DISTILLATION REGIONS FOR NON-IDEAL TERNARY MIXTURES

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ABSTRACT

This work concerns the determination of distillation boundaries. This is done comprehensively, using a bifurcation study for a single feed column. The approach used is to track all of the pinch points of rectifying and stripping profiles, mapping the branches of solutions and checking for a "jump" of composition profiles at bifurcation points. The main result is a systematic and exact method of selecting appropriate pairs of boundaries for a given type of column, which demarcate distillation regions. The distillation regions overlap. The common area of two distillation regions is parametrically sensitive and it determines the possibilities of crossing (at a finite reflux) the distillation boundaries defined for a total reflux or reboil ratio. However, such columns may be difficult to start up and control.

INTRODUCTION

Continuous distillation processes are commonly used in industry for the separation of azeotropic mixtures. The processes may necessitate a change of operating pressures between columns, the addition of entrainers or the application of recycles. Such processes can be difficult to design and require new design and synthesis methods. The synthesis of separation systems involves the successive selection of entrainers, the choice of a system structure (intermediate stream connections between columns), the design of individual columns and the selection of suitable operating parameters. A tool is needed for quick identification of feasible separations. Several researchers have attempted to determine attainable regions for azeotropic homogenous mixtures (e.g. Serafimov et al. [1]; Petlyuk and Serafimov [2]; Koehler et al. [3]; Laroche et al. [4]; Rev [5]; Stichlmair and Herguijuela [6]; Wahnschafft et al. [7]; Fidkowski et al. [8]; Poellmann and Blass [9]; Jobson et al. [10]), but a complete solution for ternary mixtures with distillation boundaries has not yet been found. Some researches use the heuristic of not crossing boundaries. Discussion about crossing distillation boundaries with batch distillation was started by Ewell and Welch [11]. Rev [5] showed that valleys and ridges in the boiling temperature surface are not the boundaries of the distillation regions. Fidkowski et al. [8] devised a method of calculating feasible distillation regions for ternary zeotropic mixtures. Recently Jobson et al. [10] showed that the separation boundaries depend on the equipment

used. Unfortunately, the nature of distillation boundaries is still not precisely understood. The present paper addresses this question.

A simple distillation process in which a multi-component liquid is boiled in an open vessel is represented by a *residue curve* in the composition space. Vapor whose composition is in equilibrium with the liquid is removed as soon as it is formed. Changes in the liquid phase composition are described by a system of nonlinear differential equations, which have singular points at azeotropic points and pure component vertices in the composition space. It has been shown (Gurikov [12], Zharov [13–14], Doherty and Perkins [15]) that these singular points can only be saddles or nodes. Generally, all residue curves begin and end at nodes. However in the case of mixtures with a saddle azeotrope, a residue curve behaving abnormally in comparison with the neighboring residue curves may connect the saddle azeotrope with a node (a pure component or an azeotrope). Such a residue curve divides the composition space into different regions and it is called a *simple distillation boundary (SDB)* in chemical engineering science or a *separatrix* in mathematics. Residue curves cannot go from one part of the composition space to another and residue curves from the same region connect the same two (unstable or stable) nodes. Acrivos and Amundson [16] provide a simple model for a continuous distillation process in packed columns. Their differential equations for composition profiles (also see Laroche et al. [4]) are identical to the residue curve equations for the limit of a total reflux or reboil ratio. In this way, simple distillation boundaries are related to the continuous azeotropic distillation process carried out in packed columns. Empirical evidence suggests that if a simple distillation boundary is curved, the steady-state composition profile (for a finite reflux or reboil ratio) can cross the boundary only from its convex side where the product composition is situated (Van Dogen and Doherty [17]). If a simple distillation boundary is linear, the composition profile cannot cross the boundary from any side. An example of a linear boundary (for the acetone–methanol–dichloromethane mixture) has been given by Kogan [18]. On the other hand, Laroche et al. [19] assert that linear boundaries do not occur in physical systems.

The crossing of simple distillation boundaries by distillation profiles (for staged columns) from the convex side prompted Fidkowski et al. [8] to propose an approximate solution for feasible separation regions for azeotropic mixtures. In their Fig. 18 [8] there are two question marks on the distillation boundary's convex side because they were unable to determine the region from which the boundary could be crossed. The missing border of this region was later strictly defined by Davydyan et al. [30] and the region's properties are described in the present paper.

TOTAL REFLUX BOUNDARY

Fidkowski et al. [8] considered continuous distillation in trayed columns (modeled by theoretical stages), whose products are saturated liquids. A constant molar overflow in each section of the column and a constant pressure along the column was also assumed. At a total reflux or reboil ratio, the mass balance equations simplify to an equality between the composition of the vapor flow rising from a stage and that of the liquid flow coming down from the stage above. Since the vapor and the liquid are assumed to be in equilibrium at each stage, the operating relations and the VLE can

be solved starting from the column's top or bottom composition (for a finite or infinite number of stages) by performing only dew or bubble point calculations. Each such trajectory is called *a finite difference curve*. Though the distillation line represents discrete composition points, it is convenient to connect the points, remembering that only vertex points on such a curve have a physical meaning and they cannot be simply removed as it was done in some studies. It is generally assumed (e.g. Van Dogen and Doherty [20], Wahnschafft et al. [7]) that residue and finite difference curves originating from the same initial point join the same pure component or azeotrope nodes and that the difference between the two kinds of curves is not
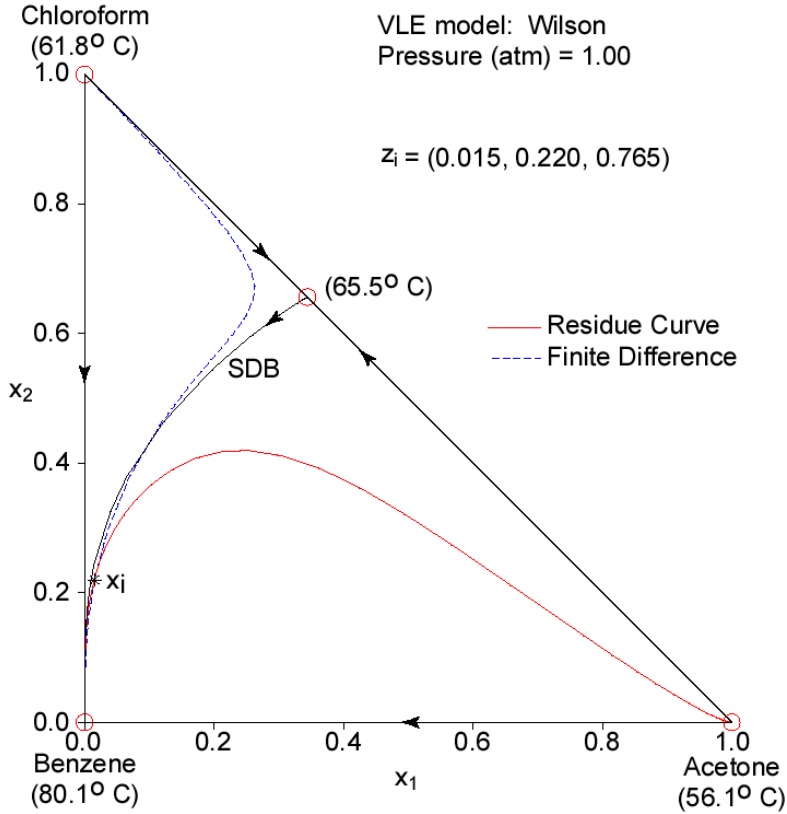
Chloroform
(61.8° C)

VLE model: Wilson
Pressure (atm) = 1.00

z_i = (0.015, 0.220, 0.765)

(65.5° C)

——— Residue Curve
– – – Finite Difference

SDB

x_2

x_i

Benzene
(80.1° C)

x_1

Acetone
(56.1° C)

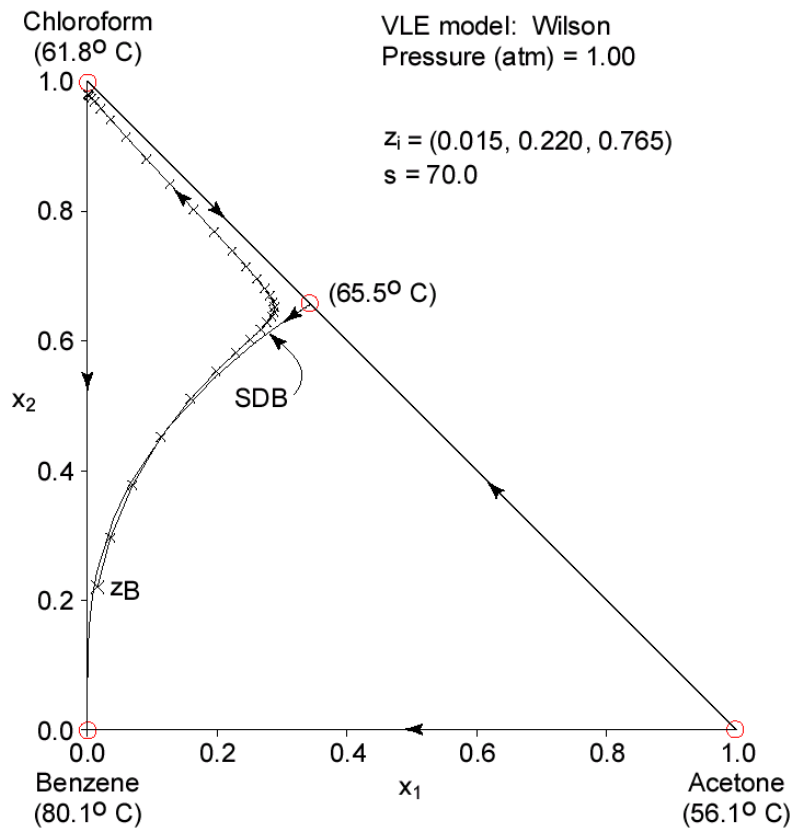Fig. 1. Residue and finite difference curves. x_i = (0.015, 0.220, 0.765).

Fig. 2. Crossing simple distillation boundary. z_B = (0.015, 0.220, 0.765), s = 70.0.

significant (as it is often the case). However, Figure 1 shows evidence to the contrary. Such results are obtained when it is impossible to make the finite differences sufficiently small (for staged columns the difference between the successive stage numbers is always equal to 1). Similarly as the residue curve map, the finite difference curve map also includes invariant curves (analogous to the separatrix for continuous systems) which start from the saddle azeotropes and join precisely the same singular points. We shall call such a curve a *total reflux boundary (TRB)*. The TRB for staged columns has properties similar to those of the simple distillation boundary for packed columns. Observations suggest that a steady-state composition profile for the staged column (for a finite reflux or reboil ratio) may cross the total reflux boundary only from the latter's convex side where the product composition lies (Kondratev et al. [21]). Similarly, a composition profile for the packed column may cross the SDB only from its convex side. Total reflux and simple distillation boundaries are often situated close to each other and an SDB is often used as a convenient approximation of a TRB, but one should be careful when marking out distillation regions. For the staged column, the SDB may sometimes be crossed by distillation profiles from its both sides. A stripping profile (originating from bottom composition z_B) which crosses the simple distillation boundary from its concave side is shown in Fig. 2. This is possible because here the TRB is situated on the SDB's concave side (Fig. 3) and the bottom composition lies between the two boundaries. For some mixtures (e.g. the acetone–chloroform–methanol mixture), the distance between the two boundaries can be more significant.
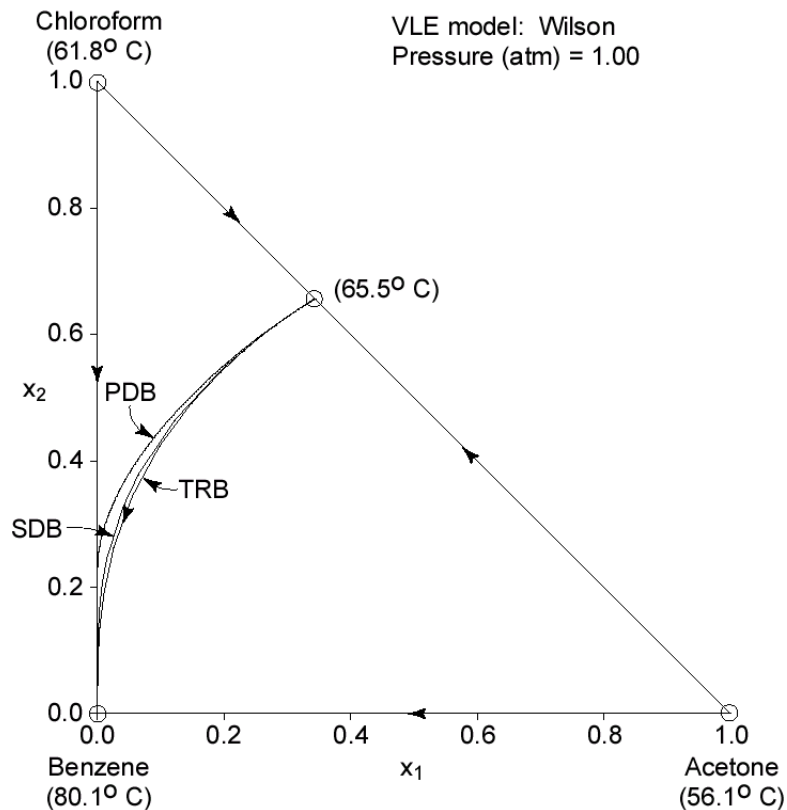
Chloroform
(61.8° C)

VLE model: Wilson
Pressure (atm) = 1.00

(65.5° C)

x_2

PDB

TRB

SDB

Benzene
(80.1° C)

x_1

Acetone
(56.1° C)

Fig. 3. Simple, total reflux and pitchfork distillation boundaries.

In the article, continuous distillation in trayed columns is modeled by theoretical stages. Constant molar overflow in each section of the column, constant pressure along the column, and the products in the form of saturated liquids are assumed. An ideal vapor phase and an activity coefficient model (with the Wilson equation) for the liquid phase are used in all the calculations. The references for the vapor–liquid equilibrium data used in all the examples are given in Table 1.

Table 1. Data Sources for Vapor–Liquid Equilibrium Parameters (p=1atm).

Mixture	DECHEMA reference (volume / part, page)		
acetone–chloroform–benzene	I/3+4, p. 128	I/3+4, p. 209	I/7, p. 72
acetone–i-propanol–water	I/1b, p. 153	I/1a, p. 251	I/2b, p. 44
acetone–chloroform–methanol	I/2e, p. 17	I/2e, p. 75	I/3+4, p. 128
acetone–methyl acetate–methanol	I/2c, p. 86	I/2e, p. 75	I/3+4, p. 163
Volume, part and page numbers refer to data collected by Gmehling at al. [22–28]			

LOCUS OF PINCHES

In the *boundary value design method* (Van Dogen and Doherty [17], Julka and Doherty [29]), distillation profiles for *finite* reflux or reboil ratios are calculated starting from product compositions and ending at pinch points. A separation is feasible if the profiles intersect. In the case of a minimum reflux ratio, the pinch point of one composition profile lies on the other profile. At any pinch point, the liquid compositions in two adjacent stages are constant, i.e. $x_j = x_{j+1}$. For packed columns, the liquid compositions at a pinch point do not change with packing height, i.e.

$dx_j/dh = 0$. In other words, a theoretical column working at a pinch point (considered as an unreachable limit) has an infinite number of stages or an infinite height of packing. The liquid composition at a pinch for staged and packed columns is given by

$$- \boldsymbol{y}(\boldsymbol{x}) + \frac{r}{r+1}\boldsymbol{x} + \frac{1}{r+1}\boldsymbol{z}_D = 0 \qquad (1)$$

for the rectifying profile and by

$$\boldsymbol{y}(\boldsymbol{x}) + \frac{s+1}{s}\boldsymbol{x} + \frac{1}{s}\boldsymbol{z}_B = 0 \qquad (2)$$

for the stripping profile (the above equation were derived from the material balance and equilibrium equations). It is convenient to write the two equations in the following general form

$$\tau\boldsymbol{x} + (1-\tau)\boldsymbol{y}(\boldsymbol{x}) = \boldsymbol{z}_P \qquad (3)$$

where $\tau = -r$ and $z_P = z_D$ for the rectifying profile or $\tau = s+1$ and $z_P = z_B$ for the stripping profile. As the value of τ is changed from $-\infty$ to $+\infty$, we obtain a set of solutions of Eq. (3), which will be called *locus of pinches (LOP)*. In Fig. 4 there are two branches of the LOP. One of them connects benzene and acetone vertices and contains product composition z_P (for $\tau = 1$). For $\tau > 1$, the points (located on the right side of product composition point z_P) on this branch correspond to the stripping profile's pinch points and if the value of τ increases, the pinch point moves closer to the acetone vertex. The points for $\tau < 0$ (they are situated on the left side of z_P)
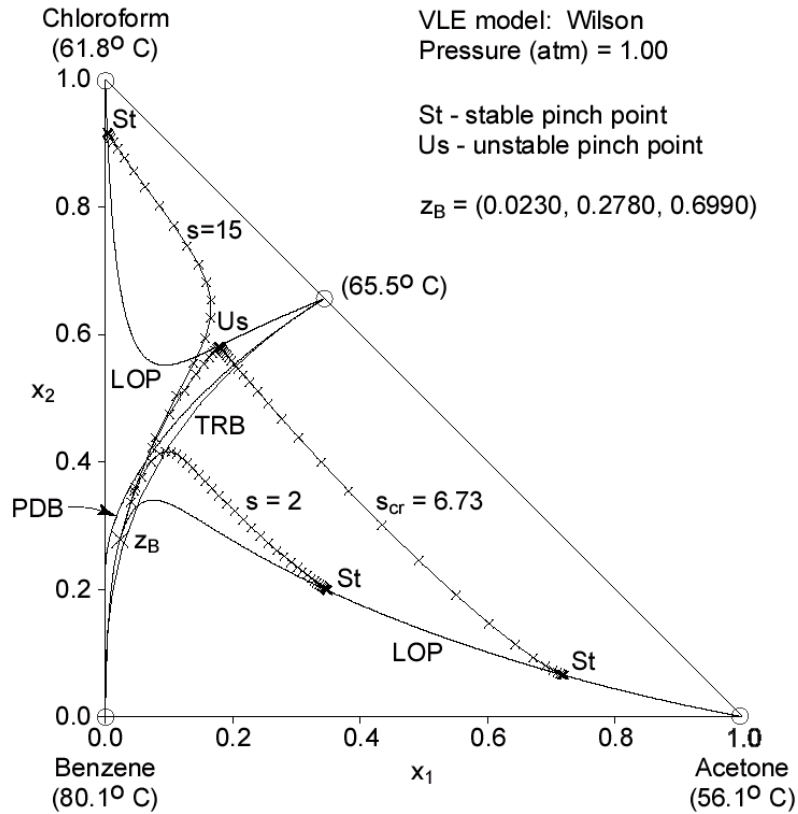
Fig. 4. Behavior of stripping profiles for staged column when z_B lies between TRB and PDB.
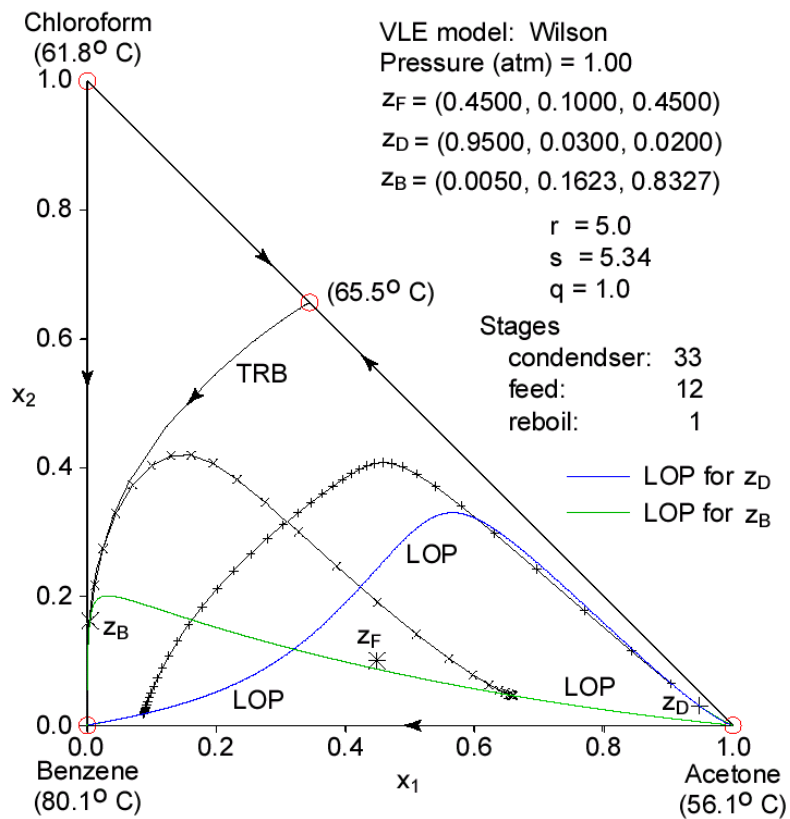

Fig. 5. Distillation profiles and product branches of LOP for distillation column.

correspond to the rectifying profile's pinch points and if the value of τ decreases, the pinch point moves closer to the benzene vertex. The other curve joins the chloroform vertex with the binary (saddle) azeotrope. There are two pinch points for every value of $\tau > \tau_{min} > 0$ on this branch. One of them is located closer to the chloroform vertex and the other closer to the azeotropic point. As the value of τ increases, the pinch points move in the directions of the respective singular points. Exemplary distillation profiles and product branches of the LOP for a distillation column are shown in Fig. 5 (only parts of the profiles situated between the product composition and the profiles' intersection point have a physical meaning).
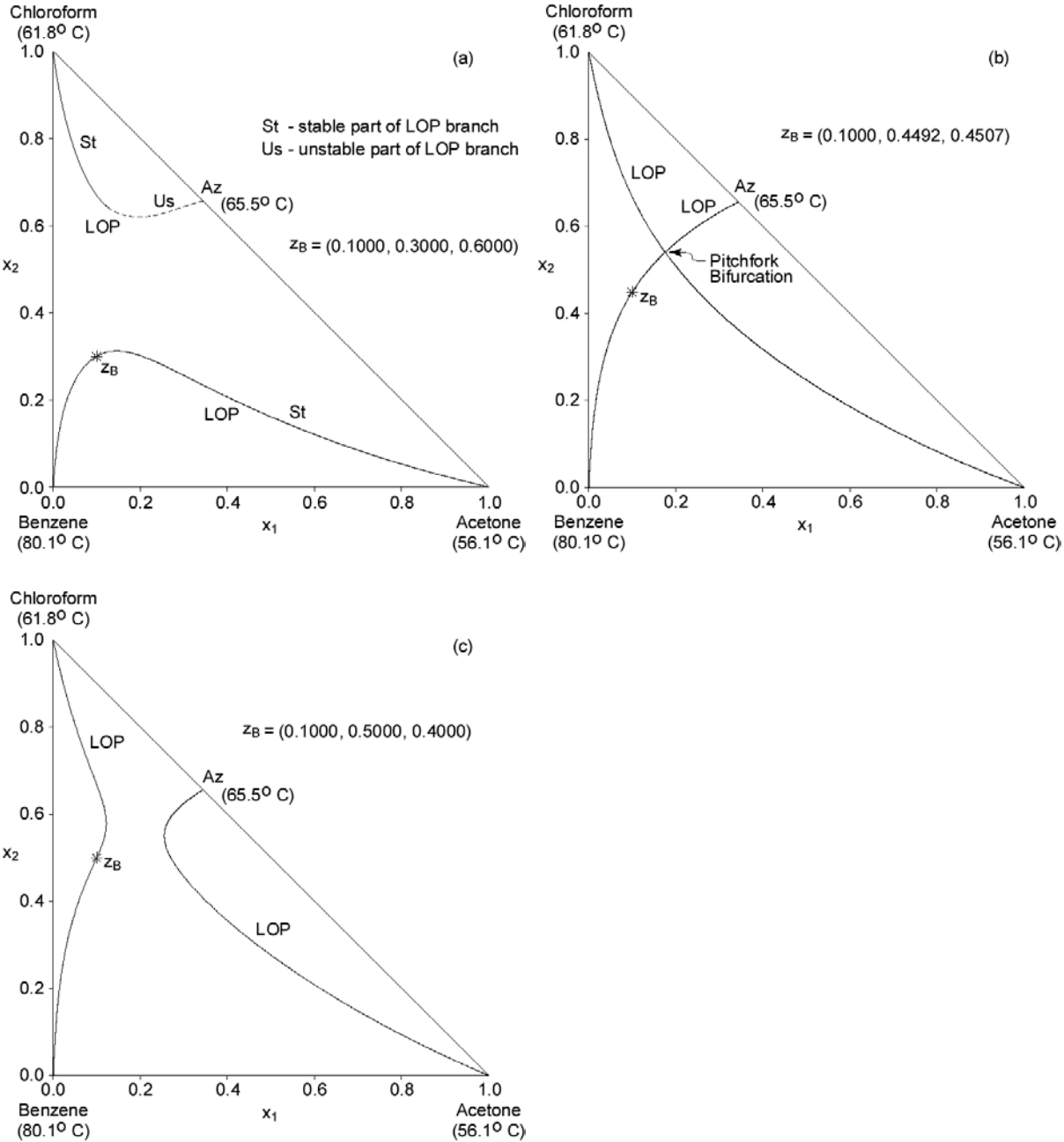

Fig. 6. Loci of pinches for various product compositions (Az – azeotrope).

Equation (3) yields more solutions for mixtures with saddle azeotropes and the solutions can be qualitatively different for different product compositions (see Fig. 6).

Product composition z_P is located on only one of the solution curves. This curve will be called a *product branch*. In general, a product branch connects pure component or azeotrope nodes, and points on this branch represent stable solutions (see Fig. 4 and 6a). If the LOP does not contain the product composition it is called an *additional branch*. This branch joins a pure component or azeotrope node with a saddle azeotrope and points nearer the node represent stable solutions whereas points closer to the saddle refer to unstable solutions. The stable and unstable parts of the branch meet at a point where one of the eigenvalues of Jacobian matrix $\boldsymbol{Y} = (\partial y_k / \partial x_l)$ satisfies relation $\lambda = \tau / (\tau - 1)$ (see Davydyan et al. [30]). Furthermore, parameter τ takes an extreme value at this point and it does not change its sign on the branch. In an exceptional case (see Fig. 6b), the product branch connects a node with an azeotrope saddle, crossing the additional branch which joins two nodes. The LOP is also interpreted as a liquid composition profile for a hypothetical reversible distillation in an infinitely long column with continuous heat exchange along its length (the column operates everywhere at pinch points) (for more information and references see Pratt [31]). Attempts to define the missing distillation boundary by means of reversible distillation were made by Petlyuk [32], Koehler et al. [3], Wahnschafft et al. [7] and Poellmann and Blass [9].

PITCHFORK DISTILLATION BOUNDARY

When the product branch crosses the additional branch (as in Fig. 6b), the intersection point is called a *pitchfork solution* or a *pitchfork bifurcation*. Then all the profiles end either on the product branch between the pitchfork solution and a pure component node (benzene) or on the additional branch between the pitchfork solution and another pure component node (chloroform) which lies on the convex side of the product branch (see Fig. 7). Each of the profiles is situated entirely above the product branch. Furthermore, almost any small change in the product composition, no matter how small, brings about an abrupt change in the LOP. After the change the LOP is as in Fig. 6c and all the profiles end on the product branch or the LOP's shape is as in Fig. 6a and the profiles may end on the product branch or on the additional branch (see Fig. 4). The exceptional product composition points for which the product branch and the additional branch intersect (bifurcate) mark a new distillation boundary, referred to as the *Pitchfork Distillation Boundary (PDB)*.

The PDB was introduced by Davydyan et al. [30]. To construct this boundary, a set of pitchfork solutions must be obtained by applying the implicit function theorem. By differentiating equation (3) we get

$$\tau \boldsymbol{I}(\boldsymbol{x} - \boldsymbol{y}) + (1 - \tau) de t(\boldsymbol{Y}) \boldsymbol{Y}^{-1}(\boldsymbol{x} - \boldsymbol{y}) = 0 \qquad (4)$$

where $\boldsymbol{x}$ is a pitchfork solution, $\boldsymbol{I}$ is an identity matrix and $\boldsymbol{Y}$ is the Jacobian matrix $(\partial y_k / \partial x_l)$ of vapor–liquid equilibrium mapping $\boldsymbol{y} = \boldsymbol{y}(\boldsymbol{x})$. As the value of τ is changed, a set of pitchfork solutions is obtained (see Fig. 8). For each of the pitchfork solutions, corresponding product composition z_P can be calculated from Eq. (3). The obtained product composition points form the pitchfork distillation boundary. One should note that the PDB is applicable to both staged and packed columns since their locus of pinches equations (3) are identical. But total reflux and simple distillation boundaries
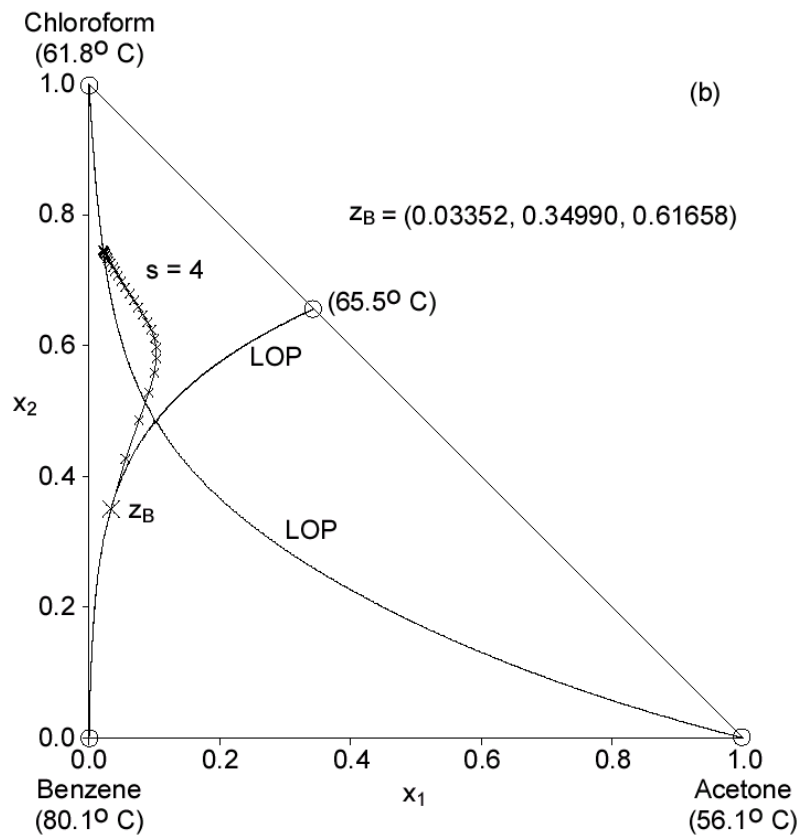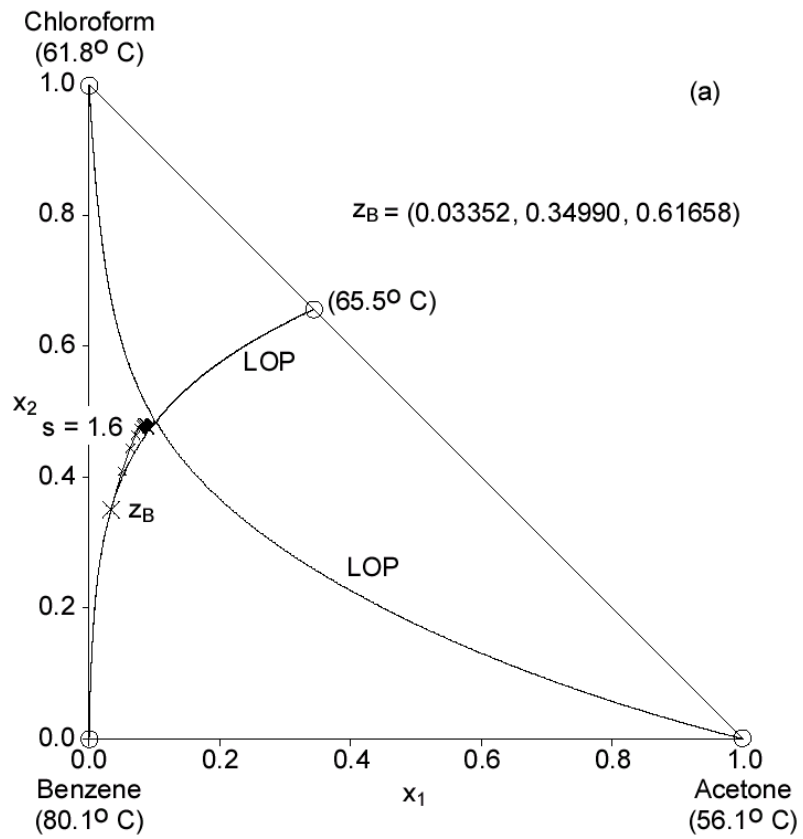
(a)

Chloroform
(61.8° C)

1.0

0.8

z_B = (0.03352, 0.34990, 0.61658)

(65.5° C)

0.6

LOP

x_2

s = 1.6

0.4

z_B

LOP

0.2

0.0

0.0   0.2   0.4   0.6   0.8   1.0

Benzene
(80.1° C)

x_1

Acetone
(56.1° C)

(b)

Chloroform
(61.8° C)

1.0

0.8

z_B = (0.03352, 0.34990, 0.61658)

s = 4

(65.5° C)

0.6

LOP

x_2

0.4

z_B

LOP

0.2

0.0

0.0   0.2   0.4   0.6   0.8   1.0

Benzene
(80.1° C)

x_1

Acetone
(56.1° C)

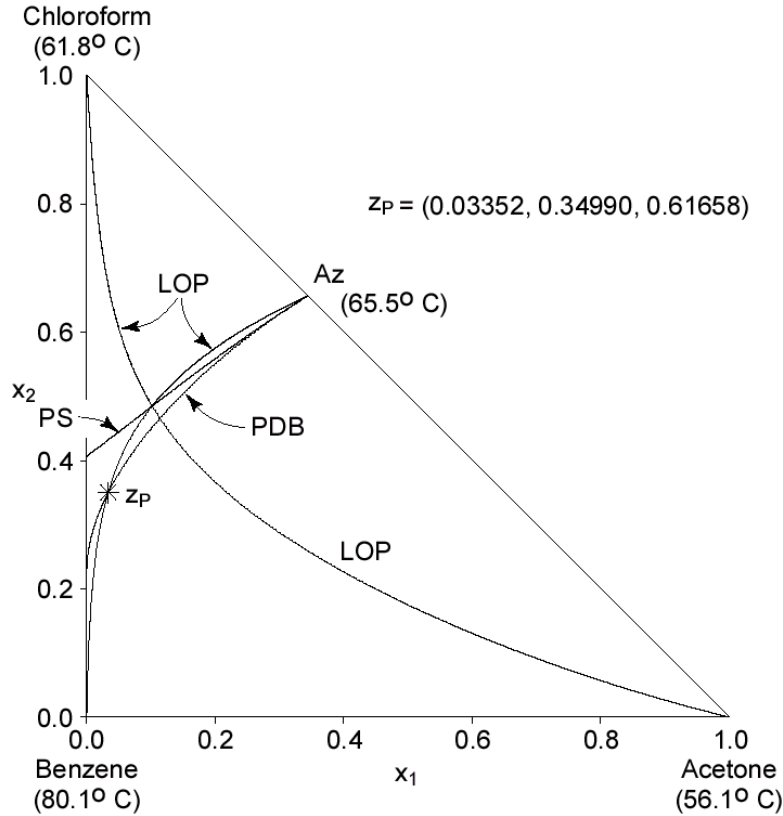*Fig. 7. Limiting case of locus of pinches and striping profiles for staged column.*

Fig. 8. Pitchfork solution (PS) and pitchfork distillation boundary (PDB).

refer to the equipment used. Hence there are two pairs of distillation boundaries: TRB and PDB for staged columns and SDB and PDB for packed columns.

Before equation (4) can be solved numerically, the initial conditions must be specified. Vectors $x - y$ along the pitchfork solution curve are the eigenvectors of matrix $Y = (\partial y_k / \partial x_l)$ with eigenvalues

$$\lambda_1 = \frac{\tau - 1}{\tau} de(Y)$$ (5)

$$\lambda_2 = \frac{\tau}{\tau - 1}$$ (6)

At singular points where $x = y(x)$, Eq. (4) is satisfied for any finite value of τ. The initial point should be taken close to a saddle azeotrope in the direction of the eigenvector calculated at the azeotropic point, which is not parallel to the edge of the composition space. Then parameter τ as a function of appropriate eigenvalue of Y should be calculated at this point from equation (5) or (6).

BEHAVIOR OF DISTILLATION PROFILES

Now we can discuss in detail the behavior of distillation profiles (which is related to the regions defined by the PDB and the TRB) for the staged column (see also [33]).

The general relations will be illustrated for the same (as above) mixture of acetone, chloroform, and benzene. The LOP shapes for different locations of product composition points for this mixture are shown in Fig. 6. If a distillate or bottom composition is located on the concave side of the TRB (Fig. 5), the profiles originating from this composition point remain entirely on the same side of this boundary and end at a pinch point on the product branch. For feasible separation, the second product of the distillation column must be situated on the same side of the TRB as the first one. When the product composition occurs on the convex side of the pitchfork distillation boundary, the shape of the LOP changes, but the composition profiles remain entirely on the same side of this boundary and end on the product branch which joins different nodes. In such a case, the second product composition must lie on the same side of the PDB as the first one. If the product composition is located between the total reflux boundary and the pitchfork distillation boundary (Fig. 9), the behavior of the composition profiles is most complex and it depends on the type of separatrix. For the considered mixture, the TRB is a stable separatrix. The rectifying profiles starting from this product composition always end on the product branch and they all lie between the TRB and the PDB for any reflux ratio value. Stripping profiles behave in a different way. For a certain critical value of reboil ratio s_{cr}, the stripping profile has a second pinch point (see Fig. 4) which lies in the unstable part of the LOP's additional branch. If the reboil ratio is increased infinitesimally, the stripping profile abruptly changes its shape and ends on the additional branch at a stable point. For $s < s_{cr}$, the stripping profile ends on the product branch, whereas for $s > s_{cr}$ the stripping profile ends on the additional branch. Then one can say that the stripping profile *jumps* from the product branch to the
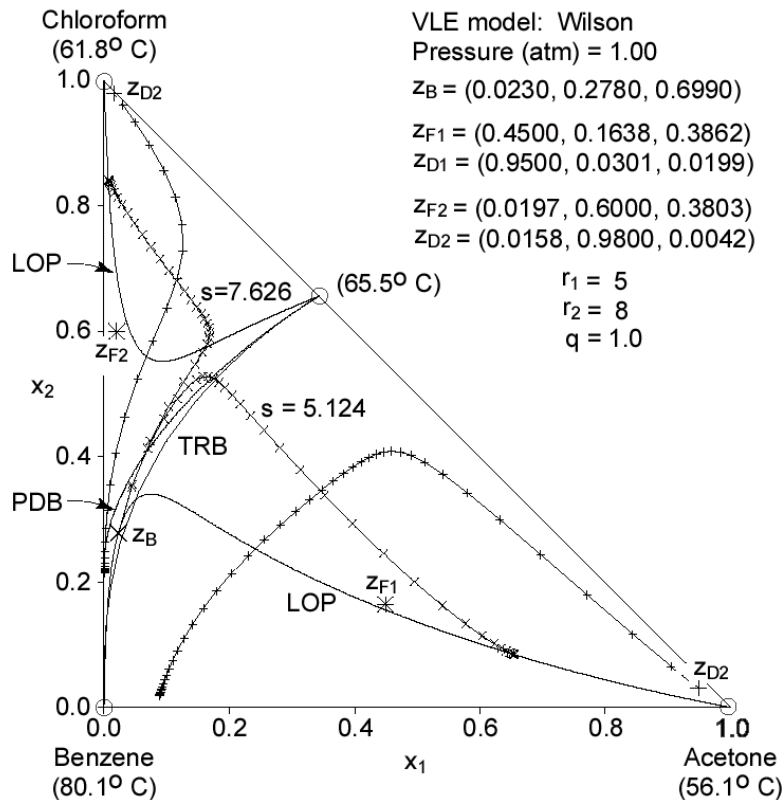
Chloroform (61.8° C)

VLE model: Wilson
Pressure (atm) = 1.00
z_B = (0.0230, 0.2780, 0.6990)
z_{F1} = (0.4500, 0.1638, 0.3862)
z_{D1} = (0.9500, 0.0301, 0.0199)
z_{F2} = (0.0197, 0.6000, 0.3803)
z_{D2} = (0.0158, 0.9800, 0.0042)
r_1 = 5
r_2 = 8
q = 1.0

Benzene (80.1° C)   Acetone (56.1° C)

Fig. 9. Distillation profiles for common bottom composition z_B and two distillate compositions z_D located in different separation regions (only LOP branches for z_B are shown).

additional branch or from one distillation region to another. This means that the distillate composition can occur on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary. If the separatrix is unstable (as in the case of the acetone–i-propanol–water mixture), only the rectifying profile is able to jump from one branch of the LOP to another. This means that if the distillate composition is located between these boundaries, the bottom composition may occur on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary. The critical values of the reboil or reflux ratio can be determined through a parametric study. A method of estimating these values was also proposed by Wahnschafft et al. [7]. The critical value of the reboil or reflux ratio decreases when the product composition point is moved from the TRB toward the PDB.

RELATIONSHIPS BETWEEN DISTILLATION BOUNDARIES

For the staged column, a TRB and a PDB originating from the same saddle azeotrope mark out two distillation regions which overlap. One of the regions lies on the concave side of the PDB and the other one on the convex side of the TRB. The area between the TRB and the PDB is the common part of the two regions. In the case of a stable separatrix (TRB), if a bottom composition is found between the TRB and the PDB, a distillate composition may occur on the concave side of the TRB or on the convex side of the PDB (see Fig. 9). Of course, not all distillate composition points are obtainable for a selected bottom composition. Furthermore, their eligibility also depends on the critical value of the reboil ratio for a given bottom composition. The case of an unstable separatrix and a rectifying profile is similar.

For packed columns, simple and pitchfork distillation boundaries, which both originate from the same saddle azeotrope, form two similar distillation regions. Since the PDB for the staged column and that for the packed column are identical and both total reflux and simple distillation boundaries lie on the concave side of the pitchfork distillation boundary, it is only natural to enquire about the interrelationships between the boundaries. For stable separatrices (SDB and TRB), the simple distillation boundary lies between the total reflux boundary and the pitchfork distillation boundary (see Fig. 3) and it may be crossed from each side by staged column stripping profiles. In the case of unstable separatrices, the total reflux boundary lies between the simple distillation boundary and the pitchfork distillation boundary and it is clear that it may be crossed from each side by packed column rectifying profiles.

MIXTURES WITH MULTIPLE AZEOTROPES

We shall discuss here only the staged column since the situation for the packed column with its simple distillation boundary is similar. In the ternary saddle azeotrope case (see Fig. 10), total reflux distillation boundaries connect the saddle to nodes. The total reflux and pitchfork distillation boundaries mark out four overlapping distillation regions. A distillation profile may jump only if the product composition lies between two appropriate distillation boundaries (e.g. TRB I and PDB I) but some additional information is needed to determine which profiles will do this. For a stable separatrix (TRB II and TRB IV), the stripping profile jumps, i.e. the distillate composition may lie in a region on the concave side of the total reflux boundary or in
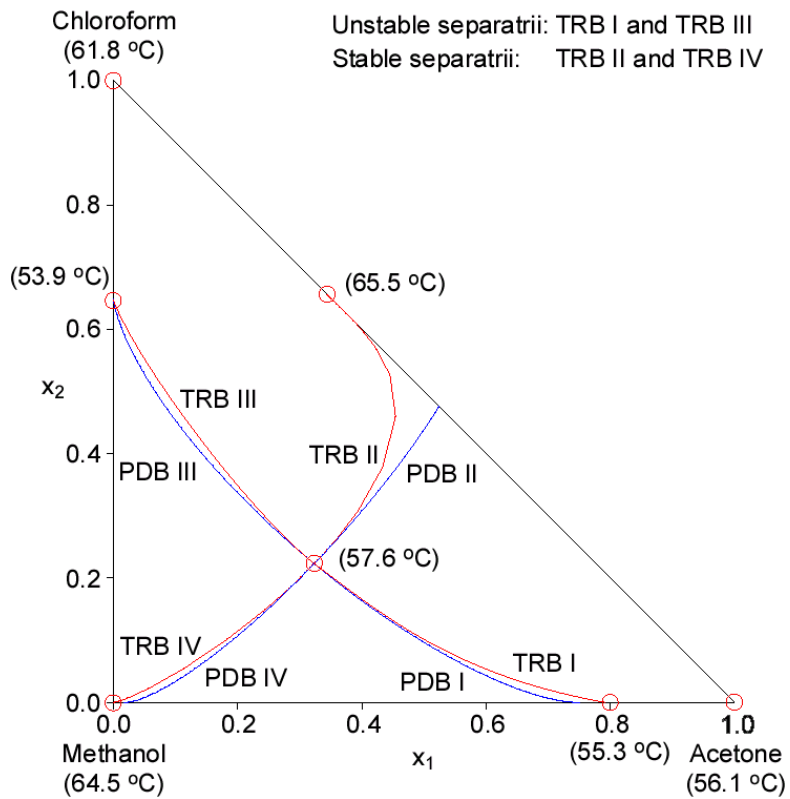
Fig. 10. Distillation boundaries for ternary saddle azeotrope (TRB I and TRB III have been distorted).
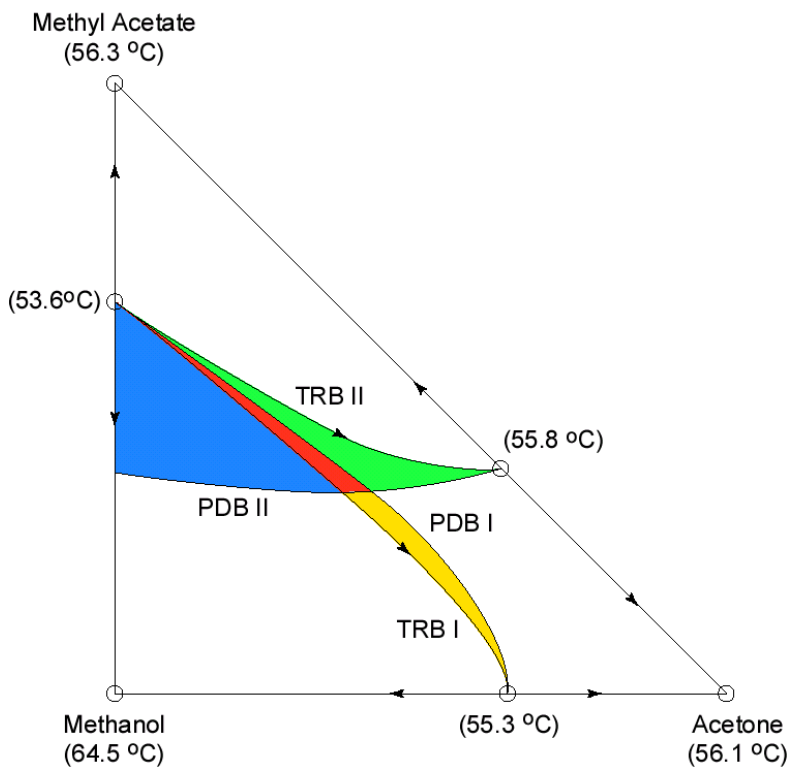

Fig. 11. Interaction of boundaries (the figure has been distorted).

a region on the convex side of the pitchfork distillation boundary. For an unstable separatrix (TRB I and TRB III), the rectifying profile jumps. In Fig. 10, TRB I and TRB III have been distorted for the purpose of clarity (in fact, they are close to PDB I and PDB III, respectively). The two regions responsible for the jump of the stripping profiles extend in the opposite directions from the ternary saddle, similarly as the two regions for the jump of the rectifying profiles.

Sometimes the regions between different TRBs and PDBs overlap. Then they interact in two possible ways. The interactions will be illustrated for a mixture of acetone, methyl acetate, and methanol. For this mixture the total reflux boundaries are unstable separatrices and as a result, there are two regions responsible for the jump of the rectifying profiles. One of them extends between TRB I and PDB I and the other between TRB II and PDB II (see Fig. 11 – the figure has been distorted for the purpose of clarity). The first kind of interaction occurs if a region between a total
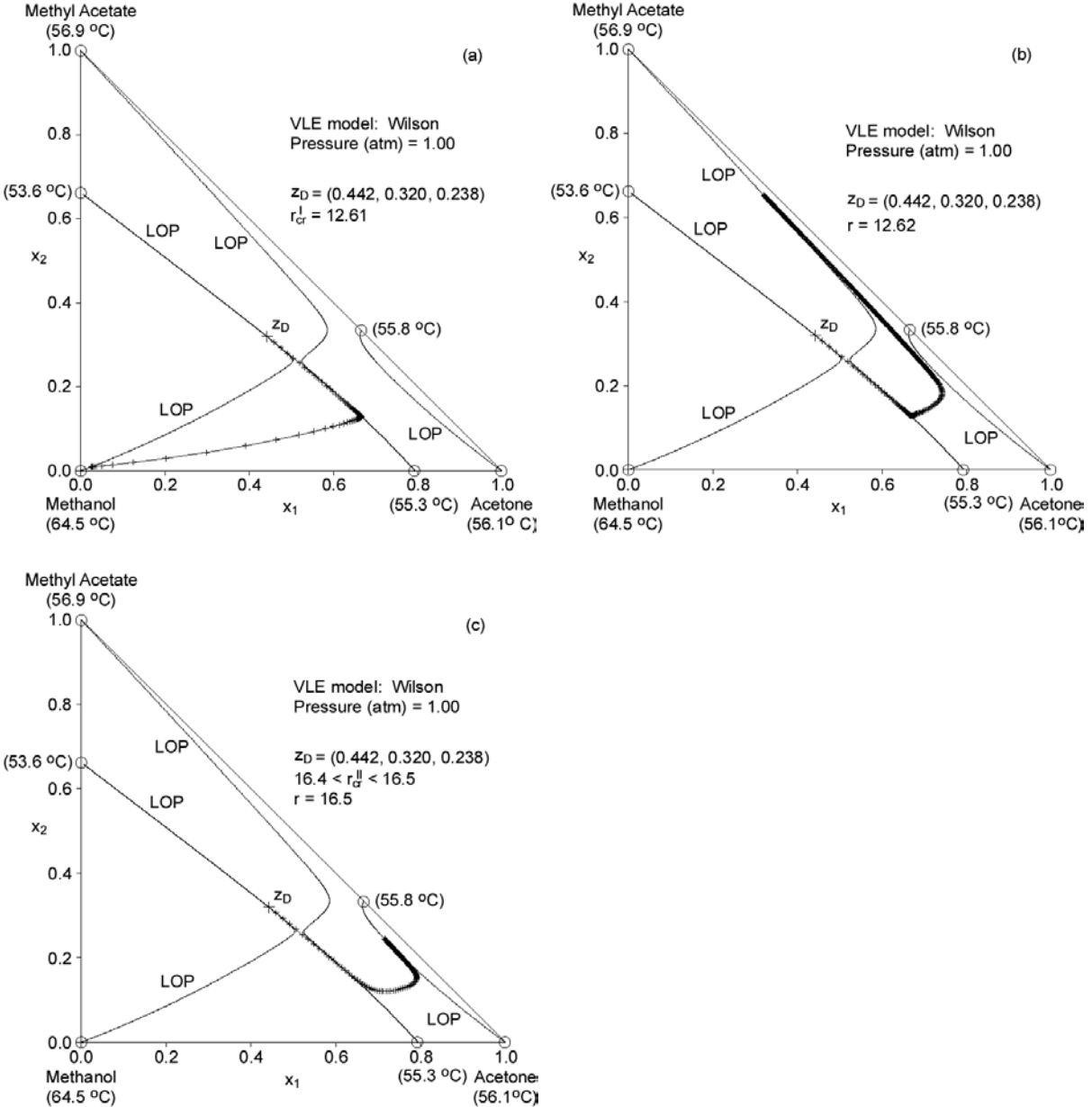

Fig. 12. Rectifying profiles for acetone–methyl acetate–methanol mixture.

reflux boundary and a corresponding pitchfork distillation boundary is crossed by another total reflux boundary. For example, TRB I crosses the region between TRB II and PDB II. Normally, the rectifying profile would jump for the distillate composition in this entire region (i.e. between TRB II and PDB II), but it does not do so in the area bounded by TRB I, PDB II and the methyl acetate–methanol edge (the blue area in Fig. 11). The second type of interaction occurs in the common part of two regions between certain total reflux and pitchfork distillation boundaries. The common part is bounded by TRB I, PDB I and PDB II (the red area in Fig. 11). If a distillate composition, e.g. z_D = (0.442, 0.320, 0.238), is put in this area, the rectifying profile will jump twice for two different values of the reflux ratio, as shown in Fig. 12. For a critical reflux ratio value r_{cr}^I = 12.61 the rectifying profile jumps from the product branch to the additional branch which joins the pure acetone vertex and the acetone–methanol azeotrope. Then for r_{cr}^{II} (16.4 < r_{cr}^{II} < 16.5) the rectifying profile jumps from the additional branch to the other additional branch which connects the pure acetone vertex with the acetone–methyl acetate azeotrope.

RULES FOR DISTILLATION REGIONS

On the basis of the above observations the following rules for determining distillation regions and predicting the behavior of distillation profiles can be formulated:

- Distillation regions are defined by total reflux and pitchfork distillation boundaries or simple and pitchfork distillation boundaries for the staged column and the packed column, respectively. The distillation regions are not disjointed – they overlap.
- All the distillation boundaries (TRB, SDB and PDB) originate from the same saddle azeotrope. Total reflux and simple distillation boundaries always end at the same node. However, a pitchfork distillation boundary may end at the same node or it may cross the edge of the composition triangle.
- If a pitchfork distillation boundary ends at a node where a total reflux boundary and a simple distillation boundary end, the distance between it and the other boundaries is small. Otherwise, the distance between a pitchfork distillation boundary and an infinite or simple distillation boundary may be large.
- For stable separatrices, the simple distillation boundary lies between total reflux and pitchfork distillation boundaries. Otherwise, the total reflux boundary lies between simple and pitchfork distillation boundaries.

The rules below apply to staged columns. For packed columns it is necessary to replace the total reflux boundary by the simple distillation boundary. If a mixture has only one binary saddle azeotrope there are two possibilities:

- If the bottom composition lies between total reflux and pitchfork distillation boundaries and the TRB is a stable separatrix, the distillate composition may occur on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary. If the bottom composition is situated on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary, the distillate composition is bound to occur on the same side of the distillation boundary (in the same distillation region).

- If the distillate composition is located between total reflux and pitchfork distillation boundaries and the TRB is an unstable separatrix, the bottom composition may occur on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary. If the distillate composition is situated on the concave side of the total reflux boundary or on the convex side of the pitchfork distillation boundary, the bottom composition is bound to occur on the same side of the distillation boundary (in the same distillation region).

Some additional rules allow us to anticipate the behavior of a mixture with multiple azeotropes:

- For a ternary saddle azeotrope, there are four pairs of total reflux and pitchfork distillation boundaries and in consequence, four overlapping distillation regions. The rules for each pair of boundaries are identical as for binary saddle azeotropes. Two areas responsible for the jump of stripping profiles extend in the opposite directions from the ternary saddle, similarly as the two areas for the jump of rectifying profiles.
- If a pair of total reflux and pitchfork distillation boundaries is crossed by another total reflux distillation boundary and the product composition lies between the pair's pitchfork distillation boundary and the concave side of the other total reflux boundary, the distillation column's second product will be located on the same side of the other total reflux boundary where the first product occurs.
- If two pairs of total reflux and pitchfork distillation boundaries originate from the same type of binary saddle azeotropes and overlap and an appropriate (for the type of separatrices) product composition lies between each pair's boundaries, the distillate profiles which start from this product composition may jump twice and the distillation column's second product may occur in different distillation regions.

The phrase: "a product (distillate or bottom) composition may (or is bound to) occur in the distillation region" used in the rules mentioned in this section does not mean that the composition will be found at each point of this region.

SUMMARY

A composition profiles behavior classification method for mixtures with azeotropes has been developed. It consists in tracking all the pinch points of rectifying and stripping profiles, mapping the branches of solutions and checking for "a jump" of composition profiles at bifurcation points. Different distillation boundaries defined for total reflux are ascribed to the particular types of column (trayed or packed). The same pitchfork distillation boundary is used for each column type. The area between two distillation boundaries which form a pair is parametrically sensitive. The area represents the common part of two distillation regions (the distillation regions overlap). If a product composition is located between two distillation boundaries which form a pair, the second product may occur in different distillation regions. A column can be designed so that distillation boundaries (defined for the total reflux) can be crossed at a finite reflux if the distance between the TRB and the PDB is

considerable. However, in such a column the TRB will not be crossed at the total reflux. Hence there is a minimum reflux ratio and a maximum reflux ratio for a desired separation. In more complicated cases (when distillation boundaries are formed by ternary azeotropes or areas bounded by different pairs of boundaries overlap), the behavior of distillation profiles can be predicted on the basis of their behavior for binary azeotropes and the bounds for the product composition can be easy calculated.

ACKNOWLEDGMENTS

NOTATIONS

Az = binary saddle azeotrope
I = identity matrix
h = dimensionless height of packing in column section
TRB = total reflux boundary
LOP = locus of pinches
PDB = pitchfork distillation boundary
PS = pitchfork solution
r = reflux ratio
s = reboil ratio
SDB = simple distillation boundary
St = stable branch of locus of pinches
Us = unstable branch of locus of pinches
x = vector of mole fractions in liquid phase
y = vector of mole fractions in vapor phase
Y = $(\partial y_k / \partial x_l)$, Jacobian matrix of vapor--liquid equilibrium mapping $y = y(x)$
z = vector of mole fractions in product

Greek letters

λ = eigenvalue of Jacobian matrix $Y = (\partial y_k / \partial x_l)$
τ = $-r$ or $s+1$, parameter

Subscripts

B = bottom
D = distillate
h = dimensionless height of packing in column section
i = initial
j = stage number

k = component number
l = component number
P = product
cr = critical value

Superscripts

I and II = numbers of related pairs of distillation boundaries

Keywords

1. distillation boundary
2. feasible separation region
3. azeotrope
4. pinch point
5. continuous distillation

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