Univolatility curves in ternary mixtures: geometry and numerical computation.

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Abstract

We propose a new non-iterative numerical algorithm allowing computation of all univolatility curves in homogeneous ternary mixtures independently of the presence of the azeotropes. The key point is the concept of generalized univolatility curves in the 3D state space, which allows the main computational part to be reduced to a simple integration of a system of ordinary differential equations.

Keywords: univolatility curves, differential continuation method, azeotropes bifurcation, double azeotropy

1. Introduction

Accurate numerical computation is essential to synthesis and design of distillation processes. The change of the volatility order between two components *i* and *j* in a ternary diagram can be detected by tracing the associated univolatility curve (or α-curve) $\alpha_{i,j}$, i.e., the set of points of equality between the distribution coefficients K_i and K_j (Kiva et al., 2003). Univolatility curves divide composition space into different *K*-order regions, even for zeotropic mixtures. Their knowledge is essential to design extractive distillation process (Gerbaud and Rodriguez-Donis, 2014).

Though the computation of univolatility curves starting at azeotropic points is straightforward, the detection of univolatility curves not associated with azeotropes is a more complicated and time-consuming process. A ternary diagram may contain up to 3 families of α-curves defined by their respective index. Zhvanetskii et al. (1988), Reshetov et al., (1990) and Reshetov and Kravchenko (2010) formulated the main principles of classification of the univolatility curves. The proposed nomenclature distinguishes the univolatility curves of type $\overline{\alpha_{i,j}}$ connecting two points on the same binary side of the composition triangle from the curves of type $\overline{\overline{\alpha_{i,j}}}$ connecting two different binary sides of the composition triangle. Transitions between types $\overline{\alpha_{i,j}}$ and $\overline{\overline{\alpha_{i,j}}}$ can occur as univolatility curves depend on pressure and temperature of VLE.

In this paper we present a new numerical algorithm for computing all univolatility curves in a ternary system independently of the presence of azeotropes. The method is based on the concept of a generalized univolatility curve in the 3D $x - T$ state space, which can be computed by integrating a system of ordinary differential equations. The efficiency of the proposed algorithm is illustrated through the study of hexafluorobenzene - methyl propionate - benzene mixture exhibiting bi-binary and bi-ternary azeotropy at 1 atm. We show the transformation of the ternary diagram with the

variation of pressure, observing the formation of tangential azeotropy, bi-ternary azeotropy, saddle-node azeotropes, as well as singular configuration of univolatility curves not yet described in the literature.

2. Geometry of univolatility curves

2.1 Definitions and notations

Consider an open evaporation of a homogeneous ternary mixture kept at thermodynamic equilibrium at constant pressure. Let $x_i, y_i,\ i = 1,2,3$ and T denote the mole fractions in the liquid and in the vapor phases and the temperature of the system. In the absence of chemical reactions a two-phase ternary mixture has three independent state variables. By selecting x_1, x_2 and T, the complete state space of the system reads $M = \{(\overline{x}, T):\ T \in [T_{min}, T_{max}],\ \overline{x} \in \Omega,\ i = 1,2\}$, where T_{min}, T_{max} are the minimum and maximum boiling temperatures of the mixture and $\Omega = \{\overline{x} = (x_1, x_2) :\ x_i \in [0,1],\ i = 1,2\}$ is the composition space. The distribution coefficients K_i describe the vapor-liquid equilibrium (VLE) in terms of molar concentrations of the components in the vapor and liquid phases: $y_i(x_1, x_2, T) = K_i(x_1, x_2, T)x_i,\ i = 1,2,3$. The following relation allows computing the temperature of the system:

$$\Phi(x_1, x_2, T) = \sum_{i=1}^{3} y_i(x_1, x_2, T) - 1 = 0. \quad (1)$$

The ratio $\alpha_{ij} = K_i/K_j$ is the relative volatility of component *i* with respect to component *j*. If $\alpha_{ij} > 1$, *i* is more volatile than *j* and vice versa. The sets of points in Ω satisfying $\alpha_{ij} = 1$ are called the univolatility curve $\alpha_{i,j}$ (or α-curve).

A ternary diagram may contain more than one univolatility curve of index "i, j". Not all these curves are related to azeotropes. However, every azeotrope belongs to at least one univolatility curve. An intersection of two univolatility curves at some point implies that this point is either a tangential binary azeotrope or a ternary azeotrope. In both cases the third univolatility curve of complementary type passes through this point. A detailed analysis of the relation between the topology of α-curves and the structure of the underlying residue curves maps (RCM) can be found in Kiva et al., 2003.

2.2. The three dimensional geometry of univolatility curves

Geometrically, Eq. (1) defines a hypersurface in the state space *M*, referred to below as the boiling temperature surface *W*. Along with the boiling temperature surface, *M* contains three univolatility hypersurfaces defined by

$$\Psi_{ij}(\overline{x}, T) = K_i(\overline{x}, T) - K_j(\overline{x}, T) = 0,\ \ i, j = 1,2,3. \quad (2)$$

Their intersections with the surface *W*, are smooth curves in *M* called the generalized univolatility curves θ_{ij}. The α-curves are merely projections of the generalized univolatility curves on the (x_1, x_2)-plane.

Fig.1 illustrates these geometrical concepts for the case of a zeotropic mixture acetone (x_1) – ethyl acetate (x_2) – benzene. Its ternary diagram is characterized by a unique univolatility curve, $\alpha_{2,3}$, between ethyl acetate and benzene. This curve is a projection on Ω of the generalized univolatility curve θ_{23} formed by the intersection of the surface *W* with the hypersurface $\Psi_{23}(\overline{x}, T) = 0$.

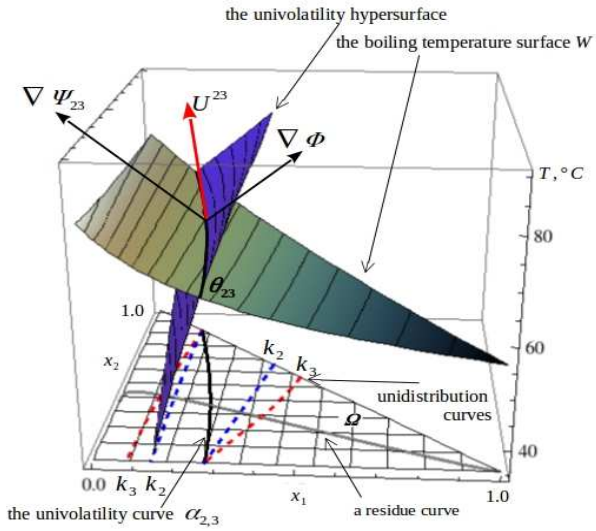

Figure 1. The univolatility curve $\alpha_{2,3}$, the boiling temperature surface W and the univolatility hypersurface $\Psi_{23} = 0$ for acetone (x_1) – ethyl acetate (x_2) – benzene

Consider a generalized univolatility curve $\theta_{ij}(\tau) = (\overline{x}(\tau), T(\tau))$ in M, solution to the pair of algebraic equations: $\Phi(\overline{x}, T) = 0$, $\Psi_{ij}(\overline{x}, T) = 0$. Let $U^{ij} = (U_1^{ij}, U_2^{ij}, U_3^{ij})$ denote a tangent vector to θ_{ij} at some point. By construction, U^{ij} is orthogonal both to the normal vector $N_w = \nabla\Phi$ to the surface W and to the normal $N^{ij} = \nabla\Psi_{ij}$ to the univolatility hypersurface, as shown in Fig.1. Hence $U^{ij} = N_w \times N^{ij}$, and:

Theorem. The generalized univolatility curve $\theta_{ij}(\tau)$ projecting on the univolatility curve $\alpha_{ij} = 1$ is an integral curve of the vector field $U^{ij} = \nabla\Phi \times \nabla\Psi_{ij}$, i.e., it is a solution to the following system of ordinary differential equations in M:

$$\dot{x_1} = U_1^{ij}(x_1, x_2, T),\ \dot{x_2} = U_2^{ij}(x_1, x_2, T),\quad \dot{T} = U_3^{ij}(x_1, x_2, T) \qquad (3)$$

Remark 1. The generalized univolatility curve θ_{ij} has isolated singularities at the points of common tangency between the surface W and the associated univolatility hyper-surface. In this case $U_1^{ij} = U_2^{ij} = U_3^{ij}$, i.e., the curve θ_{ij} degenerates into a point.

A more detailed analysis (Shcherbakova et al. 2017) shows that a point is singular for the univolatility curves if and only if it is singular for the corresponding α-curve in Ω. Such isolated singular points can be of elliptic or hyperbolic type. In the latter the resulting univolatility curve is formed by four branches meeting at the singular point. It is important to stress that singular points of univolatility curves are not necessarily related to the singular points of the underlying RCM. Section 3 and Figure 2 provide examples of these highly non-generic configurations.

Remark 2. The same geometrical argument can be directly applied to the computation of the unidistribution curves by setting $\Psi(x_1, x_2, T) = K(x_1, x_2, T) - 1$, where K is any of the distribution coefficients.

2.3.3 Numerical computation of the univolatility curves

Eqs. (3) provide an efficient tool for numerical computation of the univolatility curves using the standard Runge-Kutta schemes for the ODE integration. Initial points for such integration can be found following the idea of Kiva et al. (2003). They showed that the existence of the univolatility curves can be detected by analyzing the behavior of the binary distribution coefficients and distribution coefficient at infinite dilution along the binary sides of Ω (for more details see Shcherbakova et al., 2017).

For example, consider a curve $\alpha_{i,j}$ starting from the *13* binary side, that is, from the x_1 −axis. The starting point of this curve is a projection of a point $(x^0_{1,ij}, 0, T^0_{1,ij})$ in state space *M*. The whole curve $\alpha_{i,j}$ can be computed as the projection on Ω of the solution of the following initial value problem:

$$\frac{dx_1}{ds} = \frac{d_{ij}\, U_1^{ij}(x_1, x_2, T)}{\|U^{ij}(x_1, x_2, T)\|}, \quad \frac{dx_2}{ds} = \frac{d_{ij}\, U_2^{ij}(x_1, x_2, T)}{\|U^{ij}(x_1, x_2, T)\|}, \quad \frac{dT}{ds} = \frac{d_{ij}\, U_3^{ij}(x_1, x_2, T)}{\|U^{ij}(x_1, x_2, T)\|}, \tag{4}$$

$$x_1(0) = x^0_{1,ij}\,,\ x_2(0) = 0, \quad T(0) = T^0_{1,ij}, \quad d_{ij} = sign\left(U_2^{ij}\left(x^0_{1,ij}, 0, T^0_{ij}\right)\right). \tag{5}$$

Here s is the arc-length of the curve. The normalization of the vector field U^{ij} avoids the possible stiffness of Eqs. (3). For the curves starting from other binary sides of Ω an appropriate modification of initial conditions and direction (eq. (5)) should be made. The general algorithm can be sketched:

1. Create a list of all possible starting points of the univolatility curves on each binary side of Ω (Kiva et al., 2003).
2. Take a starting point from the list created in point 1 and solve the problem of type (4), (5) using any standard ODE solver. Continue numerical integration until the border of Ω is attained. Then both terminal points of the computed curve should be excluded from the list of starting points.
3. Go back to point 2 until the list of starting points is exhausted.

This algorithm is implemented in Mathematica 9. It uses a standard solver for a pair of non-linear algebraic equations in 2D to find the starting points of integration, and a standard ODE solver in 3D for the rest of the computation. In particular, no specific iterative procedure is needed to compute the whole curve once the starting point is detected. Any implementation using one of the standard algorithmic languages is possible, though the use of a compatible library of automatic differentiation is suggested to in order to facilitate the writing of Eqs.(4) in explicit form.

3. Case study: hexafluorobenzene – methyl propionate – benzene.

We illustrate the efficiency of the proposed algorithm in Fig. 2, which shows the transformation of the topology of α-curves under pressure variation for hexafluorobenzene (x_1) – methyl propionate (x_2) – benzene. The VLE parameters are computed according to Wilson model using the data from Myagkova (2007), the DIPPR equation and database were used for the vapor pressure computation.

At 1 atm (Fig. 2c) the binary mixture benzene - hexafluorobenzene exhibits two azeotropes A^a_{13}, A^b_{13}. Each of these gives rise to a univolatility curve of $\overline{\overline{\alpha_{1,3}}}$ type. The binary azeotrope A_{23} (benzene-methyl propionate) is the origin of a $\overline{\overline{\alpha_{2,3}}}$ curve, the other curve of the same index, of $\overline{\alpha_{2,3}}$ type, links two non-azeotropic points on the *12*-side.

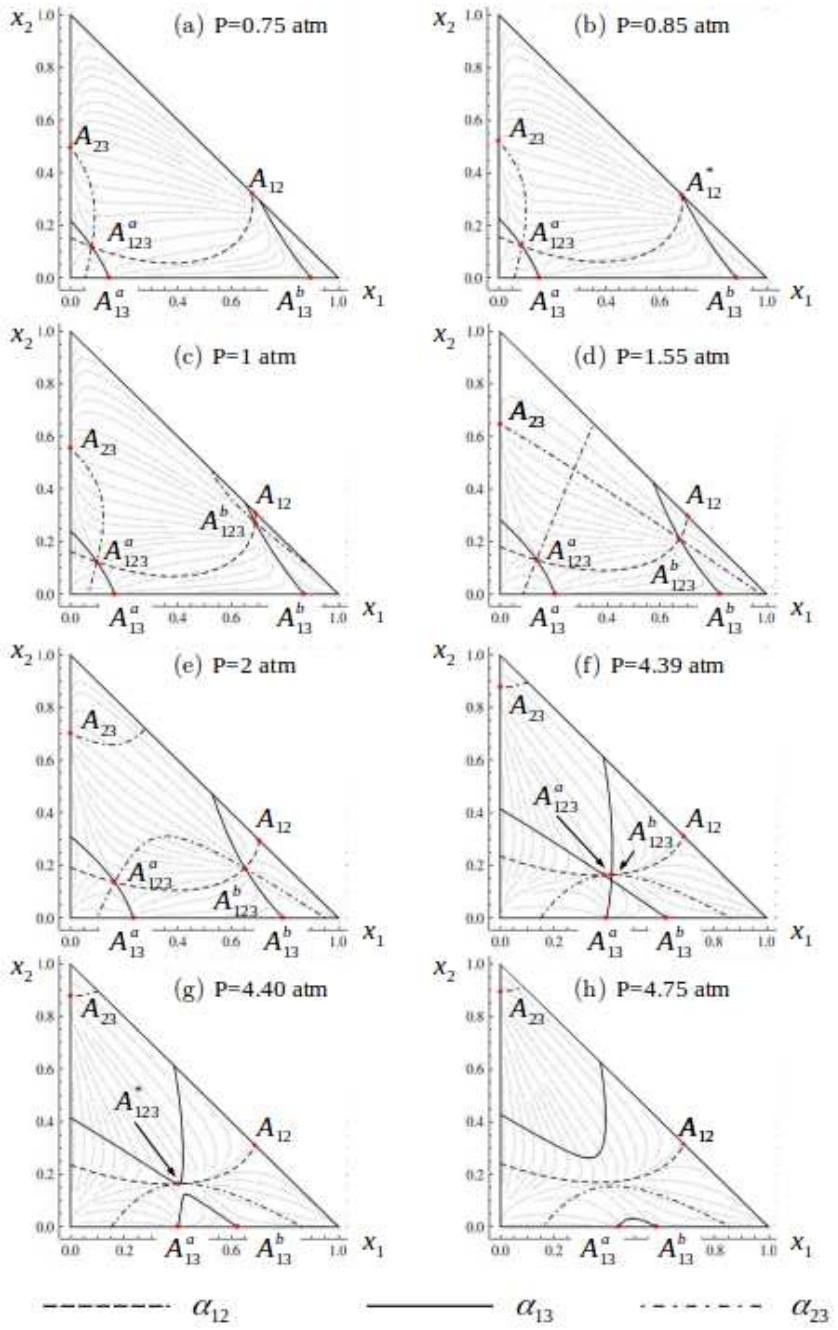

Figure 2. RCM and univolatility curves of hexafluorobenzene (x_1) - methyl propionate (x_2) – benzene

The binary azeotrope A_{12} (hexafluorobenzene – methyl propionate) gives rise to the unique $\overline{\overline{\alpha_{1,2}}}$ type curve. Such a complex structure of α-curves reflects a peculiar topology of the underlying RCM characterized by two ternary azeotropes: a saddle

(A^a_{123}) and a stable node (A^b_{123}). Lowering the pressure makes A^b_{123} and A_{12} to merge into a tangential binary azeotrope A^*_{12} at P≈0.85 atm (Fig. 2b). Three different univolatility curves meet at this point (the curve $\overline{\alpha_{2,3}}$ follows the *12* edge). The tangential azeotrope A^*_{12} disappears, as well as the curve $\overline{\alpha_{2,3}}$, at further pressure reduction (Fig. 2a). Other interesting phenomena occur at higher pressure. Indeed, raising the pressure forces the two curves $\overline{\overline{\alpha_{2,3}}}$ get closer, and at P ≈ 1.55 atm (Fig. 2d) they meet at a singular point, forming a cross-shape configuration as described in Remark 1. With the infinitesimal pressure increase, this singular configuration splits into a $\overline{\overline{\alpha_{2,3}}}$ curve connected to A_{23} and a new $\overline{\alpha_{2,3}}$ curve linking two non-azeotropic points on the *13*-side. Meanwhile the two branches of the $\alpha_{1,3}$ curve get closer as well as two ternary azeotropes. At P ≈ 4.39 atm (Fig. 2f) we again observe a particular configuration, this time with the $\alpha_{1,3}$ curve. This configuration splits into a $\overline{\overline{\alpha_{1,3}}}$ and $\overline{\alpha_{1,3}}$ branch, the latter connecting two binary azeotropes, A^a_{13} and A^b_{13}. A small pressure increase to P ≈ 4.40 atm (Fig. 2g) results in the fusion of two ternary azeotropes into a unique singular azeotrope A^*_{123} of saddle-node type, which disappears with the further pressure increase (Fig. 2h).

4. Conclusions

The topology of RCMs and associated univolatility curves is non-trivial even in the case of zeotropic ternary mixtures. Our analysis shows that 2D representation in the composition space is not always sufficient to describe the true nature of the univolatility curves. A new method for the detection of univolatility curves is proposed in this paper. It uses the concept of a generalized univolatility curve in the 3D state space. The computational efficiency of the algorithm is illustrated by tracing the bifurcation in the univolatility curves topology with pressure variation in the case of hexafluorobenzene – methyl propionate – benzene. The method allows computing detailed phenomena like the formation of tangential azeotrope, bi-ternary azeotropy, saddle-node azeotropes, as well as singular configuration of univolatility curves not yet described in the literature.

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