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Properties and thermal behavior of natural deep eutectic solvents

R. Craveiro [a], I. Aroso [b,c], V. Flammia [a], T. Carvalho [a], M.T. Viciosa [d], M. Dionísio [a], S. Barreiros [a], R.L. Reis [b,c], A.R.C. Duarte [b,c], A. Paiva [a,*]

[a] LAQV—REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] 3B's Research Group — Biomaterials, Biodegradable and Biomimetic, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, Avepark, Barco, 4805-017 Guimarães, Portugal
[c] ICVS/3B's PT Government Associated Laboratory, Braga/Guimarães, Portugal
[d] Centro de Química-Física Molecular and IN — Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Univ. Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

Natural deep eutectic solvents (NADES) have shown to be promising sustainable media for a wide range of applications. Nonetheless, very limited data is available on the properties of these solvents. A more comprehensive body of data on NADES is required for a deeper understanding of these solvents at molecular level, which will undoubtedly foster the development of new applications. NADES based on choline chloride, organic acids, amino acids and sugars were prepared, and their density, thermal behavior, conductivity and polarity were assessed, for different NADES compositions. The NADES studied can be stable up to 170 °C, depending on their composition. The thermal characterization revealed that all the NADES are glass formers and some, after water removal, exhibit crystallinity. The morphological characterization of the crystallizable materials was performed using polarized optical microscopy which also provided evidence of homogeneity/phase separation. The conductivity of the NADES was also assessed from 0 to 40 °C. The more polar, organic acid-based NADES presented the highest conductivities. The conductivity dependence on temperature was well described by the Vogel–Fulcher–Tammann equation for some of the NADES studied.

1. Introduction

Green technology requires new solvents to replace common organic media that present inherent toxicity and have high volatility. Over the past two decades, ionic liquids (ILs) have attracted great attention from the scientific community, and the number of articles focusing on ILs has grown exponentially. ILs are molten salts, liquid at room temperature, whose potential relies on the possibility to tune their properties through the combination of different cations and anions [1]. Nevertheless the "green" character of ILs is often questioned, mainly due to their poor biodegradability, biocompatibility and sustainability.

Deep Eutectic solvents (DES) are obtained upon mixing two compounds in such a ratio that the resulting substance has a significantly lower melting point than that of each individual component [2]. The most common DES are based on choline chloride (ChCl), carboxylic acids and other hydrogen-bond donors, such as urea, citric acid, succinic acid, and glycerol. DES may have similar characteristics to ILs, such as low vapor pressure, but are cheaper to produce, both due to the lower cost of the required raw materials and the simplicity of the synthesis. Furthermore, they are less toxic and often biodegradable [3]. Recently Dai and co-workers have reported on a large number of stable natural deep eutectic solvents (NADES), based on primary metabolites, such as organic acids, amino acids, and sugars [3]. Paiva and co-workers have recently reported on the cytotoxicity of different NADES, showing that it is much lower than that of commonly used imidazolium-based ILs [4]. Radošević et al. have also studied three ChCl-based DES and suggested that they can be classified as readily biodegradable presenting low to moderate toxicity [5]. These characteristics have led to growing interest in the research community in replacing ILs with DES, as solvents for biocatalysis [6,7], extraction [8] and chemical conversion [9] of organic compounds, and polymer synthesis. As regards polymer processing, DES have been shown to dissolve bioactive materials and biopolymers [2]. Bioactive DES with active pharmaceutical ingredients (APIs), such as ibuprofen [10], can be incorporated in biopolymers through the doping of the biopolymer matrix.

A more detailed characterization of DES can lead to further scientific developments. Dai et al. have characterized some NADES by nuclear magnetic resonance (NMR) spectroscopy and concluded that water played an important role in NADES formation [3]. In the case of the NADES composed by 1,2-propanediol, ChCl and water, the authors observed a strong interaction between the hydroxyl groups of all species. In addition, Dai and co-workers also determined the thermal and physical characteristics of some of NADES with water in its composition [3]. Florindo et al. also reported on the strong influence of water on the properties of ChCl:carboxylic acid-based DES [11]. The thermal

* Corresponding author.
E-mail address: alexandre.paiva@fct.unl.pt (A. Paiva).

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properties of DES were also presented by those authors, with special attention to the glass transition temperature (T_g) and decomposition temperature (T_d). Rengstl and co-workers have recently reported on the thermal behavior of DES based on different choline ILs [12].

Following the work of Dai et al. [3], we prepared NADES composed of different sugars, organic acids and ChCl, in the ratios reported and according to the procedures described by those authors. We measured a number of properties of these NADES. We also used polarized optical microscopy measurements coupled with differential scanning calorimetry analysis to better understand the thermal behavior of NADES, e.g., the influence of water on the glass transition and melting temperature. Density, polarity and conductivity measurements were also performed.

ChCl can form NADES with almost any kind of primary metabolites and has been used to prepare most of the DES reported in the literature. Therefore ChCl is present in most of the NADES we selected for our study. In addition, three sugar based NADES are also studied in this work.

2. Material and methods

2.1. Materials

Choline chloride (ChCl) (>98% purity, CAS number 67-48-1), D-(+)-xylose (99% purity, CAS number 58-86-6), citric acid monohydrate (CAS number 5949-29-1), D-(+)-glucose (99% purity, CAS number 50-99-7), Nile red (>98% purity, CAS number 7385-67-3), and Hydranal Coulomat AG were obtained from Sigma-Aldrich. D-(+)-sucrose (98% purity, CAS number 57-50-1) were obtained from Fluka. L-(+)-tartaric acid (>99% purity, CAS number 87-69-4) was obtained from Fisher scientific. All chemicals were used without further purification.

2.2. Preparation of NADES

NADES were prepared according to Table 1. Weighed amounts of each component, as required to achieve the molar ratios indicated in the table, were dissolved in water. The two solutions were mixed, and water was removed in a rotary evaporator at 50 °C under vacuum, until a clear viscous liquid was obtained. NADES were then kept under vacuum for 24 h, after which they were stored in a desiccator.

2.3. Differential scanning calorimetry analysis (DSC)

To determine the degradation temperature of the NADES (T_d), experiments were performed using a DSC Q100 equipment (TA Instruments — ELNOR). The experiments were conducted under a nitrogen atmosphere, with samples of 5–10 mg packed in aluminum pans. The samples were heated at a constant heating rate of 20 °C min^{-1}, from −40 °C up to 250 °C. The results presented are the average of at least three measurements.

To assess the thermal behavior of the NADES, calorimetric experiments were carried out with a DSC Q2000 from TA Instruments Inc. (Tzero™ DSC Technology) operating in the Heat Flow T4P option [13]. Measurements were performed under dry high purity helium, at a flow rate of 50 mL·min^{-1}. Less than 5 mg of each sample were encapsulated in Tzero aluminum pans. The set was not hermetically sealed to allow free water evaporation. At least two scans at cooling and heating rates of 20 °C·min^{-1} were performed, covering the temperature range from −90 °C to 120 °C. Each sample was kept for one additional minute at 120 °C at the end of the scan, to ensure water removal. Also each sample was kept for 10 min at −90 °C in order to obtain a better signal of the glass transition temperature, when present.

2.4. Polarized optical microscopy measurements

Polarized optical microscopy was performed on an Olympus Bx51 optical microscope equipped with a Linkam LTS360 liquid nitrogen-cooled cryostage. The microstructure of the samples was monitored by taking microphotographs at appropriate temperatures, using an Olympus C5060 wide zoom camera. A drop of each sample was positioned on a microscope slide and inserted in the hot stage. Before each measurement, the samples were heated to 120 °C and kept at least 10 min at this temperature to allow water removal; after this thermal treatment a cover slip was placed on the top of the sample. Cooling and heating thermal treatments were carried out at a rate of 20 °C·min^{-1}.

2.5. Water content determination

The water content of the NADES was determined after drying under vacuum for 24 h upon preparation. A 831 KF Coulometer with generator electrode and without diaphragm was used. The water content values given are an average of at least three measurements.

2.6. Density measurements

The density of the NADES was measured following a simple gravimetric procedure, using a calibrated volume at 23 °C.

2.7. Conductivity measurements

The conductivity of the different NADES was assessed by dielectric relaxation spectroscopy (DRS). For the DRS measurements, samples were placed between two stainless steel electrodes (10 mm diameter) in a BDS 1200 parallel plate capacitor, using two 50 μm silicon spacers to maintain sample thickness. The sample cell was mounted on a BDS 1100 cryostat, and exposed to a gas stream resulting from the evaporation of liquid nitrogen in a Dewar. Temperature control was ensured by a Quatro Cryosystem controller and performed to within ±0.5 °C (all modules supplied by Novocontrol). Measurements were carried out

Table 1
NADES prepared in this study, respective abbreviations and water content.

NADES		Mole ratio	Sample name	Water content /wt.%	Density /g·mL^{-1}
Component 1	Component 2				
Choline chloride	D-(+)-glucose	1:1	ChCl:gluc (1:1)	5.5	1.27
Choline chloride	Citric acid	1:1	ChCl:ca (1:1)	0.2	1.30
Choline chloride	D-(+)-sucrose	4:1	ChCl:suc (4:1)	0.2	1.22
Choline chloride	D-(+)-sucrose	1:1	ChCl:suc (1:1)	0.2	1.35
Choline chloride	L-(+)-tartaric acid	2:1	ChCl:ta (2:1)	1.9	1.26
Choline chloride	D-(+)-xylose	2:1	ChCl:xyl (2:1)	3.8	1.23
Choline chloride	D-(+)-xylose	3:1	ChCl:xyl (3:1)	0.2	1.22
Citric acid	D-(+)-sucrose	1:1	ca:suc (1:1)	1.2	1.43
Citric acid	D-(+)-glucose	1:1	ca:gluc (1:1)	0.5	1.45
D-(+)-glucose	L-(+)-tartaric acid	1:1	gluc:ta (1:1)	0.4	1.46