Advancing Group-Contribution Methods for Thermophysical Properties of Mixtures

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Accurate predictions of thermophysical properties are crucial for process design and optimization in chemical engineering. Therefore, group-contribution models of the Gibbs excess energy (G^E), like UNIFAC, which estimate mixture properties based on pair-interaction parameters between structural groups, are established in practice. Despite their success, these models still have substantial limitations, mainly due to incomplete parameter tables, which result, in turn, from missing experimental data and the challenging parameter fitting procedure. As a consequence, the scope of UNIFAC is still, even after decades of development and refinement, highly restricted [1].

In the present work, we address this challenge by combining Matrix Completion Methods (MCMs) from machine learning, widely used in recommender systems, with physical group-contribution methods, resulting in powerful hybrid models [2]. Specifically, we train and use an MCM for predicting the interaction parameters of UNIFAC and modified UNIFAC (Dortmund) [3], thereby filling all gaps in the parameter tables [4]. The developed models were trained end-to-end on hundreds of thousands of data points for phase equilibria from the Dortmund Data Bank. The resulting hybrid models not only have a much larger scope than the original models but also show significantly higher prediction accuracies.

We show the performance of the developed models by predicting activity coefficients and phase equilibria across a variety of binary and multi-component mixtures, demonstrating an unprecedented combination of the physical model's extrapolation capabilities and the predictive power of the MCM for previously unreported parameters.

The presented hybridization strategy is not limited to group-contribution G^E-models; it will serve as a role model for advancing models relying on binary parameters in general and, therefore, pave the way for a new generation of prediction methods for thermophysical properties.

References

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