Journal of Interdisciplinary Research in Physical Science
Vol. 01(01), November 2021, pp. 24-31

An overview of Deep Eutectic Solvents (DESs): An emerging class of green solvents

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Abstract:

Deep eutectic solvents (DESs) have been emerged as novel green and sustainable solvent and characterized by remarkable depressions in melting points in comparison to those of the neat constituent components. DESs are considered as cost effective "designer" solvents exhibiting a host of tunable physicochemical properties. The comprehensive study of the recent literature demonstrates the lack of predictive understanding of the microscopic mechanisms that execute the structure-property relationships in this class of solvents. The principal cause of the melting point depressions as well as physicochemical properties of DESs is the extensive hydrogen bonding. It is imperative to understand these systems as dynamic entities using both simulations as well as experiments. The present chapter covers the basic knowledge and recent research progresses regarding DES. It also focus on the recent progresses in the field of DES research, frames excellent scientific understanding, and recognizes potential research areas associated with the progress of the field toward predictive models and basic knowledge of these solvents.

Keywords: Deep Eutectic Solvent (DES), Green solvent, Hydrogen bonding

Introduction:

In viewpoint of green chemistry, solvents play a crucial role in the field of organic synthesis. To be considered as a sustainable solvent, solvents should possess the various salient features like easy availability, biodegradability, recyclability, non-toxicity, and cost effective in comparison to others. Up to the date, the availability of green solvents is rather limited in number. In this context, Deep Eutectic Solvents, a novel class of ionic liquids, are now rapidly emerging as a green and sustainable solvent in the field of synthetic chemistry.[1-2] A DES is a fluid generally composed of two or three easily available, cost effective and benign components that has potential for self-association, often via hydrogen bond interactions and consequently form a

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eutectic mixture exhibiting a melting point lower than that of each individual component.[3] DESs are commonly in liquid state at temperatures lower than 100 °C. These DESs show identical physico-chemical properties to the conventionally employed ionic liquids, while being much cost effective and environmentally benign. Considering to these aforementioned advantages, DESs have attracted the great interest in many areas of research. In this chapter, we compile the fundamental understanding and significant applications of DESs. All contributions covered in this chapter aim at demonstrating that DESs not only offer the design of sustainable processes but also open a straightforward access to novel chemicals and materials.

In last two decades, room temperature ionic liquids (RTILs) have attracted considerable attention especially in the field of catalysis, electrochemistry, material chemistry, and more recently for the pre-treatment of biomass.[4-5] At the early stages of these research studies, scientists particularly focused on the preparation of ionic liquids by mixing metal salts, mostly aluminium, zinc, tin and iron chlorides, with quaternary ammonium salts. However both salts exhibit very high melting points, their proper mixing leads to the formation of a liquid phase which is known as eutectic mixture. These eutectic mixtures are commonly characterized by a very large depression of freezing point, generally higher than 150 °C. With the emergence of the concept of green chemistry, the preparation of metal-free ionic liquids (ILs) is highly desirable. In this regard, numerous efforts were attempted to the design of ILs by mixing an organic cation (usually imidazolium-based cations) with a large variety of anions, the most common ones being Cl^-,BF_4^-, PF_6^-, NTf_2^-. From that time, ILs have emerged as a new class of potential solvents. The possibility to chemically transform the cationic moiety almost infinitely in combination with a very large choice of anions provides chemists a broad range of ILs possessing different physical properties like density, melting point, viscosity, solubility, conductivity, and refractivity, among others. For example, in 2009, Seddon and co-workers have reported that 1018 different ILs can be theoretically prepared, 250 of them being already commercialized.[6-7] Considering to their high boiling point and low vapour pressure, which enables their recycling, ILs were qualified as green solvents. Although, the ‘‘green affiliation’’ of these novel solvents is now greatly contested in the current literature.[8]

Indeed, many reports pointed out the hazardous toxicity and the very poor biodegradability of most ILs.[9] ILs with high purity is also needed because impurities, even in trace amounts, exert influence on their physical properties. In addition, for the synthesis of ILs

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often needs a large amount of salts and solvents to completely exchange the anions, therefore the preparation of ILs is not considered as environmentally friendly. These shortcomings along with the high price of common ILs unfortunately hamper their industrial success. Therefore new concepts are now strongly required in order to exploit these systems in a better logical way.

To overcome the toxicity and high price of ILs, a new generation of solvent, called as Deep Eutectic Solvents (DES), has emerged at the beginning of this century. Preparation of these

DESs can be obtained by simply mixing together two safe components (cheap, biodegradable and renewable), which are capable of generating a eutectic mixture. One of the most common components employed for the preparation of these DESs is choline chloride (ChCl). ChCl is a non-toxic, very cheap, and biodegradable quaternary ammonium salt which can be either extracted from biomass or smoothly synthesized from fossil reserves via a very high atom economy process. In combination with safe hydrogen bond donors such as urea, renewable carboxylic acids (e.g. oxalic, citric, succinic or amino acids) or renewable polyols (e.g. glycerol, carbohydrates), ChCl is capable of expeditiously generating a DES. However most of DESs are composed from ChCl as an ionic species, DESs cannot be treated as ILs because:

(1) DESs are not completely made up of ionic species

(2) DESs can also be obtained from non-ionic species.

In comparison to the conventional ILs, DESs derived from ChCl possess numerous advantages such as (1) low price, (2) chemical inertness with water (i.e. easy storage), (3) easy to prepare since DESs are obtained by simply mixing two components, thus by-passing all problems of purification and waste disposal often encountered with ILs and (4) most of them are biodegradable,[10] Biocompatible[11] and non-toxic,[12] reinforcing the greenness of these media.[13]

Physico-chemical properties of DESs (chemical inertness, viscosity, density, refractive index, conductivity, surface tension, etc.) are very close to those of common ILs. For this reason, DESs derived from ChCl are also intimately named “biorenewable” or “biocompatible” or ionic liquids in a few studies. Regards to their low ecological footprint and attractive price, DESs have now become of growing interest both at academic and industrial levels and the number of publications dedicated to the use of DESs is now expeditiously increasing in the current literature, further expressing the attractiveness of these media.

2. Definition of DESs

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A DES is often composed of two or three cheap and safe components which are capable of associating with each other, via hydrogen bonding, to form a eutectic mixture. The resulting DES is characterized by a melting point lower than that of each individual component. Generally, DESs are featured by a very large depression of freezing point and are liquid at temperatures lower than 150 °C. Notably most of them are liquid between room temperature and 70 °C. Mostly, a DES is produced by mixing a quaternary ammonium salt with metal salts or a hydrogen bond donor (HBD) that has the potential to generate a complex with the halide anion of the quaternary ammonium salt. Figure 1 and figure 2 summarizes the different quaternary ammonium salts that are widely employed in combination with various HBDs in the preparation of DESs.

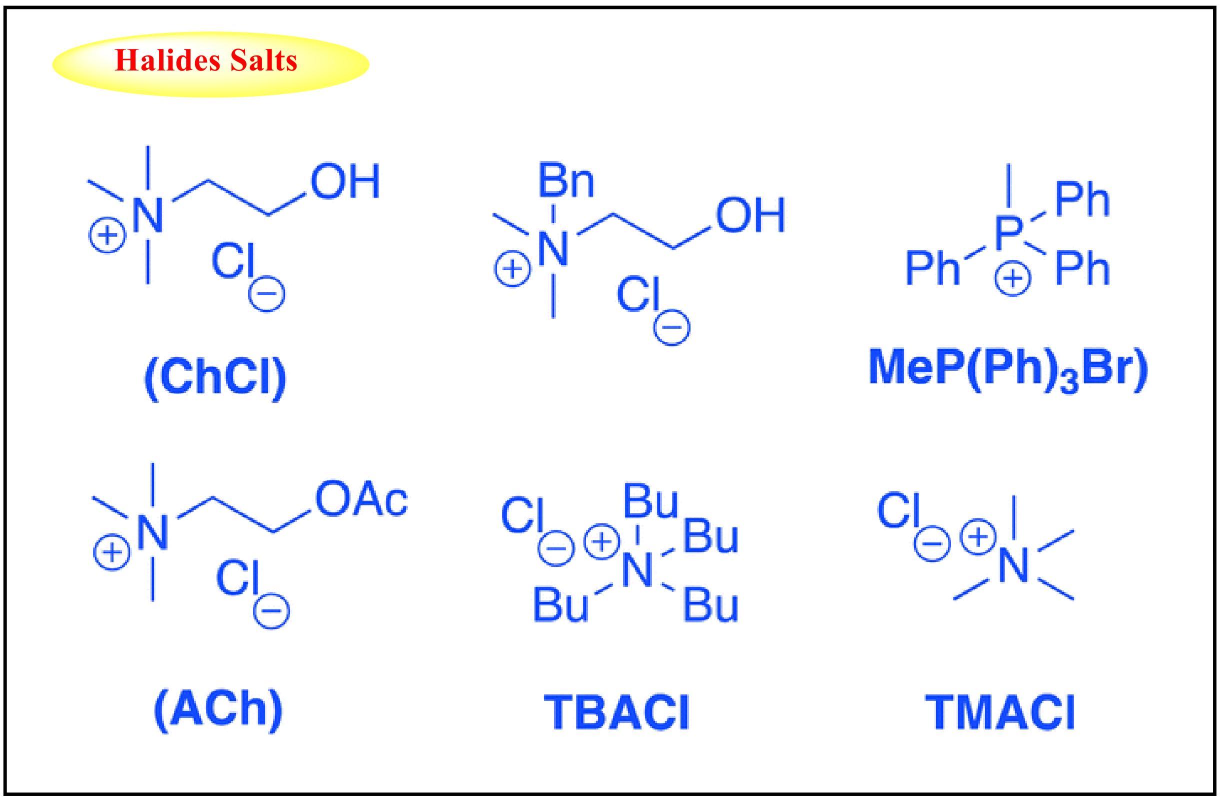

Figure 1: Representative example of the halide salts explored for the preparation of DES

In 2007, Abbott and co-workers defined DESs using the general formula $R_1R_2R_3R_4N^+X^-Y^-$.12

Type I DES Y = MClx, M = Zn, Sn, Fe, Al, Ga

Type II DES Y = MClx.yH2O, M = Cr, Co, Cu, Ni, Fe

Type III DES Y $=R_5Z$ with Z = $-CONH_2$, -COOH, -OH

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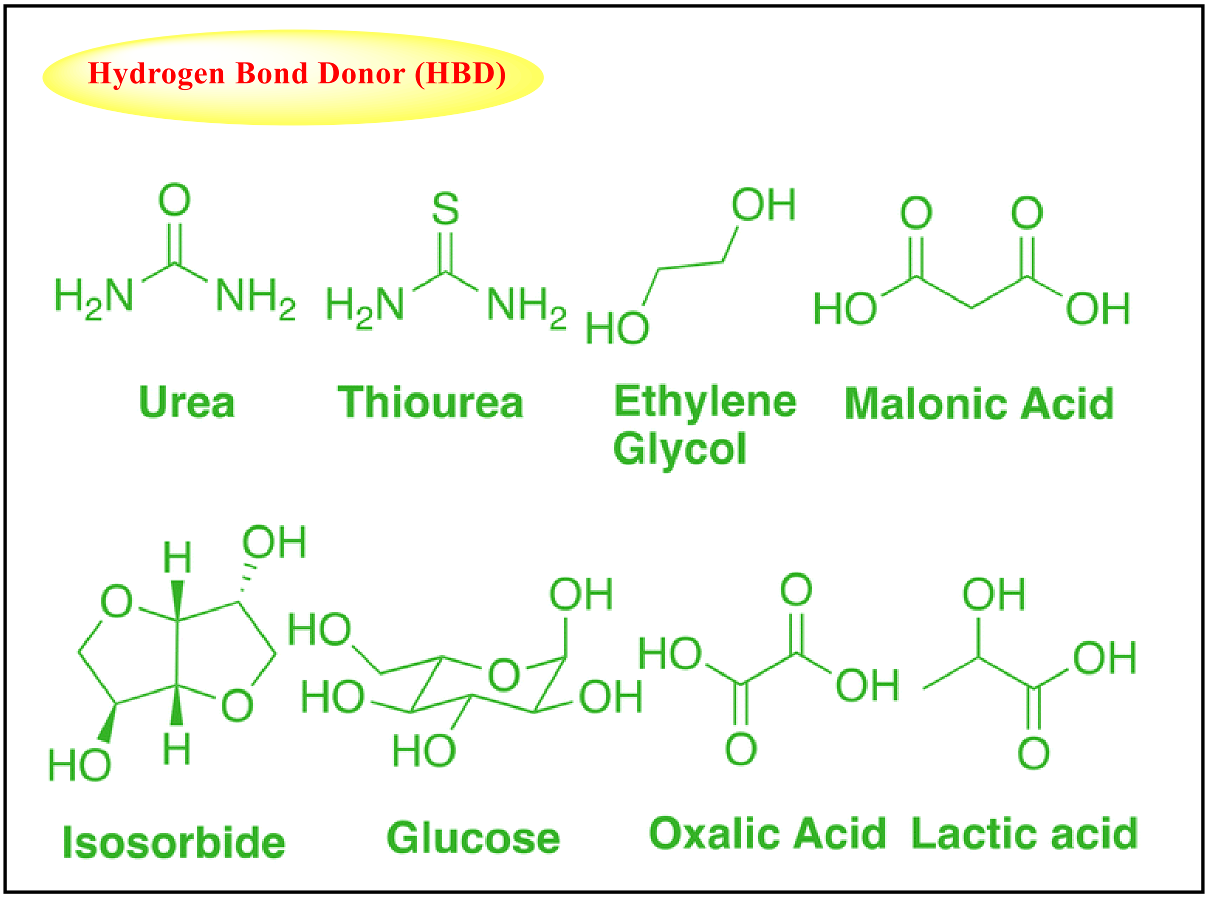

Figure 2: Selective example of hydrogen bond donors employed for the syntheses of DES

Note that the same group also defined a fourth type of DES which is composed of metal chlorides (e.g. ZnCl2) mixed with different HBDs such as urea, ethylene glycol, acetamide or hexanediol (type IV DES). Owing to its low cost, biodegradability and low toxicity, ChCl was widely used as an organic salt to produce eutectic mixtures generally with cheap and safe HBDs such as urea, glycerol, carbohydrate-derived polyols or renewably sourced carboxylic acids. These DESs are attractive since they exhibit similar physico-chemical properties to traditional imidazoliumbased ILs and thus can advantageously replace them in many applications. As compared to traditional organic solvents, DESs are not considered as volatile organic solvents and not flammable, making their storage convenient. From the view point of green chemistry, these DESs are even more attractive since some of them have been proven to be biodegradable and compatible with enzymes further increasing their interest. Additionally, synthesis of DESs is 100% atom economic, easy to handle and no purification is required, thus making their large-scale use feasible.

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From the above discussion, it is clear that DESs possess close physico-chemical properties (density, viscosity, conductivity, among others) to those of conventional ILs. Moreover, like ILs, the physico-chemicals properties of DESs can be tuned almost infinitely by changing the nature of the quaternary ammonium salt and the hydrogen-bond donor, making possible the generation of task-specific DESs. As compared to ILs, DESs have however notable advantages stemming from (1) their convenient synthesis (100% atom economy), (2) their very low price since most of DESs can be prepared from readily accessible chemicals and (3) their low toxicity, especially DESs derived from ChCl and renewable chemicals. Clearly, these notable ecological and economic advantages of DESs now open alternative routes for the emergence of ionic fluids at a larger scale. It should also be noted that although components of DESs are potentially reactive chemicals, their auto-association by a hydrogen bond drastically limits their reactivity, allowing their use in many fields of research. In the field of catalysis and organic synthesis, it is clear that DESs will definitely contribute to the design of eco-efficient processes. In particular, the possibility to (1) selectively and conveniently extract products of the reaction from the DESs phase, (2) adjust the pH of DESs, (3) dissolve not only organic and inorganic salts but also transition metal-derived complexes or nanoparticles and (4) recycle these media is among the most promising advantages of DESs. It is our opinion that development of DESs in the field of catalysis will also be drastically boosted by the need to urgently design innovative processes for the catalytic conversion of biomass. Indeed, imidazolium-based ILs have the unique ability to dissolve large amounts of cellulose and more largely lignocelluloses opening promising routes for the saccharification of biomass. However, it is also clear that the price and toxicity of ILs represent two serious drawbacks that hamper the scale-up of these processes. We are fully convinced that the recent progress made in the field of DESs for the catalytic conversion of carbohydrates will definitely open soon new methodologies for converting lignocellulosic biomass in a more rational way. In the field of material chemistry, it is also apparent that ILs can be advantageously replaced by cheap and safe DESs for the ionothermal synthesis of a wide range of inorganic materials with different textures and structures. Although a proper selection of the exactly required DESs still remains a big challenge, the above described works have clearly demonstrated that very important materials, from microporous zeotypes to carbon materials, can be synthesized in DESs. The very recent use of DESs for material synthesis demonstrates the exceptional potential of these media for the generation of novel structures and engineered materials. In these syntheses DESs may play different roles such as solvent, structure-directing agent, water inhibitor, reactant for structure crystallization, etc.

Besides excellent dissolution properties for CO2, inorganic salts, and organic molecules, many DESs can also selectively dissolve different metal oxides, which thus provide great potential for the selective recovery of pure metals, especially in electrochemistry. In the particular field of metal electrodeposition, similar results to those reported in conventional ILs were obtained in DESs.

3. Conclusion

Despite all these promising applications, much effort is still required to broaden the exploration of DESs in chemistry. For example, the instability of DESs during electrochemical processes still causes an important concern that requires to be addressed in the future. Viscosity of DESs can also be considered as a serious challenge, especially for heterogeneously-catalyzed processes. In this regard, it makes no doubt that future research will especially focus on DESs with low viscosity. Finally, a specific focus should also be provided to the reactivity of DESs that can, in many cases, lead to generation of undesirable side-products. More than a green medium, DESs can also be considered as a poorly toxic and biocompatible lipotropic agent, thus opening a new strategy for the vectorisation of pharmaceutical ingredients in the human body. This is exciting by the fact that several DESs are suspected to be prepared in living systems and responsible for unexpected mechanisms. However, DESs cannot replace ILs in all fields of chemistry. We are completely assured that low ecological footprint and attractive price will definitely contribute to the industrial emergence of this new medium in a close future.

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