Improved prediction of Fick diffusion coefficients in liquids with consistent G^E model parameters

C. Flake[1]*, A. Bardow[1]

[1]Energy and Process Systems Engineering, ETH Zurich, Switzerland
*cflake@ethz.ch

Experiments, molecular dynamic simulations, and semi-empirical predictive engineering models are the sources for diffusion coefficients [1]. Experiments give the most accurate results, and molecular simulations allow valuable insights on a molecular level. However, these two methods are expensive, especially in terms of time. In contrast to these two methods, engineering models rapidly predict diffusion coefficients based on a minimum of data, e.g., diffusion coefficients at infinite dilution. Most engineering models predict Fick diffusion coefficients with the Maxwell-Stefan approach, separating hydrodynamic and thermodynamic effects on Fick diffusion. Usually, the Maxwell-Stefan coefficients describe the hydrodynamics and are calculated with Vignes or Darken type equations, whereas the thermodynamic factors are calculated with excess Gibbs free energy (G^E) models. High uncertainties in the thermodynamic factor from G^E models hinder the widespread establishment of engineering models.

This work investigates the uncertainty of thermodynamic factors due to thermodynamically inconsistent G^E model parameters. The primary purpose of G^E models is to provide values for the activity coefficients to calculate phase equilibria. However, thermodynamic factors are calculated from the partial molar derivatives of activity coefficients. G^E models may produce correct values for the activity coefficients but not for the partial molar derivatives of the activity coefficients [2]. G^E model parameters are estimated from fitting model values to experimental phase equilibria data. As a constraint during this estimation, the model values must fulfill the isopotential criterion for phases in equilibrium, which corresponds to the local minima of the Gibbs free energy of the mixtures. However, the isopotential is only a necessary criterion for phase equilibrium and does not guarantee thermodynamic stability. The model values must fulfill a second-order necessary condition. This second-order necessary condition considers the activity coefficients' partial molar derivatives and ensures thermodynamic consistent model parameters. Only consistent model parameters obey the second law of thermodynamics. However, most reported G^E model parameters do not fulfill the second-order necessary condition [3].

A formulation for parameter estimation exists, which yields consistent G^E model parameters [4]. Here, we study the impact of thermodynamic consistent parameter estimation.

We assess the prediction of diffusion coefficients based on thermodynamic factors from consistent G^E model parameters. The prediction results depend on the system's thermodynamic nonideality.

References

[1] C. Peters, L. Wolff, T.J.H. Vlugt,. A. Bardow: *Chapter 5 diffusion in liquids: Experiments, molecular dynamics, and engineering models. Experimental Thermodynamics Volume X: Non-equilibrium Thermodynamics with Applications*. The Royal Society of Chemistry (2016)

[2] R. Taylor, H.A. Kooijman: *Composition derivatives of activity coefficients (for the estimation of thermodynamic factors in diffusion)*. Chemical Engineering Communications **102**, 87-106 (1991)

[3] A. Marcilla, J.A. Reyes-Labarta, M.M. Olaya: *Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication*. Fluid Phase Equilibria **433**, 243-252 (2018)

[4] A. Mitsos, G.M. Bollas, P.I. Barton: *Bilevel optimization formulation for parameter estimation in liquid-liquid phase equilibrium problems*. Chemical Engineering Science **64**, 548-559 (2009)