Calculation of UNIQUAC Binary Interaction Parameters from Ternary Systems in Liquid-Liquid Equilibrium

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Regression of binary interaction parameters from ternary liquid-liquid equilibrium (LLE) data, based only on the minimization of composition errors, can converge to more than one set of values. For Gibbs excess models, e.g. UNIQUAC, the LLE of the ternary system is supposed to be correctly described by using parameters assessed on binary combinations [1]. Therefore, binary parameters regressed on ternary data often provide a good representation of the ternary LLE, but in most cases can lack thermodynamic meaning [1]. This paper addresses the challenging case of methanol/benzene/n-heptane. This ternary system was shown in [1] as a case where the UNIQUAC model requires modification. We show that by applying the regression algorithm described in [2], based on the minimization of the total Gibbs energy, the original UNIQUAC model provides a fitting which is better than the modified version. There is no need of modification of the original UNIQUAC model, since the mismatch between model and data is caused only by inappropriate regression. The algorithm comprises two separate levels. The inner level is devoted to the calculation of the interaction parameters, minimizing an objective function which is a function of the activities. The outer level uses the parameters by the inner level and aims to minimize the error between experimental and calculated molar fractions through an adjustment of the experimental molar fractions, provided that the condition of common tangent to the change of the Gibbs free energy of mixing is matched. To prove the correctness of this regression approach, methanol/benzene binary interaction parameters regressed on ternary data are checked against experimental binary LLE systems.

References:

[1] T. F. Anderson and J. M. Prausnitz. Ind. Eng. Chem. Process Des. Dev., 17 (1978) 561-567.

[2] G. Santori, M. Franciolini, G. Di Nicola, F. Polonara, S. Brandani, R. Stryjek. Fluid Ph. Equilibria. 374 (2014) 79–85.