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# Geometrical study of the three-dimensional temperature–composition diagrams. An important aid to understand the behavior of the liquid–vapour equilibrium in ternary systems

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## ABSTRACT

In this work the usefulness of qualitatively studying and drawing three-dimensional temperature–composition diagrams for ternary systems is pointed out to understand and interpret the particular behavior of the liquid–vapour equilibrium of non-ideal ternary systems. Several examples have been used in order to highlight the interest and the possibilities of this tool, which should be an interesting support not only for lecturers, but also for researchers interested in experimental equilibrium data determination.

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**Keywords:** Liquid–vapour equilibrium; Residue curve maps; Ternary systems; Three-dimensional diagrams

## 1. Introduction

The importance and interest in using residue curve maps, the distillation lines and boundaries, the distillation regions and the feasible product regions for the synthesis and design of ternary distillation operations, especially in the case of highly non-ideal mixtures, as in azeotropic and extractive distillation, has been recognized for years (Pham and Doherty, 1990a,b,c; Bossen et al., 1993; Doherty and Malone, 2001). A residue curve can be defined as the graphical representation, in a composition ternary diagram, of the evolution of the composition of the liquid phase in a simple batch distillation process, whereas a distillation line consists in the graphical representation in the ternary diagram of the liquid composition profile in a stage column at total reflux (Pelkonen et al., 1997; Foucher et al., 1991). The trajectories of the lines, in both cases, are only dependent on the liquid–vapour equilibrium characteristics and therefore, although the complete information (i.e., the temperature or pressure and the composition of both phases) cannot be represented in the corresponding maps, enough information to carry out predictions about the behavior of several processes, and representation of profiles in distillation operations can be performed (Widadgo and Seider,

1996; Seader and Henley, 2006). The procedures for the calculation of such maps are widely described in the bibliography (Foucher et al., 1991; Widadgo and Seider, 1996; Seader and Henley, 2006).

Thus, the residue curve maps and distillation line maps are useful and interesting alternatives in the face of the difficulty of completely representing the liquid–vapour equilibrium data of ternary systems in one plane. However, despite the fact that liquid–vapour equilibrium behavior is clearly reflected in the shape of such maps, the equilibrium characteristics of ternary systems are not as clearly shown as in the classical binary temperature–composition diagrams, and there are few works describing such ternary temperature–composition diagrams. As an example, Pham and Doherty (1990a) present an interesting analysis, from a qualitative point of view, of the ternary temperature composition diagram of systems having liquid–liquid and liquid–vapour equilibrium, with one binary azeotrope, in two cases: with and without liquid–liquid–vapour equilibrium. Reading the work of Pham and Doherty (1990a), it is clear that on seeing the ternary diagrams it is relatively easy to interpret the qualitative behavior as a function of the temperature and composition and to deduce the shape of the residue

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curve maps, although it is difficult to perform quantitative calculations in such diagrams. In this way, [Tiang et al. \(1998\)](#) (<http://www.owl.net/~wgchap/Phase/v3dcmnt.htm>) recognize that two-dimensional phase diagrams are familiar and easy to construct, but limited to only one independent variable, whereas three-dimensional phase diagrams require more thought and are more difficult to construct but can show the effects of a second independent variable. These authors develop ways to obtain quantitative phase-equilibrium three-dimensional diagrams drawings compatible with chemical process simulators and standard graphical software packages. On the other hand, the residue curves and the distillation lines, and the corresponding maps, can be easily calculated ([Seader and Henley, 2006](#)), their calculation can even be carried out through commercial chemical process simulation software packages such as CHEMCAD (<http://www.chemstations.com/>). However, the knowledge from a qualitative point of view of the behavior of the ternary system (i.e., the shape of the corresponding three-dimensional diagram) can, with some difficulty, be deduced from these maps, especially in the case of systems having several binary azeotropes and homogeneous or heterogeneous ternary azeotropes. In this sense, [Stichlmair and Fair \(1998\)](#) explain in detail the characteristics of the saturated liquid surfaces of several typical ternary systems and also include a figure corresponding to the complete diagram, i.e., the diagram with both surfaces, that of saturated liquid and that of the saturated vapour, despite recognizing that only the dew point surface and the visible part of the underlying boiling point surface can be observed.

In this work, the drawing of the qualitative shape of the three-dimensional phase equilibrium temperature–composition diagrams at constant pressure for several ternary systems is illustrated through several examples, and their relationship with the corresponding residue curve maps and distillation boundaries are pointed out. This could be an interesting practice for lecturers and exercises for undergraduates in order to assist in the understanding of the fundamentals and the characteristics of the maps. Moreover, it provides valuable information related to the general behavior of the system which should be taken into account in order to plan the experimental study of the liquid–vapour equilibrium in ternary systems. The construction of such three-dimensional diagrams can be facilitated by attempting to draw the equilibrium surfaces as an extension from the binary equilibrium curves toward the inner part of the temperature–composition prism. The result obtained from this can yield useful information in order to (a) understand the behavior of the system, (b) adequately interpret the residue curves and distillation lines maps and (c) adequately plan the experimental study of the phase equilibrium. The explanation of these three-dimensional diagrams has been included as a preparatory step for learning about the residue curves maps and their use for the assessment of feasible distillation regions and distillation column sequences. Thus, the students have improved their understanding of some concepts which are especially hard for them, such as the nature and characteristics of the liquid–liquid–vapour region, the tie-triangles and the vapour curve. On the other hand, if the characteristics of the three-dimensional temperature–composition diagrams at constant pressure are not taken into account, some existing different regions could be ignored, yielding erroneous phase diagrams at constant temperature.

## 2. Construction of the temperature–composition three-dimensional diagrams. Relationship with the residue curve maps

Consider, as an example, a ternary system  $L$ – $I$ – $H$  having three maximum temperature binary azeotropes and one homogeneous saddle ternary azeotrope ( $L$ ,  $I$  and  $H$  refer to the lower, intermediate and higher volatility components, respectively). The three-dimensional temperature–composition phase equilibrium diagram at constant pressure consists of a triangular prism, whose three limiting lateral surfaces are the three binary temperature–composition diagrams corresponding to the three binary pairs  $L$ – $I$ ,  $L$ – $H$  and  $I$ – $H$ . If the relative bubble point temperatures for pure components and azeotropes are in the order  $L < I < \text{ternary azeotrope} < \text{binary azeotrope } L$ – $I < H < \text{binary azeotrope } L$ – $H < \text{binary azeotrope } I$ – $H$ , then, the temperature composition diagrams for the three binary systems are as those shown in [Fig. 1a](#). The saturated liquid and saturated vapour surfaces (i.e., the ternary equilibrium surfaces) must start in these saturated liquid and saturated vapour curves of the binary systems, evolving through the inner part of the prism. Moreover, the existence of a ternary azeotrope implies the need of a contact point between both surfaces in such a ternary azeotropic point. These considerations allow us to obtain the qualitative three-dimensional diagram shown in [Fig. 1b](#). In this diagram, five different distillation zones can be observed (see [Fig. 1c](#)). In fact, it can easily be deduced that a ternary mixture in the zone containing the pure component  $H$  could not be separated in order to yield pure components  $L$  or  $I$ . Moreover, the diagram suggests that the highest degree of separation attainable from such a mixture would be a distillate of pure  $H$  and the binary azeotrope  $I$  $H$  as the residue, which are the points with lower and higher boiling temperature, respectively, in the zone considered. Similar comments for the other regions could be pointed out. Therefore, a simple visual inspection of the three-dimensional equilibrium diagram allows the understanding of the qualitative behavior of the system. [Fig. 1b](#) shows, in the base of the prism, the lines corresponding to the projection of the valleys (similar curves could be drawn for the ridges) in both surfaces; these lines are related, in some extent, to the distillation boundaries of the ternary system. These distillation boundaries will appear as straight lines if the qualitative drawing proposed by [Foucher et al. \(1991\)](#) is carried out, or as curved or straight lines if the quantitative calculation of the map is performed. Therefore, as can be seen, not only does a clear relationship exist between the boundaries and distillation regions with the shape of the temperature–composition diagram, but it is a clear consequence of this shape. A similar analysis could be performed for every ternary system, and the structure of the corresponding temperature–composition diagram and the residue curve map as well as their relationship could be deduced.

On the other hand, the knowledge of the three-dimensional diagrams is also a very useful tool in order to plan any systematic experimental phase equilibrium study. Consider, as an example, the same ternary system shown in [Fig. 1](#). [Fig. 2](#) shows the expected liquid–vapour equilibrium zones existing at different temperatures. These regions result from the isothermal sectional planes (i.e. horizontal sectional planes) in the three-dimensional diagram at constant pressure, and illustrate the existence of the different regions in the

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