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## Insights into the Solid-Liquid Equilibria of Eutectic and Deep Eutectic Mixtures

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**PURPOSE OF THE ABSTRACT**

Eutectic mixtures present interesting properties and have been widely applied due to the liquefaction and enhanced solubility provided by the decrease of the melting point of the mixture when compared to those of the starting pure constituents [1?3]. In 2003, Abbott and co-workers [4] coined for the first time the term deep eutectic solvents (DES) to describe mixtures of amides with quaternary ammonium salts that had melting points much lower than those of their pure compounds, allegedly due to the formation of a hydrogen bonding complex between a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) on a well-defined stoichiometric proportion. Later, the term was extended [5], and a number of reviews on DES and their applications is available nowadays [5?7]. DES were reported to be very versatile solvents, easy to prepare from widely available compounds, and are nonreactive with water. They have been touted as a cheap and greener alternative to ionic liquids and the concept became, meanwhile, widely used with more than one thousand references today in ISI Web of Science. However, due to the absence of a strict and clear definition of what a 'deep eutectic solvent' is, this term is often abused nowadays. This problem is related to the limited number of works devoted to understand the DES nature and what is their difference to conventional eutectic mixtures. The applications of these solvents have been the only target of most works published so far. The thermodynamic characterization, namely information about their solid-liquid phase diagrams (SLE) and an understanding of their interactions in the liquid phase, essential for the efficient design and selection of the best DES for a given application, remains poorly studied, while the melting properties of their pure constituents are many times unknown. This communication aims at contributing to deepen the understanding of eutectic and deep eutectic mixtures concerning their definition, thermodynamic nature and modelling.

In this work the SLE phase diagrams for mixtures reported as DES in the literature, involving different classes of compounds, were analyzed and discussed in order to contribute to a better understanding of the nature of the liquid phase of these mixtures, in particular in what concerns to their liquid phase non-ideality. Regarding terpene based mixtures (eg. thymol+ibuprofen, menthol+testosterone), and unlike previous pharma oriented works, the recent publications under the DES concept fail to study the SLE, focusing essentially on the application. Thus, despite their important hydrophobic label, most of these mixtures present a quasi-ideal behaviour. Choline chloride, [Ch]Cl, the most widely used HBA in DES formulations, decomposes before/upon melting [8] what precludes the direct measurement of its melting properties. Thus, their melting temperature and enthalpy were indirectly estimated [8] and here evaluated by using the SLE phase diagrams of choline chloride with fatty alcohols, fatty acids, sugars, sugar alcohols or polycarboxylic acids. A detailed evaluation on the relevance of heat capacity change upon melting was also performed, showing that in many cases this value is not negligible. Finally, mixture of quaternary ammonium chlorides and fatty acids were analyzed and described by thermodynamic models. Results show extreme negative deviations to the ideal solubility for the ammonium salt

solubility curve, while the experimental solubility curve of the acid is very well described assuming ideality. In most of the cases studied, the SLE phase diagrams were compared with the predictions assuming ideality, and with correlations using the Perturbed Chain-Statistical Associating Fluid Theory (PC-SAFT) equation of state.

## FIGURES

### FIGURE 1

### FIGURE 2

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### KEYWORDS

Deep eutectic solvents | Solid Liquid equilibria | Eutectic Mixtures

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