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An outline of DESs, or deep eutectic solvents: A new family of environmentally friendly solvents

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Abstract:

Deep eutectic solvents (DESs), which are distinguished by their notable melting point depressions relative to their pristine constituent components, have emerged as a revolutionary green and sustainable solvent. With a variety of adjustable physicochemical characteristics, DESs are regarded as affordable "designer" solvents. The inability to foresee the microscopic processes executing the structure-property connections in this class of solvents is demonstrated by a thorough analysis of the recent literature. In DESs, the substantial hydrogen bonding is the main source of the physicochemical characteristics and melting point depressions. Understanding these systems as dynamic entities through simulations and experiments is essential. The current chapter discusses the fundamentals of DES as well as current research developments. Additionally, it highlights the latest developments in DES research, presents a high level of scientific comprehension, and identifies possible research directions related to the field's advancement towards predictive models and fundamental understanding of these solvents.

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

Introduction:

In viewpoint of green chemistry, solvents play decisive task 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 that is often made up of two or three readily accessible, reasonably priced, and safe components capability to self-assemble through interactions of hydrogen bond and produce a eutectic mixture with a low melting point.3 DESs are frequently found in liquid form at temperatures below 100 °C. These DESs are far more affordable and ecologically friendly than the commonly used ionic liquids, and they exhibit the same physico-chemical characteristics. Because of these benefits, DESs have garnered a lot of attention in a variety of scientific fields. We summarise the essential knowledge and important uses of DESs in this chapter. The goal of every contribution discussed in this chapter is to show that DESs provide easy access to new chemicals and materials in addition to enabling the design of sustainable processes.

Room temperature ionic liquids (RTILs) have garnered a lot of interest over the past 20 years, particularly in material chemistry fields, catalysis, and electrochemistry. More recently, they have also been used for biomass pre-treatment.4-5 In the early phases of these investigations, researchers concentrated especially on creating ionic liquids by combining quaternary ammonium salts with metal salts, including iron, zinc, tin, and aluminium chlorides. Despite the fact that both salts have extremely high melting temperatures, a eutectic mixture—a liquid phase—is created when they are properly mixed. Typically, these eutectic mixes have a very substantial freezing point depression that is more than 150 °C. The creation of metal-free ionic liquids (ILs) is very desirable as the idea of "green chemistry" gains traction. Numerous attempts have been made to create ILs in this respect by combining a wide range of anions—NTf^{2-}, $BF4^{-}$, Cl^{-}, and $PF6^{-}$—with an organic cation, often based on imidazolium. Since then, ILs have become a novel class of possible solvents. With a wide variety of anions and the ability to chemically change the cationic moiety nearly infinitely, chemists can create a wide variety of ILs with a variety of physical characteristics, including density, melting point, viscosity, solubility, conductivity, and refractivity. For instance, Seddon and colleagues reported in 2009 that 250 of the 1018 ILs that might be produced theoretically were currently on the market.6-7 ILs were considered green solvents because of their high boiling point and low vapour pressure, which allow for recycling. However, there is now much debate in the literature regarding these innovative solvents' "green affiliation."8.

In fact, several reports have shown the dangerous toxicity and extremely low biodegradability of the majority of ILs.9 High-purity ILs required less impurities, even in minute quantities, influence their physical characteristics. Furthermore, the production of ILs is not thought to be ecologically beneficial because it frequently requires a significant quantity of solvents and salts to fully switch over the anions. Unfortunately, these drawbacks and the elevated cost of typical ILs prevent them from being successful in the market. As a result, new ideas are now desperately needed to better logically use these systems.

In recent century, a new class of solvent known as Deep Eutectic Solvents (DES) was developed in order to address the toxicity and high cost of ILs. These DESs comprises combination of safe, affordable, biodegradable, and renewable ingredients that can combine to form a eutectic combination. Choline chloride (ChCl) is one of the most often used ingredients in the production of these DESs. ChCl is a quaternary ammonium salt that is non-toxic, inexpensive, and biodegradable. It can be easily synthesised from fossil fuels using a very high atom economy approach, or it may be extracted from biomass. ChCl may quickly produce a DES when combined with hydrogen bond donors like urea and renewable polyols (like glycerol, polysaccharides), or carboxylic acids (like citric, oxalic, amino acids or succinic,). DESs cannot be belongs to ILs since (1) they are not completely constituted of ionic species, and (2) they may also be generated from non-ionic species, even if the majority of DESs are composed of ChCl as an ionic species.

DESs made from ChCl have many advantages over conventional ILs, including: (1) minimum cost; (2) simple preparation; (3) chemical inertness with water (i.e., easy storage), as DESs are made by simply mixing two components, avoiding the purification and waste disposal issues that are frequently associated with ILs; and (4) the fact that the majority of them are biocompatible, non-toxic, and biodegradable, which furthers the media's greenness.13.

Chemical inertness, conductivity, viscosity, surface tension, density, refractive index, and other physico-chemical characteristics of DESs are quite similar to those of typical ILs. As a result, in certain research, DESs made from ChCl are also referred to as "biorenewable," "biocompatible," or ionic liquids. Due to their low environmental impact and appealing cost, DESs are currently gaining attention from both academic and industry sectors. Several recent reports devoted to DES employ is quickly rising in the current development in this field, which further demonstrates the media's allure.

2. Definition of DESs

A DES is often made up of amalgation of inexpensive and protected constituents that may create a eutectic mixture by hydrogen bonding with one another. The melting point of the resultant DES is comparatively lower than each constituents. DESs typically showed liquid nature at below 150 °C temperatures and have a very big depression in freezing point. The majority of DEs are notably liquid in nature at 37 °C to 70 °C. A DES is typically created by combining a quaternary ammonium salt with hydrogen bond donor (HBD) or metal salts that may form a complex with the quaternary ammonium salt's halide anion. The numerous quaternary ammonium salts that are often used in conjunction with different HBDs in the production of DESs are summarised in Figures 1 and 2.

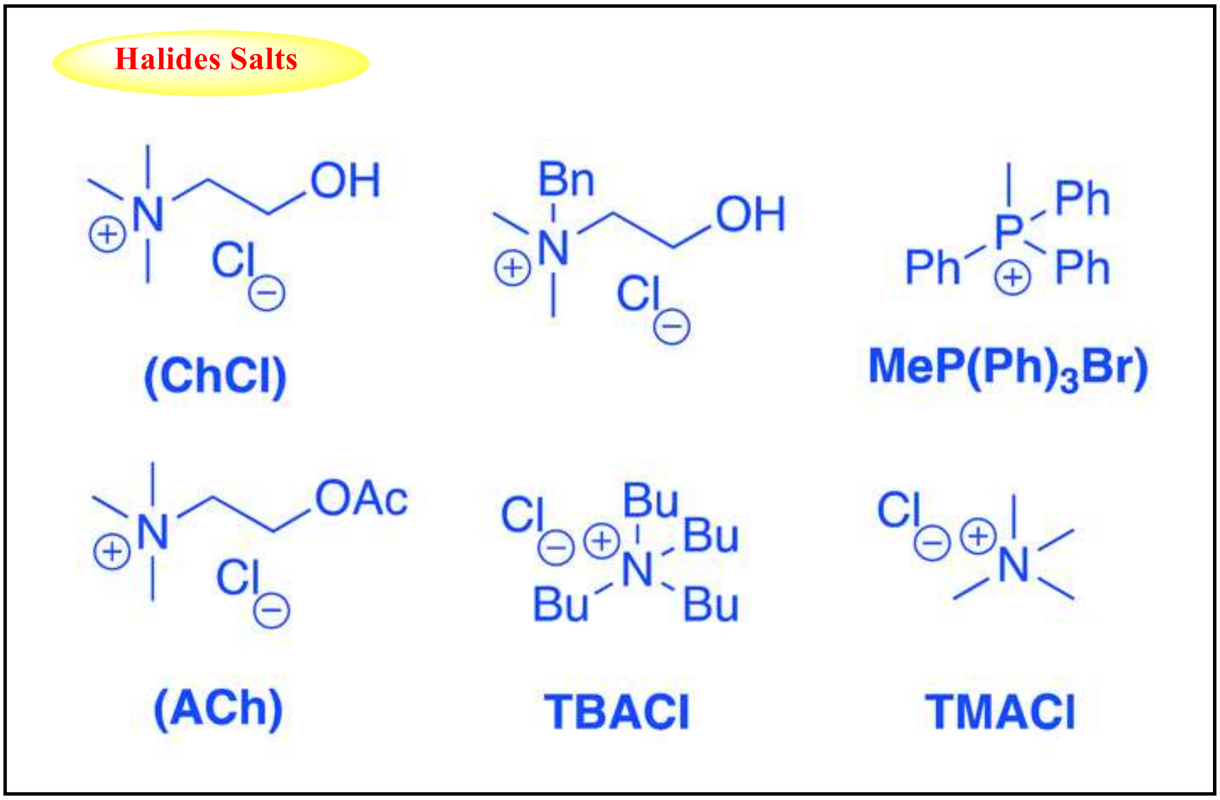

Figure 1: Representative example of the halide salts explored for the preparation of DES

Abbott and colleagues used the generic formula R1R2R3R4N+X-Y- to define DESs in 2007.12
Type I DES, M = Fe, Zn, Al, Sn, Ga, Y = MClx
Type II DES Y = MClx.yH_2O, M = Co, Ni, Cr, Cu, Fe,
Type III DES Z = -OH, -COOH, -$CONH_2$, Y = R5Z

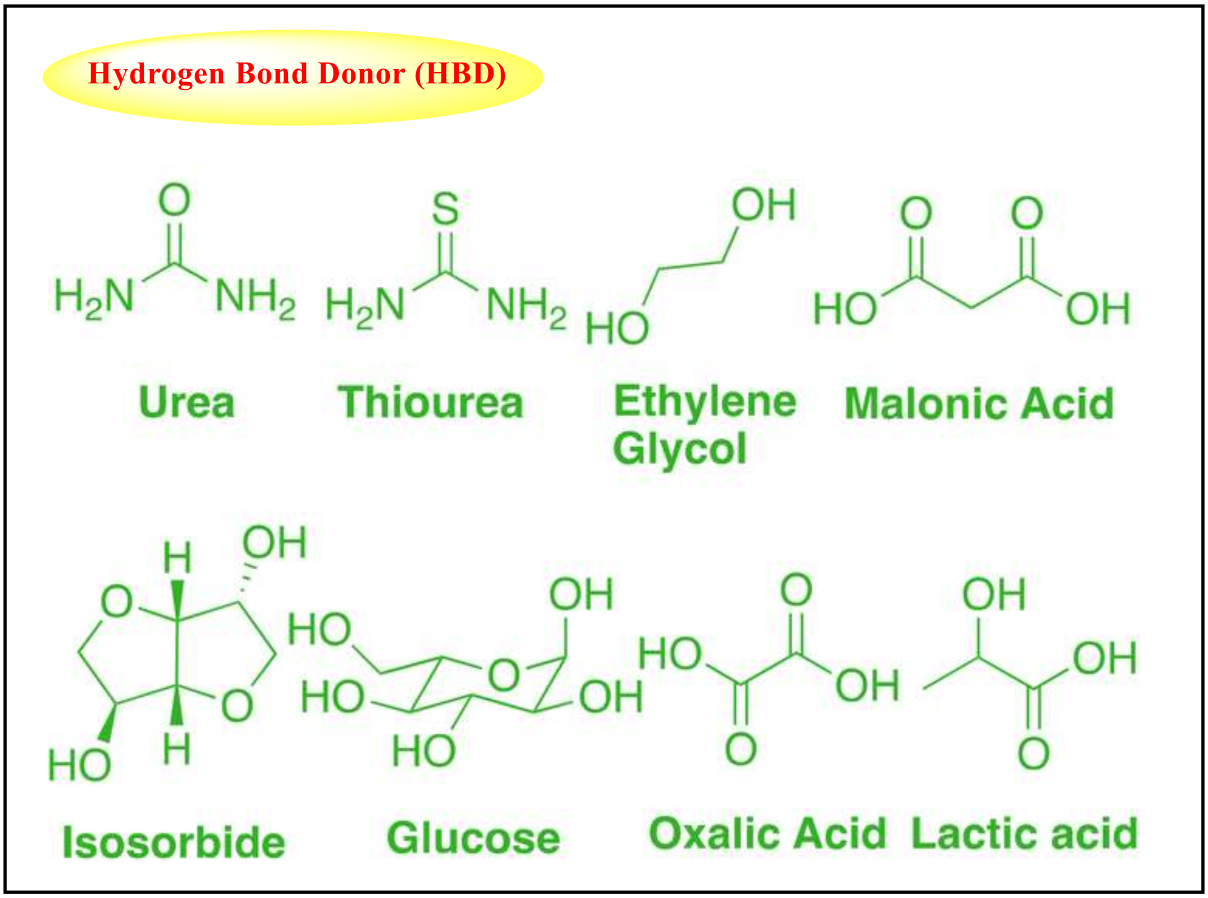

Figure 2: Selective example of hydrogen bond donors employed for the syntheses of DES

Keep in mind that same group of DES were identified as 4th form/type IV DES, which is made up of metal chlorides (such $ZnCl_2$) combined with other HBDs including urea, acetamide, ethylene glycol, or hexanediol. an organic salt such as ChCl was utilised to create eutectic mixes with like carbohydrate-derived polyols, glycerol, carboxylic acids or urea. These DESs are appealing because they can effectively replace conventional imidazolium-based ILs in a variety of applications due to their comparable physico-chemical characteristics. Because DESs are neither combustible or regarded as volatile organic solvents like conventional organic solvents, they are easier to store. These DESs are even more alluring from the perspective of green chemistry since some of them have been shown to be biodegradable and enzyme-compatible, which heightens interest in them. Large-scale application of DESs is also possible due to their 100% atom-economic synthesis, ease of handling, and lack of purification requirements.

It is evident from the description above that DESs and traditional ILs have many physico-chemical characteristics, including density, viscosity, and conductivity. Furthermore, by altering the characteristics of the hydrogen-bond donor and the quaternary ammonium salt, DESs' physico-chemical characteristics may be adjusted nearly endlessly, just like ILs, enabling the creation of task-specific DESs. DESs have some significant advantages over ILs, though, including (1) simple synthesis procedure, (2) extremely low cost because required chemicals obtained easily, and (3) less toxic, particularly those made from renewable resources and ChCl. These significant economic and ecological benefits of DESs undoubtedly create new pathways for the larger-scale rise of ionic fluids. Additionally, despite the fact that DES components are reactive compounds, their self-association via a hydrogen bond significantly reduces own reactivity, enabling its application in a variety of study domains. It is obvious that DESs will undoubtedly aid in the development of eco-friendly procedures in the fields of organic synthesis and catalysis. Specifically, the ability to (1) easily and selectively remove reaction products from the DESs phase, (2) modify the DESs's pH, (3) dissolve complexes or nanoparticles produced from transition metals in addition to organic and inorganic salts, and (4) One of the most capable reimbursement of DESs is their capability to recycle these media. We believe that the imperative need to generate novel techniques for the catalytically biomass conversion that will accelerate the advancement of DESs. Although, imidazolium-based ILs have extraordinary capacity to dissolve significant quantities of cellulose, and more specifically lignocelluloses, which opens up exciting possibilities for biomass saccharification. It is evident, therefore, that two significant obstacles to the expansion of these procedures are the cost and toxicity of ILs. We firmly believe that new approaches for the more sensible conversion of lignocellulosic biomass will soon become available because to the recent advancements in DESs for the catalytic conversion of carbohydrates.

For the ionothermal synthesis of a variety of inorganic materials with varying textures and architectures, it is also evident in the field of material chemistry that inexpensive and secure DESs may be used to replace ILs in a beneficial way. The efforts mentioned above have made it abundantly evident that crucial materials, such as carbon and microporous zeotypes, can be synthesised in DESs, even though choosing the right DESs is still a difficult task. The remarkable capicity of DESs for the creation of innovative structures and tailored materials is demonstrated by their relatively recent application in material synthesis. DESs can operate as a solvent, water inhibitor, structure-directing agent, reactant for structure crystallisation, and more in these syntheses.

Many DESs have the ability to selectively dissolve various metal oxides in addition to having excellent dissolving qualities for CO2, inorganic salts, and organic molecules. This offers significant promise for pure metals recovery, particularly in electrochemistry. Similar outcomes to those documented in traditional ILs were achieved in DESs in the specific field of metal electrodeposition.

3. Conclusion

Even with all of these encouraging uses, there is still more work to be done to expand DES research in chemistry. For instance, DES instability during electrochemical operations remains a significant issue that has to be resolved in the future. Another significant issue with DESs is their viscosity, particularly in processes that are heterogeneously catalysed. In this sense, it is obvious that DESs with low viscosity will be the primary focus of future study. Lastly, particular attention should be paid to DESs' reactivity, which frequently results in the production of unwanted byproducts. In addition to being a green medium, DESs are a lipotropic agent that is biocompatible and weakly poisonous, which creates a novel avenue for the human body to absorb medicinal substances. The fact that a number of DESs are thought to be present in biological systems and in charge of surprising mechanisms makes this intriguing. DESs cannot, however, take the role of ILs in every area of chemistry. We have every confidence that this new medium's minimal environmental impact and alluring pricing will soon play a part in its industrial rise.

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