Development and Analysis of Original UNIFAC-CI and Modified (Dortmund) UNIFAC-CI Models for Predictions of VLE and SLE Systems

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Development and Analysis of Original UNIFAC-CI and Modified (Dortmund) UNIFAC-CI Models for Predictions of VLE and SLE Systems

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Prediction of properties is important in chemical process-product design. Reliable property models are needed for increasingly complex and wider range of chemicals. Group-contribution methods provide useful tool but there is a need to validate them and improve their accuracy when complex chemicals are present in the mixtures.

In accordance with that, a combined group-contribution and atom connectivity approach that is able to extend the application range of property models has been developed for mixture properties. This so-called Group-Contribution^{Plus} (GC^{Plus}) approach is a hybrid model which combines group contribution and molecular descriptor theories (such as connectivity indices – CI). Connectivity indices are formalisms defined via graph theoretical concepts intended to describe the topological characteristics of molecular structures. The main idea is the use of connectivity indices to describe the molecular fragmentation that relates properties which is the molecular interactions with the molecular structures. One well known and established group-contribution method is the UNIFAC model, used to predict liquid phase activity coefficients for mixtures. The needed values of the group interaction parameters (GIPs) are obtained by fitting phase equilibrium data. There are, however many gaps in the UNIFAC parameter table due to lack of data. Alternative to performing measurements, which may not be feasible, values of the missing GIPs, can be predicted through the GC^{Plus} approach. The predicted values for the GIPs are then used in the UNIFAC model to calculate activity coefficients. This approach can increase the application range of any “host” UNIFAC model by providing a reliable predictive model towards fast and efficient product development.

In this work, the model parameters for using the GC^{Plus} approach to the original UNIFAC and Modified (Dortmund) UNIFAC have been regressed against vapor-liquid equilibrium (VLE) data alone and simultaneously against VLE and solid-liquid equilibrium (SLE) data for groups formed by C, H, O, N, Cl and S atoms. Initially all the VLE data used to regress those parameters are checked using a quality assessment algorithm which combines four widely used consistency tests which are the Herington, Van Ness, Point (Differential) and Infinite Dilution tests and also a check on the consistencies of the data with the pure component vapor pressures. The overall quality factors, Q_{VLE} obtained for each dataset indicate the quality of each datasets. These quality factors are then used as weighting factors, in the objective function for the parameter regression with VLE data (and with SLE data). Therefore, the performance of the CI-models using parameters regressed against VLE data alone and simultaneously against VLE and SLE data are compared in terms of the uncertainties of the parameters regressed against the predicted properties and the accuracy of the predictions. In addition, the model performances are evaluated and compared with their reference UNIFAC models and a version of the NIST-UNIFAC model.

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