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Deep Eutectic Solvents: Background, Properties and Applications

Abstract

DESs are novel solvents that can replace ionic liquids and other VOCs, because they are less toxic and biodegradable. Different mixtures could provide tunable and interesting properties.

Introduction

Eutectics are alloys of inorganics (mostly hydrated salts) and/or organics. They have a single melting temperature, which is usually lower than that of any of the individual compounds and form one single common crystal when crystallized. One of the most important characteristics of eutectics is their capability to melt/freeze congruently without phase segregation. During research carried out by Abbott et al. they noted that when they mixed a certain proportion of hydrogen bond donors (HBDs) and acceptors (HBAS), there was an unusually deep depression of the melting point of the eutectic composition. This is when deep eutectic solvents (DESs) started receiving more attention, a class of green solvents related to ionic liquids (ILs) [1, 2].

DE mixtures melt at low enough temperatures (as shown in Figure 1), some of them at room temperature, making them viable as solvents and/or electrolytes for new and existing chemistries; the major interest for these mixtures is focused in their liquid state therefore they’re commonly called “deep eutectic solvent” (DES) as a general name for these materials. DESs are often acknowledged as a class of ILs because they share many of the same general characteristics, including generally high thermal stabilities, low volatility, low vapor pressures, and tunable polarity, making DESs promising candidates for potential replacement of the 600 or so existing volatile organic compounds (VOCs) used widely throughout research and industry. DESs are expected to replace ILs, because they tend to be expensive, are often nonbiodegradable, and can have high toxicities, whereas DESs are typically inexpensive, biodegradable, non-toxic, and easier to prepare than ILs. Although, DESs cannot be considered ILs because they are not entirely composed of ionic substances; they can also be obtained from non-ionic substances [3, 4].

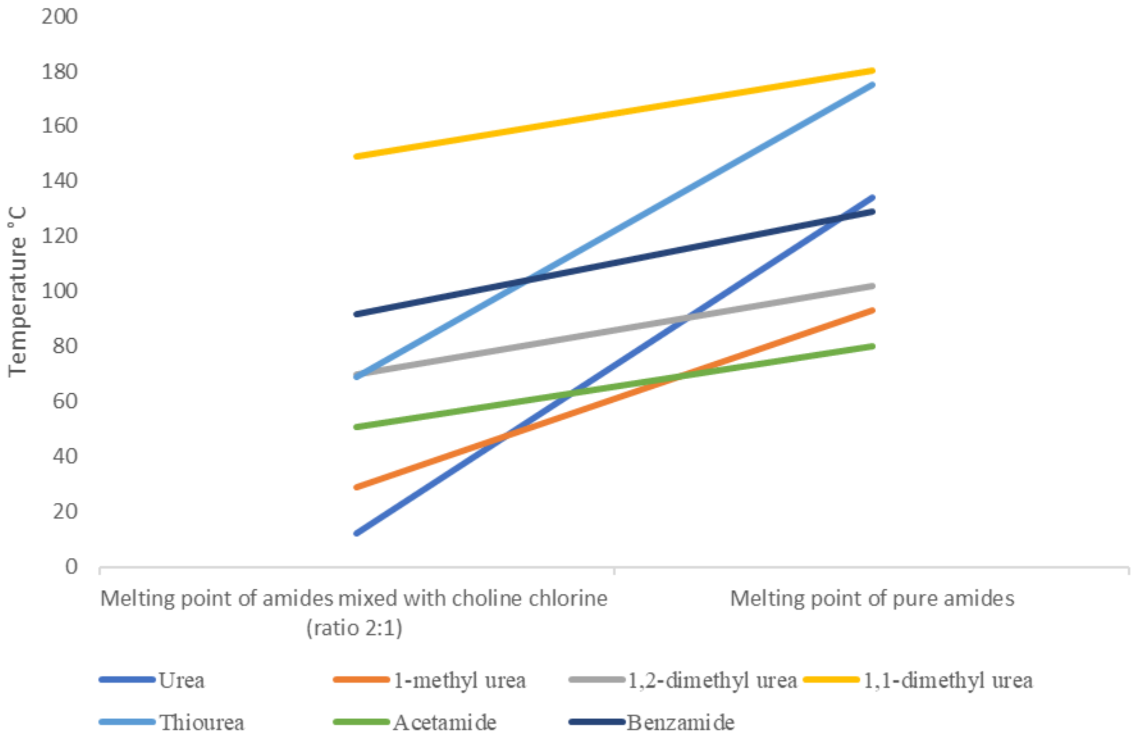


*Figure 1 Plot of melting points of pure amides and the same amides mixed with choline chloride (MP=302 °C) in a ratio of **2:1**, adapted from [1].*

The majority of DESs that have been prepared and studied thus far are traditionally classified as Type I, which combines a quaternary ammonium salt and a metal chloride, Type II, consisting of a quaternary ammonium salt and a metal chloride hydrate, Type III, consisting of a quaternary ammonium salt and a hydrogen bond donor (typically an organic molecular component such as an amide, carboxylic acid, or polyol), Type IV, consisting of a metal chloride hydrate and HBD, and Type V, which are a relatively new class composed of only nonionic, molecular HBAs and HBDs.

The most common preparation involves heating and stirring the constituents of the DES together under an inert atmosphere until a homogeneous liquid is formed. Other methods of preparation of DESs include vacuum evaporation, grinding, and freeze-drying. In appearance, DESs are typically viscous, clear liquids and have different colors ranging from white to amber and other colors, or as cloudy, opaque solids below T_{eut}.

A large number of known DESs have been identified and from a library of potential constituents it was estimated 10^6-10^8 possible binary combinations. Tertiary DESs are also reported but have thus far been minimally explored. Given the huge number of combinations of HBAs and HBDs, finding "optimal" mixtures for a given application would currently require decades of exhaustive trial-and-error through millions of possible binary combinations. Because of this, a primary objective of current DES research is to develop a fundamental understanding and ultimately build predictive models to recognize DESs as inexpensive, renewable, and green solvents that could be design for specific purposes.

DES generally contains larger asymmetric ions, which have lower lattice energy. The charge delocalization through the hydrogen bond between the halide ion and the hydrogen donor moiety is the cause of the decrease in the melting point of the mixture relative to the melting point of each component. There is also a subclass of DES called natural deep eutectic solvents (NADESs), these eutectic mixtures are formed by primary cellular constituents, such as sugar, alcohols, amino acids, and carboxylic acids. These NADESs may play a role in all types of cellular processes, explaining various mechanisms and phenomena that are otherwise difficult to understand, such as the biosynthesis of water-insoluble small and large molecules.

Until 2015, most DESs (including NADESs) reported in the literature were generally composed of hydrophilic compounds. Because water has a strong ability to form hydrogen bonds, it can destroy the hydrogen bonds between the DES components. Therefore, hydrophilic DESs are unstable in aqueous solutions and cannot be used in aqueous systems, greatly limiting their practical applications in analytical chemistry. In certain situations, compounds of interest can only be extracted from non-aqueous liquid and solid samples due to the phase separation from the DESs.

In 2015 a new subclass of DESs with hydrophobic character were presented. These solvents are formed by long alkyl chain quaternary ammonium salt and decanoic acid. Another hydrophobic DESs that was reported consisted of two neutral components: DL-menthol and natural acids. The goal of both studies was to create hydrophobic phases that could be used in analytical chemistry as hydrophobic extraction media [5].

Applications

DESs can be used in a wide range of applications. These solvents offer the advantage to be tailored and tuneability which is one of the greatest advantages of DESs. Physicochemical properties, especially polarity is highly related to the efficiency of extraction solvents. Thankfully, DESs' polarity can be adjusted according to the characteristics of the target compound.

It has been reported, polyol-based DESs which have free hydroxyl groups can interact with the free and etherified hydroxyl groups of lignin, this interaction enables the high lignin fractionation efficiency and enhanced cellulose accessibility to cellulase enzymes [6]. Extraction of lignocellulosic biomass and polysaccharides such as lignin, cellulose, starch, agar, agarose, chitin, chitosan, xylan, pectin, and inulin is a potential application of DESs due to advantages compared to the conventional extraction process. DESs involved extraction methods for lignocellulosic biomass and polysaccharides have already been reported in several papers lately [7].

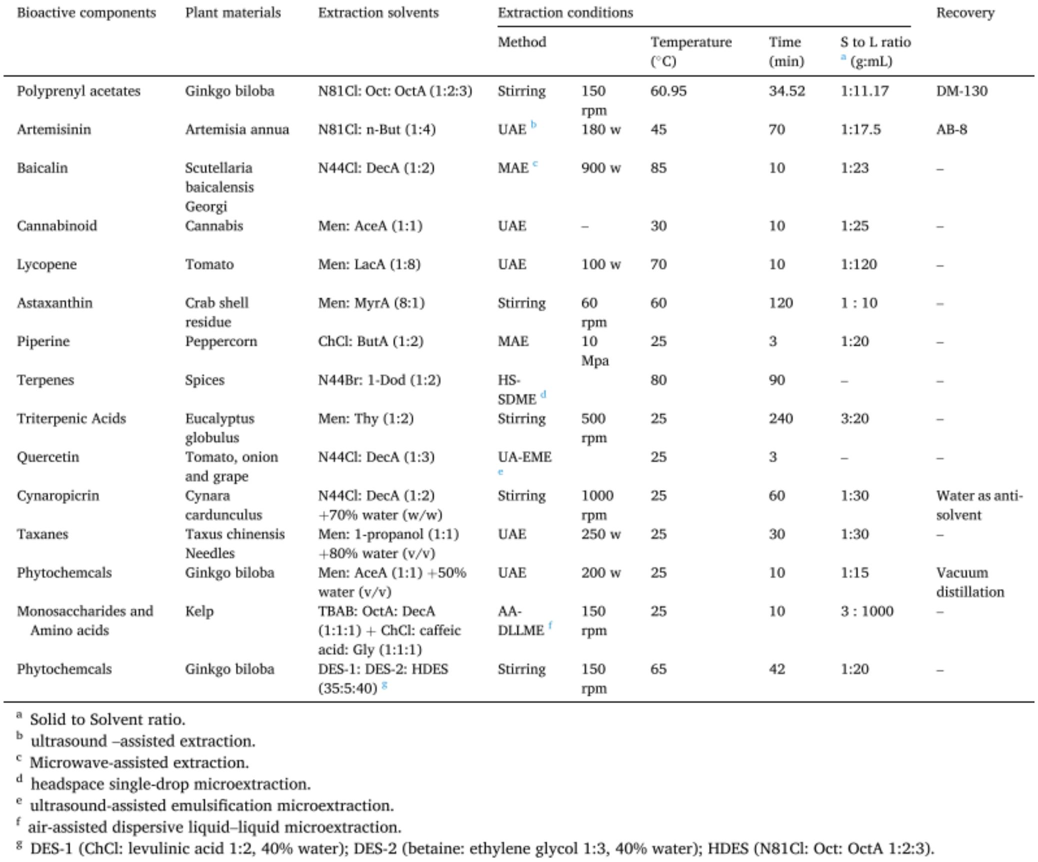
Related to this, another potential successful area of DESs is the extraction of natural compounds such as secondary metabolites from living organisms that are of interest in the pharmaceutical, cosmetic, agrochemical and food industries. DESs have been used for a wide range of bioactive extraction due to properties of DESs such as low price, low toxicity.

For example, switchable natural DESs successfully extracted the main carotenoid in pumpkin, β-carotene, characterized by poor solubility in water and low temperature oil, sensitive to light, oxygen, and heat, thus making it difficult to be recovered in high quantities, and incorporated in food products [8]. Other examples of extractions with DESs are shown in Table 1.

DESs can also successfully dissolve some metal salts such as copper (II) oxide and lithium chloride. Hence, DESs are a potential solvent as a metal cleaner before electroplating. Additionally, DESs are a potential media for nanomaterial synthesis as a dispersion medium for nanoparticles and media for electrochemical deposition for different metals such as Ag, Zn, Sn, Cr, and Cu.

Another research topic related to the environmental ecology of DESs involves using DESs as potential sorbents for CO_2 capture and storage, dissolving agent of phenolic compounds and are excellent solvents for a variety of chemical processes, for example, organic syntheses, separation processes, catalysis, biomass processing and more. DESs can also be utilized as media during the storing of unstable compounds [9].

Table 1 Applications of hydrophobic DESs for the extraction of bioactive compounds, edited from [9].



Bioactive components	Plant materials	Extraction solvents	Extraction conditions					Recovery
			Method		Temperature (°C)	Time (min)	S to L ratio [a] (g:mL)	
Polyprenyl acetates	Ginkgo biloba	N81Cl: Oct: OctA (1:2:3)	Stirring	150 rpm	60.95	34.52	1:11.17	DM-130
Artemisinin	Artemisia annua	N81Cl: n-But (1:4)	UAE [b]	180 w	45	70	1:17.5	AB-8
Baicalin	Scutellaria baicalensis Georgi	N44Cl: DecA (1:2)	MAE [c]	900 w	85	10	1:23	–
Cannabinoid	Cannabis	Men: AceA (1:1)	UAE	–	30	10	1:25	–
Lycopene	Tomato	Men: LacA (1:8)	UAE	100 w	70	10	1:120	–
Astaxanthin	Crab shell residue	Men: MyrA (8:1)	Stirring	60 rpm	60	120	1 : 10	–
Piperine	Peppercorn	ChCl: ButA (1:2)	MAE	10 Mpa	25	3	1:20	–
Terpenes	Spices	N44Br: 1-Dod (1:2)	HS-SDME [d]		80	90	–	–
Triterpenic Acids	Eucalyptus globulus	Men: Thy (1:2)	Stirring	500 rpm	25	240	3:20	–
Quercetin	Tomato, onion and grape	N44Cl: DecA (1:3)	UA-EME [e]		25	3	–	–
Cynaropicrin	Cynara cardunculus	N44Cl: DecA (1:2) +70% water (w/w)	Stirring	1000 rpm	25	60	1:30	Water as anti-solvent
Taxanes	Taxus chinensis Needles	Men: 1-propanol (1:1) +80% water (v/v)	UAE	250 w	25	30	1:30	–
Phytochemcals	Ginkgo biloba	Men: AceA (1:1) +50% water (v/v)	UAE	200 w	25	10	1:15	Vacuum distillation
Monosaccharides and Amino acids	Kelp	TBAB: OctA: DecA (1:1:1) + ChCl: caffeic acid: Gly (1:1:1)	AA-DLLME [f]	150 rpm	25	10	3 : 1000	–
Phytochemcals	Ginkgo biloba	DES-1: DES-2: HDES (35:5:40) [g]	Stirring	150 rpm	65	42	1:20	–

[a] Solid to Solvent ratio.
[b] ultrasound –assisted extraction.
[c] Microwave-assisted extraction.
[d] headspace single-drop microextraction.
[e] ultrasound-assisted emulsification microextraction.
[f] air-assisted dispersive liquid–liquid microextraction.
[g] DES-1 (ChCl: levulinic acid 1:2, 40% water); DES-2 (betaine: ethylene glycol 1:3, 40% water); HDES (N81Cl: Oct: OctA 1:2:3).

Physicochemical properties

High conductivities, viscosities, surface tensions and lower vapour pressure are characteristic properties of DESs and they differ from other solvents with these beneficial properties. To date, the viscosities of DESs have tended toward impractically high values, which makes their ready use in commercial applications more difficult and expensive than other options.

Related to density, typically DESs have exhibited higher densities than that of water. It can be observed that increasing the number of −OH functional groups on the hydrogen bond donor part results in the formation of more H-bonds, which presumably decreases the free volume available.

Regarding pH, it has been reported that neutral mixtures (for example, ChCl with D-glucose) at room temperature can change their pH when exposed to higher temperatures. Researchers have observed this behavior and noted a similar pattern exhibiting a linear decrease of pH with temperature increase, this relationship held for different DES mixtures, although it was found that there is a significant difference in pH values depending on the HBD used.

Studies have revealed that while the vapor pressures of DESs are much lower than common volatile organic solvents (e.g., acetonitrile, toluene), they are indeed significantly higher than their IL counterparts.

Relating to the ionic conductivity of a DESs, they tend to be lower than that of high-temperature molten salts. According to Abbott et al., this difference in conductivity can be attributed to both size of ions and viscosity, which are both related to hole theory [3].

Eutectogels

Eutectogels are a new type of ionic gels, with good conductivity and ductility have great potential in the field of smart sensing and flexible electronics. DESs can act as solvents by directly introducing polymers or polymerizing monomers to form gels. It is also possible to directly prepare monomers into DES, and then initiate polymerization to form a gel. Based on different DESs, the prepared gels have different properties and applications.

DESs eutectogels can be roughly divided into three types: (1) polymer gels in which DESs only act as solvents (Eutectogels-S); (2) polymer gels in which DESs act as solvents and polymerized monomers (Eutectogels- P); (3) supramolecular gels in which DESs act as solvents (Supramolecular Eutectogels) [10].

Due to the good conductivity and excellent stability of DESs themselves, the gels prepared by DESs have a wide range of applications in the fields of energy materials and wearable flexible devices. DESs have good electrical conductivity, nonflammability, environmental friendliness, and stable voltage window, which are ideal materials for supercapacitors. The applications of DESs eutectogels in flexible wearable devices have also received extensive attention. They could be used in the design of transparent, conductive, and stretchable electronic products, and have high application potential in the design of advanced sensors and corresponding electronic facilities. Another advantage of eutectogels is that it is well known hydrogels have a signicant disadvantage because their properties can change due to the evaporation of water during gel preservation, which limits their application. In contrast, eutectogels containing DESs are reported to have a strong ability to bind water [11].

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