Journal of the Taiwan Institute of Chemical Engineers 61 (2016) 64–74

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Novel amino acids based ionic liquids analogues: Acidic and basic amino acids

Farouq S. Mjalli*

Department of Petroleum and Chemical Engineering, Sultan Qaboos University, Al Khoudh, Muscat 123, Oman

ARTICLE INFO

Article history:
Received 30 July 2015
Revised 27 November 2015
Accepted 14 December 2015
Available online 13 January 2016

Keywords:
Amino acids
Ionic liquids
Eutectic
Aspartic
Glutamic
Arginine

ABSTRACT

Deep eutectic solvents (DES) are one of the immerging promising industrial green solvents that are gaining considerable attention. These novel liquids have been synthesized from a variety of quaternary ammonium and phosphonium salts in combination with one or more complexing agents. Amino acids may act as good hydrogen bond donors and hence can be used as the complexing agent in the synthesis of type III DES. In this work a variety of ammonium quaternary salts have been investigated in forming amino acids-based DESs by combining with acidic or basic amino acids. Five of the common basic and acidic amino acids were used for this purpose. Three amino acids (glutamic acid, aspartic acid and arginine) were successful in forming DESs with the salt tetrabutylammonium chloride. The successful molar ratios of these DESs were characterized by measuring their melting point, density, viscosity, surface tension, refractive index, and conductivity in the temperature range 303.15–353.15 K. The presented novel data for these DESs can be utilized for customizing these solvents for probable chemical or industrial applications.

1. Introduction

Room temperature ionic liquids (RTIL) are unanimously considered among the promising green solvents that have great impact on the chemical and pharmaceutical industries [1]. These extremely low volatile, thermally stable and non-flammable liquids have attracted scientists in diverse disciplines for utilizing their favorable properties in the chemical synthesis, separation, electrochemical as well as pharmaceutical applications [2–6]. The ability of customizing these liquids for certain applications encouraged researchers to design them by modifying their constituting ions and tuning their properties for specific applications. This brought up the idea of task-specific ionic liquids (TSIL). This option has introduced tremendous opportunities of successful applications, some of which have seen commercialization [7]. Nevertheless, serious limitations confronting the widespread application of these ILs manifest in their toxic and non-biodegradable nature, not to mention the high production cost of these chemicals [8].

Natural amino acids which are considered as the building blocks of the proteins in humans as well as animals are important organic species that are used in many applications. Their ability to oxidize enables them to be utilized by the body as a store of energy [9]. In the industry, they have been used in the formulation of animal feedstock, as well as in the food, cosmetic, polymers production and pharmaceutical fields [10–12].

Conventionally, the twenty essential naturally occurring amino acids can be grouped into different categories depending on their chemical structure and properties [12]. A major group of the twenty essential amino acids is one having acidic or basic side chains at neutral pH conditions. This group involves five of the essential amino acids namely, glutamic acid, aspartic acid (acidic) and arginine, histidine and lysine (basic). These safe, biodegradable acids were utilized in functionalizing some of the ILs [13,14]. This category of ILs is termed amino acid-based ionic liquids (AAILs). The first attempt to incorporate amino acids in the structure of some ILs was reported by Fukumoto et al. (2005). In their work [15], the cation 1-ethyl-3-methylimidazolium $[C_2mim]^+$ was used to prepare imidazolium hydroxide to neutralize a group of amino acids forming the corresponding AAILs. Their study revealed that the ionic liquids functionalized with amino acids are capable of forming strong hydrogen-bonds and dissolve many bio-species like DNA and carbohydrates. This new category of ILs may have immense role in serving the pharmaceutical, medical and bio-industries. However, much work is needed to simplify their synthesis procedure and replace the used toxic solvents (needed to exchange the anions) with more environmental friendly and cost effective materials.

Another successful methodology for preparing ionic liquids is by the coupling of a phosphonium or ammonium quaternary salts

* Corresponding author. Tel.: +968 24142558; fax: +968 24141354.
E-mail address: farouqsm@yahoo.com

http://dx.doi.org/10.1016/j.jtice.2015.12.020
1876-1070/

with a compound that is capable of donating hydrogen bonds. If successfully coupled, the mixture will form a homogeneous liquid at room temperature. These liquids are termed deep eutectic solvents (DES). They possess many of the favorable properties of ionic liquids in addition to their low cost of synthesis. By carefully selecting the type of salt and complexing agent involved in the synthesis of the mixture, a DES with low environmental impact can be prepared. Many varieties of these DESs have been reported that vary in the type of salt and complexing agent involved [16]. Four different categories are available namely: Type I (quaternary ammonium or phosphonium salt + metal halide), Type II (quaternary ammonium or phosphonium salt + hydrated metal halide), Type III (quaternary ammonium or phosphonium salt + hydrogen bond donor) and Type IV (metal halide + hydrogen bond donor). Out of these four different varieties of possible DES, the third type DES has been studied thoroughly in the literature and a variety of applications have been reported [17–20]. For successfully applying these DESs in future applications, a thorough investigation needs to be made on their physical–chemical characteristics. Some studies are already available [21–23].

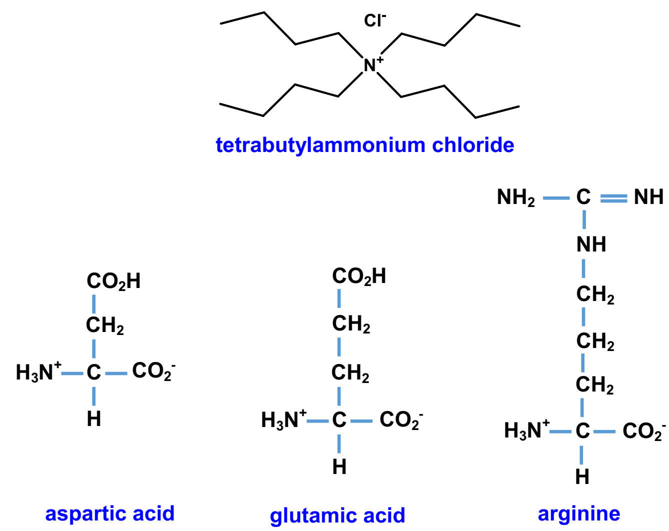
The previous studies on the synthesis and characterization of type III DESs involved many types of hydrogen bond donors such as: sugars [22], alcohols [24], polyols [25], acids [26]. Amino acids have been mixed with other naturally occurring compounds to form what's called natural deep eutectic solvents (NADES). NADES were proposed as possible solvents or reaction medium for a variety of applications such as drug delivery systems, enzymatic and pharmaceutical applications [27].

In this work, the members of a group of the essential amino acids that are categorized based on their acid–base character are used as possible H-bond donors for synthesizing type III DESs in combination with selected quaternary ammonium salts. The successful DESs are characterized in terms of their basic properties including melting point, density, viscosity, conductivity and refractive index within the temperature range (303.15–353.15 K). Similar studies will be conducted on other types of amino acids in future works.

2. Experimental methodology

2.1. Chemicals used

Salts involving: choline chloride, ChCl ($C_5H_{14}NO.Cl$), tetrabutyl ammonium bromide TBAB, ($(CH_3CH_2CH_2CH_2)_4$ N.Br), tetrapropyl ammonium bromide, TPAB ($(CH_3CH_2CH_2)_4$ N.Br) all > 98%, tetrabutylammonium chloride, TBAC ($(CH_3(CH_2)_3)_4$ N.Cl) were supplied by Merck Chemicals (Darmstadt, Germany). The amino acids: glutamic acid ($C_5H_9NO_4$), aspartic acid ($C_4H_7NO_4$), arginine ($C_6H_{14}N_4O_2$), histidine ($C_6H_9N_3O_2$) and lysine ($C_6H_{15}N_2O_2$) (>99.0%), were supplied by Sisco Research Lab (Mumbai, India). The chemical structures of the quaternary ammonium salt and amino acids are shown in Scheme 1 and their basic data are given in Table 1. All chemicals were pretreated by drying for a minimum of 3 h in a vacuum oven to guarantee minimal moisture content of less than 200 ppm prior to being used. Pretreated chemicals were then kept in sealed bottles and stored in a dissector.



Scheme 1. Chemical structure of the successful DES component.

2.2. Synthesis of amino acids based DES

The four ammonium based salts were screened for possible coupling with the five mentioned amino acids to form successful DESs. In each screening experiment, the selected salt was mixed with one of the amino acids one at a time with a pre-screening (salt: amino acid) molar ratio in the range 10:1–1:10. The pre-screening ratios were mixed at 400 rpm in an incubator shaker (Brunswick Scientific Model INNOVA 40R) at 353.15 K for 2 h. Successful ratios were those that formed homogeneous liquids. The mixing was done in a moisture-controlled atmosphere with maximum water content of 500 ppm. Only successful ratios were refined by selecting tighter salt: amino acid molar ratios. Among all four tested salts, only the TBAC salt mixtures were successful in forming homogeneous liquid phases upon mixing. Hence, the other three salts ChCl, TBAB and TPAB were discarded from further analysis. Three of the used amino acids (aspartic acid, glutamic acid and arginine) formed consistent homogeneous liquids when mixed with TBAC.

The least successful DES ratios of the TBAC based DESs were 9:1, 8:1, and 6:1 with aspartic acid, glutamic acid and arginine respectively. Starting at these minimum successful ratios, two more ratios of each combination were prepared. The three prepared molar ratios of each DES are given in Table 3. Looking at the successful molar ratios of these DESs, we notice that all of them have TBAC content higher than the corresponding amino acid. This

Table 1
Basic data for the used amino acids and ammonium based salts.

Chemical specie	Abbreviation	Molecular formula	Molecular weight	Density (g/cm^3)	Melting point (K)
L-aspartic acid	Asp	$C_4H_7NO_4$	133.10	1.7000	543.15[28]
L-glutamic acid	Glu	$C_5H_9NO_4$	147.13	1.4601	433.15[28]
L-arginine	Arg	$C_6H_{14}N_4O_2$	174.20	1.3000	517.15[28]
L-histidine	His	$C_6H_9N_3O_2$	155.15	1.4850	560.15[28]
L-lysine	Lys	$C_6H_{14}N_2O_2$	146.19	1.1250	497.15[28]
Choline chloride	ChCl	$C_5H_{14}ClNO$	139.62	1.2050	578.15
Tetrabutyl ammonium bromide	TBAB	$C_{16}H_{36}BrN$	322.37	1.1480	376.15
Tetrabutyl ammonium chloride	TBAC	$C_{16}H_{36}ClN$	277.92	0.9800	353.15
Tetrapropyl ammonium bromide	TPAB	$C_{12}H_{28}NBr$	266.26	-	543.15