Journal of Molecular Liquids 223 (2016) 845–852

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Physical properties of benzyl tri-methyl ammonium chloride based deep eutectic solvents and employment as catalyst

M. Bengi Taysun, Emine Sert *, Ferhan S. Atalay

Ege University, Department of Chemical Engineering, 35100 İzmir, Turkey

ARTICLE INFO

Article history:
Received 27 April 2016
Accepted 28 July 2016
Available online 03 September 2016

Keywords:
Deep eutectic solvent
Benzyl tri-methyl ammonium chloride
Oxalic acid
p-toluene sulfonic acid
Citric acid
Esterification

ABSTRACT

Deep eutectic solvents (DES) are a type of ionic solvents composed of two components and that have a melting point lower than either of the individual components. DES's can be prepared combining a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). In this study, benzyl tri-methyl ammonium chloride (BTMAC) is used as the hydrogen bond acceptor, and p-toluene sulfonic acid (PTSA), citric acid (CA), and oxalic acid (OX) are used as the HBD. The physical properties of DES 1 (BTMAC-PTSA), DES 2 (BTMAC-CA), and DES 3 (BTMAC-OX) were investigated at their respective eutectic points. The refractive index, conductivity, density, viscosity, and pH values were measured for the three DES between 293.15 and 333.15 K. As expected, the density, refractive index, and viscosity decreased and the ionic conductivity increased with increasing temperature, whereas, the pH values remained constant. The catalytic activities of the DES were tested in the esterification reaction between acetic acid and butanol. The results showed the superiority of DES 1 (BTMAC: PTSA) which gave the highest conversion of acetic acid and a further parametric study including the effects of catalyst loading, mole ratio, alcohol type, and reusability were conducted using DES 1. The obtained results showed a high applicability of DES for catalytic applications.

1. Introduction

Since the emergence of the “Green Chemistry” concept in the early 90s, there is a growing interest in environmentally friendly or at least partially/relatively “green” solvents and catalysts. Part of this interest fell upon ionic liquids (IL). ILs have some advantages such as high solubility, low volatility, inflammability, high polarity, high thermal stability, and a relatively low melting point [1–5]. Despite these advantages, the usage and implementation of ILs is hampered by their toxicity and low biodegradability [6–8] and subsequent purification problems [9]. In contrast, owing to their low cost, ease of use and preparation, environmentally friendly nature, and non-toxicity, DES are becoming more relevant each day [10–13]. The current and potential future applications of DES include biodiesel production, waste oil purification, separation processes, and employment as an acidic catalyst or solvent [11,12,14–16].

DES show many similarities with ionic liquids, such as low vapor pressure, non-combustible, and a non-toxic nature [17,18]. Due to the flexibility of selecting different HBAs and HBDs, DES can be tailored to specific applications [19]. The preparation of DES is completely mole efficient and relatively easy compared to the ionic liquids and this broadens their usage areas.

Despite their relative novelty, DES are used as solvents and catalysts in many areas. Early applications include the usage of DES as electrolytes in electro-finishing processes [20], and due to their high ability to dissolve organic materials, even complex ones like cellulose [21], DES were used as extraction solvents [22]. Also, the employment of DES on the production and purification of biodiesel was studied [23,24].

As with any novel chemical product, precise data on the physical properties of DES must be obtained in order to be employed on any industrial application. Properties like viscosity, density, and melting point have a great effect on how and where DES could or could not be employed. It is very hard to imagine any process where a catalyst or solvent is not subjected to pumping, mixing, storing, and flowing through pipes. Therefore, it is imperative to investigate density and viscosity. Also, the density and refractive index of a DES can provide information on the molecular interactions within the liquid and purity of the DES [25,26].

Due to a growing interest, there is a proliferation on the studies focusing on the physical properties of DES like density, viscosity, refractive index, ionic conductivity, and pH [9,27–29]. Despite this, studies on the physical properties of carboxylic acid based DES are rather scarce. The melting points of choline chloride (ChCl) based DES were reported by Abbot et al. [13] which showed melting point depressions as high as 160 K. The viscosity of tri-methyl benzyl ammonium methane sulfonate-PTSA based DES was reported by De Santi et al. [30]. The viscosities of the sulfonate-PTSA system varied from 1700 to 100 cP in the

* Corresponding author.
E-mail address: emine.sert@ege.edu.tr (E. Sert).

http://dx.doi.org/10.1016/j.molliq.2016.07.148
0167-7322/

temperature range between 308 and 353 K. The densities of DES made from ChCl-ethylene glycol and ChCl-malonic acid and the viscosities of ChCl and glycerol were investigated by Yadav et al. [29]. They found that the ChCl-malonic acid system densities varied from 1.19 g/cm^3 at 283 K to 1.14 g/cm^3 at 363 K. The physical properties like density, viscosity, and ionic conductivity of tetra-butyl ammonium bromide based DES was investigated by Yusof et al. [9]. However, there is no any study about the physical properties and also catalytic activity of benzyl tri-methyl ammonium chloride (BTMAC) based DES in the literature.

Esterification reactions between carboxylic acids and alcohols require acidic catalysts. Traditionally acid catalysts like sulfuric and hydrofluoric acid were employed. Although these acids have a higher catalytic performance [31]; their usage is hampered with problems such as the recovery of the catalyst, a high volume of acidic waste, and general difficulties caused by working with highly potent acids. For the same reasons, these types of manufacturing processes require large purification and treatment efforts for products and waste. As a more modern alternative, acidic ion exchange resins are widely employed in these reactions. Although ion exchange resins offer relatively high conversions, ease of separation and reusability, their temperature sensitive structure prevents their employment in high temperature operations [32].

There is a very limited literature background on the catalytic employment of DES. Yadav et al. [12] studied the employment of a DES composed of choline chloride-oxalic acid on some organic synthesis reactions and reported very high yields within very short times and high reusability of the DES catalyst. Also employment of ChCl:PTSA and ChCl:urea DES on the supercritical esterification of waste tire pyrolysis oil and subsequent improvement in fuel properties were reported by Alhassan et al. [33]. Converting potent acids such as PTSA to DES provides advantages like decreasing hygroscopicity, increasing reusability and pumping, and transporting conveniences due to the liquid nature of the DES [24]. The introduction of solid acid based DES as catalysts have some unique advantages. Although solid acids, like p-toluene sulfonic acid, offer a high catalytic activity [30], in esterification reactions they dissolve into the liquid reaction mixture. This complicates recovery of the catalyst. DES can provide phase separation within the reaction mixture. This greatly simplifies the catalyst recovery process. De Santi et al. [30] investigated the application of the PTSA based DES as dual solvent-catalyst and reported the ease of reusability and high yield [34]. However, there is no reported study in the literature about the physical properties and catalytic performance of the BTMAC based DES.

To present the DES high potentials as an acidic catalyst on the esterification reactions, this study investigates the physical properties of three different BTMAC based DES, namely the refractive index, conductivity, density, viscosity, and pH at temperature ranges from 293.15 to 333.15 K at their respective eutectic points and the catalytic performances of DES in the esterification reactions of acetic acid with different alcohols. All three DES studied, in this study, are composed of common HBA (BTMAC) and different HBDs (PTSA, CA, OX). The molecular representation of DES is represented graphically in Fig. 1. Current literature lacks information on both the physical properties and catalytic performance of BTMAC based DES, especially on the esterification reactions.

2. Experimental

2.1. Materials

The following were used for the preparation of DES in the study: Citric acid monohydrate (Sigma Aldrich, 99%), *p*-toluene sulfonic acid monohydrate (ABCR, 98%), oxalic acid di-hydrate (Sigma Aldrich, 99%), and benzyl tri-methyl ammonium chloride (Merck, 99%). The reactants used for the esterification reactions were methanol (Merck, 99%), *n*-butanol (Merck, 99%), *n*-hexanol (Merck, 99%), and 2-ethyl-1-hexanol (ABCR, 99%). For the gas chromatographic calibration, methyl acetate (ABCR, 99%), butyl acetate (ABCR, 99%), hexyl acetate (ABCR, 99%), and 2-ethyl-hexyl acetate (ABCR, 99%) were used. All chemicals were used without further purification.

2.2. Determination of eutectic point

The samples from 30 to 70 molar percent with 10 molar percent intervals were analyzed to measure the freezing points of the DES using a laboratory setup. The setup consisted of a modified temperature controlled alcohol bath, which was loaded with pure ethanol, to provide low temperatures. The schematic representation of the setup is shown in Fig. 2. The prepared DES were placed in glass vials and immersed into the alcohol reservoir. The temperature was decreased at the rate of 2 °C/h. The vials were taken from the reservoir and placed horizontally for 5 s to see any flow behavior. The temperature at which flow was not observed was considered as the freezing point.

2.3. Preparation of DES

The HBA and HBD were placed in a flask at the eutectic molar ratio and to ensure the homogeneity, the content of the flask was mixed with a Dragon Lab™ MX-S vortex mixer. The solid mixture was heated to 80 °C and stirred with a temperature controlled magnetic stirrer until the entire solid was dissolved and the mixture attained a consistent clear liquid structure. At periodic time intervals, the mixture was weighted to ensure evaporation of the water content within the DES. To prevent humidification of the prepared DES by atmospheric vapor, the DES were placed into glass vials with airtight aluminum – Teflon caps and stored in a dehumidification chamber.

2.4. Measurement of physical properties

The density measurements were performed with an Anton Paar™ DMA 35 model vibrating borosilicate U-tube density meter. Prior to and after measurement calibrations were performed using deionized water and methanol. The *viscosity measurements* were performed using a Fungilab™ Expert R model rotating spindle viscosity meter. The viscometer calibration was performed using the built-in test function of the device. The *conductivity measurements* were carried out using the Hanna™ HI 9033 model EC and TDS meter. The calibration were performed using sample solutions of known conductivity. The *refractive index measurements* were performed using a SOIF WYA-2S digital abbe refractometer. Calibrations were performed before and after the measurements using deionized water and ethanol. The *pH measurements* were performed using a WTW pH 7110 model pH meter. Calibrations were performed prior to and after the measurements using appropriate buffer solutions.

2.5. Esterification reactions

2.5.1. Procedure

Experiments were performed in a batch reactor which was placed upon a magnetic heater-stirrer and consisted of a 500 mL three necked flask fitted with a condenser to prevent loss of material during the experiment. Also in order to prevent concentration gradients across the reaction mixture, vigorous stirring were employed at 1000 rpm for each experimental run. In the experiments, the alcohol and catalyst (DES) were charged into the reactor and the mixture was quickly heated to the reaction temperature. After obtaining the constant temperature, the preheated acid was added. This method gives the best results to maintain the reaction temperature in the initial reaction step and also made it possible to avoid an auto catalyzed reaction occurring between the acid and alcohol if they had been heated together [31]. The temperature was controlled by a temperature controller. The samples, around 1 mL, were taken during the experiment for gas chromatographic analysis.