Plait point in ternary system with a miscibility gap: Analysis of the procedures involved in its determination and development of novel procedures

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ABSTRACT

Ternary miscibility data, usually reported in the Roozeboom triangular diagram, have been analyzed in Cartesian coordinates defined by $X = (x_i - x_j)/3$ and $Y = x_k$ where x_i, x_j, and x_k are the mole fractions of the two solvents and of the solute, respectively. This has allowed for an easy analytical representation of all the elements which are characteristic of the system: binodal curve, tie lines, plait point. Three novel methods for determining the plait point composition have been proposed based only on its fundamental properties. The results have been presented by applying the methods to some systems described in the literature. Differences between the values obtained with the proposed methods and those obtainable with the NRTL and UNIQUAC models have been found and are discussed.

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1. Introduction

Extraction is a general separation technique extensively used in chemical [1,2], environmental [3], biochemical [4—6], polymer and pharmaceutical industry [7]. At this aim, multicomponent liquid--liquid equilibrium (LLE) data are very important for the design and operation of extraction equipments. In the simplest situation, a solute (component 2) dissolved in a solvent (component 1), must be transferred in a second solvent (component 3) nearly immiscible with the first one. Thus, ternary LLE data are shown to be essential for describing correctly the extraction process, as well as for being used as a predictive tool for multicomponent systems [8,9].

Among the different ternary systems in which a miscibility gap occurs, the most frequent is the Type 1 system, as described by the Treybal classification [10] and displayed in the Roozeboom triangular diagram [11,12], a typical example of which is reported in Fig. 1a. A different representation [13—15] that has proved to be very useful for the purposes of the present paper, uses a Cartesian

coordinate system having the coordinates (X,Y) expressed in terms of the mole fractions

$$X = \frac{x_1 - x_3}{\sqrt{3}}$$

$$Y = x_2$$

This representation has the advantage of treating the two solvents (1 and 3) in a symmetrical way and is directly proportional to the Roozeboom representation, with a linear magnification factor equal to $2/\sqrt{3}$. Fig. 1b reports the same Type 1 system shown in Fig. 1a in the Cartesian representation described.

In Fig. 1 the miscibility gap region is delimited by a dashed curve representing the so-called binodal curve: this curve separates the external stable monophasic compositions from the internal two-phase region. Every line connecting two conjugated (*i.e.* in thermodynamic equilibrium) compositions is called tie line. Its knowledge, obtained experimentally, is essential for planning extraction procedures and for describing the system investigated.

Starting from the 1—3 side (*i.e.* compositions in the absence of the solute 2) and progressively increasing the amount of the solute, the tie line lengths are reduced as well as the extension of the two-
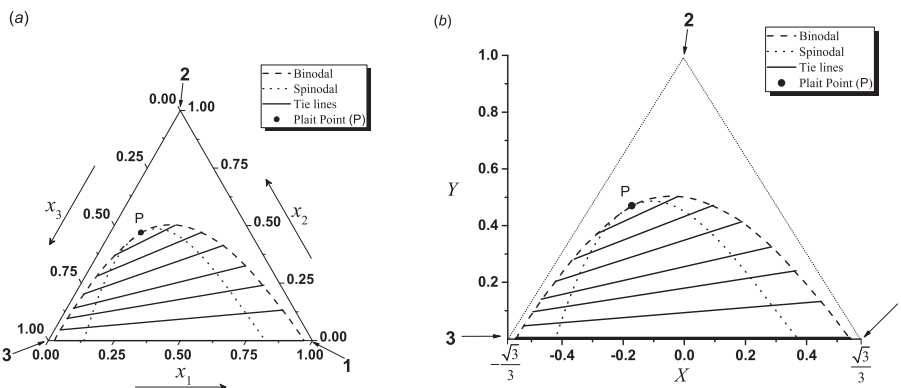

Fig. 1. Typical Type 1 ternary system phase diagram, with a miscibility gap occurring between components 1 and 3. Pure component compositions 1, 2, and 3 are indicated by bold numbers. In (*a*) the system is represented by means of the Roozeboom equilateral triangle. In (*b*) the same system is displayed in the Cartesian coordinate system: all the compositions having physical meaning are those inside the equilateral triangle whose slanting sides are indicated by thin dotted lines. The two figures are reported in scale, with (*b*) magnified by a linear factor of $2/\sqrt{3}$ with respect to (*a*).

phase region. Tie line lengths shrink to zero in a point called plait point, dividing the binodal curve in two branches, conventionally referred as right and left branch. At this point (indicated with P in Fig. 1) the two conjugated phases have identical composition and the system is invariant, provided that temperature and pressure are pre-fixed. The plait point has also another important property; beside the binodal curve that separates the monophasic from the biphasic region, another curve characterizes the properties of Type 1 ternary systems: the so-called spinodal curve, internal to the two-phase region and tangent to the binodal curve at the plait point, dividing the intermediate metastable region from the inner unstable one [8]. In Fig. 1 the spinodal curve is indicated by thick dotted lines.

Thus in Type 1 ternary systems, the determination of plait point coordinates from the experimental conjugated compositions is recognized to be very important from both practical and theoretical sides. In fact: *i*) its position on the binodal curve, being correlated to the derivatives of the free energy of mixing, can provide information about the intermolecular interactions existing among the three components [8]; *ii*) its position is fundamental for studying critical dynamics of fluids and mixtures [16,17]; *iii*) it can be used to check for the reliability of theoretical expressions used in the description of multicomponent solutions, such as Wilson, NRTL, and UNIQUAC excess functions [18–20]; *iv*) it is also useful in evaluating, by using appropriate models, the spinodal curve. At this aim, very recently some of us have proposed [21], by using the Wheeler-Widom model, a calculation procedure using the plait point position for obtaining the spinodal curve from the knowledge of the binodal one [22–24].

Whereas a direct experimental determination of the plait point is only rarely performed [25], the most used procedures involve tie line correlations and/or graphical plots with subsequent extrapolation that can be performed with a much better accuracy. At this aim, different approaches have been proposed in the literature. Coolidge [26] has suggested a graphical method consisting in building up, on each experimental tie line, a virtual triangle with the other two sides parallel to those oblique of the Roozeboom triangle: a smooth curve joining the apices of all the virtual triangles drawn crosses the binodal curve at the plait point. This method makes use of points some of which are external to the triangle delimiting the region of physical compositions $0 \leq x_i \leq 1$. A modification of the Coolidge procedure, adopted by Sherwood [27], uses virtual triangles with at least one horizontal side.

Brancker [28] has proposed a different graphic method to evaluate the plait point, whose position is subsequently used to

correlate and interpolate tie lines: the proposed procedure is based on variably dimensioned concentration scale, such to make linear the relationship existing between conjugate solution concentrations. Bachman [29] has recognized the considerable plotting efforts necessary for analyzing ternary systems with Brancker's procedure and has introduced an empirical linear equation correlating conjugate solution concentrations: this equation works well when the immiscibility between the two solvents is almost complete. Othmer and Tobias [30], in their well-known paper, have analyzed the Bachman equation providing an extension to systems with partial miscibility between the solvents and showing the consistency of an equation due to Hand [31]. Fleming and Vinatieri [32] have proposed a different approach based on equations derived from a theory of critical phenomena [33]: they are able to determine the composition of the plait point from the experimental knowledge of tie lines. Nevertheless, the approach proposed is quite tricky and works well only if tie lines selected for the fitting procedure are close to the plait point. Very recently, Goutaudier [34] and Bahramian [35] have presented two new approaches for the determination of the plait point coordinates. While Goutadier uses the barycentric weighting of the binodal points [36], the rectilinear diameter method, and the tie line "modulus", the approach of Bahramian is based on the assumption that the composition of the interfacial phase between two bulky liquid phases is independent of the compositions of these latter and is identical to the plait point composition. This supposition has been proved only for binary regular solutions and has been extended for generic multicomponent systems.

Most of the investigations performed by the authors mentioned, have the aim to propose linear relations between the concentrations of conjugate solutions. However, the equations proposed have to be intended as empirical attempts to correlate tie line data, since no theoretical background is offered. Indeed, Carniti [37] has analyzed the Hand and Othmer–Tobias equations on 83 aqueous and 26 non-aqueous ternary systems, concluding that both of them are not suitable as a check of experimental data reliability. The Hand equation may be used only for locating approximately the position of plait point.

Whereas Hand, Bahramian, and Othmer–Tobias approaches are easy to implement from a numerical point of view, on the other hand they are based on empirical equations and can lead to uncorrected results. On the contrary, Coolidge, Sherwood and Branker's methods are exact, but they require considerable plot efforts, especially when performed in a Roozeboom diagram representation. Regarding the recent paper of Goutaudier [34], it is to be noted