



PITFALLS ON COMPUTING LIQUID-LIQUID PHASE EQUILIBRIA USING THE K-VALUE METHOD

A. Marcilla, J.A. Reyes-Labarta, M.D. Serrano and M.M. Olaya*

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, Alicante 03080, Spain.

Telf. (34) 965 903867 Fax (34) 965 903826. e-mail: maria.olaya@ua.es

<http://iq.ua.es/gcef.htm>

Summary

In the past, many strategies have been proposed to solve liquid-liquid equilibrium (LLE). Nevertheless, some papers and process simulation software packages still show inconsistent procedures for LLE regressions that lead to apparent solutions which are not true tie-lines. This study illustrates some of the pitfalls of the LLE data correlation and proposes some ideas to overcome them.

Isoactivity criterion

- ✓ The **necessary but not sufficient isoactivity criterion** (K-value method) is the most frequently used equilibrium condition for LLE calculations.
- ✓ It specially fails when the Gibbs energy of mixing function (g^M) is very linear between the equilibrium points or when the equilibrium compositions are very close.

Minor common tangent criterion

The Gibbs *minor common tangent criterion* is the **necessary and sufficient condition** for solving phase equilibria.

Convergence efficiency comparison in LLE calculations

The following example illustrates the problem: methanol (1) + diphenylamine (2) + cyclohexane (3) system at 25°C. More precisely, the tie-line obtained from the global mixture M ($z_1=0.5365$; $z_2=0.0230$; $z_3=0.4405$, molar fractions) will be calculated. The NRTL model is used with $\alpha=0.2$ and the values for the binary interaction parameters obtained from DECHEMA Chemistry Data Series [1].

- ✓ The **activity objective function** (O.F.(a)) is evaluated close to the LLE solution (Figure 1). A variety of false tie-lines can be obtained that correspond with very low values of the activity objective function although, obviously, the true tie-line is unique.

The activity function provides a **poor definition** of the objective function minimum (O.F.(a) $< 10^{-12}$ in Figure 2), because the g^M surface for this system is very flat.

$$O.F.(a) = \sum_{i=1}^3 (a_i^I - a_i^{II})^2 = 0 \quad (1)$$

- ✓ Next, a combination of the **activity and the minor common tangent condition** (O.F.(t) in Figure 2) based on Iglesias-Silva et al. [2] is used, and a sharper minimum for the objective function value is obtained. The common tangent line contribution to the objective function is:

$$O.F.(t) = \left[\left(\frac{\partial g^M}{\partial x_3} \right)_{P,T,D}^I - \left(\frac{\partial g^M}{\partial x_3} \right)_{P,T,D}^{II} \right]^2 + \left[g^{MI} - g^{MII} + \left(\frac{\partial g^M}{\partial x_3} \right)_{P,T,D}^{II} - \left(\frac{\partial g^M}{\partial x_3} \right)_{P,T,D}^I \right] x_3 \quad D = \frac{x_2^{II} - x_2^I}{x_3^I - x_3^I} = \frac{x_2^M - x_2^I}{x_3^M - x_3^I} \quad (2)$$

PROPOSED METHOD

- ✓ Finally, we present a **modification of the vector method** [3] developed by Eubank et al. [4]. The original work used the vector method combined with the maximum area criterion as equilibrium condition (later proved to be only applicable for binary systems [5]).

Our algorithm, that is applicable to the ternary systems, uses the minor common tangent equilibrium condition (O.F.(t)) [2]:

- An α -angle range for each ternary global mixture M (Figure 3) is defined.

- For a sheaf of straight lines passing through M, the two common tangent points (I, II) to the g^M function in the corresponding sectional plane are obtained (necessary condition).

- Among all pairs of calculated compositions, the "true" tie-line corresponds to the O.F.(a) equal to zero (sufficient condition) which corresponds to the minimum value for the Gibbs energy of mixing (g^{TL}).

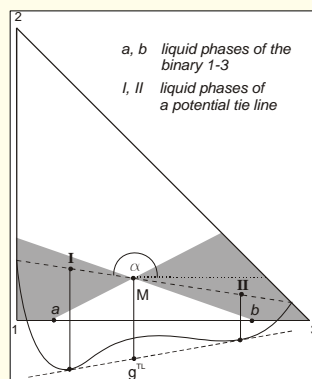


Figure 3. Graphical representation of the suggested method

- ✓ The O.F.(a) is evaluated for each α -angle at the two common tangent points. Those values (suggested method O.F.(a)) are compared to the other previous approaches (Figure 2) showing that a **sharper minimum** is obtained.

References:

- ✓ [1] Sorensen, J.M.; Aitl, W. DECHEMA Chemistry Data Series, Vol. V: Frankfurt, 1980.
- ✓ [2] Iglesias-Silva, G.A.; Bonilla-Petriciolet, A.; Eubank, P.T.; Holste, J.C.; Hall, K.R. Fluid Phase Equilib. 2003, 210, 229.
- ✓ [3] Olaya, M.M.; Ibarra, I.; Reyes-Labarta, J.A.; Serrano, M.D.; Marcilla, A. Chem. Eng. Educ. 2007, 41, 3, 218.
- ✓ [4] Eubank, P.T.; Elhassan, A.E.; Barrufet, M.A.; Whiting, W.B. Ind. Eng. Chem. Res. 1992, 31, 942.
- ✓ [5] Elhassan, A.E.; Tsvetkov, S.G.; Craven, R.J.B.; Stateva, R.P.; Wakeham, W.A. Ind. Eng. Chem. Res. 1998, 37, 1489.

Acknowledgements: Vicepresidency of Research (University of Alicante) and Generalitat Valenciana (GV/2007/125).

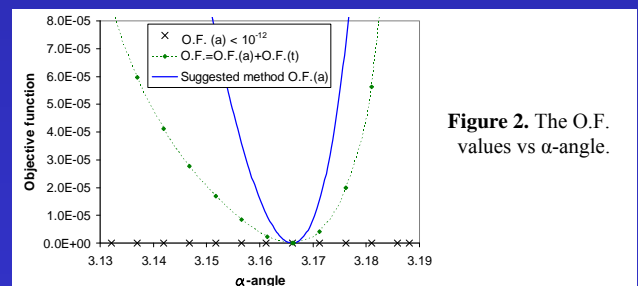
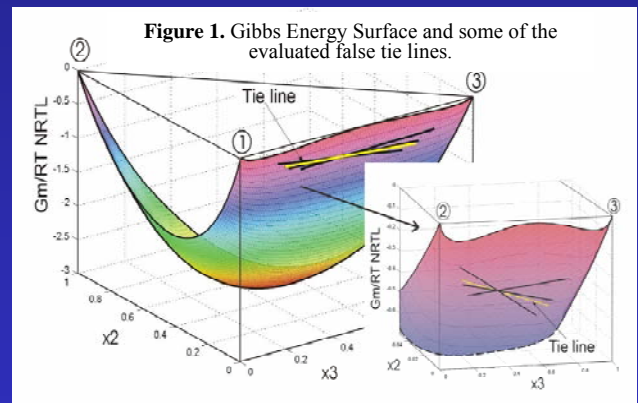


Figure 2. The O.F. values vs α -angle.

RESULTS

- ✓ When the activity condition is combined with the common tangent line criterion, either simultaneously (eq 2) or sequentially (vector method), a **more efficient equilibrium calculation** can be carried out, avoiding false solutions with very low values of the O.F.(a).

- ✓ The **suggested method improves the convergence** of the optimization.