Journal of Molecular Liquids 204 (2015) 76–83

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Zinc (II) chloride-based deep eutectic solvents for application as electrolytes: Preparation and characterization

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ARTICLE INFO

Article history:
Received 4 October 2014
Received in revised form 29 November 2014
Accepted 14 January 2015
Available online 16 January 2015

Keywords:
Ammonium
Phosphonium
Zinc (II) chloride
Deep eutectic solvents
Characterization
Electrical window

ABSTRACT

Deep eutectic solvents (DESs) have gained interest due to their favorable electrochemical properties. This work introduced a new group of zinc (II) chloride based DESs and characterized their melting temperatures, viscosities, electrical conductivities, refractive indices, as well as electrical window over a wide range of temperatures. The ammonium-based deep eutectic solvents possessed lower melting temperatures, lower viscosities and higher electrical conductivities in comparison to phosphonium-based ones. The deep eutectic solvent made from choline chloride and zinc (II) chloride at a mole ratio of 1:1 possessed high conductivities, 574–4779 $\mu S \cdot cm^{-1}$, relatively low viscosities, 0.8278–0.2842 $Pa \cdot s$, and wide electrochemical window, 3.74 V within the studied temperature range. The attained measurements were compared with other reported deep eutectic solvents in the literature.

1. Introduction

Developing a cost effective and environmentally benign solvent system is of utmost importance in contemporary organic synthesis [1]. One of the proposals is the replacement of conventional volatile organic solvents by non-volatile alternatives so that they do not emit toxic or flammable vapors at a wide range of temperatures [1]. Ionic liquids (ILs) and their analogous known as deep eutectic solvents (DESs) with favorable properties were recognized as potential candidates to be used as "green" solvents for industrial processes [2–7]. DESs include simple eutectics made from a combination of quaternary ammonium salts, like choline chloride (ChCl), with either hydrogen bond donors like urea and glycerol, or with metal halides (complexing agent) like zinc chloride. Such eutectic mixtures have emerged as biodegradable, economical alternatives and efficient replacement for conventional solvents and molten salts. Due to their high polarity, metal halide based DESs have outstanding salvation properties and can serve as high temperature electrolytes, reusable or homogeneous catalysts, and as solvent in biodiesel applications. This indicates the wide industrial horizon in which they can play essential roles [7–14].

ChCl:$ZnCl_2$ DESs as inexpensive and moisture stable benign solvents were successfully utilized in transesterification of soybean to biodiesel. It was found that the synthesis of biodiesel using zinc chloride-based DESs favored over conventional ILs owing to its simple preparation method [15]. Additionally, same DESs have been applied as efficient and reusable catalysts in the synthesis of α-aminophosphonates under solvent-free condition at room temperature. Despite carrying out the reaction in far shorter time with higher yields over 95% compared to the other alternatives, it is noticeable that $ZnCl_2$-based catalysts were recycled by simple extraction from the reaction mixture. The viscous eutectic mixtures that remained in the reaction flask were thoroughly washed with ether and reused in subsequent reactions without further purifications [16]. Add to this, ChCl:CuCl DESs became attractive homogeneous catalysts in view of their ease of applications and low costs in the palladium-free Sonogashira-type cross-coupling reactions. The use of this catalyst led to the formation of substituted aromatic alkynes in excellent yields about 97% under palladium-free conditions [17]. Besides, the electrochemical screening of both ammonium and phosphonium-based DESs on the potential applications of redox flow batteries was conducted. It was observed that DESs synthesized from ammonium salts provided a larger potential window in comparison to the phosphonium-based counterparts [18]. In addition, ChCl-based DESs were utilized by different groups as an electrolyte in lithium ion batteries, electric double layer capacitors, and as electrolytic media in electropolishing of metals [17–20].

In this work, new $ZnCl_2$ based-DESs made from four different quaternium salts were prepared and characterized by measuring some of their important physical and electrochemical properties. These DESs were introduced to replace high cost ILs in the preparation of biodiesel

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http://dx.doi.org/10.1016/j.molliq.2015.01.025
0167-7322/

as well as potential electrolytes in electrochemical processes such as down's cell [21]. Thus, their measured physical properties were evaluated to conclude about their suitability for such application. The melting point, viscosity, electrical conductivity and refractive index were measured and reported for these DESs at different salt:metal halide molar composition and temperature. In addition, the electrochemical windows of these DESs were determined so as to evaluate the stability of studied DESs in electrochemical processes.

2. Experiment

2.1. Chemicals

Choline chloride and N,N-diethylethanolammonium chloride (purity > 99%) purchased from Merck chemicals (Darmstadt, Germany) were recrystallized from absolute ethanol then filtered and dried under vacuum. Anhydrous zinc (II) chloride was purchased from Merck chemicals (Darmstadt, Germany), ethyltriphenylphosphonium bromide and tetrabutylphosphonium bromide were acquired from Sigma Aldrich (St. Louis, USA). These chemicals are of synthesis grade (purity > 99%) and were used without further purifications.

2.2. Preparation of DESs

The preparation of the DESs was carried out inside a glove box (Innovative Technology, USA) in which the humidity is controlled to less than 0.4 ppm. This is to ascertain that no contamination with atmospheric water vapor occurs to the salt and the HBD and consequently to the prepared eutectic solvent. The DESs in this research were prepared based on the preparation method described previously in the literature [1]. The two components of which the DES is made (salt and metal halide) are mixed mechanically in a jacketed vessel. The preparation temperature was at a maximum of 363.15 K and was achieved by passing heating fluid through the jacket of the vessel. The DES is considered to be fully prepared when the mixture turns into homogeneous liquid phase. For the purpose of protecting the prepared DESs from contamination by atmospheric water vapor, the DESs were placed in tight and humidity-safe screw-capped bottles and stored in a dehumidified chamber. Table 1 shows the salt:HBD combinations used in this work along with their molar ratios and abbreviations.

2.3. Characterization of DESs

2.3.1. Melting temperature measurement

The melting temperatures were measured using a Mettler Toledo Differential Scanning Calorimetry (DSC) device. The accuracy of measurement of the equipment was tested by measuring the melting temperatures for samples of known freezing points (distilled water and 2-propanol). The uncertainty in freezing point measurements was ±0.02 K.

2.3.2. Viscosity measurement

Viscosities were measured at a range of temperatures using a Brookfield R/S plus Rheometer. The device was calibrated by a zero-calibration method. Viscosity values were taken between 343.15 K and 368.15 K at 5 K interval. The variation in the temperature is achieved by utilizing an external water bath and circulator (Protech HC-10). The uncertainty in the viscosity and temperature measurements was ±0.0005 Pa·s and ±0.01 K, respectively.

2.3.3. Electrical conductivity measurement

The electrical conductivity is measured by a multi parameter analyzer (DZS-708, Cheetah) with a resolution of 0.001 ($\mu S \cdot cm^{-1}$). The cell constant was calibrated by measuring the conductivities of aqueous solutions of KCl at different concentrations according to the IUPAC recommended procedure [21]. The measurements of the conductivity were taken at a range of temperature. The temperature of DES samples was varied using an oil bath. The uncertainty in the electrical conductivity and temperature measurements was ±1 $\mu S \cdot cm^{-1}$ and ±0.02 K, respectively.

2.3.4. Refractive index measurement

The measurements of the refractive index are carried out using an ABBE SASTEC refractometer (ST-WYA-25) at a range of temperatures. This range usually starts from few degrees Kelvin above the melting temperature of the DES up to a maximum of 363.15 K. To vary the temperature of measurement, the refractometer was connected to an external water bath. The meter was calibrated by measuring the refractive index of glycerol at 298.15 K, which was found to match reported values of glycerol in the literature [22]. The uncertainty in refractive index measurements was ±0.00001. Three measurement replicates of viscosity, conductivity and the refractive index were conducted, and the average value was recorded.

2.3.5. Cyclic voltammetry

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about the electrochemical behavior of electrolytes [23,24]. It offers a rapid location of redox potentials of the electroactive species. In the current work, the electrolytic behaviors of $ZnCl_2$-based DESs were investigated. The electrochemical cell consisted of a typical three-electrode set-up. The counter electrode was a Pt wire, and an Ag wire (immersed in 65% HNO_3 prior to experiments, then rinsed thoroughly with water and ethanol) was used as a quasi-reference electrode. A glassy carbon (GC, 3 mm diameter) was used as

Table 1
DESs studied in this work with their abbreviations and melting points.

	Salt:HBD	Salt:$ZnCl_2$ mole ratio	Abbreviation	Melting temp. (K)
Ammonium-based DESs	Choline chloride:$ZnCl_2$	1:1	DES1	314.77
	Choline chloride:$ZnCl_2$	1:2	DES2	325.33
	Choline chloride:$ZnCl_2$	1:3	DES3	320.37
	Choline chloride:$ZnCl_2$	1:4	DES4	318.97
	N,N-diethylethanolammonium chloride:$ZnCl_2$	1:1	DES5	313.39
	N,N-diethylethanolammonium chloride:$ZnCl_2$	1:2	DES6	307.56
	N,N-diethylethanolammonium chloride:$ZnCl_2$	1:3	DES7	310.47
	N,N-diethylethanolammonium chloride:$ZnCl_2$	1:4	DES8	312.26
Phosphonium-based DESs	Ethyltriphenylphosphonium bromide:$ZnCl_2$	1:2	DES9	341.5
	Ethyltriphenylphosphonium bromide:$ZnCl_2$	1:3	DES10	338.98
	Ethyltriphenylphosphonium bromide:$ZnCl_2$	1:4	DES11	340.27
	Ethyltriphenylphosphonium bromide:$ZnCl_2$	1:5	DES12	345.29
	Tetrabutylphosphonium bromide:$ZnCl_2$	1:2	DES13	340.95
	Tetrabutylphosphonium bromide:$ZnCl_2$	1:3	DES14	343.01
	Tetrabutylphosphonium bromide:$ZnCl_2$	1:4	DES15	341.55
	Tetrabutylphosphonium bromide:$ZnCl_2$	1:5	DES16	344.99