Prediction of Missing UNIFAC Group-Interaction Parameters through Connectivity Indices

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Group contribution methods, such as UNIFAC, for calculation of liquid phase activity coefficients are popular and suitable for preliminary screening purposes. The main advantages of the GC method are: acceptable reliability, predictive power, their current analytical form, and ease of use in molecular design applications. However, because of limited experimental data, a large percentage of UNIFAC group interaction parameters are still missing, so the delivery of new and reliable parameters is a big challenge. If not all group parameters are available, which is very likely for new chemicals, one option is to collect or measure experimental data and then determine the new interaction parameters by data fitting. This, however, can be time-consuming, expensive, and sometimes infeasible, as it may not be possible to perform the necessary experiments.

In this work, a new methodology for predicting UNIFAC parameters using connectivity indices has been explored. Connectivity indices are formalisms defined via graphed theoretical concepts intended to describe topological characteristics of molecular structures. The following steps are involved:

1) A relation is derived between the group-interaction parameters and:
   - The number of each type of atoms in each group
   - The valence connectivity indices for each group
   - Atom interaction parameters
2) Existing VLE data is used to regress the atom-interaction parameters
3) Using the regressed atom-interaction parameters and the derived relation, the missing group interaction parameters are predicted.

The main advantage of using connectivity indices is that the need for new experimental data is reduced and the existing VLE data is used to determine the atom connectivity index interaction parameters. After this, the regressed parameters are combined together to predict the missing group interaction parameters. The paper highlights the regressed atom connectivity parameter matrix and its applications in VLE calculations where missing group interaction parameters have been automatically generated.