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REVIEW

Basics and properties of deep eutectic solvents: a review

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Abstract

Deep eutectic solvents have emerged in green chemistry only seventeen years ago and yet resulted in a plethora of publications covering various research areas and diverse fields of application. Deep eutectic solvents appear as promising alternatives to conventional organic solvents due to their straightforward preparation using highly accessible and natural compounds. They display also high tunability. Here we present the classification and preparation methods of deep eutectic solvents. We detail their physicochemical properties such as phase behavior, density, viscosity, ionic conductivity, surface tension, and polarity. Properties are controlled by the choice of the forming compounds, molar ratio, temperature, and water content.

Keywords Deep eutectic solvents · Eutectic point · Phase behavior · Natural deep eutectic solvents · Hydrogen bond acceptor · Hydrogen bond donor · Choline chloride · Physicochemical properties · Water · Supramolecular network

Abbreviations

DES	Deep eutectic solvents
NADES	Natural deep eutectic solvents
Tm	Melting temperature

Introduction

The discovery of deep eutectic solvents has been a major breakthrough in green chemistry. Deep eutectic solvents are frequently defined as binary or ternary mixtures of compounds that are able to associate mainly via hydrogen bonds. Combining these compounds at a certain molar ratio results in a eutectic mixture (Zhang et al. 2012). The word "eutectic" comes from the Ancient Greek εὔτηκτος or *eútēktos* which means easily melted and a eutectic point represents the chemical composition and temperature at which a mixture of two solids becomes fully molten at the lowest melting temperature, relative to that of either compound. However, defining a deep eutectic solvent is still a controversial subject and there are various reported definitions that do not really distinguish deep eutectic solvents from other mixtures, since all the mixtures of immiscible solid compounds present a eutectic point and considering that numerous compounds are able to form hydrogen bonds when put together (Coutinho and Pinho 2017). Given that the presence of a eutectic point or hydrogen bonding between components is not sufficient conditions to define a "deep eutectic solvent" and in order to clarify what a deep eutectic solvent is and what makes it special compared to other mixtures, Martins et al. recently defined deep eutectic solvent as "a mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from ideality ($\Delta T_2 > 0$)", where ΔT_2 stands for the temperature depression which is the difference between the ideal and the real eutectic point (Martins et al. 2019). The same authors stated that it is important that the temperature depression results in a liquid mixture at operating temperature, regardless of the mixture composition. The fact that there is no fixed composition offers an even greater tunability for these systems.

Although deep eutectic solvents were extensively studied, especially in the past decade, there is still a lack of understanding the principle behind deep eutectic solvent's formation and properties. It all started almost twenty years

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ago, when Abbott et al. were looking for liquids that can overcome the moisture sensitivity and high cost of some common ionic liquids (Abbott et al. 2001). In this study, numerous mixtures based on different quaternary ammonium salts and metal salts were tested and it turned out that choline chloride mixed with zinc chloride in a 1:2 molar ratio presents the lowest freezing point (23–25 °C). Thereafter, the same authors investigated eutectic mixtures of quaternary ammonium salts and hydrogen bond donors and named them "deep eutectic solvents" (Abbott et al. 2003). The lowest freezing point (12 °C) was obtained with 1:2 choline chloride:urea. This significant depression of the freezing point, compared to that of choline chloride (302 °C) or urea (133 °C), is due to hydrogen bonding between urea molecules and chloride ion as proved by nuclear magnetic resonance spectroscopy. What is interesting about these solvents is that they are not only liquid at ambient temperature but also tunable and highly solubilizing. After that, other deep eutectic solvents based on choline chloride and carboxylic acids were characterized and were also shown to have important solubilizing ability toward some metal oxides (Abbott, Boothby, et al. 2004a, b). Other liquids were also obtained when mixing choline chloride with a hydrated metal salt like chromium (III) chloride hexahydrate (Abbott, Capper, et al. 2004). Later on, an additional class of ambient temperature solvents based on metal salts and hydrogen bond donors such as amides (urea and acetamide) and diols (ethylene glycol and 1,6-hexanediol) were reported, but it turned out that only a restricted number of metal salts and hydrogen bond donors can lead to their formation (Abbott, Barron, et al. 2007).

A few years later, Choi et al. coined the term "natural deep eutectic solvents" (Choi et al. 2011). This category covers the deep eutectic solvents that are made of primary metabolites such as organic acids, amino acids, sugars, polyols, and choline derivatives (Choi et al. 2011; Dai et al. 2013). Besides, water can also be part of natural deep eutectic solvents' composition. They were introduced as a way to explain the omnipresence of metabolites in high concentrations in cells. Further, their consideration is highly encouraged owing to the advantages that they provide from an environmental and economic point of view. Indeed, deep eutectic solvents and their natural counterparts found applications in environmental protection (Fahri et al. 2020; Krishnan et al. 2020; Malolan et al. 2020; Moura et al. 2017), extraction (Nakhle et al. 2021), and the pharmaceutical industry (Nguyen et al. 2021; Santos and Duarte, 2021), among others. This article is an abridged version of the chapter by El Achkar et al. (2021).

Classification

In order to differentiate between the possible eutectics, deep eutectic solvents were classified into four types based on the general formula Cat$^+$ X$^-$ zY, where Cat$^+$ is generally an ammonium, phosphonium, or sulfonium, while X is a Lewis base, usually a halide anion. Y represents a Lewis or Brønsted acid and z is the number of Y molecules that interact with the corresponding anion (Fig. 1) (Abbott, Barron, et al. 2007; E. L. Smith et al. 2014).

Type III eutectics are the most studied in literature and are usually based on choline chloride and various hydrogen bond donors. Choline chloride has been extensively adopted since it is relatively cheap, non-toxic, and biodegradable, considering it is approved as a natural additive for several animal species ("Scientific Opinion on Safety and Efficacy of Choline Chloride as a Feed Additive for All Animal Species," 2011). In fact, the first type III deep eutectic solvent was primarily based on choline chloride. Since then, a plethora of compounds has been successfully used in deep eutectic solvents' formation. The hydrogen bond acceptors mainly include quaternary ammonium or phosphonium salts, whereas the most common hydrogen bond donors are amides, alcohols, and carboxylic acids. In addition, compounds like sugars, sugar alcohols, and amino acids are also considered for natural deep eutectic solvents' preparation (Dai et al. 2013). More recently, hydrophobic deep eutectic solvents were introduced and they are based on the use of hydrophobic compounds such as tetrabutylammonium

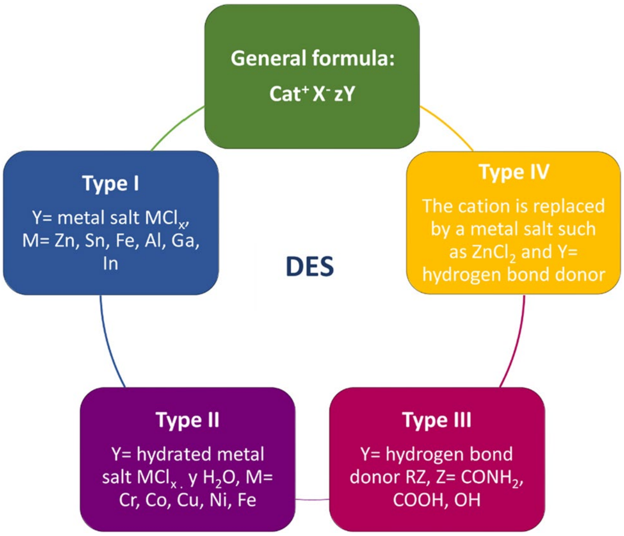


Fig. 1 Four types of deep eutectic solvents (DES) based on the general formula Cat$^+$ X$^-$ zY, where Cat$^+$ (cation) is generally an ammonium, phosphonium, or sulfonium, while X is a Lewis base, usually a halide anion. Y represents a Lewis or Brønsted acid and z is the number of Y molecules

bromide, menthol, thymol, and fatty acids as hydrogen bond acceptors together with long alkyl chain alcohols and carboxylic acids as hydrogen bond donors (Florindo et al. 2019; Osch et al. 2015). Furthermore, deep eutectic solvents can be made of active pharmaceutical ingredients like ibuprofen, lidocaine, and phenylacetic acid. In that event, the solvents are named therapeutic deep eutectic solvents (Duarte et al. 2017; Paiva et al. 2014). Some of the frequently used hydrogen bond acceptor and hydrogen bond donor counterparts described in the literature are illustrated in Fig. 2.

On the other hand, although natural deep eutectic solvents can sometimes be considered as type III deep eutectic

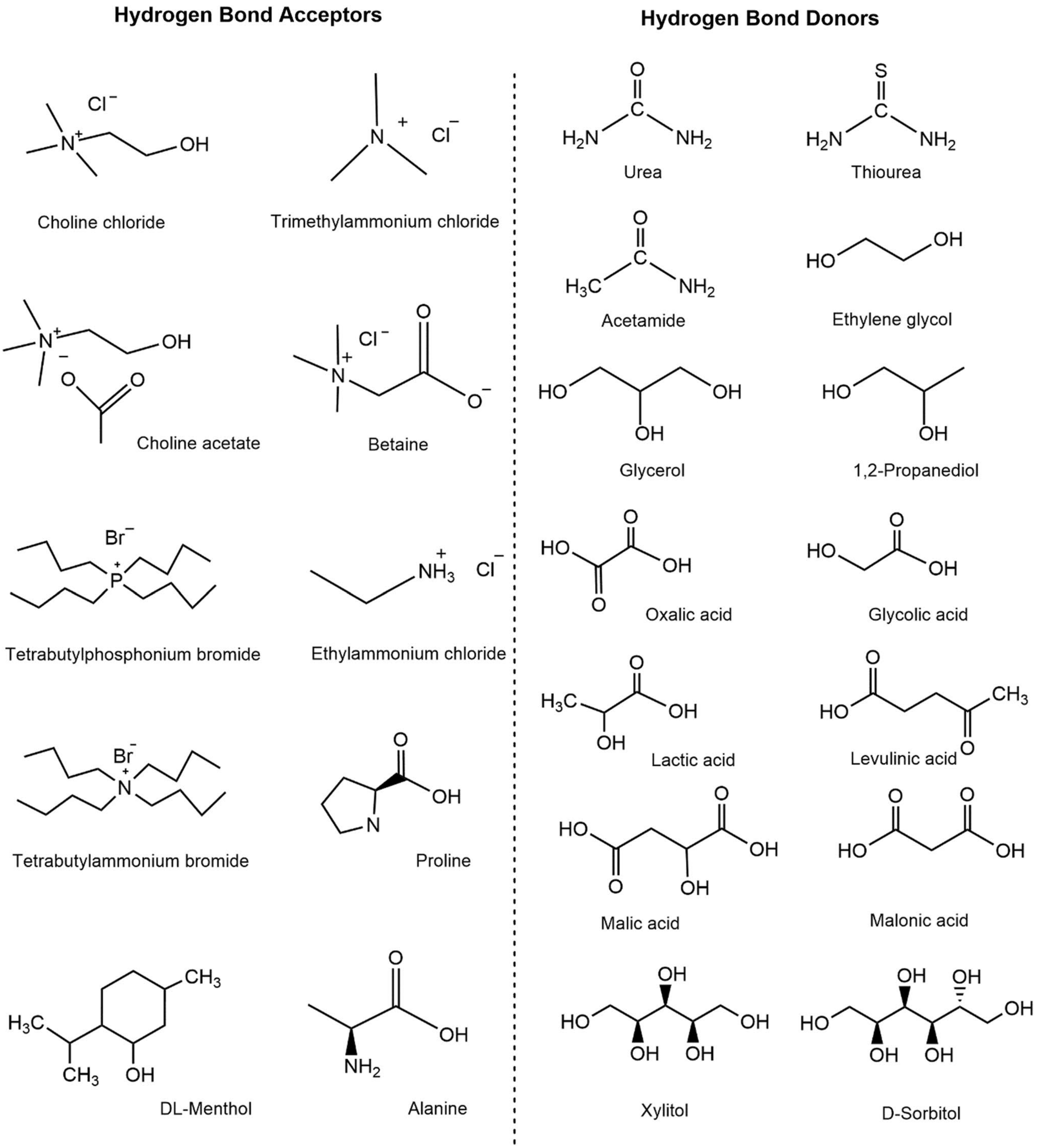


Fig. 2 Common hydrogen bond acceptors and hydrogen bond donors used for preparation of deep eutectic solvents

solvents, it is not always the case. That said, natural deep eutectic solvents were recently classified into five main groups (Dai et al. 2013; González et al. 2018):

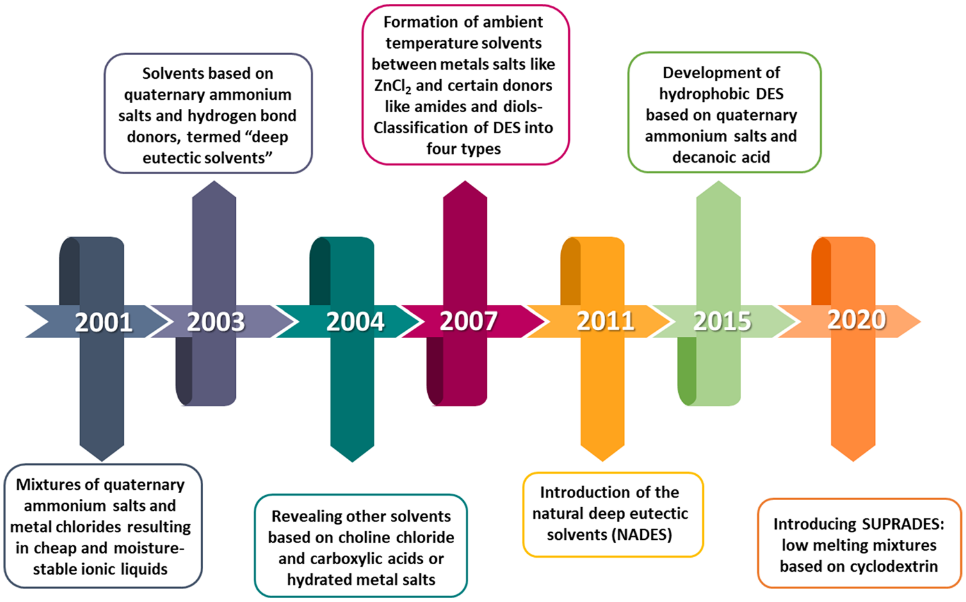
- Ionic liquids, made of an acid and a base;
- Neutral, made of only sugars or sugars and other polyalcohols;
- Neutral with acids, made of sugar/polyalcohols and organic acids;
- Neutral with bases, made of sugar/polyalcohols and organic bases;
- Amino acids-containing natural deep eutectic solvents, made of amino acids and sugars/ organic acids.

Nevertheless, the reported deep eutectic solvents do not certainly fall into one of the above-mentioned classes given their versatility and the myriad of the considered starting compounds. As a result, Coutinho and coworkers proposed a type V deep eutectic solvents composed of non-ionic species such as thymol and menthol (Abranches et al. 2019). On another note, two recent studies reported the use of cyclodextrins, which are non-toxic cyclic oligosaccharides, as hydrogen bond acceptors resulting in the formation of liquid supramolecular mixtures at room temperature (El Achkar, Moufawad, et al. 2020a, b; El Achkar, Moura, et al. 2020a, b). The important events marking the development of deep eutectic solvents so far are presented in Fig. 3 (Abbott et al. 2001, 2003; Abbott, Capper, et al. 2004; Abbott, Boothby, et al. 2004a, b; Abbott, Barron, et al. 2007; Choi et al. 2011; El Achkar, Moufawad, et al. 2020a, b; Osch et al. 2015).

Methods of preparation

Researchers generally use one of the two main methods to prepare deep eutectic solvents: the heating method and the grinding method. The heating method consists of mixing and heating the compounds, under constant stirring, until a homogeneous liquid is formed (Abbott, Boothby, et al. 2004a, b). The heating temperature usually ranges between 50 and 100 °C. However, a high temperature may potentially lead to a degradation of the deep eutectic solvent due to an esterification reaction regardless of the preparation method, as demonstrated by Rodriguez et al. for solvents based on choline chloride and carboxylic acids (Rodriguez Rodriguez et al. 2019). The grinding method is based on mixing the compounds at room temperature and crushing them in a mortar with a pestle until a clear liquid is formed (Florindo et al. 2014). Another method based on the freeze-drying of the aqueous solutions of the components of deep eutectic solvents was also revealed by Gutierrez et al. (Gutiérrez et al. 2009). An evaporation method was also reported by Dai et al. consisting of dissolving the components of deep eutectic solvents in water, followed by evaporation at 50 °C. The resulting liquid is then placed in a desiccator in presence of silica gel (Dai et al. 2013). Considering the optimization of time and energy consumption, a greener microwave-assisted approach was proposed for the preparation of natural deep eutectic solvents within seconds (Gomez et al. 2018). Lastly, an ultrasound-assisted synthesis of natural deep eutectic solvents was recently introduced (Santana et al. 2019).

Fig. 3 Milestones of the history of deep eutectic solvents (DES)



Physicochemical properties

The physicochemical properties of deep eutectic solvents are one of the main reasons behind the rising researchers' interest in these solvents. Besides having low volatility, nonflammability, low vapor pressure, and chemical and thermal stability, deep eutectic solvents are chemically tunable meaning they can be designed for specific applications given the wide variety of the possible deep eutectic solvents' forming compounds. Herein, the main physicochemical properties of deep eutectic solvents, namely their phase behavior, density, viscosity, ionic conductivity, surface tension, and polarity, are presented and discussed.

Phase behavior

As mentioned above, deep eutectic solvents are not pure compounds but mixtures of two or more pure compounds. This system is represented by a solid–liquid phase diagram, which shows the melting temperature in function of the mixture composition. Therefore, if we consider a binary mixture of compounds A and B, the eutectic point represents the composition and the minimum melting temperature at which the melting curves of both compounds meet (Fig. 4).

According to Martins et al. the deep eutectic solvent appellation should only cover mixtures with a melting point lower than the ideal eutectic temperature; otherwise, deep eutectic solvents would not be called "deep" and could not be differentiated from other mixtures (Martins et al. 2019). In addition, they stated that a deep eutectic solvent must be liquid at operating temperature even if this requires a different composition than the eutectic one. Consequently, having a phase diagram is essential, and knowing the melting properties of the pure compounds is necessary to determine the ideal solubility curve. Nevertheless, very little is reported about the thermodynamic behavior of the deep eutectic solvents to date. The freezing points of most of the deep eutectic solvents usually range between −69 and 149 °C, but all of them present a freezing point lower than 150 °C (Zhang et al. 2012). The choice of the hydrogen bond donor (Abbott, Boothby, et al. 2004a, b; Abbott et al. 2003), the nature of the organic salt and its anion (Abbott et al. 2003), and the organic salt/ hydrogen bond donor molar ratio (Shahbaz et al. 2011) can all affect the freezing point of the mixture. The method of preparation can also influence the value of the freezing point, but not the eutectic composition which must remain unchanged no matter the method used (Abbott et al. 2006). On the other hand, no correlation was found between the freezing point of a deep eutectic solvent and the melting points of its pure components (Abbott, Boothby, et al. 2004a, b; Zhang et al. 2012). The hydrogen bond donor did, however, affect the freezing point depression ΔT (Abbott, Boothby, et al. 2004a, b; E. L. Smith et al. 2014). For instance, Abbott et al. found that the lower the hydrogen bond donor's molecular weight, the greater is the depression of the freezing point (Abbott, Boothby, et al. 2004a, b). But unlike Abbott and coworkers who considered the temperature depression as the difference between the linear combination of the melting points of the pure components and the real eutectic point (ΔT_1), Martins et al. thought it would be more appropriate to define the temperature depression as the difference between the ideal and the real eutectic point (ΔT_2); otherwise, any mixture of compounds would be referred as a deep eutectic solvent (Fig. 5) (Martins et al. 2019).

Nevertheless, several other reported mixtures presented only a glass transition, and no melting point was detected

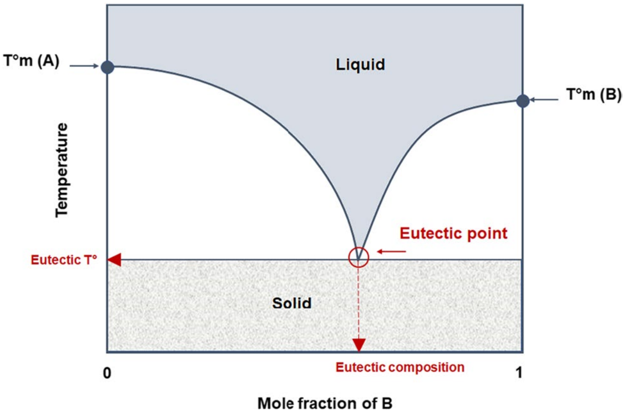


Fig. 4 General solid–liquid phase diagram of a binary mixture. Tm(A) and Tm(B) represent the melting temperatures of compounds A and B, respectively. The eutectic point represents the composition and the minimum melting temperature at which the melting curves of both compounds meet

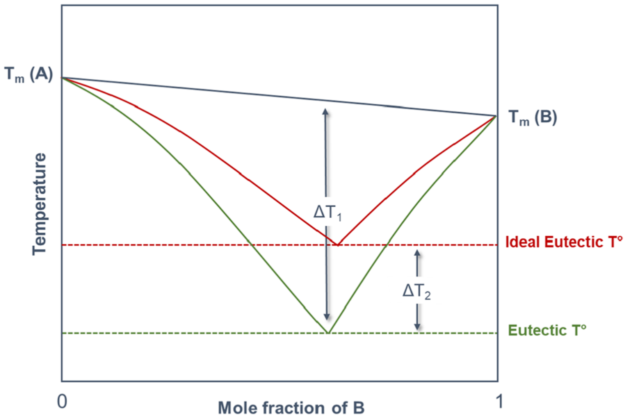


Fig. 5 Solid–liquid phase diagram representing a simple ideal eutectic mixture (red line) and a deep eutectic mixture (green line). ΔT stands for the considered freezing point depression (Adapted from Martins et al. 2019)

(Dai et al. 2013; Florindo et al. 2014; Francisco et al. 2012; Savi, Carpiné, et al. 2019a, b; Savi, Dias, et al. 2019a, b).

Density

Density is one of the fundamental physical properties of liquids. Most of the reported deep eutectic solvents present higher densities than water with values ranging between 1.0 and 1.3 g.cm^{-3} at 25 °C, while deep eutectic solvents based on metal salts have densities in the 1.3–1.6 g.cm^{-3} range (Tang and Row, 2013). Contrarily, lower densities than water are obtained for hydrophobic deep eutectics (Florindo et al. 2019). The deep eutectic solvent's density shows a temperature-dependent behavior; it decreases linearly with the increasing temperature (Cui et al. 2017; Florindo et al. 2014; Ibrahim et al. 2019; Shahbaz et al. 2012). Moreover, the density depends on the choice of the hydrogen bond donor (Abbott, Harris, et al. 2007a, b; Cui et al. 2017; Florindo et al. 2014; García et al. 2015), and the molar ratio (Abbott et al. 2011).

Viscosity

The viscosity is another important and extensively studied property of deep eutectic solvents. Most of the reported deep eutectic solvents to date are highly viscous at room temperature ($\eta > 100$ mPa.s) which is mainly ascribed to the extensive hydrogen bond network taking place between deep eutectic solvents' components. In addition, they present a very broad viscosity range. In fact, choline chloride:ethylene glycol (1:2) is known to have a very low viscosity (37 mPa.s at 25 °C), while sugar-based deep eutectic solvents present extremely large viscosities (12,730 mPa.s for 1:1 choline chloride:sorbitol at 30 °C and 34,400 mPa.s for 1:1 choline chloride:glucose at 50 °C) and even higher viscosities were recorded for metal salts-based deep eutectic solvents (85,000 mPa.s for 1:2 choline chloride:zinc chloride at 25 °C) (Zhang et al. 2012). Yet, very low viscosities were recorded for hydrophobic deep eutectic solvents based on DL-menthol (7.61 mPa.s at 25 °C for 1:3 DL-menthol:octanoic acid) (Nunes et al. 2019; Ribeiro et al. 2015). The viscosity of a eutectic mixture is clearly affected by the nature of its components (Abbott, Barron, et al. 2007; D'Agostino et al. 2011), their molar ratio (Abbott et al. 2011), the temperature (Abbott, Boothby, et al. 2004a, b; Abbott et al. 2003, 2006; Dai et al. 2015; Kareem et al. 2010) and the water content (D'Agostino et al. 2015; Dai et al. 2015; Du et al. 2016; Florindo et al. 2014; Shah & Mjalli, 2014). On a separate note, it is worthy to mention that large differences were noticed when comparing the viscosity data obtained by different researchers for the same deep eutectic solvent (e.g., 152 mPa.s vs 527.28 mPa.s for 1:2 choline chloride:urea at 30 °C and 202 mPa.s vs 2142 mPa.s for 1:1 choline chloride:oxalic acid at 40 °C) (García et al. 2015). These major differences can be attributed not only to the preparation method as stated by Florindo et al. (Florindo et al. 2014) but to the experimental method and the impurities as well (García et al. 2015).

Ionic conductivity

Since the viscosity is the main controller of the conductivity, most of the deep eutectic solvents tend to have poor ionic conductivities ($\kappa < 2$ mS cm^{-1} at room temperature). Therefore, increasing the temperature results in a decrease in the viscosity and an increase in the conductivity (Lapeña et al. 2019; Zhang et al. 2012). This property is also affected by the hydrogen bond acceptor/hydrogen bond donor molar ratio (Abbott, Boothby, et al. 2004a, b), the nature of both the organic salt and the hydrogen bond donor as well as the salt's anion (García et al. 2015) and of course the water addition (Dai et al. 2015).

Surface tension

The studies related to the surface tension of deep eutectic solvents are quite limited compared to the studies dealing with other physicochemical properties. Yet, it is an essential property since it is highly dependent on the intensity of the intermolecular forces taking place between the hydrogen bond donor and the corresponding salt. That said, highly viscous liquids present high surface tensions. The values relative to the reported deep eutectic solvents generally vary between 35 and 75 mN m^{-1} at 25 °C (García et al. 2015; Ibrahim et al. 2019). Once again remarkable high values were recorded for sugar-based deep eutectic solvents such as choline chloride:D-glucose (Hayyan et al. 2013) and choline chloride:D-fructose (Hayyan et al. 2012), reflecting their extensive hydrogen-bond network. Besides, the surface tension is influenced by the salt mole fraction and the cation type since an additional hydroxyl group or a longer alkyl chain in the quaternary ammonium salt leads to higher surface tensions. Also, the surface tension linearly decreases with increasing temperature (García et al. 2015; Lapeña et al. 2019; Nunes et al. 2019).

Polarity

Polarity is a key property since it reflects the overall solvation capability of solvents. Despite its significance, the polarity of the deep eutectic solvents was not considerably studied and was not addressed until recently. This property is often estimated via the solvatochromic parameters which consider the hypsochromic (blue) shift or bathochromic (red) shift of UV−vis bands for the negatively solvatochromic dyes (e.g., Reichardt's betaine dye) or the positively solvatochromic dyes (e.g., Nile red), respectively, as a function of the solvent's polarity (Reichardt 1994). The most frequently used scales are the polarity scales of Dimroth and Reichardt (E_T and E_TN) (Reichardt 1994) and the multiparameter scale of Kamlet and Taft (the hydrogen bond donating ability α, the hydrogen bond accepting ability β and dipolarity/polarizability π*) (Kamlet et al. 1977; Kamlet and Taft, 1976). However, it is worthy to mention that the polarity scales are not universal and are probe dependent which means that we cannot compare polarity parameters obtained by different solvatochromic probes (Valvi et al. 2017).

Effect of water

Given the omnipresence of water and the hygroscopic character of some deep eutectic solvents and their forming compounds, the water uptake by the eutectic solvents is inevitable (Du et al. 2016; Florindo et al. 2014). While traces of water in deep eutectic solvents are usually considered as impurities, a plethora of papers intentionally added water to their solvents in order to fine-tune their properties so they can respond to the requirements of some desired applications and water allowed, in many cases, to improve the performance of deep eutectic solvents. On the other hand, the presence of water not only affects the physicochemical properties but may also jeopardize the integrity of deep eutectic solvents (El Achkar et al. 2019), which explains the inconsistency in the literature given that deep eutectic solvents are prepared in different operating conditions. Therefore, studying the effect of water on the eutectic systems is of utmost importance. This section highlights the impact of water on the physicochemical properties of deep eutectic solvents and the characteristics of their supramolecular organizations.

Effect on deep eutectic solvents' physicochemical properties

Herein, the effect of water on the main physicochemical properties (melting point, density, viscosity, conductivity, surface tension, and polarity) will be discussed according to the reported studies so far. Some investigated the effect of low water content that can naturally be present in the deep eutectic solvent and others considered a full range of water content. After being in contact with the atmosphere for three weeks, choline chloride:urea deep eutectic solvent absorbed up to 20 wt% water. That said, Meng et al. tested the effect of water (up to 10 wt%) that can be naturally absorbed by the deep eutectic solvents, on the melting point of choline chloride:urea. A linear decrease in the melting point was observed as a function of the water content. The melting point of the mixture dropped from 30 °C for the dry deep eutectic solvent to 15 °C in the presence of 5 wt% of water. This tremendous water effect can explain the dissimilarities obtained by different studies for the same deep eutectic solvent (Meng et al. 2016). These results were somehow in accordance with the findings of Smith et al. who also followed the variation in the melting point of the same deep eutectic solvent but with a full range of water content. Though a similar linear trend was obtained up until 10 wt% of water by the two studies, a further increase in the water content yields a minimum melting point of -48 ± 2 °C at 0.67 mol fraction of water. Above this point, the melting temperature linearly increased. Owing to the behavior of the studied mixture, the authors proposed that 1:2:6 choline chloride:urea:water makes a ternary deep eutectic solvent (P. J. Smith et al. 2019).

On the other hand, all the studies have agreed that unlike the density, both viscosity and conductivity are highly sensitive to the presence of water in deep eutectic solvents. Agieienko et al. noticed a slight decrease of 0.14% in the density of choline chloride:urea at around 0.008 mass fraction of water while 0.005 water mass fraction decreased its viscosity by around 22% (Agieienko and Buchner 2019). Du et al. showed that both viscosity and conductivity of choline chloride:urea are highly sensitive to water. In fact, the viscosity and the conductivity were 13 times lower and 10 times higher in the hydrated deep eutectic solvent, respectively, at only 6 wt% water content (Du et al. 2016). Likewise, Shah et al. found that within 10 wt% of water, the viscosity of choline chloride:urea was reduced by more than 80% and the conductivity was 3 times higher compared to the dried deep eutectic solvent (Shah and Mjalli 2014). A significant decrease in the viscosity and a linear decrease in the density of several natural deep eutectic solvents were also observed in the presence of water, while the conductivity of five selected ternary natural deep eutectic solvents made of choline chloride, organic acids, sugars, and water firstly increased with the increasing water content and then decreased after reaching a peak value of around 10–100 times higher than that of pure natural deep eutectic solvent at 60–80 wt% water (Dai et al. 2015). The viscosity and conductivity of choline chloride-based deep eutectic solvents with different glycols as hydrogen bond donor were also massively affected by the water content. In fact, the viscosity value was halved after the addition of about 7–10 wt% water. On the other hand, the conductivity of deep eutectic solvents firstly increased with the increasing of water content, reached a maximum at 60 wt% water, at which values were 6–15 times higher than that of pure deep eutectic solvents, and then decreased. The ionic dissociation of deep eutectic solvents' components caused the initial increase in the conductivity which was later decreased owing to the dilution of the electrolytes at higher water content. The polarity linearly increased with the increasing water content for all three solvents (Gabriele et al. 2019). Similar non-monotonic behavior of the ionic conductivity was observed with aqueous solutions of choline chloride:urea and choline chloride:ethylene glycol via molecular dynamics simulations. The values reached the maximum also at 60 wt% water (Celebi et al. 2019).

Rublova et al. conducted an in-depth study about the effect of water on the surface tension of binary mixtures of “choline chloride + water”, “choline chloride + ethylene glycol”, “ethylene glycol + water” and a ternary mixture of “choline chloride + ethylene glycol + water”. The interpretation of the variation in the surface tension and the thermodynamic characteristics of adsorption at the interface “solution/air” led to some interesting findings. When comparing the aqueous solution of choline chloride to that of ethylene glycol, stronger adsorption of choline cation was obtained owing to the choline cation- water hydrophobic interactions. The ternary mixture results revealed interactions between deep eutectic solvents’ constituents in an adsorbed surface layer formed at the interface air/diluted solution of choline chloride:ethylene glycol which explains the way higher values of equilibrium adsorption constants for the ternary mixture compared to those related to “choline chloride + water” and “ethylene glycol + water” mixtures (Rublova et al. 2020). When studying the effect of water on the surface tension of DL-menthol:octanoic acid deep eutectic solvent, Nunes et al. detected two consecutive behaviors: a decrease in the surface tension while increasing the water content reaching a minimum value at around 4000 ppm of water, followed by an increase in the surface tension (Nunes et al. 2019). The same behavior was observed by Sanchez-Fernandez et al. when studying the surface tension of choline chloride:malonic acid as a function of water (Sanchez-Fernandez et al. 2017).

The papers dealing with the effect of water on the deep eutectic solvents’ polarity are rather limited. The polarity of choline chloride:urea, choline chloride:glycerol, and choline chloride:ethylene glycol was investigated through the solvatochromic behavior of different absorbance and fluorescence probes in deep eutectic solvents -water mixtures. This approach would inform us about the interactions dominating these mixtures. The water addition happens to increase the dipolarity/polarizability and decrease the hydrogen bond- basicity of all three solvents. The behavior of the fluorescent probes further revealed more relevant hydrogen-bond interactions between added water and deep eutectic solvents’ constituents for choline chloride:glycerol and choline chloride:ethylene glycol when compared to choline chloride:urea. The structural differences between the adopted hydrogen bond donors as well the interstitial accommodation of water molecules within choline chloride:urea would explain the greater influence of water addition on choline chloride:glycerol and choline chloride:ethylene glycol, rather than choline chloride:urea (Pandey and Pandey 2014).

Effect on deep eutectic solvents’ network

As discussed above, water clearly impacts the physicochemical properties of the deep eutectic solvents, whether present in low or large amounts. Furthermore, investigating deep eutectic solvent–water interactions is crucial, especially that binary mixtures of deep eutectic solvents and water have been commonly adopted in many applications already. In fact, the presence of water allows the circumvention of some of the shortcomings of deep eutectic solvents like their relatively high viscosity while maintaining their unique and appealing properties, which explains the rising interest in deep eutectic solvents–water mixtures over the past few years. However, the high polarity of water and its propensity to interact with the hygroscopic components of the eutectic system makes it of paramount importance to check out if and how water affects the intra- and intermolecular bonds lying behind the supramolecular network of deep eutectic solvents. Despite their relevance, the investigations of the effect of water on deep eutectic solvent’s system are rather restricted and mostly cover choline chloride-based eutectics. This effect was examined via multiple techniques mainly nuclear magnetic resonance, Brillouin spectroscopies, and neutron total scattering, not to mention the molecular dynamics simulations. Some studies proposed a passage from a deep eutectic solvent to an aqueous solution of its individual components while adding water and others suggested that a transition from a “water-in-deep eutectic solvent” to a “deep eutectic solvent-in-water” system occurs at a certain hydration level. In the former system, water is seen as another hydrogen bond donor (Hammond, Bowron, Jackson, et al. 2017a, b; López-Salas et al. 2019; Zhekenov et al. 2017), thus integrating into the deep eutectic solvent’s network and subsequently strengthening the hydrogen bonds taking place between the hydrogen bond acceptor and the hydrogen bond donor at a low water content (Hammond, Bowron, and Edler, 2017a, b; Weng and Toner 2018). However, further dilution results in the weakening of the interactions that usually dominate in a deep eutectic solvent supramolecular structure owing to the tendency of water to interact with the deep eutectic solvent’s forming compounds. The preferential hydration of chloride anions was reported in numerous papers dealing with different choline chloride-based deep eutectic solvents like choline chloride:urea, choline chloride:glycerol, choline chloride:ethylene glycol, and choline chloride:lactic acid (Alcalde et al. 2019; Fetisov et al. 2018; Kaur et al. 2020; Kumari et al. 2018; Weng and Toner, 2018). Yet, when it comes to the hydration level at which the transition happens, the values are not always consistent for the same deep eutectic solvent. For instance, the transition point varied between 15 and 51 wt% for choline chloride:urea (Hammond, Bowron, and Edler, 2017a, b; Kumari et al. 2018; Posada et al. 2017; Shah and Mjalli

2014). There are not enough studies to compare between the transition points of other deep eutectic solvents. Few studies also proved that temperature does not affect the structure of deep eutectic solvent–water mixtures (Celebi et al. 2019; Weng and Toner 2018). Further studies must be conducted on other deep eutectic solvents because although this transition is likely to occur in all the aqueous mixtures of deep eutectic solvents, the changeover water content obviously depends on the hydrogen bond acceptor and hydrogen bond donor types as well as their molar ratio (Gabriele et al. 2019). Besides, a deep understanding of the impact of water on the deep eutectic solvent's structural arrangement will surely expand the possibility of tuning the deep eutectic solvent–water mixtures according to the desired applications.

Conclusion

The quest for green solvents is a rising topic contributing to the goals of green chemistry. Deep eutectic solvents constitute the most considered and investigated solvents nowadays. These solvents possess quite interesting properties thus increasing their possibility to replace other conventional solvents in numerous academic and industrial sectors. This review article provides a general and comprehensive overview of the basics and properties of deep eutectic solvents. Their updated definition, classification, and preparation methods were elucidated. At a second stage, their main physicochemical properties, particularly their phase behavior, density, viscosity, ionic conductivity, surface tension, and polarity, are summarized. This segment also highlights the great tunability of these systems which properties can be modeled by several parameters. From the choice of the hydrogen bond donor, hydrogen bond acceptor, and their molar composition to the temperature and water content, these solvents can be designed to meet the requirements of the targeted applications. Finally, given the ubiquity of water and the wide consideration of binary mixtures of deep eutectic solvents and water in plenty of applications, the impact of water on both the physicochemical properties and the structure of the deep eutectic systems was emphasized. The presence of water significantly affects the properties of deep eutectic solvents. Even though it can present some beneficial outcomes, the presence of water may disturb the supramolecular network of the eutectic mixtures. Several studies engaged in understanding the behavior of aqueous mixtures of deep eutectic solvents have recently emerged. A transition from one system to another upon the addition of water is proposed by several studies. A deeper understanding of deep eutectic solvents still requires further studies, especially that there are a countless number of combinations that can lead to their formation.

Declarations

Conflicts of interests The authors have no conflicts of interest to declare that are relevant to the content of this article.

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