Feasibility of Separations for Distillation of Nonideal Ternary Mixtures

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The product compositions in single-feed distillation columns can be specified only in certain regions of the composition space, which depend only on the pressure, feed, and vapor-liquid equilibrium for the mixture. In nonideal mixtures, even without azeotropes, the regions may allow unusual product distributions. For example, the distillate in a "direct split" is composed primarily of the lightest component. Intuition and experience with relatively ideal mixtures suggest that the next most plentiful component is the intermediate boiler. In nonideal mixtures, however, with or without azeotropes, the next most plentiful component may be the highest-boiling species with only trace amounts of the intermediate boiler. For azeotropic mixtures, distillation boundaries may give rise to additional restrictions on the product compositions. We describe how simple distillation boundaries deform into continuous distillation boundaries and, in a limited number of cases, how the simple distillation boundaries can be crossed in continuous columns for certain ranges of the design variables. Unfortunately, such designs may be quite sensitive to model uncertainties or to disturbances in the parameters.

Introduction

The most important issue in designing a chemical process is *feasibility*. A design is usually performed by solving a mathematical model of the process which is normally subject to constraints such as nonnegative flow rates and mole fractions, upper bounds on temperature because of thermal degradation, on pressure, or on the cost of the design. Some constraints are subtler than these, and it is necessary to assess process feasibility *before* the design specifications are made. This, however, is not always a simple task. The worst scenario is that after extensive and lengthy simulations one discovers that the desired specifications cannot be met, and significant changes must be made to the flowsheet structure to achieve the process goals.

Until recently, distillation systems for all, but the simplest, mixtures were designed often by performance or "rating" simulations, where all the input variables such as feed flow rate, composition and thermodynamic state and process parameters such as pressure, number of stages, feed stage, reflux and reboil ratio are specified, and the compositions and flows of the products are calculated. This technique is very robust for simulating the performance of an existing column. For design purposes, however, it requires estimation of process parameters, and usually the Fenske-Underwood-Gilliland approach is used to compute the minimum reflux ratio and minimum number of stages, which is not applicable for nonideal mixtures.

A more widely applicable design algorithm for ternary mixtures, known as the "Boundary Value Design Procedure" (Levy et al., 1985), can be used to find the number of stages in a column when the reflux ratio and product compositions are specified. A related geometric approach to minimum reflux calculations and design (Julka and Doherty, 1990) enables us to estimate, with high accuracy, the minimum reflux ratio and rapidly compute a spectrum of column designs (with various numbers of stages and feed stage locations) that satisfy the given specifications on product purities. These methods, together with the use of a continuation technique to track branches of fixed points (pinches) and the application of bifurcation analysis for tangent pinches provide convenient and robust tools for solving the design problem *explicitly* (Fidkowski et al., 1991).

It is well known that not all splits are possible even for an ideal mixture. For example, when a ternary mixture of say A, B and C is being separated, where components are arranged in decreasing order of volatilities, one cannot obtain pure intermediate component B in a simple distillation column nor is it possible to obtain a mixture of A and C. This statement seems to be so trivial that no exact proof was ever necessary, and specifications for high-purity splits of ideal mixtures can be made according to boiling points. Some problems arise in the case of sloppy splits of ideal mixtures for which the feasible ranges of product compositions are not so obvious. On the other hand, sequences performing sloppy splits can be much more efficient than conventional sharp-split sequences (Westerberg, 1985). A lot more difficulties are encountered in nonideal mixtures, where the volatilities can vary to such an extent that the "order" of components changes locally. This may seriously affect a procedure that attempts to synthesize a separation system.

For synthesis of nonideal systems, the state of the art is summarized in two recent articles. Foucher et al. (1991) presented a global topological analysis of the structure of residue curve maps that can be used to determine feasible regions of operation (in composition space) for azeotropic distillation of ternary mixtures. Knowledge of these regions is very useful for column sequencing, but they do not contain complete information about product compositions that is necessary for design. Therefore, this approach gives only sufficient conditions for a separation to be feasible and has been discussed by others such as Rev (1992). The much more general approach of Wahnschafft et al. (1991) provides a useful synthesis tool for the development of nonideal separation systems, but again provides no guidance on the existence and extent of feasible separation regions.

The aim of this work is to describe a systematic method for the determination of feasible product composition regions (*separation regions*) for the distillation of ternary mixtures in a single-feed distillation column for any reflux ratio and any number of stages.

Total Reflux Separation

It is convenient to begin with the case of total reflux, which has been discussed previously by Van Dongen (1983) and by Laroche et al. (1992).

For staged columns at total reflux, passing streams have equal composition and the liquid composition profiles can be determined from the mass-balance equations:

$$x_j = y_{j+1} \tag{1}$$

together with an equilibrium relation:

$$y_j = f(x_j) \tag{2}$$

Equation 1 requires an initial condition. For example, calculations for $j \geq 1$ can be started from the bottom of the column, where $x_0 = x_B$. Alternatively, the system can be solved backward from the top of the column down where the liquid composition on the top stage, x_N is chosen to satisfy $y(x_N) = x_D$. The latter is the most common convention for making residue curve maps because this proceeds in the direction of increasing temperature; this direction is indicated by arrows in subsequent figures.

Equation 1 is equivalent to:

$$\frac{x_{j+1} - x_j}{\Delta\xi} = x_{j+1} - y_{j+1} \tag{3}$$

for $\Delta\xi = 1$; for the staged columns ξ denotes a stage number. Equation 3 is a finite difference approximation of:

$$\frac{dx}{d\xi} = x - y \tag{4}$$

Here, we can assign two meanings to ξ (see also Laroche et al., 1992; Julka, 1993):

(1) ξ may be defined as the dimensionless height of a packed column. In this case, the solutions of Eq. 4 are the profiles in a packed column at total reflux.

(2) ξ may also be defined as the dimensionless time for an open evaporation process. In this case, the solutions of Eq. 4 are the simple distillation residue curves.

Therefore, liquid composition profiles, in a staged column at total reflux, can be approximated by simple distillation residue curves. The difference between these two types of curves is determined by the accuracy of the differential approximation, Eq. 4, of the finite difference model in Eq. 3. Julka (1993, Appendix B) has shown that the discrete and continuous problem formulations for the steady-state operation of a multicomponent distillation column are topologically equivalent and that all geometric results can be obtained using either approach. We shall assume that differences between these types of curves are negligible unless stated otherwise. This assumption is completely incidental to our arguments and can be abandoned without difficulty. A comparison of the residue curve map with the finite difference map is shown in Figure 1 for the system acetone, chloroform and methanol. [The vapor-liquid equilibrium (VLE) data for all the examples are collected in Table 1.] In this map, acetone and chloroform are saddles, and methanol is a stable node. The maximum-boiling

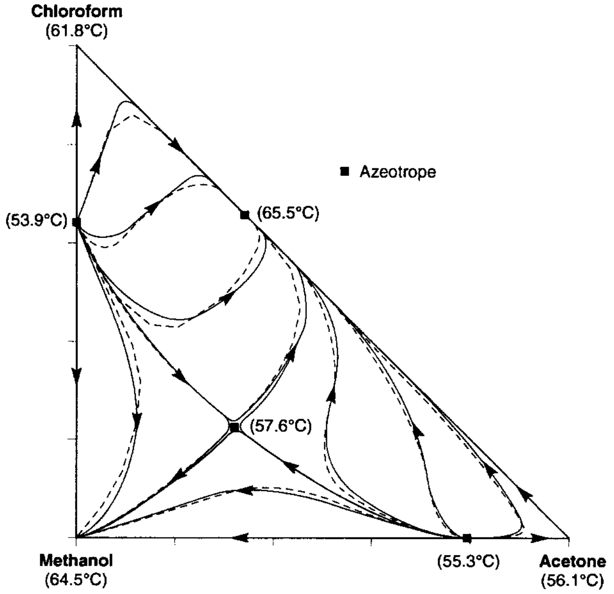

Figure 1. Residue and finite difference curves for a mixture of acetone, chloroform and methanol at a pressure of 1 atm.

Table 1. Examples and Sources of Data for the Vapor-Liquid Equilibrium Parameters*

Mixture	Pres. atm	Model	Model Parameters Ref. or Data	Figure
1) Acetone 2) Chloroform 3) Methanol	1.0	Wilson Equation	Vol. I/2e, p. 17 Vol. I/2e, p. 75 Vol. I/3+4, p. 128	1
1) A 2) B 3) C	–	Constant Volatility	$\alpha_{AC}=4$ $\alpha_{BC}=2$	3-7
1) Acetone 2) B 3) Water	2.0	Wilson for 1-3; 1-2 and 2-3 obey Raoult's law	Vol. I/1b, p. 153	8-12
1) Acetone 2) Chloroform 3) Benzene	1.0	Wilson Equation	Vol. I/3+4, p. 128 Vol. I/3+4, p. 209 Vol. I/7, p. 72	2b 16-24
1) Ethanol 2) Water 3) Ethylene Glycol	1.0	Wilson Equation	Vol. I/1, p. 165 Vol. I/1b, p. 127 Vol. I/2c, p. 297	14-15
1) Acetaldehyde 2) Methanol 3) Water	1.0	Margules Equation (parameters in K)	$M_{12}=-316.699$ $M_{21}=-384.657$ $M_{13}=350.100$ $M_{31}=290.200$ $M_{23}=307.000$ $M_{32}=143.000$	13

*Ideal behavior in the vapor phase was assumed in all calculations and the Antoine equation for vapor pressure along with activity coefficient models were used to describe the liquid phase. The volume, part, and page numbers refer to the data collection by Gmehling et al. (1977, 1979, 1980, 1982, 1988), where the form used for the Wilson and Antoine equations can also be found. The form of the Margules equation is $T \ln \gamma_k = \Sigma_i M_{ki} x_i^2 + 2\Sigma_i M_{ik} x_i x_k - 2\Sigma_i \Sigma_j M_{ij} x_i x_j^2$

acetone-chloroform azeotrope is also a stable node, while the other two binary azeotropes are unstable nodes. The ternary azeotrope is a saddle.

At total reflux, the feed and product flow rates are zero, but it is convenient to consider an asymptotic case where these flow rates are vanishingly small. Since the feed flow rate is infinitesimally small, the location of the feed stage is not relevant and the column can be treated as either a stripper or a rectifier. The liquid compositions throughout the column have to be located on the same residue curve. The composition of the distillate corresponds to a vapor in phase equilibrium with a liquid on the top stage in the column and lies on the vapor boil-off curve corresponding to the residue curve. Since the feed and product compositions are collinear on account of the lever rule, the situation is as shown in Figure 2a. (Also see Van Dongen, 1983, p. 104.) The design procedure for total reflux is quite simple. Knowing the feed composition, z^F, and the composition at the bottom of the column, x^B, a trajectory of solutions for Eq. 1 can be computed. As a result, we obtain the (minimum) number of stages required for this separation ($N=N_{\min}$) and the distillate composition. More than two intersections are possible when the residue curves have inflections as shown in Figure 2b. This situation corresponds to total reflux and reboil in two different columns, one with a larger number of stages. When the feed composition, feed quality and pressure are known, there remain four degrees of freedom in a design problem at finite reflux (Fidkowski et al., 1991). At total reflux, both the reflux, *and* the reboil ratios are indefinitely large, and there remain *two* degrees of freedom; in the example above, we chose x_i^B, $i=1, 2$. Note that each feasible separation at total reflux can be accomplished with a finite number of stages, unless one or more of the products is specified to be exactly at a pure component or an azeotrope. In the case of constant volatility mixtures, this is equivalent to Fenske's procedure.

Finite Reflux

In the boundary value design procedure, the rectifying and stripping profiles are calculated from specified product compositions (initial conditions) up to their respective stable nodes. There are three degrees of freedom for product specifications and one for the reflux (or reboil) ratio (Fidkowski et al., 1991). Typical design specifications are x_1^D, x_2^D, x_1^B, r or x_1^B, x_2^B, x_1^D, s. A design is feasible if the profiles intersect, which will not happen if the reflux ratio is too small *or too large*. The latter case of "maximum reflux" is common even in ideal mixtures and happens when the product composition specifications would require the profiles to lie on different residue curves, which is almost always the case. The existence of a maximum reflux for almost all product specifications is obvious.

Geometry of Splits at Minimum Reflux—Transition Line

Consider the isobaric separation of a ternary mixture, where the components A, B and C are ordered from the lowest to the highest boiling point (we will sometimes number these components as 1, 2 and 3 for convenience). The liquid composition profiles for a direct split (A/BC) are shown in Figure 3a, where we see that the stripping profile pinches the rectifying profile with its stable node. In this case, there are an infinite number of stages or "pinch" in the stripping section (a stable node in the stripping profile) just below the feed stage. For high-purity splits when there is a vanishingly small amount of component C in the distillate, there is *also* a pinch in the rectifying section (a saddle in the rectifying profile) above the feed stage. If the composition of component A in the bottom product is also vanishingly small, there is a third pinch (a saddle on the stripping trajectory) in the stripping section below the feed stage. We call this case a "direct geometry."

The geometry of profiles at minimum reflux for an indirect

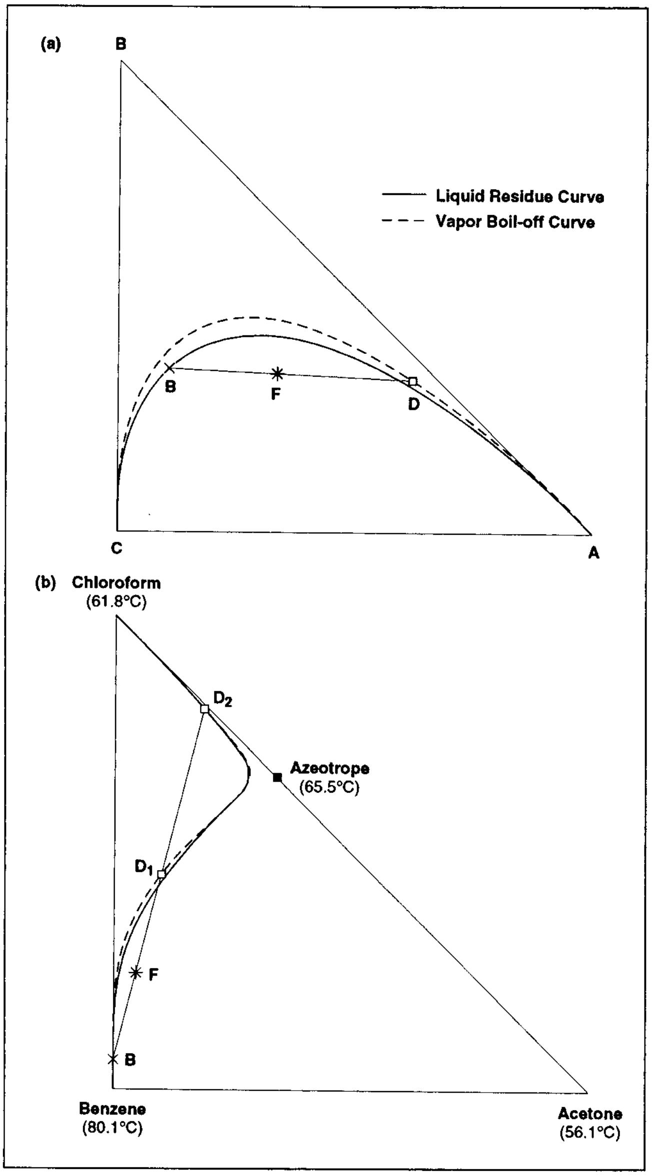

Figure 2. Total reflex separation: (a) ideal and (b) non-ideal mixture with inflectional residue curves.

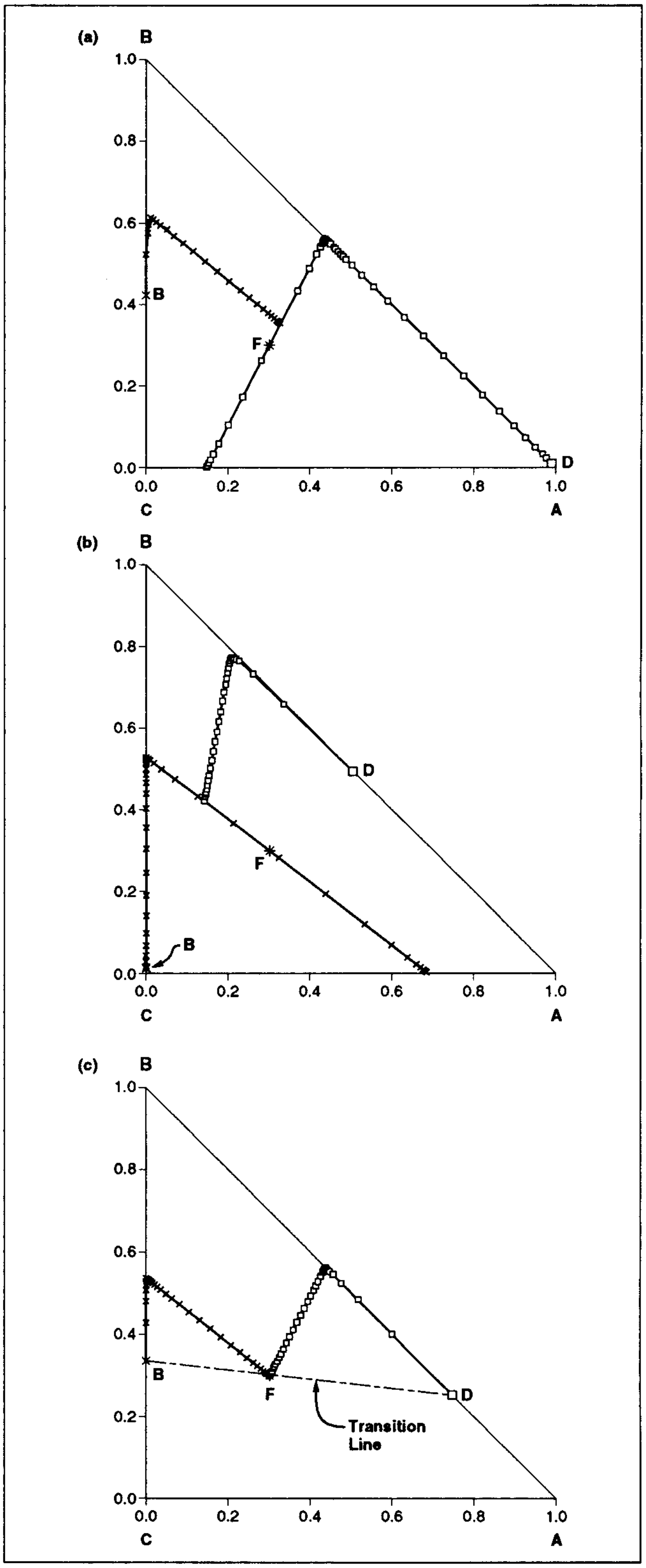

Figure 3. Liquid composition profiles at minimum reflux for (a) direct, (b) indirect and (c) transition geometry for a saturated liquid feed, $q = 1$.

split (*AB/C*) is shown in Figure 3b. In this case, the rectifying profile pinches the stripping profile with its stable node, and there are an infinite number of stages in the rectifying section in the vicinity of the feed stage. The two other regions of infinite number of stages, close to the saddles on both profiles, are also possible for high-purity splits. We will refer to this situation as the "indirect geometry."

Levy and Doherty (1986) showed that there exists a unique "transition line" which divides the direct from indirect geometry. This is called the "transition geometry" (*AB/BC*), as shown in Figure 3c. We see that at minimum reflux, for the transition split, the stable nodes of both profiles coalesce: there are an infinite number of stages in each section with two pinches at the feed stage. It is also worth noting that if the product specifications are changed continuously so that the geometry changes from direct to indirect, the minimum reflux (reboil) ratio reaches its smallest value at the transition split. This feature of the transition split has been used in optimization of complex distillation systems (Glinos and Malone, 1985; Fidkowski and Krolikowski, 1986).

From the fixed point (pinch) equation for the rectifying section (Fidkowski et al., 1991):

$$r+1=\frac{x_i^D-\hat{x}_i^r}{\hat{y}_i^r-\hat{x}_i^r} \qquad i=1,\,2 \tag{5}$$

(where $\hat{x}$ and $\hat{y}$ denote liquid and vapor mole fractions at the fixed point) we can show that the extension of the tie line at a pinch goes through the distillate composition:

$$\frac{x_1^D-\hat{x}_1^r}{\hat{y}_1^r-\hat{x}_1^r}=\frac{x_2^D-\hat{x}_2^r}{\hat{y}_2^r-\hat{x}_2^r} \tag{6}$$

Similarly, for the stripping section, the tie line at a pinch goes through the bottoms composition:

$$s=-\frac{x_i^B-\hat{x}_i^s}{\hat{y}_i^s-\hat{x}_i^s} \qquad i=1,2 \tag{7}$$

$$\frac{x_1^B-\hat{x}_1^s}{\hat{y}_1^s-\hat{x}_1^s}=\frac{x_2^B-\hat{x}_2^s}{\hat{y}_2^s-\hat{x}_2^s} \tag{8}$$

Equations 5-8 are satisfied at any pinch regardless of geometry or type of split.

At the transition split, the stable nodes for both profiles are located at the same point, namely, at the feed stage:

$$\hat{\mathbf{x}}^r=\hat{\mathbf{x}}^s=\hat{\mathbf{x}}^f \tag{9}$$

Therefore, both tie lines must coalesce with the material balance line joining $\mathbf{x}^D$, $\mathbf{z}^F$, and $\mathbf{x}^B$.

$$\frac{z_1^F-\hat{x}_1^f}{\hat{y}_1^f-\hat{x}_1^f}=\frac{z_2^F-\hat{x}_2^f}{\hat{y}_2^f-\hat{x}_2^f} \tag{10}$$

The transition line is, therefore, the line formed by extending the tie line between $\hat{\mathbf{x}}^f$ and $\hat{\mathbf{y}}^f$ up to the edges of the composition triangle. To find the coordinates of the node $\hat{\mathbf{x}}^f$ that is common to both profiles, we use Eqs. 5, 7, and 9, and the following energy balance for constant molar overflow:

$$s=(r+q)\left[\frac{x_i^B-z_i^F}{z_i^F-x_i^D}\right]+q-1 \qquad i=1,\,2 \tag{11}$$

which gives:

$$q\,\hat{\mathbf{x}}^f+(1-q)\hat{\mathbf{y}}^f-\mathbf{z}^F=\mathbf{0} \tag{12}$$

Equations 9, 10 and 12 are valid only for the transition split. Knowing the overall feed composition, $\mathbf{z}^F$, the feed quality, q, $(-\infty<q<\infty)$ and the equilibrium relation, Eq. 2, one can solve Eq. 12 for $\hat{\mathbf{x}}^f$. For $0\le q\le 1$, this is a simple adiabatic flash calculation. For a boiling liquid feed ($q=1$), both nodes coalesce at the feed composition, $\mathbf{z}^F$. Of course, there is no transition line for an azeotropic feed, since there is no separation whatsoever in this case and the tie line reduces to a point $\hat{\mathbf{x}}^f=\hat{\mathbf{y}}^f$. More information on the transition line is included in the Appendix.

For the transition split, both product compositions must lie on the transition line. If the distillate composition is located below the transition line (or the bottoms composition is above the transition line) on the composition triangle labeled as in Figure 3, we have the *direct geometry* at minimum reflux. On the other hand, if the distillate composition lies above the transition line, the profiles at minimum reflux will follow the *indirect geometry*.

For ideal mixtures, the direct geometry in Figure 3a is characteristic only for direct splits of components (A/BC) and the indirect geometry in Figure 3b always corresponds to indirect splits (AB/C). For nonideal systems, however, the order of volatilities of components may change locally in the column and *the minimum reflux geometry does not necessarily correspond to the type of split.* For example, for the direct split A/BC, the profiles at minimum reflux may form the indirect *geometry*. The type of minimum reflux geometry can be determined by comparing the locations of product compositions with the location of the transition line on the composition triangle. This does not rely on any assumption about the vapor-liquid equilibrium, and all of the conclusions about the transition split hold for ideal and nonideal mixtures alike.

Limits for Single Column Sections—Sloppy Splits

The terminology used in the literature for describing various splits is based on intuition rather than on strict definitions and can therefore cause some misunderstandings. For example, splits might be characterized as high or low purity, high or low recovery, sharp or nonsharp, sharp or sloppy, and so on. Some of these terms are used in an interchangeable way, although their meanings may not be the same for each reader. The existing terminology is not precise enough for the material presented in this work, but there is little incentive to introduce even more. We will use existing concepts and hope to define them precisely so that their usage in this article is clear.

The general problem of separating one feed stream into n products by distillation has been the subject of many publications and has been reviewed by Westerberg (1985). We deal here with the more specific case of separating a ternary mixture into two product streams. The aim of a conventional column with one feed and two products is usually to separate two "key" components. If there are more than two components in the feed, their compositions in the products depend on the equilibrium and balance relations and on the split specified between the key components. The conventional notation for splits, A/BC or AB/C is sometimes confusing; for example, all of the components in the feed will actually be present in both products although the amounts may vary by orders of magnitude. If the objective of a process is to separate components A and B, we actually make the $A(B)/(A)BC$ split. This notation means that in the distillate we have mostly component A, a small amount of component B, and practically no component C. The bottom product contains mostly components B and C, and a small amount of component A.

Simple combinatorial analysis gives eight types of splits for a ternary mixture: $A(B)/(A)BC$, $A(B)/ABC$, and so on. The type of split will depend on the product composition being either close to a pure-component vertex or located on the edge or inside the composition triangle, and it is more convenient to classify the product purities and to define the feasible choices.

When the residue curves do not have inflection points, the composition profile in a rectifier has a shape like one of those shown in Figure 4. (Note that the distillate composition is in

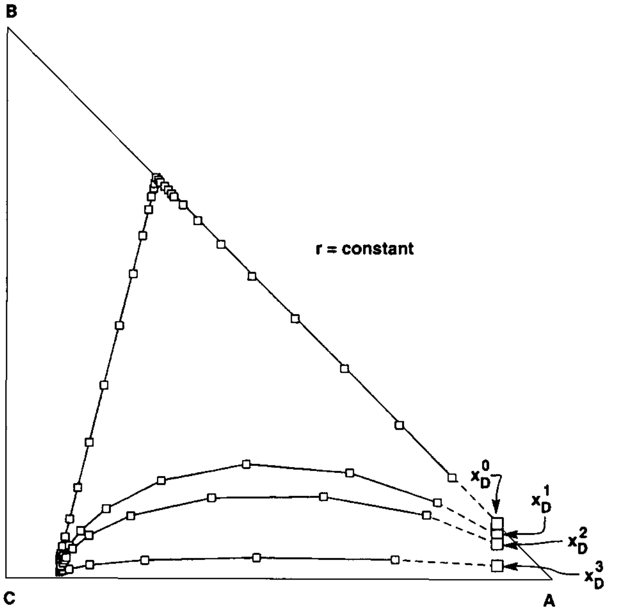

Figure 4. Rectifying profiles at constant reflux ratio; x^{D0} is a "sharp" split, while x^{D1}, x^{D2}, x^{D3} are "sloppy."

phase equilibrium with the liquid on the top stage as mentioned above for the total reflux case; this is indicated by the dashed line joining the distillate composition and the liquid composition profile.) The profile beginning at the distillate composition x^{D0} is characteristic of a "sharp" split; the subsequent profiles beginning at x^{D1}, x^{D2}, x^{D3}, correspond to situations where the separation becomes more and more "sloppy," that is, a heavier component appears in the distillate.

The composition profiles for one sloppy split are shown in Figure 5 at various values of the reflux ratio: (a) minimum, (b) maximum, and (c) above maximum. It is possible to meet the given specifications *exactly* for $x_1^{D1} = [x_1^{D1}, x_2^{D1}]$ with a finite number of stages using only a stripping section in case b. The given specifications cannot be met in case c, but a higher-purity distillate can be produced, which contains the specified mole fraction of B and a larger fraction of A than $D1$. The maximum reflux is different than the minimum, since the product purity for the key component can be exceeded at a reflux above the maximum, while it cannot be achieved for a reflux ratio below the minimum.

As the distillate composition gets richer in C at a fixed composition of A, the range of feasible reflux ratios narrows until finally, for the distillate at x^{D2} (Figure 6b) the stripping node pinches at a liquid composition in equilibrium with a vapor at x^{D2}. In this case, the minimum reflux ratio is equal to the maximum reflux, and the separation can only be accomplished using a stripper with an infinite number of stages. Furthermore, rectifying and stripping profiles never intersect for distillate specifications below x^{D2}; instead, they look like the profiles shown in Figure 6a or 6c. However, it is possible to exceed the specifications for C, that is, have less of it in the distillate, using a stripping section operated at some large but finite reflux and reboil ratios.

For a stripper with a pinch in equilibrium with the distillate composition (or for a rectifier with a pinch at the bottoms composition), we can use Eq. 8 (or Eq. 6) together with the overall material balance relating x^D, x^B and z^F to show that the tie line at the pinch goes through the feed composition:

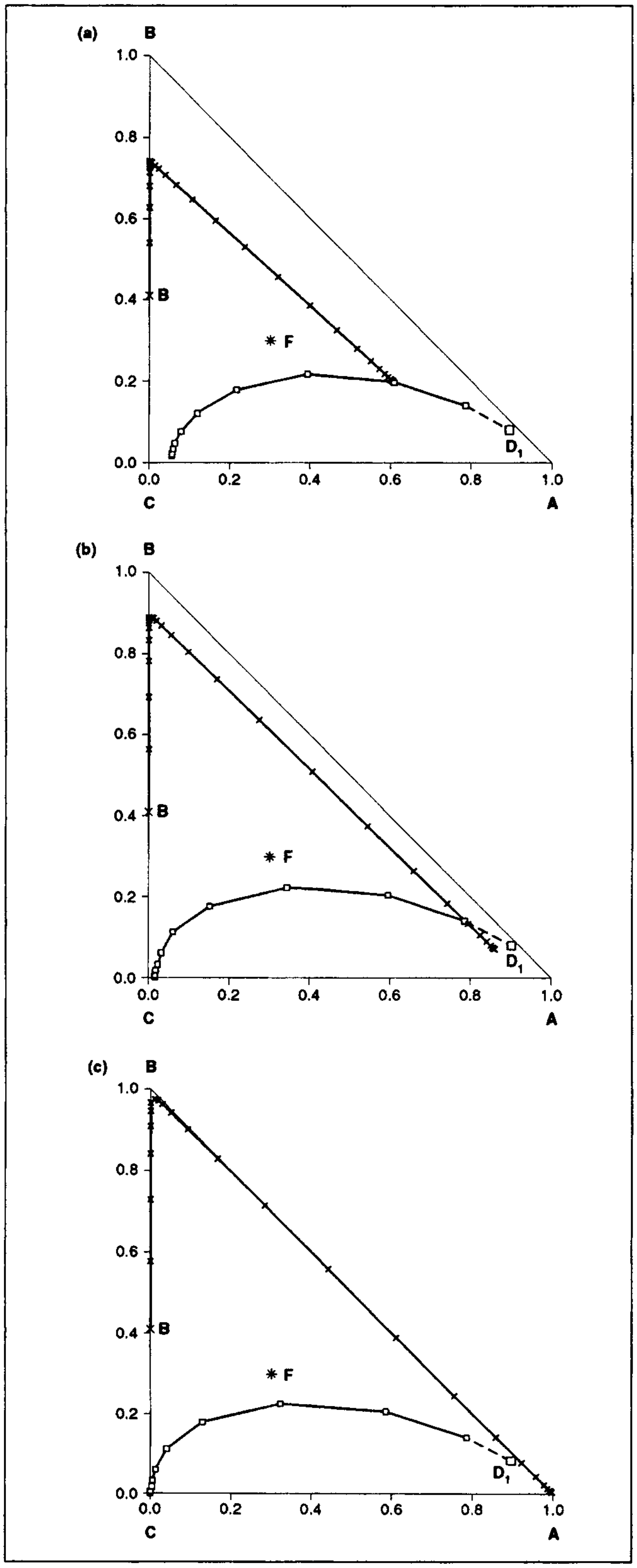

Figure 5. Liquid composition profiles for a sloppy split corresponding to composition x^{D1} in Figure 4.

The reflux ratio is (a) minimum, (b) maximum, and (c) above maximum.

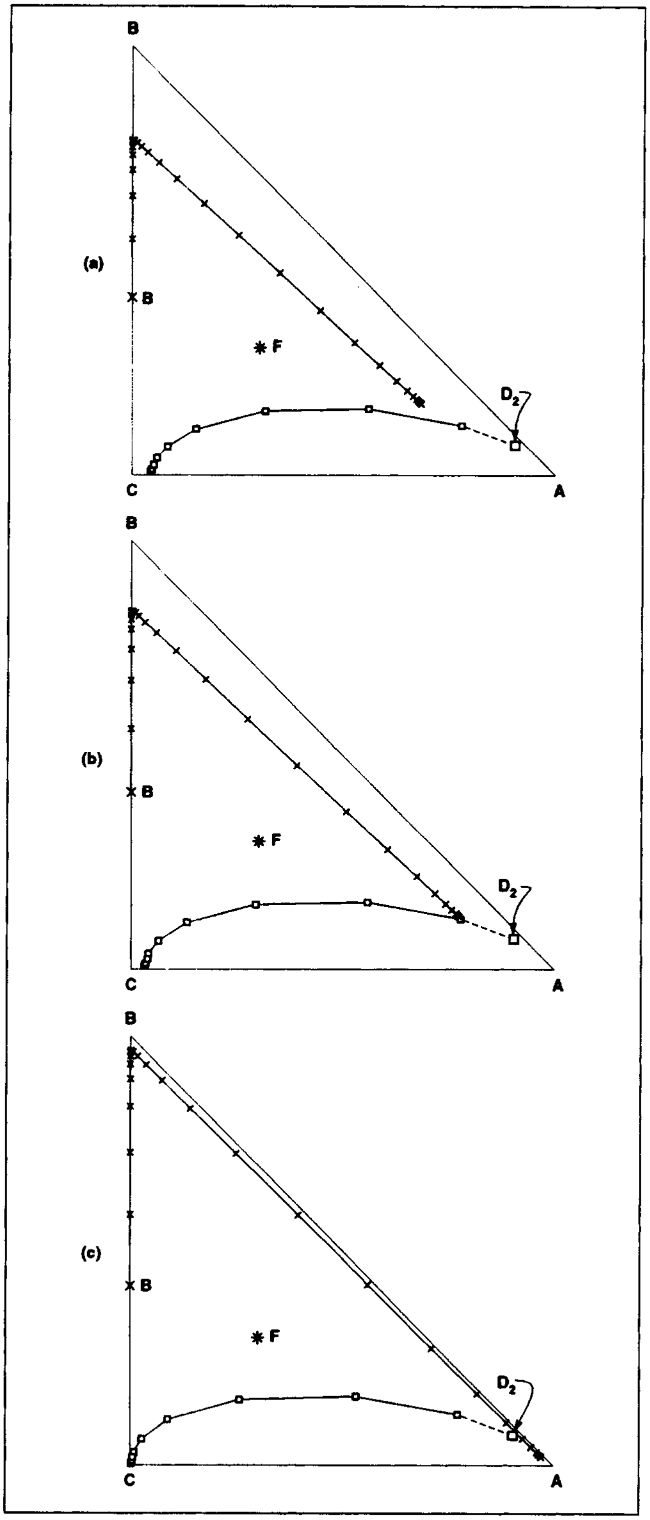

Figure 6. Liquid composition profiles for a sloppy split corresponding to composition x^{D2} in Figure 4.

The reflux ratio is (a) below minimum, (b) minimum reflux = maximum reflux, (c) above maximum.

$$\frac{z_1^F-\hat{x}_1}{\hat{y}_1-\hat{x}_1}=\frac{z_2^F-\hat{x}_2}{\hat{y}_2-\hat{x}_2} \tag{13}$$

Equation 13 can be solved for a locus of points $\hat{x}_2$ vs. $\hat{x}_1$, and Eq. 2 gives the corresponding vapors as shown in Figure 7a. These curves encompass the most sloppy splits permissible and delimit regions not accessible by distillation. The bottoms compositions are encompassed by $\hat{x}$ and the distillates by $\hat{y}$. We call this set of curves the *distillation limit*. Together with the transition line and mass balances, this determines the *separation regions*. An example is shown in Figure 7 for an ideal mixture with a saturated liquid feed and the relative volatilities given in Table 1. The distillation limit begins and ends at the nodes of the residue curve map and passes through the overall feed composition z^F and through the points $\hat{x}^f$ and $\hat{y}^f$ (See the Appendix).

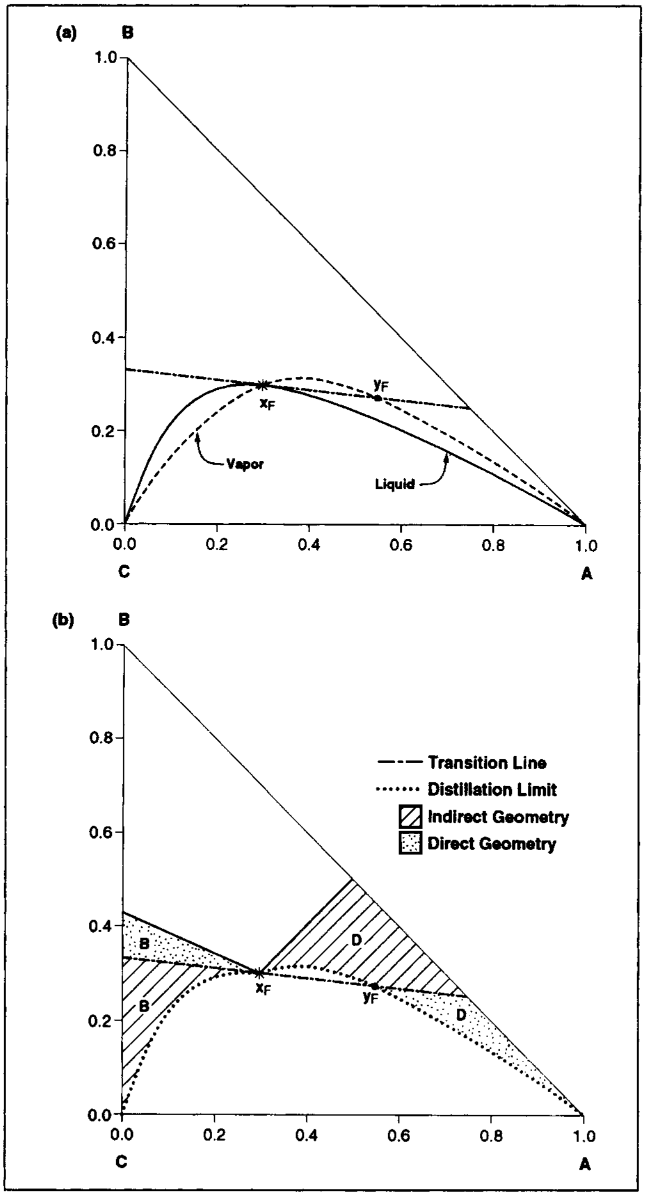

Figure 7. Feasible separation regions for constant relative volatility mixture and for saturated liquid feed $(q-1)$.

A convenient method to determine the solutions of Eq. 13 and the corresponding vapor compositions is to solve Eqs. 12 and 2 with q as a free parameter. This can be proven easily following the methods outlined in the Appendix.

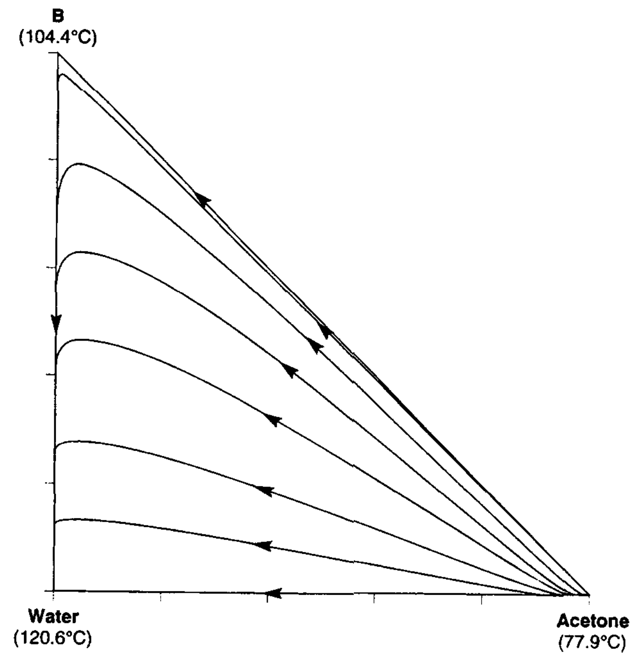

Figure 8. Residue curve map for the mixture acetone, B and water.

Nonideal Mixtures without Azeotropes

The geometry of separation regions for nonideal mixtures is similar to that for constant volatility mixtures, if the residue curves do not have inflection points. It is easiest to show what happens if there are inflections, using an example. We take this to be a ternary mixture of acetone (light component-A) and water (heavy component-*C*) with a hypothetical intermediate boiling component *B* selected to have a vapor pressure equal to that of benzene. The binary mixtures *A*-*B* and *B*-*C* are ideal (obey Raoult's law), while *A*-*C* is nonideal. The vapor-liquid equilibrium for the mixture is represented by $Py_i = p_i^{sat} x_i \gamma_i$ with the activity coefficients represented by the Wilson equation and the column pressure taken to be 2 atm (See Table 1). The Wilson parameters for the *A*-*B* and *B*-*C* mixtures are set in such a way as to make the activity coefficients equal to unity for these pairs. This sort of description commonly arises when the activity coefficient parameters are missing for some binary pairs in a multicomponent mixture. In such cases, it is common practice to assume that the "unknown" pairs obey Raoult's Law as an expedient, though this may have unexpected consequences as shown below.

The residue curves for this mixture are shown in Figure 8. In the vicinity of the pure-acetone vertex the residue curves are tangent to the *A*-*C* edge of the triangle, that is, the light-heavy side, instead of the light-intermediate side, as in ideal systems. This results in inflections of the residue curves and indicates the possibility of tangent pinches. Inflections also occur frequently in azeotropic systems, especially in four-sided regions.

The separation regions for two different feed compositions are shown in Figure 9. The regions in Figure 9a are similar to the ideal case. For the feed in Figure 9b, however, almost all splits have an indirect geometry. The slope of the transition line has also changed significantly in this case, and the line intersects the acetone-water edge instead of the acetone-*B* edge. This gives rise to the possibility of splits, in which there is an "abnormal" order of components in the distillate: acetone (lightest) and water (heaviest) with a trace amount of *B* (intermediate).

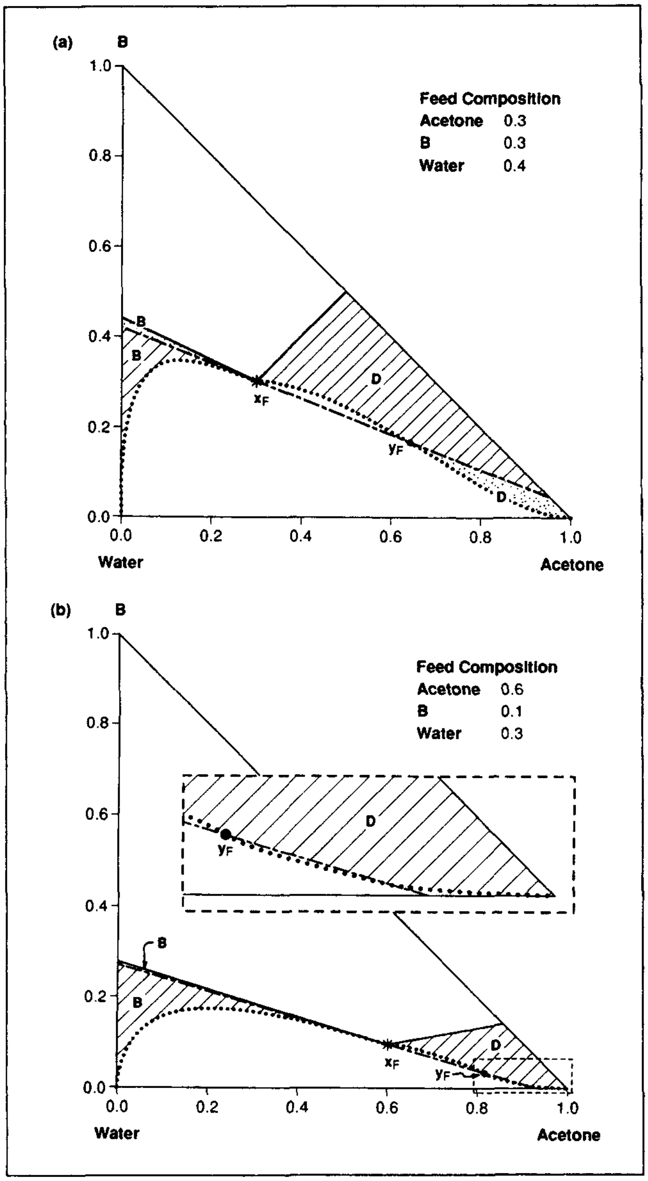

Figure 9. Feasible separation regions of a mixture of acetone, B and water for two different feed compositions ($q = 1$).

The slope of the transition line depends on the feed composition, and we can classify feed compositions depending on which edges of the triangle the transition line intersects, as shown in Figure 10. This classification gives regions of feed compositions which may result in a different order of abundance for the components in one of the products. Feeds in region I will give mostly components *A* and *B* in the distillate, while in region II there are two possibilities, distillates containing mostly *A* and *B* and distillates containing *A* and *C*. The "abnormal" order of components in one of the products is frequently encountered in the separation of azeotropic mixtures, but it is less common for nonazeotropic systems.

To confirm our analysis, we used the boundary value design

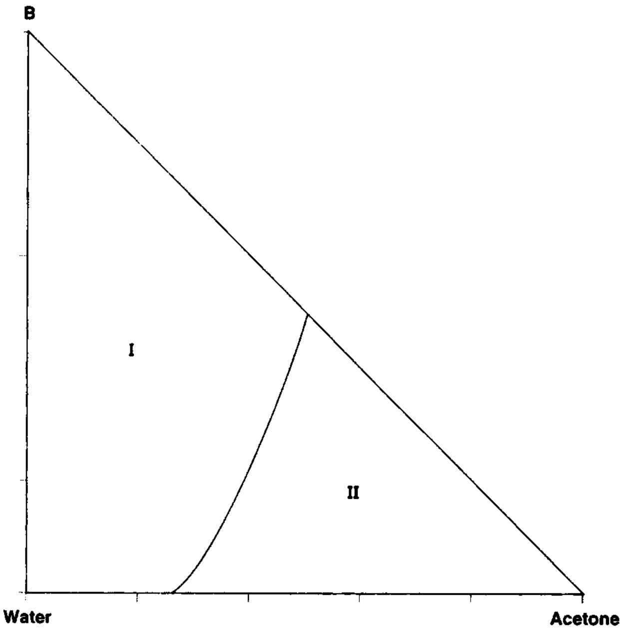

Figure 10. Regions of feed compositions: (I) transition line intersects the acetone-B and B-water edge and (II) transition line intersects the acetone-water and B-water edge.

procedure to find designs for various product compositions. Profiles beginning outside separation regions never intersected. Examples of some feasible designs are discussed below.

The separation of acetone from this mixture would conventionally be treated as a "direct" split (sometime called "lightest out first"), but the shape of profiles follows the indirect geometry, as discussed earlier. This information is essential for minimum reflux calculations and to point out the possibility of unusual product distributions. The minimum reflux can be calculated using the "Zero-Volume Method," in which turning points in the fixed-point volume, shown in Figure 11a, indicate the presence of a tangent pinch (Fidkowski, Malone and Doherty, 1991). This is confirmed by calculating profiles at a reflux ratio very close to the minimum as shown in Figure 11b. We made several designs, changing the specification for the mole fraction of *B* and maintaining a constant mole fraction of acetone in the distillate. An example with a very small amount of *B* in the distillate is shown in Figure 12a, and an example with the distillate on the *AB* edge is shown in Figure 12b. After making a series of designs (later confirmed by rigorous simulations), we conclude that *A* (*C*)/*BC* splits require much smaller reflux ratios but a much larger number of stages than conventional *A* (*B*) /*BC* splits. Sensitivity calculations for both types of splits show that the *AC*/*BC* splits can be very sensitive to the parameters in the process model. Small changes in the reflux ratio, the number of stages, or the feed composition may cause the amount of *B* in the distillate to increase sharply, resulting in an *AB*/*BC* split.

An example of real mixture that behaves in this way is acetaldehyde-methanol-water, although the effects are not as large as in the example above. The classification of feeds for this mixture and an example of the separation regions for one specific feed are shown in Figure 13 (see Table 1 for the VLE data).

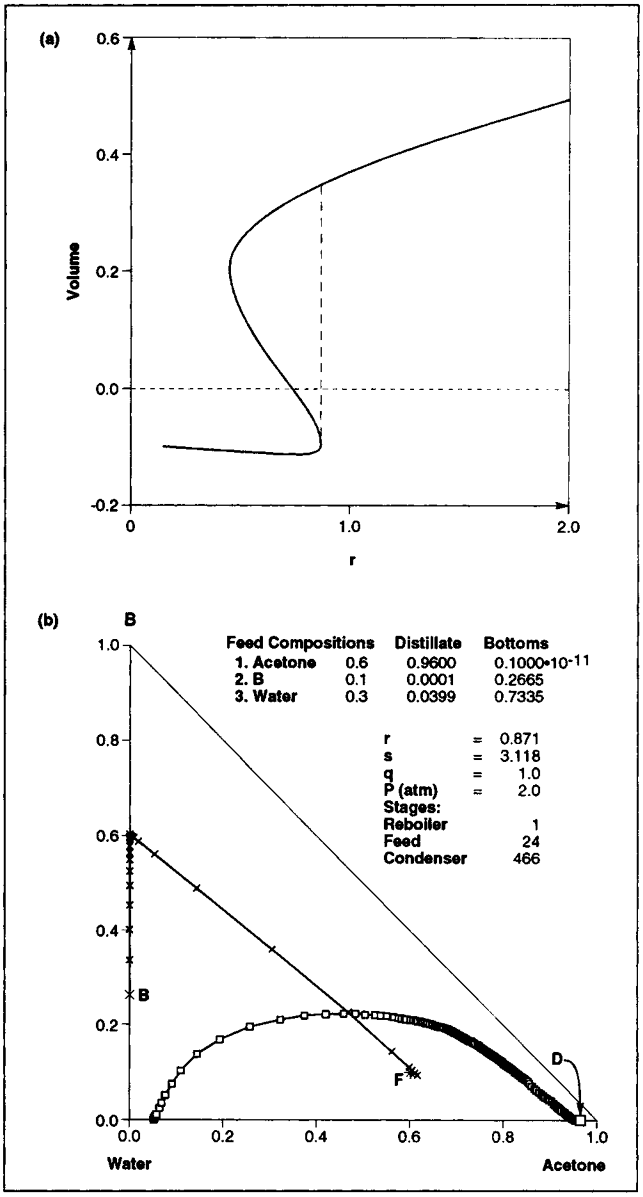

Figure 11. (a) Turning points on the fixed point volume vs. reflux diagram and (b) corresponding tangent pinch on liquid composition profile at a reflux ratio slightly above minimum.

Azeotropic Mixtures without Distillation Boundaries

The mixture ethanol-water-ethylene glycol has been studied extensively in extractive distillation (Knight and Doherty, 1989; Knapp and Doherty, 1992). The VLE data are given in Table 1, and the residue curve map is shown in Figure 14. The transition line always intersects the ethanol-water and water-ethylene glycol edges of the composition triangle and the separation regions are shown in Figure 15. Figure 15a is similar to the ideal case, but with the minimum-boiling azeotrope playing the role of the "lightest component." In Figure 15b, the distillate compositions for splits with direct geometry is deformed toward the pure-ethanol vertex, but high-purity ethanol cannot be obtained as the product of a single-feed distillation column for either feed.

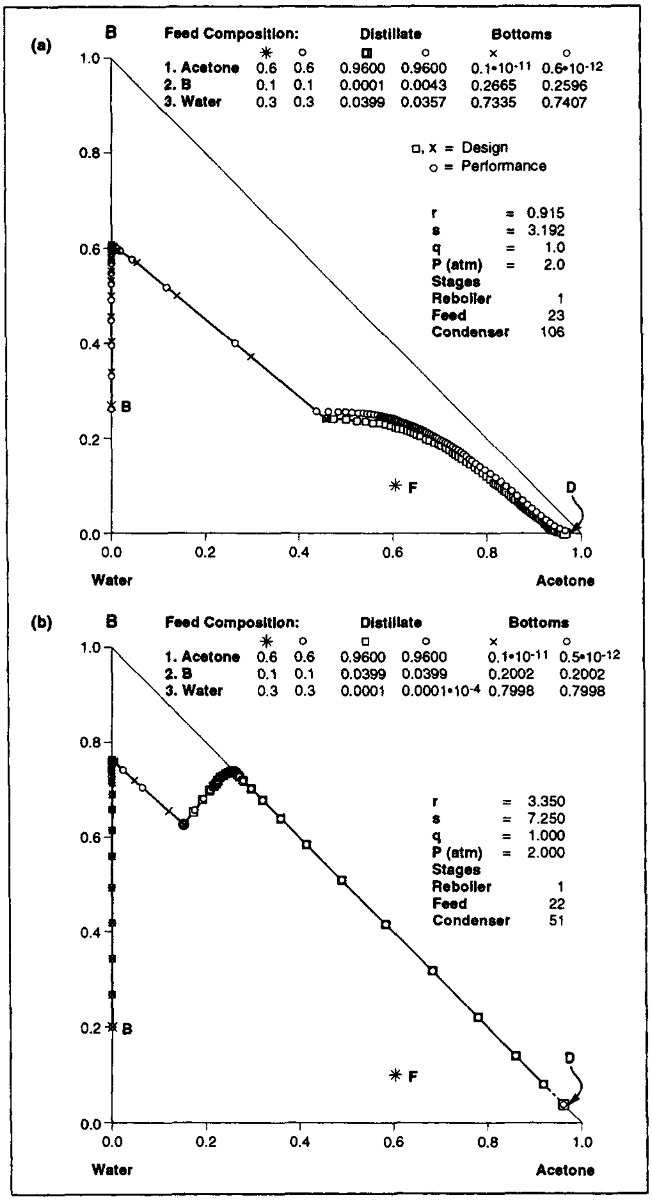

Figure 12. Results of design and rigorous performance simulations for the mixture described in Figure 8: (a) abnormal and (b) normal order of components in the distillate.

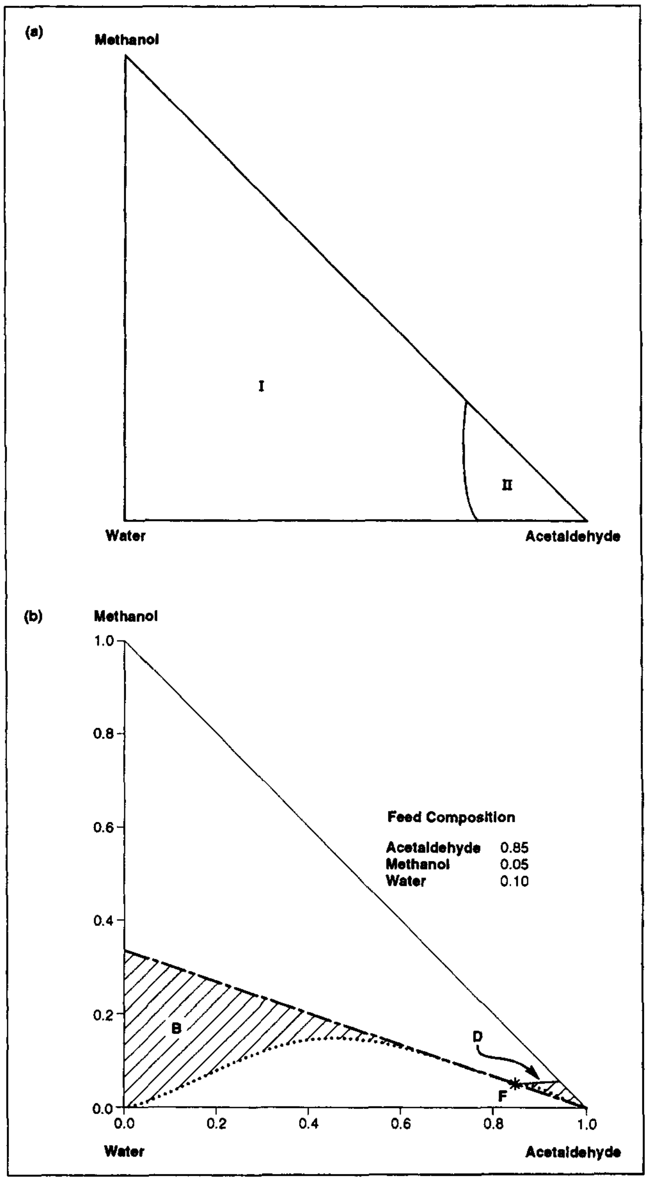

Figure 13. Results for a mixture of (A) acetaldehyde, (B) methanol, and (C) water.

Regions of the feed compositions, where (I) the transition line intersects AB and BC edges and (II) the transition line intersects the AC and BC edges. The feasible separation regions (b) for a saturated liquid feed with a composition in region II ($q=1$).

Azeotropic Mixture with a Simple Distillation Boundary

A single distillation boundary is found in the mixture acetone (A), chloroform (B), and benzene (C) at 1-atm pressure; the VLE data are given in Table 1. The residue curve map for this system is shown in Figure 16a, where we can see the simple distillation boundary connecting the binary acetone–chloroform azeotrope with the benzene vertex. The classification of feeds for this mixture is shown in Figure 16b; there are three different regions of feed compositions where the transition line intersects the edges AB and AC (region I), AB and BC (region II), or BC and AC (region III). We are able to find separation regions for any particular feed. The locus of liquid pinch compositions that satisfy Eq. 13 are shown in Figure 17 for several feeds. In Figures 17a and 17b, the locus connects the unstable node (A) and the stable node (C) in the region of compositions below the simple distillation boundary. There is also another solution of Eq. 13, which connects the unstable node B with the saddle azeotrope AB. This solution is located on the upper side of the simple distillation boundary and does not determine a feasible separation region for the given feed, since this line does not connect the appropriate nodes. However, as the feed composition is moved toward chloroform, the solutions bifurcate as shown in Figure 17c, until the line connecting nodes B and C determines the feasible separation regions, now located above the simple distillation boundary (Figure 17d).

The information in this picture is incomplete: if we attempt to separate acetone from benzene and chloroform we know

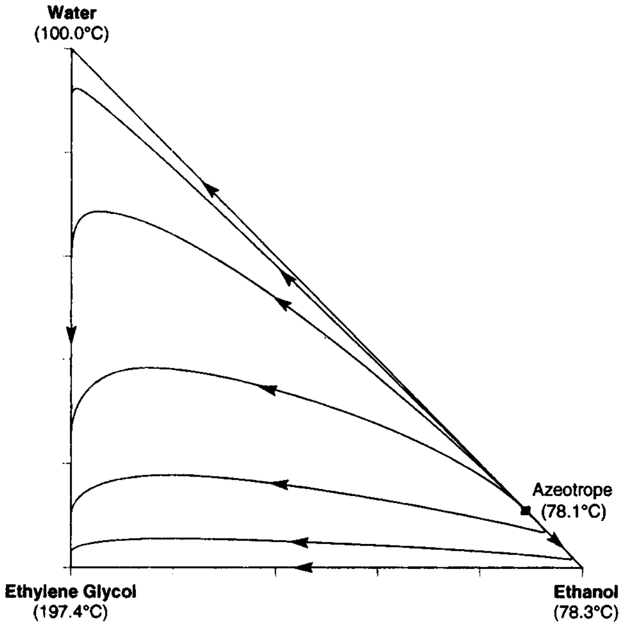

Figure 14. Residue curve map for ethanol, water and ethylene glycol at a pressure of 1 atm.

the region of possible distillate compositions (*D* in Figure 18), but the bottoms compositions (*B* in Figure 18) are harder to determine because of the boundary. The difficulty arises because we do not know exactly where the *continuous* distillation boundary is located. One way to *estimate* its location is with that of the simple distillation boundary, as shown in Figure 18. We may even assume that this simple distillation boundary is a straight line, although it would cause a significant error in this example. The curved boundary in this mixture permits a much better purity of the bottom product. We may also attempt to cross a simple distillation boundary, but this requires a more detailed analysis.

Discussions about crossing simple distillation boundaries in batch distillation began in 1945, when Ewell and Welch found the phenomenon experimentally. Simple distillation boundaries were confused for a long time with valleys and ridges in the boiling temperature surfaces. In 1984, Van Dongen and Doherty proved that ridges and valleys in the boiling temperature surface do not coincide with azeotropic distillation region boundaries, and this was also discussed in more detail recently by Rev (1992). Levy (1985) showed several examples of calculations where liquid composition profiles cross a simple distillation boundary. He interpreted the results using an explanation proposed originally by Nikolaev et al. (1979) that simple distillation boundaries must differ from continuous distillation boundaries and that the location of the boundaries for continuous distillation change with process parameters (reflux ratio and product composition). Levy also used the fact that tie lines are everywhere tangent to simple distillation residue curves to show how a curved simple distillation boundary must be straddled by (straight) tie lines connecting liquid and vapor compositions that lie on different sides of this boundary. He concluded that it is "easier" to cross a simple distillation boundary that is more curved and it is impossible to cross a boundary that is perfectly straight. The discussions were revived in 1990, when Laroche et al. pointed out that simple distillation boundaries are usually not straight and that they can be crossed, but usually with significant efforts (like enormous reflux or reboil ratios) and large uncertainty because of the sensitivity of such a design to the parameters in the VLE model.

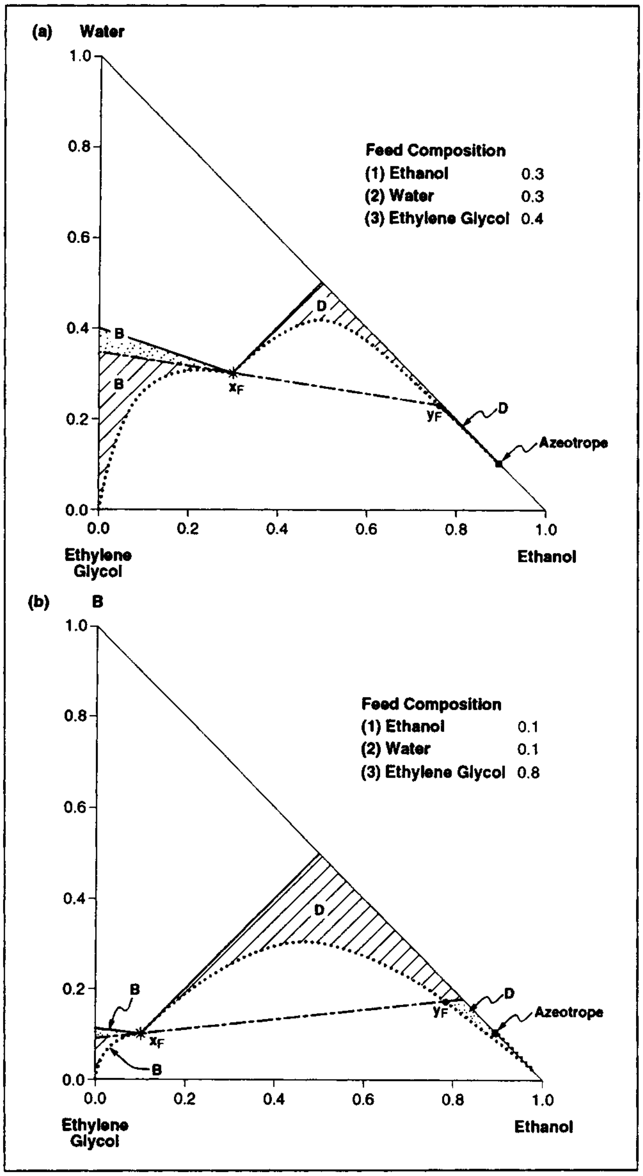

Figure 15. Feasible separation regions for the mixture of ethanol, water, and ethylene glycol for two feed compositions ($q = 1$).

Ethanol cannot be recovered in high purity using a single-feed column.

Since the residue curves correspond to liquid composition profiles at total reflux, a simple distillation boundary corresponds to the continuous distillation boundary *at total reflux*. Whether it is straight or curved, it cannot be crossed by profiles at total reflux because residue curves do not intersect. If the reflux ratio is finite, however, the boundary moves as well; moreover, it splits into at least two different boundaries—one for the rectifying profiles and the other for the stripping profiles. Examples of the phase plane for the rectifying and strip-

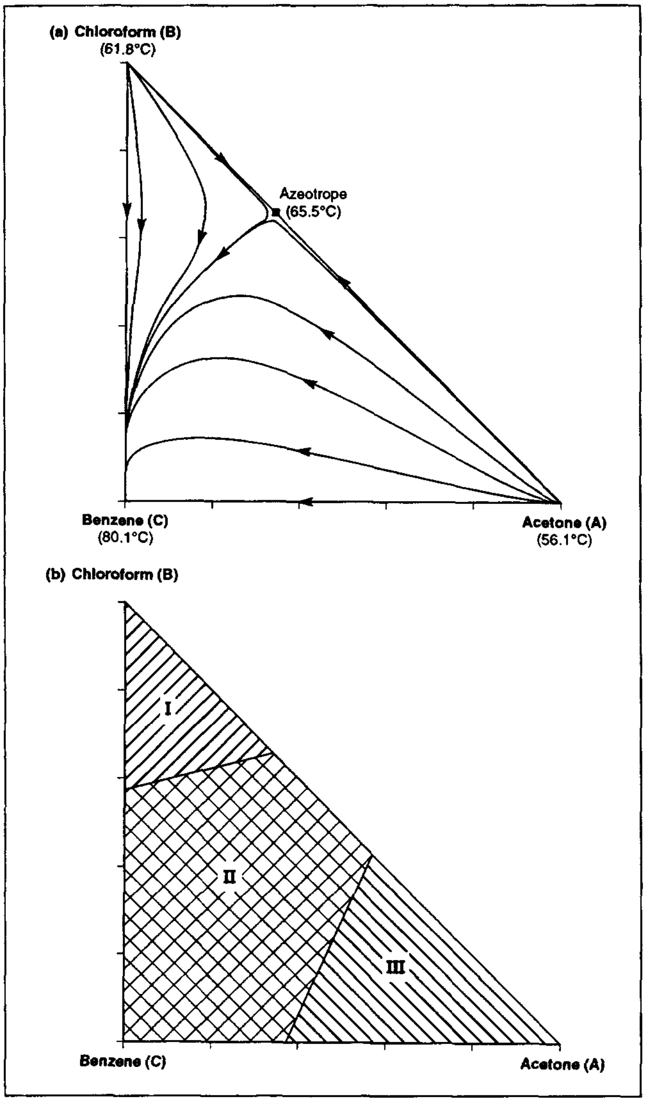

Figure 16. Results for a mixture of (A) acetone, (B) chloroform, and (C) benzene.

The residue curve map (a) and regions of feed compositions (b) where the transition line intersects (I) and the AB and AC edges, (II) the AB and BC edges, and (III) the BC and AC edges.

ping sections are shown in Figures 19 and 20, respectively. Note that the boundary for the stripping profile moves toward the chloroform-benzene edge of the triangle as the reboil ratio decreases (Figures 20 and 21a), and it finally vanishes at a reboil ratio $s=3$, when the ternary saddle bifurcates with a binary node on the chloroform-benzene edge. Thus, a reboil ratio of $s \approx 3$ may be regarded as the maximum reboil for this separation. The boundary for a rectifying section cannot be crossed by the rectifying profile, but it can be crossed (and frequently is) by the stripping profile and *vice versa*. The simple distillation boundary (straight or curved) may be crossed by either one of the profiles, depending on the geometry of the phase plane at a given reflux ratio. A phase plane for the rectifying and stripping sections with feasible profiles is shown in Figure 21b. Indeed, we can design a sequence of distillation columns to accomplish a separation that crosses the simple distillation boundary. This sequence consists of two columns as shown in Figure 22a; the first column separates acetone, giving a bottoms product of benzene and chloroform on the other side of the simple distillation boundary. The liquid composition profiles for this column are shown in Figure 22b. The second column performs the separation of the binary mixture of chloroform and benzene.

We have discussed above how and why the simple distillation boundary can be crossed with continuous distillation. In fact, we do not really need to cross the simple distillation boundary to separate this mixture into pure components. This can be accomplished in a three-column sequence shown in Figure 23. The first column separates acetone (D_1) from the mixture acetone-chloroform-benzene giving the bottom product (B_1) close to the simple distillation boundary. Then, we separate benzene (B_2) from the mixture of acetone and chloroform (D_2) in the second column. This separation has nothing to do with boundary crossing, since both products and the profiles in the second column are contained entirely above the simple distillation boundary. (This is only possible because the simple distillation boundary is concave.) Finally, D_2 is separated in the third column into chloroform (D_3) and azeotrope (B_3) which is recycled to the feed of the first column. This third column would not be needed if the simple distillation boundary was crossed in the first column and $B1$ did not contain acetone. More detailed process parameters are given in Table 2, and flow rates and compositions of streams are listed in Table 3.

We can also use the same sequence of columns to separate the acetone-chloroform azeotrope, with benzene as a separating agent as shown in Figure 24a; a similar separation at total reflux was proposed by Laroche et al. (1992). The parameters for distillation at finite reflux are given in Table 4, and flow rates and compositions of streams are listed in Table 5. This separation is possible because of the curvature of the boundary. This scheme differs from the one shown in Figure 22, and this flowsheet has better operability characteristics, because it still works even in the case when we cannot cross the boundary to a satisfactory extent. The sequences presented in Figures 23 and 24 are simply examples of feasible designs and are not optimized in any way.

From the foregoing discussion, a misleading conclusion would be that simple distillation boundaries can always be crossed to such an extent that it leads to an attractive application. This all depends on how the boundaries (or fixed points) in the phase plane move with reflux (reboil) ratio and on the desired purity of the products. More often than not, the effects are small, the energy requirements can be enormous and, most important, there remains a high degree of uncertainty of the design. For instance, some VLE models predict that a boundary can be crossed, but others suggest that it cannot. In our example, for feed compositions of $x^F = (0.12, 0.22, 0.66)$, we could not cross the boundary when the Wilson model was used, but we could do it easily using the Van Laar model. Moreover, for very small changes in a product composition the design may become infeasible. The steady-state performance (rating) predictions for product purity are also sensitive to disturbances, and we expect the column may be difficult to control.

We conclude that it is better engineering practice not to attempt to cross a simple distillation boundary unless all other alternatives have been explored.

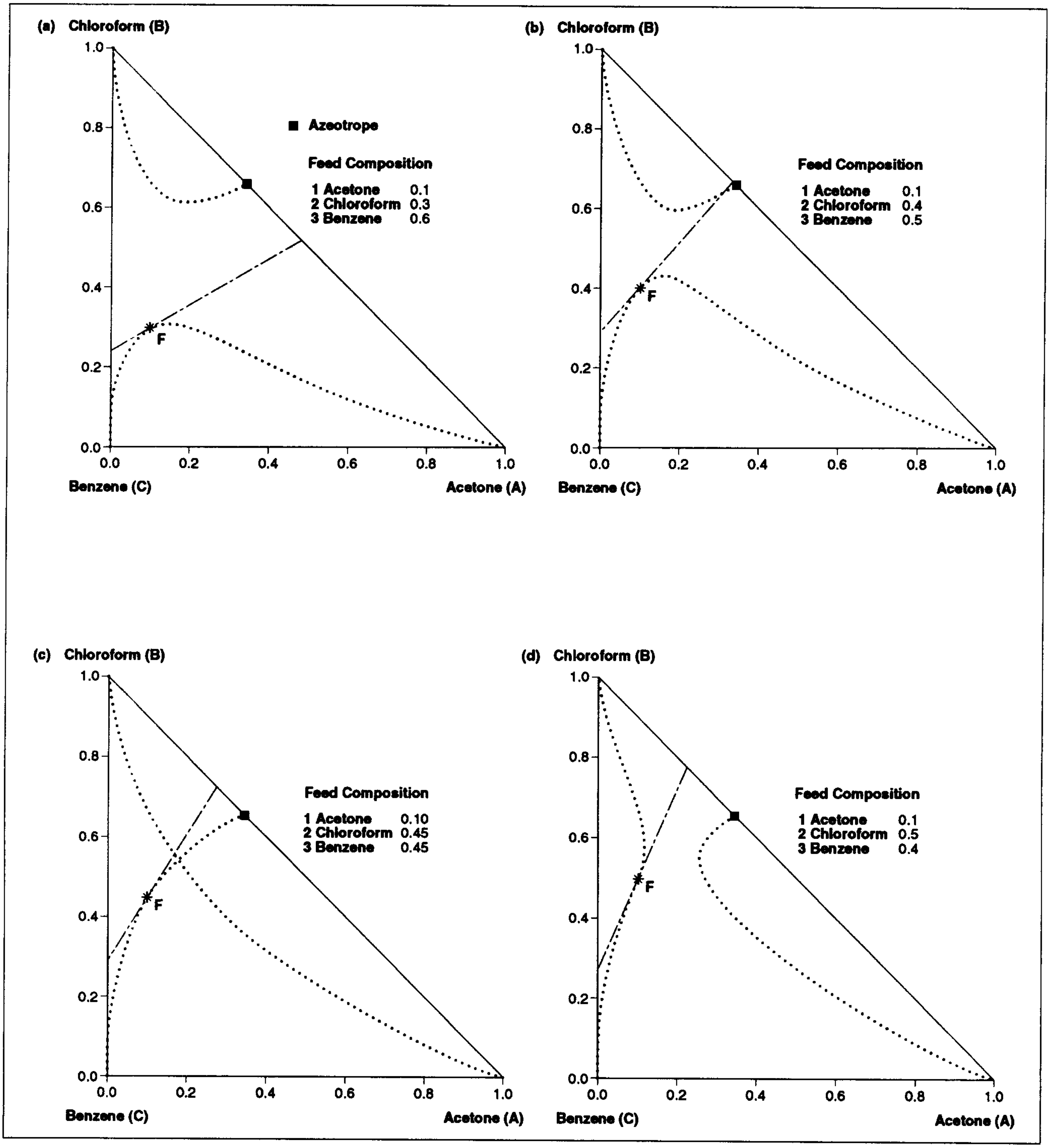

Figure 17. Liquid solutions of Eq. 13 for mixtures of acetone, chloroform and benzene at various feed compositions and for saturated liquid feeds.

How to Determine Separation Regions

The procedure for determination of separation regions can be summarized as follows:

1) Given the feed composition, z^F, feed quality, q, and column pressure, P.

2) Calculate $\hat{x}^f$ and $\hat{y}^f$ from Eqs. 2 and 12 and draw the transition line on the composition triangle.

3) Determine the distillation limits. There are two ways of doing this: i) Solve Eqs. 2 and 13 simultaneously; there is one degree of freedom and solutions form a curve in the composition triangle. ii) Solve Eqs. 2 and 12 simultaneously, varying q in the range $-\infty < q < \infty$. (For practical purposes, the range $-100 < q < 100$ is usually sufficient, and the corresponding values of x^f cover the entire curve of distillation limits.)

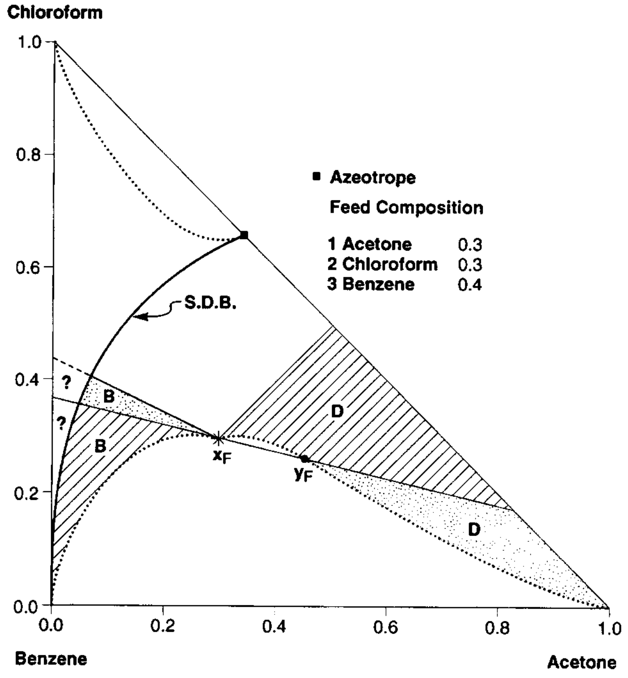

Figure 18. Example of feasible separation regions for the mixture of acetone, chloroform, and benzene ($q = 1$). The simple distillation boundary is superimposed.

This calculation is easily carried out using a continuation from the known initial condition at $x^f = z^F$ for $q = 1$.

A *necessary* condition for the separation to be feasible is that product compositions lie in the feasible separation regions. However, before we will be able to pick feasible product compositions, we need also to find distillation boundaries. A sufficient condition for feasibility can be formulated as a heuristic rule: *choose product compositions which lie within the distillation limits and on the same side of the simple distillation boundary.* Note that we are also able to determine the type of the split geometry (direct, indirect, or transition), once the product compositions are chosen; this information is essential for minimum reflux calculations.

If an attempt is made to cross the simple distillation boundaries, a trial-and-error technique is needed to determine *whether* the boundary can be crossed or how closely it can be approached. Phase planes can be calculated to determine the exact location of a continuous distillation boundary. Unfortunately, these phase planes depend on the product purities and reflux or reboil ratios so this is not a very efficient procedure, although it does give useful information. We think that the picture of continuous distillation boundaries is still not complete and additional research may provide simpler procedures to determine if and to what extent the simple distillation boundary can be usefully crossed.

Conclusions

A simple equation-based procedure has been developed for calculating feasible separations for the distillation of nonideal ternary mixtures in single-feed columns. The method is most useful for azeotropic mixtures where feasible separations are difficult to anticipate. The technique is useful for process synthesis (column sequencing) and process design (calculating minimum reflux by geometric methods). Extension of the ideas to mixtures with more components or to columns with multiple feeds (such as extractive distillation) appears promising, but has not been attempted here.

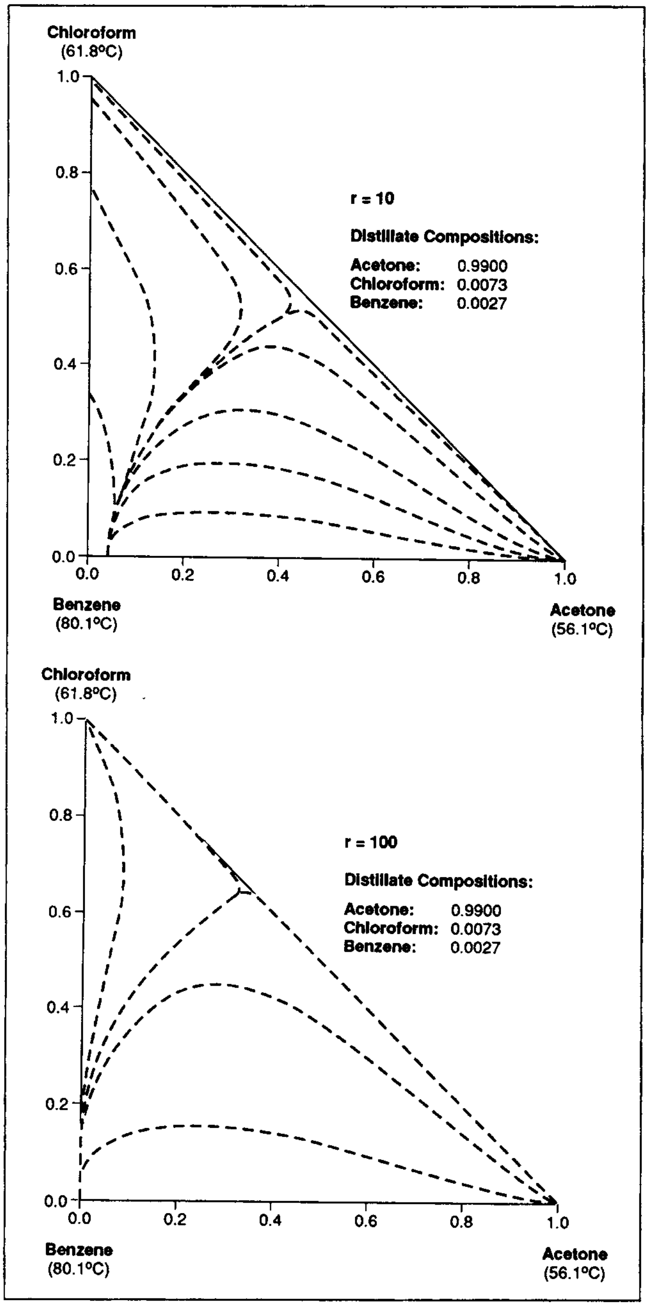

Figure 19. Phase planes for the rectifying profiles in a mixture of acetone, chloroform and benzene at two reflux ratios.

Acknowledgment

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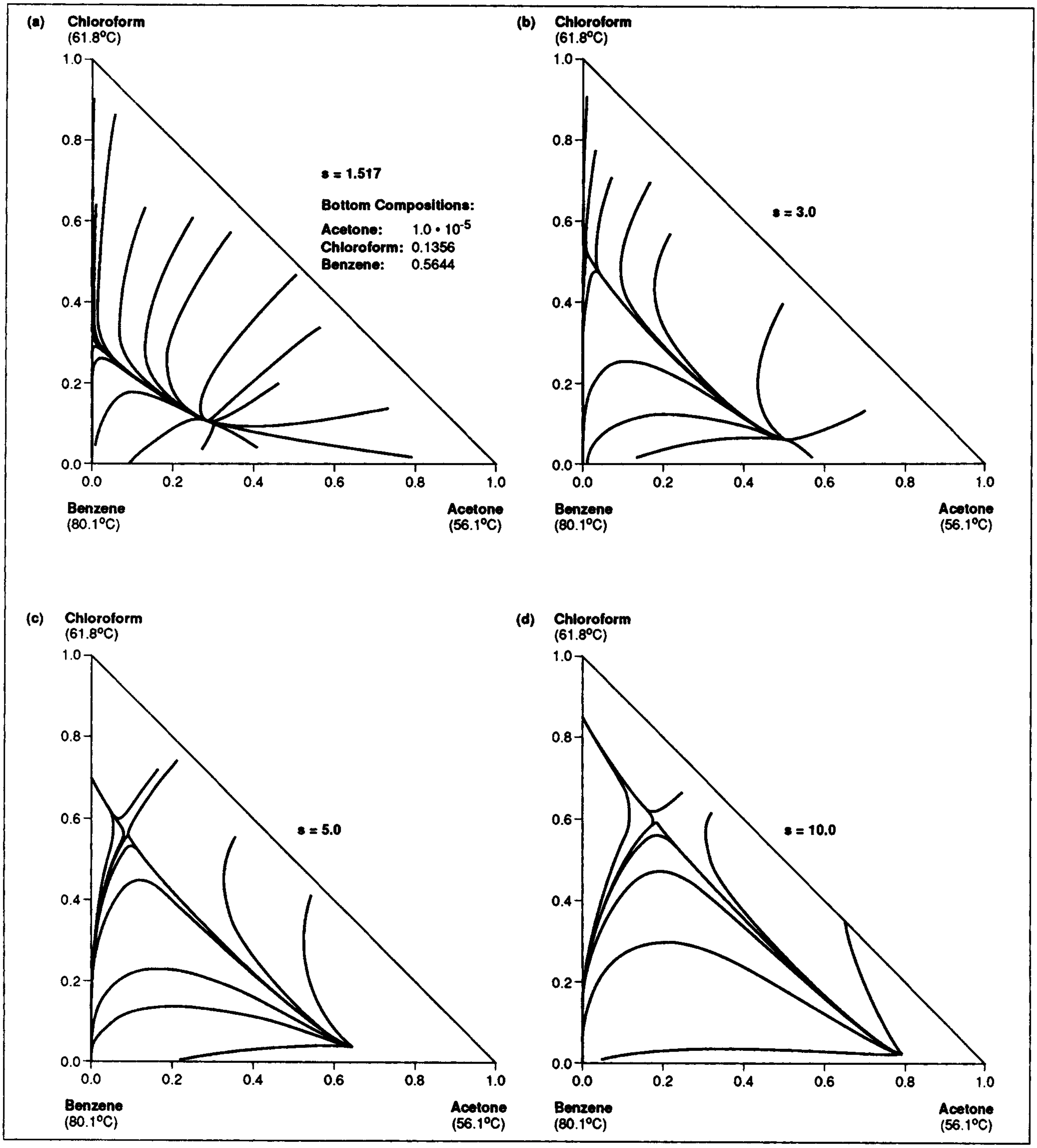

Figure 20. Phase planes for the stripping profiles in a mixture of acetone, chloroform and benzene at various reboil ratios.

Note

After this article was submitted, three related publications appeared by Wahnschafft et al. (1992), Stichlmair and Herguijuela (1992), and Laroche et al. (1992). Each contains some important results and should be read in conjunction with this article.

Notation

A = lowest boiling component
B = intermediate boiling component
C = highest boiling component
f = equilibrium relation
M = parameter of Margules equation, K
N = number of stages

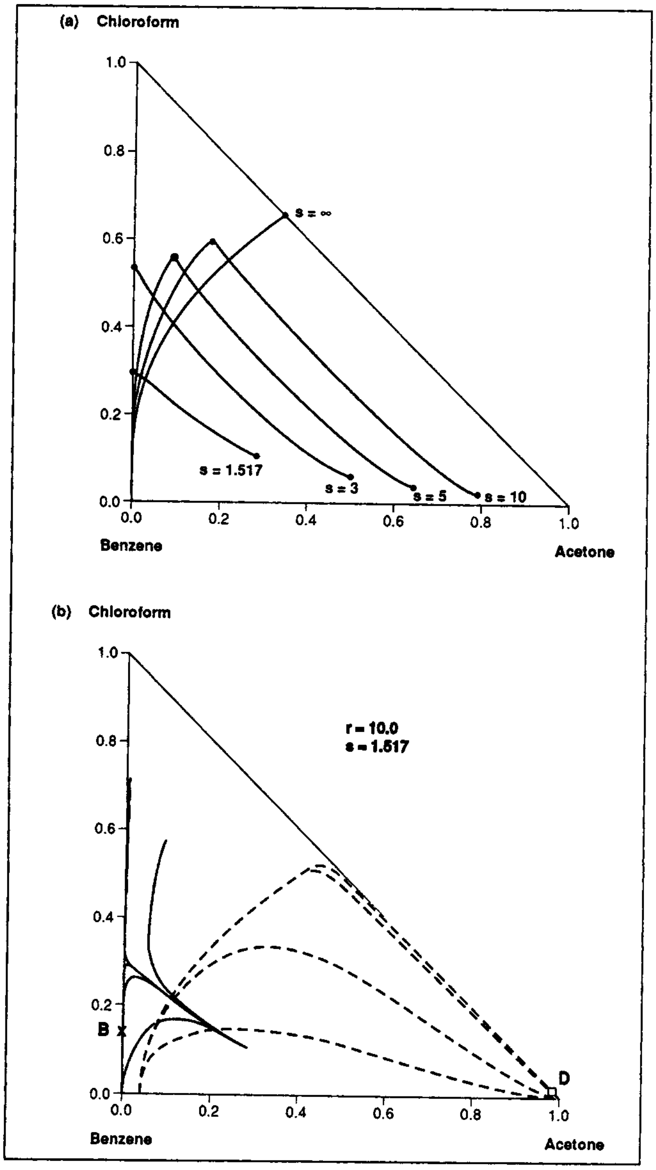

Figure 21. (a) Continuous distillation boundaries for the stripping section at various reboil ratios and (b) phase planes for the rectifying and stripping section showing feasible profiles that cross the simple distillation boundary.

p^{sat} = saturation pressure
P = pressure
q = thermodynamic state of the feed
r = reflux ratio
s = reboil ratio
T = temperature, K
x = mole fraction in the liquid phase
$\mathbf{x}$ = $[x_1, x_2]^T$, vector of mole fractions in the liquid phase
$\hat{\mathbf{x}}$ = $[\hat{x}_1, \hat{x}_2]^T$, vector of liquid mole fraction at a fixed point
y = mole fraction in the vapor phase
$\mathbf{y}$ = $[y_1, y_2]^T$, vector of mole fractions in the vapor phase
$\hat{\mathbf{y}}$ = $[\hat{y}_1, \hat{y}_2]^T$, vector of vapor composition at a fixed point
$\mathbf{z}$ = $[z_1, z_2]^T$, vector of feed mole fractions

Greek letters

α = relative volatility

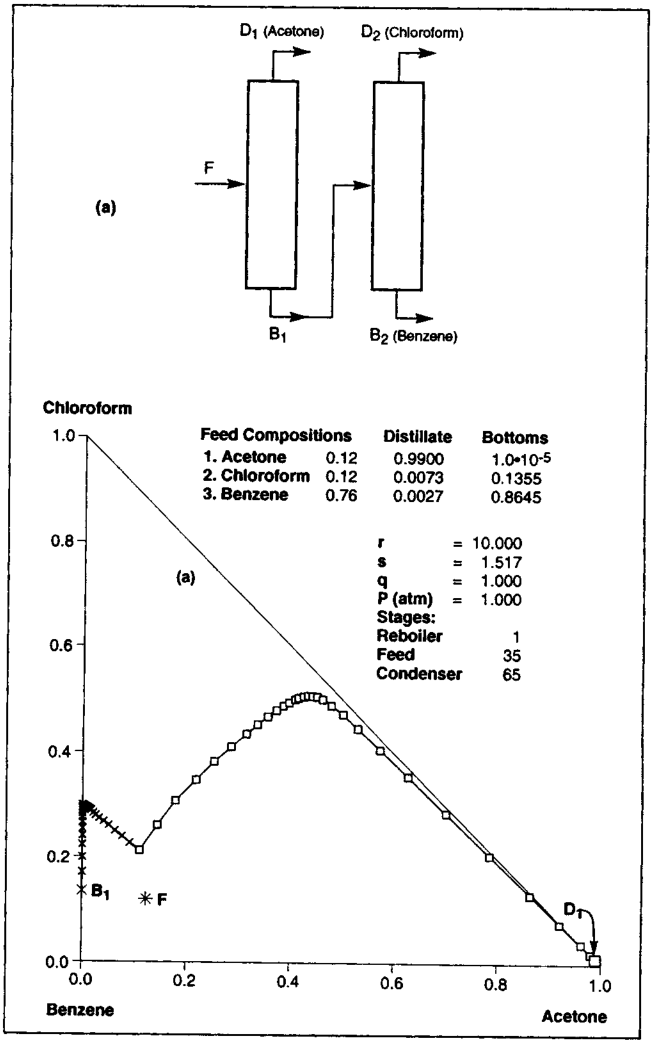

Figure 22. Liquid composition profiles that cross the simple distillation boundary.

γ = activity coefficient
ξ = stage number, dimensionless height of packed column, or dimensionless time of an open evaporation

Subscripts

A = lowest-boiling component
B = intermediate-boiling component
C = highest-boiling component
i = component index
j = stage number
min = minimum
N = total number of equilibrium stages
1, 2, 3 = component numbers, in order of lowest to highest boiling point

Superscripts

B = bottoms
D = distillate
f = feed pinch
F = feed
r = rectifying section
s = stripping section
sat = saturation
T = tranpose

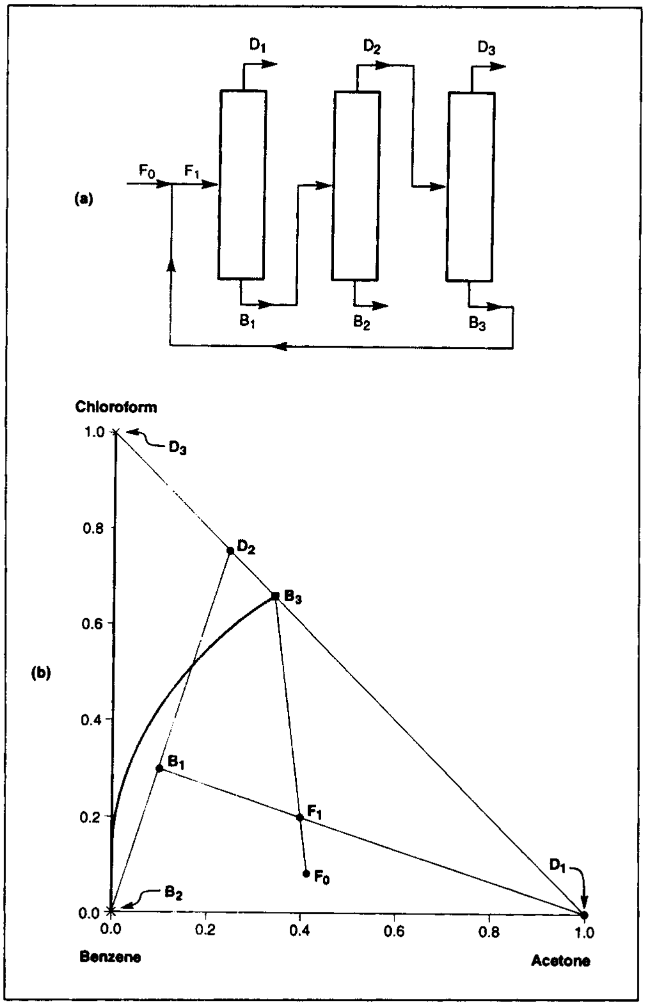

Figure 23. Example of separation of a mixture of acetone, chloroform and benzene in a three-column sequence: (a) sequence of columns (b) corresponding composition diagram.

Table 2. Parameters for the Three-Column Sequence in Figure 23*

Column	Reflux Ratio	Reboil Ratio	Feed Quality	Pres. atm	No. of Stages	Feed Stage
1	5.000	3.051	1.0	1.0	56	6
2	15.00	10.27	1.0	1.0	42	10
3	15.00	6.432	1.0	1.0	34	29

*The stages are counted upward from the reboiler which is stage number 1; the total condenser is not counted in the number of stages.

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Table 3. Flow Rates and Composition of Streams for the Three-Column Sequence in Figure 23

Stream	Flow Rate mol/s	Acetone mole frac.	Chloroform mole frac.	Benzene mole frac.
F0	80.975	0.4166	0.0896	0.4938
F1	100.000	0.4000	0.2000	0.4000
D1	33.710	1.0000	1.8×10^{-14}	3.0×10^{-6}
B1	66.290	0.0949	0.3017	0.6034
D2	25.910	0.2428	0.7567	0.0005
B2	40.38	4.8×10^{-7}	0.0097	0.9903
D3	6.885	0.0036	0.9964	3.0×10^{-6}
B3	19.025	0.3389	0.6604	0.0007

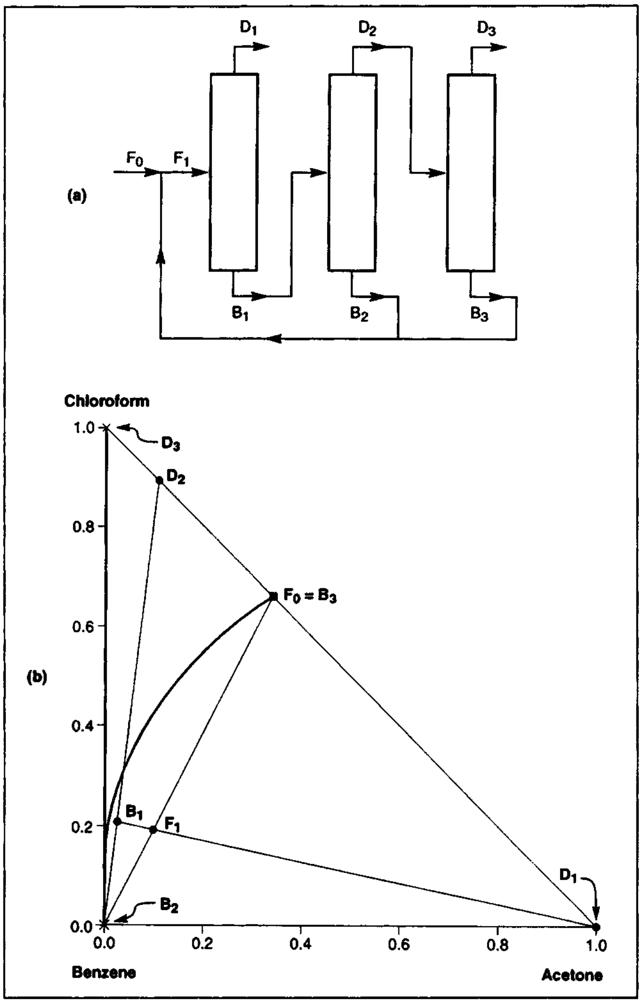

Figure 24. Example of separation of a binary azeotropic mixture of acetone and chloroform, using benzene as an entrainer, in a three-column sequence: (a) sequence of columns (b) corresponding composition diagram.

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Table 4. Parameters for the Three-Column Sequence in Figure 24*

Column	Reflux Ratio	Reboil Ratio	Feed Quality	Pres. atm	No. of Stages	Feed Stage
1	10.00	9.270	1.0	1.0	42	14
2	30.00	8.936	1.0	1.0	39	8
3	3.000	8.464	1.0	1.0	32	20

*The stages are counted upward and the reboiler is stage number 1; the total condenser is not included in the number of stages.

Table 5. Flow Rates and Composition of Streams in the Three-Column Sequence in Figure 24

Stream	Flow Rate mole/s	Acetone mole frac.	Chloroform mole frac.	Benzene mole frac.
F0	21.783	0.3394	0.6596	0.0009
F1	100.000	0.1000	0.1910	0.7090
D1	7.773	0.9923	0.0050	0.0027
B1	92.227	0.0248	0.2066	0.7686
D2	20.640	0.1108	0.8889	0.0003
B2	71.587	7.1×10^{-7}	0.0100	0.9900
D3	14.010	0.0027	0.9973	7.8×10^{-7}
B3	6.630	0.3394	0.6596	0.0009

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Appendix

We show that the distillation limit begins at an unstable node, ends at a stable node, and intersects the transition line at the points z^F, $\hat{\mathbf{x}}^f$ and $\hat{\mathbf{y}}^f$.

The first part of this statement is obvious if we recall that residue curves begin at the unstable node and end at the stable node. Both of these nodes are reachable for profiles at total reflux and infinite number of stages, where they are the fixed points for the column profile. Thus, the curve determining the limit of feasible separation regions must include these nodes.

The distillation limit must also go through the feed composition, which is the other limiting case where there is no separation (for example, there are no theoretical stages) and where the product compositions are equal to the feed composition. The proof is immediate if we make $\hat{\mathbf{x}}=z^F$ in Eq. 13.

We show that Eq. 13 is also satisified for $\hat{\mathbf{x}}=\hat{\mathbf{x}}^f$:

$$\frac{z_1^F-\hat{x}_1^f}{\hat{y}_1^f-\hat{x}_1^f}=\frac{z_2^F-\hat{x}_2^f}{\hat{y}_2^f-\hat{x}_2^f} \tag{A1}$$

Using Eq. 12, we obtain:

$$\frac{qx_1^f+(1-q)y_1^f-\hat{x}_1^f}{\hat{y}_1^f-\hat{x}_1^f}=\frac{qx_2^f+(1-q)y_2^f-\hat{x}_2^f}{\hat{y}_2^f-\hat{x}_2^f} \tag{A2}$$

and after simple rearrangements, this gives an identity. Similar arguments can be used to show that y^f is on the distillation limit.

For a boiling liquid feed, $q=1$ and the points z^F and x^f coalesce, and the liquid solutions of Eq. 13 are tangent to the transition line. The tangency can be proved by a simple differentiation of Eq. 13 at $\hat{\mathbf{x}}=\hat{\mathbf{x}}^f=z^F$.

In the case of nonideal mixtures, there may be multiple solutions for the curve determining the limit of feasible separations if Eq. 13 is used (see also Figure 17). We may easily identify and eliminate spurious solutions which do not pass through the feed composition or which do not connect stable and unstable nodes on the composition diagram.

A more convenient way of determining the distillation limit, which does not give multiple solutions, is to use parametric continuation in q to solve Eq. 12 with Eq. 2 relating the liquid and vapor compositions.

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