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Thermal stability analysis, experimental conductivity and pH of phosphonium-based deep eutectic solvents and their prediction by a new empirical equation

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ABSTRACT

Deep eutectic solvents (DESs) are derived from two or more salts as the hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). Because of many unique features, DESs can be a versatile alternative to ionic liquids and traditional solvents. In this work, DESs were prepared namely allyltriphenylphosphonium bromide-diethylene glycol (ATPPB-DEG) and allyltriphenylphosphonium bromide-triethylene glycol (ATPPB-TEG) into three mole ratios 1:4, 1:10, and 1:16 salt to HBDs. The thermal stability was comprehensively analysed under the temperature range of (30–800) °C. The conductivity and pH values were determined within the temperature range of 293.15 K–343.15 K. The results revealed that the amount and type of HBDs have an effect on these properties. Moreover, the effect of temperature was studied on these properties. As the temperature increases, the conductivity values increase while the pH values decrease. Finally, a new empirical equation was applied to correlate the experimental conductivity and pH data. It was found that this equation is powerful and reliable to correlate these properties of DESs.

1. Introduction

Deep eutectic solvents (DESs) are derived from two or more salts as the hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) including amides, amines, alcohols, and carboxylic acids. In 2003, Abbott et al. [1] introduced DESs by the preparation of urea and a range of quaternary ammonium salts.

Recently, DESs have gained popularity between researchers for many purposes, especially in CO_2 capture [2–12] in comparison with ionic liquids (ILs) which have a low melting point, high solvency power for both polar and non-polar solvents, high ionic conductivity, high thermal and chemical stability, tuneable physicochemical character, low flammability and volatility [13–22]. However, in spite of the unique properties of ILs, they have some drawbacks such as the high price for their industrial applications in the large scale, the complex reaction steps and purification procedures for synthesizing, high viscosity, potential toxicity, limited biodegradability and low CO_2 loading capacity (in comparison with traditional alkanolamines) [23,24]. That is why researchers are trying to find new solvents as alternative to ILs. Similar to ILs, DESs have many unique properties, for instance, non-volatile, thermally stable, highly conductive and also composed of low-cost, nontoxic, natural, easy preparation way, lower melting point than the constituents of the mixture, a wide liquid range, high solvation capacity, biodegradable constituents which are important for the environmental and economical perspective [2,25–33]. Therefore, DESs can be regarded as the alternative to ILs for many purposes.

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature or mass loss). The thermogravimetric analysis of the DESs used for CO_2 capture is of utmost importance. This provides information about the decomposition of the solvents. The solvent, being used for CO_2 absorption, should be thermally stable over a wide range of absorption temperatures for its effective usage.

There is very rare information regarding the thermal stability of DESs in literature. Zhao et al. [34] analysed the thermal stability of DESs consisting of mixtures of choline salts (chloride or acetate

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form) and glycerol. Their results showed that these DESs are generally stable up to nearly 200 °C and the decomposition temperature (T_{dcp}) values for choline chloride/urea (1:2), choline chloride/glycerol (1:2), choline acetate/glycerol (1:1.5), and choline acetate/glycerol (1:2) all fall in the range from 205 to 216 °C. Florindo et al. [35] measured the T_{dcp} of choline chloride-based DESs with several carboxylic acids (levulinic, glutaric, malonic, oxalic, and glycolic). Their results showed that the DESs exhibit a very close T_{dcp}. The lowest value was pertinent to choline chloride/malonic acid (397.83 K) and the highest was for choline chloride/glutaric acid (397.83 K). Abbas and Binder [36] studied the thermal stability of choline chloride-based DESs with ethylene glycol (EG), glycerol (GL), DMSO, DMF and urea as HBDs. Their results showed that DESs are stable up to 300 °C, except for choline chloride/DMSO mixture that shows decomposition below 100 °C. Francisco et al. [37] reported the thermal stability of choline chloride/lactic acid. Their results showed that this type of DES is stable up to about 400 K.

Electrochemical applications are major fields for DESs to have significant roles in industry, so there is a great demand for information concerning their electrical and electronic properties, including their electrical conductivity. Hayyan et al. [28] measured the conductivity of triethylene glycol based-DESs with different salts at temperature in the range of (25–80) °C. Their results showed that the temperature and molecular structure of the salts and HBDs has an impact on the conductivity. They reported the highest conductivity for choline chloride/triethylene glycol with mole ratio of (1:3) at room temperature and at 80 °C from 1.41 to 8.77 $mS{\cdot}cm^{-1}$. Mjalli et al. [38] measured the conductivity of potassium carbonate-based DESs at different temperatures from 293.15 K to 353.15 K. Their results disclosed that conductivity values increase by increasing the temperature and amount of HBDs in the DES. The ethylene glycol DESs had the higher conductivity than the glycerol-based DESs at all temperatures. Further, there was an increasing trend on the conductivity of DESs as both temperature and the quantity of HBD in the DES increased.

Siongco et al. [39] measured the conductivity of N,N-diethylethanol ammonium chloride–glycerol (DEAC-Gly), N,N-diethylethanol ammonium chloride–ethylene glycol (DEAC-EG) and their aqueous mixtures at various temperatures. Their results showed that the conductivity values decrease as DES concentrations increase at a specific temperature. AlOmar et al. [27] measured the conductivity of glycerol-based DESs at the temperature range of 298–348 K. their results showed that DES with the salt of allyltriphenylphosphonium bromide has the higher refractive index values than other types of DESs. Abbott et al. [40] measured the conductivity of choline chloride mixtures with glycerol at various temperatures. Their results revealed that by increasing the amount of salt and temperature, the conductivity values increase. Kareem et al. [26] reported the conductivity of phosphonium-based DESs at several temperatures. Although there is generally an increasing trend on the conductivity value of DESs by increasing temperature, they stated that there is a decreasing trend on their conductivity values as the temperature increases for benzyltriphenylphosphonium chloride/glycerine (1:5) and benzyltriphenylphosphonium chloride/ethylene glycol (1:3). They did not mention a reason for this behaviour of DESs. Guo et al. [41] reported the conductivity of several deep eutectic solvents (DES) base on three different hydrogen-bond donors (HBD), namely phenol, *o*-cresol, and 2,3-xylenol, and choline chloride. The conductivity values of the DES were from (1.40 to 7.06) $mS{\cdot}cm^{-1}$ and increases with an increase of temperature. Bahadori et al. [42] investigated an exponential behaviour of conductivity with temperature for all measured DESs containing ammonium-based salts and HBDs such as acid, amine, amide, and nitrate. Yusof et al. [43] measured the conductivity of tetrabutylammonium bromide (TBABr) as a salt with some HBDs, for example, ethylene glycol, 1,3-propanediol, 1,5-pentanediol and glycerol. By increasing the amount of HBDs in DESs, the conductivity of DESs increases at all temperatures except for TBABr/glycerol.

Knowledge of pH as a physical property is important in applications related to catalytic reactions, biochemical reactions, pharmaceutical preparations and corrosive studies. The literature did not cover the pH measurement of DESs. Hayyan et al. [44] measured the pH of the different types of d-fructose-based DES of choline chloride (2-hydroxyethyl-trimethylammonium) at different mole ratios temperatures. Their results revealed that DES with the lower mole fraction of HBD in mixture has the lowest pH value tend to be more acidic steadily with the increase in temperature. Kareem et al. [26] measured the pH of phosphonium-based DESs at several temperatures. Their result revealed that although there was a decreasing trend on pH values by increasing temperature, the pH value of methyltriphenylphosphonium bromide/2,2,2-triflouraceta mide with mole ratio of 1:8, increased as the temperature increased from about 2.5–3.5. Mjalli et al. [38] measured the pH of potassium carbonate-based DESs at different temperatures from 293.15 K to 353.15 K. their results disclosed that the DESs were basic and their basicity decreased with increasing the temperature and amount of HBDs (glycerol and ethylene glycol) in DESs.

Therefore, in the present work, six DESs were prepared at three mole ratios of 1:4, 1:10 and 1:16 by mixing HBDs such as diethylene glycol (DEG), triethylene glycol (TEG) with allyltriphenylphosphonium bromide (ATPPB) salt as a HBA. The conductivity and pH were measured at several temperatures from 293.15 K to 343.15 K. The thermal stability of DESs was conducted at the temperature range from 30 °C to 800 °C.

2. Experimental

2.1. Chemicals

Allyltriphenylphosphonium bromide (ATPPB) was purchased from Angene International Limited supplier. All HBDs including diethylene glycol (DEG) and triethylene glycol (TEG) (>99% purity) were supplied by *R* & *M* Chemicals. Table 1 lists the specification of

Table 1
Specification of chemical samples used in this study.[a]

Chemical name and Linear formula	CAS No.	Supplier	Mass fraction purity[a]	Water and peroxide	Purity analysis
Allyltriphenylphosphonium bromide $H_2C{=}CHCH_2P(C_6H_5)_3Br$	1560-54-9	Angene International Limited	>99%	None[b]	None
Diethylene glycol $(HOCH_2CH_2)_2O$	111-46-6	*R* & *M* Chemicals	>99%	<0.3%[c]	GC[e]
Triethylene glycol $HO(CH_2CH_2O)_2CH_2CH_2OH$	112-27-6	*R* & *M* Chemicals	>99%	<0.005%[d]	GC

[a] The purity values of all components are provided by the suppliers.
[b] Supplier did not provide this information.
[c] This number is water content and was measured by Karl Fischer (KF) method (stated by supplier).
[d] This number is peroxides (as H_2O_2) (stated by supplier).
[e] Gas chromatography.