



# A novel method for detecting and computing univolatility curves in ternary mixtures



Nataliya Shcherbakova<sup>a</sup>, Ivonne Rodriguez-Donis<sup>b,\*</sup>, Jens Abildskov<sup>b</sup>, Vincent Gerbaud<sup>c</sup>

<sup>a</sup> Laboratoire de Génie Chimique, Université Paul Sabatier – INP ENSIACET, 4, allée Emile Monso, 31432 Toulouse, France

<sup>b</sup> CAPEC-PROCESS, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark

<sup>c</sup> Laboratoire de Génie Chimique, CNRS, 4, allée Emile Monso, CS 84234, 31432 Toulouse, France

## HIGHLIGHTS

- 3D generalized univolatility surfaces are defined.
- Ternary RCM univolatility curves are the loci of relative composition critical points.
- Ordinary differential equations describe the univolatility curves.
- A new algorithm based on an initial value problem is proposed.
- The method finds univolatility curves not connected to any azeotrope.

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## ABSTRACT

Residue curve maps (RCMs) and univolatility curves are crucial tools for analysis and design of distillation processes. Even in the case of ternary mixtures, the topology of these maps is highly non-trivial. We propose a novel method allowing detection and computation of univolatility curves in homogeneous ternary mixtures independently of the presence of azeotropes, which is particularly important in the case of zeotropic mixtures. The method is based on the analysis of the geometry of the boiling temperature surface constrained by the univolatility condition. The introduced concepts of the generalized univolatility and unidistribution curves in the three dimensional composition – temperature state space lead to a simple and efficient algorithm of computation of the univolatility curves. Two peculiar ternary systems, namely diethylamine – chloroform – methanol and hexane – benzene – hexafluorobenzene are used for illustration. When varying pressure, tangential azeotropy, bi-ternary azeotropy, saddle-node ternary azeotrope, and bi-binary azeotropy are identified. Moreover, rare univolatility curves starting and ending on the same binary side are found. In both examples, a distinctive crossing shape of the univolatility curve appears as a consequence of the existence of a common tangent point between the three dimensional univolatility hypersurface and the boiling temperature surface.

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## 1. Introduction

Separation of liquid mixtures is one of the most important tasks in the process industry where distillation is the most widely used technique. Remarkably, almost every product on the market contains chemicals that have undergone distillation (Kiss, 2014). Beyond conventional distillation of binary and multi-component mixtures, several additional distillation techniques are developed for breaking azeotropes or separating close boiling mixtures: pressure swing distillation, azeotropic and extractive distillation. These

techniques are covered at length in several textbooks and reviews (Skiborowski et al., 2014; Gerbaud and Rodriguez-Donis, 2014; Artl, 2014; Olujic, 2014).

Preliminary conceptual design of distillation processes is based on the knowledge of the mixture thermodynamics and on the analysis of the residue curve maps (RCMs). RCMs are useful to assess the feasibility of splits since they approximate the column composition profiles under total reflux (Doherty and Malone, 2001; Petlyuk, 2004). RCMs also display azeotropes and distillation boundaries, as well as unidistribution and univolatility manifolds. These geometrical concepts have been reviewed in several works. Particularly, the review paper of Kiva et al. (2003) provides a comprehensive historical review of RCMs mainly taking into account

\* Corresponding author.

E-mail address: [ivonnerd02@gmail.com](mailto:ivonnerd02@gmail.com) (I. Rodriguez-Donis).

the Serafimov's classification of 26 RCM diagrams of ternary systems (Hilmen et al., 2002). The important role of RCMs, unidistribution and univolatility manifolds has been well described by Widagdo and Seider (1996), Ji and Liu (2007), Skiborowski et al. (2014) for azeotropic distillation process design and by Rodriguez-Donis et al. (2009a, 2009b, 2012a, 2012b), Luyben and Chien (2010) and Petlyuk et al. (2015) for extractive distillation design purposes. Noteworthy, the existence and the position of the univolatility curve, a particular type of isovolatility curve, determine the component to be drawn as distillate as well as the configuration of the extractive distillation column.

*Isovolatility* curves are curves along which the relative volatility of a pair of species is constant:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \text{constant}, \quad i \neq j$$

Along *univolatility* curves  $\alpha_{ij} = 1$ . As their properties are closely related to those of residue curves (Kiva et al., 2003), univolatility, isovolatility, and isodistribution curves are useful for studying the feasibility of distillation processes. For example, the most volatile component is likely to be recovered in the distillate stream with the so-called direct split whereas the least volatile is likely to be in the bottom stream with the so-called indirect split. In azeotropic and extractive distillation processes an entrainer is added to the liquid mixture to be separated, in order to enhance the relative volatility between the components. If the isovolatility rate increases towards the entrainer vertex, it is a good indicator of an easy separation (Laroche et al., 1991; Wahnschafft and Westerberg, 1993; Luyben and Chien, 2010). Furthermore in extractive distillation, the location of the univolatility curve and its intersection with the composition triangle edge determine the component to be withdrawn as a distillate product from the extractive column as well as the proper column configuration (Laroche et al., 1991; Lelkes et al., 1998; Gerbaud and Rodriguez-Donis, 2014).

As shown by Kiva and Serafimov (1973), univolatility curves divide the composition space,  $\Omega$ , into different K-order regions. Zhvanetskii et al. (1988) proposed the main principles describing all theoretically possible structures of univolatility curves for zeotropic ternary mixtures and their respective location according to the thermodynamic relationship between the distribution coefficients of the light component  $i$ , the intermediate  $j$  and the heavy component  $m$ . 33 possible structures of univolatility curves were reported under the assumption that for every pair of components there exists only one univolatility curve. In the succeeding paper from the same group (Reshetov et al., 1990), the classification was refined by introducing the following nomenclature:

- $\overline{\alpha}_{ij}$ : an arc shape univolatility curve whose terminal points belong to the same binary side of the composition triangle;
- $\overline{\overline{\alpha}}_{ij}$ : the univolatility curve connecting two different binary sides of the composition triangle.

Later Reshetov and Kravchenko (2010) extended their earlier analysis to ternary mixtures having at least one binary azeotrope. Their main observations are:

- (a) more than one univolatility curve having the same component index “ $i, j$ ” can appear in a ternary diagram;
- (b) the univolatility curve that does not start at the binary azeotrope can be either  $\overline{\alpha}_{ij}$  or  $\overline{\overline{\alpha}}_{ij}$  type. An  $\overline{\overline{\alpha}}_{ij}$  curve can cross a separation boundary of the RCM;
- (c) a ternary azeotrope can be crossed by any type of univolatility curve;

- (d) if two univolatility curves intersect at some point, this point is a tangential binary azeotrope or a ternary azeotrope. In both cases there is a third univolatility curve of complementary type passing through this point;
- (e) transitions from  $\overline{\alpha}_{ij}$  to  $\overline{\overline{\alpha}}_{ij}$  (or vice versa) can occur as univolatility curves depend on pressure and temperature of vapor – liquid equilibrium (VLE).

Despite the increasing application of univolatility curves in conceptual design, there still lacks a method allowing:

- (1) detection of the existence of univolatility curves independently of the presence of azeotropes, which is particularly important in the case of zeotropic mixtures;
- (2) simple and efficient computation of univolatility curves.

In fact, numerical methods available in most chemical process simulators allow mainly the computation of the univolatility curves linked to azeotropic compositions. Missing univolatility curves not connected to azeotropes will result in improper design of the extractive distillation process. This problem can be solved by a fully iterative searching in the ternary composition space providing the composition values with equal relative volatility (Bogdanov and Kiva, 1977). Skiborowski et al. (2016) have recently proposed a method to detect the starting point of the univolatility curve. They locate all pinch branches that bifurcate when moving from the pure component vertex along the corresponding binary sides. The robustness of this approach to handle complex cases, such as biazeotropy when more than one univolatility curve ends on the same binary side, is well demonstrated. Their algorithm is based on MESH equations, including mass and energy balances, summation constraints, and equilibrium conditions.

A less tedious and less time-consuming method is proposed in this paper. It is based on the geometry of the boiling temperature surface constrained by the univolatility condition. This approach will also require the computation of starting binary compositions independently of the azeotrope condition. Such starting points can be easily computed with a vapor-liquid equilibrium model by using the intersections of the distribution coefficient curves on each binary side of the ternary diagram (Kiva et al., 2003).

This paper is organized as follows: First, we revisit the properties of the univolatility curves in RCMs, and prove that they are formed by critical points of the relative compositions. Then, we show that the topology of unidistribution and univolatility curves follows from both the global geometrical structure of the boiling temperature surface and the univolatility condition considered in the full three-dimensional composition – temperature state space. Such a consideration leads to a simple algorithm for the numerical computation of the univolatility curves and other similar objects by solving a system of ordinary differential equations. The starting points of the univolatility curves computation can be detected from the relationship between the distribution coefficients related to the binary pair “ $i, j$ ”: the binary distribution coefficients  $k_i^{ij}$ ,  $k_j^{ij}$  and the ternary coefficient  $k_m^{\infty, ij}$  describing the ternary mixture with the third component “ $m$ ” at infinite dilution. Finally, we illustrate our approach by considering several topological configurations of RCM for two distinctive ternary mixtures (thermodynamic model parameters for both mixtures are available online as the [supplementary material](#) to this article). The ternary mixture diethylamine – chloroform – methanol at different pressures has two univolatility curves with the same component index “ $i, j$ ” and one univolatility curve of type  $\overline{\alpha}_{ij}$ . We also applied our method to the well-known (though uncommon) case of the binary mixture benzene – hexafluorobenzene exhibiting two azeotropes at

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