Fingerprinting and Thermodynamic Modeling of Poorly Specified Mixtures with NMR Spectroscopy and Machine Learning

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Poorly specified mixtures, of which the composition is unknown, are common in many fields of process engineering. Dealing with such mixtures in process design is challenging as their fluid properties cannot be described with classical thermodynamic models, which require the knowledge of the composition. The common way to tackle this – by introducing ad-hoc pseudo-components – has many drawbacks. In this work, we present a new approach for the thermodynamic modeling of poorly specified mixtures [1-5]. It is based on fingerprints of the mixtures that give quantitative information on the structural groups, which is much simpler to obtain than information on the speciation. NMR spectroscopy is used for that purpose and automated methods for identifying the groups and assigning to signals in the NMR spectra were developed using the machine-learning concept of support vector classification. In the second step, the obtained group-specific information is used in combination with results from diffusion-ordered (DOSY) NMR experiments for the rational definition of pseudo-components. To the best of our knowledge, this is the first generic approach for this purpose. The resulting characterizations of poorly specified mixtures are finally used in combination with thermodynamic group-contribution methods to predict fluid properties of the mixtures. The applicability of the approach is demonstrated by considering a variety of aqueous mixtures, which are inspired by fermentation broths as a prominent class of poorly specified mixtures in process engineering, and the prediction of different fluid properties, such as activity coefficients, liquid-liquid partition coefficients, and separation factors. Surprisingly good results are obtained.

References

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