DISTILLATION, AZEOTROPIC, AND EXTRACTIVE

1. Introduction

Distillation (qv) is the most widely used separation technique in the chemical and petroleum industries. Not all liquid mixtures are amenable to ordinary fractional distillation, however. Close-boiling and low relative volatility mixtures are difficult and often uneconomical to distill, and azeotropic mixtures are impossible to separate by ordinary distillation. Yet such mixtures are quite common (1,2) and many industrial processes depend on efficient methods for their separation (see also SEPARATIONS PROCESS SYNTHESIS). This article describes several special distillation techniques for economically separating low relative volatility and azeotropic mixtures.

Vapor–liquid phase equilibrium (VLE) in a c-component mixture can be represented by

$$y_i \phi_i^V P = x_i \gamma_i P_i^{\mathrm{sat}} \phi_i^{\mathrm{sat}} \exp \int_{P_i^{\mathrm{sat}}}^{P} \frac{V_i^L dP}{RT} \qquad \text{for} \quad i = 1, \ldots, c \tag{1}$$

where y_i is the mole fraction of component i in the vapor phase; ϕ_i^V is the vapor-phase fugacity coefficient of component i; P is the total system pressure; x_i is the mole fraction of component i in the liquid phase; γ_i is the liquid-phase activity coefficient of component i; P_i^{sat} is the vapor pressure of component i; ϕ_i^{sat} is the saturation fugacity coefficient of component i; and the exponential term is the Poynting correction factor (Poy_i). At low to moderate pressures, the value of the term $\phi_i^{\mathrm{sat}}/\phi_i{}^*Poy_i$ is typically close enough to unity that it can be ignored and equation 1 reduces to

$$y_i P = x_i \gamma_i P_i^{\mathrm{sat}} \qquad \text{for} \quad i = 1, \ldots, c \tag{2}$$

For simplicity, this is the VLE equation that will be used throughout the rest of this article.

The activity coefficient (γ_i) is a measure of the liquid-phase nonideality of a mixture and its value varies with both temperature and composition. When $\gamma_i = 1$ the liquid phase is said to form an ideal solution and equation 2 reduces to Raoult's law. Nonideal mixtures ($\gamma_i \neq 1$) can exhibit either positive ($\gamma_i > 1$) or negative ($\gamma_i < 1$) deviations from Raoult's law. Positive deviations are more common and occur when the molecules of the different compounds in the solution are dissimilar and have no preferential interactions between them. Negative deviations occur when there are preferential attractive forces (hydrogen bonds, etc.) between the molecules of the different species that do not occur in the absence of the other species (3). If these deviations are large enough, the pressure-composition (P-x,y) and temperature-composition (T-x,y) phase diagrams exhibit a minimum or maximum point (Fig. 1). At these minima and maxima the liquid

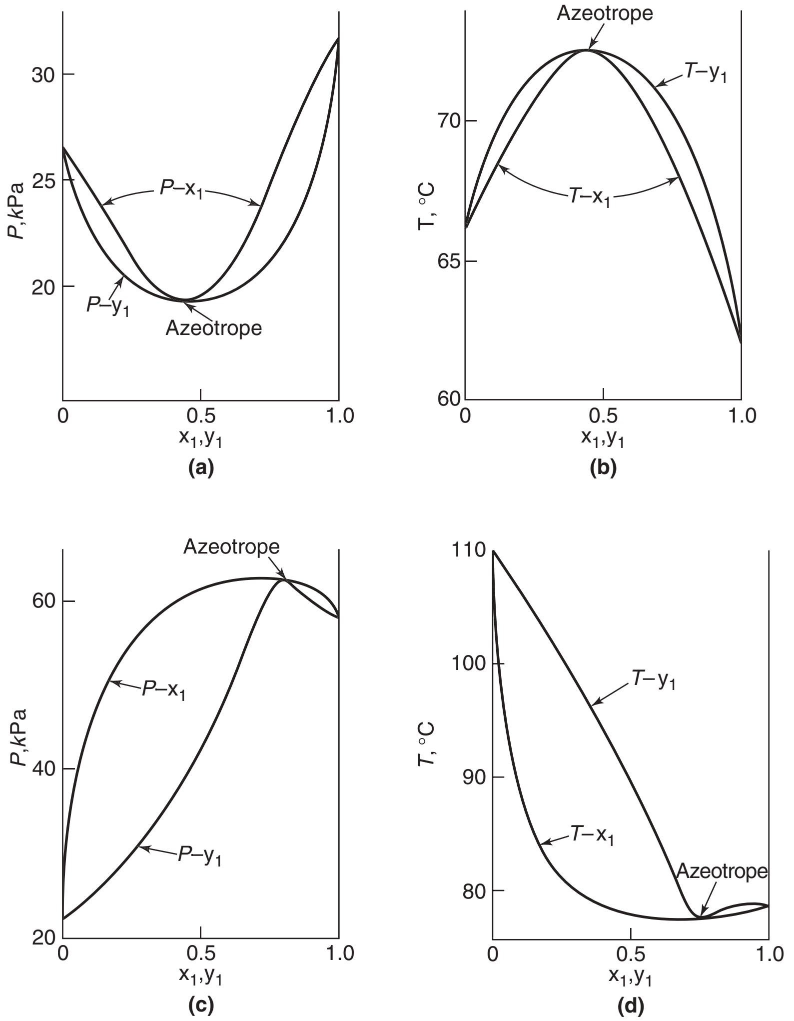


Fig. 1. *P-x,y* and *T-x,y* phase diagrams showing binary, homogeneous, maximum, and minimum azeotropes. (**a**) Chloroform (1)-tetrahydrofuran (2) at 30°C; (**b**) chloroform (1)-tetrahydrofuran (2) at 101 kPa; (**c**) ethanol (1)-toluene (2) at 65°C; and (**d**) ethanol (1)-toluene (2) at 101 kPa (from Ref. 6). To convert kPa to atm, multiply by 9.87×10^{-3}.

phase and its equilibrium vapor phase have the same composition, ie,

$$y_i = x_i \qquad \text{for} \quad i = 1, \ldots, c \tag{3}$$

the mixture boils at constant temperature, and the dew-point (vapor) and bubble-point (liquid) curves are tangent with zero slope. These are the defining conditions for a homogeneous azeotrope where a single liquid phase is in equilibrium with a vapor phase. Note that a maximum boiling azeotrope (Fig. 1**b**) is equivalent to a minimum pressure azeotrope (Fig. 1**a**) and a minimum boiling azeotrope (Fig. 1**d**) is also a maximum pressure azeotrope (Fig. 1**c**). Minimum boiling azeotropes occur in mixtures with positive deviations from Raoult's law and maximum boiling azeotropes occur in mixtures with negative deviations. The vast majority of the known azeotropes are minimum boiling (see 1,2). Combining equations 2 and 3 gives an alternative criterion for a homogeneous azeotrope, in this case, a binary azeotrope:

$$\frac{\gamma_2}{\gamma_1} = \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} \tag{4}$$

Equation 4 illustrates that, (*1*) only small deviations from Raoult's law are necessary for an azeotrope to exist in a close boiling mixture (ie, compounds with similar vapor pressures) and (*2*) the larger the difference in boiling points of the compounds, the more nonideal the mixture must be to form an azeotrope and, hence, the less likely that an azeotrope will exist. Generally, mixtures of compounds with boiling points more than $\sim 30^\circ$C apart do not exhibit azeotropes (4). Exceptions to this heuristic do exist, however. For example, hydrogen chloride and water form a maximum boiling azeotrope and their normal boiling points differ by 185°C. Martin (5) showed that a binary mixture forms a minimum boiling azeotrope when the infinite dilution activity coefficient of the less volatile component is greater than the ratio of the pure component vapor pressures, ie,

$$\gamma_2^{\infty} > \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} \tag{5}$$

Partially miscible mixtures are more nonideal than completely miscible mixtures and thus are more likely to form azeotropes. Usually, these will be heterogeneous azeotropes where two (or more) liquid phases are in equilibrium with a vapor phase, the mixture boils at constant temperature and at constant composition, but the composition of the equilibrium phases are all different (see Fig. 17**b**). The *overall* liquid-phase composition is, however, identical to the vapor-phase composition. Since positive deviations from Raoult's law are necessary for liquid phase immiscibility, only minimum boiling heterogeneous azeotropes can exist. When the immiscibility exists only over a limited composition range, the azeotrope can lie outside of the two-liquid-phase region, giving rise to a homogeneous azeotrope. The methyl acetate–water and methyl ethyl ketone–water mixtures are two such examples.

Separation by distillation depends on the vapor and liquid phases having different compositions when a liquid (vapor) mixture is partially vaporized (condensed). The vapor phase becomes enriched in the more volatile components and depleted in the less volatile components while the opposite occurs in the equilibrium liquid phase. By successively repeating these partial vaporizations and condensations in a countercurrent cascade, it is often possible to achieve the desired degree of separation. A common measure of the degree of enrichment or the ease of separation is the relative volatility defined as:

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} = \frac{\gamma_i P_i^{\text{sat}}}{\gamma_j P_j^{\text{sat}}} \tag{6}$$

The relative volatility of most mixtures changes with temperature, pressure, and composition. The larger the value of α_{ij}, the easier it is to separate component i from component j. From equation 3, at a c-component (ie, binary, ternary, etc) homogeneous azeotrope, $y_i = x_i$ for all c components in the mixture. Therefore, $\alpha_{ij} = 1$ for all components i and j and no enrichment of the vapor takes place during a partial vaporization. Thus, homogeneous azeotropes cannot be separated by ordinary fractional distillation. Similarly, any mixture, be it ideal, nonideal, close-boiling, etc where the relative volatilities are close to unity will be difficult to separate by ordinary distillation because little enrichment occurs with each partial vaporization step. Although the actual minimum relative volatility necessary for an economical separation is a function of a number of variables (most notably, the required product purities, but also the value of the products and the cost of the materials of construction and the heating and cooling mediums, etc), alternatives to ordinary fractional distillation should generally start to be investigated when α_{ij} is less than ~1.15–1.2.

Most methods for distilling azeotropic and low relative volatility mixtures rely on the addition of specially chosen chemicals or “mass separating agents” to facilitate the separation. These separating agents can be divided into distinct classes that define the principal distillation techniques used to separate such mixtures. The five categories of distillation-based methods for separating low relative volatility and/or azeotropic mixtures are (*1*) extractive distillation and homogeneous azeotropic distillation where the liquid separating agent is completely miscible. In extractive distillation, the separating agents, variously known as solvents, extractive agents, extractants, and sometimes entrainers, are high boiling, non-azeotrope-forming, liquids that alter the relative volatility of the mixture to be separated. (*2*) Heterogeneous azeotropic distillation or, more commonly, azeotropic distillation, where the liquid separating agent, called the entrainer, forms one or more azeotropes with the other components in the mixture and causes two liquid phases to exist over a broad range of compositions. This immiscibility is the key to making the distillation sequence work. (*3*) Salt-effect distillation, which is a variation of extractive distillation, where the separating agent is an ionic salt. The salt dissociates in the liquid mixture and alters the relative volatilities to make the separation possible. (*4*) Pressure-swing or pressure-sensitive distillation where a series of distillation columns operating at different pressures is used to separate mixtures containing azeotropes whose composition changes appreciably over a moderate pressure range. (*5*) Reactive distillation where the separating agent reacts preferentially and reversibly with one of the components in the mixture. The reaction product is then distilled from the nonreacting components and the reaction is reversed to recover the initial component. An example is the separation of isobutene from butanes by etherification (7). This last method is not discussed in this article. All five of these techniques can be used in batch as well as continuous distillations.

Distillation can also be combined with other separation methods such as liquid–liquid extraction (see EXTRACTION, LIQUID–LIQUID), absorption, adsorption/molecular sieves (qv), melt crystallization (qv), or membrane-permeation-based methods like pervaporation (8–10) to separate azeotropic mixtures. Ordinary fractional distillation is used for the separation over the composition range where the relative volatility is appreciable and the separation is easy. One of the other separation techniques, whose efficacy does not depend on relative volatility, is then used to achieve the separation over the “pinched” (low relative volatility) or azeotropic composition range where distillation would be difficult or impossible.

2. Residue Curve Maps

The most basic form of distillation, called simple distillation, is a process in which a multicomponent liquid mixture is slowly boiled in an open pot and the vapors are continuously removed as they form. At any instant in time the vapor is in equilibrium with the liquid remaining in the still. Because the vapor is always richer in the more volatile components than the liquid, the liquid composition changes continuously with time, becoming more and more concentrated in the less volatile species. A simple distillation residue curve is a graph showing how the composition of the liquid residue in the pot changes over time. A residue curve map is a collection of residue curves originating from different initial compositions. Residue curve maps contain the same information as phase diagrams, but present it in a way that is more useful for understanding how to create a distillation sequence to separate a mixture. Simple distillation residue curves represent the liquid composition profiles of packed distillation columns operating at total (infinite) reflux. Some authors (11,12) prefer to use distillation lines, which represent liquid composition profiles in trayed distillation columns operating at total reflux, instead of residue curves. For practical purposes, there is little difference between the two types of curves and either can be used for distillation sequence synthesis. (Residue curves and distillation lines have identical fixed points, ie, the pure components and azeotropes in a mixture, and, except for regions with high curvature, the two lines typically lie very close to each other). Residue curves are used here.

Residue curves can only originate from, terminate at, or be deflected by the pure components and azeotropes in a mixture. Pure components and azeotropes that residue curves move away from are called unstable nodes (UN), those where residue curves terminate are called stable nodes (SN), and those that deflect residue curves are called saddles (S).

The simplest residue curve map for a ternary mixture is shown in Fig. 2. All ternary nonazeotropic mixtures, including ideal and constant relative volatility mixtures, are qualitatively represented by this map. All of the residue curves originate at the light (lowest boiling) pure component, move toward the intermediate boiling component, and end at the heavy (highest boiling) pure component. Residue curves point in the direction of increasing temperature and must always move in such a way that the mixture boiling temperature continuously increases along every curve. (Distillation lines are typically given the opposite orientation. That is, the arrows on a distillation line point in the direction of decreasing boiling temperature. Consequently, the discussion in the text has to be reversed if distillation lines are used). From this property and the direction of the arrows in Fig. 2, the light component is an unstable node; the intermediate component, which deflects the residue curves, is a saddle; and the heavy component is a stable node.

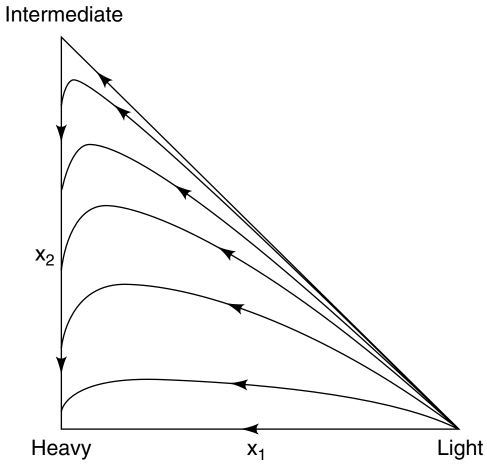


Fig. 2. Residue curve map for a ternary nonazeotropic mixture.

Many different residue curve maps are possible when azeotropes are present (see 13–15). For example, there are six possible residue curve maps for ternary mixtures containing a single azeotrope. These six maps differ by the binary pair forming the azeotrope and by whether the azeotrope is minimum or maximum boiling. Figure 3 represents the case where the intermediate and heaviest components (A and B) form a minimum boiling binary azeotrope. Pure component D is an unstable node, pure components A and B are stable nodes, the minimum boiling binary azeotrope C is a saddle, and the boiling point order from low to high is D→C→A or B. The residue curve connecting component D

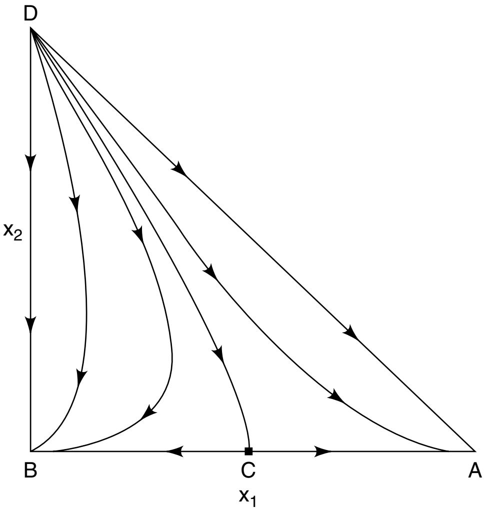


Fig. 3. Residue curve map for a ternary mixture with a distillation boundary running from pure component D to the binary azeotrope C.

to the azeotrope C has the special property that it divides the composition triangle into two separate distillation regions. Any initial mixture charged to the stillpot of the simple distillation apparatus with a composition lying to the left of the curve D–C will result in the last drop of liquid being pure B; whereas any initial mixture with a composition lying to the right of the curve D–C will yield pure A as the last drop of liquid. Residue curves like D–C that divide the composition space into different distillation regions are called simple distillation boundaries, infinite reflux boundaries, separatrices, or, most commonly, distillation boundaries. The residue curve map for a binary mixture is the one-dimensional line connecting the two pure components and an azeotropic point is a boundary in the composition space that limits how far a distillation can proceed. (Consider, for example, the binary mixture of A and B, which forms the minimum-boiling azeotrope C, represented by the bottom edge of the triangle in Fig. 3). In a ternary mixture, the composition space is a two-dimensional triangle and a distillation boundary is a one-dimensional curve that similarly restricts how far a distillation can proceed. There must be a saddle on at least one end of every distillation boundary and each distillation region must contain a stable node, an unstable node, and at least one saddle. As seen in Fig. 3, different distillation regions can have some saddles and nodes in common.

Residue curve maps would be of limited usefulness if they could only be generated experimentally. Fortunately that is not the case. The simple distillation process can be described (16) by the set of equations:

$$\frac{dx_i}{d\xi} = x_i - y_i \qquad \text{for} \quad i = 1, \ldots, c \tag{7}$$

where x_i and y_i are the liquid and vapor mole fractions, respectively, of component i, ξ is a nonlinear time scale that is related to the fraction of liquid remaining in the pot at any instant in time, and c is the number of components in the mixture. Note that the pure components and azeotropes in the mixture correspond to the steady-states or singular points of equation 7 (where the derivative goes to zero) and they are all either nodes or saddles. A detailed mathematical treatment of simple distillation residue curve maps and their properties can be found in the literature (16,17). Given a method for calculating the VLE for the mixture of interest, equation 7 can be numerically integrated forward and backward in time from a number of different initial compositions to generate a residue curve map. An alternative method for sketching residue curve maps that only requires knowledge of the boiling points of the pure components and azeotropes in the mixture has also been published (18–21). This latter method is well suited to mixtures lacking detailed VLE data and thus can be useful in preliminary separation feasibility studies.

Even though the simple distillation process is not a practical method for separating mixtures, simple distillation residue curve maps are extremely useful. They can be used to test the consistency of experimental azeotropic data (18,19,22); to predict the sometimes nonintuitive order and content of the cuts from batch distillations of azeotropic mixtures (23–26); to determine whether a given mixture is separable by distillation; to help identify feasible separating agents; to predict the attainable product compositions; and to synthesize the corresponding distillation sequences (4,13,18,27–36). By helping to identify the limits of distillation, residue curve maps can also be useful in synthesizing separation sequences where distillation is combined with other methods.

Residue curve maps exist for mixtures having any number of components, though they cannot be visualized when there are more than four components. Fortunately, many mixtures of industrial importance contain only three or four key components and can thus be treated as pseudo-ternary or pseudo-quaternary mixtures. Quaternary residue curve maps (three-dimensional tetrahedrons with two-dimensional surfaces as distillation boundaries) are more complicated than their ternary counterparts, but can still be understood using just the boiling point temperatures of the pure components and azeotropes (37). Mathematical (ie, non-graphical) methods for calculating all of the azeotropes, distillation boundaries, and distillation regions in mixtures containing any number of components are available (38–43).

3. Homogeneous Azeotropic Distillation

The most general definition of homogeneous azeotropic distillation is the distillation of any mixture containing one or more azeotropes into the desired pure component or azeotropic products without exploiting any liquid-phase immiscibilities that might be present. Thus, homogeneous azeotropic distillation includes the distillation of azeotropic mixtures in which the desired separation can be achieved without the addition of a separating agent, azeotropic mixtures to which a separating agent that may or may not form new azeotropes is added to facilitate the separation, and non-azeotropic mixtures to which an azeotrope-forming separating agent is added to more easily distill one or more of the compounds away from the others in the original mixture. (When liquid-phase immiscibility is used to make the distillation sequence work, the separation is classified as a heterogeneous azeotropic distillation. These systems are discussed later in the article).

The first step in synthesizing a homogeneous azeotropic distillation sequence is to determine the desired separation objective. For example, sometimes it is desirable to recover all of the constituents in the mixture as pure components; other times it is sufficient to recover only some of the components as pure products. In still other cases, an azeotrope may be the desired product. Not every objective is attainable and those that are feasible may require different distillation sequences (see SEPARATIONS PROCESS SYNTHESIS).

The next step is to sketch or calculate the residue curve map for the mixture to be separated. This will allow one to determine whether the desired separation can be achieved and, if so, how to achieve it or, if not, to determine that the separation objective needs to be changed. (See pp. 223–227 in Ref. 21 for an instructive example). Note that the decision to add a separating agent to a mixture in order to achieve a separation objective also requires that an effective method be found for recovering the agent for reuse.

As mentioned above, simple distillation boundaries are the same as the distillation boundaries of a distillation column operated at total reflux. While the two are not equivalent at finite reflux ratios, the simple distillation boundaries remain a very good approximation to the finite-reflux distillation boundaries, except in regions where the boundaries are extremely curved. Although the composition profile of a distillation column operating at finite reflux can cross a curved simple distillation (infinite reflux) boundary to a limited degree (28–33,44,45) the resulting distillation sequences typically require large reflux (reboil) ratios and/or large recycle flowrates and, thus, are not normally economical. Mixtures such as nitric acid–water–sulfuric acid that have extremely curved boundaries (see Fig. 15) can be exceptions. A good rule-of-thumb, therefore, is that the compositions of the distillate and bottom streams from a distillation column should lie in the same simple distillation region in order for the separation to be feasible. Crossing of simple distillation boundaries should only be attempted as a last resort and only with caution, because the feasibility of such column designs can be sensitive to small inaccuracies in the VLE model and, once built, the column may be sensitive to disturbances.

An overall material balance for a continuously operated distillation column requires that the feed, distillate, and bottoms compositions lie on a straight line in the composition space (the composition triangle for ternary mixtures). Thus, a feasible distillation sequence for separating a homogeneous azeotropic mixture can be identified by determining whether or not the desired products lie in the same distillation region and then can be synthesized by superimposing material balance lines onto the distillation residue curve map. When setting the compositions of the distillate and bottom streams leaving each column in the sequence: (*1*) the distillate composition must have a lower boiling temperature than the bottoms composition, however the component with the lowest (highest) boiling point is not necessarily removed as the distillate (bottoms); (*2*) pure components and azeotropes that are nodes on the residue curve map are easier to obtain as pure products than saddles; and (*3*) a double-feed column is almost always required in order for a saddle on the residue curve map to be the product from a distillation column, eg, extractive distillations. For simplicity, only "sharp" splits, where a pure component or azeotrope is the product from at least one end of the distillation column, are considered here. (This excludes situations where a nonsharp or sloppy split is acceptable, such as when a small amount of impurities are removed in a small distillate or bottoms stream. The complete range of product compositions that can be reached in a single column for a given feed can be determined by calculating the "bow-tie"-shaped separation region (4,21,29,31–34,44).

As an example, consider the residue curve map for the nonazeotropic mixture shown in Fig. 2. It has no distillation boundary so the mixture can be separated into pure components by either the direct or indirect sequence (Fig. 4). In the direct sequence, the unstable node (light component, L) is taken overhead in the first column. The bottom stream composition is determined by following the material balance line (the straight line through the distillate and feed compositions) until a distillation boundary or the edge of the composition space (the composition triangle here) is reached. Thus, the bottom stream from the first column is a binary mixture of the intermediate, I, and heavy, H, components (plus a trace amount of the light component). In the binary I–H mixture, I has the lowest boiling temperature (unstable node) so it is recovered as the distillate in the second column and the stable node, H, becomes the corresponding bottoms stream. The

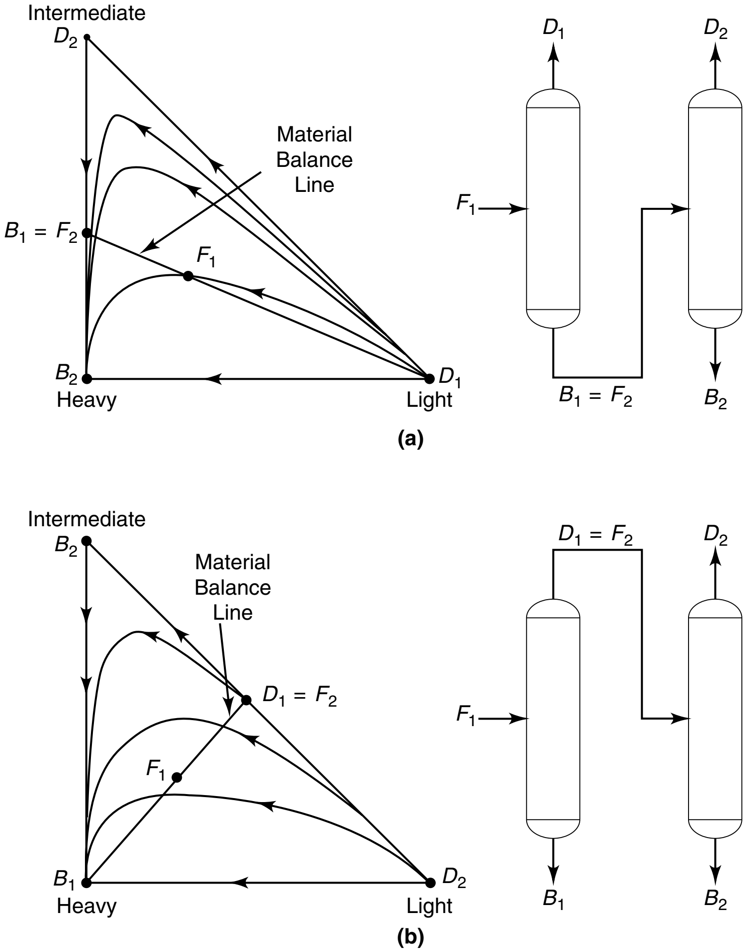
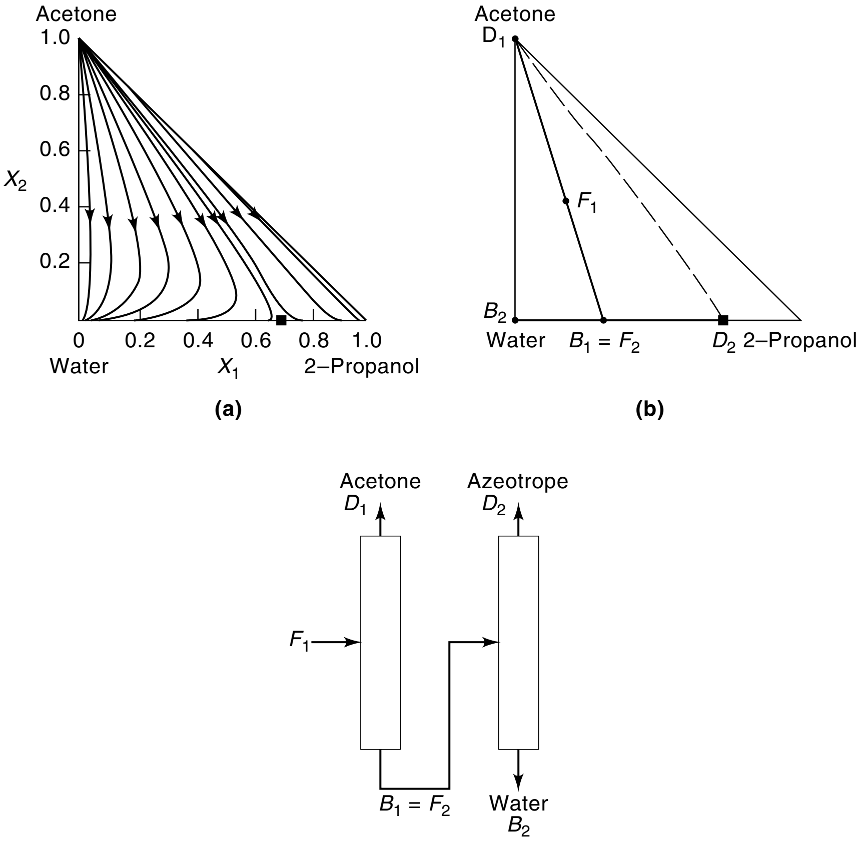


Fig. 4. Column sequences and material balance lines for the (**a**) direct and (**b**) indirect sequences for separating nonazeotropic mixtures.

indirect sequence removes the stable node (heavy component, H) from the bottom of the first column. The composition of the distillate stream is determined by following the material balance line through the bottom and feed compositions until a distillation boundary or the edge of the composition space is reached. Thus, the overhead stream from the first column is a binary mixture of L and I (plus a trace amount of H). In the second column, the unstable node, L, is taken overhead and component I, the stable node in the binary mixture, is recovered as the bottoms. The relative flowrate of any of the streams can be determined by the well-known lever-arm rule. For example, in Fig. 4**b**, the flowrate of stream B_1 is represented by the length of the line segment from F_1 to D_1 and the flowrate of stream D_1 is represented by the length of the line segment from F_1 to B_1. In this example the distillate and bottoms flows are roughly equal, but that is frequently not true.

A second example is the azeotropic mixture of acetone, water, and 2-propanol encountered in the production of acetone by 2-propanol dehydrogenation. The



(a) **(b)**

(c)

Fig. 5. The acetone–2-propanol–water system where ■ represents the 2-propanol–water azeotrope. (**a**) Residue curve map (46); (**b**) material balance line and distillation boundary (---); and (**c**) the column sequence.

goal is to recover the acetone product, recycle the unreacted 2-propanol to the reactor, and discard the wash water. From the residue curve map (Fig. 5**a**), it is clear that, unlike the previous example, the three pure components cannot be recovered because of the distillation boundary running from the acetone vertex to the 2-propanol–water azeotrope, which divides the triangle into two distillation regions. However, by modifying the separation objective to accept recycling the 2-propanol–water azeotrope to the reactor instead of pure 2-propanol, a feasible separation sequence is possible (Fig. 5**b** and **c**). The acetone (unstable node) is taken overhead in the first column, leaving a 2-propanol–water mixture to be distilled in the second column. In this binary mixture, the azeotrope is an unstable node so it becomes the distillate and the stable node, water, is removed from the bottom of the second column. If some up-stream modification were made which reduced the amount of water in the feed to the first distillation column enough to move the feed composition into the other distillation region, the desired separation would no longer be possible. Acetone could still be recovered as the distillate in the first column (assuming there are sufficient stages and reflux), but it would no longer be possible to get pure water from the base of the second column. Instead, 2-propanol would be come out of the bottom of the second column. The binary azeotrope would continue to be distilled overhead in the second column. This means there would no longer be a way to remove pure water from the process.

The overwhelming majority of all ternary mixtures that can potentially exist are represented by only 125 different residue curve maps (15, see also 13, 14). (The rare mixtures in which a pair of compounds form two binary azeotropes (47–51) are exceptions). For each type of separation objective, these 125 maps can be subdivided into those that can potentially meet the objective (ie, the residue curve maps where the desired pure component and/or azeotropic products lie in the same distillation region) and those that cannot. Knowing the structure of the residue curve map for a mixture is thus sufficient to determine if a given separation objective is feasible. (There is, however, no guarantee that a feasible separation will be economical).

The seven most favorable residue curve maps for the common task of distilling a mixture containing a binary minimum-boiling azeotrope into its two constituent pure components by adding a suitable separating agent are shown in Fig. 6. (Favorable residue curve maps for separating binary maximum-boiling azeotropes are given in Ref. 4 and Fig. 14). Other maps that exploit distillation boundary curvature, namely those with a low boiling separating agent that forms a highly curved boundary ending at the azeotrope, have the potential to meet the stated objective (28–33). However, as described earlier, distillation sequences based on such maps have a number of potentially serious drawbacks. Thus, for initial screening purposes, only compounds that yield one of these seven maps need to be considered as possible separating agents for separating binary minimum-boiling azeotropes. Five of the candidate maps require the separating agent to form a maximum-boiling azeotrope with one of the other components. Since maximum-boiling azeotropes are much less common than minimum-boiling azeotropes, these five maps will also be relatively rare. Two examples are adding formic acid to valeric acid–water mixtures (4) and adding hydrazine to water–aniline mixtures (52). The map shown in Fig. 6**a** requires the separating agent to have a boiling point between the other two compounds, but not form any azeotropes. Such separating agents will also be fairly uncommon. Because the likelihood that two compounds will form an azeotrope increases the closer their boiling points are and because the compounds of the original mixture already boil close enough to form an azeotrope, many potential intermediate-boiling separating agents will also form azeotropes with one or both of the original compounds. Benzene is an example of a feasible intermediate-boiling separating agent for separating acetone–heptane mixtures (29,30,32). Thus, of the seven favorable residue curve maps for separating binary minimum-boiling azeotropes into their two constituent pure components, the map representing extractive distillation (Fig. 6**b**) is by far the most common and the most important. Notice that, in this map, the azeotrope is an unstable node (lowest boiling), the two desired pure components are saddles, and the high boiling separating agent is a stable node.

For other separation objectives or when homogeneous azeotropic distillation is combined with other non-distillation separation methods, additional

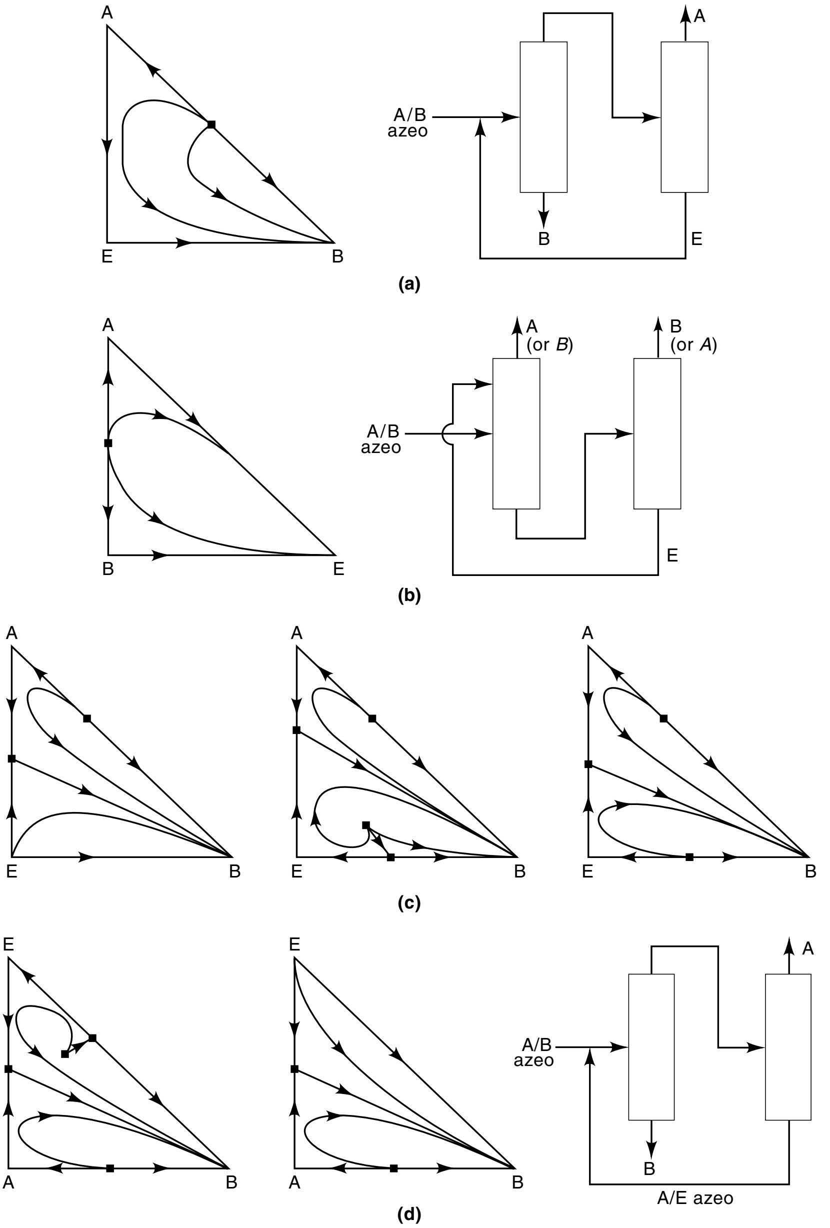
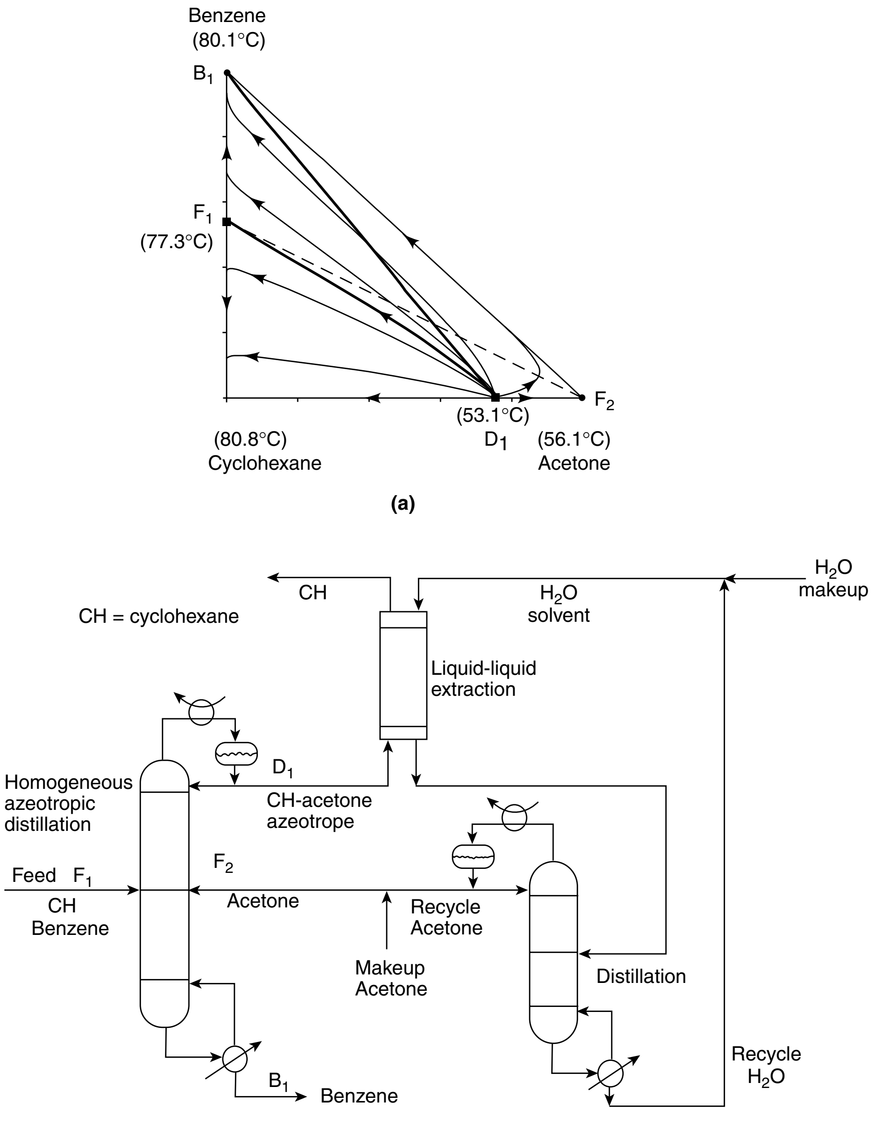


Fig. 6. The seven most favorable residue curve maps and corresponding column sequences for the homogeneous azeotropic distillation of a minimum-boiling binary azeotrope using a mass separating agent E to recover the two constituent pure components A and B (18). The symbol ■ represents an azeotrope. (**a**) Case I, where the separating agent is intermediate boiling and does not introduce any new azeotropes: (**b**) Case II, extractive distillation with a heavy solvent that does not introduce any new azeotropes. In some cases, B will come off the top of the first column instead of A; (**c**) Case III, where the separating agent is intermediate boiling and forms a maximum boiling azeotrope with the lighter of the two pure components (ie, A). The agent may or may not form a minimum boiling azeotrope with B, and there may or may not be a minimum boiling ternary azeotrope lean in A; and (**d**) the same column configuration as case III, but the separating agent is lower boiling.

residue curve maps can lead to successful separations and need to be considered. For example, the minimum-boiling homogeneous azeotrope formed by cyclohexane and benzene can be separated by adding acetone (53), despite the fact that acetone and cyclohexane form a binary minimum-boiling homogeneous azeotrope that introduces a distillation boundary running from the acetone–cyclohexane azeotrope to the benzene–cyclohexane azeotrope, which divides the desired pure components into different distillation regions (Fig. 7**a**). Acetone (F_2) is fed to the first distillation column along with the benzene–cyclohexane azeotrope (F_1) so that the overall feed to the column ($F_1 + F_2$) lies within the upper distillation region on the residue curve map. Benzene, the stable node in this distillation region, is recovered from the bottom of the first distillation column (B_1) and a mixture near the acetone–cyclohexane azeotrope is distilled overhead (D_1). (See the material balance lines on Fig. 7**a**). Next liquid–liquid extraction with water is used to separate the acetone–cyclohexane azeotrope (Fig. 7**b**). Acetone is extracted into the aqueous phase and nearly pure cyclohexane is recovered as the raffinate. Finally, acetone and water are separated by distillation with the acetone recycled to the first column and the water recycled to the extractor.

When neither or only one of the components needs to be recovered as a pure product, separating agents that form azeotropes and introduce distillation boundaries that divide the pure components into different distillation regions can sometimes be used without resorting to a nondistillation step. For example, even though methyl acetate and water form a minimum-boiling homogeneous azeotrope, water is commonly used in polyvinyl alcohol plants to separate the minimum-boiling homogeneous azeotrope formed by methyl acetate and methanol (54). (Methyl acetate and water are only partially miscible but, unlike most acetate–water mixtures, the methyl acetate–water azeotrope lies outside of the immiscible region). The methyl acetate–methanol–water mixture contains a distillation boundary running from the methyl acetate–methanol azeotrope to the methyl acetate–water azeotrope, placing pure methyl acetate and methanol into different distillation regions and making it impossible to recover both components as pure products (Fig. 8). Notice that the larger distillation region is bounded by the methyl acetate–methanol azeotrope (unstable node), pure methanol (saddle), the methyl acetate–water azeotrope (saddle) and the high boiling separating agent, water (stable node). In other words, this four-sided distillation region has the same structure as the extractive distillation residue curve map (Fig. 6**b**), except that one of the saddles is an azeotrope. As long as the overall feed to the column lies in this distillation region, the column sequence will also be identical to that shown in Fig. 6**b**. In the first column, a double-feed column with water as the upper feed, the methyl acetate–water azeotrope is the overhead product. (A wet methyl acetate stream is acceptable here because the methyl acetate is sent to a hydrolysis reactor where more water is added). A mixture of methanol and water leaves the bottom of the first column and becomes the feed to the second column. Methanol is recovered as the distillate in the second column. Water leaves the bottom of the second column and is recycled to the first column, completing the sequence. This process and others with separating agents that give rise to similarly structured four-sided distillation regions are thus a variation of extractive distillation where only one of the azeotropic-constituents is recovered as a pure product. Another example is using



(a)

(b)

Fig. 7. Hybrid process for separating the benzene-cyclohexane azeotrope using acetone as the separating agent. (**a**) The residue curve map for the acetone–benzene–cyclohexane mixture at 101 kPa with superimposed feed (----) and column (——) material balance lines for the homogeneous azeotropic distillation step. Azeotropes are denoted by ■. (**b**) The complete separation sequence (53).

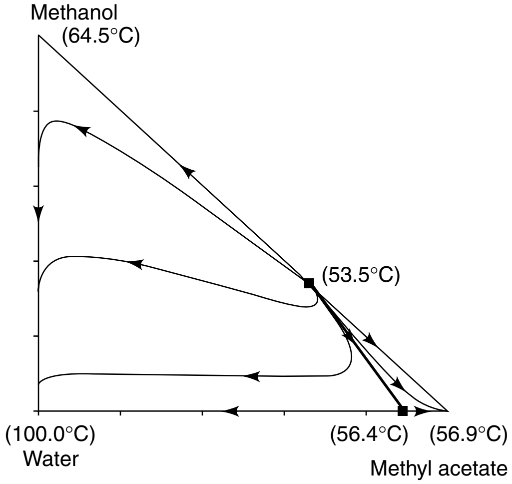


Fig. 8. Residue curve map for the methyl acetate–methanol–water mixture at 101 kPa, where ■ represents an azeotrope. The immiscible region is not shown.

methyl ethyl ketone (MEK) to separate the acetone–methanol azeotrope (21,55). Methanol and MEK form a minimum boiling azeotrope and the ternary mixture contains a distillation boundary running between the two azeotropes, which puts acetone and methanol into different distillation regions, ie, the residue curve map is analogous to Fig. 8. This extractive distillation sequence distills the methanol–MEK azeotrope overhead in the first (double-feed) column while acetone is recovered from the top of the second column. Successful separating agents with residue curve maps similar to the one shown in Fig. 8 will have the same attributes as those described later for extractive distillation solvents, except for the prohibition against azeotrope formation.

4. Extractive Distillation

Extractive distillation is defined as distillation in the presence of a miscible, higher boiling, liquid separating agent, commonly called the solvent, which does not form azeotropes with the other components in the mixture (27). Extractive distillation is widely used in the chemical and petrochemical industries for separating azeotropic, close-boiling, and other low relative volatility mixtures, including those whose phase diagram shows the presence of a severely “pinched” (low relative volatility) region over a limited composition range (ie, a tangent pinch).

Extractive distillation works because the solvent is specially chosen to interact differently with the components of the original mixture, thereby altering their relative volatilities. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that it is present at an appreciable concentration in the liquid phase on all of the trays below. The mixture to be separated is added through a second feed point further down the column (see Fig. 6**b**). In the extractive column, the component with the higher volatility in the presence of the solvent (not necessarily the component with the lowest boiling point) is distilled overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is then separated from the remaining components, typically by distillation in a second column, and recycled back to the first column. The product leaving the top of the solvent recovery column is relatively free of both the compound distilled overhead in the extractive column and the solvent.

Many examples of extractive distillation can be found in the literature. A selected few are included here to give the reader an idea of the breadth of possible applications. Extractive distillation has been widely used since the 1940s to separate butanes, butenes, and butadiene. (Butadiene and *n*-butane form an azeotrope while the various butanes and butenes have low relative volatilities). Industrially used solvents have included furfural (56,57), acetone, acetonitrile (58), dimethylformamide (59), dimethylacetamide (60), N-methylpyrrolidone (61), and dimethylsulfoxide (62). Other extractive distillation examples include: distilling nonaromatics away from aromatics using phenol (63), sulfones (64), *N*-methylpyrrolidone (65), or dimethylformamide (66); separating toluene from methylcyclohexane using phenol (67); removing close-boiling heptane isomers from cyclohexane, an important raw material for manufacturing nylon intermediates (68); separating the phenol–cyclohexanone azeotrope using adipic acid diester (69); separating the cumene–phenol azeotrope using trisubstituted phosphates (70); separating the low relative volatility mixture of propylene and propane using acrylonitrile (71); the Ryan-Holmes process for separating the ethane–carbon dioxide azeotrope that arises when carbon dioxide is used for enhanced oil-field recovery (72); separating the azeotropes formed by alcohols and their esters using aromatic hydrocarbons (73); separating the methanol–methylene bromide azeotrope using ethylene bromide (74); dehydrating ethanol using ethylene glycol (75–77); separating acetone and methanol using water (78); separating the pyridine–water azeotrope using bisphenol (79); dehydrating tetrahydrofuran using monopropylene glycol (80) or 1,4-butanediol (81); separating close-boiling vinyl acetate and ethyl acetate using phenol (82); separating mixtures of dimethyl ether and chloromethane, obtained by reacting methanol and HCl, using water (83) or methanol (84) as the extractant; purifying crude propylene oxide reaction mixtures using propylene glycol (85); and purifying a variety of fluorocarbons used as refrigerants, blowing agents, and aerosol propellants (86–91).

Extractive distillations can be divided into three general categories: (*1*) the separation of minimum-boiling azeotropes, (*2*) the separation of maximum-boiling azeotropes, and (*3*) the separation of low relative volatility nonazeotropic mixtures. For separating binary mixtures into pure components, each category is represented by a single, unique residue curve map.

4.1. Minimum Boiling Azeotropes. Every extractive distillation that separates a binary minimum boiling azeotropic mixture into its pure components has a residue curve map and column sequence like the one shown in Fig. 6**b**. Typical tray-by-tray composition profiles are shown in Fig. 9. Notice that the concentration of the solvent remains high throughout the extractive section of the

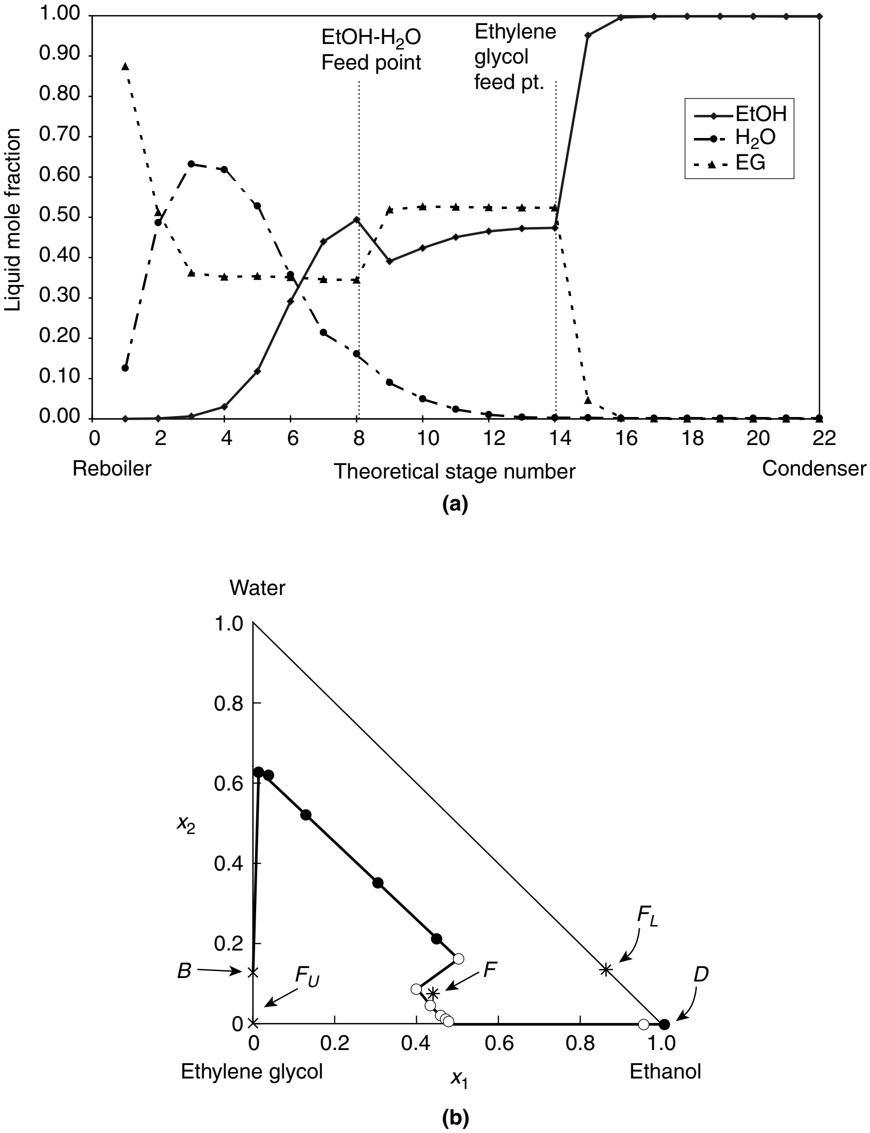


Fig. 9. Extractive distillation column profiles for separating ethanol (EtOH) and water (H_2O) using ethylene glycol (EG) as the extractive agent. (**a**) Liquid compositions versus theoretical stage number where (—◆—) represents ethanol, (-- -●-- -) water, and (-- ▲ --) ethylene glycol; and (**b**) liquid composition profiles in mole fraction coordinates where (*) represents the feeds, (●) is the distillate, (X) is the bottoms, and (●) and (○) are the tray compositions. (From Example 5.4 in Ref. 21.)

column, ie, the section between the two feed points (Fig. 9**a**). This is a characteristic of all extractive distillations and is due to the need for the solvent to be present in sufficient quantity on the trays to alter the relative volatilities of the components being separated. Most of the separation of the components that form the azeotrope takes place here in the extractive section. The purpose of the stripping section (below the lower feed) is to strip out the remaining "light" component(s) to complete the separation of the key components begun in the extractive section. The rectifying section (above the upper or solvent feed point) separates the high-boiling solvent from the "light" component(s) so the solvent won't contaminate the distillate.

When distilling ideal mixtures, the component with the lowest boiling point is always the one recovered as the distillate. That is not always the case in extractive distillation. Neither can the design engineer freely pick which azeotropic component to recover in the distillate, despite the apparent symmetry of the residue curve map (Fig. 6**b**). For a given solvent, one and only one component can be recovered overhead in the extractive column and it need not be the pure component with the lowest boiling point. For example, the extractive distillation of ethanol and water using gasoline (76), some phenols (92), cyclic ketones, or cyclic alcohols (93) causes water to distill overhead in the extractive column while the lower boiling ethanol leaves in the bottom stream with the solvent. Similarly, ketones distill the higher boiling methanol overhead from methanol–acetone mixtures (55,94) and furfural reverses the natural volatility difference of butane–butadiene mixtures (56). This phenomenon where the intermediate boiling pure component distills overhead in the extractive column is entirely due to the way in which the relative volatilities of the components in the mixture are altered by the liquid-phase interactions between the solvent and the other components.

One way to identify which component will distill overhead with a given solvent is to draw pseudo-binary y–x phase diagrams for the mixture to be separated. A pseudo-binary phase diagram is one in which the VLE data for the azeotropic constituents (components 1 and 2) are plotted on a solvent-free basis. When no solvent is present, the pseudo-binary y–x diagram is the true binary y–x diagram (Fig. 10**a**). At the azeotrope, where the VLE curve crosses the 45° line, $\alpha_{12} = 1.0$. To determine which component will be the distillate, a series of pseudo-binary y–x plots are drawn at increasing solvent concentrations until the pseudo-azeotrope, the point where the solvent-free VLE curve crosses the 45° line, ie, where $\alpha_{12} = 1.0$, disappears into one of the pure component corners. The resulting pseudo-binary phase diagram will either resemble Fig. 10**b** where the solvent increases the volatility of component 1 relative to component 2, making component 1 the distillate, or Fig. 10**c**, where the solvent has the opposite effect, making component 2 the distillate. For example, aniline increases the volatility of cyclohexane (nbp = 80.8°C) relative to benzene (nbp = 80.1°C) (Fig. 10**d**). Thus, with aniline as the extractive agent, the higher boiling cyclohexane will distill overhead in an extractive distillation. Pseudo-binary y–x phase diagrams can also be used to determine which component will be the distillate in extractive distillations of non-azeotropic mixtures.

Some authors (95) prefer to use "isovolatility" curves to determine which component will become the distillate in an extractive distillation. For a mixture of components 1 and 2 and an extractive distillation solvent S, an isovolatility curve is simply the locus of points where $\alpha_{12} = 1.0$ in the ternary composition space, ie, with different amounts of solvent present. The isovolatility curve starts at the binary azeotrope and ends on one of the faces of the composition triangle. If it ends on the 1-S face, then component 1 will distill overhead. Likewise,

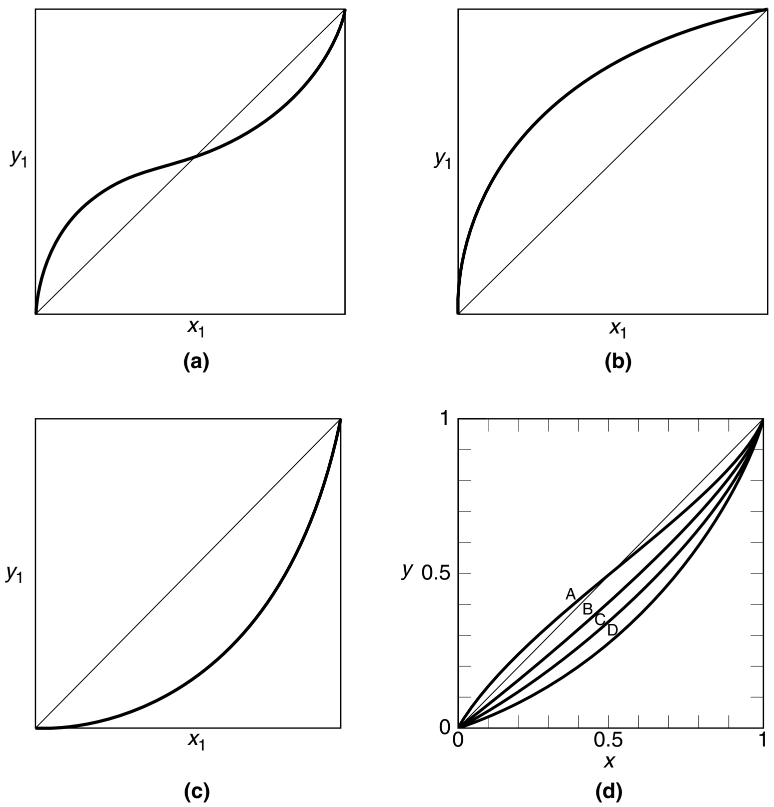


Fig. 10. Pseudo-binary (solvent-free) y–x phase diagrams for determining which component will be the distillate. (**a**) No solvent present; (**b**) and (**c**) with sufficient solvent present to eliminate the pseudo-azeotrope with component 1 and component 2, respectively, becoming the distillate (96); and (**d**) experimental VLE data for cyclohexane–benzene where A, B, C, and D represent 0, 30, 50, and 90 mol% aniline, respectively (97).

component 2 will be the distillate if the isovolatility curve ends on the 2-S face. Pseudo-binary y–x phase diagrams and isovolatility curves are simply different ways of visualizing the same information. When plotted on a solvent-free basis, points along an isovolatility curve become the pseudo-azeotropic points on a series of pseudo-binary phase diagrams.

Extractive distillations exhibit unexpected behavior at large reflux ratios. In ordinary distillations, the number of stages required to achieve a given separation decreases monotonically as the reflux ratio increases. Equivalently, in an operating distillation column where the number of stages is fixed, the distillate purity monotonically increases as the reflux ratio increases. Consequently, it is very common to increase the reflux when higher purity products are desired. In extractive distillations, however, the behavior is more complex. As the reflux ratio increases from its minimum value, the number of theoretical stages necessary to achieve a given separation initially decreases—the same behavior observed with ordinary distillations. Eventually, however, a minimum in the number of stages required is reached and further increases in the reflux ratio require an *increasing* number of stages (essentially all in the extractive section) in order to continue to achieve the same separation. Fig. 11**a** illustrates this behavior in the ethanol–water–ethylene glycol separation from Fig. 9. For azeotropic mixtures, beyond a certain large reflux ratio, called the maximum reflux ratio, an infinite number of stages would be required to achieve the same separation. During the operation of an extractive distillation column, two different types of behavior can also be observed, depending on where the column is operating along its distillate purity vs. reflux ratio curve (Fig. 11**b**). At lower reflux

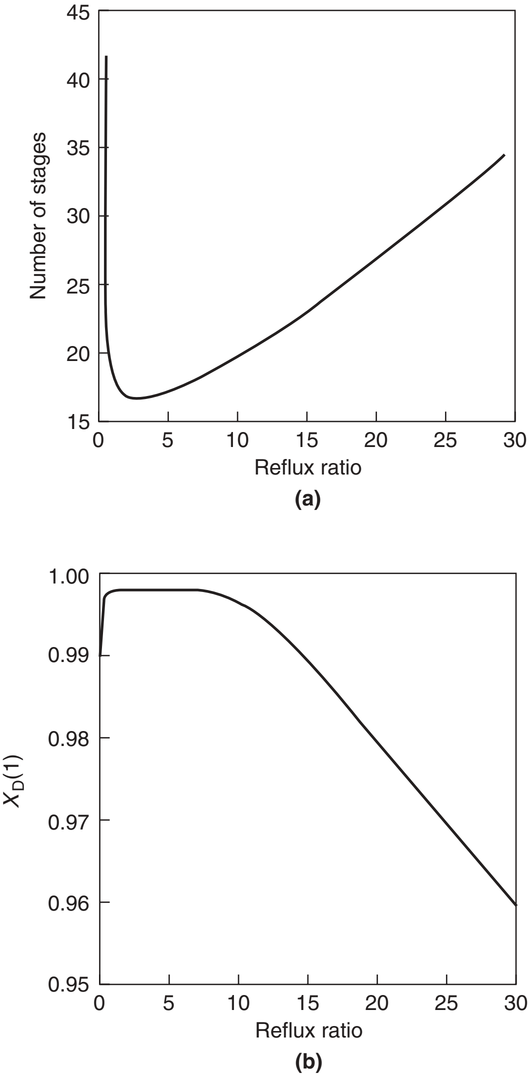


Fig. 11. Ethanol–water separation using ethylene glycol as the solvent (from Example 5.4 in Ref. 21). (**a**) Number of theoretical stages in the extractive column as a function of reflux ratio. (**b**) Distillate mole fraction of ethanol as a function of reflux ratio.

ratios, the column behaves normally. Increasing the reflux increases the product purity. At larger reflux ratios, however, the inverse behavior occurs. Increases in reflux ratio result in *decreased* product purities. As might be imagined, standard distillation control systems will have trouble controlling an extractive distillation column operating in this inverse response region or, worse still, in the vicinity of the inflection point where the response to reflux ratio changes switches from the expected to the inverse. Thus, an important step in the design of an extractive distillation sequence is to locate where the inverse behavior begins for the chosen solvent and to design the column to operate well away from this point. The range of reflux ratios over which the normal response occurs increases with the solvent-to-feed ratio and, in most cases, the inverse response region is easily avoided. This unexpected increasing stage requirement or decreasing product purity with increasing reflux ratios is caused by the dilution of the solvent concentration in the column (which makes the separation more difficult) as more and more of the solventless reflux is fed back into the column.

4.2. Design Optimization. Optimization is an important yet often neglected step in the design of extractive distillation sequences. The cost of the solvent recovery step affects the optimization and thus must also be included. Optimization not only yields the most efficient extractive distillation design, but is also necessary for meaningful comparisons with other separation sequences and methods.

When several simple heuristics are used, the optimization procedure usually reduces to a single-variable optimization of the feed ratio, ie, the ratio of the solvent to process feed flow rates, which has the greatest effect on the sequence cost (77,98). The simple heuristics are for (*1*) setting the purity of the solvent recycle stream midway between unity and the minimum required purity, calculated by assuming that all of the intermediate volatility component in the bottom of the solvent recovery column (water in the ethanol–water–ethylene glycol system) ends up in the distillate of the extractive column (see Eqs. 3–6 of Ref. 77); (*2*) setting the temperature of the solvent feed 5–15°C below the boiling temperature of the distillate leaving the extractive column; (*3*) setting the fractional recovery of the component recovered at the top of the extractive column to between 99.5% and 99.99%; and (*4*) setting the reflux ratios in all of the columns to 1.2–1.5 times the minimum. Minimum reflux ratios for extractive distillations can be calculated using the methods presented in Refs. 99 and 100 to solve the equations given by Refs. 101 and 102.

Because homogeneous azeotropic mixtures cannot be separated into pure component products by isobaric distillation without a solvent, but can be separated in the presence of a sufficient amount of a suitable solvent, there is clearly some minimum amount of solvent that just makes the separation possible. This minimum solvent flow, or minimum solvent-to-feed ratio, depends on the solvent used and the effectiveness with which it alters the relative volatility of the components being separated. A solvent yielding a smaller minimum feed ratio is a better solvent and should result in a lower cost design than a solvent with a larger minimum feed ratio. The solvent composition required to just make the pseudo-azeotrope disappear on a pseudo-binary y–x phase diagram, ie, to "break" the azeotrope, can be taken as a qualitative measure of the minimum solvent flow. A simple method for estimating minimum solvent flows has been published

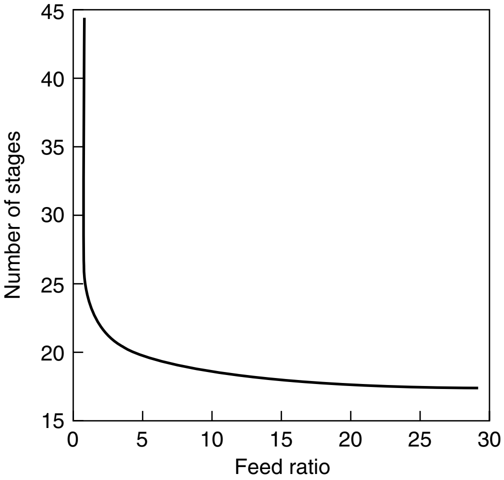


Fig. 12. Number of theoretical stages in the extractive column as a function of the solvent-to-feed ratio for the extractive distillation of ethanol and water using ethylene glycol as the solvent (21).

(95) as has an exact quantitative method (96,98). As a rough rule-of-thumb, the economically optimal feed ratio is often between two and four times the minimum feed ratio (96,98). Many industrial extractive distillations operate with feed ratios between 1 and 5, though we know of commercial units operating with feed ratios as low as 0.15 and as high as 20. Fig. 12 shows how the number of stages in the extractive column varies with feed ratio for the ethanol–water separation shown in Fig. 9. The relationship between stages required and feed ratio is the same for all extractive distillations of azeotropic mixtures. The number of stages required is infinite at the minimum feed ratio, rapidly drops at feed ratios slightly above the minimum, and then continues to decrease at a slowing rate at higher feed ratios until, eventually, an asymptotic region is reached where further increases in solvent flow has little or no effect on the number of stages required. Sometimes the number of stages required in the extractive column will start to increase again at sufficiently high feed ratios. Fig. 13 shows how the feed ratio influences the total annualized cost (TAC) [defined in Ref. 103] of an extractive distillation sequence for dehydrating ethanol using ethylene glycol. Cost diagrams for all extractive distillations have this same distinctive shape. The cost is very high near the minimum feed ratio, but then rapidly decreases to a minimum before starting to increase again at higher feed ratios, as the costs associated with the increasing solvent recirculation rate (increased heating and cooling loads and larger diameters in both columns), begin to exceed the cost savings from the reduction in the number of stages in the extractive column.

4.3. Maximum Boiling Azeotropes.

Maximum boiling azeotropes are far less common than minimum boiling azeotropes and so are successful extractive distillations of maximum boiling azeotropes using high boiling solvents. Adding a high boiling solvent to a mixture containing a maximum boiling

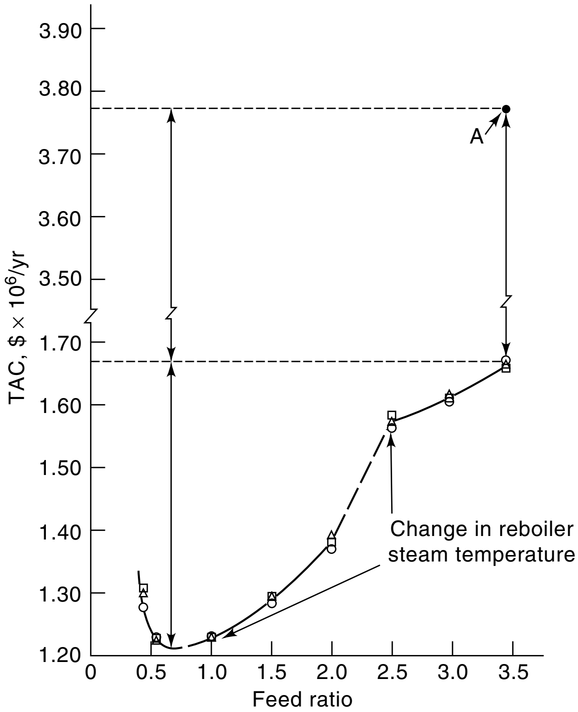


Fig. 13. Extractive distillation sequence cost as a function of the solvent-to-feed ratio for producing anhydrous ethanol from azeotropic ethanol using ethylene glycol at reflux ratios of $\Delta = 1.15\ r_{\min}$, $\bigcirc = 1.2\ r_{\min}$, and $\square = 1.3\ r_{\min}$ (77). Point A represents another published design for the same mixture (75).

azeotrope causes a distillation boundary running from the maximum boiling azeotrope to the heavy solvent (Fig. 14), which divides the desired pure components into different distillation regions. The only way a high boiling solvent can yield an economically viable means for separating a maximum boiling azeotrope is if the resulting distillation boundary is extremely curved. Classic examples include using sulfuric acid to concentrate aqueous nitric acid (104–106) or hydrochloric acid (107) mixtures. *N*-formylmorpholine has also been proposed for breaking the maximum-boiling formic acid–water azeotrope (108). Figure 15 shows that the distillation boundary in the nitric acid–water–sulfuric acid mixture is indeed highly curved. Applying the lever arm rule to the material balance lines superimposed on the residue curve map in Fig. 15**a** shows that the internal recycle flow rates (B_1 and B_2) in this process are relatively high compared with the product flow rates (D_1 and D_2).

4.4. Nonazeotropic Mixtures. Extractive distillation is widely used in the petrochemical industry to separate close-boiling but non-azeotropic mixtures. Common examples include the purification of aromatics, the separation of olefins and paraffins, diolefins and olefins, paraffins and napthalenes, styrenes and aromatics, and a number of other hydrocarbon mixtures (109).

The extractive distillation of any close-boiling or other low relative volatility, but non-azeotropic, mixture using a high boiling solvent is represented

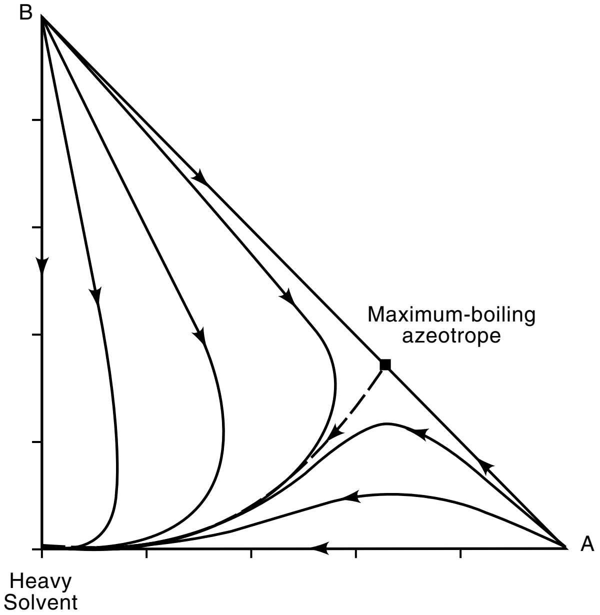
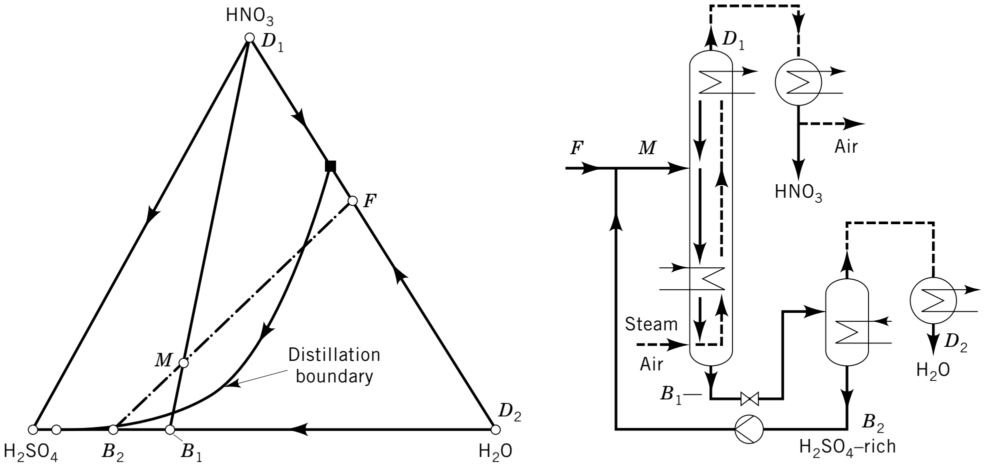


Fig. 14. Residue curve map for separating a maximum boiling azeotrope using a high boiling solvent where (- - - -) represents the distillation boundary and ■ the azeotrope.

by the residue curve map shown in Figure 2. Although this map is different than the one for the extractive distillation of minimum boiling azeotropes, the distillation sequence is identical (see Fig. 6**b**) and the process works for the same reason. The solvent alters the relative volatilities of the components to be separated via liquid-phase interactions. Depending on the nature of these interactions, either



(a) (b)

Fig. 15. Extractive distillation of nitric acid, HNO_3, and water, H_2O, using sulfuric acid, H_2SO_4, as the solvent. (**a**) Residue curve map and material balance lines where ■ represents the maximum boiling azeotrope and (**b**) the column sequence (11).

the low boiling or the intermediate boiling pure component will be distilled overhead in the extractive column. Pseudo-binary y–x phase diagrams can again be used to determine which component will distill overhead in the extractive column. When the composition of the lower boiling component is plotted and increasing solvent concentrations cause the pseudo-binary VLE curve to lie above the true binary VLE curve, then this solvent accentuates the natural volatility difference and will cause the lower boiling component to distill overhead. If the pseudo-binary VLE curve lies below the true binary VLE curve, then this solvent reverses the natural volatility difference of the mixture and, at sufficiently high solvent concentrations, the intermediate boiling component will distill overhead.

Because there is no azeotrope, these mixtures could in theory be separated without adding a solvent, though it would be a difficult and expensive separation. Consequently, there is no minimum feed ratio (minimum solvent flow). Curves relating the number of stages in the extractive column to the feed ratio (eg, Fig. 12) end at a large but finite number of stages when the solvent flow rate goes to zero. By using the heuristics provided earlier, optimization of extractive distillation sequences for separating non-azeotropic mixtures usually reduces to a one-variable optimization of the feed ratio. These extractive distillations can also exhibit inverse response at sufficiently large reflux ratios, due to dilution of the solvent concentration in the column. (See p. 447 of Ref. 110 for additional information).

References 109 and 112 provide additional information on the extractive distillation of close-boiling, non-azeotropic mixtures and the use of mixed-solvent systems.

4.5. Solvent Selection. The most important step in developing a successful (ie, economical) extractive distillation sequence is identifying an effective solvent for the separation. The solvent selection procedure is typically carried out in several stages. In the first step, simple qualitative methods are used to identify general classes of compounds or functional groups that may make effective solvents for a given separation. In the next step, individual compounds are evaluated, typically by experimental methods, and then ranked to identify the most promising candidates. In the final step, detailed vapor–liquid equilibrium measurements are made for several of the top candidates, the separation is simulated using chemical process simulation software and/or tested in a lab-scale or miniworks column, and then the final solvent selection is made. The final selection process should include an economic comparison of the optimal separation sequence with each of the final solvent candidates, because differences in the solvent recovery costs can influence the decision. The remaining discussion focuses on the first two stages.

As described earlier, extractive distillation works because the presence of the solvent alters the relative volatilities of the components being separated. Consequently, an important measure of the effectiveness of an extractive distillation solvent is its selectivity, S_{ij},

$$S_{ij} = \frac{(\alpha_{ij})_s}{\alpha_{ij}} = \frac{(\gamma_i P_i^{\text{sat}}/\gamma_j P_j^{\text{sat}})_s}{\gamma_i P_i^{\text{sat}}/\gamma_j P_j^{\text{sat}}} \cong \frac{(\gamma_i/\gamma_j)_s}{\gamma_i/\gamma_j} \tag{8}$$

which is simply the ratio of the relative volatilities of the key components with and without the solvent present. Solvents with selectivities farthest from unity are generally preferred. Since interactions with the solvent predominantly occur in the liquid phase—affecting the ratio of the liquid-phase activity coefficients (γ_i/γ_j)—and the ratio of the pure component vapor pressures is normally not significantly affected by changes in the boiling temperature caused by the presence of the solvent, equation 8 is often expressed as the ratio of the key component activity coefficients with and without the solvent present. Alternatively, since the denominator in equation 8 is the same for all solvents, the solvent selectivity is sometimes written as just the ratio of the key component activity coefficients in the presence of the solvent. While it is possible to find solvents that increase or decrease the ratio of activity coefficients, it is usually preferable to select a solvent that accentuates the natural difference in vapor pressures of the components to be separated. In other words, a solvent that increases γ_i relative to γ_j when $P_i^{\mathrm{sat}} > P_j^{\mathrm{sat}}$ ($S_{ij} > 1$) is favored over one that increases γ_j relative to γ_i ($S_{ij} < 1$). In the latter case, adding small amounts of the solvent actually makes the separation more difficult, and relatively large quantities may be required to completely overcome the natural volatility difference and enhance the separability of the original mixture (105). Such solvents will cause the intermediate boiling pure component to distill overhead in the extractive column. A heuristic, therefore, is to favor solvents that cause the more volatile (lower boiling) component to distill overhead (ie, solvents with selectivities greater than 1.0).

To force the naturally more volatile component i overhead, the solvent should either behave essentially ideally with component j and cause positive deviations from Raoult's law for component i ($\gamma_j \sim 1$ and $\gamma_i > 1$), or behave essentially ideally with component i and cause negative deviations from Raoult's law for component j ($\gamma_i \sim 1$ and $\gamma_j < 1$). Compounds of similar type and size, eg, pentane–hexane or methanol–ethanol, tend to behave ideally in the liquid phase and thus have activity coefficients close to unity. Dissimilar molecules tend to repel each other, causing positive deviations from Raoult's law and, in the extreme, resulting in liquid-phase immiscibilities. Compounds that tend to associate in the liquid phase exhibit negative deviations from Raoult's law. Because systems showing positive deviations are more common, the usual approach is to force the lower boiling component overhead by selecting a solvent which is chemically similar to the higher boiling species and dissimilar to the lower boiling species.

Homologues, polarity, and hydrogen-bonding tendencies can be used for a crude screening of candidate solvents by qualitatively predicting the types of deviations from ideality that can be expected. When the compounds being separated are chemically dissimilar, suitable solvents may be found among the higher boiling homologues of either compound, though homologues of the less volatile compound are generally favored, as they enhance the natural volatility difference. The molecular similarity of two members of the same chemical family causes them to form relatively ideal solutions, while the molecular dissimilarity of the homologue and the other compound tend to cause positive deviations. For example, higher boiling alcohols could be used to force acetone overhead from the acetone–methanol azeotrope while the higher boiling ketones would force

Table 1. **Relative Polarities of Functional Groups**[a]

most polar	water
	organic acids
	amines
	polyols
	alcohols
	esters
	ketones
	aldehydes
	ethers
	aromatics
↓	olefins
least polar	paraffins
Effect of branching	
most polar	normal
	secondary
least polar	tertiary

[a] From Ref. 4.

methanol overhead (94). Choosing the lowest boiling homologue that does not azeotrope with the other components (94) or the homologue that just barely remains miscible (111) have both been recommended.

Mixtures of liquids with similar polarity typically form nearly ideal solutions while liquids with different polarities exhibit positive deviations from ideality. The degree of deviation from ideality is roughly proportional to the difference in polarity. Table 1 gives a qualitative ranking of the polarity of various functional groups. Note that steric hindrance diminishes the polarity of a compound. Other more quantitative measures of a molecule's polarity include the dipole moment, the dielectric constant (112), and the solubility parameter (3,4,113). Dipole moment interactions in hydrocarbon systems are discussed in Ref. 113. In general, adding a more polar solvent increase the volatility of the least polar compound in the original mixture. The reverse is true when a less polar solvent is added. As an example, consider the azeotropic mixture of acetone and methanol. Methanol is more polar than acetone (Table 1) so, by adding an even more polar compound like water, the relative volatility of acetone to methanol can be increased enough to "break" the azeotrope. If, on the other hand, a nonpolar compound like an alkane were added, the volatility of methanol relative to acetone would increase (105). Since acetone has a lower boiling point than methanol, the heuristic to favor solvents that enhance the natural volatility difference tells us that a polar solvent like water is preferred.

Carlson and Stewart's (114) guidelines for choosing potential extractive distillation solvents based on polarity arguments are given below. Be aware, however, that exceptions do occur. (*1*) If the mixture to be separated is highly polar (like acetic acid and water), choose a polar solvent or a nonpolar solvent (like a hydrocarbon) that is more soluble with the higher boiling component. (*2*) For nonpolar mixtures (like cyclohexane–benzene) choose a polar solvent (like aniline) that is more soluble with the higher boiling component. (*3*) For a mixture where the more volatile component is polar and the less volatile component is nonpolar, choose a nonpolar or a polar solvent. Be aware that polar solvents may reverse the relative volatility. (*4*) For mixtures where the more volatile component is nonpolar and the other component is polar, choose a polar solvent. (*5*) For mixtures of compounds that are moderately polar, choose a polar solvent or a nonpolar solvent that is more soluble with the higher boiling component. For cases where either a polar or a nonpolar solvent is recommended, polar compounds are often preferred because they typically cause the solution to be more nonideal.

Strong deviations from ideality are often associated with hydrogen bonding between molecules and many successful extractive distillation solvents are compounds capable of forming strong hydrogen bonds such as phenols, aromatic amines like aniline, higher alcohols, glycols, etc (115). Several authors have published tables based on the hydrogen-bonding tendency of different classes of compounds and functional groups for qualitatively predicting the type of deviation likely to occur in a mixture (4,115–118). Table 2 is representative. To distill the more volatile component overhead, use Table 2 to select classes of compounds that cause positive deviations with the more volatile component or negative deviations with the less volatile component.

Once several potentially promising families of compounds have been identified using the above qualitative methods, individual solvent candidates need to

Table 2. **Predicted Deviations from Raoult's Law for Different Functional Groups Based on Hydrogen-Bonding Interactions**[a]

		Solvent Class[b]											
Solute Class		1	2	3	4	5	6	7	8	9	10	11	12
	H-Donor Groups												
1	phenol	0	0	–	0	–	–	–	–	–	–	+	+
2	acid, thiol	0	0	–	0	–	–	0	0	0	0	+	+
3	alcohol, water	–	–	0	+	+	0	–	–	+	+	+	+
4	active H on multihalogen paraffin	0	0	+	0	–	–	–	–	–	–	0	+
	H-Acceptor Groups												
5	ketone, amide with no H on N, sulfone, phosphine oxide	–	–	+	–	0	+	+	+	+	+	+	+
6	tertiary amine	–	–	0	–	+	0	+	+	0	+	0	0
7	secondary amine	–	0	–	–	+	+	0	0	0	0	0	+
8	primary amine, ammonia, amide with 2H on N	–	0	–	–	+	+	0	0	+	+	+	+
9	ether, oxide, sulfoxide	–	0	+	–	+	0	0	+	0	+	0	+
10	ester, aldehyde, carbonate, phosphate, nitrate, nitrite, nitrile, intramolecular bonding, eg, *o*-nitrophenol	–	0	+	–	+	+	0	+	+	0	+	+
11	aromatic, olefin, halogen aromatic, multihalogen paraffin without active H, monohalogen paraffin	+	+	+	0	+	0	0	+	0	+	0	0
	Non-H-Bonding Groups												
12	paraffin, carbon disulfide	+	+	+	+	+	0	+	+	+	+	0	0

[a] From Reference 117.

[b] – = Negative deviation. + = Positive deviation. 0 = No deviation.

be identified and ranked. As a starting point, elminate all compounds with boiling points lower than the compounds to be separated. This ensures that, throughout the column, the solvent will be predominantly present in the liquid phase where it can alter the activity coefficients of the mixture being separated. The likelihood that a potential solvent will form azeotropes with any of the mixture components can be minimized by selecting compounds that boil 30–50°C or more above the mixture. On the other hand, the solvent should not boil so high that excessive temperatures or high vacuum are required in the solvent recovery column.

Group contribution methods such as modified UNIFAC (Dortmund) (119,120) can be used to predict activity coefficients in mixtures and thus provide a nonexperimental method for *estimating* solvent selectivities. Bear in mind, however, that all group contribution methods have weaknesses and they sometimes give, not only quantitatively inaccurate, but also qualitatively incorrect results. COSMO–RS (121,122) is a promising, though relatively new, method for *a priori* predicting activity coefficients and other thermophysical properties based on unimolecular quantum chemical calculations. It has the advantage of often being applicable to those problems where group contribution methods fail. Currently, however, on mixtures for which they are well-suited, group contribution methods give more accurate predictions than COSMO-RS (123).

The infinite-dilution selectivity provides a convenient quantitative method for comparing the effectiveness of different solvents. Since activity coefficients are composition dependent, a fair comparison of the candidate solvents requires that their selectivities be determined at a consistent solvent concentration and key component ratio. Most commonly, the activity coefficient of each of the key components is determined at infinite dilution in each of the potential solvents. The infinite-dilution selectivity, $S_{ij}{}^{\infty}$, is then simply the ratio of these infinite-dilution activity coefficients.

$$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \tag{9}$$

In most systems, the selectivity steadily, and often almost linearly, increases with solvent concentration so that the solvent with the largest infinite-dilution selectivity usually also has the largest selectivity at the lower solvent concentrations used in extractive distillation. In other words, solvents with the largest infinite-dilution selectivities are generally preferred. Be aware, however, that some systems exhibit a maximum in selectivity at finite solvent concentrations (eg, *n*-butane and butene in furfural) while in other systems, typically those that approach the point of immiscibility at high solvent concentrations, the selectivity increases rapidly (ie, nonlinearly) with solvent concentration (eg, 2,4-dimethyl pentane–benzene–aniline) (110,124). For such mixtures, the infinite-dilution selectivity is not an accurate indicator of the solvent's effectiveness in an extractive distillation. Fortunately, these systems are relatively rare.

Gas–liquid chromatography (glc) is one of the most common experimental methods used for screening potential extractive distillation solvents and/or for determining infinite-dilution activity coefficients (125–127). The selectivity is determined by measuring the retention time of each solute on an inert chromatographic column that has been preloaded with enough of the candidate solvent to approximate infinite dilution conditions. Other methods for measuring infinite-dilution activity coefficients include ebulliometry (127,128), the dilutor technique (129), and the dew point method (130). The dilutor technique is the only one that can determine infinite-dilution activity coefficients in solvent mixtures.

Potential extractive distillation solvents can also be evaluated by experimentally measuring the selectivity or relative volatility of a fixed composition mixture of the components to be separated (often 50% each) in the presence of a constant amount of each candidate solvent (114). Solvent-to-feed ratios of 1:1 to 3:1 are typically used. The preferred experimental apparatus is a modified Othmer still operated to yield one theoretical stage of separation (114,131). As before, the objective is to find the candidate solvents that cause the largest increase in relative volatility (ie, the highest selectivities).

While good selectivity at reasonable solvent concentrations is essential, it is not the only important property when selecting an extractive distillation solvent. A solvent's *capacity* (ie, its ability to solubilize the components in the mixture being separated) is also important. If a solvent causes a second liquid phase to form during the distillation, much of the selectivity enhancement can be lost. Since higher selectivities are by achieved by increasing the nonideality between the solvent and one of the key components, and mixtures with large nonidealities often have limited miscibilities, solvents with the highest selectivities can have lower capacities. Thus, a compromise between high selectivity and high capacity sometimes has to be made. Another alternative is to use a mixture of solvents where one of the solvents is chosen for its high selectivity and the other is chosen to maintain high capacity (109,112). The solvent which provides the high selectivity is usually the predominant component in the solvent mixture. Because of its limited solubility with many compounds, the reverse is true when water is used as the highly selective solvent. For example, aromatics are separated from aliphatics using *N*-methyl-2-pyrrolidone (NMP) with a small amount of water added to increase the selectivity.

In addition to having a high selectivity at reasonable concentrations and a high capacity, desirable extractive distillation solvents should: (*1*) not form azeotropes with the components in the mixture to be separated—this can almost be guaranteed by picking solvents with boiling points 30−50°C or more above the other compounds, (*2*) be easily separated from the other components at reasonable temperatures and pressures, (*3*) be thermally stable at the temperatures encountered in the distillation columns, (*4*) be nonreactive with the other compounds, (*5*) be nontoxic, (*6*) inexpensive, (*7*) readily available (perhaps a compound already in the process), (*8*) noncorrosive to commonly used materials of construction, and (*9*) have a low latent heat of vaporization (114). In practice, some compromise in solvent properties is almost always required.

5. Salt-Effect Distillation

Salt-effect distillation (also called salt extractive distillation or salt rectification) is another form of extractive distillation, where, rather than using high boiling liquids to alter the relative volatility of the mixture being separated, the separating agent is a soluble, nonvolatile ionic salt or mixture of salts. Because the added salt is completely nonvolatile, no stages are needed above the salt feed point to keep it out of the overhead product. The salt is normally dissolved in the reflux stream and added at the top of the column so that it is present on all of the trays of the extractive column. The salt is removed from the bottom of the column along with the less volatile component(s) in the feed mixture and sent to the salt recovery step where evaporation and/or drying is used to recover the salt so it can be recycled to the top of the extractive column.

The principal advantage of an ionic salt over a liquid separating agent is that the salt ions typically cause much larger changes in relative volatility than do liquid separating agents (132). Consequently, much less salt is typically needed—sometimes as little as a few percent as compared with 50–90% of the liquid phase, as can be the case with some liquid separating agents (133). This, in turn, leads to shorter, smaller diameter columns and/or higher purity products, and noticeably smaller energy requirements (132,133).

Salt-effect distillation also has several significant disadvantages compared with traditional extractive distillation. Foremost is the relatively limited number of systems for which there is a known salt that is both soluble in the components being separated and effective at altering their relative volatility. The solubility constraints are the most limiting, as it can be difficult to find a salt that is adequately soluble in both components throughout the range of compositions encountered in the extractive column. The search for suitable salts is also hindered by the complexities of the liquid-phase interactions which make it difficult to predict or model vapor–liquid equilibrium in such systems without experimental data. It is also more difficult to transport and accurately meter solids than liquids and it can be difficult to achieve rapid dissolution of the salt after it has been added. For these reasons, there have been only a limited number of industrial applications of salt-effect distillation (132,134–140). Reference 135 demonstrates that, as with liquid separating agents, certain salts will reverse the natural volatility difference of a mixture, causing the higher boiling compound to distill overhead.

Mixed-agent extractive distillations in which one separating agent is a liquid and one a salt has found some interest and shown some promise in China (141). Such processes combine the advantages of extractive distillation (ie, the ease of recovering, transporting and mixing the separating agent) with those of salt-effect distillation (ie, the more pronounced effect on relative volatility so less separating agent, less energy, and smaller equipment are needed). At least two industrial plants are mentioned in which ethylene glycol–potassium acetate mixtures are used to dehydrate ethanol or *tert*-butanol.

See the articles by Furter (132,133,142–144) for additional information on salt-effect distillation.

6. Pressure-Swing Distillation

It is well known that varying the system pressure can affect the composition of an azeotrope. When the change in azeotropic composition is appreciable over a

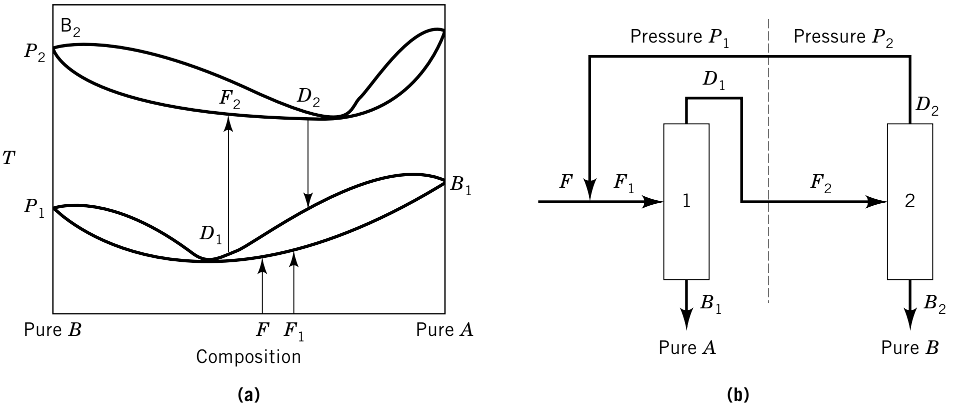


Fig. 16. Pressure-swing distillation of a minimum boiling binary azeotrope. (**a**) Temperature–composition phase diagram showing the effect of pressure on the azeotropic composition; (**b**) column sequence (145).

moderate pressure range, this effect can be exploited to separate both minimum- and maximum-boiling binary azeotropes using a two-column sequence with the columns operated at different pressures. This process, called pressure-swing or pressure-sensitive distillation, is illustrated by Fig. 16. For a binary mixture forming a pressure-sensitive, minimum-boiling azeotrope, the fresh feed, F, is mixed with the recycled stream from the second column to form the feed stream, F_1, to the first column, which operates at pressure P_1. (Alternatively, these two streams can be fed to separate points in the first column). Because F_1 lies to the right of the azeotrope at pressure P_1 (Fig. 16**a**), pure component A is removed as the bottom product, B_1, and a mixture near the azeotropic composition at pressure P_1 is the distillate, D_1. Stream D_1 is changed to pressure P_2 and fed to the next column as stream F_2. Because F_2 now lies to the left of the azeotropic composition at pressure P_2 (Fig. 16**a**), the other pure component, B, can be recovered in the bottom stream, B_2, and a near azeotropic mixture becomes the distillate, D_2, which is recycled to the first column. The greater the shift in azeotropic composition, the smaller the recycle flow rate will be relative to the product flow rates, and thus, the smaller the column diameters and the more economical the process will be. An analogous procedure is used for binary maximum boiling azeotropes (110), except the pure component products are recovered as distillates and the near azeotropic streams come out of the bottom of each column.

Systems amenable to pressure-swing distillation include: tetrahydrofuran (THF) and water (146,147), acetonitrile and water (148), a variety of alcohol–ketone azeotropes, including the methanol–acetone azeotrope, which is known to disappear at both low and high pressure (149), methanol and methyl ethyl ketone (150), the alcohol–acetate azeotropes arising from transesterification reactions (151), ethanol and water (76,152), and the maximum-boiling hydrogen chloride–water azeotrope (153,154). Additional pressure-sensitive azeotropes can be found in Refs. 1,2,145 and 150. Only a fraction of the known azeotropes, however, are sufficiently pressure-sensitive for pressure-swing distillation to be economical. References 96 and 150 provide methods for estimating the effect of pressure on azeotropic composition.

Pressure-swing distillation can also be applied to multicomponent mixtures containing distillation boundaries as long as at least one end of the boundary terminates at an azeotrope whose composition changes with pressure. Now when the pressure is varied, the position of the distillation boundary moves along with the pressure-sensitive azeotrope to which it is attached. This enables the distillation boundary to be circumvented by using a multi-pressure distillation sequence analogous to the one in Fig. 16**b** [see Fig. 4 in Ref. 145]. Reference 155 includes a four-component example. Similarly, an azeotrope whose composition is insensitive to pressure can be separated into pure components by adding a separating agent that forms a pressure-sensitive azeotrope with one of the constituents of the original mixture and introduces a pressure-sensitive distillation boundary (145). Like their binary counterparts, these ternary pressure-swing distillation sequences are prone to having large recycle flowrates, requiring larger column diameters, unless the movement of the distillation boundary is appreciable over a moderate pressure range.

7. Heterogeneous Azeotropic Distillation

Heterogeneous azeotropic distillation, or simply azeotropic distillation, is widely used for separating nonideal mixtures. The technique uses minimum boiling azeotropes and liquid–liquid immiscibilities in combination to overcome the effect of other azeotropes or tangent pinches in the mixture that would otherwise prevent the desired separation. The azeotropes and liquid heterogeneities that are used to make the desired separation feasible may either be induced by the addition of a separating agent, usually called the entrainer, or they may be intrinsically present, in which case the mixture is sometimes called self-entrained. The most common case is the former; it includes such classic separations as ethanol dehydration using either benzene, cyclohexane, toluene, heptane, ethyl ether, etc, as the entrainer, and acetic acid recovery from water using either 1-propyl acetate, isopropyl acetate, 1-butyl acetate, or isobutyl acetate as the entrainer. In ethanol dehydration the entrainer is used to break the homogeneous minimum boiling azeotrope between ethanol and water; in the acetic acid recovery process the entrainer is used to overcome the tangent pinch between acetic acid and water.

The first successful application of heterogeneous azeotropic distillation was in 1902 (156) and involved using benzene to produce absolute alcohol from a binary mixture of ethanol and water. This batch process was patented in 1903 (157) and later converted to a continuous process (158). Good reviews of the early development and widespread application of continuous azeotropic distillation in the pre-World War II chemical industry are available (159).

Historically azeotropic distillation processes were developed on an individual basis using experimentation to guide the design. The use of residue curve maps as a vehicle to explain the behavior of entire sequences of heterogeneous azeotropic distillation columns, as well as the individual columns that make up the sequence, provides a unifying framework for design. This process can

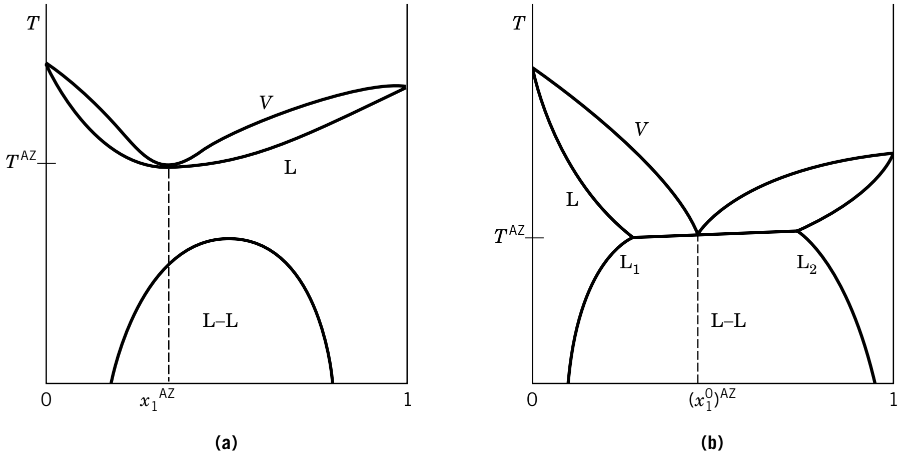


Fig. 17. Schematic isobaric phase diagrams for binary azeotropic mixtures (AZ). (**a**) Homogeneous azeotrope; (**b**) heterogeneous azeotrope.

be applied rapidly, and produces an excellent starting point for detailed simulations and experiments.

7.1. Phase Diagrams. For binary mixtures, it is well known that when a liquid–liquid envelope merges with a minimum boiling vapor–liquid phase envelope the resulting azeotropic phase diagram has the form shown in Fig. 17. When the liquid composition (x_1) is equal to x_1^{AZ}, as in Fig. 17**a**, then the vapor composition, y_1, is also equal to x_1^{AZ} and the mixture boils at constant temperature and at constant (and equal) composition in each phase. Thus a homogeneous azeotrope is formed. When the overall liquid composition $x_1^0 = (x_1^0)^{AZ}$, as in Fig. 17**b**, then y_1 is also equal to $(x_1^0)^{AZ}$ and again the mixture boils at constant temperature and at constant composition in each phase. However, the liquid of composition $(x_1^0)^{AZ}$ splits into two liquid phases, L_1 and L_2, so that there are three coexisting equilibrium phases (two liquids and one vapor) that have different compositions. That is, a heterogeneous azeotrope is formed. Homogeneous and heterogeneous azeotropes share the common property that the overall liquid composition is equal to the vapor composition, which provides a means for identifying azeotropes experimentally and computationally.

The properties of ternary heterogeneous vapor–liquid–liquid equilibrium (VLLE) phase diagrams are important for understanding azeotropic distillation. The simplest VLLE phase diagram, where a liquid–liquid envelope merges with a VLE surface containing a single minimum boiling binary azeotrope, is shown in Fig. 18. The region, where the LLE and VLE surfaces merge is called the heterogeneous liquid boiling surface, Fig. 18**b**. Note that the boiling temperature varies over this surface, so the surface is not flat. When the overall liquid composition lies inside the heterogeneous boiling envelope, and the temperature lies on the heterogeneous boiling surface, then the liquid boils and splits into two equilibrium liquid phases (connected by a tie-line) and one coexisting vapor phase. The Gibbs phase rule requires that the locus of all the equilibrium vapor compositions forms a curve in *T*-*y* space (called the vapor-line) and *not* a surface, as happens in the homogeneous region.

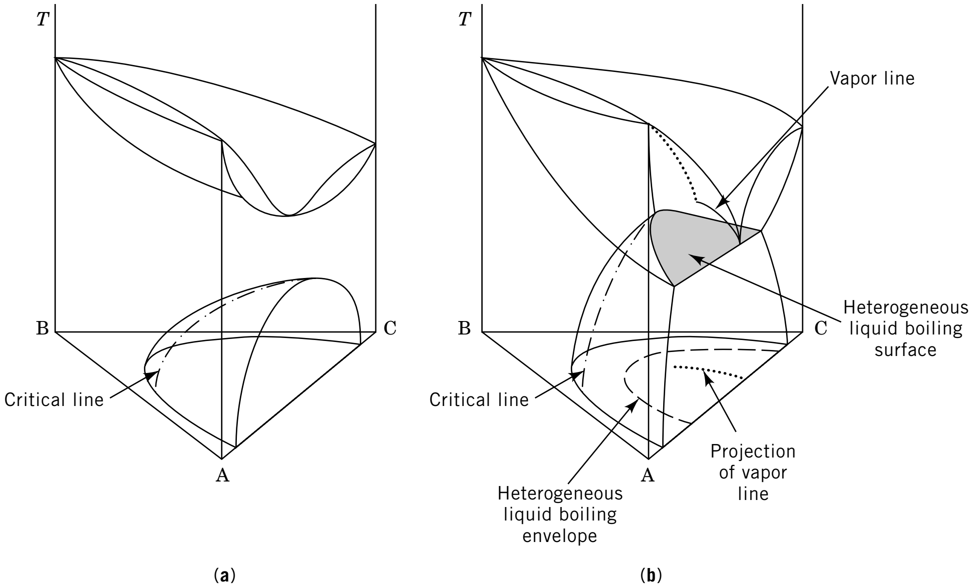


Fig. 18. Schematic isobaric phase diagrams for ternary (A,B,C) azeotropic mixtures. (**a**) Homogeneous liquid phase at all boiling points; (**b**) heterogeneous liquid phase for some boiling points.

A convenient way of representing the *T-x-y* phase diagram (Fig. 18**b**) is by projection onto the composition triangle at the base of the figure. It is understood that the temperature varies from point to point on the projected vapor line and on the projected boiling envelope. The latter looks like an isothermal liquid–liquid binodal envelope, but is not. Each tie line across the boiling envelope is associated with a different boiling temperature (Fig. 19).

Little experimental VLLE phase data for ternary mixtures has been published (see Table 8.1 in 21) and thus good model parameters are not available for most VLLE mixtures. Fig. 19**a** shows a model predicted phase diagram for the ethanol–water–benzene mixture at 101.3-kPa (1 atm) pressure (160). In this diagram, the liquids and vapors in equilibrium with each other are signified by a common number. For example, the coexisting liquids on tie-line number 2 are in equilibrium with vapor number 2 at a boiling temperature of 68.55°C. The ethanol–water–benzene mixture forms a minimum boiling heterogeneous ternary azeotrope. Experimental VLLE data for this mixture are shown in Fig. 19**b** (160). Ternary heterogeneous saddle azeotropes are also possible, eg, formic acid–water–*m*-xylene (161), water–acetone–chloroform (162), however, maximum boiling heterogeneous azeotropes cannot exist (163). This differs from homogeneous azeotropes where all three types are found in Nature.

The typical phase equilibrium problem encountered in distillation is to calculate the boiling temperature and the vapor composition in equilibrium with a liquid phase of specified composition at a given pressure. If the liquid separates into two liquid phases, then the problem is to calculate the boiling temperature and the compositions of the two equilibrium liquid phases plus the coexisting

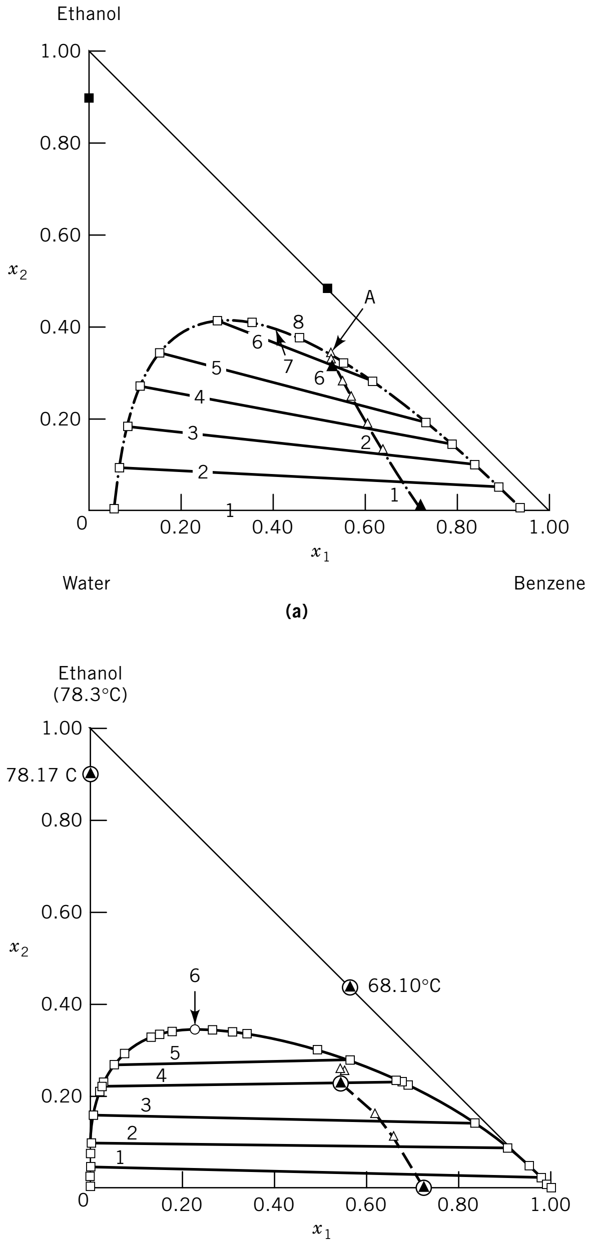


Fig. 19. Isobaric VLLE phase diagrams for the ethanol–water–benzene system at 101.3 kPa; (□-□) represent liquid–liquid tie-lines; (△—△), the vapor line; ■, homogeneous azeotropes; ▲, heterogeneous azeotropes; ▲⃝, Horsley's azeotropes. (**a**) Calculated, where A is the end point of the vapor line and the numbers correspond to boiling temperatures in °C of 1, 70.50; 2, 68.55; 3, 67.46; 4, 66.88; 5, 66.59; 6, 66.46; 7, 66.47, and 8, the critical point, 66.48. (**b**) Experimental, where the numbers correspond to boiling temperatures in °C of 1, 67.0; 2, 65.5; 3, 65.0; 4, 64.85; 5, 64.9; and 6, the critical point, 69.9.

vapor phase at the specified overall liquid composition. Robust and practical numerical methods have been devised for solving this problem (164–171).

Thus, using these techniques and a nonideal solution model that is capable of predicting multiple liquid phases, it is possible to produce phase diagrams comparable to those of Fig. 19. These predictions are not, however, always quantitatively accurate (160,172–175).

7.2. Residue Curve Maps. Residue curve maps are useful for representing the infinite reflux behavior of continuous distillation columns and for getting quick estimates of the feasibility of carrying out a desired separation. In a heterogeneous simple distillation process, a multicomponent partially miscible liquid mixture is vaporized in a still and the vapor that is boiled off is treated as being in phase equilibrium with the coexisting liquid phases. The vapor is withdrawn from the still as distillate. The changing liquid composition is most conveniently described by following the trajectory (or residue curve) of the overall composition of all the coexisting liquid phases (176). An extensive amount of valuable experimental data for the water–acetone–chloroform mixture, including binary and ternary LLE, VLE, and VLLE data, and both simple distillation and batch distillation residue curves are available (162,177). Experimentally determined simple distillation residue curves have also been reported for the heterogeneous system water–formic acid–1,2-dichloroethane (178).

Using the new generation of VLLE computation techniques, it is possible to calculate residue curve maps for heterogeneous liquid systems (Fig. 20). In this map, the heterogeneous liquid boiling envelope has been superimposed on the residue curves in order to distinguish the homogeneous and heterogeneous regions of the triangular diagram.

Systems Having a Ternary Heterogeneous Azeotrope. Binary or ternary heterogeneous azeotropes are restricted to being either unstable nodes or saddles in the residue curve map (163). An example is the computed residue curve map for the ethanol–water–benzene mixture that exhibits a ternary minimum boiling heteroazeotrope (see Fig. 20). This map exhibits three distillation regions. The three distillation boundaries all begin at the minimum boiling ternary heteroazeotrope and end at each of the binary azeotropes. If ethanol is the desired product of the separation, the initial condition for the simple distillation must lie in the upper region of Fig. 20, which is bounded by the ternary azeotrope, the binary azeotropes between benzene + ethanol and water + ethanol, and the pure ethanol vertex. The computed phase diagram is shown in Fig. 19**a**. Other mixtures with a minimum-boiling ternary heteroazeotrope include, ethanol–water–toluene, ethanol–water–cyclohexane, 2-propanol–water–benzene, and related mixtures. The water–acetone–chloroform system exhibits a ternary heterogeneous saddle azeotrope (162), but such systems are rare and will not be discussed futher in this article.

7.3. Column Sequences. The analysis of residue curve maps and distillation boundaries for homogeneous azeotropic mixtures provides a simple and useful technique for distinguishing between feasible and infeasible sequences of distillation columns, and many of the same insights apply to heterogeneous mixtures. Residue curves cross continuously through the liquid boiling envelope from one side to the other. Thus a simple distillation boundary inside the heterogeneous region does not stop abruptly or exhibit a discontinuity at the liquid

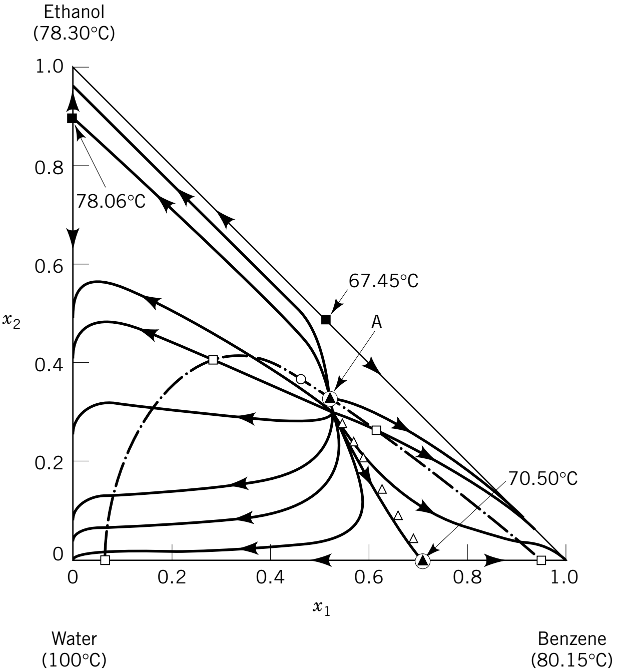


Fig. 20. Residue curve map calculated for the ethanol–water–benzene mixture where A is the end point of the vapor line; ■ represents a homogeneous azeotrope; ⓐ, heterogeneous azeotropes; (△—△), the vapor line; (- ● -), the heterogeneous liquid boiling envelope; ○, the critical point; and □, the end points of tie-lines (179).

boiling envelope but passes continuously through it, becoming a homogeneous distillation boundary thereafter (see Figs. 20 and 22**b**). As in homogeneous systems, residue curves cannot cross heterogeneous distillation boundaries. However, if a point x°, on a residue curve inside of the heterogeneous region phase splits into two equilibrium liquid phases that lie in two different distillation regions, then a liquid–liquid phase separation can be exploited to jump across heterogeneous distillation boundaries in a way that is not possible for homogeneous systems. This is the key to devising feasible sequences of columns for separating heterogeneous mixtures.

Binary Mixtures. A binary mixture containing a homogeneous azeotrope can be distilled up to, but not beyond, the azeotropic composition. If the binary azeotrope is heterogeneous however, the situation is more favorable and a simple sequence of columns, shown in Fig. 21, is capable of isolating each pure component. The process feed, x_F, is fed as a saturated or sub-cooled liquid to a decanter where it phase-separates into an A-rich phase and a B-rich phase. The A-rich phase, x_{F1}, is then fed to column 1; the B-rich phase, x_{F2}, is fed to column 2. As can be seen in Fig. 21**a**, because of the liquid–liquid phase split the compositions of these two feed streams lie on either side of the azeotrope. Therefore, column 1 produces pure A as a bottoms product and the azeotrope as distillate, whereas column 2 produces pure B as a bottoms product and the azeotrope as

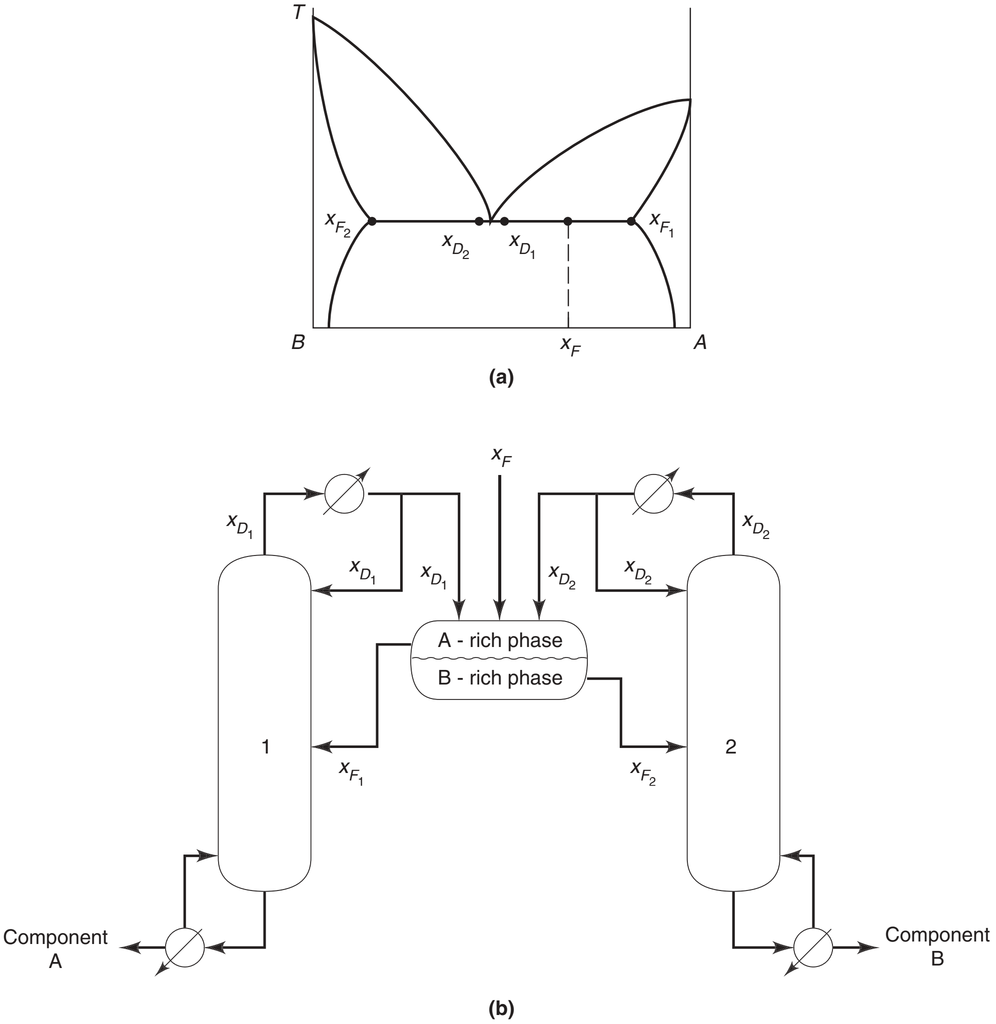


Fig. 21. Column sequence for separating a binary heterogeneous azeotropic mixture, *A* and *B*, where x_F represents the process feed mole fraction. (**a**) Phase diagram; (**b**) column sequence.

distillate. The two distillate streams are fed to the decanter along with the process feed to give an overall decanter composition partway between the azeotropic composition and the process feed composition according to the lever rule. This arrangement is well suited to purifying water–hydrocarbon mixtures, such as a C_4–C_{10} hydrocarbon, benzene, toluene, xylene, etc; water–alcohol mixtures, such as butanol, pentanol, etc; as well as other immiscible systems.

If the process feed does not lie in the liquid–liquid region it can be made to do so by deliberately feeding either pure A or pure B to the decanter, as required. This may only be necessary during start-up or for control purposes because the recycled azeotrope has the beneficial effect of dragging the decanter composition further into the liquid–liquid region.

Ternary Mixtures. When the binary mixture containing the minimum boiling azeotrope is completely homogeneous, ie, the liquid is homogeneous for all compositions, the method given in Fig. 21 requires modification. In this case, a third component, called the entrainer, is added which induces a liquid–liquid phase separation over a limited portion of the ternary composition diagram. Many options for sequencing ternary heterogeneous azeotropic distillation systems exist (159). These sequences generally consist of two, three, or four columns using various techniques for handling the entrainer recycle stream. The feasibility of such sequences rests on the use of liquid–liquid phase splits to provide each column with a feed composition in a different distillation region. In this regard, the sequences for ternary mixtures resemble the sequences for binary mixtures. In all cases the heart of the process is the azeotropic column and its decanter.

The classical example is the separation of ethanol from water using benzene as the entrainer. Many other separations fit this mold, eg, ethanol–water–carbon tetrachloride, 2-propanol–water–benzene, and 2-propanol–water–cyclohexane (180). The task is to separate a homogeneous binary mixture of ethanol and water, which contains a minimum boiling binary azeotrope, into its pure components. An entrainer, which has limited miscibility with one of the components, in this case water, is used. In addition, benzene (and a number of other entrainers such as cyclohexane and carbon tetrachloride) causes two more minimum boiling binary azeotropes (one homogeneous, the other heterogeneous) to form together with a ternary minimum boiling heterogeneous azeotrope. The resulting residue curve map is similar to that shown in Fig. 20, in which there are three distillation regions. Figure 22 shows a schematic of the azeo-column and the material balance lines for this system (note that the points x_B, x_F, and x_D lie on a straight line by the lever rule). The map indicates that the components to be separated (ethanol and water) lie in two different distillation regions, I and II.

The azeo-column must be designed to meet the following target compositions: (*1*) the bottoms composition is specified to be almost pure ethanol, ie, x_B is specified to lie close to the vertex of distillation region II; and (*2*) the overhead vapor composition leaving the last vapor–liquid equilibrium stage of the column, y_N, must lie in the wedge-shaped portion of region II inside the heterogeneous region near the ternary azeotrope. Typical target values for x_B and y_N are shown in Fig. 22. The final values of x_B and y_N are subject to optimization and may differ slightly from those shown. All values of y_N inside the wedge-shaped region, except those special values which lie on the vapor line, are in equilibrium with a homogeneous liquid. Therefore, the liquid composition leaving the top tray, x_N, lies in the homogeneous portion of region II as shown (Fig. 22). The azeo-column is therefore designed so that the steady-state liquid composition profile runs from x_B to x_N. This can normally be done in such a way that every stage inside the column is homogeneous, ie, has only one liquid phase. A method for doing this is given in Ref. 181. Not all azeo-columns, however, are designed to have a single liquid phase on all the trays. Neither do columns that have been designed in this manner necessarily remain homogeneous under the action of disturbances (168,172–174,182–188). For some azeotropic distillations there can be a significant savings in energy and/or stages by designing the column

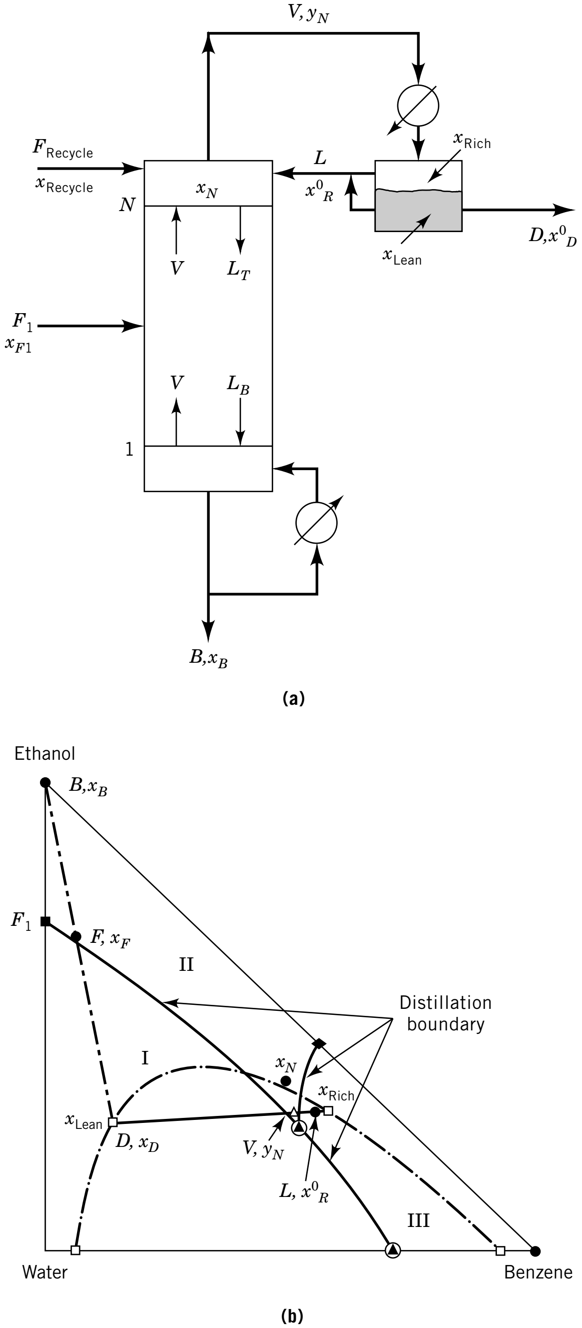


Fig. 22. Separation of ethanol from an ethanol–water–benzene mixture using benzene as the entrainer. (**a**) Schematic representation of the azeo-column; (**b**) material balance lines where ■ denotes the homogeneous and ◬ the heterogeneous azeotropes; □, the end points of the liquid tie-line and △, the overhead vapor leaving the top of the column. The distillation regions, I, II, and III, and the boundaries are marked. Other terms are defined in the text.

so that the entrainer penetrates down the rectifying section causing some of the stages in the rectifying section to exhibit multiple liquid phases (180,189,190). One such case is the acetic acid + water + n-butyl acetate separation discussed at the end of this article.

The overhead vapor of composition y_N is totally condensed and sent to a decanter where it splits into two equilibrium liquid phases, an entrainer-rich phase of composition x_{rich} and an entrainer-lean phase of composition x_{lean}. The relative proportion of these two liquid phases in the decanter, ϕ, is given by the lever rule, where ϕ represents the molar ratio of the entrainer-rich phase to the entrainer-lean phase in the decanter. The overall composition of the liquids in the decanter is the same as y_N. The temperature of the liquid in the decanter is normally held constant at a value below the VLLE boiling temperature.

The two decanter liquid phases are used to provide the reflux and distillate streams. Normally, the reflux ratio, r, is chosen so that $r = \mathrm{L/D} \geq \phi$. This requires that the reflux rate be greater than the condensation rate of entrainer-rich phase and that the distillate rate be correspondingly less than the condensation rate of entrainer-lean phase. This means that the reflux stream consists of all the entrainer-rich phase plus some of the entrainer-lean phase, and the distillate stream consists of the balance of the entrainer-lean phase, ie, $x_{\mathrm{D}} = x_{\mathrm{lean}}$. Thus, the overall composition of the reflux stream, $x_{\mathrm{R}}{}^0$, lies on the decanter tie-line between the entrainer-rich phase, x_{rich}, and the overall decanter composition, y_N, as shown in Fig. 22.

Completing the Separation Sequence. To close the material balance around the separation sequence, the distillate stream leaving the azeotropic column (column 2 in Fig. 23**a**) is separated (in column 3) into a product stream, B_3, and an entrainer recycle stream, D_3. The amount of benzene needed to move the composition of stream F_1 to F is equal to the amount of benzene lost in the aqueous distillate D_2 and recovered in the stream D_3.

Kubierschky Three-Column Sequence. If only simple columns are used, ie, no side-streams, side-rectifiers/strippers etc, then the separation sequence can be completed by adding an entrainer recovery column, column 3 in Fig. 23**a**, to recycle the entrainer, and a preconcentrator column (column 1) to bring the feed to the azeotropic column up to the composition of the binary azeotrope.

The entrainer recovery column takes the distillate stream, D_2, from the azeo-column and separates it into a bottoms stream of pure water, B_3, and a ternary distillate stream, D_3, for recycle to column 2. The overall material balance line for column 3 is shown in Fig. 23**b**. This sequence was one of two original continuous processes disclosed in 1915 (191). More recently, it has been applied to other azeotropic separations (76,192,193).

Extensive design and optimization studies have been carried out for this sequence (193). The principal optimization variables, ie, the design variables that have the largest impact on the economics of the process, are the reflux ratio in the azeo-column; the position of the tie-line for the mixture in the decanter, determined by the temperature and overall composition of the mixture in the decanter; the position of the decanter composition on the decanter tie-line [see Ref. 181 for a discussion of the importance of these variables]; and the distillate composition from the entrainer recovery column.

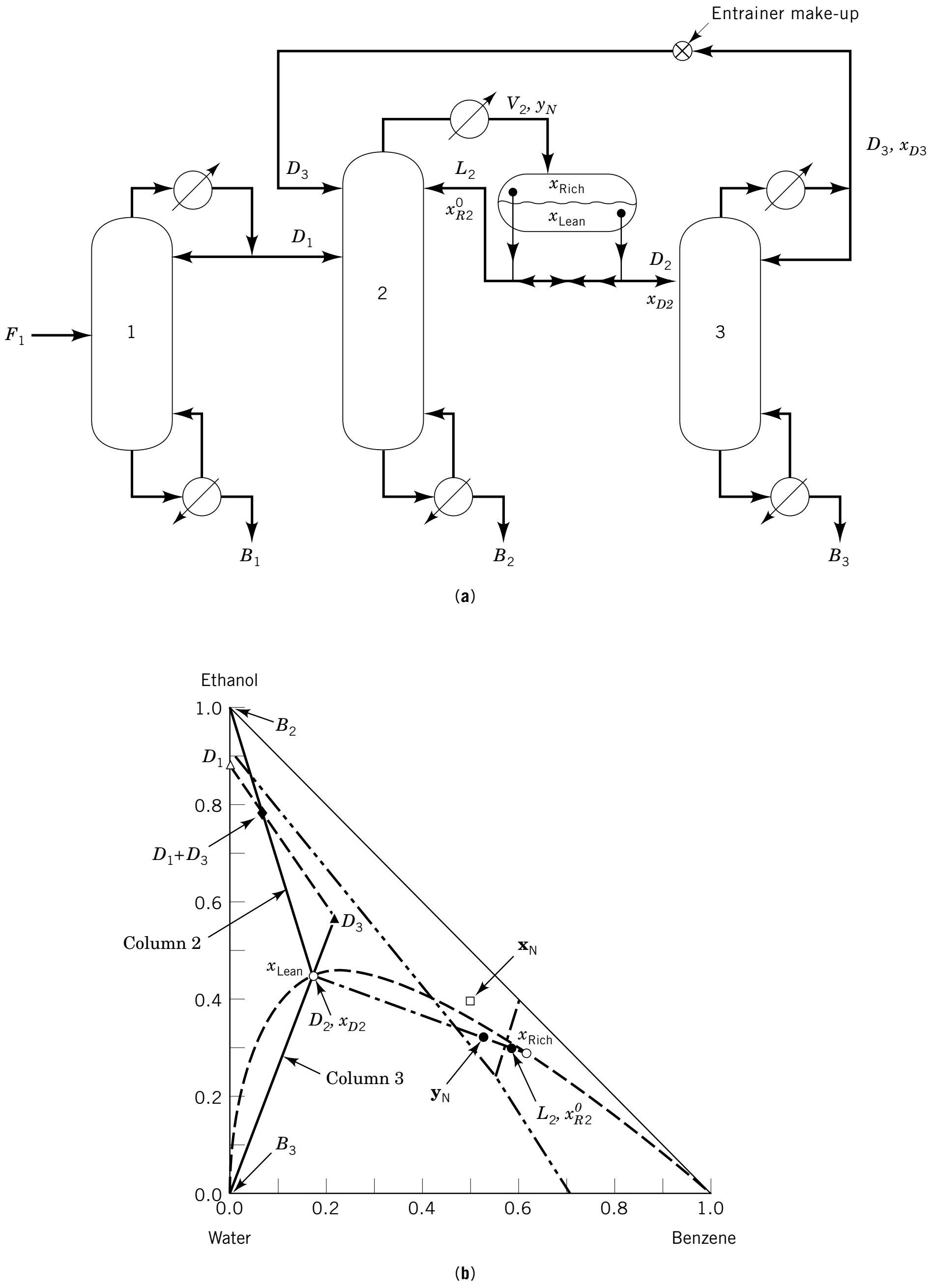


Fig. 23. Separation of ethanol and water from an ethanol–water–benzene mixture. Bottoms B_1 and B_3 are water, B_2 is ethanol. (**a**) Kubierschky three-column sequence where columns 1, 2, and 3 represent the preconcentration, azeotropic, and entrainer recovery columns, respectively. (**b**) Material balance lines for the azeotropic and entrainer recovery columns where ● represents the overall vapor composition from the azeo-column, V_2, y_N; □ the liquid in equilibrium with overhead vapor composition from the azeo-column, x_N; ▲, distillate composition from entrainer recovery column x_{D3}; and ◆, overall feed composition to the azeo-column, $D_1 + D_3$.

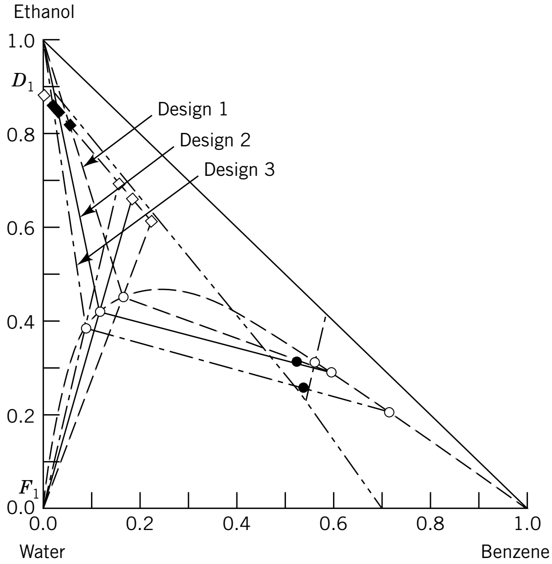


Fig. 24. Three sets of material balance lines for the Kubierschky three-column sequence where design 1 corresponds to the upper tie-line having $r_{\min} = 8.78$; design 2, to the subcooled upper tie-line having $r_{\min} = 12.23$; and design 3, to the lower tie-line having $r_{\min} = 17.31$; ● represents the overall decanter composition; ◆, the overall feed composition to the azeo-column; ◇, the distillate composition from the entrainer recovery column; and ○, the end points of the liquid–liquid tie-lines.

Figure 24 shows material balance lines for three different decanter tie-lines. The process feed to the preconcentrator in each sequence is a binary mixture of 4.2 mol% ethanol and 95.8 mol% water. The product purity from the azeo-column (column 2) is set at 99.9 mol% ethanol, and the water purity leaving the entrainer recovery column is set at 99.5 mol% water. These specifications are essentially identical to those used for studying the optimal extractive distillation sequences (77,78). For design 1, the decanter tie-line is set at the bubble-point of the mixture leaving the top of the azeo-column, having composition y_N. This temperature is 64.4°C. For design 2, the decanter composition is the same as for design 1 but it is subcooled to 25°C. For design 3 the decanter composition is placed closer to the ternary azeotrope than for designs 1 and 2, and the decanter temperature is set at the bubble-point of the mixture. In each design, the distillate composition from the entrainer recovery column is placed close to the distillation boundary. The position of the tie-line has a significant influence on the distillate composition from the azeo-column, which in turn influences the position of the material balance line for the entrainer recovery column. The position of the distillate composition from the entrainer recovery column also influences the overall feed composition to the azeo-column ($D_1 + D_3$ in Fig. 23).

Optimization studies indicate that the distillate composition from the entrainer recovery column has a strong influence on the process economics and the optimum position is always close to the distillation boundary. By the lever rule, this minimizes the amount of water in the entrainer recycle stream, or equivalently, makes the overall feed to the azeo-column richer in ethanol. For each tie-line, the optimal position of the decanter liquid composition is found by the method proposed in Ref. 181. The minimum reflux ratio for a given tie-line can be reduced by as much as 50% by making small changes in the decanter composition. Calculations indicate that the optimal reflux ratio for the azeo-column is normally in the range 1.1–1.5 $r_{\min}$ and that the cost of the sequence is insensitive to this factor. This leaves the position of the decanter tie-line as the sole remaining optimization variable.

The intra-sequence flows, compositions, and reflux ratios are quite sensitive to relatively small changes in the position of the decanter tie-line as evidenced by the $r_{\min}$ value for the azeo-column: 8.78 for design 1, 12.23 for design 2, and 17.3 for design 3. Based on knowledge of homogeneous distillations, the vapor rate and total annualized cost for sequence 1 would appear to be the lowest. For homogeneous distillations the feed and product flow rates, as well as their compositions, can be held constant as the reflux ratio is changed from one design to another. Thus there is a direct relationship between increased minimum reflux ratio and increased costs. However, such a relationship does not occur for heterogeneous distillations so we can't conclude that design 1 will have the lowest cost.

A good approximation for the vapor rate leaving the reboiler, V, for any type of distillation is

$$V = (r+1)D \tag{10}$$

where r is the reflux ratio and D is the distillate flow rate. For homogeneous distillations, D is constant so that V increases as r increases. For azeotropic distillation, however, both r and D change from one tie-line to another. These effects may tend either to reinforce or to cancel each other depending on the mixture. There is no general rule and each mixture must be treated separately. In the ethanol-water-benzene system, the reflux ratio increases from one design to another, but the distillate flow rate, D_2, decreases, as can be seen by application of the lever rule to the material balance lines for the azeo-column in Fig. 24. The net effect is that the vapor rate in the azeo-column hardly changes from one design to another. All the sequences shown in Fig. 24 have approximately the same cost. This fortuitous cancellation of effects does not occur in general. It is always worthwhile exploring the economic impact of variations in the position of the decanter tie-line.

Other Sequences. The Kubierschky sequence is not the only way to perform the separation. Alternatives include: (*1*) If the process feed already has a composition at or near the composition of the binary azeotrope then the preconcentrator is not needed. (*2*) The distillate stream from the entrainer recovery column can be recycled directly to the decanter, which is analogous to the binary process shown in Fig. 21. This recycle alternative causes the reflux ratio in the azeotropic column to be much larger than necessary (194) and should be avoided, even though it has been studied extensively in the literature (172,182,195–199). (*3*) Use of the Kubierschky two-column sequence (191), in which the preconcentration and entrainer recovery steps are combined into a single column. For the ethanol–water–benzene system, this alternative has lower capital costs but higher operating costs than the Kubierschky three-column sequence so that the total annualized cost is about the same for both sequences (193). (*4*) Use of the Steffen three-column sequence, the basic layout of which is the same as the Kubierschky three-column sequence. The essential new feature is to replace the single decanter in the Kubierschky sequence by multiple decanters, adding fresh or recycled water to each. The entrainer-rich phase from each decanter is returned to the azeo-column as reflux and the aqueous-rich phase from each decanter is fed to the next decanter in the train. This effectively replaces the decanter by a liquid–liquid extraction step which pushes the "effective decanter tie-line" deeper into the liquid–liquid region than it could possibly go by distillation alone. (*5*) Use of the Ricard-Allenet four-column sequence (3,159,191, 193,194,200). The first two columns in this sequence are the same as the first two columns in the Kubierschky three-column sequence. The third column in the Ricard-Allenet sequence takes the water-rich phase from the decanter and splits it into a distillate stream containing the ternary azeotrope, and by material balance, a bottoms stream consisting of water and ethanol. The ternary azeotrope is recycled to the azeo-column decanter, and the ethanol-water stream is fed to a fourth column, which recovers pure water as bottoms and the binary azeotrope as distillate. This azeotropic distillate stream is recycled to the feed into the azeo-column. Ricard-Allenet proposed a variation on this sequence (191) in which the overhead vapors from the entrainer recovery column (third column in the sequence) are provided with a separate condenser–decanter system, similar to the one provided for the overhead vapors from the azeo-column. (*6*) Use of the Ricard-Allenet three-column sequence in which the fourth column is eliminated and the bottom stream from the third column (containing only ethanol and water) is recycled to the preconcentrator column. This alternative has good economic possibilities, but there are no available studies of this alternative.

In summary, for systems of the ethanol–water–benzene type, the three most attractive sequences for carrying out azeotropic distillation are the Kubierschky three-column sequence, the Kubierschky two-column sequence, and the Ricard-Allenet three-column sequence. For each of these there is the added possibility of replacing the decanter with a liquid–liquid extraction step.

Other Classes of Entrainers. Not all heterogeneous azeotropic mixtures are of the ethanol–water–benzene type. The number of azeotropes in the mixture may vary from system to system as may their character, ie, maximum or minimum boiling, hetereogeneous or homogeneous. In addition, the size and shape of the liquid–liquid region varies greatly from system to system. The feasibility and sequencing strategy for each new system is most conveniently established using residue curve maps such as those shown in Fig. 25.

Any entrainer that does not divide the components to be separated into different distillation regions is normally a feasible entrainer, and remains feasible even if it induces a region of partial miscibility. Examples are shown in Fig. 25**a** and **b** and it is possible to construct many more such maps by strategically placing heterogeneous regions on the feasible residue curve maps given in Fig. 6. Sequences based on these maps normally have multiple liquid phases on some of the stages in the column, which *may* lower the mass-transfer efficiency on those stages. In practice, mass-transfer efficiency and hydrodynamic performance of three-phase columns does not present a problem. As early as 1938 it

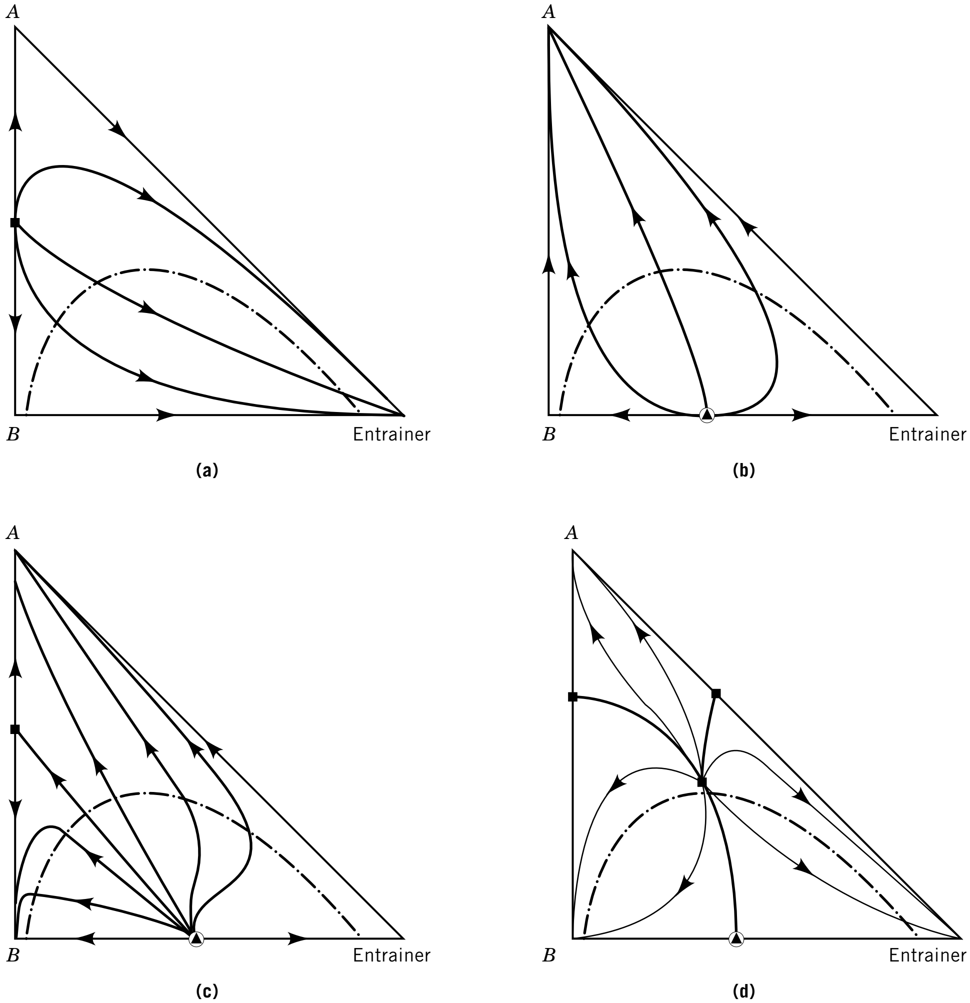


Fig. 25. A selection of feasible residue curve maps for ternary heterogeneous mixtures where ■ represents homogeneous and ◬ heterogeneous azeotropes. See text.

was stated that "The efficiency of the plates was apparently undiminished by the heterogeneity of the boiling liquid and that was undoubtedly due to the violent agitation produced on the plates by the rapid bubbling of the vapours through the liquid..." (159). A more recent study and assessment of the literature from a practitioner's viewpoint is available (201). However, at the conceptual design stage of process development, mass-transfer efficiency is of secondary importance to feasibility.

The map shown in Fig. 25**b** is relevant to the separation of acetic acid and water which is of commercial significance. Although this binary mixture does not form an azeotrope, it does have a severe tangent pinch at high water compositions, which makes it difficult to produce an acid-free water stream. It is not economical to separate this mixture into pure product streams without the aid of an entrainer. All known commercial entrainers for this separation are heterogeneous and most produce residue curve maps similar to the one shown in Fig. 25**b**.

Clarke-Othmer Process for Acetic Acid–Water Separation. Large amounts of dilute acetic acid are purified industrially (see ACETIC AND ITS DERIVATIVES, also see Ref. 202). Feasible entrainers include ethylene dichloride (nbp 83.7°C), chloroform (npb 61.8°C), ethyl ether (nbp 34.5°C), also called ether or diethyl ether), 1-propyl acetate (nbp 101.6°C), isopropyl acetate (nbp 88.4°C), and 1-butyl acetate (nbp 125.9°C). All except 1-butyl acetate have residue curve maps similar to Fig. 25**b**. The azeo-column has a process feed consisting of acetic acid (component A in Fig. 25**b**) and water (component B in Fig. 25**b**). The entrainer is charged to the column, typically via the reflux stream, and remains captive within the column. The bottom stream from the column is pure acetic acid, and the overhead vapor is close to the composition of the minimum boiling heterogeneous binary azeotrope formed by the entrainer and water (see Fig. 25**b**). The azeotropic vapors are condensed and decanted into a water stream that leaves as distillate, and an entrainer-rich stream that is returned to the column as reflux. In some process alternatives, part of this stream is also recycled to the column feed (see p. 67 of Ref. 202). Additional reflux, if needed, is achieved by returning some of the water phase. It is typical for these systems to have multiple liquid phases present on some stages in the rectifying section. This process was invented by Clarke and Othmer (203); more detailed operating information and entrainer comparison for this separation is available (204). Ethyl acetate (nbp 77.1°C) is sometimes mentioned as a feasible entrainer for separating acetic acid–water mixtures and, although it does give a residue curve map similar to Fig. 25**b**, the liquid–liquid region is so small that it is not nearly as attractive an entrainer as those cited above. It is for this reason that many users of this system employed multicomponent entrainers, adding for example cyclohexane and/or methylene chloride to ethyl acetate so as to enlarge the liquid-liquid region while retaining as much as possible the favorable distribution coefficients (tie-line slopes) of the ethyl acetate system. Another entrainer that is sometimes used industrially is n-butyl acetate that has a normal boiling point of 126°C, which is 8°C higher than acetic acid. This is a feasible entrainer but the residue curve map is different than the one shown in Fig. 25**b** (see the section below, Self-Entrained Systems, for more details).

Wentworth Process for Ethanol–Water Separation. In the Wentworth process ethyl ether is used as the entrainer for ethanol–water separation, producing a residue curve map similar to the one shown in Fig. 25**c** (A and B represent ethanol and water, respectively). Ethyl ether and water form a minimum boiling heterogeneous azeotrope at 34.15°C containing 98.75 wt% ether and 1.25 wt% water at atmospheric pressure. There is no azeotrope between ethyl ether and ethanol and no ternary azeotrope. The dilute ethanol process feed is first preconcentrated up to the composition of the ethanol–water azeotrope in a preconcentrator column. This stream is fed to the azeo-column that produces pure ethanol as bottoms product and an overhead vapor close to the composition of the ethyl ether–water azeotrope. The overhead vapors are condensed and decanted into an ether-rich layer that is returned to the column as reflux, and a water-rich layer that leaves as distillate. The distillate contains no alcohol and very little ether. Pure water may be obtained from this stream by sending it to a stripping column where water is recovered as the bottom product and the overhead vapor has a composition near the ethyl ether–water azeotrope. These vapors are condensed and recycled to the decanter. The azeo-column is normally operated at ~700 kPa (7 atm) pressure because, (*1*) this increases the amount of water in the ether–water azeotrope, thereby reducing the amount of ether needed in the system, and (*2*) it allows for cooling water to be used in the condenser.

This process is described in the literature in more detail (205–207). Its main advantage was a lower energy consumption (~6000 kJ/L (20,000 Btu/gal) ethanol product) relative to the benzene process (12,000 kJ/L (43,000 Btu/gal) ethanol) (206). Since the 1940s the gap has been narrowed by better designs for the benzene process that is now capable of producing 99.8 mol% ethanol at an energy consumption of 8,400 kJ/L (30,000 Btu/gal) ethanol product (78,193), or using thermally integrated columns for 5000 kJ/L (18,000 Btu/gal) ethanol product (78,208). In recent years, homogeneous separating agents have shown great promise for the ethanol–water separation, and extractive distillation processes using ethylene glycol as the solvent have been designed with energy consumptions of ~6000 kJ/L (22,000 Btu/gal) ethanol product (78), or using thermally integrated columns for 2200–3300 kJ/L (8,000–12,000 Btu/gal) ethanol product (78,209,210).

Rodebush Sequence for Ethanol–Water Separation. When ethyl acetate is used as the entrainer to break the ethanol–water azeotrope the residue curve map is similar to the one shown in Fig. 25**d**, ie, the ternary azeotrope is homogeneous. Otherwise the map is the same as for ethanol–water–benzene. In such cases the liquid leaving the azeo-column condenser does not separate into two liquid phases, and the sequence is infeasible unless special tricks are employed. In the Rodebush sequence, water is continuously added to the decanter in order to shift the overall composition into the two-liquid phase region. The water-rich phase from the decanter is fed to a distillation column where pure water is recovered in the bottom stream (some of which is recycled to the decanter) and the distillate, which lies near the ternary azeotrope, is recycled to the azeo-column. The ethyl acetate-rich phase from the decanter is returned to the azeo–column as reflux (191). Pure ethanol is recovered in the bottom stream of the azeo-column. More recently, a clever variation on this sequence was patented (211) for separating a ternary feed consisting of ethanol, water, and diethoxymethane. This variation also has a residue curve map similar to the one shown in Fig. 25**d**.

More Complex Mixtures. All the sequences discussed are type I liquid systems, ie, mixtures in which only one of the binary pairs shows liquid–liquid behavior. Many mixtures of commercial interest display liquid–liquid behavior in two of the binary pairs (type II systems), eg, secondary butyl alcohol–water–di-secondary butyl ether (SBA–water–DSBE), and water–formic acid-*meta*-xylene (162). Sequences for these separations can be devised on the basis of residue curve maps. The SBA–water–DSBE separation is practiced by ARCO and is considered in detail in the literature (183,184,188,212).

Self-Entrained Systems. It is quite common to find that the feed mixture to an azeotropic distillation column is not a binary azeotropic mixture but a ternary mixture that already contains a third component that can act as an entrainer. Such systems are called self-entrained. The presence of the third component may be unavoidable on account of the reaction chemistry [eg, acetic acid–water–vinyl acetate (213–215); ethanol–water–diethoxy methane, (211)], or may be present on purpose due to the choice of process technology. For example, in some process alternatives for separating acetic acid–water mixtures by azeotropic distillation part of the entrainer-rich phase from the decanter is recycled back to the column feed (202, p. 67), thereby creating a self-entrained feed to the column. In other process alternatives for separating the same mixture, solvent extraction is used to remove almost all the acetic acid from the water, creating an extract stream that contains almost all of the acetic acid that entered with the process feed, some water, and all of the solvent used in the extractor (202, p. 68; 216,217). This extract stream is then fed (as a self-entrained ternary mixture) to an azeotropic distillation column where glacial acetic acid (>99.7 wt%) is recovered as the bottom product. In these kinds of separation sequences, the third component is chosen to be both a good solvent in the extractor and a good entrainer in the azeotropic distillation. Minotti et al. (218) give a detailed description of the process alternatives and process economics of using diethyl ether to separate acetic acid–water mixtures using a combination of extraction and azeotropic distillation flow sheets.

Two typical self-entrained azeotropic distillation systems are described below.

Separation of Acetic–Water–Isopropyl Acetate Mixtures. At 1 atm pressure, isopropyl acetate boils at 88.4°C and forms a binary heterogeneous azeotrope with water that boils at 77.2°C and contains ~40 mol% water. Isopropyl acetate is the lightest boiling component in the mixture and the residue curve map, calculated using the NRTL activity coefficeint model, is shown in Fig. 26.

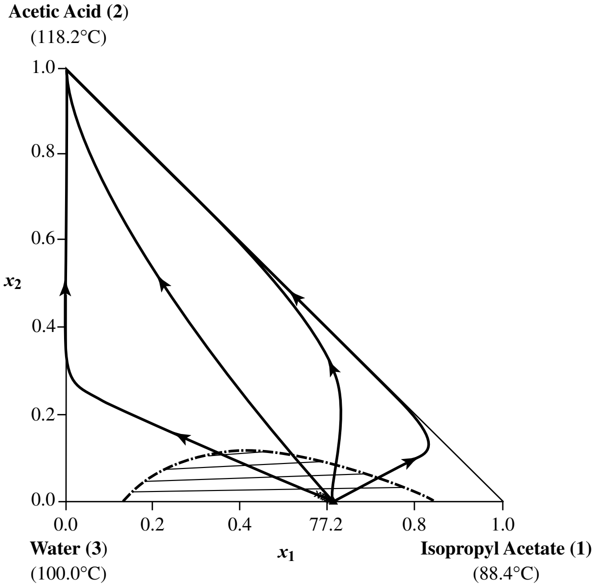


Fig. 26. Residue curve map and liquid–liquid boiling envelope for acetic acid + water + isopropyl acetate at 1-atm pressure.

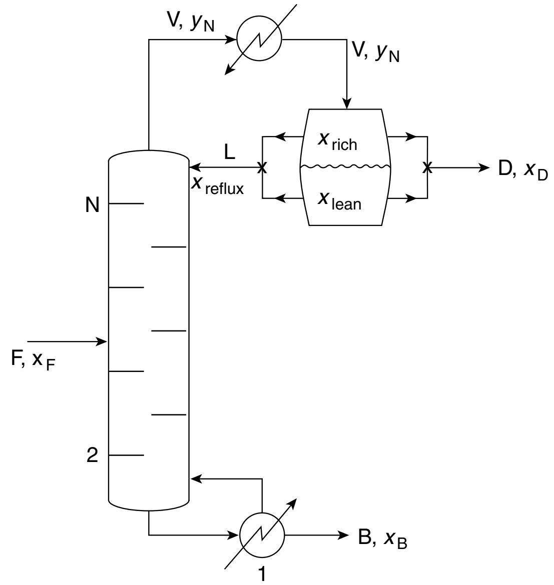


Fig. 27. Schematic column configuration for self-entrained azeotropic distillation.

(Note that several other light-boiling entrainers, such as vinyl acetate, diethyl ether, chloroform, etc, generate similar residue curve maps and have qualitatively similar azeotropic distillations. Thus, the isopropyl acetate entrainer is representative of other entrainers of the light-boiling type). For illustration, a saturated liquid ($q = 1$) feed composition of 20 mol% isopropyl acetate, 40 mol% water and 40 mol% acetic acid is assumed. The desired purity of the bottoms stream is glacial acetic acid containing ~99.9 mol% acetic acid. Two design alternatives exist. With the same feed composition, the column can be designed to operate with either an entrainer-rich or an entrainer-lean composition profile. In either case the column configuration is the same as shown in Fig. 27, and the distillate composition (determined by material balance with the feed and bottoms compositions) is essentially the same in both cases. (Note that the distillate composition of acetic acid determines which tie-line in the liquid–liquid region corresponds to the decanter tie-line, but the relative proportion of phases in the decanter is determined by the position of the overhead vapor composition on the decanter tie-line, see Fig. 28). The decanter composition, which is the same as the overhead vapor composition, is, however, quite different in the two designs, as is the reflux composition (ie, the proportion of the two decanter liquid phases returned to the column is different), and the reflux ratios.

The first entrainer-rich design is shown in Fig. 28. The distillate is selected so it contains some acetic acid in order to make the decanter tie-line visible on the diagram and the relationship between the various points on it more obvious. The bottom stream, the acetic acid product, contains more isopropyl acetate (0.001 mole fraction) than water (0.0001 mole fraction). This distribution of the trace components forces the stripping section composition profile to move along the acetic acid–isopropyl acetate edge of the diagram and intersect with the

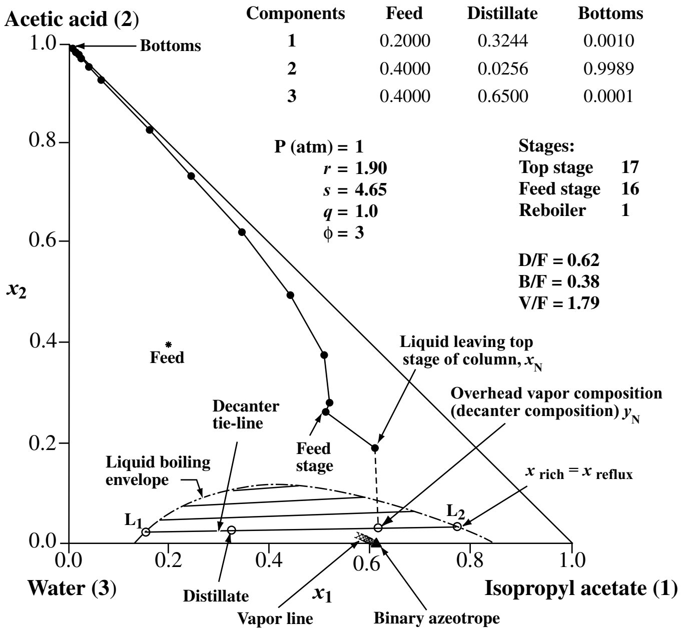
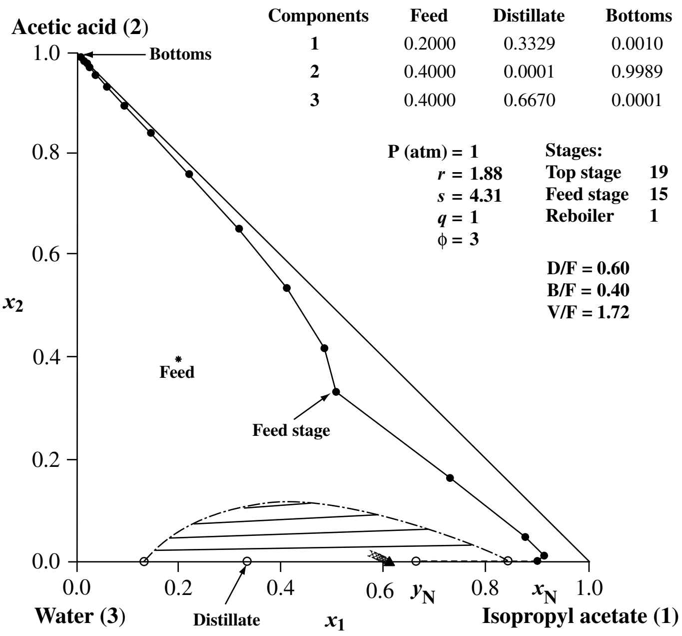


Fig. 28. Azeo-column liquid composition profile (●—●) and design data for the acetic acid + water + isopropyl acetate separation. Entrainer-rich design with low recovery of acetic acid (2.56 mol % acetic acid in the distillate).

rectifying section composition profile in the entrainer-rich region of the diagram. The result is a column design where the liquid on all of the stages throughout the column contains more entrainer than water. The top of the column is designed so that the overhead vapor composition (which becomes the feed to the decanter) lies to the entainer-rich side of the azeotrope on the decanter tie-line. This causes the liquid on the top tray of the column to be rich in entrainer (see Fig. 28). The ratio, ϕ, of entrainer-rich phase (L_2) to entrainer-lean phase (L_1) in the decanter is 3:1 (this is determined by the design value of the decanter composition). Part of the entrainer-rich decanter liquid is refluxed to the column, the balance is mixed with the entrainer-lean decanter liquid to produce a distillate composition at the required point along the decanter tie-line. There is a simple algebraic material balance relationship between the reflux ratio and the reflux composition (which also contains the distillate composition and the decanter composition as known parameters). Therefore, a chosen value of **r** implies that the reflux composition is determined, and vice-versa. When we select the reflux composition to be equal to the composition of the entrainer-rich phase the corresponding value of the reflux ratio is $r = 1.9$. This entrainer-rich design requires 17 theoretical stages to perform the separation at a reflux ratio of 1.9. Sixteen stages are in the stripping section and only 1 is in the rectifying section. A key measure of economic performance (energy use) is the internal vapor rate relative to the feed rate (V/F), which is 1.79 for this design. Generally in distillation, values of $V/F < 1$ are considered very attractive, while values greater than 3 are unattractive. Values in between are normal.

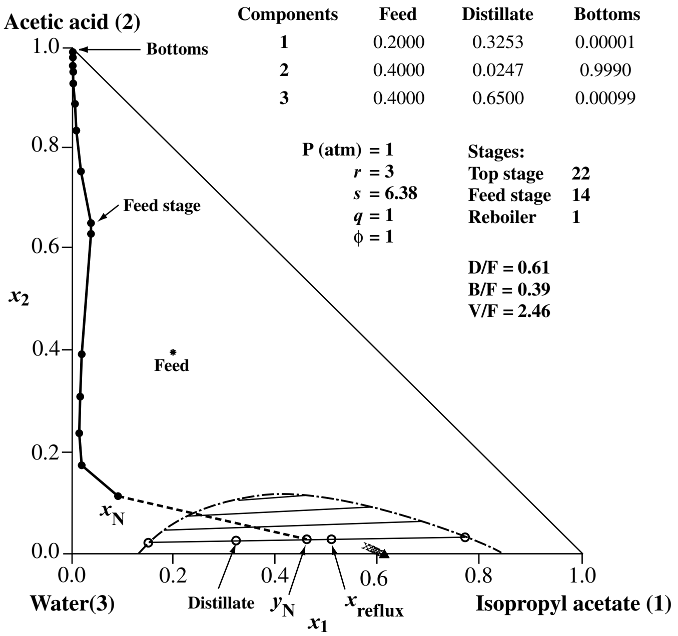


Components	Feed	Distillate	Bottoms
1	0.2000	0.3329	0.0010
2	0.4000	0.0001	0.9989
3	0.4000	0.6670	0.0001

Fig. 29. Azeo-column liquid composition profile and design data for the acetic acid + water + isopropyl acetate separation. Entrainer-rich design with high recovery of acetic acid (100 ppm (molar) acetic acid in the distillate).

A more realistic entrainer-rich design is shown in Fig. 29, where the distillate is selected to have only a small amount of acetic acid present (mole fraction of 0.0001). The decanter tie-line lies almost on top of the isopropyl acetate-water edge of the diagram. In this design, the feed and bottom composition are the same as before, so is $\phi = L_2/L_1 = 3$. We again choose to reflux only the entrainer-rich phase (which determines the reflux ratio to be $r = 1.88$), giving a column with a total of 19 theoretical stages (15 in the stripping section and 4 in the rectifying section), and $V/F = 1.72$. This design, therefore, produces high purity glacial acetic acid at high recovery (ie, with very little acetic acid lost in the distillate) in a column with both a reasonable number of stages and a reasonable boilup.

By contrast, entrainer-lean designs require more stages and more boilup. The entrainer-lean designs described below have exactly the same feed composition, and almost the same acetic acid purity in the bottoms stream and acetic acid composition in the distillate as the entrainer-rich designs. The first case is shown in Fig. 30. It is the entrainer-lean analog of the design in Fig. 28. The overhead vapor composition is selected to lie on the entrainer-lean side of the azeotrope so that the composition of the liquid on the top stage of the column is also on the lean side of the diagram. (A phase ratio of 1:1 in the decanter achieves this). The minimum reflux for this separation is ~1.8 and the corresponding value of $(V/F)_{\min}$ is 1.7. Choosing a reflux ratio, $r = 3$, gives $V/F = 2.5$, and also determines that the reflux stream contains roughly equal amounts (on a molar



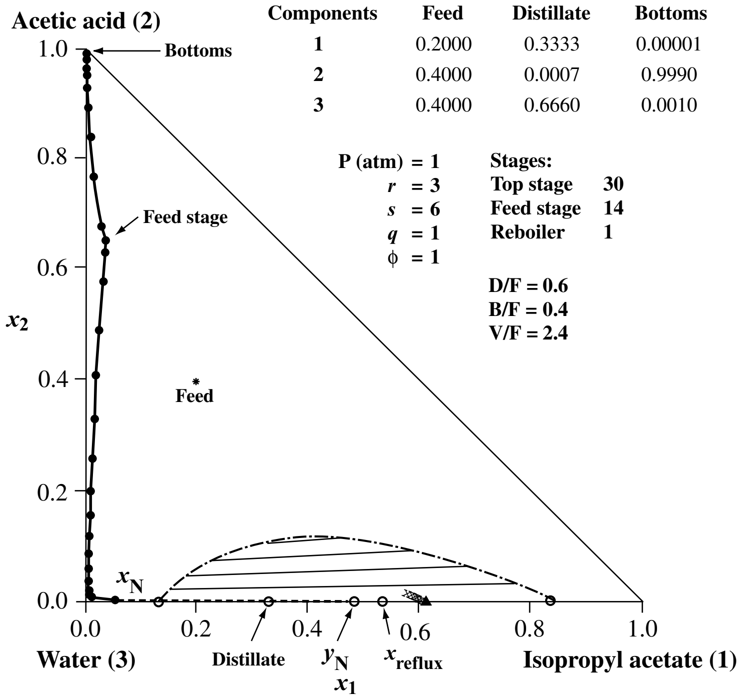
Components	Feed	Distillate	Bottoms
1	0.2000	0.3253	0.00001
2	0.4000	0.0247	0.9990
3	0.4000	0.6500	0.00099

Fig. 30. Azeo-column liquid composition profile and design data for the acetic acid + water + isopropyl acetate separation. Entrainer-lean design with low recovery of acetic acid (2.47 mol% acetic acid in the distillate).

basis) of the two decanter phases (see Fig. 30). This design requires a total of 22 theoretical stages for the separation. The distribution of stages is very different than the design in Fig. 28, with 14 in the stripping section and 8 in the rectifying section. Therefore, this design requires more stages and more boilup to deliver the same product specifications as the entrainer-rich design. Note that the trace components in the bottom stream for this design consist mainly of water (0.001 mole fraction versus 0.00001 mole fraction of isopropyl acetate). This trace component distribution forces the stripping section composition profile to move along the acetic acid-water edge of the diagram and intersect with the rectifying composition profile in the entrainer-lean region of the diagram. The result is a column design where the liquid on all of the stages contains less entrainer than water.

An entrainer-lean design that delivers high purity acetic acid at high recovery is shown in Fig. 31. Thirty stages (14 in the stripping section and 16 in the rectifying section) are required at a reflux ratio of $r = 3$ (V/F = 2.4). Again, the minimum reflux ratio for this separation is ~1.8. It is possible to reduce the number of stages by increasing the reflux ratio, eg, when $r = 5$, V/F = 3.6, and the total number of stages is reduced to 25. However, compared to the corresponding entrainer-rich design in Fig. 29, the entrainer-lean design requires more stages and more boilup to deliver the same acetic acid product purity and recovery.

As more entrainer is added to the feed (keeping the relative proportions of acetic acid and water roughly equal), it remains possible to generate both



Components	Feed	Distillate	Bottoms
1	0.2000	0.3333	0.00001
2	0.4000	0.0007	0.9990
3	0.4000	0.6660	0.0010

P (atm) = 1
r = 3
s = 6
q = 1
ϕ = 1

Stages:

Top stage	30
Feed stage	14
Reboiler	1

D/F = 0.6
B/F = 0.4
V/F = 2.4

Fig. 31. Azeo-column liquid composition profile and design data for the acetic acid + water + isopropyl acetate separation. Entrainer-lean design with high recovery of acetic acid (700 ppm (molar) acetic acid in the distillate).

entrainer-rich and entrainer-lean designs, although the entrainer-rich design is always the better of the two. However, as the composition of water in the feed increases, it eventually becomes impossible to generate an entrainer-rich design and, as the composition of isopropyl acetate in the feed increases, it eventually becomes impossible to generate an entrainer-lean design.

One final possibility for the design of the azeo-column is to put the overhead vapor composition exactly on the vapor line, causing the liquid on the top stage of the column (and possibly the next several stages below it) to be heterogeneous. The rectifying composition profile then moves through the liquid–liquid region rather than around the outside of it. This may be advantageous for some systems such as the n-butyl acetate case that follows.

Separation of Acetic Acid–Water–n–Butyl Acetate Mixtures. At 1-atm pressure, *n*-butyl acetate boils at 126°C and forms a binary heterogeneous azeotrope with water that boils at 91°C and contains ~72 mol% water. *N*-Butyl acetate is the highest boiling component in the mixture and the residue curve map, calculated using the NRTL activity coefficient model, is shown in Fig. 32. This map is quite different than the map shown in Fig. 26 for light-boiling entrainers, and the feasible splits and azeotropic column designs are also different. Only entrainer-lean designs are possible. This is due to the fact that acetic acid is the stable node (high boiler) and the entrainer is a saddle (intermediate boiler) in Fig. 26, while acetic acid is a saddle and the entrainer is a stable node in Fig. 32.

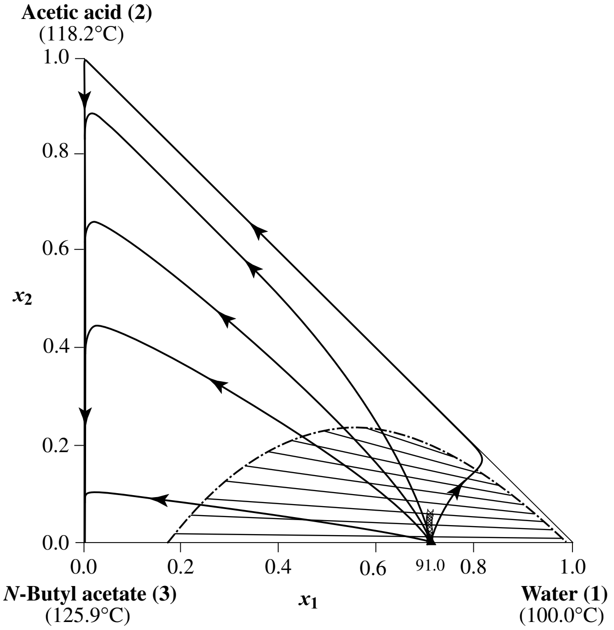


Fig. 32. Residue curve map and liquid–liquid boiling envelope for acetic acid + water + n-butyl acetate at 1-atm pressure.

Consider a saturated liquid feed containing 20 mol% n-butyl acetate, 40 mol% water and 40 mol% acetic acid. The desired purity of the bottoms stream is again glacial acetic acid containing ~99.9 mol% acetic acid. The column configuration is the same as in Fig. 27, and the distillate composition is again chosen to have some acetic acid present in order to make the decanter tie-line visible on the triangular diagram. A typical design is shown in Fig. 33. The distillate composition determines the position of the decanter tie-line, and the overhead vapor composition is selected to lie on the entrainer-lean side of the azeotrope (the ratio of entrainer-rich phase (L_2) to entrainer-lean phase (L_1) in the decanter is 1:3), which gives a liquid on the top tray of the column that is also lean in entrainer. The rectifying profile starts at this point and moves toward the stable node (high boiler) at n-butyl acetate (ie, in the direction of increasing temperature down the column). It intersects the stripping profile which moves from the acetic acid corner of the diagram along the acetic acid–water edge before turning into the diagram towards the azeotrope (ie, in the direction of decreasing temperature up the column). The minimum reflux at which these profiles just intersect is ~1. A reasonable trade-off between stages and reflux occurs at $r = 2$ ($V/F = 1.84$), giving 30 theoretical stages in the column (23 in the stripping section and 7 in the rectifying section), see Fig. 33. As can be seen in this Fig., the reflux stream and the liquid composition on all of the stages are entrainer-lean. It is not possible to design a column with an entrainer-rich profile because rectifying profiles that start near the entrainer-rich end of the decanter tie-line will move directly to pure n-butyl acetate (in the direction of increasing temperature down the column). The rectifying profile can never intersect the stripping profile,

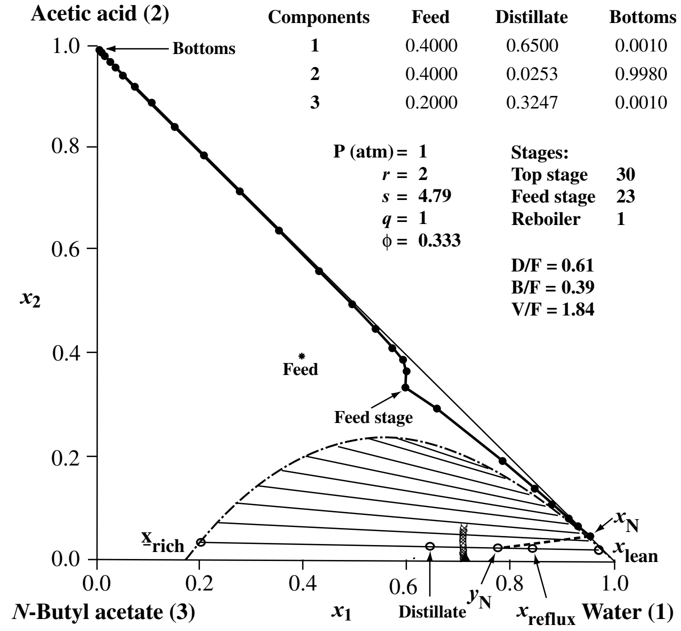
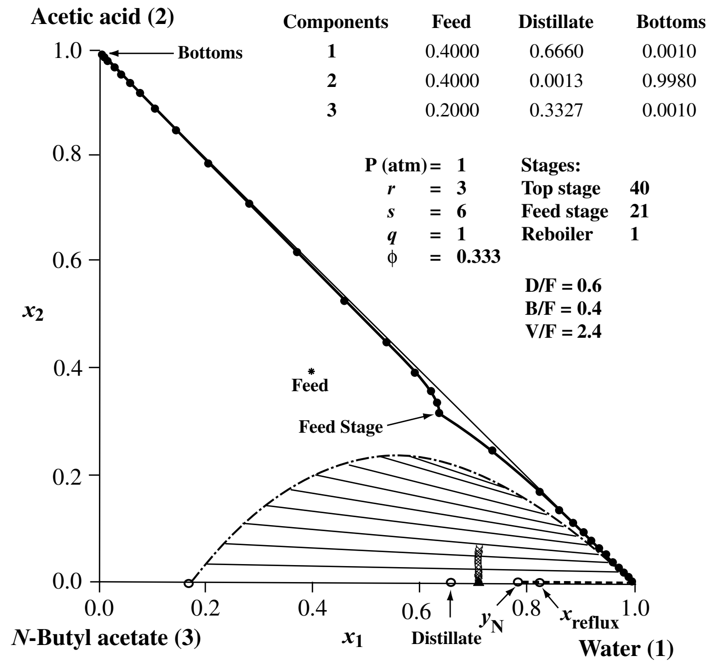


Fig. 33. Azeo-column liquid composition profile and design data for the acetic acid + water + *n*-butyl acetate separation. Low recovery of acetic acid (2.53 mol % acetic acid in the distillate).

which starts at acetic acid and moves toward the azeotrope (in the direction of decreasing temperature up the column). Another way of saying this is that heavy entrainers cannot be forced up the column to generate entrainer-rich designs.

With *n*-butyl acetate as the entrainer, high recovery of acetic acid is possible only with larger reflux ratios (in the range of $r = 3–5$, giving V/F in the range of 2.4–3.6) and larger numbers of theoretical stages (40–34, respectively), eg, see Fig. 34. Reflux ratios < 3 increase the number of stages dramatically (eg, $r = 2$ requires 50 theoretical stages). This effect is due to the proximity of the column composition profile to the tangent pinch between acetic acid and water located in the vicinity of pure water. When the distillate contains very little acetic acid, the decanter tie-line lies on the *n*-butyl acetate-water edge of the triangle, and this puts the composition of the liquid on the top stage of the column right on top of the tangent pinch where the separation per stage is very small, see Fig. 34.

For this system there is a clear advantage to having multiple liquid phases on the top several trays of the rectifying section. Such designs put the top portion of the rectifying profile inside of the liquid–liquid region of the diagram, well away from the tangent pinch. This has the effect of simultaneously reducing both the reflux ratio and the total number of theoretical stages, see Fig. 35. Parten and Macpherson Ure (189) disclose a process for achieving this by only refluxing the organic phase. Urdaneta and co-workers (180) and Wasylkiewicz and co-workers (190) propose methodologies for systematically designing such azeotropic distillations with multiple liquid phases on some of the stages inside



Components	Feed	Distillate	Bottoms
1	0.4000	0.6660	0.0010
2	0.4000	0.0013	0.9980
3	0.2000	0.3327	0.0010

P (atm) = 1
r = 3
s = 6
q = 1
ϕ = 0.333

Stages:	
Top stage	40
Feed stage	21
Reboiler	1

D/F = 0.6
B/F = 0.4
V/F = 2.4

Fig. 34. Azeo-column liquid composition profile and design data for the acetic acid + water + n-butyl acetate separation. Higher recovery of acetic acid (0.13 mol % acetic acid in the distillate).

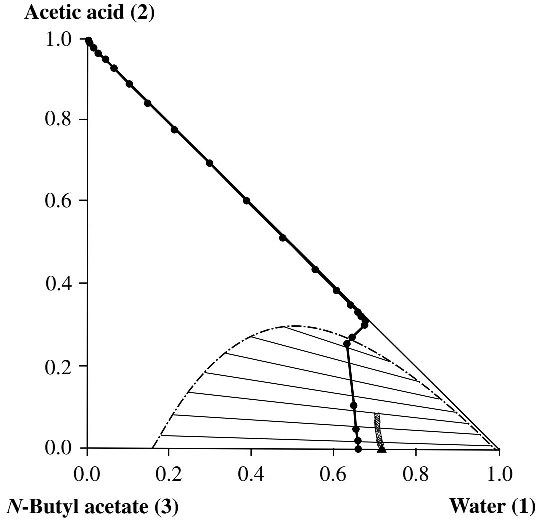


Fig. 35. Azeo-column liquid composition profile for the acetic acid + water + n-butyl acetate separation with two liquid phases on the top stages in the rectifying section. Taken from reference (190). The heterogeneous binary azeotrope and vapor-line are also shown.

the column. Designs for the acetic acid-water-n-butyl acetate system are considered in detail in (190), and one is reproduced in Fig. 35.

Whereas there is extensive literature on design methods for azeotropic and extractive distillation, much less has been published on operability and control. It is, however, widely recognized that azeotropic distillation columns can be difficult to operate and control because some of these columns can exhibit complex dynamic behavior, multiple steady-states, and parametric sensitivity (172–174,182–187,219). In contrast, extractive distillations typically do not exhibit such complex behavior and even highly optimized columns are typically no more difficult to control than ordinary distillation columns producing high purity products (220). Exceptions do exist, however. Multiple steady-states have been observed in at least one industrial extractive distillation (221).

8. Nomenclature

B	bottom stream or bottoms flow rate
c	number of components in a mixture
D	distillate stream or distillate flow rate
F	feed stream or feed flow rate
L	liquid flow rate
P	pressure
P_i^{sat}	vapor pressure of component i
R	gas constant
r	reflux ratio
S_{ij}	selectivity of a solvent for solutes i and j (defined by eq. 8)
S_{ij}^{∞}	selectivity of a solvent with the solutes present at infinite dilution (defined by eq. 9)
T	temperature
TAC	total annualized cost (see Ref. 103)
V	vapor flow rate
V_i^{L}	liquid-phase molar volume of component i
x_i	liquid-phase composition of component i (mol fraction)
y_i	vapor-phase composition of component i (mol fraction)
α_{ij}	volatility of component i relative to component j (defined by eq.6)
γ_i	liquid-phase activity coefficient of component i
γ_i^{∞}	infinite dilution liquid-phase activity coefficient of component i
ξ	nonlinear time scale (see eq.7)
ϕ	the ratio of the two phases in a decanter
ϕ_i^{v}	vapor-phase fugacity coefficient of component i
ϕ_i^{sat}	liquid-phase saturation fugacity coefficient of component i

Subscripts

B	bottom
D	distillate
F	feed
lean	entrainer-lean phase
min	minimum
N	stage number N
R	reflux
rich	entrainer-rich phase
S	in the presence of solvent

Superscripts

AZ	denotes an azeotrope or azeotropic condition
o	overall composition

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