Journal of Molecular Liquids 178 (2013) 137–141

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Glucose-based deep eutectic solvents: Physical properties

Adeeb Hayyan [a,b], Farouq S. Mjalli [a,*], Inas M. AlNashef [c], Yahya M. Al-Wahaibi [a], Talal Al-Wahaibi [a], Mohd Ali Hashim [b]

[a] Petroleum and Chemical Engineering Department, Sultan Qaboos University, Muscat 123, Sultanate of Oman
[b] Department of Chemical Engineering, Centre for Ionic Liquids (UMCiL), University of Malaya, Kuala Lumpur 50603, Malaysia
[c] Chemical Engineering Department, King Saud University, Riyadh 11421, Saudi Arabia

ARTICLE INFO

Article history:
Received 15 April 2012
Received in revised form 22 November 2012
Accepted 23 November 2012
Available online 10 December 2012

Keywords:
Glucose
Monosaccharides
Deep eutectic solvents
Ionic liquids

ABSTRACT

Deep eutectic solvents (DESs) are considered nowadays as green ionic liquid (IL) analogues. Despite their relatively short period of introduction as a special class of ILs, they have been under an increasing emphasis by the scientific community due to their favorable properties. In the present study, a glucose based DES of choline chloride (2-hydroxyethyl-trimethylammonium chloride) with the monosaccharide sugar D-glucose anhydrous was synthesized at different molar ratios. The physical properties of density, viscosity, surface tension, refractive index, and pH were measured and analyzed as function of temperature in the practical temperature range of 298.15–358.15 K. The analysis of these physical properties revealed that these novel DESs have the potential to be utilized for several possible industrial applications involving processing and separation of food constituents, pharmaceutical applications, as well as mediums for chemical reactions.

1. Introduction

Ionic liquids (ILs) have received escalating attention in organic synthesis, due to their unique physicochemical properties and their availability compared with conventional solvents. ILs have many favorable merits that distinguish them from conventional solvents. Not to mention all, ILs are known to have undetectable vapor pressure, wide liquid temperature range, special solubility for many organic or inorganic compounds, and less toxicity[1–3]. ILs have been used in many chemical applications such as CO_2 capture [4], battery development [5], electrochemical applications [6] and biological applications such as biocatalysis [7]. ILs can be applied in many chemical and industrial processes [8]. Recently, ILs were applied in the separation of food constituents such as separation of sugars from natural fruits [9]. This is due to the fact that their physical and chemical properties can be tailored by the judicious selection of their basic building block (cation, anion and substituent) [9].

Deep eutectic solvents (DESs) are relatively new class of ionic liquids that can be simply synthesized via mixing of a salt with a hydrogen bond donor compound. A common example is the DES between choline chloride and urea [10,2]. Due to their favorable properties, DESs were reported in many industrial applications as attractive alternatives to ILs. DESs share with ILs many of their intrinsic merits such as their biodegradable components, non-flammability due to their low or none measurable vapor pressure, and low toxicity [1,2,11]. Additionally, DESs are much cheaper than ILs which makes them readily available for large scale industrial applications. DESs were introduced in many applications and product preparations. Examples of such are in the synthesis of zeolite analogues [12], liquid–liquid extraction for aromatic separation from naphtha [13], mediums for the deposition of specific metals in the electro and electroless plating of metals [14,15] and in the removal of excess glycerol from biodiesel fuel [16]. Moreover, it was found that DES can be used as template-delivery agents in a controlled manner for the synthesis of materials [17].

The sugar industry sector is a very promising field which contributes much to the food and pharmaceutical industry. Research and development in the field of sugar separation and fractionation from natural bio-resource materials such as local fruits are necessary to improve the sugar industry and utilize the abundant bio-resource. Conventional sugar separation and fractionation technologies are expensive, complicated and sometimes not suitable to deal with sensitive food ingredients. There exists a great need for improving these technologies and introducing new separation methods. The key concept that contributes in this direction is the adoption of green engineering methodologies which improve the sustainability, efficiency, biodegradability, and environmental friendliness [2,18–20]. Recently, AlNashef et al. [9] patented a novel process for the separation of sugars from mixtures of fructose and glucose from a liquid phase or a solid mixture containing the fructose and glucose using ionic liquids. The patent claimed that ionic liquids work as selective agents that can separate glucose and fructose under ambient conditions. For example solubility of 1,3-dimethylimidazolium dimethylphosphate is 2–6 times higher than that of fructose [9].

The next step in improving this technology is by reducing its cost to make it practically available for industrial scale applications. DESs can contribute much in this area. These new and environmental friendly

* Corresponding author. Tel.: +968 2414298 1558; fax: +968 24141354.
E-mail address: farouqsm@yahoo.com (F.S. Mjalli).

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http://dx.doi.org/10.1016/j.molliq.2012.11.025

Table 1
Compositions and abbreviations for the studied DESs.

Molar ratio	Abbreviation	Appearance at room temperature
1:1	DES1	Colorless liquid
1.5:1	DES2	Colorless liquid
2:1	DES3	Colorless liquid
2.5:1	DES4	Turbid white liquid
1:1.5	DES5	White semisolid
1:2	DES6	White semisolid
1:2.5	DES7	White semisolid

solvents can be used as successful alternatives to ILs in the separation of sugars. In a similar analogy to the separation of glycerol from biodiesel [16], where a glycerol-based DES was utilized as a solvent, a sugar-based DES can be used to capture selectively sugar molecules from sugar mixtures. Since most natural fruits contain monosaccharide sugars (mainly glucose, fructose or both), sugar-based DESs should be synthesized from the same type of sugars. Harris [21] studied the freezing points of glucose based DES without further investigation of physical properties such as density, viscosity, surface tension, refractive index, and pH. To initiate research in this area, the physical properties of sugar-based DESs must be known and analyzed. In a recent study, the physical properties of phosphonium-based DES were studied by Kareem et al. [2]. In another work, Abbott et al. [10] reported the physical properties of DES formed between choline chloride and carboxylic acids. Physical properties of quaternary ammonium salt such as choline chloride and hydrogen bond donor of natural sources such as D-glucose were not yet studied. Therefore, the first objective of this study is to synthesize a new class of DESs based on ammonium salts at different ratios with a sugar as a hydrogen bond donor such as D-glucose. The other objective of this study was to investigate the most important physical properties such as density, viscosity, surface tension, refractive index, and pH as functions of temperature. This study investigated the effect of the mole ratios of salt and hydrogen bond donor on these physical properties. The findings of this study highlight the characteristics, nature/features of these DESs as probable new solvents. The availability of physical property data of such new classes of DESs will help investigating further related applications and in the design of chemical processes involving these DESs.

2. Experimental

2.1. Chemical

Choline chloride (2-hydroxyethyl-trimethylammonium) and D-glucose anhydrous with purity (>98%), were supplied by Merck Chemicals (Darmstadt, Germany). Both chemicals were used without any further purification.

2.2. Preparation of glucose based DES

In this study, DES samples were synthesized in different ratios of choline chloride to D-glucose as shown in Table 1. An incubator shaker (Brunswick Scientific Model INNOVA 40R) was used to mix choline chloride salt and the hydrogen bond donor (D-glucose). The mixture of choline chloride and D-glucose was shaken at 400 rpm and 353.15 K for a period of 2 h until a homogenous transparent colorless liquid was formed. DES samples were synthesized at atmospheric pressure and under tight control of moisture content.

2.3. Physical properties measurement

All samples were kept in well-sealed vials after preparation and fresh samples were used for analysis to avoid any structure changing and to avoid humidity effects from the environment which may affect the physical properties of DES. In this study, the temperature range of all physical properties was between 298.15–358.15 K.

Table 2
Experimental uncertainies in measurments.

Property	Estimated uncertainty
Density at solid phase	$\pm$0.001 g cm^{-3}
Density	$\pm$0.0001 g cm^{-3}
Viscosity (relative)	(3 to 5) % of measured value
Surface tension	$\pm$0.01 mN m^{-1}
Refractive index	0.0001
pH	0.05

The densities of choline chloride and D-glucose in solid powder form were measured at room temperature using a Quantachrome instrument BoyNTon. Choline chloride and D-glucose were dried under vacuum overnight in order to eliminate the moisture in both powders before measuring the density. The densities of all samples of DESs were measured using Anton Paar DMA4500M while the viscosities of the DESs were measured using Anton Paar Rheolab Qc. The temperature was controlled using external water-circulator type Techne-Tempette TE-8A. The surface tension of DES samples was measured using an automated tensiometer Krüss K10ST classification B with Du Noüy ring method. Refractive indices were obtained using a Bellingham and Stanley Abbe Refractometer (model 60/ED) with a sodium D1 line. The temperature was controlled in the refractometer using Techno TE-8D water circulator. Deionized water was used for calibration before each experiment. pH of synthesized DESs was measured using Thermo Scientific 3 star pH Bench top. The pH meter was calibrated using a standard pH buffer. The temperature of each sample was controlled using a water circulator (Julabo Labortechnik). Table 2 shows the estimated uncertainties for the experimental measurement of each physical property.

3. Results and discussion

Different molar ratios of choline chloride to D-glucose were used to prepare 7 samples of DESs and were described in Table 1 along with their abbreviations and our observations during preparation stage.

The different DES composition ratios were prepared by varying D-glucose composition at a fixed amount of salt. DES5, DES6, and DES7 were not successful as the two components did not mix properly and the products were in a white semisolid form. The probable reason for these ratios to be in solid phase after mixing, is that the amount of salt was not enough to build hydrogen bonding for all available sugar. Consequently, the mixture was saturated with sugar and no further reduction in freezing point was achieved. The high concentration of hydrogen bond donor compared to salt makes the mixture heterogeneous and even after long time of shaking under high temperature the mixture stayed as semisolid phase. After cooling DES5, DES6, and DES7 to room temperature they transform to white solid phase.

This leads to the conclusion that these ratios are not recommended for sugar based DES synthesis and therefore the three samples of DES were discarded from further consideration in this study. On the other hand, the DES1, DES2, DES3, and DES4 appeared as colorless liquid phase and easy to handle although DES4 was close to a semisolid form

Table 3
Freezing points of the salt (choline chloride) and D-glucose [21].

	Freezing point/K
DES1	304.15
DES2	297.15
DES3	288.15
DES4	317.15