Determination of Distillation Regions for Non-Ideal Ternary Mixtures

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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. An algorithm determining the distillation regions, which takes into account properties of distillation boundaries, has been formulated. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 532–544, 2006

Keywords: distillation boundary, residue curve map, distillation line map, trayed column, packed column

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] and Jobson et al.[10]), but a complete solution for ternary mixtures with distillation boundaries has not yet been found. Some researchers 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. Jobson et al.[10] showed that the separation boundaries depend on the equipment used. Castillo and Towler,[12] Taylor et al.,[13] and Baur et al.[14] described the influence of mass transfer on distillation boundaries. Unfortunately, the nature of distillation boundaries is still not precisely understood. The present article 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,[15]

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Zharov,[16,17] Doherty and Perkins[18]) 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[19] provide a simple model for a continuous distillation process in packed columns. Their differential equations for composition profiles (also see Laroche et al.[7]) 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 (Levy et al.[20]). 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.[21] On the other hand, Laroche et al.[22] assert that linear boundaries do not occur in physical systems. A comprehensive survey of simple equilibrium phase transformations and their properties is given by Kiva et al.[23]

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. It was done 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.,[24] and the region's properties are described in the present article.

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 vapor–liquid equilibrium (VLE) relation 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 "discrete distillation line" or a "tie-line curve." Though the distillation line represents discrete composition points, it is convenient to connect the points with line segments (equilibrium vectors), remembering that only vertex points on such a curve have a physical meaning. Similar to the residue curve map, the distillation line 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).

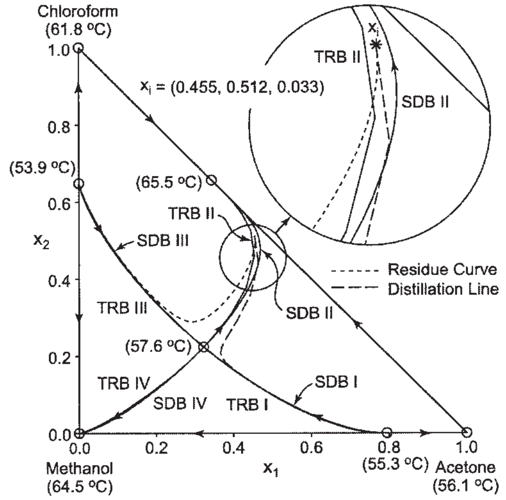

Figure 1. Residue curve and distillation line. x_i = (0.455, 0.512, 0.033).

It is generally assumed (e.g., Van Dogen and Doherty,[25] Wahnschafft et al.[7]) that residue and distillation lines 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 significant (as is often the case). However, Figure 1 shows evidence to the contrary. This is possible because for the acetone–chloroform–methanol mixture, the TRB II is situated on the concave side of the SDB II and the initial point lies between the two boundaries (relative location of different boundaries is given by Kiva et al.[23]). In this case, the distance between the two boundaries is significant but for remaining pairs of corresponding boundaries is small. 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.[26]). 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 both its sides. A stripping profile (originating from bottom composition z_B) that crosses the simple distillation boundary from its concave side is shown in Figure 2. Such results are obtained when the TRB is situated on the SDB's concave side and the bottom composition lies between the boundaries.

In this article, continuous distillation in trayed columns is modeled by theoretical stages. Constant molar overflow (CMO) 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

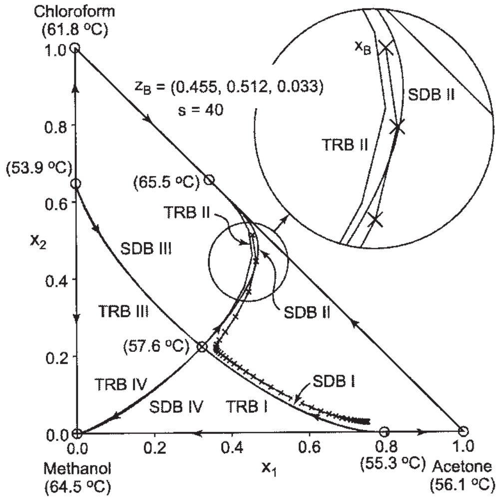

Figure 2. Crossing simple distillation boundary. z_B = (0.455, 0.512, 0.033), s = 40.0.

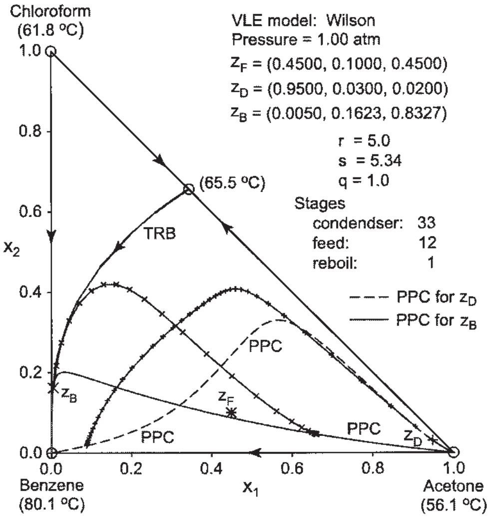

Figure 3. Distillation profiles and product branches of PPC for distillation column.

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.

Pinch-Point Curve

In the "boundary value design method" (Van Dogen and Doherty,[25] Julka and Doherty[31]), 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, that is, $\boldsymbol{x}_j = \boldsymbol{x}_{j+1}$. For packed columns, the liquid compositions at a pinch point do not change with packing height, i.e., $d\boldsymbol{x}_j/dh = 0$. 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[32] and packed[20] columns is given by

$$-\boldsymbol{y}(\boldsymbol{x}) + \frac{r}{r+1}\boldsymbol{x} + \frac{1}{r+1}z_D = 0 \tag{1}$$

for the rectifying profile and by

$$\boldsymbol{y}(\boldsymbol{x}) - \frac{s+1}{s}\boldsymbol{x} + \frac{1}{s}z_B = 0 \tag{2}$$

for the stripping profile (the above equations were derived from the material balance and equilibrium equations assuming: isobaric separation, CMO, saturated liquid products, and theoretical stages in trayed column). It is convenient to write the two equations in the following general form:

$$\tau\boldsymbol{x} + (1-\tau)\boldsymbol{y}(\boldsymbol{x}) = z_P \tag{3}$$

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 the "pinch-point curve" (PPC). Exemplary pinch-point curves for a distillation column and distillation profiles are shown in Figure 3 (only parts of the profiles situated between the product composition and the profiles' intersection point have a physical meaning). Both of the PPCs connect acetone and benzene vertices. One of the PPC contains (for $\tau = 1$) product composition z_B, whereas the second PDB contains product composition z_D. 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) correspond to the rectifying profile's pinch points; and if the value of τ decreases, the pinch point moves closer to the benzene vertex. Eq. 3 yields more solutions for mixtures with saddle azeotropes, and the solutions can be qualitatively different for different product compositions (see Figures 4a-c). 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

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

Mixture	DECHEMA Reference (volume/part, page)		
acetone–chloroform–benzene[27,28]	I/3 + 4, p. 128	I/3 + 4, p. 209	I/7, p. 72
acetone–chloroform–methanol[29,27]	I/2e, p. 17	I/2e, p. 75	I/3 + 4, p. 128
acetone–methyl acetate–methanol[30,29,27]	I/2c, p. 86	I/2e, p. 75	I/3 + 4, p. 163

Volume, part, and page numbers refer to data collected by Gmehling et al.

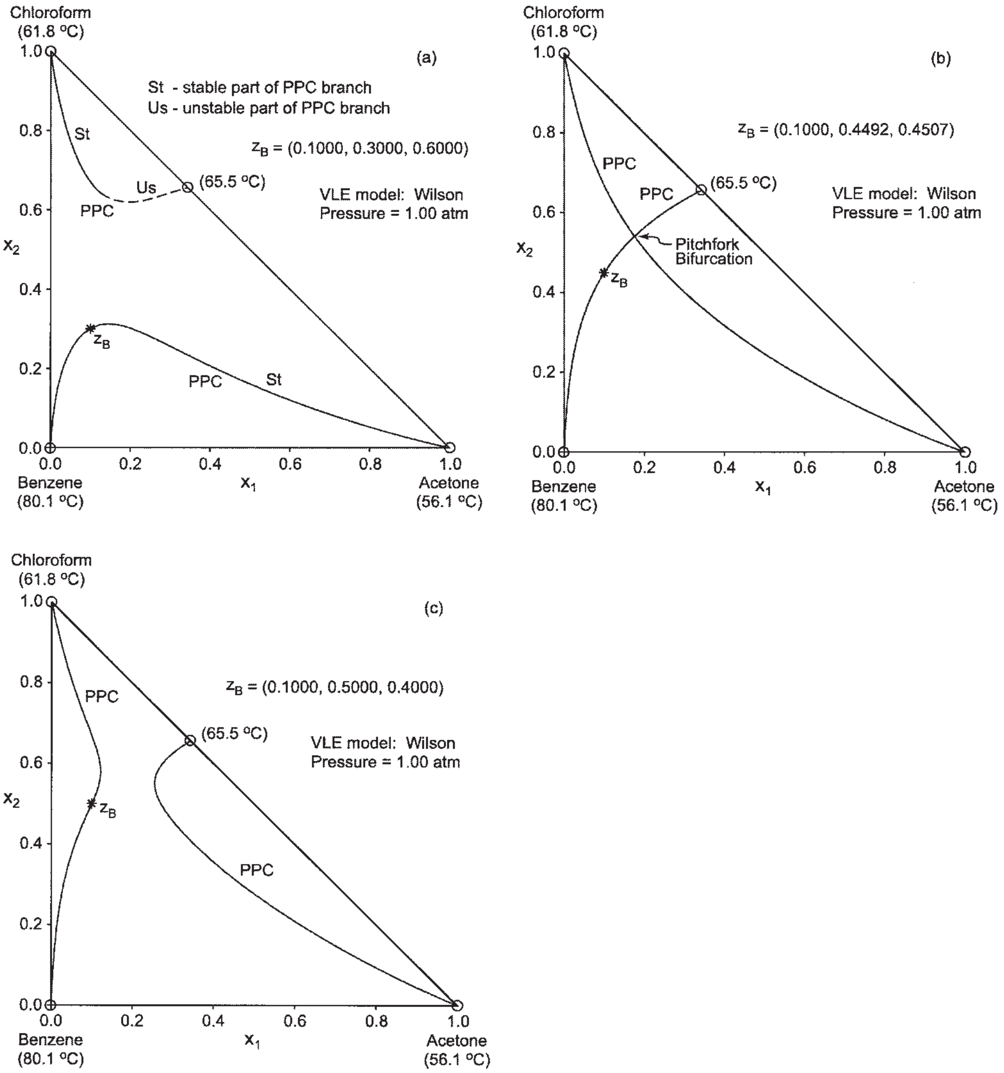

Figure 4. Pinch-point curves for various product compositions.

(a) $\mathbf{z}_B$ = (0.1000, 0.3000, 0.6000), (b) $\mathbf{z}_B$ = (0.1000, 0.4492, 0.4507), (c) $\mathbf{z}_B$ = (0.1000, 0.5000, 0.4000).

or azeotrope nodes (benzene and acetone vertices in Figure 4a), and points on this branch represent stable solutions.

If the PPC 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 (chloroform vertex with the acetone–chloroform azeotrope in Figure 4a), 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 $\boldsymbol{Y} = (\partial \boldsymbol{y}_k/\partial \boldsymbol{x}_l)$ satisfies relation $\lambda = \tau/(\tau - 1)$ (see Davydyan et al.[24]). Parameter τ takes an extreme value at this point, and it does not change its sign on the branch. Therefore, 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. In an exceptional case (see Figure 4b), the product branch connects a node with an azeotrope saddle, crossing the additional branch that joins two nodes. The PPC 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. In every cross section the column operates at pinch point (for more information and references, see Pratt[33]). Attempts to define the missing distillation boundary by means of reversible distillation were made by Petlyuk,[34] 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 Figure 4b), the intersection point is called a "pitchfork solution" or a "pitchfork bifurcation." In this case, almost any small change in the product composition, no matter how small, brings about an abrupt change in the PPC. After the change, the PPC's shape is as in Figure 4c and all the profiles end on the product branch, or the PPC's shape is as in Figure 4a and the profiles usually end on the product branch or sometimes on the additional branch. For the bifurcation case, all the profiles end either on the product branch between the pitchfork solution and

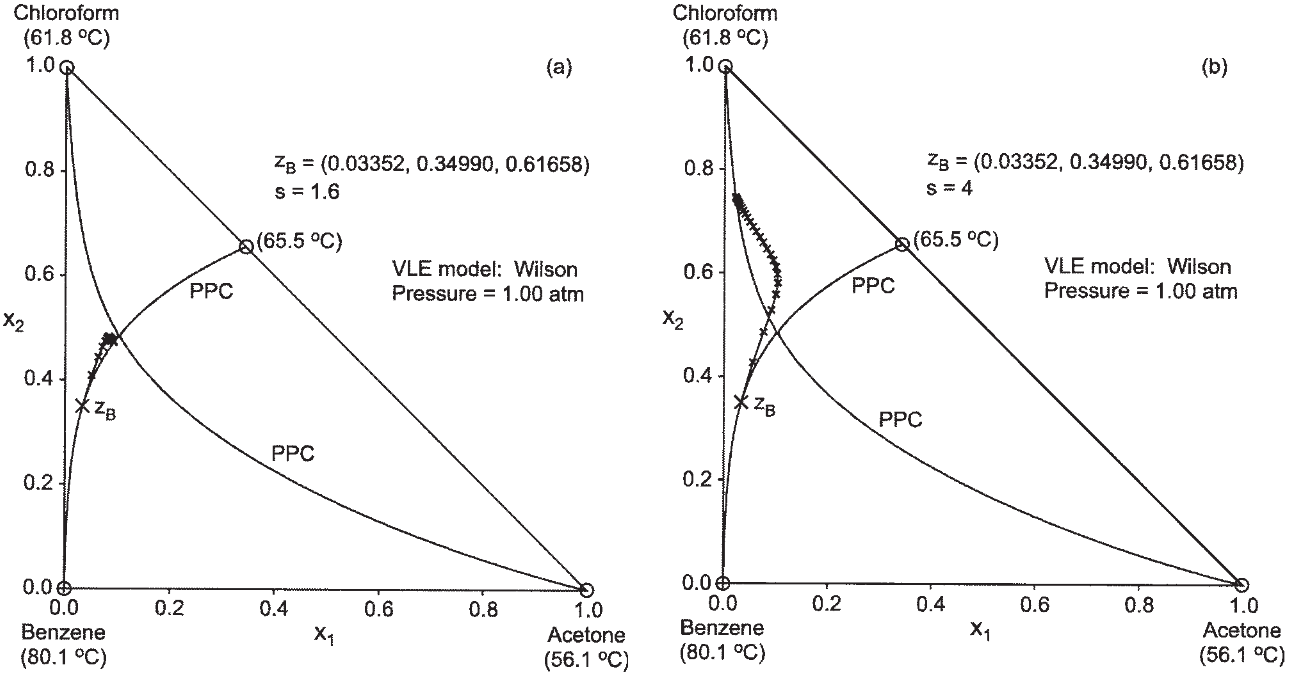

Figure 5. Limiting case of pinch-point curve and stripping profiles for staged column.
(a) s = 1.6, (b) s = 4.0.

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 Figures 5a and b). If the value of reboil ratio increases, the pinch point moves smoothly from the product branch to the additional branch. Each of the profiles is situated entirely above the product branch.

A set of pitchfork solutions is obtained, as the value of τ is changed, from the following relation (see Davydyan et al.[24]):

$$\tau(\boldsymbol{x} - \boldsymbol{y}) + (1 - \tau)det(\boldsymbol{Y})\boldsymbol{Y}^{-1}(\boldsymbol{x} - \boldsymbol{y}) = 0 \tag{4}$$

where $\boldsymbol{x}$ is a pitchfork solution and $\boldsymbol{Y}$ is the Jacobian matrix $(\partial \boldsymbol{y}_k/\partial \boldsymbol{x}_l)$ of vapor–liquid equilibrium mapping $\boldsymbol{y} = \boldsymbol{y}(\boldsymbol{x})$. The set of pitchfork solutions forms a curve, which is shown in Figure 6. For each of the pitchfork solutions, corresponding product composition z_P can be calculated from Eq. 3. Those 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 pitchfork distillation boundary was introduced by Davydyan et al.[24] and is presented in Figure 6. One should note that the PDB is applicable to both staged and packed columns since their pinch equations (Eq. 3) are identical. But total reflux and simple distillation boundaries 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 Eq. 4 can be solved numerically, the initial conditions must be specified. Vectors $\boldsymbol{x} - \boldsymbol{y}$ along the pitchfork solution curve are the eigenvectors of matrix $\boldsymbol{Y} = (\partial \boldsymbol{y}_k/\partial \boldsymbol{x}_l)$ with eigenvalues

$$\lambda_1 = \frac{\tau - 1}{\tau} det(\boldsymbol{Y}) \tag{5}$$

$$\lambda_2 = \frac{\tau}{\tau - 1} \tag{6}$$

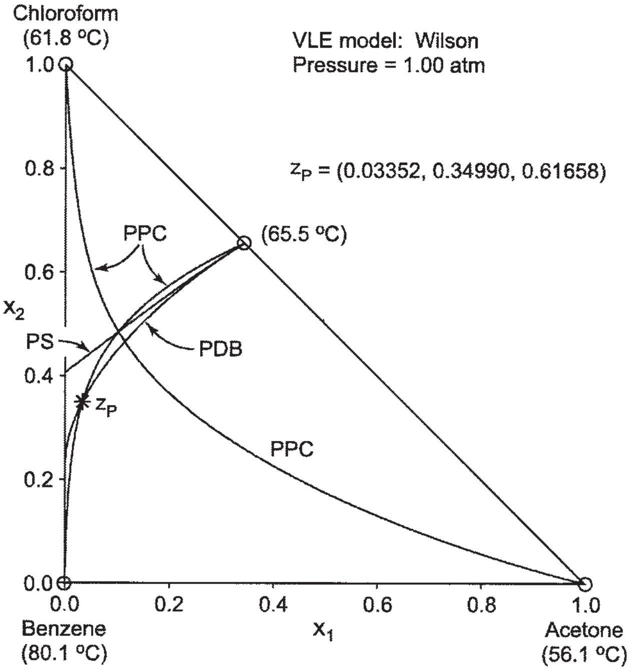

Figure 6. Pitchfork solution (PS) and pitchfork distillation boundary (PDB).

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 the appropriate eigenvalue of Y should be calculated at this point from Eq. 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. The general relations will be illustrated for the same (as above) mixture of acetone, chloroform, and benzene. The PPC's shape for this mixture depends on the location of the product composition point, as was shown above. If the product composition is located between the total reflux boundary and the pitchfork distillation boundary, 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 Figure 7), which lies in the unstable part of the PPC'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 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 (Figure 8). 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 PPC 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.

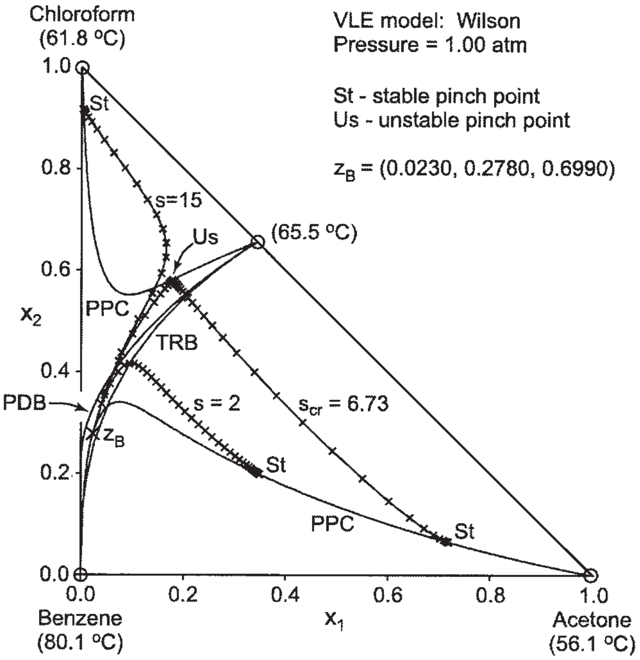

Figure 7. Behavior of stripping profiles for staged column when z_B lies between TRB and PDB.

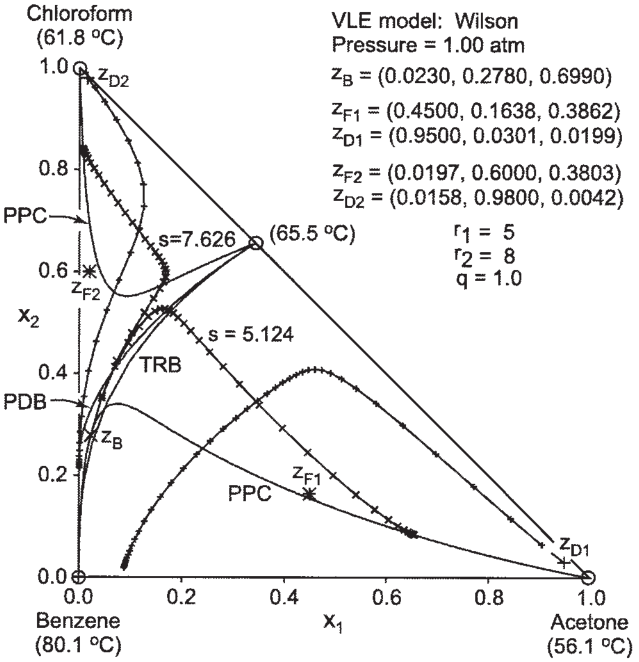

Figure 8. Distillation profiles for common bottom composition z_B and two distillate compositions z_D located in different separation regions (only PPC branches for z_B are shown).

If a distillate or bottom composition is located on the concave side of the TRB (Figure 3), 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 PPC changes, but the composition profiles remain entirely on the same side of this boundary and end on the product branch that joins different nodes. In such a case, the second product composition must lie on the same side of the PDB as the first one.

Relationships Between Distillation Boundaries

For the staged column, a TRB and a PDB originating from the same saddle azeotrope mark out two distillation regions,

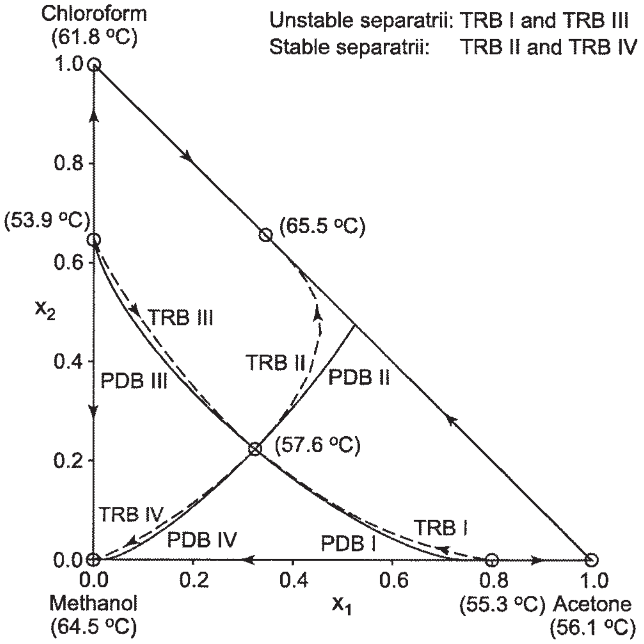

Figure 9. Distillation boundaries for ternary saddle azeotrope (TRB I and TRB III have been distorted).

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 Figure 8). 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 inquire 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, 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 Figure 9), 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, that is, the distillate composition may lie in a region on the concave side of the total reflux boundary or in 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 Figure 9, 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 Figure 10—the figure has been distorted for the purpose of clarity). The first kind of interaction occurs if a region between a total 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 dotted area in Figure 10).

The second type of interaction occurs in the common part of the two regions between certain total reflux and pitchfork distillation boundaries. The common part is bounded by TRB I, PDB I, and PDB II (the gray area in Figure 10). 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

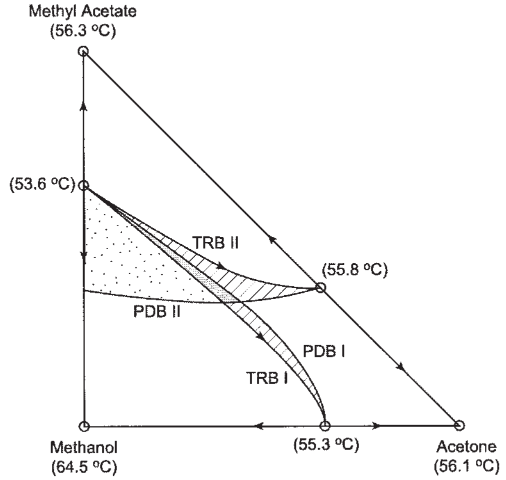

Figure 10. Interaction of boundaries (the Figure has been distorted).

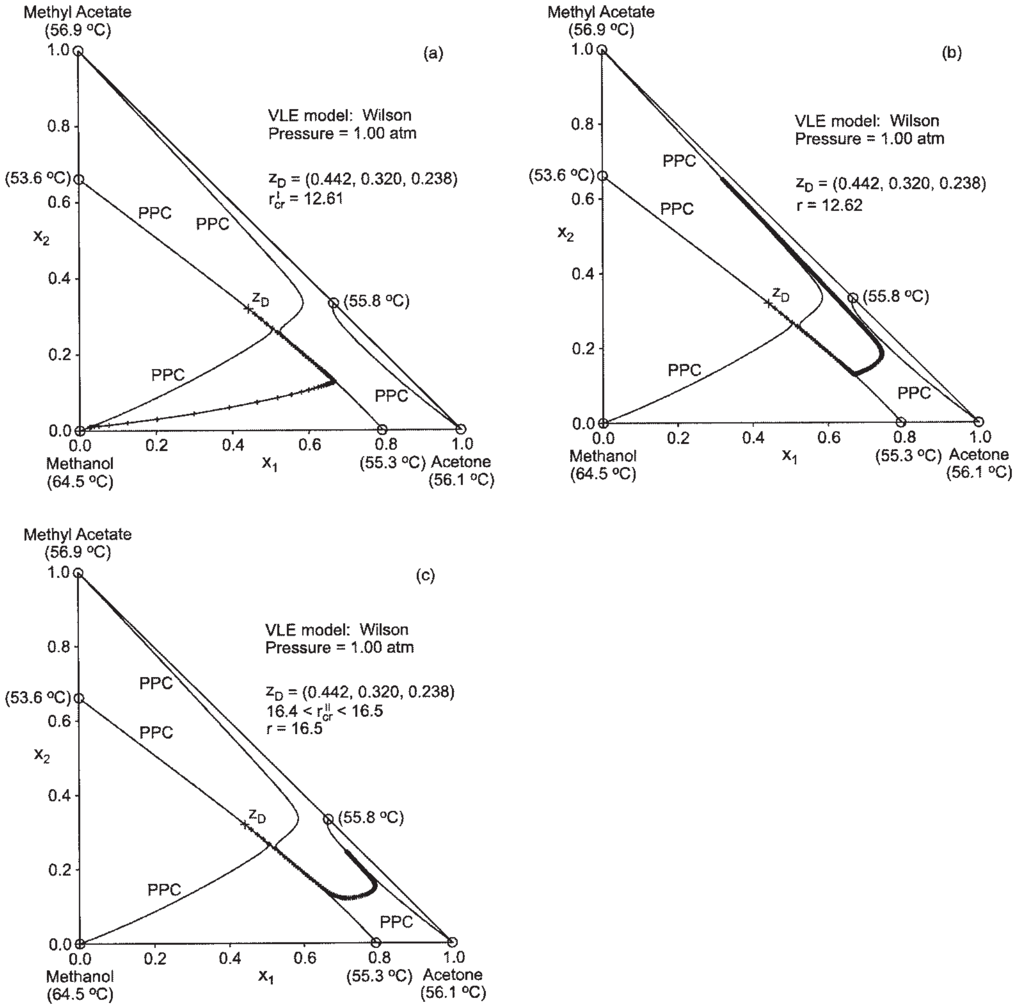

Figure 11. Rectifying profiles for acetone–methyl acetate–methanol mixture.

(a) r = 12.61, (b) r = 12.62, (c) r = 16.5.

values of the reflux ratio, as shown in Figures 11a-c. For a critical reflux ratio value $r_{cr}^{I} = 12.61$, the rectifying profile jumps from the product branch to the additional branch that joins the pure methyl acetate 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 that 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 a total reflux 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 the 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

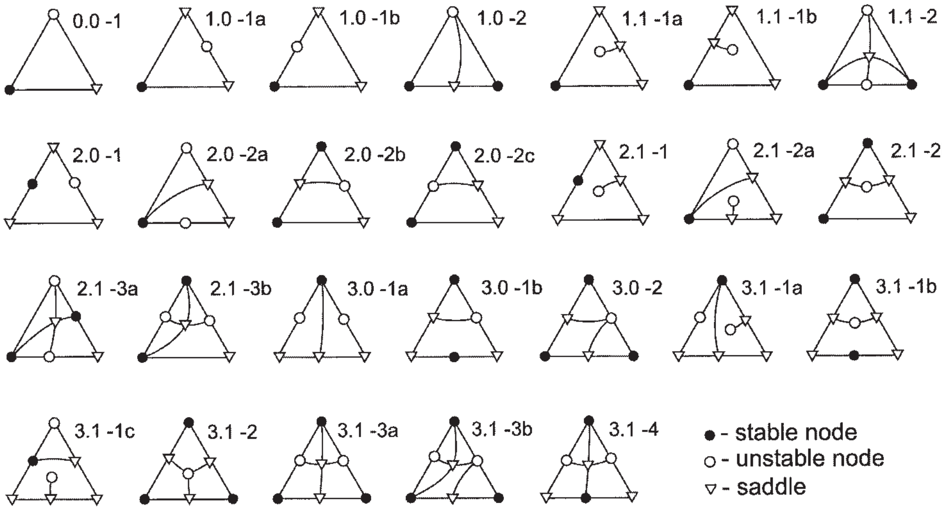

Figure 12. Serafimov's classification of structures of VLE diagrams.

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 the 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 to those 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 that 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.

In the literature, the term "distillation region" means a subspace of the composition space defined by a family of distillation lines that join a stable and unstable node. A distillation region founded with the aid of the presented rules does not fulfill the requirements of the above definition, and we shall call it a "primary distillation region."

Algorithm to Determine the Primary Distillation Regions

Rules for distillation regions and Serafimov's classification of structures of VLE diagrams[35] (see Figure 12) make it possible to formulate an algorithm to determine the primary distillation regions for ternary mixtures. Serafimov's classification does not distinguish between antipodal structures that are formed by exchange stable and unstable nodes and change the direction of residue curves. Structures of the residue curve map and distillation line map can be represented by graphs. In that case, pure component and azeotrope points correspond to graph vertices, whereas segments of the composition space border and distillation boundaries, which connect pure component and azeotrope points, correspond to graph edges. This representation allows using basic notions of graph theory and, in effect, simplifies both algorithm description and its computer implementation. Algorithms to determine the distillation regions for individual column type differ in used distillation boundaries (TRB for stage column and SDB for packed column).

In the case of a staged column, an algorithm can take the following form:

(1) If a mixture contains saddle azeotropes, go to step 3.

(2) The whole composition space constitutes a primary distillation region (the mixture is of class 0, 1.0–1a, 1.0–1b, or 2.0–1). The algorithm ends.

(3) For all saddle azeotropes find TRB_i ($i = 1, 2, \ldots, n_S$, where $n_S = n_{BS} + 4n_{TS}$, n_{BS} is the number of binary saddle azeotropes, and n_{TS} is the number of ternary saddle azeotropes).

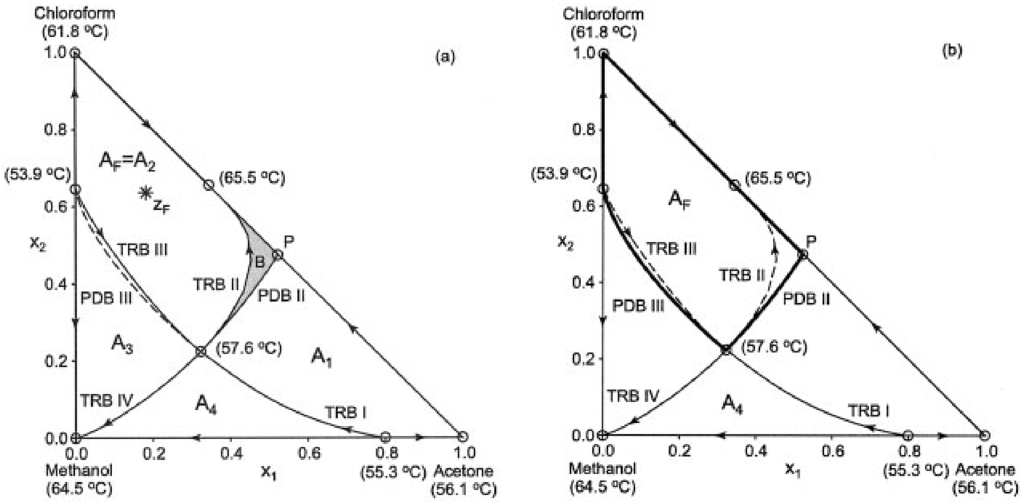

Figure 13. Determination of the primary distillation region (Example 1, $z_B \in A_2$).

(a) Common part of distillation regions A_1 and A_2, (b) the border of the primary distillation region. TRB III has been distorted.

(4) Find all distillation regions A_j ($j = 1, 2, \ldots, m$) determined by TRB_i ($i = 1, 2, \ldots, n_S$) and the composition space border. Use the algorithm described by Rooks et al.[36]

(5) From among the regions A_j pick a region (let's call it A_F) that contains the feed composition point z_F.

(6) If the border of A_F does not contain any TRB_i then A_F is a primary distillation region (e.g., a mixture of class 1.1–1a). The algorithm ends.

(7) If there exists such TRB_i that is contained in the border of A_F and joins two saddle azeotropes (a mixture of class 3.1–3a), then the algorithm cannot determine a primary distillation region. The algorithm ends.

(8) For each TRB_i that belongs to the border of A_F, determine corresponding PDB_i and perform the following operations:

(a) If PDB_i and TRB_k (which is different from TRB_i) intersect, add their intersection point P to the set of graph vertex. Then add a part of PDB_i, lying between intersection point P and the azeotrope point (which creates that boundary), to the set of graph edges. Go to step d.

(b) If PDB_i and the border of composition space intersect at a point P (which is not a pure component or node azeotrope point), add the intersection point to the set of graph vertex. Then add the PDB_i to the set of graph edges. Go to step d.

(c) Add PDB_i to the set of graph edges. Go to step e.

(d) From the set of graph edges, remove the edge that has been divided by intersection point P (i.e., TRB_k or a segment of the composition space border). Then add both parts of the divided edge to the set of graph edges.

(e) In modified graph find the circuit of the shortest length (definition of a circuit is given in the Appendix) that contains TRB_i and corresponding PDB_i or the part of PDB_i. A subset B of composition space bounded by that circuit is a common part of two distillation regions.

(f) If A_F does not contain the common part B, add B to A_F, i.e., $A_F = A_F \cup B$.

(9) A_F is the calculated primary distillation region. The algorithm ends.

Determination of primary distillation regions relies on modification of distillation regions (marked out by distillation lines) or residue curve regions, which may be found for mixtures with any number of components (Rooks et al.[36]). Therefore, it should be possible to generalize the presented algorithm (which is limited for ternary systems) for multicomponent mixtures. The algorithm performance will be presented for mixtures of two different classes.

Example 1. Mixture of acetone–chloroform–methanol (class 3.1–4)

We start from step 1. Because our mixture has ternary saddle azeotrope, we go to step 3 and find four TRB. Doing step 4 we get four regions A_i. Then we go to step 5 where we chose a region (let's denote it as A_F) containing feed composition point z_F (see Figure 13a). Step 6 is skipped because the border of region A_F contains TRB II and TRB III. Step 7 is also omitted since both TRB II and TRB III join ternary saddle azeotrope and binary node azeotrope. On the other hand, step 8 is performed twice. In the first place, for TRB II, corresponding PDB II is determined. Step a is disregarded because PDB II does not intersect any TRB_k. We go to step b. PDB II and the border of composition space intersect at a point P (see Figure 13a). We add the point P to the set of graph vertex and PDB II to the set of graph edges. Next, go to step d. A segment determined by acetone and acetone–chloroform azeotrope points is removed from the set of graph edges. On the other hand, two segments determined by acetone and P points and acetone–chloroform azeotrope and P points are added to the set of graph edges. We go to step e. A circuit of the shortest length that contains TRB II and PDB II represents the border of common part B of two distillation regions. Let us go to step f. Set B is not a subset of A_F; therefore, we add B to A_F, i.e., $A_F = A_F \cup B$. We repeat step 8 for TRB III. After doing it, A_F is the calculated primary distillation region (see Figure 13b). The algorithm ends.

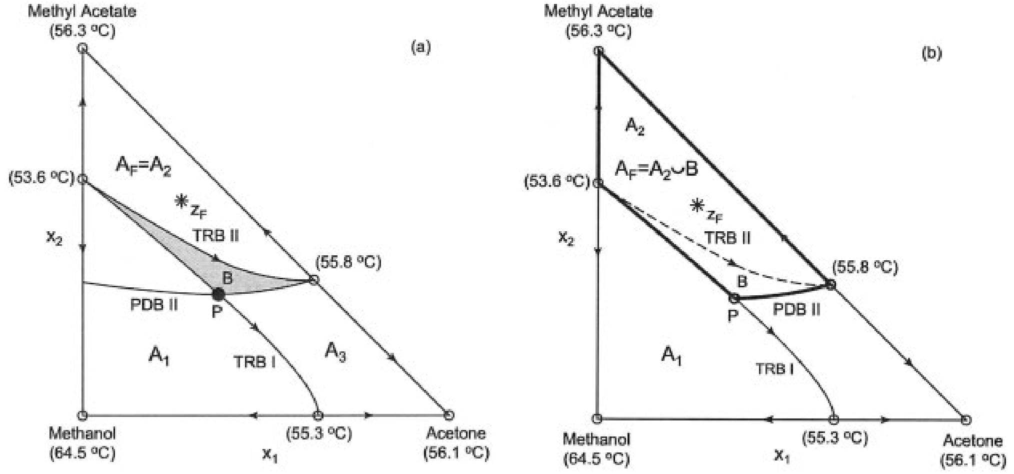

Figure 14. Determination of the primary distillation region (Example 2, Case A, $z_B \in A_2$).

(a) Common part of distillation regions A_2 and A_3, (b) the border of the primary distillation region. The figures have been distorted.

Example 2. Mixture of acetone–methyl acetate–methanol (class 3.0–2)

Case A

The mixture contains two binary saddle azeotropes. Therefore, from step 1 we go to step 3 and find two TRB. Doing step 4, we get three regions A_i. Then we go to step 5 where we chose a region (let's denote it as A_F) containing feed composition point z_F (see Figure 14a). Step 6 is skipped because the border of region A_F contains TRB II. Step 7 is also omitted since TRB II joins binary saddle azeotrope and binary node azeotrope. Now we perform step 8. Only TRB II belongs to the border of A_F. PDB II corresponding to TRB II is determined. Because PDB II and TRB I intersect at point P (see Figure 14a), we go to step a. The intersection point P is added to the set of graph vertex. The part of PDB II that lies between intersection point P and acetone–methyl acetate azeotrope point is added to the set of graph edges. We go to step d. TRB I is removed from the set of graph edges. The two parts of divided (by the intersection point P) TRB I are added to the set of graph edges. We go to step e. The circuit of the shortest length that contains TRB II and the part of PDB II (which lies between intersection point P and acetone–methyl acetate azeotrope point) represents the border of common part B of two distillation regions. Let us go to step f. Set B is not a subset of A_F; therefore, we add B to A_F, i.e., $A_F = A_F \cup B$. A_F is the calculated primary distillation region (see Figure 14b). The algorithm ends.

Case B

The initial steps of the algorithm are identical to those in Case A. For this reason we omit them and begin the description from step 5. We select a region containing a feed composition point z_F (i.e., A_3 in Figure 15a) and denote it as A_F. Step 6 is omitted because the border of region A_F contains two distillation boundaries: TRB I and TRB II. Step 7 also is skipped since both TRB I and TRB II join binary saddle azeotrope and binary node azeotrope. On the other hand, step 8 is performed twice. In the first place, for TRB I, corresponding PDB I is determined. Step a is disregarded because PDB I does not intersect any TRB_k. Similarly, step b is omitted since PDB I ends in

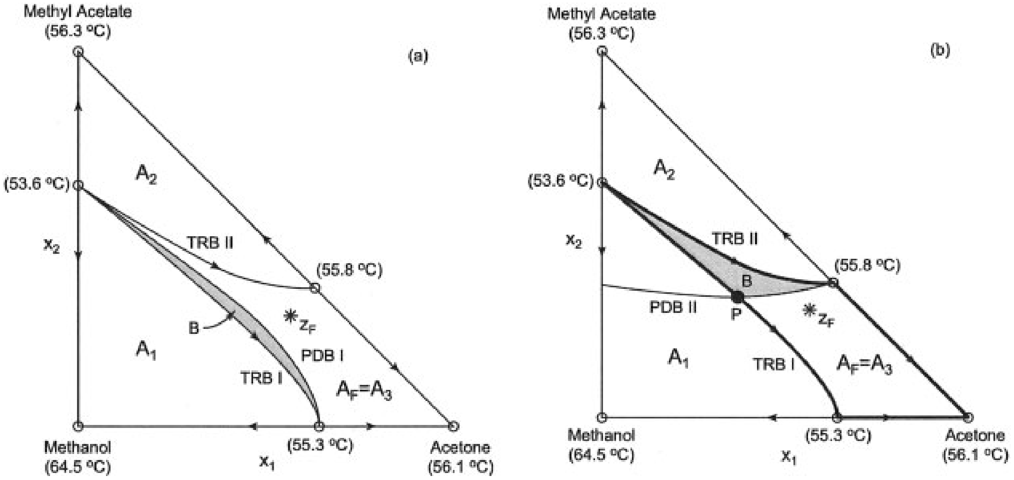

Figure 15. Determination of the primary distillation region (Example 2, Case B, $z_B \in A_3$): common part of distillation regions.

(a) A_1 and A_3, (b) A_2 and A_3. The Figures have been distorted.

methyl acetate–methanol azeotrope point. We go to step c. PDB I is added to the set of graph edges. Next, go to step e. A circuit of the shortest length that contains TRB I and PDB I represents the border of common part B of two distillation regions. Let us go to step f. Set B is a subset of A_F; therefore, A_F remains unchangeable. We repeat step 8 for TRB II. Respective steps are exactly the same as in Case A except for step f, where set B is a subset of A_F and A_F is not changed again (see Figure 15b). Consequently, the primary distillation region is identical with distillation region A_3. The algorithm ends.

Summary

A composition profiles behavior classification method for mixtures with azeotropes has been developed. It consists of 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 that 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 binary azeotrope cases and a few additional rules. Characteristics of distillation boundaries and behavior of distillation profiles have provided facilities for formulating an algorithm to determine the primary distillation regions for ternary mixtures. The distillation regions obtained from the algorithm can be used for calculating the exact bounds for product composition.

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Notation

$\boldsymbol{I}$ = identity matrix
h = dimensionless height of packing in column section
q = feed quality
r = reflux ratio
s = reboil ratio
$\boldsymbol{x}$ = vector of mole fractions in liquid phase
$\boldsymbol{y}$ = vector of mole fractions in vapor phase
$\boldsymbol{Y} = (\partial \boldsymbol{y}_k/\partial \boldsymbol{x}_l)$ = Jacobian matrix of vapor–liquid equilibrium mapping $\boldsymbol{y} = \boldsymbol{y}(\boldsymbol{x})$
$\boldsymbol{z}$ = vector of mole fractions in product

Greek letters

λ = eigenvalue of Jacobian matrix $\boldsymbol{Y} = (\partial \boldsymbol{y}_k/\partial \boldsymbol{x}_l)$
$\tau = -r$ or $s + 1$, parameter

Subscripts

$\boldsymbol{B}$ = bottom
$\boldsymbol{D}$ = distillate
h = dimensionless height of packing in column section
i = initial
j = stage number
k = component number
l = component number
$\boldsymbol{P}$ = product
cr = critical value

Superscripts

I *and* II = numbers of related pairs of distillation boundaries

Acronyms

CMO = constant molar overflow
PDB = pitchfork distillation boundary
PPC = pinch-point curve
PS = pitchfork solution
SDB = simple distillation boundary
TRB = total reflux boundary
VLE = vapor–liquid equilibrium

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Appendix: Definition of a Circuit

An undirected graph G = (V, E) consists of a finite set V of vertices and a finite set E of edges. A "circuit" in a graph G = (V, E) is a finite alternating sequence of vertices and edges v_0, e_1, v_1, e_2, . . . , v_{k-1}, e_k, v_k satisfying the following conditions:

(1) All edges begin and end with vertices such that v_{i-1} and v_i are the end vertices of the edge e_i, $1 \leq i \leq k$,

(2) All edges are distinct ($e_i \neq e_j$ for $i \neq j$),

(3) Vertices $v_0, v_1, \ldots, v_{k-1}$ are distinct from one another ($v_i \neq v_j$ for $i \neq j$ and $i, j < k$),

(4) End vertices v_0 and v_k are the same vertex ($v_0 = v_k$)

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