

Topic of a Bachelor / Master thesis

Revision and extension of UNIFAC-IL model by simultaneous correlation to different thermodynamic properties

Experimental / theoretical

Magdeburg, xx.xx.20xx

Motivation:

Ionic liquids (ILs) possess many unique physico-chemical properties such as non-volatility, non-flammability, high thermal/chemical stability, wide liquid range, and high solvent capacity, etc. More importantly, desired properties of ILs can be achieved by careful selection of cation, anion and substitute groups, making ILs 'designer' solvents. Because of these attractive characters, ILs are regarded as promising alternatives to organic solvents and have attracted significant interest across a wide variety of separation systems.

To identify suitable ILs towards a specific separation task, the experimental trial-and-error method is very time-consuming and expensive, and thus theoretical methods that can be applied to estimate the thermodynamic properties (e.g., activity coefficient, phase equilibria, etc.) of IL-solute systems is of great significance. In our previous work^[1], the UNIFAC-IL model was largely introduced to cover 21 conventional functional groups, 9 cation skeleton groups, and 29 anion groups. This is as far as we concern the most complete UNIFAC-IL model in literature. However, it should be pointed out that the obtained UNIFAC-IL model is purely regressed from infinite dilution activity coefficient (γ^∞) data. Such a γ^∞ -based model has two limitations. (1) As the temperature and concentration independent character of the group interaction parameters assumed by the original UNIFAC model is not perfect and various thermodynamic properties deliver different information about real mixture behaviors, the extrapolation of γ^∞ -based model to predict other types of thermodynamic properties such as vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) may lose the quantitative accuracy to some extent. (2) Some ILs involved in the VLE and LLE data are not covered in the γ^∞ data. That is to say, if one regresses ILs only based on γ^∞ data, some group interaction parameters that can be fitted from experimental VLE and LLE will be missed. Considering the above-mentioned facts, it would be desirable to revise and extend the UNIFAC-IL model by correlating to the data of γ^∞ , VLE and/or LLE simultaneously.

Problem definition:

The task is to revise and extend the UNIFAC-IL model by simultaneous correlation to different thermodynamic properties (γ^∞ , VLE and/or LLE). This simultaneous fitting method could balance the effect of temperature and concentration on the group interaction parameters. The final objective is to

provide a larger and more versatile UNIFAC–IL model which could be used reliably for the IL solvent and process design of different separation tasks.

Task list:

- Complete the experimental γ^∞ , VLE and LLE database currently stored in our group (latest literature review, binary VLE and VLE data).
- Revise and extend the UNIFAC–IL model by simultaneously correlating to γ^∞ , VLE and/or LLE data. Different combinations of databases can be tested for the regression. Comparisons can be made to finally present the UNIFAC–IL model either suited for one specific type of property or versatile for different thermodynamic properties.

Start: Summer 2019 / autumn 2019 / immediately

Duration: 4 months (compare to your exam guidelines)

Prior knowledge:

- Basics of chemical thermodynamics and thermodynamic modelling
- Programming using Matlab or other mathematic modelling tools.

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References:

[1] Song, Z., Zhang, C., Qi, Z., Zhou, T., Sundmacher, K. Computer–aided design of ionic liquids as solvents for extractive desulfurization. *AIChE Journal*. 2018; 64(3): 1013–1025.