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

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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 regression that lead to apparent solutions which are not true tie-lines. The necessary but not sufficient *isoactivity criterion* (K-value method) is in practice the most frequently used equilibrium condition for LLE calculations. However, 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. This criterion can lead to many different solutions corresponding to very low values of the activity objective function, depending on initial guess-values used, although the stable equilibrium solution is unique (i.e. false ternary tie-lines have not a common tangent line on the g^M surface). The *minor common tangent criterion is* the necessary and sufficient condition for solving phase equilibria.

In this respect, the present study illustrates some of the pitfalls of the LLE data correlation and proposes some ideas to overcome them. Convergence efficiency is compared for different strategies to calculate the LLE. First, the activity objective function (O.F.(a)) evaluated close to the LLE solution, uses to provide a poor definition of the objective function minimum (O.F.(a)$<10^{-12}$), as shown in the example of Figure 1a. Next, a combination of the activity and the *minor common tangent condition* O.F.(t) based on Iglesias-Silva et al. (2003) is used, and a sharper minimum for the objective function value is obtained. Finally, we present a modification of the vector method developed by Eubank et al. (1992). The original work used the vector method combined with the maximum area criterion as equilibrium condition, although it was later proved to be only applicable in the case of binary systems. Our algorithm, that is applicable for ternary systems, uses the *minor common tangent equilibrium condition* (see Olaya et al., 2007). First, an α-angle range for each ternary global mixture M (Figure 1b) is defined. For a sheaf of straight lines passing through the composition of a mixture 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 minimum value for the Gibbs energy of mixing (g^{TL}) (sufficient condition) and the objective function of activity must be minimum and equal to zero. The O.F.(a) is evaluated for each α-angle at the two common tangent points to look for the minimum (O.F.(a)=0). Those values (suggested method O.F.(a)) are compared to the other previous approaches (Figure 1a) showing that a sharper minimum, corresponding with the "true" tie-line, is obtained when the suggested method with the minor common tangent condition is used to obtain the activity objective function.

a)
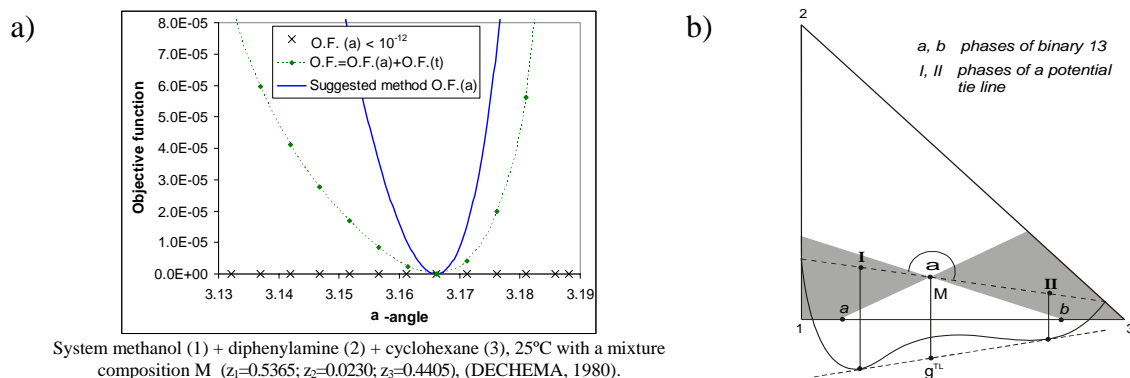
System methanol (1) + diphenylamine (2) + cyclohexane (3), 25ºC with a mixture composition M (z_1=0.5365; z_2=0.0230; z_3=0.4405), (DECHEMA, 1980).

b)

Figure 1. a) The O.F. values vs α-angle. ***a)*** Graphical representation of the suggested method.

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