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Research article

ACIDITY, SALINITY AND TOTAL DISSOLVED SOLIDS FOR TRIETHYLENE GLYCOL BASED DEEP EUTECTIC SOLVENTS

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ABSTRACT: Neoteric green solvents alternate ionic liquids (ILs) and conventional solvents have been emerged in the field of green chemistry. Recent studies reported the properties of deep eutectic solvents (DESs) such as low vapor pressure, non-toxicity, inflammability, biodegradability and friendly relationship with the environment. In this article, five types of phosphonium and ammonium salts, namely methyltri Phenylphosphonium bromide (MTPB), benzyltri Phenylphosphonium chloride (BTPC), allyltri Phenylphosphonium bromide (ATPB), choline chloride (2-hydroxyethyl-trimethylammonium) (ChCl) and N,N-diethylenethanol ammonium chloride (DAC) were mixed with triethylene glycol (TEG) as a hydrogen bond donor (HBD) to form DESs. The acidity (pH), salinity and total dissolved solids (TDS) of the five DESs were investigated in this article. The experiments were conducted at different temperatures, i.e. 25 to 80°C. It was reported that DESs show promising implementation in green technology. This article is a further study to the work published by Hayyan et al. investigating the physical properties of the same DESs.

Key words: Deep eutectic solvent; Ionic liquid; Triethylene glycol; Choline chloride; Phosphonium salt; Hydrogen bond donor

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INTRODUCTION

In recent years, DESs have been reported as neoteric solvents replacing ILs and conventional solvents (Aissaoui T 2015, Hayyan M et al, 2015) . Due to their biodegradability, non-toxicity, low vapor pressure and inflammability, DESs were studied by several research groups around the globe. Their attractive properties make them promising solvents for future chemical and engineering applications (Aissaoui T 2015, Hayyan M et al, 2015). DESs are a mixture of HBD with hydrogen bond acceptor (HBA)at atmospheric pressure and specific temperature and molar ratio to form a solvent with lower melting point comparing to that of HBD and HBA (Kareem MA et al, 2010, Zhang Q et al, 2012).

Recently, Tayeb Aissaoui and Inas M. AlNashef have investigated the chemical structure of phosphonium and ammonium based DESs by conducting fourier transform infrared spectroscopy (FT-IR) for both phosphonium and ammonium based DESs (Aissaoui T 2015, Aissaoui T, AlNashef IM 2015). In addition, Sun et al. have reported a theoretical investigation on the structures and properties of mixtures of ChCl: urea. Their results indicate reasonable explanation for the low melting point of the eutectic mixture of ChCl: urea with a ratio of 1:2 (Sun H et al, 2013). Many other studies dealing with the nanostructure of DESs have been published by several research groups (Yue D et al, 2012, Shah D, Mjalli FS 2014).

Furthermore, physiochemical properties for different types of DESs have been recently investigated (Aissaoui T 2015 Zhang Q et al, 2012). The published results prove the capacity of DESs to be implemented in several industrial applications (Aissaoui T 2015 Zhang Q et al, 2012). DESs are used for CO_2 capturing technology, biodiesel production, pharmaceutical reactions, electrochemistry and many other technologies (Aissaoui T 2015 Zhang Q et al, 2012).
In this study, the acidity, salinity and TDS of TEG Based DESs were reported. Hayyan et al. have studied different properties for the same DESs Hayyan M et al, 2015). This article is a further work to deeply investigate TEG Based DESs. The results found in this article confirms the conclusion given by Hayyan et al. that DESs have suitable properties to be used in industrial processes such as separation, extraction, biochemical, petroleum and gas technology Hayyan M et al, 2015).

EXPERIMENTAL WORK

CHEMICALS

TEG with purity 99% was supplied by R&M Chemicals Ltd., UK. MTPB, BTPC, ATPB, ChCl and DAC with purity 98% were synthesized and supplied by Merck, Germany Table2 shows the salts, HBD, abbreviations, molar ratios, symbols and phases of the five selected DESs.

EXPERIMENTAL METHOD

In this work, each of the five HBA_s (MTPB, BTPC, ATPB, ChCl and DAC) were mixed with the HBD (TEG) in an incubator shaker (Brunswick Scientific Model INNOVA 40R) to form the studied DES_s; DES_1, DES_2, DES_3, DES_4, DES_5 [2]. The mixture of the HBA_s and HBD was shaken at 350 rpm and 80°C until the DES became a homogeneous mixture without any precipitation [2]. The synthesized DES_s were kept in a controlled area to avoid humidity that may affect the physical properties of the DES_s [2]. PH, salinity and TDS were measured by Multi-Parameter Analyzer (DZS-708) with a temperature range 25-80°C. Table 1 shows the experimental accuracy of measured physical properties.

RESULTS AND DISCUSSION

pH

The chemical nature of the HBD has a strong effect on the acid or basic strength of the DESs [4]. Figure 1 depicts the pH of the investigated DESs as a function of temperature. The range of the pH for the five DESs was 1.5 to 5.2 at room temperature and 0.6 to 4.1 at 80°C. The main trend of pH of the five DESs decreases with the temperature increase. TEG at room temperature has a pH=7. The decrease of pH after HBAs and HBD combination may be due to the chemical structure of the HBAs that may free the protons which increase the acidity of the DES_s. DES_3 and DES_5 were more acidic compared to other DESs. The highest pH value was for DES_2 (i.e. 5.2) at room temperature. The pH of DES_1, DES_2 and DES_3 as phosphonium-based DESs were lower than previous studies for MTPB: GL at 1:1.75 molar ratio and BTPC: GL at 1:5 molar ratio and BTPC:EG at 1:3 molar ratio [3]. This indicates that molar ratio has also an impact on the pH of DES_s. Additionally, the type of HBD has also an impact on the acidity of DES_s, and this may be due to the increase or decrease of H atom in the HBD.
The temperature and pH relationship was linearly fitted according to the following relationship:

$$pH = a(t/°C) + b \quad (1)$$

Where:
T: is temperature in °C
a and b are constants that vary according to the type of DES

Table 1: Estimated uncertainty

Property	Estimated uncertainty
TDS	± 0.5 % FS
Salinity	± 0.1 %
pH	± 0. 02 pH

Table 2: Composition and abbreviation of DESs investigated in this research.

Salts	Abbreviation	HBD	Molar ratio	Symbol
Methyltri Phenylphosphonium Bromide	MTPB	TEG	1:4	DES_1
Benzyltri Phenylphosphonium Chloride	BTPC	TEG	1:8	DES_2
Allyltri Phenylphosphonium Bromide	ATPB	TEG	1:10	DES_3
Choline Chloride	ChCl	TEG	1:3	DES_4
N,N-diethylenethanolammonium Chloride	DAC	TEG	1:4	DES_5

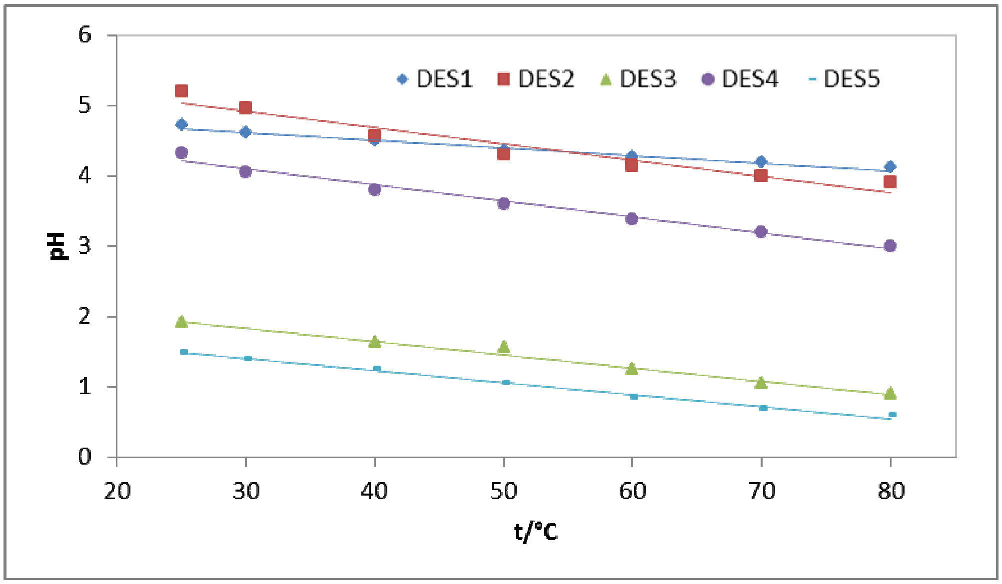

Figure 1: pH for the studied DESs as a function of temperature t at the range of 25 to 80 °C.

TDS

TDS is a measure of the combined content of all inorganic and organic substances contained in a liquid. The two principal methods of measuring TDSs are gravimetry and conductivity [9]. However, since TDSs are not easily measured, except under controlled conditions in reputable laboratories, a common alternative method is to utilize the simple permeate electrical conductivity reading and multiply by a standard correction factor (typically 0.7) to obtain the required TDS results [9]. The measured TDS by the gravimetric method and conductivity/TDS meter is expected to be the same [10]. Figure 2 demonstrates that DES_4 has the highest TDS value with the interval of 0.714 $mg.L^{-1}$to 4.39 $mg.L^{-1}$. The lowest TDS value was 0.1062 $mg.L^{-1}$ for DES_2. Consequently, the high purity of DES_2 and DES_3 makes them potential solvents to be used in industrial applications such as pre-treatment separation, biochemical and biodiesel processes. In contrast, DES_4 and DES_5 show less purity which affects their potential use in the industry. However, it should be noted that the impurities of the studied DES_s may affect the results of TDS especially when the DES_s were not kept in a controlled area. Arrhenius-like equation was used to predict the TDS behaviour for the five DES_s.

$$D = D_0\, e^{\left[-\frac{E_D}{RT}\right]} \quad (2)$$

Where:
T: temperature in Kelvin.
R: gas constant in J/molK
ED: activation energy in $Pa.L.mol^{-1}$
Do: constant in $mg.L^{-1}$
D: Total Dissolved Solids in $mg.L^{-1}$
The values of D_0 and E_D are shown in Table 3 along with the sum of squares of deviations.

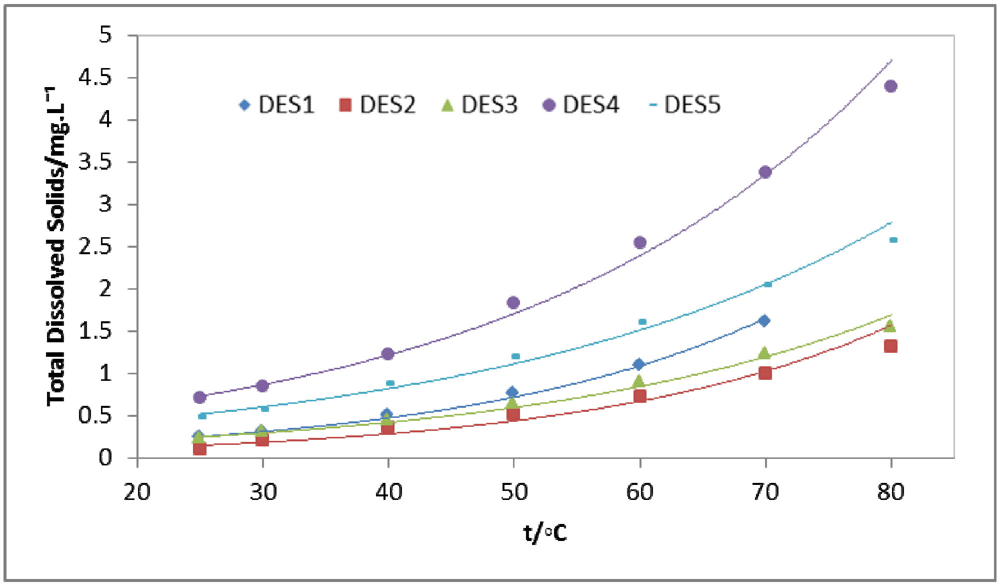

Figure 2: Total Dissolved Solids, TDS, of DESs as a function of temperature t in the range of 25 to 80 °C with the Arrhenius Equation.

Table 3: Regression parameters for TDS.

DES	D_0	E_D	R^2
	mg.L^{-1}	Pa.L.mol^{-1}	
DES_1	7.3E+05	3.6E+05	1
DES_2	4.31E+09	6.02E+06	0.932
DES_3	1.05E+04	3.2E+05	0.992
DES_4	5.6E+03	2.7E+05	0.9987
DES_5	1.15E+05	3.06E+04	0.996

SALINITY

Salinity is the dissolved salt content in a liquid. Figure 3 illustrates the salinity of DESs as a function of temperature t in the range of (25 to 80) °C. It was illustrated in figure 3 that the salinity behaviour of the studied DESs was very similar to TDS. The salinity of the DESs increased with temperature increase. DES_4 has the highest amount of salts followed by DES_5. DES_2 and DES_3 have an approximate values and minimum amount of salts in comparison with other DESs. The lowest salinity was for DES2. The low salinity of DESs makes them promising solvents for industrial use for liquid separation and superoxide ion [11].

Arrhenius-like equation was used to predict the salinity behaviour for the five DESs.

$$S = S_0\, e^{\left[-\frac{E_S}{RT}\right]} \quad (3)$$

Where:
T: temperature in Kelvin.
R: gas constant in J/mol K
ES: activation energy in Pa.L.mol^{-1}
So: constant in mg.L^{-1}
S: Salinity in mg.L^{-1}

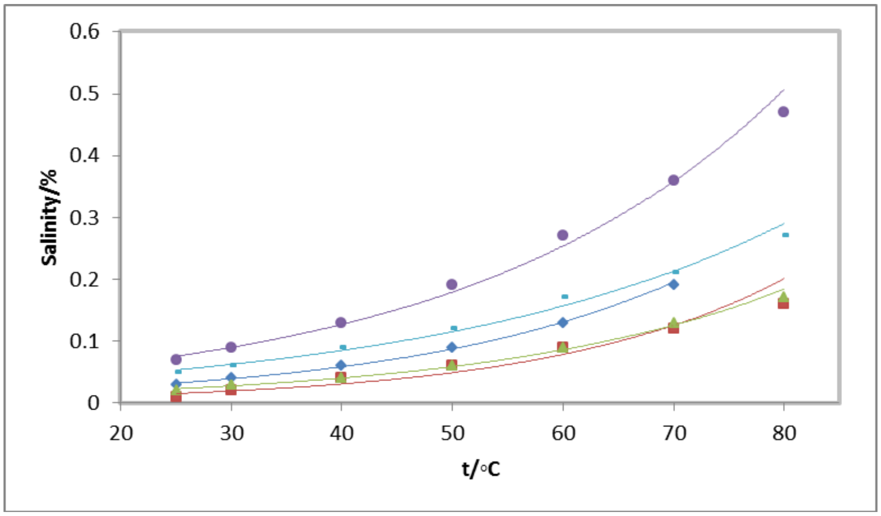

Figure 3: Salinity of DESs as a function of temperature t in the range of (25 to 80) °C.

CONCLUSION

In this study, acidity, salinity and TDS for TEG based DESs were studied. All studied DESs were acidic. The purity of phosphonium based DESs were better than that of ammonium based DESs in terms of TDS and salinity values. The findings of this article confirm that DESs have promising applications in many industrial applications such as separation, extraction, biochemical, and petroleum and gas technology.

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