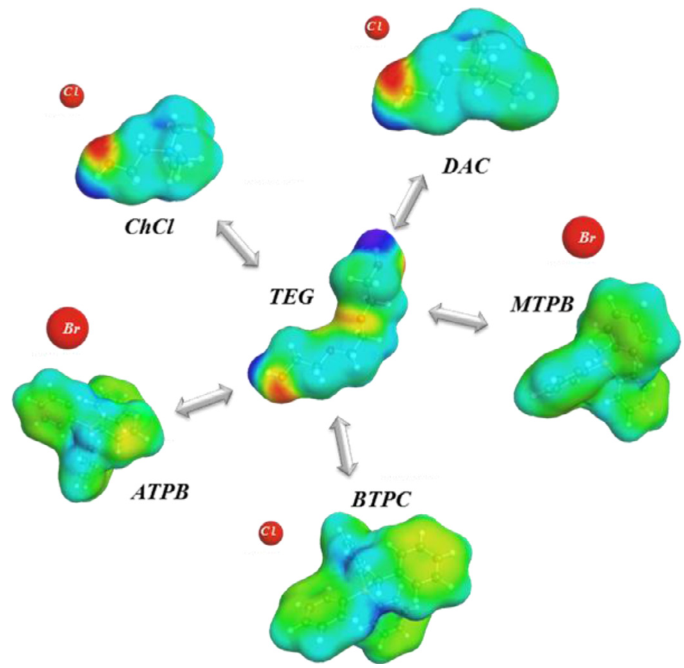
2. Experimental work

2.1. Chemicals

MTPB, BTPC, ATPB, ChCl and DAC with purity 98% were synthesized and supplied by Merck, Germany TEG with purity 99% was supplied by R&M Chemicals Ltd, UK. Table 1 shows the salts, HBD, abbreviations, molar ratios, symbols and phases of the five selected DESs. Scheme 1 shows the molecular structure of the five salts and HBD.

Table 1
Composition and abbreviation of DESs analyzed in this research.

Salts	Abbreviation	HBD	Molar ratio	Symbol	Phase
Methyltriphenylphosphonium bromide	MTPB	TEG	1:4	DES_4	Liquid
Benzyltriphenylphosphonium chloride	BTPC	TEG	1:8	DES_{18}	Liquid
Allyltriphenylphosphonium bromide	ATPB	TEG	1:10	DES_{30}	Liquid
Choline chloride	ChCl	TEG	1:3	DES_{35}	Liquid
N,N-Diethylenethanolammonium chloride	DAC	TEG	1:4	DES_{46}	Liquid



Scheme 1. TEG and salts molecular structures.

2.2. Experimental method

Table 1S (Supporting Information) shows the 52 synthesized DESs. Different phases appeared during and after preparing the DESs such as solid, semi-solid, crystal and liquid. Only five synthesized DESs were selected.

All chemicals were dried prior to the preparation stage and kept in a glove box to control the moisture. Each of the five salts (MTPB, BTPC, ATPB, ChCl and DAC) was mixed with the HBD (TEG) in an incubator shaker (Brunswick Scientific Model INNOVA 40R). The mixture of the salt and HBD was shaken at 350 rpm and 80 °C until the DES became a homogeneous mixture without any precipitation. The synthesized samples were kept in a glove box to avoid humidity that may affect the physical properties of the DESs.

Differential scanning calorimetry (DSC) (DES1 STAR^e System) METTLER TOLEDO was used to measure the freezing point for the five selected DESs. Rotational viscometer (Anton Paar Rheolab QC) was used for measuring the viscosity. The variation in the temperature was controlled by external water circulator (Techne-Tempette TE-8A) with a temperature range 25–80 °C. Tensiometer KRUSS (K100M) was used to measure the density with a temperature range 25–75 °C controlled by the external water circulator. Conductivity was measured by Multi-Parameter Analyzer (DZS-708) with a temperature range 25–80 °C. Water content of the five DESs was measured by Karl Fisher (Coulometric KF Titrator C30) at room temperature. FT-IR