Design Rules for Recyclable Eutectic Systems

Mise en forme de solvants eutectiques recyclables

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Modern chemical processes need to be sustainable and environmentally acceptable, and a major line of research towards these goals involves new solvents and reaction media as replacement of current volatile or toxic solvents.

Ionic liquids are low-melting salts composed of large organic ions and have been the object of intensive research because of the non-volatility, stability and versatility of many of them as solvents. Nonetheless, most ionic liquids remain expensive whereas availability in large scale is a prerequisite for a successful alternative to presently used commodity chemicals. The so-called deep eutectic solvents are another class of separation and reaction media. Although imperfect, we retain here this designation of "deep eutectic solvent" (DES) to encompass the broader class of low-melting mixed solvents. DESs are formed by mixing two substances: often a salt with a molecular compound, both of which may be solid at room temperature, to obtain a low-melting mixture near the eutectic composition. They are mostly made of cheap, readily available and rather safe starting compounds.

The temperatures for which the mixture is a liquid, the solvation performance, and the sustainability of the DESs can be adapted by the appropriate selection of (1) the constituents and (2) the composition of the mixture. However, exploring this vast chemical space experimentally is challenging. Current predictive models seldom capture the complex structure and interaction needed to accurately predict phase equilibria and partition coefficients, which would allow the rapid choice of a DES, its use, and subsequent recovery. Hence, DESs have so far failed to meet important green engineering principles, such as the conservation of complexity and the minimization of material diversity, as far as their design and recycling are concerned.

The aim of this thesis is to propose a robust design strategy for novel task-specific and easily recyclable DESs for temperature swing and liquid-liquid extraction processes. Firstly, the conditions under which the DES is liquid must be screened using improved thermodynamic models to ensure its adequacy for a given application. Secondly, the presence of other components and their effect on the DES constituents partitioning needs to be considered to allow its recyclability, which previously has not been taken into account as a design criterion. To attain these objectives, a set of experimental phase equilibrium data of carefully chosen DESs will be obtained and comprehended following two fundamental aspects: (1) thermophysical properties of the pure component or formed solids—such as a cocrystal—and (2) the activity coefficients for all liquid phase constituents.

The main scientific difficulties anticipated concern: i) the experimental determination of the pure component properties as they often decompose before melting; ii) the description of the activity coefficients of components in such complex liquid mixtures (DES + solute + recovery solvent); iii) the scarcity of recyclability studies.

A combined experimental and modelling effort will take place in the Theoretical Chemistry and Molecular Thermodynamics group at *Laboratoire de Chimie de l'ENS Lyon* and this thesis will mainly concern the experimental approach. Experimental methods that will be used include characterisation of thermodynamic and solvation properties of DESs through phase diagrams of the DES without and with solutes (obtained by differential scanning calorimetry), solubility measurements, heats of mixing and heats of dissolution. The candidate will interact with an active international network of collaborators in the field of sustainable chemistry, ionic liquids and DES.