Extension of COSMO-RS for the prediction of the salt effect on liquid-liquid equilibria

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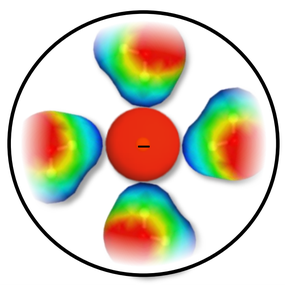
Introduction

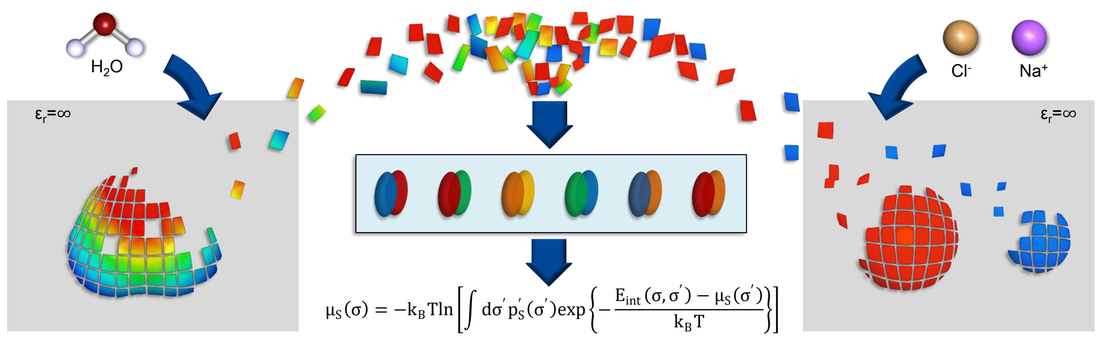
- Strong influence of electrolytes on solubility of organic species in aqueous solutions
- Extraction of hydrophilic species with polar organic solvents possible upon addition of salts
- Reduction of experimental effort with predictive thermodynamic models



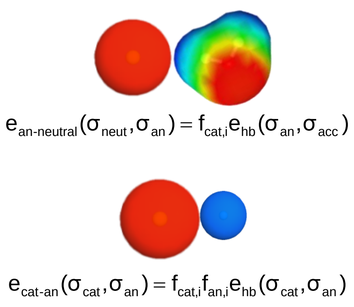
- Very few electrolyte models allow the prediction of liquid-liquid equilibria (LLE)
- Extension of the predictive thermodynamic model COSMO-RS
- Refinement of the model particularly for the prediction of liquid-liquid equilibrium data

Modelling of Electrolyte Systems with COSMO-RS

Prediction of thermodynamic properties using COSMO-RS

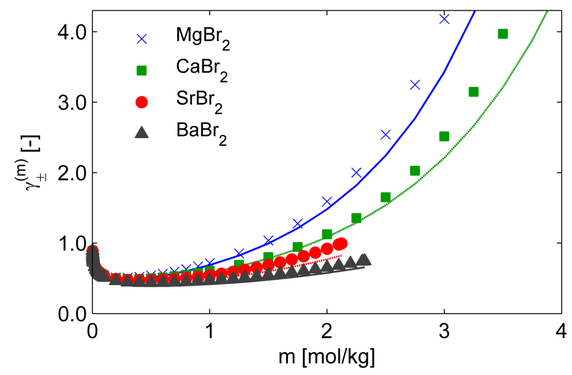


Extension for electrolyte systems



- Pitzer-Debye-Hückel contribution
- Parametrization :
  - Cation radii
  - Interaction energy

Prediction of Ion Activity Coefficients in Aqueous Solution

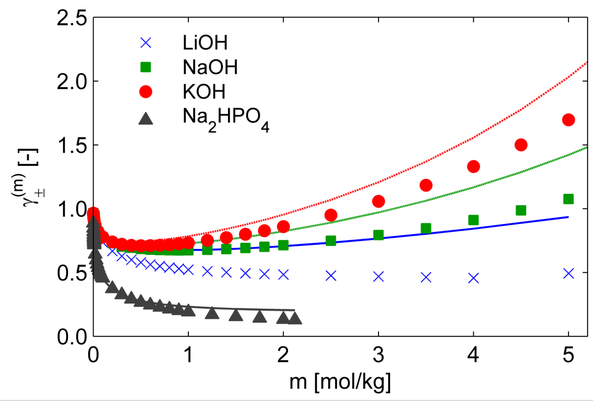


Correlation

- Modelling of a variety of salts possible
- Comparatively few parameters necessary

Prediction

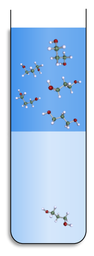
- Application of the model to ions that were not used in the training set
- Predictions possible even for non-parameterized ions

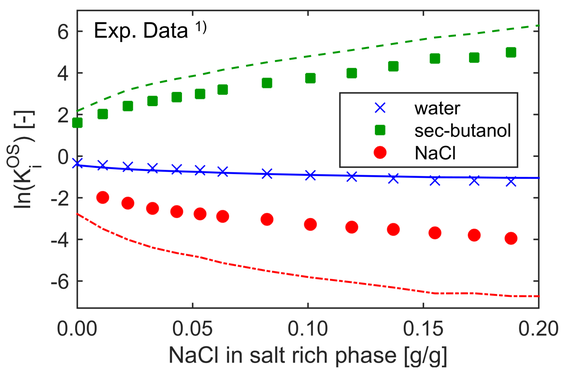


Refinement of the Model for Liquid-Liquid Equilibria

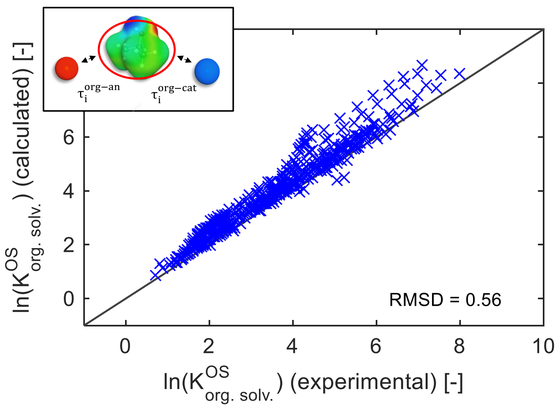
$$K_i^{OS,exp} = \frac{x_i^O}{x_i^S}$$

$$K_i^{OS,calc} = \exp\left(\frac{\mu_i^E(\mathbf{x^S}) - \mu_i^E(\mathbf{x^O})}{RT}\right)$$



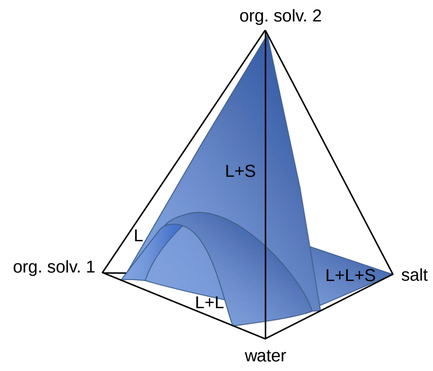


- New algorithm for the efficient parameterization of ion-solvent interaction parameters
- Improved predictions for solvent partition coefficients in alcohol + water + salt systems

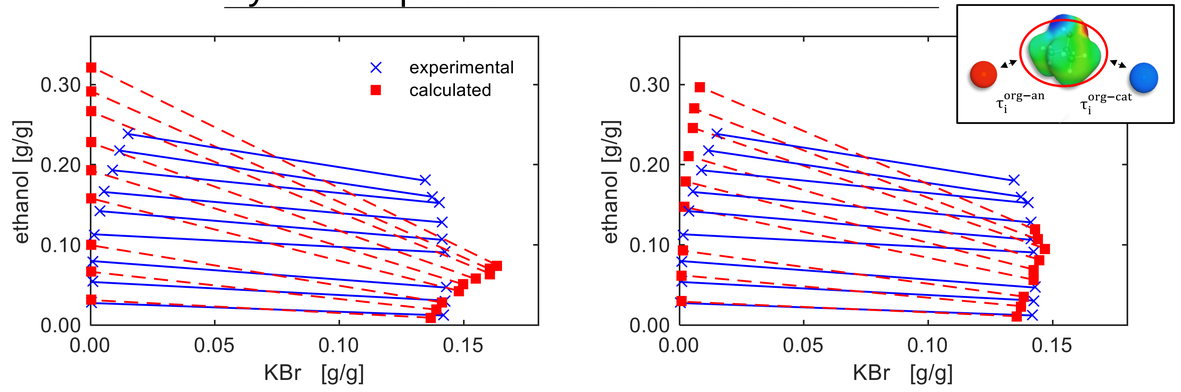


Prediction of LLE in Quaternary Systems

- Quaternary systems relevant for extraction processes
- The model can be applied to predictions in such complex systems



System: n-pentanol – ethanol – water – KBr 2)



Conclusions

- An electrolyte extension of COSMO-RS for the prediction of thermodynamic properties in aqueous systems was developed.
- The model can be successfully applied to the prediction of mean ionic activity coefficients in different systems.
- A refinement of the model based on liquid-liquid equilibrium data can lead to quantitative improvements of the predictive quality for these complex systems.

References:
[1] De Santis et al., Chem. Eng. J, 1976, 11, 207-214
[2] Aznar et al., J. Chem. Eng. Data, 2000, 45, 1055-1059

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