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From green chemistry to nature: The versatile role of low transition temperature mixtures

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ABSTRACT

In 1998, the concept of “green chemistry” was established through twelve principles with the aim of improving the eco-efficiency of chemical processes and to judge, whether or not, a chemical process is sustainable. Currently, numerous processes do not obey to most of these principles (large energy usage, formation of waste, usage of hazardous solvents and reagents, etc ...), which have forced the scientists to develop and implement new strategies for upcoming researches. One of the most attractive challenges is finding, creating and developing new and green media. Over the last decades, the scientific community has mainly focused on two different classes of solvents (namely, Ionic liquids and Eutectic Solvents). These solvents share advantageous characteristics (low vapor pressure, thermally stable, non-flammable, etc ...) making them an attractive option to implement sustainable chemistry and engineering. Mainly due to its environmental and economic features, DES are now growing much more interest. Indeed, although their ecotoxicological profile is still poorly known, DES are classified as “green” solvents because they are composed of molecules which are considered to be eco-friendly. The fast, numerous and broad scope of studies on these new liquids make the literature rather complex to understand. Here, we attempted to establish a succinct history and a presentation of these liquids with emphasis on their role, classification, importance and application in biological systems.

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1. Eutectic

Fundamentally, the term “eutectic” is used to describe a mixture of two or more compounds which, at a well-defined composition, displays a unique and minimum melting point in the phase diagram (Fig. 1). This minimum melting point is typically, significantly lower than the melting points of the individual components, and reflect non-covalent affinities at the molecular level. These interactions lead to energy reduction characterized by a decrease, sometimes very substantial, of the melting point of the mixture. Nevertheless, the same word might suggest (usually wrongly) that the system has the eutectic composition or is at the eutectic temperature. In principle, any system containing a liquid phase must be at or above an appropriate eutectic temperature. Although the precise nature of the driving forces for eutectic formation is not well understood, the non-covalent intermolecular interactions between the components (such as hydrogen-bonding and van der

Waals' interaction) are supposed to play a fundamental role.

2. From eutectic to Deep Eutectic Solvents (DES)

The term “Deep Eutectic Solvent (DES)” was originally introduced in literature by the team of Prof. A. P. Abbott to describe any mixture characterized by a significant (“deep”) decrease in the transition temperature (liquid–solid) compared to the individual melting point of the substances [1,2]. The first liquids were obtained by mixing an ammonium salt with a metal salt or a hydrogen-bond donor (HBD). In most cases, these solvents may be used liquid at room temperature or at a temperature below 70 °C. In the specific case where a HBD is used to form the eutectic, the charge delocalization occurring between the HBD molecule and the anionic species provided by the salt is responsible of the significant depression in the melting point of the starting molecules. It is hereafter assumed that the HBD acts as complexing agent and interact with the anionic species which increases its effective size, which in turn decreases the interactions with the cation, leading to this characteristic freezing point depression in the mixture. Thus,

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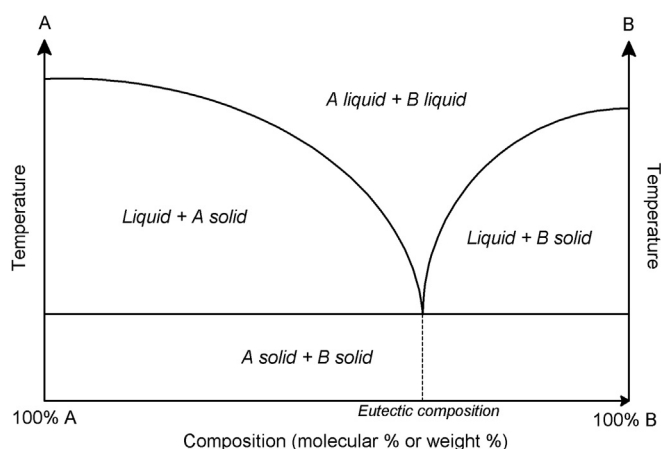


Fig. 1. Schematic phase diagram for binary eutectic mixture.

DES may be designed and improved upon using Hole theory, where the viscosity and surface tension of the medium will be related to its free volume and the probability of finding holes of suitable dimension for molecules or ions to move into [3]. Historically, the DES can be defined according to the general formula $R_1R_2R_3R_4N + X \cdot zY$ and classified according to the type of compound associated with the ammonium salt:

- Type 1: metal salts. $Y = MCl_x$, $M = Zn, Sn, Fe, Al, Ga$;
- Type 2: hydrated metal salts. $Y = MCl_x \cdot yH_2O$, $M = Cr, Co, Cu, Ni, Fe$;
- Type 3: hydrogen-bond donors. $Y = R_5Z$, $Z = CONH_2, COOH, OH, NH_2$

Similarly, these authors defined a type 4 DES, consisting of a metal chloride (eg. $ZnCl_2$) associated with a HBD such as urea, ethylene glycol, acetamide or hexanediol. More recently, a study showed that it was possible to synthesize DES by substituting the ammonium salt with a phosphonium salt, combined with a HBD such as glycerol, ethylene glycol or 2,2,2-trifluoroacetamide [4]. There are numerous opportunities to prepare DES because of the high flexibility to choose their individual components. As a consequence, myriad of new DES are now available to design a task-specific solvents.

However, literature may often be confusing when dealing with these new liquids. Ionic Liquids (IL), Deep Eutectic Solvents (DES), Natural Deep Eutectic Solvents (NADES) and Low Transition Temperature Mixtures (LTTM) are different terms used in studies, sometime wrongly or referring to the same solvent. It is actually tricky to differentiate all the terms, most likely because all four may in some circumstances refer to the same solvent. For example, one may claim that DES and some NADES may be assimilated to IL because some of IL, especially those obtained from pyridinium or imidazolium halides combined with aluminium chloride ($AlCl_3$), share the same principle of creation. Indeed, their formation may be summarized as an association of the coordinating anion (e.g. halides) with a complexing agent (e.g. Lewis or Brønsted acids), promoting the charge delocalization and decrease of the interaction with the cation [3]. Yet, although in this case the liquids share the very same mechanism of depression of the melting point, they may display dissimilarity since the IL will be reactive to water whereas the DES will not be. Recently, most of the IL are exclusively formed with discrete ionic molecules often obtained after multi-step syntheses, and thus cannot be compared with a binary mixture of unmodified molecules leading to a DES where the hydrogen

bonding appear to be the main driving forces. In those IL, the decreases in melting points and heats of formation are mainly the result of a change in charge distribution, degrees of freedom of the ions, and increases in nonparticipating portions of the cation that do not contribute to Coulombic charge–charge attraction and stabilization of the crystal [5]. Concomitantly, because most of the mixtures showed glass transitions instead of melting points, some solvents were named LTTM [6,7], and not DES. Nevertheless, some authors have used (randomly?) the term DES or LTTM without any characterization of the transition temperature. Finally, the term NADES was recently used to describe a liquid obtained by combining molecules abundantly present in the nature. However, the boundary between NADES and DES is somewhat hazardous and difficult to determine. Also, DES was defined as mixtures of components that form a eutectic point in the phase diagram, but it is not clear whether all the NADES form such eutectic mixtures. A more striking difference is that some NADES are exclusively formed by non-ionic species, which suggest different driving forces to create the liquid since the Hole theory put forward to explain the molecular motion in DES is difficult to contemplate in such NADES. In summary, there are some evident connections between all the terms and we are even convinced that some of them are labeled with different names in Literature whereas they are precisely the same. Lack of physical descriptions of the transition temperature associated with imprecisions and approximate semantic make the Literature very confusing. A suggested classification of these new liquids is illustrated in Fig. 2. Mixture of molecules resulting in a low transition temperature (liquid–solid) is the unique common property of these solvents. That is why, the term LTTM appears to be the most representative to characterize this large family of solvents. Thus, and without a detailed investigation of the physico-chemical properties, these newly discovered liquids should be called LTTM in order to avoid any ambiguity. NADES, DES and IL may be seen as different subfamilies of LTTM linked together because they may share similar physico-chemical properties (e.g. low vapor pressure, non-volatility, etc.) and/or theory of formation for some of them. NADES and DES are very similar (sometime equivalent) and may share the same properties and definition, but we believe that some NADES may retain different features, as previously outlined. The same conclusion may be drawn with DES and IL, or NADES and IL. Finally, it might be noticed that most of the LTTM consist of at least two molecules with one mainly hydrogen-bond acceptor and one mainly hydrogen-bond donor and thus, a huge diversity of molecules can be potentially combined to form such liquids.

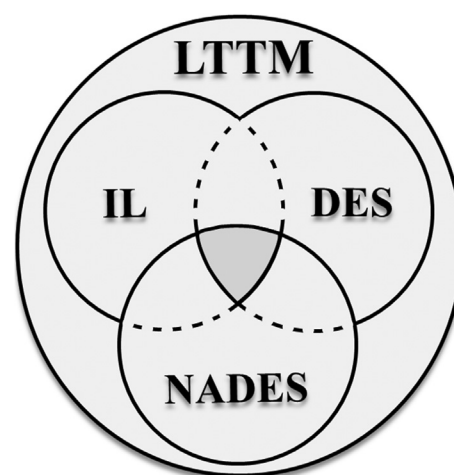


Fig. 2. Classification of low transition temperature mixtures.

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