Deep Eutectic Solvents

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Contributor: Victoria Samanidou , Orfeas-Evangelos Plastiras , Eirini Andreasidou

Deep eutectic solvents (DESs), were introduced in 2001 as an alternative to ILs. These showed a stronger ecofriendly profile, with easier and cheaper production, while having similar properties. DESs contain large, asymmetrical ions that have low lattice energy and, thus, low melting points. They are often acquired by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between, for instance a halide ion and the hydrogen-donor moiety, is responsible for the decrease in the melting point of the mixture, in relation to the melting points of the individual components. Since 2001, many scientists around the globe pursed the utilization of DESs and published a variety of studies.

The use of DESs in analytical microextraction techniques is on the rise, due to the many benefits they provide, such as lower cost and easier synthesis than ILs and an environmentally friendly profile, because of the low toxicity reported, although they need further investigation. To this day, the number of HBAs and HBDs is quite limited, so more studies ought to be carried out to present a plethora of DESs available for use. Moreover, DESs are not commercially available yet, substantially affecting and further limiting their usage for routine analyses in industrial or certified laboratories.

The extraordinary high relative recoveries, selectivity, low LODs and decent repeatability they offer, render them appropriate for the determination and quantification of lots of compounds in either simple or complex matrices. As seen, most applications regard liquid phase microextractions rather than solid phase microextractions, because of their liquid nature, as it is simpler to use them as supporting solid adsorbents. The fact that the sample preparation of complicated matrices is of high interest makes them ideal for the research.

Hopefully, DESs will be available for purchase in the foreseeable future and will replace organic solvents in some analytical methods commonly used nowadays, while more studies are carried out about their properties.

Our aim in this review will be towards the use of DESs in analytical extraction and microextraction techniques, while briefly presenting some frequently used DESs, their synthesis methods and their properties.

The ever-increasing use of deep eutectic solvents (DES) in microextraction techniques will be discussed, focusing on the reasons needed to replace conventional extraction techniques with greener approaches that follow the principles of green analytical chemistry.

deep eutectic solvents
microextraction
liquid phase microextraction
liquid–liquid microextraction
dispersive liquid–liquid microextraction

1. Introduction

Sample preparation is considered to be the bottleneck of the whole analytical process, because it covers a plethora of operations that are essential to modify the sample, to make it amenable for chromatographic analysis, or to improve the analytical parameters, such as precision and accuracy. [1][2] Furthermore, it eliminates typical problems like possible interferences and low sensitivity. Samples can be considered as being made from two distinct parts, the analytes of interest and the matrix. The analytes of interest are the compounds to be determined, while the matrix is the rest of the sample, which not only does not necessitate analysis, but also may contain interfering substances. Sample preparation may focus on the analytes' extraction, on the matrix transformation, or on both, in order to achieve dissolution, cleanup, preconcentration, or chemical modifications of the sample, so as to obtain better analytical results [3].

In recent years, more and more attention has been devoted to replacing conventional extraction techniques with the so-called "green" extraction techniques. This started with the introduction of green analytical chemistry (GAC) and the 12 principles, formulated by P. Anastas in 1998, the main concern of which was to create environmentally friendly analytical techniques, especially extraction techniques [4]. Greener approaches to extraction techniques include more inexpensive, quicker, and environmentally safe practices in environmental, clinical, and food analysis [5]. The adverse environmental impact of analytical procedures has been reduced in three different ways: reduction of the volume of solvents required in sample preparation; reduction in the amount and the toxicity of solvents and reagents employed in the measurement step, especially with automation and miniaturization; and the development of different direct analytical techniques not requiring solvents or reagents [6]. Thus, newly developed extraction techniques, which have a greener approach, are on the rise. Moreover, microextraction techniques, for example solid phase microextraction (SPME) and liquid phase microextraction (LPME), which will be discussed below, are considered to be green extraction techniques, owing to the use of very small quantities of solvents of the extraction phase in relation to the volume of the sample or to the solvent volume used in classical approaches [7].

The development and application of sustainable solvents has been a hot topic in different scientific and technological areas [8][9][10][11][12][13][14][15]. In this regard, remarkable advances towards the replacement of volatile organic solvents have been achieved by a group of organic salts with melting points below 100 °C, generally referred to as ionic liquids (ILs) [16]. Nevertheless, the problems with their biodegradability, toxicity, stability, and the expensive synthesis make them less than perfect solvents [17]. Therefore, deep eutectic solvents (DESs), were introduced in 2001 as an alternative to ILs. These showed a stronger ecofriendly profile, with easier and cheaper production, while having similar properties [18]. DESs contain large, asymmetrical ions that have low lattice energy and, thus, low melting points. They are often acquired by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between, for instance a halide ion and the hydrogen-donor moiety, is responsible for the decrease in the melting point of the mixture, in relation to the melting points of the individual components [19][20]. Since 2001, many scientists around the globe pursed the utilization of DESs and published a variety of studies [21][22][23][24][25][26][27][28][29][30][31].

2. Synthesis and Properties of Deep Eutectic Solvents

2.1. Synthesis of Deep Eutectic Solvents

One of the approaches used to synthesize DESs is by mixing and heating two or more salts to form a homogenous solution. Typically, ambient temperature molten salts have been formed by mixing quaternary ammonium salts, a hydrogen bond acceptor (HBA) with metal salts [32][33]. Hence, four main different types of DES occur: I. quaternary salt with a metal chloride, II. quaternary salt with a hydrated metal chloride, III. quaternary salt (HBA) with an HBD compound and IV. metal chloride with an HBD. The respective general formulas of the four types are shown at Table 1. The first two types are used to synthesize hydrophilic DESs, whilst the other two for hydrophobic DESs [20][34]. Due to the stability in the aquatic solutions which type III and IV provide, they are often utilized in many papers, with choline chloride (ChCl) being the most used HBA. In Figure 1, some common HBA and HBD are shown.

Table 1. The four types of deep eutectic solvents.

Type	Formula	Terms
I	$Cat^{+}X^{-} + zMCl_{x}$	M = Zn, Sn, Al, Ga, Fe, In
II	$Cat^{+}X^{-} + zMC_{lx} \cdot yH_{2}O$	M = Co, Cu, Ni, Fe, Cr
III	$Cat^{+}X^{-} + zRZ$	Z = OH, COOH, $CONH_2$
IV	$MCl_{x} + RZ = MCl_{x-1}{}^{+} \cdot RZ + MCl_{x+1}{}^{-}$	M = Zn, Al and Z = OH, $CONH_2$

Cat^{+} = any phosphonium, ammonium or sulfonium cation, X^{-} = a Lewis base, generally a halide anion, MCl_x = metal chloride, RZ = organic compound.

2.2. Properties of Deep Eutectic Solvents

Various interactions (such as anion exchange, weak non-covalent interactions, π-π and/or hydrogen bonding) take place, amongst an HBD and an HBA in various combinations and molar ratios that contribute to some of the physicochemical properties discussed below [35]. Those properties are viscosity, density, conductivity, acidity, surface tension, volatility, and melting or freezing point. There is also an intensive study explaining the effect of hydrogen bonding proton transfer mechanism on the physical and chemical properties [36]. Other properties taken into account before selecting the optimal DES are biodegradability, toxicity, and thermal stability [37]. Moreover**,** both ILs and DESs can exhibit different physicochemical properties as binary mixtures, depending on the selected co-solvent, such as water or organic solvents. The interactions that may occur from the solute–solvent combination are defined as solvatochromic properties, which can further aid in the comprehension of chemical reactions through preferential solvation (PS) [38]. A useful tool to investigate the PS parameters and interactions, like hydrogen bond between molecules and ions, is the molecular dynamics (MD) simulation, which can be used as completion and confirmation of experimental results. For instance, Aryafard et. al. conducted an extensive investigation for three different DESs and their binary mixtures with polyethylene glycol (PEG 400) as co-solvent, through MD simulations analysis, while showing that PEG 400 can make a strong hydrogen bond with DESs [39].

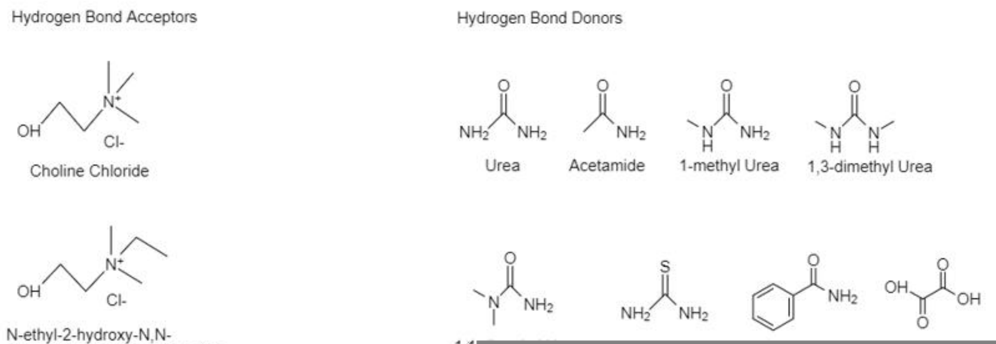

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Figure 1. Structures of some halide salts (HBAs) and hydrogen bond donors (HBDs) used in the formation of deep eutectic solvents.

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