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 = MClx, M = Zn, Sn, Fe, Al, Ga
Type II DES Y = $MClx \bullet yH_2O$, 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.

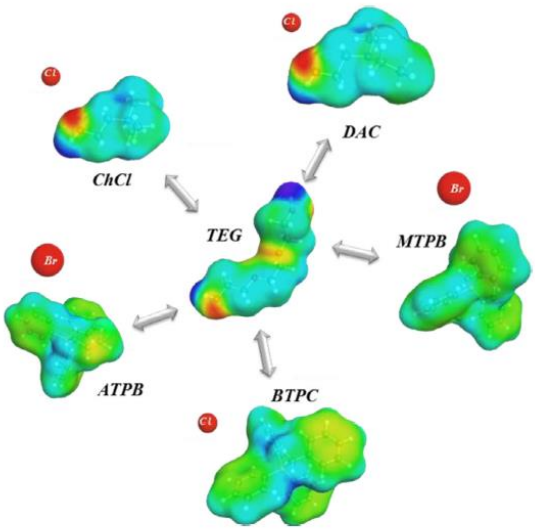
2. Experimental work

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

Spectrometer (Perkin-Elmer) was used to analyze the functional group of the DESs at room temperature.

The estimated uncertainty for the freezing point is ±0.19 °C, for the viscosity ±1% of full scale range. The uncertainty for the conductivity is ±0.5% F.S. +1 digit, for the density it is ±0.00001 g/cm. The water content uncertainty is ±0.5%.

3. Results and discussion

In this study, 52 DESs were synthesized in different molar ratios (1:1–1:10, salt:HBD). However, precipitates were observed in some DESs after synthesis, Table 1S (Supporting Information). Therefore, the selection of the desired molar ratio was the minimum molar ration that provided the most stable homogeneous mixture, as illustrated in Table 1.

3.1. Freezing point

The liquid state of DES is resulted through freezing point depression. Hydrogen bonding and complex interaction between the halide anion of the salt and HBD is more energetically favored relative to the lattice energies of the pure constituents [4]. Similar to the HBD, the nature of the salt also affects the DES freezing point [8]. The freezing point depressed in a considerable manner following the general behavior of DES combination. The range for the five DESs is −16.59 to −19.83 °C. The highest freezing point was for DES_{45} and the lower freezing point was for DES_{35}. The freezing points for DES_{18}, DES_{30} and DES_{35} are −19.49, −19.52 and −19.83 °C, respectively. Thus, DES_{18}, DES_{30} and DES_{35} have potential industrial applications. The freezing point of TEG is -7 °C and the salt MTPB is 234 °C. The freezing point of resulted DES_4 was deceased to −18.17 °C. The result of DES_4 was in agreement with previous studies reported DESs MTPB:TEG and ChCl:EG [19,21]. The freezing point for the salt BTPC is 239 °C after forming DES_{18} the freezing point was −19.49 °C. Similar freezing points were found for DES_{30} and DES_{35}. These results are in agreement with a previous study reported DESs formed by DAC:TEG at a ratio of 1:3 and 1:4 [19]. The freezing point for the salt DAC is 136 °C whereas after preparing DES_{46} the freezing point decreased to −16.59 °C which is close to the value reported by Abbot et al. (2003) for ChCl:urea [22].

3.2. Viscosity

The viscosity of DESs is an important property to be addressed. Fig. 1 shows that the temperature has a significant effect on viscosity. The viscosity decreased with temperature increment. The viscosity of DESs followed the order, $DES_4 > DES_{18} > DES_{35} > DES_{46} > DES_{30}$. Owing to their potential applications as green media, the development of DESs with low viscosities is desirable [8]. The viscosity behavior in function with temperature is shown in Fig. 1. The viscosities of eutectic mixtures are mainly affected by the chemical nature of the DES components (*i.e.* salts and HBDs) [8].

The lowest viscosities for the studied DESs, DES_{30}, DES_{46}, DES_{35}, DES_{18} and DES_4 are 49.9, 84.6, 110.4, 116.7 and 136.1 mPa s, respectively at 80 °C. At room temperature DES_{46} has the lowest viscosity 610 mPa s comparing to other DESs. DES_{30} (using ATPB as a salt) is a novel DES giving the lowest viscosity 49.9 mPa s at 80 °C comparing to the other synthesized DESs. The viscosity of DES_{30} at room temperature was compared with D'Agostino et al. (2011) for ChCl:urea at molar ratio of 1:2 and ChCl:malonic acid at molar ratio of 1:2 [23] and Chen et al. (2013) for imidazolium-based ILs [23,24]. It was found that the viscosity of the DES_{30} is lower. The high viscosity of DESs is often attributed to the presence of an extensive hydrogen bond network between components, which results in a lower mobility of free species within the DES [8].

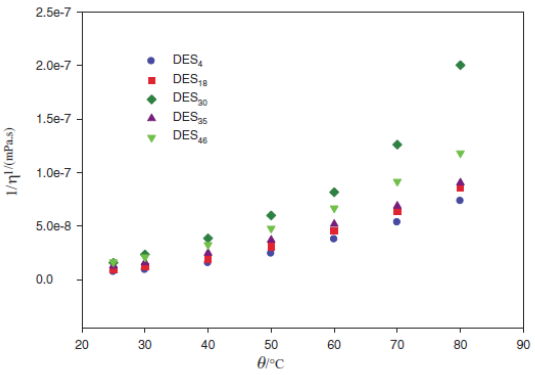


Fig. 1. Dynamic viscosity, η, of five DESs as a function of salt/HBD with temperature range 25–80 °C.

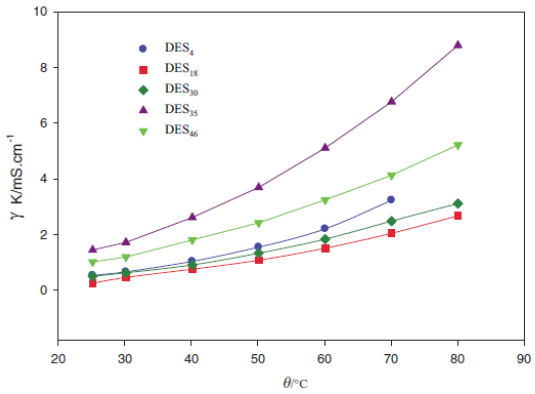


Fig. 2. Conductivities, γ, of DESs as a function of temperature in the range of 25–80 °C.

The viscosities of the studied DESs were fitted using the Arrhenius model as shown below:

$$\eta = \eta_0 \, e^{\left[-\frac{E_\eta}{RT}\right]} \quad (1)$$

where:

T: temperature in K,
R: gas constant in J/mol K,
E_η: activation energy in Pa L/mol,
η_0: pre-exponential constant in mPa s,
η: viscosity in mPa s.

3.3. Conductivity

Owing to their high viscosities, most of DESs display poor ionic conductivities (lower than 2 mS/cm at room temperature) [8]. In this study, the five DESs have conductivities in the range 0.212–8.77 mS/cm increasing with temperature increase. The molecular structure of the salts and HBDs has an impact on the conductivity.

The tendency of the conductivity for DES_{18} and DES_{30} was increasing with approximate values. Fig. 2 shows that the conductivity increases from 0.212 to 2.46 mS/cm for DES_{18} and from 0.464 to 3.08 mS/cm for DES_{30}. On the other hand, DES_{35} has the highest conductivity at room temperature and at 80 °C; Fig. 2 also shows the dramatic increase from 1.41 to 8.77 mS/cm for DES_{35}. Consequently,

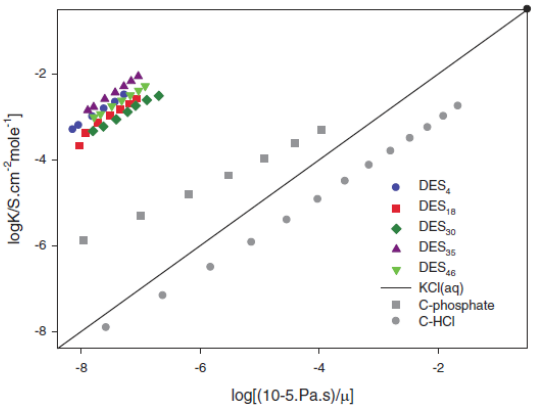


Fig. 3. Walden plot for KCl(aq), salts and DESs at temperatures 25–80 °C.

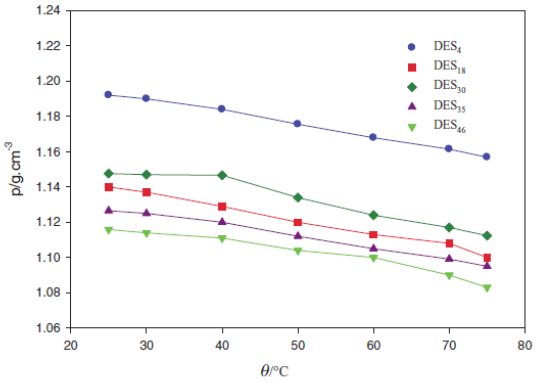


Fig. 4. Densities ρ of DESs as a function of temperature of the range of 25–75 °C.

it can be employed in electrochemical applications. The conductivity of DES_{46} as an ammonium based DESs was compared with Siongco et al. (2013) for *N*,*N*-diethylethanolammonium chloride:Gl and *N*,*N*-diethylethanolammonium chloride:EG at 1:2 molar ratio [25]. It was found that DES_{46} has higher conductivity.

Arrhenius-like equation was used to predict the conductivity behavior of the five DESs.

$$\gamma = \gamma_0 \, e^{\left[-\frac{E_\gamma}{RT}\right]} \tag{2}$$

where:

T: temperature in K,
R: gas constant in J/mol K,
E_γ: is the activation energy in Pa L/mol,
γ_0: constant in mS/cm,
γ: conductivity in mS/cm.

3.4. Walden rule

The Walden plot has been used increasingly in the last years to illustrate the conductivity–viscosity relationship of pure ILs [26]. Walden rule is often obeyed well empirically, especially by solutions of large and only weakly coordinating ions in solvents with nonspecific ion–solvent interactions [26]. The Walden rule relates the mobility of ions to the fluidity of their surrounding medium according to following equation [27]:

$$\Lambda \eta = k \tag{3}$$

where Λ is the molar conductivity and η is the viscosity; k is a temperature dependent constant. On a logarithmic plot of Λ, representing the ion mobility, versus the fluidity ϕ ($\phi = \eta^{-1}$) one can compare the tendency to form ions of non-aqueous electrolyte solutions, molten salts and ILs [27].

The question of whether DESs are ILs or not has been raised recently [8]. Therefore, investigating the Walden rule would help to categorize the family of DESs. An "ideal" reference line, established by using dilute aqueous KCl solutions, is representative for independent ions without any interionic interactions [27]. The proximity of the plotted values to the KCl reference line is an indicator of the interionic interactions between solvent's anions and cations [27]. Solvents with high tendency to form ions are located close to the reference line while solvents with low tendency to form ions are situated further away [27]. Fig. 3 shows that all the studied DESs are not located close to the KCl reference line. The far locations of the DESs indicate the non-ionic structure of the DESs and support the argument that DESs could not be considered as ILs. This work was compared with two salts of carvedilol carvedilol-hydrochloride (C-HCl) and carvedilol-dihydrogen phosphate (C-phosphate) [28]. It was noticed that these salts were located closer to the KCl(aq) reference line comparing to the five studied DESs and this is due to their high ionic mobility [28].

3.5. Density

Fig. 4 depicts the density of DESs. In general, the density decreases with temperature increase. The highest density was for DES_4. In contrast, the lowest density was for DES_{46}. The results for DES_{35} are less than recent densities measured for ChCl-based DESs in different molar ratio [19]. As for DES_4, the results were compared with Hayyan et al. (2012) for ChCl:D-fructose at a molar ratio 2.5:1, the results are in agreement [6]. The densities of the two novel DESs, DES_{18} and DES_{30} were compared with Królikowska and Hofman (2012) for thiocyanate-based ILs [29]. It was found that DES_{18} and DES_{30} have higher densities at room temperature and this is because of the large molecular size of the salts; BTPC and ATPB.

The behavior of the five DESs was linear and the results were fitted by a linear relationship as follows:

$$\rho/g/cm^3 = a(\theta/^\circ C) + b \tag{4}$$

where:

θ: temperature in °C,
b: constant depends on the type of the DES,
ρ: density in g/cm^3.

3.6. Water content

Water has a significant impact on the physical properties of DESs. Therefore, it is essentially important to measure the water content of DESs. The water content range was between 6.958 and 10.340 mg/g. The highest value was for DES_4 10.340 mg/g and the lowest value was for DES_{30} 6.958 mg/g. DES_{30} can be considered as less hygroscopic comparing to other DESs. The water content for DES_{18}, DES_{35} and DES_{46} were 8.128, 7.062 and 9.173 mg/g, respectively. The results of DES_4 and DES_{35} were compared with a previous study for ChCl:Gl at molar ratio 1:1 and 1:3 [30]. DES_{35} was in agreement with a previous study [30]. In contrast, the result of DES_4 (MTPB as salt) was in disagreement for MTPB:EG at molar ratio 1:3, 1:4 and 1:5 [30]. This can be implied to the strength of the H-bonding interaction that

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