



Assessing solute partitioning in deep eutectic solvent-based biphasic systems using the predictive thermodynamic model COSMO-RS



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ABSTRACT

The prediction quality of COSMO-RS for the thermodynamic properties needed for the design of a liquid-liquid chromatographic process was evaluated for systems containing deep eutectic solvents (DES). Therefore activity coefficients, liquid-liquid equilibrium data, and partition coefficients of different solutes were computed and compared to experimental data from literature or measurements. The calculations were performed using TZVP and TZVPD-FINE parameterizations and fully dissociated and non-dissociated representations of the H-bond acceptor molecules. It was found that the predictions qualitatively resemble the trend of the experimental data. The TZVPD-FINE parameterization did not yield significantly lower deviations from the experimental values than TZVP, while calculations with the latter were up to ten times faster. Although DES constituents exhibit strong H-bond interactions, the representation as an electroneutral mixture is preferable. It could be shown that the predictions of partition coefficients are in good agreement with the measured values in the preferred working range of liquid-liquid chromatography. The overall prediction quality is sufficient to use the predictive model for the screening procedure for the solvent system selection.

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1. Introduction

Deep eutectic solvents (DES) are a combination of hydrogen bond donor (HBD) and hydrogen bond acceptor molecules (HBA), which in mixture have a substantially lower melting point than the pure components. The term refers to such combinations with a melting point below 100 °C. After Abbott et al. reported the interesting properties of this new solvent class in 2003, DES gained a lot of attention [1]. Because of their high solving capacity, low volatility and relatively low price, many new applications have been described and their number is rapidly increasing [2–7]. The most abundantly used HBA is choline chloride, a non-toxic quaternary ammonium salt. It can be combined to form a DES with various HBD, such as urea, carboxylic acids and sugar-based polyols [8]. The resulting mixtures are considered biocompatible and less environmentally harmful green solvents [3]. Those advantages also led to the application of biphasic solvent systems containing DES in solid-support free liquid-liquid chromatography [9]. This technique, also known as countercurrent or centrifugal partition

chromatography (CCC or CPC), uses the two liquid phases of a biphasic solvent system in thermodynamic equilibrium as the mobile and stationary phases for a chromatographic separation process [10]. A mixture can be separated according to the difference in the partition coefficient of each component in this liquid biphasic system. DES can be used to form water free biphasic liquid systems with, for example, alkanes and alcohols or nitriles, which can be utilized for the separation of hydrophobic compounds [9]. Since DES have shown interesting characteristics, it is worth increasing the accessibility of DES-based biphasic systems. Due to the large number of possible combinations of DES and possible biphasic solvent systems formed with DES and other solvents, systematic screening methods are needed for solvent system selection.

In liquid-liquid chromatography the most crucial step in the design of a separation process is the selection of a biphasic liquid system, which phases will be used as the mobile and stationary phases for the separation. Choosing such a system may involve many experiments if it is done by a trial and error approach. Therefore the exploration of systematic methods to reduce the efforts for this selection process came into the focus of research. There are many strategies for solvent system selection, for example by classifying the large amount of possible biphasic solvent systems by their composition or by comparison of the partition coefficient

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of different standard substances in those systems [10–13]. These solvent system evaluations have significantly eased the selection process; however, they can only assess a finite number of solvent systems and still involve a lot of measurements until a final solvent system is chosen. In many cases no pure substances from the mixture to be separated are available to determine partition coefficients in many different solvent systems. Due to those limitations, model-based approaches for the selection of a biphasic solvent system were developed. Thermodynamic models have been used to predict liquid-liquid equilibria (LLE) of multicomponent mixtures and the partitioning of solutes between the phases of a biphasic system. In previous work, our group has shown that thermodynamic models can drastically reduce the experimental effort in the solvent system selection process [14,15].

Publications on the application of thermodynamic models to systems involving DES have rapidly increased in the last few years. Gonzalez et al. performed a correlation to reflect the phase behavior of two different DES combined with hexane and benzene, toluene or ethyl acetate with varying temperature using UNIQUAC [16]. The group of Hadji-Kali investigated the extraction of aromatics from aliphatics and denitrication of diesel using NRTL and COSMO-RS for LLE calculation [17–19]. Rodriguez et al. presented phase equilibrium data for chloride quaternary ammonium salts and polyol-based DES and performed COSMO-RS calculations to predict the phase equilibria [20]. Gouveia et al. investigated an application of DES as azeotrope breakers for mixtures of aliphatics and aromatics using COSMO-RS and experimentally [21], and Aissaoui et al. used COSMO-RS in the investigation of DES for an application in natural gas dehydration [22]. Since the interactions between the HBA and HBD are of great interest for the choice of a DES for a specific process, molecular dynamics simulations have been applied to study the characteristics of DES solutions, such as self-diffusion or hydrogen bonding. The most abundantly investigated DES, choline chloride-urea, was used to gain an insight into the hydrogen bonding between the donor and acceptor molecules and later molecular dynamics and experimental analysis were performed for three further HBD [23,24]. Ullah et al. investigated the intermolecular interactions in the DES composed of choline chloride and levulinic acid, which was used in CO₂ capturing, and characterized a network of H-bonds between the donor and acceptor molecules [25]. Although predictive models have been applied in the design of different separation processes, they have not yet been applied to solvent system screening involving DES-based solvent systems for liquid-liquid chromatography. The most important properties needed for the design of a liquid-liquid chromatographic separation process are LLE and partition coefficients of target molecules within a biphasic system. In contrast to extraction processes a moderate partition coefficient in the range of $-0.4 < \log P_i < 0.4$ is preferred and usually biphasic systems closer to the plait point are used. It has been shown that COSMO-RS can be applied in the selection of a biphasic solvent system composed of water and organic solvents for a liquid-liquid chromatographic separation [14,15,26]. However, the approach needs to be validated for complex biphasic systems containing DES.

In this work the prediction quality of COSMO-RS is evaluated for solvent systems containing DES. The most important thermodynamic parameters for the design of a liquid-liquid chromatographic separation process are calculated and compared to experimental data taken from literature or measurements. Those thermodynamic properties include activity coefficients, LLE data and partition coefficients. For the COSMO-RS calculations different parameterizations and methods to represent the DES in the software are compared.

2. Material and methods

2.1. Experimental details

2.1.1. Chemicals

Choline chloride, betaine and levulinic acid were purchased from Alfa Aesar. All compounds used for the DES had purities $\geq 98\%$. Methanol, 1-propanol and heptane (99.9%) were purchased from VWR Chemicals, ethanol ($\geq 99.9\%$) was obtained from Merck KGaA, acetonitrile ($\geq 99.9\%$) from J.T. Baker. Vanillin (99%) and α -tocopherol ($\geq 97\%$) from Alfa Aesar and β -ionone (96%) from Aldrich were used for the partitioning experiments.

2.1.2. Preparation of deep eutectic solvents

For the DES preparation HBA and HBD were weighed in at a molar ratio of 1:2 and heated to 80–85 °C in a hermetically closed vial for approximately 25 min. The mixtures were stirred and heated until a clear homogenous liquid was obtained. A more detailed description of the procedure can be found in Ref. [9]. Betaine or choline chloride were used as HBA, the HBD in both cases was levulinic acid. The DES composed of betaine and levulinic acid (1:2 mol:mol) will further be referred to as BLA, the DES containing choline chloride and levulinic acid (1:2 mol:mol) as CLA.

2.1.3. Biphasic solvent systems

The biphasic solvent systems were prepared by mixing the solvents in the respective amounts. The composition of the solvent systems and the solutes used for the shake flask experiments can be found in Table 1. The biphasic systems were mixed using an automatic shaker for 30 min and were afterwards allowed to settle for another 1.5 h.

2.1.4. Partition coefficients

The partition coefficient K of a solute i is defined as the ratio of the solute's mole fraction in each phase at thermodynamic equilibrium:

$$K_i^{\alpha\beta} = \frac{x_i^\alpha}{x_i^\beta} = \frac{\gamma_i^\beta}{\gamma_i^\alpha} \quad (1)$$

where x_i and γ_i are the mole fraction and activity coefficient of compound i , and α and β are the two phases of a biphasic liquid system. For low concentration of the solute in the biphasic system the solute distribution shows linear behavior and the partition coefficient can be assumed as a constant.

In experimental screenings of the partition coefficient it is more convenient to use concentrations c instead of mole fractions:

$$P_i^{\alpha\beta} = \frac{c_i^\alpha}{c_i^\beta} = \frac{x_i^\alpha \rho^\alpha}{x_i^\beta \rho^\beta} \quad (2)$$

where ρ is the molar density of the phase.

For the calculation of the partition coefficient the compositions of the two phases without solute has to be known. These were taken from literature data or calculated using the LLE function in COSMOtherm.

The experimental partition coefficients of vanillin, β -ionone and α -tocopherol were determined using the shake flask method described in our previous work [9]. For the shake flask experiments α -tocopherol, vanillin or β -ionone were added to the systems at a concentration of 5 mmol l⁻¹. UV-Vis spectroscopy was utilized to assess the concentrations of the respective solute in the phases of the solvent systems. The experiments were conducted in triplicate.

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