

Thermodynamic representation of ternary liquid–liquid equilibria near-to and far-from the plait point

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Abstract

Common classical expressions for the molar excess Gibbs energy of mixing g^E do not contain a contribution from composition fluctuations that are significant in the vicinity of the plait point for a ternary system. We propose a correction to g^E based on reasonable phenomenological assumptions. This correction requires three ternary constants, but two are obtained from stability relations provided that we know the composition of the plait point. While the method proposed here is not predictive, it provides a consistent thermodynamic procedure for calculating the liquid–liquid phase diagram of a ternary system with a plait point. The proposed method is illustrated for three ternaries. When calculations are based on the classical expressions for g^E alone, calculated results are in serious disagreement with experiment near critical conditions. Inclusion of the proposed correction for g^E provides dramatic improvement.

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1. Introduction

For typical separation by extraction, rational process design calculations require multicomponent liquid–liquid equilibria (LLE). In the simplest extraction system, we have three components: two nearly immiscible solvents (1 and 2) and a solute (3) that we want to transfer from one solvent to the other. We present here a thermodynamic procedure for calculating LLE in a ternary system with a plait point. The goal of this procedure is to provide reliable representation of LLE near-to and far-from critical conditions that prevail near and at the plait point. Our procedure is similar to that proposed by de Pablo [1], but, because we only use algebraic equations, it is much more convenient for engineering-oriented calculations.

2. Theoretical framework

As illustrated in Fig. 1, it is convenient to show ternary experimental LLE data in an equilateral triangle diagram where the

binary 1–2 is represented by the horizontal bottom edge and solute (3) is represented by the upper apex. The curved line shows the connodal curve that separates the one-phase region (outside) from the two-phase region (inside). The ends of a tie-line give the compositions of two coexisting liquid phases at equilibrium. Somewhere in the top region of the connodal curve, we have a plait point where the length of tie-line has shrunk to zero, that is, when the two liquid phases become identical. As discussed in numerous textbooks (e.g. Prausnitz et al. [2]), we can readily calculate the connodal line and all tie-lines provided that we have available an expression for the molar excess Gibbs energy g^E of the ternary mixture at the temperature and pressure of interest; g^E is usually given as a function of mole fractions x_1 , x_2 and x_3 . The well-known equations of equilibrium are

$$x'_i \gamma'_i = x''_i \gamma''_i, \quad i = 1, 2, 3 \quad (1)$$

where, at equilibrium, prime (') indicates one liquid phase and double prime (") indicates the other. Activity coefficient γ_i is obtained from g^E according to

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T, P, n_j} \quad (2)$$

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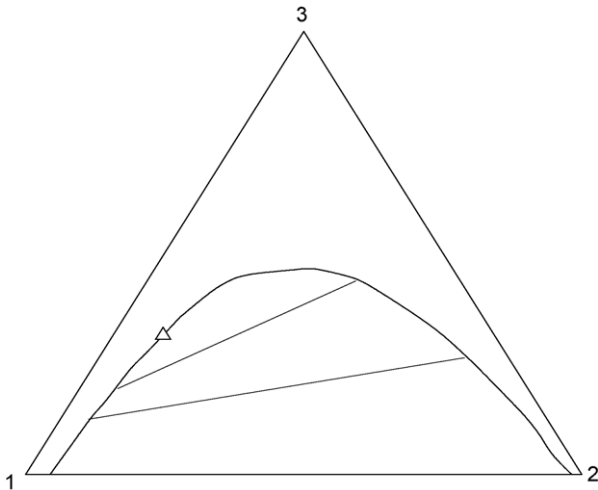


Fig. 1. Ternary Liquid-Liquid Equilibria (LLE). The tie lines connect the compositions of two liquid phases at equilibrium. (Δ) Plait point.

where n_i is the number of moles of component i , n_T the total number of moles ($n_T = \sum n_i$) and RT has the usual meaning. To obtain a solution to the three equations of equilibrium, we also use the obvious relations

$$x_i = \frac{n_i}{n_T}, \quad x'_1 + x'_2 + x'_3 = x''_1 + x''_2 + x''_3 = 1 \quad (3)$$

The essential key to ternary LLE calculation lies in the expression for ternary g^E . To minimize experimental effort, it is attractive to use an expression for ternary g^E that uses only adjustable binary parameters, that is, parameters obtained from experimental data for the three binaries 1–2, 1–3 and 2–3. As discussed in standard textbooks, a simple way to achieve that attractive goal is to assume

$$g^E(x_1, x_2, x_3) = g_{12}^E(x_1, x_2) + g_{13}^E(x_1, x_3) + g_{23}^E(x_2, x_3) \quad (4)$$

where g_{ij}^E is the molar excess Gibbs energy of the ij binary. Another common simple approximation is given later in Eq. (18).

Typical expressions for g^E of a binary system contain two or three adjustable binary parameters. For the 1–2 binary, these parameters are fixed from experimental data for mutual solubilities (solubility of 1 in 2, and solubility of 2 in 1). For the 1–3 and 2–3 binaries, whenever possible, the adjustable parameters are obtained from binary vapor-liquid equilibrium (VLE) data, all at (or near) the temperature of interest. Because at normal conditions the properties of liquids are not sensitive to changes in pressures, we do not here consider the effect of pressure on g^E .

The large advantage of Eq. (4) is that, in principle, no ternary experimental data are required. Because experimental data for binary systems are much more plentiful than experimental data for ternary systems, in principle, Eq. (4) can be used to predict ternary liquid-liquid equilibria from binary data alone.

However, such predictions are rarely successful, in part, because reduction of binary VLE data cannot yield a unique set of binary parameters; given the inadequacy of the model for g^E and, given experimental uncertainties, many sets of binary

parameters can equally well represent the experimental VLE data for a binary system. When calculating ternary LLE using Eq. (4), which sets of binary parameters shall we use? Regrettably, that choice can significantly affect calculated ternary LLE. In practice, therefore, it is usually not possible to predict ternary LLE from binary data alone.

However, there is another, more fundamental problem that makes thermodynamic calculation of ternary LLE difficult. Common expressions for g^E have an inherent deficiency: they are based on mean-field models that neglect fluctuations in composition. In typical cases, at conditions remote from the plait point, fluctuations are insignificant. However, the plait point is a critical point where the two equilibrated liquid phases become identical; in the vicinity of a critical point, composition fluctuations contribute to the excess Gibbs energy. Because these fluctuations are ignored in all common models for g^E , calculated ternary LLE that give good results far-from the plait point are often in serious error near the plait point, regardless of what binary parameters are used. In a typical calculation that ignores composition fluctuations, the two-phase region is too large; the calculated mole fraction x_3 at the plait point is likely to be much larger than that found experimentally. While it is possible to choose six binary parameters that correctly reproduce the experimental plait point, that choice yields poor (often very poor) results remote from the plait point.

We propose here a semi-empirical expression for g^E that includes contributions from composition fluctuations. This expression is not predictive. In addition to six binary parameters (preferably obtained from binary data), we require the experimental coordinates of the plait point. The advantage of our procedure is that it provides a thermodynamic self-consistent method for representing ternary LLE data.

3. Contribution of composition fluctuations to the excess gibbs energy

For the ternary mixture we write

$$g^E = g_{cl}^E + g_{co}^E \quad (5)$$

where cl stands for classical and co stands for correction. For g_{cl}^E we use Eq. (4) with all g_{ij}^E given by any one of the well-known models such as Van Laar, NRTL or UNIQUAC. For g_{co}^E we propose a second-order Taylor-series expansion in mole fractions x_1 and x_2 .

$$g_{co}^E = \frac{1}{2} \frac{\partial^2 g_{cl}^E}{\partial x_1^2} (\overline{\delta x_1})^2 + \frac{1}{2} \frac{\partial^2 g_{cl}^E}{\partial x_2^2} (\overline{\delta x_2})^2 + \frac{1}{2} \frac{\partial^2 g_{cl}^E}{\partial x_1 \partial x_2} (\overline{\delta x_1})(\overline{\delta x_2}) + \dots \quad (6)$$

where δ indicates fluctuation and the bar indicates a time average. The derivative with respect to x_1 is taken at constant x_2 and the derivative with respect to x_2 is taken at constant x_1 . The first-order derivatives in the Taylor expansion vanish because, by definition, $\overline{\delta x_1}$ and $\overline{\delta x_2}$ are zero. In a ternary system we assume that δx_1 and δx_2 are not correlated, that is, $\overline{\delta x_1 \cdot \delta x_2} = \overline{\delta x_1} \cdot \overline{\delta x_2}$.

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