Thermodynamic Insights on the Feasibility of Homogeneous Batch Extractive Distillation. 4. Azeotropic Mixtures with Intermediate Boiling Entrainer

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ABSTRACT: This paper shows how knowledge of the univolatility and unidistribution line location and residue curve analysis help to assess the feasibility of batch extractive rectifying or stripping distillation of azeotropic mixtures by using an intermediate boiling entrainer. We consider five minimum boiling (minT) azeotropic mixtures AB with entrainer E, namely, acetone−heptane with benzene, methanol−toluene with triethylamine, methyl acetate−cyclohexane with carbon tetrachloride, dichloromethane−ethanol with acetone, and ethyl acetate−heptane with benzene; and one maximum boiling (maxT) azeotropic mixture, namely, chloroform−ethyl acetate with either 2-chlorobutane, isobutylchloride, bromopropane, or bromochloromethane. All ternary diagrams A−B−E belong to the 1.0-1b class, for which all three possible univolatility, α_{AB}, α_{BE}, and α_{AE}, and unidistribution lines, K_A, K_B, and K_E can exist. With application of the general feasibility criterion of Rodriguez-Donis et al. (*Ind. Eng. Chem. Res.* **2009**, *48* (7), 3544−3559), both azeotropic components, A and B, accomplish the criterion, and they can be recovered, A in an extractive rectifier and B in an extractive stripper. The process efficiency of each alternative depends strongly on the location of the α_{AB} univolatility line interception with the triangle edge, and also depends on the α_{BE} (α_{AE}) in the minT (maxT) case and of the unidistribution line K_E closeness to the (E−B) (A−E) edge. Besides, choice of the rectification of A instead of the stripping of B is set by the ratio of α_{AE}/α_{BE}, the ratio of relative volatility variation of the binary mixtures between A or B and E.

1. INTRODUCTION

Over the years, extractive distillation has been considered for the separation of azeotropic and low relative volatility mixtures as a fairly simple process for synthesis, design, and industrial implementation. Indeed, almost all industrial extractive distillation processes have been designed based on a single rule, namely, the choice of a heavy boiling entrainer forming no new azeotrope for the separation of a minimum boiling azeotropic mixture. The restriction of not forming new azeotrope is not a strict condition anymore[1] but is not discussed here. We have also shown in parts 1−3[2−4] of this article series that light or heavy entrainers can lead to a feasible process as well.

With an entrainer (E) added to a binary mixture (A−B) and forming no new azeotrope, the resulting ternary diagram belongs to Serafimov's class 0.0-1[5,6] for the separation of a low volatility mixture, to class 1.0-1a for the separation of a minimum boiling temperature (minT) azeotropic mixture with a heavy entrainer (the most common industrial case) or of a maximum boiling temperature (maxT) azeotropic mixture with a light entrainer, to class 1.0-2 for the separation of a maxT azeotropic mixture with a heavy entrainer or a minT azeotropic mixture with a light entrainer, and finally to class 1.0-1b for the separation of either a minT or a maxT azeotropic mixture with an intermediate entrainer.[2] Classes 1.0-1a, 1.0-2, and 1.0-1b amount to one-third of occurring ternary azeotropic mixtures.[6]

Extractive distillation differs from azeotropic distillation because the entrainer is fed at another location than the main feed. Thus, it defines an extractive section between both feeds. When no entrainer is added, we call the process simply "distillation".

The extractive distillation process is more complicated than what the industry thinks from the single rule applied in industry: choosing an entrainer forming no new azeotrope with the components to be separated, either a heavier one for separating a minimum boiling azeotrope or a lighter one for separating a maximum boiling azeotrope. First, good performance is strongly related to the entrainer's ability to selectively enhance the A−B volatility.[3,7] Until recently, the process synthesis and design key questions (which product is first distilled, is there a limiting entrainer flow rate, is the product recovery complete?) were assessed by computing the liquid profile in each column section via a discrete[8] or continuous[9,10] model. In parallel, thermodynamic features of the diagrams could be used to design an extractive distillation process.[11,12] By combining univolatility line location and residue curve map analysis only, a general feasibility criterion suitable for infinite reflux operation and infinite number of stages was enounced by
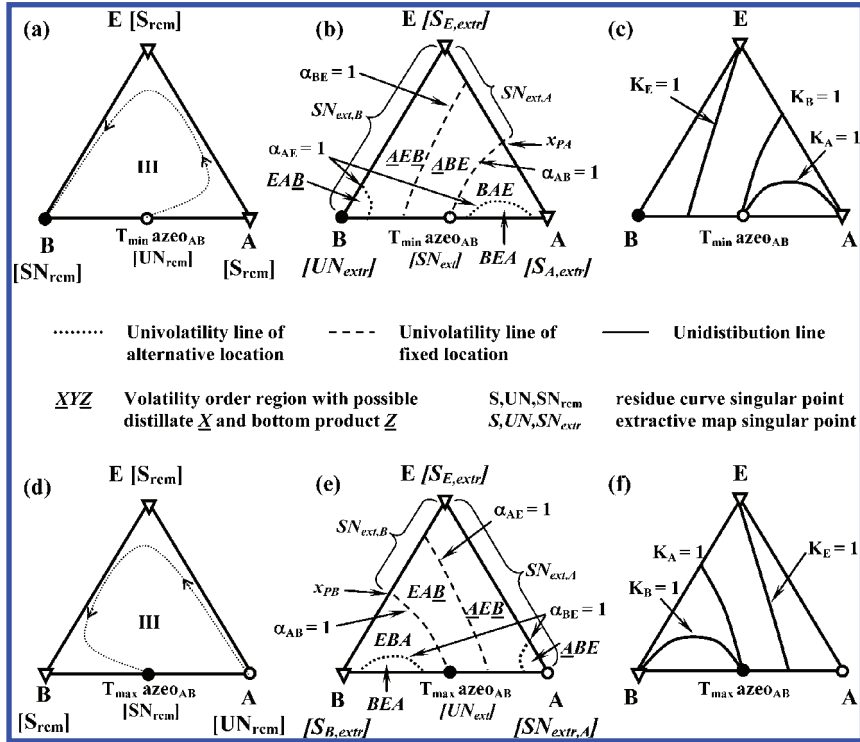
Figure 1. Residue curve and extractive profile maps with unidistribution and univolatility lines for the ternary diagram 1.0-1b: (a, b, c) minimum boiling azeotropic mixture; (d, e, f) maximum boiling azeotropic mixture.

Rodriguez-Donis et al.[2] in part 1 of this article series. Parts 1[2] and 2[3] investigated the separation of minT or maxT azeotropic mixtures and low relative volatility mixtures, respectively, using a heavy entrainer in either batch rectifying or stripping column configurations. Part 3 looked at the use of light entrainers for extractive distillation.[4] In those works, finite reflux operation impact on the process feasibility was also considered, and reflux policies were suggested.

In this paper, we consider using an intermediate boiling entrainer for separating azeotropic mixtures without inducing a new azeotrope. The diagram belongs to Serafimov's class 1.0-1b. We illustrate our study by considering batch distillation, but the feasibility analysis under infinite reflux also holds for continuous operation as well.

2. STATE OF THE ART

Bernot et al. stated that batch azeotropic distillation with an intermediate entrainer E loaded initially with the azeotropic mixture (A−B) is always feasible.[13] Indeed the whole 1.0-1b ternary diagram has a single basic distillation region (Figure 1). For a minT azeotropic mixture, the heavy original component B is a stable node of the residue curve map and is recovered in the bottom of a batch stripper. Conversely, for a maxT azeotropic mixture, the light original component A is an unstable node and can be distilled overhead in a batch rectifier.

For continuous extractive distillation, Laroche et al.[11] studied feasibility in the light of univolatility line originating at the azeotrope and pointed out that intermediate entrainers provide several alternatives: (1) a direct sequence to obtain the light component A, (2) an indirect sequence for the heavy component B, and (3) the use of a single column for separating both components A and B as top and bottom products, respectively, if a small amount of the entrainer remains inside the column. Alternative 3 operation could be

extrapolated to batch by using a middle vessel column. Later, the importance of the univolatility line was confirmed theoretically[12] and helped to develop a short cut method for finding the minimum flow rate and ratio of extractive distillation under finite reflux ratio[7] for separating minT with heavy entrainer (class 1.0-1a). The use of an intermediate entrainer was not considered in those two works.

The use of an intermediate entrainer (class 1.0-1b) has been better investigated in batch operation. Rev et al. found that batch extractive rectification was a superior alternative to azeotropic distillation in a batch stripper for separating minT azeotropes like methyl acetate−cyclohexane using tetrachloride.[14] The separation of the key components can be performed with less operating steps because the first distillate cut given by the azeotrope can be avoided by feeding the entrainer continuously at a given position of the distillation column providing higher purity and recovery yield as well. At the same time, Lelkes et al. demonstrated that batch rectification of the chloroform−ethyl acetate maxT azeotrope with 2-chlorobutane could be impossible by azeotropic distillation and proposed extractive distillation instead.[15] Later, Varga et al. studied an extractive stripper for separating the same mixture as Lelkes and the methanol−toluene minT azeotrope with triethylamine.[16] By computing stripping and extractive section profiles for several reboil ratios, they found that a minimum reboil ratio value was required for the minT case whatever the entrainer feed position and also noticed that an extractive rectifier could give a better performance. The maxT case showed a narrow feasible region and a minimum reboil ratio as well. However, a high purity bottom product could be obtained.[17]

All those works on batch operation did not pay special attention to the existence and location of univolatility lines α_{AB}, α_{AE}, or α_{BE} and unidistribution lines $K_i = 1$ despite their occurrence in all ternary diagram classes.[5,6] This is done in this

article, and additional ternary mixtures are considered to elucidate the most controversial results.

Univolatility and unidistribution lines, residue curve maps, singular point stability, rectifying and extractive composition profiles at a given reflux ratio, and entrainer flow rate were computed with Residue and drawn with the freeware ProsimTernaryDiagram.[18] Stripping profiles were computed with SimulisThermodynamics in Microsoft Excel.[18] The NRTL thermodynamic model was used for computing the liquid–vapor equilibrium. NRTL parameters are given in Table 1.

Table 1. NRTL Parameters for Computing the Ternary Liquid–Vapor Equilibrium

	binary coefficients [cal/mol]		
	A_{ij}	A_{ji}	α_{ij}
acetone (A)–benzene (E)	−193.34	569.931	0.3007
acetone (A)–heptane (B)	881.932	297.031	0.2892
benzene (E)–heptane (B)	576.066	−75.5819	0.3469
methanol (A)–triethylamine (E)	−642.811	1272.83	0.2793
methanol (A)–toluene (B)	907.825	1025.08	0.4315
triethylamine (E)–toluene (B)	−255.684	348.946	0.2876
methyl acetate (A)–CCl$_4$ (E)	173.308	175.367	0.3013
methyl acetate (A)–cyclohexane (B)	588.521	455.901	0.2953
CCl$_4$ (E)–cyclohexane (B)	696.570	−570.815	0.3048
dichloromethane (A)–acetone (E)	−186.400	−74.59	0.3056
dichloromethane (A)–ethanol (B)	1332.80	−153.100	0.3057
acetone (E)–ethanol (B)	36.2965	434.823	0.2987
ethyl acetate (A)–benzene (E)	−273.017	383.126	0.3196
ethyl acetate (A)–heptane (B)	608.053	205.900	0.3000
benzene (E)–heptane (B)	576.066	−75.5819	0.3469

Validation of the feasibility assessed through preliminary thermodynamic insight is done through rigorous simulation using ProSim BatchColumn.[18] In all cases, the following assumptions were kept: theoretical plates, negligible liquid hold-up on the trays and condenser (for the rectifying column configuration), no pressure drop inside the column, adiabatic column, boiling entrainer is fed at intermediate tray, and the liquid contained in the top vessel (for the stripping column configuration) is kept at its boiling temperature. All these assumptions were retained in order to keep closer the conditions for short-cut simulation (without heat balance) and rigorous simulation in order to compare the main results (component to be drawn as first product, liquid composition profile into each section of the column, and the trajectory of the composition into the boiler or into the top vessel for batch rectifier or batch stripper, respectively).

3. THERMODYNAMIC AND TOPOLOGICAL STRUCTURES FOR INTERMEDIATE BOILING ENTRAINER

Figure 1 shows the ternary diagram class 1.0-1b residue curve map and volatility order regions with the unidistribution map, which holds for the separation of minT (Figure 1a) or maxT (Figure 1d) azeotropic mixture by using an intermediate boiling entrainer forming no new azeotrope. Notice that the intermediate entrainer is always a saddle. One of the original components and the azeotrope is either an unstable or a stable node of the residue curve map. The remaining original component is a saddle point. The residue curve map contains one single elementary cell, III, in which the residue curve

reaches the stable node from the unstable node passing through two consecutive saddle points. Reported occurrence of diagram class 1.0-1b is only 0.4%,[6] incidentally explaining the difficulty of finding intermediate entrainers. The 1.0-1b class diagram (Figure 1) displays up to three unidistribution lines (K_A, K_B, K_E) and up to three univolatility curves (α_{AB}, α_{AE} and α_{BE}).[5] In the case of a minT (maxT) azeotrope (Figure 1b (e)), the α_{AB} = 1 curve starts at the azeotrope and ends at the binary side (A–E (B–E)) limited by the entrainer and the light (heavy) azeotropic component. Univolatility line α_{BE} (α_{AE}) always exists parallel to the corresponding binary side (B–E (A–E)). Occasionally, α_{AE} (α_{BE}) appears on the edge of the azeotropic components or around either A or B apex. Therefore, up to four volatility order regions exist as shown in Figure 1b,e for each type of azeotropic mixture.

Through the rest of this article, the existence of the univolatility line α_{AE} in Figure 1b (α_{BE} in Figure 1e) is not discussed because it has no effect on the feasibility of the separation of the minT (maxT) azeotrope to recover A or B by extractive distillation. It does not change the A versus B volatility order.

Both minT and maxT cases are studied now.

4. SEPARATION OF MINIMUM AZEOTROPES

4.1. Feasibility Analysis. In part 1 of this article series, a general feasibility criterion was enounced: "homogeneous batch extractive distillation of a A–B mixture with entrainer E feeding is feasible if there exists a residue curve connecting E to A or B following a decreasing (a) or increasing (b) temperature direction inside the region where A or B are the most volatile (a) or the heaviest (b) component of the mixture". The volatility order is set by the univolatility curves. The criterion was shown to hold for 1.0-1a and 1.0-2 classes.[2,3]

For the 1.0-1b class, rectifying and stripping extractive column configurations are considered. The first one with a rectifying and an extractive section withdraws products as a sequence of distillate cuts (Figure 2a). The second one with an
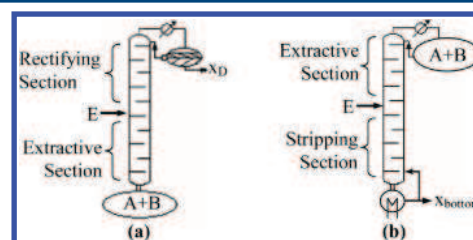
Figure 2. Batch column configurations for homogeneous extractive distillation processes: (a) batch rectifying column; (b) batch stripping column.

extractive and a stripping section recovers components as consecutive bottom products (Figure 2b). If the entrainer is fed into the still during the process (the top vessel), no extractive section exists. However, the process behaves differently from azeotropic distillation because it has a different still (top vessel) composition trajectory. That is the case of separation of minimum boiling azeotropes using light entrainers.[9] Batch extractive distillation usually proceeds with an infinite reflux step 1 with no entrainer feeding, then infinite reflux step 2 with entrainer feeding, then product removal step 3 with entrainer feeding, and finally, step 4 with the separation of the entrainer from the nonproduct initial component.[19−21] The first two

steps can be merged to reduce energy and entrainer consumption.[22,23]

Extractive map singular points have the opposite stability of the residue curve map singular points.[10−12] So, the minimum boiling azeotrope (UN_{rcm}) is the stable extractive node (SN_{extr}), the SN_{rcm} vertex B is the unstable extractive node (UN_{extr}) and the S_{rcm} vertices A and E are saddle extractive points, $S_{A,extr}$ and $S_{E,extr}$, respectively.[4]

When we overlap Figure 1a on Figure 1b, the region between the binary edge (E−B) and the univolatility line α_{BE} encompasses volatility order region AEB. Inside this region, B is the least volatile component of the mixture and a residue curve connects component E with B, following the expected increasing temperature toward B. Hence, component B satisfies the general feasibility criterion, and it can be drawn as a first bottom product cut using a batch extractive stripper similarly to the case involving light entrainer (see part 3[4]). The size of the region where B can be removed as bottom product is determined by the location of the univolatility line $\alpha_{BE} = 1$. Under infinite reboil ratio, the liquid profile inside the stripping section follows closely a residue curve running over the E−B edge, and it intercepts the liquid profile into the extractive section near the stable node $SN_{extr,B}$ located somewhere on the binary side E−B (Figure 1b). At the same time, the extractive liquid profile ends at the top vessel actual composition.

As hinted by the extent of the $SN_{extr,B}$ location range over the edge B−E, no minimum entrainer flow rate ($F_{E,min}$) is required for separating B, and the process is feasible even if $F_E = 0$. Indeed, since B is the sole residue curve map stable node SN_{rcm} of the ternary diagram, separation by batch azeotropic distillation adding E along with the initial charge (A+B) is viable in a batch stripper, as well.[24]

In the volatility order regions AEB and ABE, A is the most volatile component and a residue curve goes from E to A with a decreasing temperature direction. Therefore, the general feasibility criterion is also valid for recovering a distillate A at the top of a rectifying extractive column. In this case, the extractive and rectifying section liquid profile intersects near the binary side E−A at a stable extractive node $SN_{extr,A}$ located between x_{PA} and the E vertex. As detailed in parts 1−3 for the extractive distillation of minT or maxT azeotropes or close boiling mixtures by using heavy or light entrainers,[2−4] a limiting (minimum or maximum) value for entrainer flow rate exists when x_P is a binary mixture and finishes at the edge A−E or B−E. That was already proposed by Rev et al.[14] who suggested to use batch extractive rectifier instead of an azeotropic distillation in a batch stripper for the separation of a minT azeotrope by using an intermediate entrainer.

In conclusion, the combined analysis of the residue curve map and of the univolatility lines α_{AB} and α_{BE} hints at two alternatives to recover as product either component A or B using an extractive rectifying or stripping column configuration, respectively. On all figures, possible products satisfying the feasible criterion are underlined in each volatility order region. For example, in region AEB, compound A is a possible distillate product in a extractive rectification column and B is a possible bottom product in an extractive stripper.

Regarding the number of trays in each sections, a large number of trays was recommended in the extractive section for heavy or light entrainers studied elsewhere,[2−4] so that $SN_{extr,A}$ or $SN_{extr,B}$, the ending composition of the extractive profile, lies as close as possible to the binary side (A-E) or (E-B), respectively. However, this could not be the best option with

intermediate boiling entrainer because of its typical low relative volatility of E with both azeotropic components. Besides, special care must be taken for separating A (respectively B) in the minT (respectively maxT) case because the topological condition of saddle point imposes a maximum number of trays in the rectifying (respectively stripping) section above which the composition profile may turn away from A (respectively B) toward the azeotrope (A-B). For the stable node B (respectively unstable A), no maximum trays number exists. However, those assertions are further more complicated because effective recovery of A and B under a finite reflux ratio will affect the extractive profile maps, with singular points moving and extractive boundaries emerging inside the ternary diagram, thus limiting the recovery of both components as we now present in an example.

4.2. Thermodynamic Features for Preferable Recovery of A.
4.2.1. Separation of Acetone (A)−Heptane (B) with Benzene (E) as an Intermediate Boiling Entrainer. The separation of acetone (56.1 °C)−n-heptane (98.4 °C) minimum boiling azeotrope (55.8 °C at $x_{acetone} = 0.93$) was studied by Laroche et al. with benzene (80.1 °C) as an intermediate entrainer using an indirect and direct sequence of continuous distillation column.[11] The ternary diagram belongs to the 1.0-1b class, so recovery of acetone (A) (heptane (B)) using a batch extractive rectifier (a batch azeotropic or extractive stripper) is possible.

The residue curve map and univolatility and unidistribution lines of the ternary mixtures are displayed in Figure 3. In this
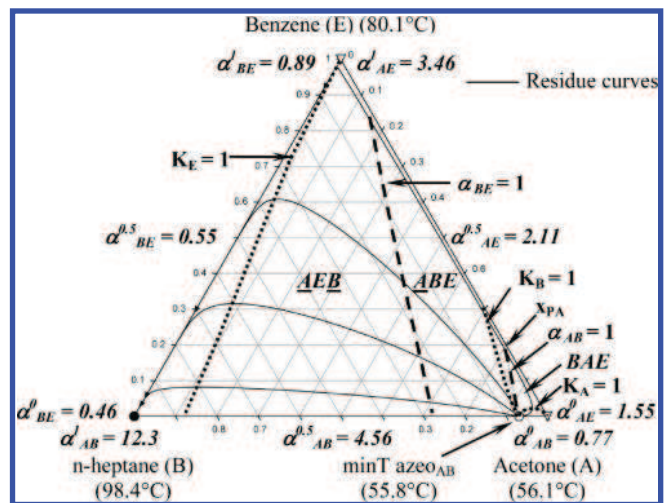
Figure 3. Acetone (A)−n-heptane (B) with benzene (E) 1.0-1b residue curve map and unidistribution and univolatility lines.

case, only two univolatility lines exist, α_{AB} and α_{BE}, dividing the ternary composition space in three volatility order regions, AEB, ABE, and BAE. Other values of α_{AB}, α_{AE}, and α_{BE} are reported in Figure 3 for $x_E \rightarrow 0$ (α^0), $x_E = 0.5$ ($\alpha^{0.5}$), and $x_E \rightarrow 1$ (α^1). Indeed, addition of benzene improves significantly the relative volatility of both A and B at infinite dilution in E to reach $\alpha^1_{AE}/\alpha^1_{BE} = 3.9$. Adding E increases α_{AE} ($\alpha^0_{AE} = 1.55$ to $\alpha^1_{AE} = 3.46$) more than α_{BE} ($\alpha^0_{BE} = 0.46$ to $\alpha^1_{BE} = 0.89$). The average relative volatility between benzene and each original component, $\bar{\alpha}_{AE}$ and $\bar{\alpha}_{BE}$, is 2.25 and 0.56, respectively, giving a ratio $\bar{\alpha}_{AE}/\bar{\alpha}_{BE} = 4$. The combination of those values brings the unidistribution line $K_E = 1$ near the E−B edge, indicating that
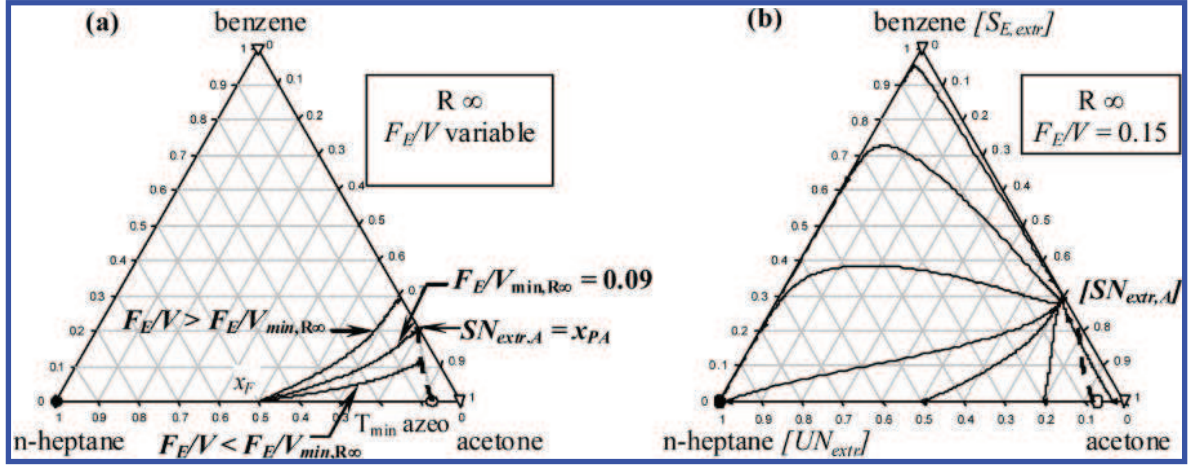
Figure 4. Acetone–n-heptane with benzene extractive composition profile map at infinite reflux ratio: (a) several values of F_E/V; (b) feasible extractive region for $F_E/V = 0.15$.
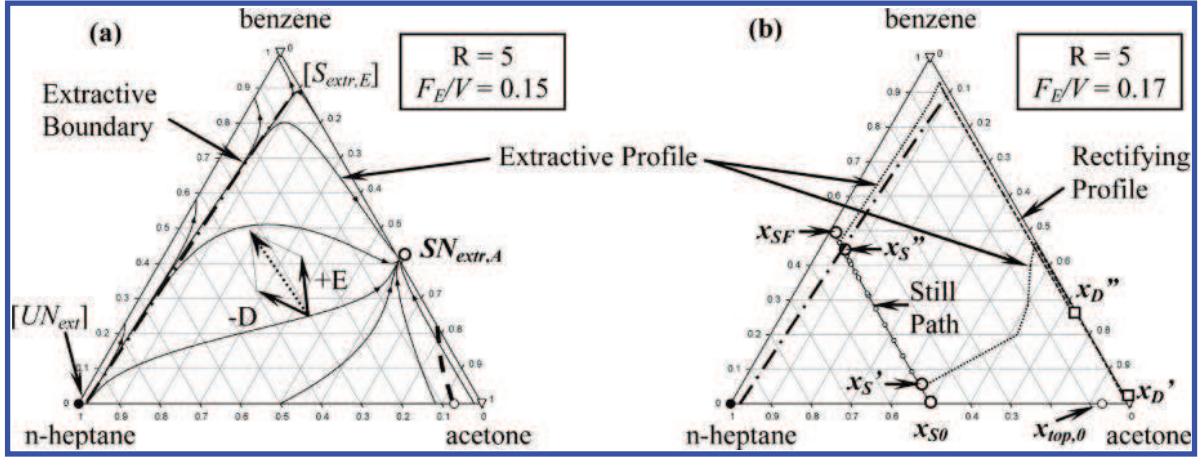

Figure 5. Acetone–n-heptane with benzene extractive composition profiles map: (a) simplified model with $F_E/V = 0.15$, $R = 5$; (b) validation via rigorous simulation by ProSim Batch of extractive batch rectification of acetone (A).

separation of E–B in the stripping section (see Figure 2b) will require a high number of trays and reflux ratio.

The location of the $x_{PA} = 0.80$ intercept not far from A indicates that separation of acetone may be practical in a batch extractive rectifier above a minimum limit value of benzene flow rate, which should be moderate. Otherwise, within the large AEB volatility order region heptane (B) is the least volatile and can be drawn as a bottom product in a batch stripper, either azeotropic or extractive as discussed before.

For an extractive rectification column (Figure 2a), extractive composition profiles are computed according eq 1 and depend on the reflux value R, the entrainer feed (F_E) to boiler vapor (V) flow rate ratio, and the distillate composition (x_D):[9]

$$\frac{dx_i}{dh} = \frac{R+1}{R + (R+1)(F_E/V)}\left[\left(\frac{R}{R+1} + (F_E/V)\right)x_i \right.$$
$$\left. + \frac{1}{R+1}x_D - (F_E/V)x_E - y_i^*\right] \tag{1}$$

where h is the dimensionless column height and y_i^* is the vapor composition in equilibrium with the liquid composition x_i. Nonextractive composition profiles in the rectifying section are computed from eq 1 by setting $F_E/V = 0$.

For an extractive stripping column (Figure 2b), it is more convenient to define a reboil ratio and consider the bottom

product composition x_N. Therefore, the extractive section composition profiles are computed according eq 2 and depend on the reboil ratio, S, computed as the ratio of the boiler vapor, V_N, and the difference between the liquid flow pouring into the boiler, L_{N-1}, and V_N, the entrainer feed, F_E, to top vessel liquid, L_R, flow rate ratio, and the bottom product composition, x_N:[17]

$$\frac{dx_i}{dh} = \left(1 + \frac{\left(\frac{F_E}{L_R} - 1\right)\left(\frac{1}{S+1}\right)}{\frac{F_E}{L_R} + 1}\right)\left[\frac{S+1}{S}x_i - \frac{1}{S}x_N\right.$$
$$\left. - \frac{S+1}{S}\left(\frac{\frac{F_E}{L_R}}{\frac{F_E}{L_R}+1}\right)x_E - y_i^*\right] \tag{2}$$

Nonextractive composition profiles in the stripping section are computed with the same equation by setting $F_E/L_R = 0$.

Figure 4a shows extractive liquid composition profiles from an equimolar composition mixture of acetone–heptane, x_F, for several values of benzene flow rate (F_E) under infinite reflux. Because $(F_E/V) < (F_E/V)_{min,R\infty}$, the extractive liquid profile ends at the stable extractive node $SN_{extr,A}$ that moves along the univolatility line α_{AB}. The minimum value of the benzene flow rate, $F_{E,min}$, is defined by the coincidence of $SN_{extr,A}$ and x_{PA}. In
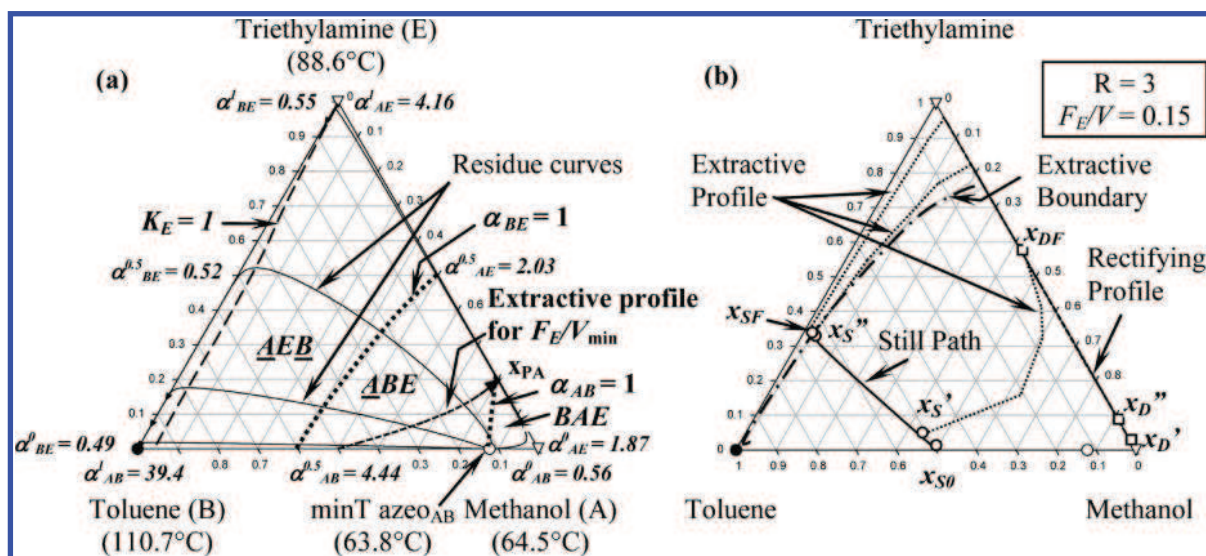
Figure 6. Methanol (A)−toluene (B) with triethylamine (E) 1.0-1b residue curve map and univolatility lines α_{AB} and α_{BE}. (a) and simulation results with $F_E/V = 0.15$ and $R = 3$ to recover A by extractive batch rectification (b).

this case, $(F_E/V)_{min,R\infty} = 0.09$. Above $(F_E/V)_{min,R\infty}$ (like in Figure 4b, $F_E/V = 0.15$), any composition into the ternary diagram can reach $SN_{extr,A}$ through an extractive liquid composition profile under infinite reflux, and the whole ternary diagram is a feasible region for separating acetone (A).

As for the 1.0-1a and 1.0-2 class diagrams,[2,3] the size of the feasible region becomes smaller at finite reflux ratio, limited by the arising of an unstable extractive separatrix. At $R = 5$ and $(F_E/V) = 0.15$ for acetone−heptane−benzene, the unstable separatrix linking UN_{extr} and $S_{E,extr}$ have moved inside the triangle. On its left, the region is unfeasible because extractive profiles do not reach $SN_{extr,A}$. It also prevents complete recovery of acetone in the distillate when the initial still composition moves from the feasible region on the right, toward the unfeasible region on the left because the still path is determined by the combination of entrainer feeding, +E, and distillate removal, −D (Figure 5a). Distillation stops when the still path crosses it, preventing complete recovery of A.

Figure 5 displays results of a rigorous simulation with ProSim BatchColumn simulator considering a column with 30 equilibrium stages, whereas benzene is fed at tray 12 counted from the top. An initial charge of 6 L of equimolar composition of acetone−heptane (x_{S0}) is considered. The heat duty was fixed in 1.5 kW, and the benzene flow rate was set to provide a relationship of $F_E/V = 0.17$ inside the extractive column section, above the F_E/V_{min} value. Start up under infinite reflux sets the unstable azeotrope acetone−n-heptane ($x_{top,0}$) into the total condenser. Step 2 with benzene feeding under infinite reflux shifts after a few minutes x_{S0} to x_S' and $x_{top,0}$ to x_D' with a 98.5% acetone molar purity: the extractive process operation has replaced the rcm unstable binary azeotrope by a composition near the rcm saddle (A). Distillate is then removed at $R = 5$ and $F_E/V = 0.17$, and its purity is maintained whenever the still composition is located inside the feasible region. Once the still path crosses the unstable extractive separatrix (x_S''), the instantaneous distillate acetone molar fraction quickly falls (x_D''). But distillate removal goes on until the average distillate acetone molar fraction drops below 95% molar, taking 56 min. Only, 2% molar fraction of acetone remains in the still (x_{SF}) providing a 96% recovery yield. The average acetone/benzene/n-heptane molar composition in the

distillate was $x_{dist,avg} = 0.950/0.044/0.006$. Due to the accumulation of entrainer in the still, the final still volume is 6.9 L, a suitable 15% increase of the initial charge volume that could be readily handled in practice.

4.2.2. Separation of Methanol (A)−Toluene (B) with Triethylamine (E) as an Intermediate Boiling Entrainer. A similar case, namely, the separation of the minT azeotropic mixture methanol (64.5 °C)−toluene (110.7 °C) ($x_{azeo,methanol}$ = 0.88 at 63.6 °C) with intermediate boiling triethylamine (88.2 °C) was studied theoretically by Varga et al.[16] using an extractive stripper to recover the heavy boiler toluene (B). However, conditions for recovering A are more favorable. Figure 6a displays the residue curve map and the location of the univolatility and unidistribution lines. As in the previous example, both A and B can be obtained by extractive rectification or stripping, respectively. Interception of the α_{AB} = 1 curve with the A−E edge at $x_{PA} = 0.79$ is similar to the previous example, and the minimum value of entrainer flow rate $(F_E/V)_{min} = 0.1$ is the same (0.15 for the previous mixture), in agreement with the value of literature.[16] On the other hand, the ratio $\bar{\alpha}_{AE}/\bar{\alpha}_{BE} = 5.8$ is greater than that for the previous ternary mixture because the increase of α_{BE} ($\alpha_{BE}^0 = 0.49$ to $\alpha_{BE}^1 = 0.55$) with E molar fraction is much lower than the case of α_{AE} ($\alpha_{AE}^0 = 1.87$ to $\alpha_{AE}^1 = 4.16$). Overall, those features indicate that methanol (A) removal by using a batch extractive rectifier is preferable to removal of B by using a batch extractive stripper. Indeed, in their study of batch extractive stripping of toluene (B),[16] Varga et al. quoted that this process was "feasible, but practically not promising", because high purity of toluene could not be obtained due to a very narrow feasible region under finite reflux. This fact is linked to the position of the unidistribution line $K_E = 1$, which is much closer to the E−B edge than in the first example (compare Figure 3 to Figure 6a).

Figure 6b shows rigorous simulation results obtained with ProSim BatchColumn, keeping the same operating conditions in the distillation column as those specified earlier for the mixture acetone−benzene−n-heptane ($N = 30$, $Q = 1.5$ kW, initial charge = 6 L). For the equimolar mixture methanol−toluene (x_{S0}), boiling triethylamine is fed at tray 10, while setting an F_E/V value inside the extractive column section near 0.15. Methanol (A) distillation is run under a lesser $R = 3$ until

the still methanol molar fraction drops below 0.01 (x_{SF}), taking 1.1 h. Molar methanol recovery equals 98.4% with an average methanol/triethylamine/toluene molar composition in the distillate $x_{dist,avg}$ = 0.962/0.038/0.000. The final still content is 8 L. Figure 6b also shows the liquid profile inside the extractive and rectifying section at different times for the still composition (x_S', x_S'', x_{SF}) and the related distillate purity (x_D', x_D'', x_{DF}).

4.2.3. Separation of Methyl Acetate (A)−Cyclohexane (B) with Carbon Tetrachloride (E) as Intermediate Boiling Entrainer. Rev et al. compared the separation of the minT azeotropic mixture methyl acetate (57.1 °C)−cyclohexane (80.8 °C) ($x_{azeo,methyl\ acetate}$ = 0.78 at 54.9 °C) with intermediate boiling carbon tetrachloride (76.7 °C) by (a) batch azeotropic distillation (BAD) and (b) batch extractive distillation (BED) in a rectifier.[14] They performed a complete parametric study of the extractive distillation process but without considering the effect of the univolatility lines. A total of 95% molar A could be distilled by BAD, but it required a prohibitively high amount of entrainer added along with the initial still charge in order to reach the feasible region. For BED, continuously feeding carbon tetrachloride at an intermediate column position enabled recovery of A in an extractive rectifier because component A fulfills the general feasibility criterion. According to Figure 1a, a stripping column would also allow recovery of the rcm stable node B as a bottom product.

Figure 7 displays the residue curve map of methyl acetate−cyclohexane−carbon tetrachloride using the same binary
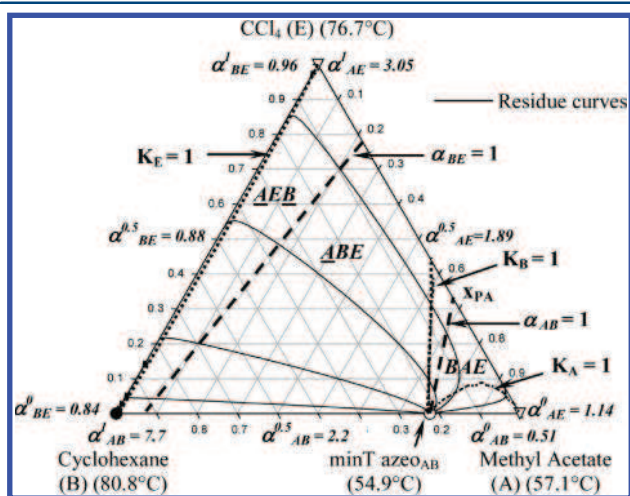
Figure 7. Methyl acetate (A)−cyclohexane (B) with carbon tetrachloride (E) 1.0-1b residue curve map and unidistribution and univolatility lines.

coefficients reported by Rev. et al.[14] Several features explain why recovery of B could be difficult. First, the region wherein B is the least volatile is small. Indeed, the values of α_{BE}^0 = 0.84 to α_{BE}^1 = 0.96 on the binary side E−B are greater than both preceding examples, and they are closer to unity, resulting in the unidistribution line K_E = 1 being located very close to the E−B edge (compare Figures 3, 6a, and 7). The unidistribution line passes through extreme of residue curves,[5] and thus residue curves first approach the E−B edge before turning toward the stable node B. Besides, the average relative volatility between B and E is $\bar{\alpha}_{BE}$ = 0.88, close to unity, and indicating a close-boiling mixture difficult to split by conventional distillation. Hence, separation of component B in an extractive stripper (Figure 2b) could be highly demanding in reflux ratio and in tray number in

the stripping section, where the binary separation E−B will mainly take place.

Recovery of component A using an extractive rectifier (Figure 2a) is likely easier thanks to a suitable $\bar{\alpha}_{AE}$ = 2 and ratio $\bar{\alpha}_{AE}/\bar{\alpha}_{BE}$ = 2.2. Besides, the x_{PA} = 0.67 intercept is farther from A than previous ternary mixtures but still close enough to hint at a moderate entrainer flow rate minimum. Rev et al. computed a $(F_E/V)_{min,R\infty}$ = 0.166 from the composition profile diagrams.[14]

Rev et al. also carried out rigorous simulation by using ChemCAD software.[14] With a rectifier column having 30 theoretical plates and feeding carbon tetrachloride at the middle plate, they obtained 90% molar methyl acetate (A), starting from an equimolar methyl acetate−cyclohexane mixture, with F_E/V = 0.5 and R = 10. Acceptable recovery of methyl acetate was achieved in 1.98 h, and the main impurity in the distillate was cyclohexane.

4.3. Thermodynamic Features for Preferable Recovery of B. In the three examples explained in the section above, the position of the univolatility line α_{AB} and the closeness of x_{PA} to A suggested that A recovery in an extractive rectifier with a small entrainer amount would be preferable to B recovery. Besides, the location of the unidistribution line K_E close to the edge B−E indicates that separation of B could be very tricky using extractive or azeotropic distillation in a batch stripper. The next section investigates the favorable conditions for separating B instead of A as first product cut and two examples of separating minimum boiling azeotropic mixtures using a middle boiling entrainer will be presented.

4.3.1. Separation of Dichloromethane (A)−Ethanol (B) with Acetone (E) as an Intermediate Boiling Entrainer. The possibility of separation of the minT azeotropic mixture dichloromethane (39.7 °C)−ethanol (78.3 °C) ($x_{azeo,dichloromethane}$ = 0.98 at 39.6 °C) with intermediate boiling acetone (56.1 °C) was first proposed by Rodriguez-Donis et al.[24] using an azeotropic batch stripper. But an extractive distillation process can be used as well. The residue curve map and the univolatility and unidistribution lines are shown in Figure 8. The position of the univolatility line α_{BE} = 1 gives rise to a large volatility order region AEB wherein B is the least volatile component and can be recovered in a batch extractive stripper. Because $\bar{\alpha}_{BE}$ = 0.4 is far from unity, separation of the mixture E−B should be easy, as also hinted from the shape of
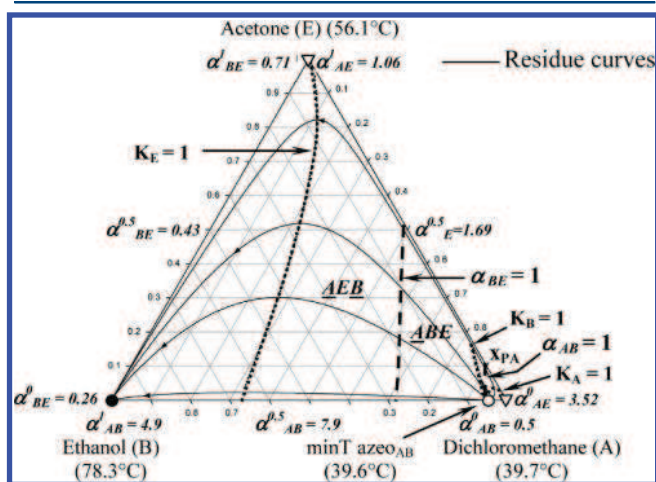
Figure 8. Dichloromethane (A)−ethanol (B) with acetone (E) 1.0-1b residue curve map and unidistribution and univolatility lines.

the residue curves because they reach the B vertex without nearing the E−B edge, thanks to the unidistribution line K_E located on the center of the ternary diagram. Besides as recalled in Figure 1b, there is no minimum acetone flow rate value for B recovery and either an extractive or an azeotropic stripper can be used.

Regarding the recovery of A in an extractive rectifier, the average relative volatility value for A and E is moderate at $\overline{\alpha}_{AE}$ = 1.8. The interception of α_{AB} = 1 stays close to the dichloromethane vertex A thanks to the good value of α^0_{AE} = 3.52, and the entrainer flow rate minimum value does not seem to be high. However, addition of entrainer acetone depresses the volatility of dichloromethane noticeably from α^0_{AE} = 3.52 to α^1_{AE} = 1.06. The ratio $\overline{\alpha}_{AE}/\overline{\alpha}_{BE}$ = 1.8/0.4 = 4.5 provides a promising separation of dichloromethane (A) by using an extractive batch rectifier. But, this good ratio of $\overline{\alpha}_{AE}/\overline{\alpha}_{BE}$ is mainly determined by the lower value of $\overline{\alpha}_{BE}$, and regarding the favorable location of the unidistribution line K_E, it seems that separation of B will be easier than separation of component A.

We now compare the recovery of ethanol (B) using a batch extractive stripper (BES) and the recovery of dichloromethane (A) using a batch extractive rectifier (BED) by carrying out simulations using ProSim BatchColumn.

For BES, the total number of theoretical plates in the column is 30. An equimolar mixture x_0 of dichloromethane−ethanol is split between the top vessel (7.2 mol) and the boiler (5 mol). Several preliminary tests were done in order to define an adequate distribution of the total initial charge between both vessels in order to provide better results for purity, recovery yield, and operating time. The heat duty in the boiler was set at 205 W.

After 0.6 h of infinite reflux operation, high-purity ethanol is settled in the boiler (step 1). The trajectory of the top vessel (from x_0 to $x_{top,R\infty}$) and of the still composition (from x_0 to $x_{boiler,R\infty}$) is shown in Figure 9. In step 2, acetone is fed
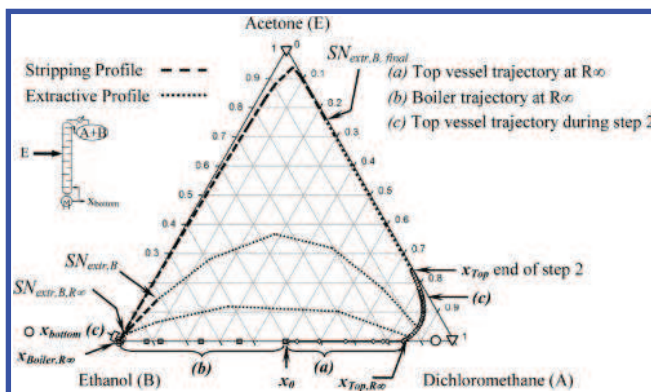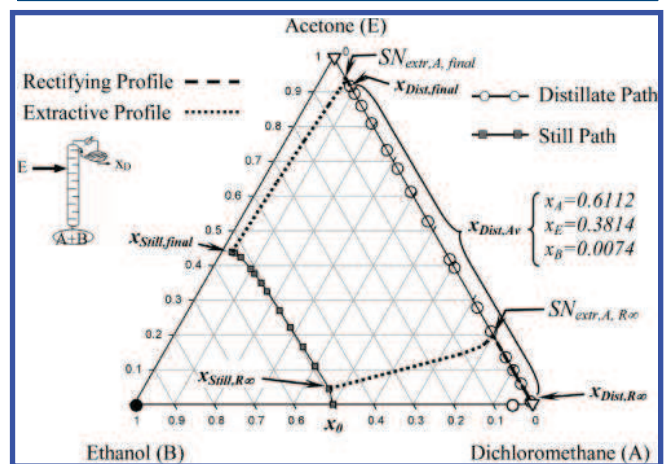

Figure 9. Simulation results for separating dichloromethane (A)−ethanol (B) with acetone (E). Recovery of B by using an extractive stripper.

continuously at tray five from the top while ethanol is removed from the top vessel (x_{top} (path c in Figure 9). The reboil ratio S at the bottom of the column starts at 15 at the beginning of step 2 and reaches gradually 150 at the end of step 2. The liquid flow rate, L_R, coming from the top vessel toward the column top is set slightly higher than V_N leaving the boiler, whereas the ratio F_E/L_R = 0.05 is kept approximately constant inside the extractive section. Liquid composition profiles inside the extractive and stripping section are reported along with the

location of the stable extractive node ($SN_{extr,B}$) at their intersection. At the beginning of step 2, the extractive profile almost reaches the ethanol apex, but later, the stripping section becomes decisive to keep greater than 0.99 M ethanol in the bottom product. Finally, 99.2% of the ethanol is recovered inside the boiler after 3 h (x_{bottom}). The main impurity in the boiler is acetone with a molar fraction of 0.0099. The extractive process required the addition of 2.04 mol of acetone for the total initial charge (12.2 mol) of dichloromethane−ethanol mixture.

Finally, a 30 equilibrium tray BED rectifier with an entrainer feeding at tray five is used to distill dichloromethane (A), and rigorous simulation is performed using ProSim BatchColumn. The whole amount (12.2 mol) of the same equimolar mixture x_0 is now introduced into the boiler with a heat duty of 205 W. The start up under infinite reflux (step 1) brings the minimum boiling azeotrope dichloromethane−ethanol toward the total condenser. Then, keeping an infinite reflux, acetone is fed equally at tray five and only in a few minutes breaks the azeotrope (step 2) and brings almost pure dichloromethane at the column top ($x_{dist,R\infty}$). The ratio F_E/V equals 0.14 in step 2, and it is above the minimum value taking into account the position of x_{PA} in Figure 8, so that the extractive node $SN_{extr,A}$ is located near the binary side A−E (see Figure 10). The still path

Figure 10. Simulation results for separating dichloromethane (A)−ethanol (B) with acetone (E). Recovery of A using an extractive batch rectifier.

and the liquid profile inside the column at the end of step 2 for the still composition $x_{still,R\infty}$ is displayed in Figure 10. In step 3, withdrawal of dichloromethane is performed under R = 10 while keeping acetone feeding with a lower value, F_E/V = 0.08. After 1.8 h, the dichloromethane molar fraction drops below 0.98 in the distillate, which is then polluted progressively with the entrainer acetone. Fortunately, the distillate path shows that the distillate product has almost no ethanol. However, compared with BES, depleting the still pot from the product (dichloromethane) below a molar fraction of 0.025 ($x_{still,final}$) is longer (4 h) in this BED process. A recovery yield of 95.3% of dichloromethane with average molar fraction equals to 0.61 is finally obtained but at the expense of a significant pollution of the distillate pot with acetone. The total acetone consumption is considerable (8.6 mol) and represents 70.5% of the initial charge into the still. Moreover, the ending still mixture ($x_{still,final}$) also requires further purification process.

As this example shows, ethanol (B) removal by batch stripping column is preferable over dichloromethane (A) distillation by batch rectifying column. Indeed, the unidistribution line K_E, the univolatility line α_{AB} and α_{BE} locations and the variation of α_{AE} and α_{BE} over the corresponding binary side are a reliable indication of the convenience of the separation of one original azeotropic component over the other one using a batch stripping or a rectifying column configuration in extractive distillation.

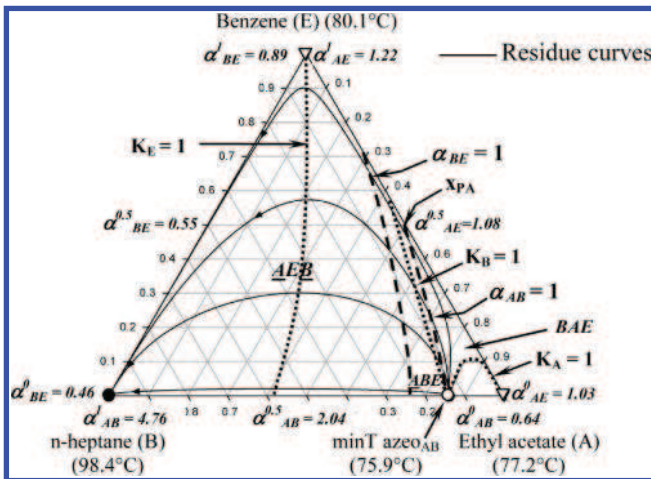*4.3.2. Separation of Ethyl Acetate (A)−Heptane (B) with Benzene (E) as an Intermediate Boiling Entrainer.* Figure 11

Figure 11. Ethyl acetate (A)−n-heptane (B) with benzene (E) 1.0-1b residue curve map and unidistribution and univolatility lines.

displays the residue curve map of the ternary mixture ethyl acetate (77.2 °C)−n-heptane (98.4 °C) with benzene (80.1 °C) along with the unidistribution and univolatility lines. Ethyl acetate forms a minT azeotrope with n-heptane at 75.9 °C having ethyl acetate molar fraction of 0.85. Again, BES and BED processes for separating B and A, respectively, are compared.

The choice of benzene does not seem practical because it forms a close-boiling mixture with ethyl acetate as $\overline{\alpha}_{AE}$ (= 1.1) is very close to unity. Besides, the univolatility line α_{AB} intercepts the edge ethyl acetate−benzene at an x_{PA} position very far from A, hinting at a benzene entrainer minimum flow rate greater than in the former examples to recover A. Those indications are not in favor for a preferable recovery of A by extractive batch rectifier.

On the other hand, the low $\overline{\alpha}_{AE}$ value opens a large volatility order region AEB in which n-heptane (B) is the least volatile component of the ternary mixture delimited by α_{BE} = 1. By comparison with the range of $\alpha_{AE}^0-\alpha_{AE}^1$, α_{BE}^0 and α_{BE}^1 show a wider interval over the binary side B−E providing an $\overline{\alpha}_{BE}$ = 0.67 appearing to be an adequate value. Due to the unidistribution line K_E lying in the middle of the ternary diagram, the recovery of n-heptane (B) seems to be more favorable by using an extractive batch stripper.

First, a BES column with 30 equilibrium trays is studied to recover n-heptane (Figure 12) using ProSim BatchColumn. Ethyl acetate−n-heptane equimolar mixture (x_0) is split into the boiler (3.2 mol) and the top vessel (5 mol). Again, distribution of the initial amount into the top vessel and the boiler was set by preliminary trial and error tests in order to achieve better results. Heat duty in the boiler was set at 205 W. After 1.5 h of
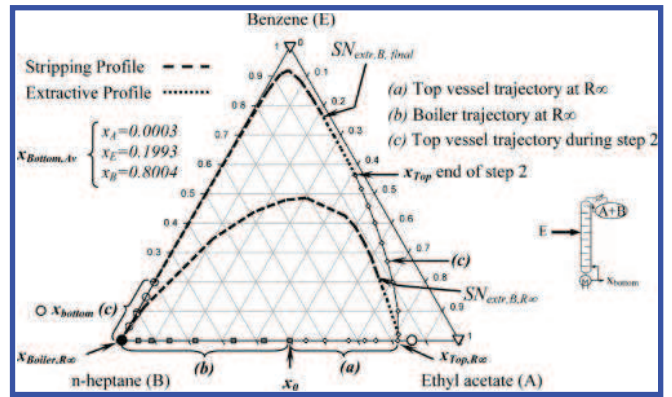

Figure 12. Simulation results for separating ethyl acetate (A)−n-heptane (B) with benzene (E). Recovery of B by using an extractive batch stripper.

infinite reflux operation (step 1), pure n-heptane (stable node) stays in the boiler ($x_{boiler,R\infty}$). Composition paths (boiler and top vessel) and the final composition profiles of step 1 are shown in Figure 12. In the next step (step 2), benzene is continuously fed at tray five counted from the top with an average value of the ratio F_E/L_R inside the extractive section of 0.051. In order to deplete the column from n-heptane, (x_{top} below 0.025), the reboil ratio S gradually increased during 6.55 h from 20 to a significant value of 680, showing how difficult the separation becomes, whereas the top vessel is being exhausted of B. Notice that compared with the previous example (Figure 9), separation of n-heptane is harder than separation of ethanol by extractive batch stripper mainly due to the lower value of $\overline{\alpha}_{BE}$ = 0.4 for ethanol. Besides, the stripping section is predominant during the whole process as the intercept between extractive and stripping composition profiles at the stable extractive node $SN_{extr,B}$ is situated closer to the edge A−E instead of E−B. Simulations with more extractive trays provided no improvement of the process. Finally, n-heptane recovery reaches 94%, but the ending product in the boiler, $x_{bottom,avg}$, contains 0.8 heptane molar fraction and benzene as main impurity, and it requires further purification. The entrainer benzene consumption is high, at 6.55 mol, representing 81% of the initial charge amount.

Finally, a BED rectifier is considered to recover ethyl acetate (A) in the distillate, and rigorous simulation is performed using ProSim BatchColumn. Because the binary mixture ethyl acetate−benzene (A−E) is a low relative volatility mixture ($\overline{\alpha}_{AE}$ = 1.1), preliminary computations suggest a 50 tray column. From 8.2 mol of ethyl acetate−n-heptane equimolar mixture (x_0) loaded in the still, infinite reflux operation sets the minimum boiling azeotrope ethyl acetate−n-heptane staying at the column top (step 1) (see Figure 13). Heat duty was kept at 205 W. Then, benzene feeding at tray 10 under infinite reflux with F_E/V = 0.09 (close to the minimum value) shifts the top composition to $x_{dist,R\infty}$ and the still composition to $x_{still,R\infty}$ (step 2) (see column liquid profile in Figure 13). Later in step 3, while F_E/V = 0.09, an ethyl acetate−benzene mixture is distilled out at reflux ratio R = 10 until the still molar fraction of ethyl acetate into the boiler drops below 0.025 ($x_{still,final}$), taking 5 h (see Figure 13). The recovery yield of ethyl acetate is 95.1%. The column liquid profile at the end of step 3 is shown in Figure 13. The average distillate composition ($x_{dist,avg}$) shows that the entrainer is the major component. Additionally, there is a significant amount of benzene in the still at the end of the
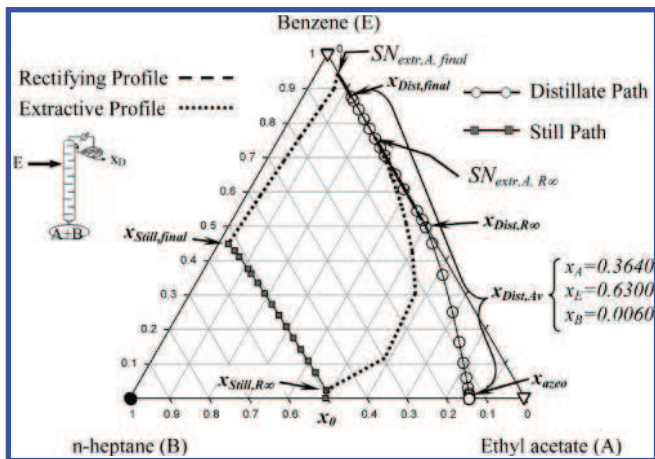
Figure 13. Simulation results for separating ethyl acetate (A)−*n*-heptane (B) with benzene (E). Recovery of A by using an extractive batch brectifier.

process. Therefore, even if BED of ethyl acetate from *n*-heptane is possible, it requires a substantial amount of benzene (10.4 mol) representing 127% of the initial charge amount.

In conclusion, the less favorable location of the univolatility line α_{AB} for the mixture ethyl acetate−benzene−*n*-heptane compared with the previous dichloromethane−acetone−ethanol mixture makes the separation of the light azeotropic component A by using an extractive rectifier more demanding in the number of theoretical trays, total amount of entrainer, and distillation time. However, like the previous example, separation of the heavy azeotropic component B in a stripping column configuration is a better option.

5. SEPARATION OF MAXIMUM AZEOTROPES

5.1. Feasibility Analysis. Similarly to the minT azeotropic mixture case, the general extractive distillation feasibility criterion can be applied to the maxT azeotrope case. If Figure 1d,e are superimposed, it can be demonstrated that there is a residue curve going in the inverse sense from E toward A with a decreasing temperature path in the region between the binary side (AE) and the univolatility line α_{AE} encompassing volatility order regions AEB and ABE wherein component A is the most volatile component. Hence, A can be drawn as a first distillate cut either in a batch extractive rectifier, without any lower limit for the entrainer flow rate, or in a batch azeotropic rectifier because component A is the only $[UN_{rcm}]$ of the ternary diagram.

In Figure 1e, the volatility order region EAB and AEB between the univolatility lines α_{AE} and α_{BE} (or the E−A edge if the α_{BE} is not present), component B is now the least volatile component, and an increasing temperature residue curve goes from E toward B. So, the saddle component B can also be recovered as a first bottom product in an extractive batch stripper, provided that the entrainer flow rate is above a minimum determined by the intercept of x_{PB} and α_{AB} at the binary side B−E as in the 1.0-1a class case.[2] Once more, the location of the unidistribution line K_E hints about the complexity of the separation of the binary mixtures A−E or B−E in a batch rectifier or in a batch stripper, respectively.

5.2. Separation of Chloroform (A)−Ethyl Acetate (B) Using 2-Chlorobutane (E) as an Intermediate Boiling Entrainer. Lelkes et al. were the first to work on the separation of maximum boiling azeotropic mixtures using an intermediate

boiling entrainer.[15] They selected the maxT azeotropic mixture chloroform (A) (61.7 °C)−ethyl acetate (B) (77.2 °C) ($x_{azeo,chloroform}$ = 0.12 at 77.3 °C). By using 2-chlorobutane (E) (68.1 °C), they compared distillation of chloroform (A) by classical azeotropic rectification, BAD, and by extractive rectification, BED, but considering the entrainer feeding into the still. They observed that BAD failed to recover 90% molar purity chloroform in the distillate, even in a column with 100 equilibrium trays and a very large reflux ratio (*R* = 70). BED was not much better to recover high-purity chloroform in the distillate, but the preliminary feasibility study using extractive composition profile maps demonstrated that the feasible region was bigger than for azeotropic distillation because the feeding of entrainer into the still kept the still composition inside the feasible region longer. Consequently, they targeted a chloroform−2-chlorobutane mixed distillate and compared both BAD and BED by rigorous simulation using ChemCAD. Similar recovery yield and molar fraction of chloroform in the distillate (0.386) were obtained for both alternatives, but extractive distillation required 11.4% less operating time and 17.1% less entrainer. We will now show that difficulties of recovering high-purity chloroform are related to the location of the univolatility and unidistribution lines in the ternary diagram.

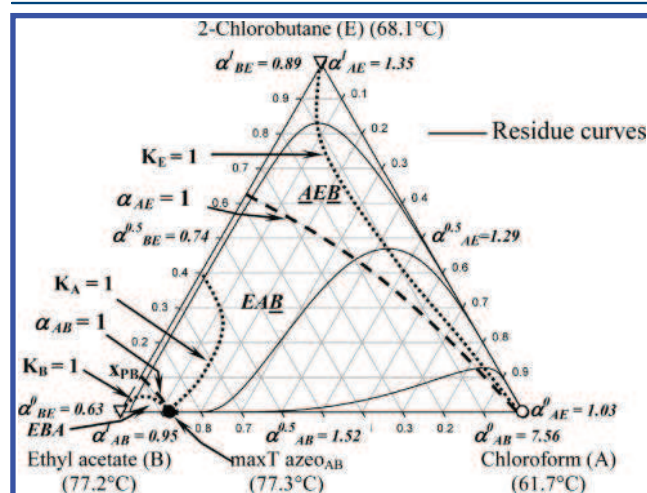Figure 14 displays the thermodynamics features for the ternary mixture chloroform−ethyl acetate−2-chlorobutane

Figure 14. Chloroform (A)−ethyl acetate (B) with 2-chlorobutane (E) 1.0-1b residue curve map and unidistribution and univolatility lines.

using the same binary coefficients for the NRTL model reported by Lelkes et al.[15] Both the univolatility line α_{AE} and the unidistribution line K_E get close to the binary side A−E and almost finish at the chloroform vertex A. Chloroform−2-chlorobutane (A−E) mixture could be considered as a low-relative-volatility mixture with $\overline{\alpha}_{AE}$ = 1.25 (α_{AE}^0 = 1.03 and α_{AE}^1 = 1.35). Therefore, the recovery of chloroform (A) by using any azeotropic or extractive distillation process with a rectifying column configuration, will require many trays and a high reflux ratio.

5.3. Comparison of Four Different Entrainers for the Separation of maxT Chloroform (A)−Ethyl Acetate (B).
5.3.1. Analysis of Ternary Diagrams. Figure 15 displays the 1.0-1b class residue curve map, univolatility and unidistribution lines, and volatility order regions for four intermediate boiling entrainers, namely, 2-chlorobutane (68.1 °C), isobutylchloride
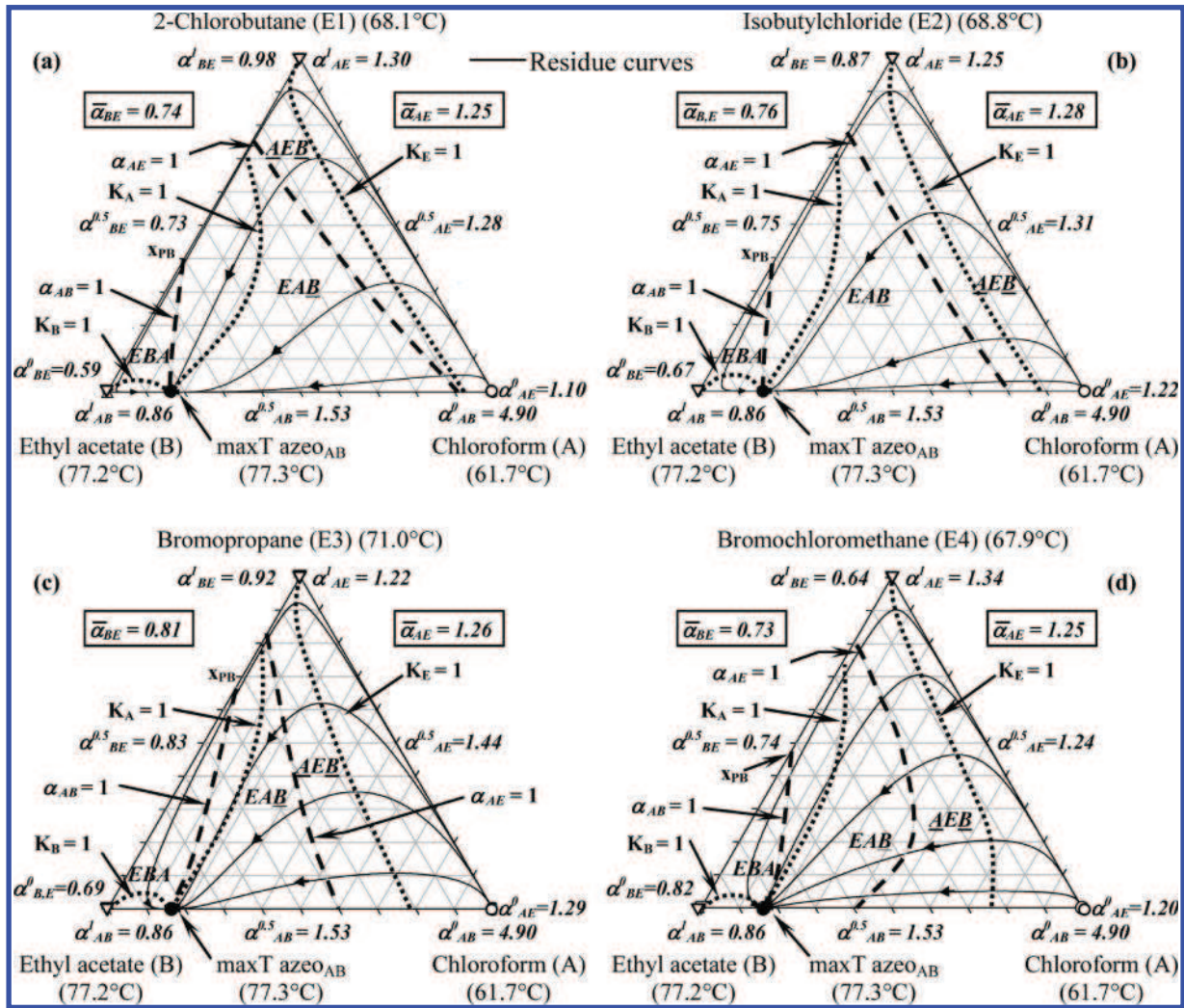
Figure 15. The 1.0-1b residue curve map and unidistribution and univolatility lines for the mixture chloroform−ethyl acetate using four intermediate boiling entrainers: (a) 2-chlorobutane, (b) isobutylchloride, (c) bromopropane, and (d) bromochloromethane.

(68.8 °C), bromopropane (71 °C), and bromochloromethane (67.9 °C). The modified UNIFAC Dortmund 1993 model is considered instead of NRTL because of missing NRTL binary parameters for some mixtures.

First, NRTL (figure 14) and UNIFAC (figure 15a) predictions are compared for 2-chlorobutane. Among noteworthy differences, the x_{PB} interception of the $\alpha_{AB} = 1$ line contains much more entrainer, indicating that the minimum entrainer flow rate is higher to recover B in the bottom of an extractive batch stripper. Otherwise, the univolatility line α_{AE} reaches the edge E−B at a higher concentration of ethyl acetate because the range $\alpha_{BE}^0 - \alpha_{BE}^1$ is wider, diminishing the size of the region wherein A is the most volatile component. Nevertheless, the range for $\alpha_{AE}^0 - \alpha_{AE}^1$ and $\overline{\alpha}_{AE}$ are almost identical. Recovery of chloroform in an extractive rectifier should be carry out with the same efficiency whatever the VLE model is.

Second, the ternary diagrams for all four entrainers are compared as well. They are similar, but a few differences affect the process feasibility and efficiency. Concerning ethyl acetate (B) recovery in an extractive batch stripper, bromopropane exhibits the highest value of x_{PB} because of the highest $\overline{\alpha}_{BE}$. A higher value of $\overline{\alpha}_{BE}$ means that entrainer increases the volatility of component B, which is not favorable when the component has to be drawn as bottom product, requiring a higher

concentration of entrainer inside the extractive section. Concerning chloroform (A) recovery by azeotropic or extractive rectification, the three new entrainers give a volatility order region AEB wherein A is the most volatile component, bigger than the one obtained for 2-chlorobutane (Figure 15a). Indeed, they all have a α_{AE}^0 value higher than the 1.10 corresponding to 2-chlorobutane. Therefore, the univolatility line α_{AE} is located farther from A−E and apex A. The position of unidistribution line K_E is the most favorable, mainly, for bromopropane. A noticeable fact is that bromochloromethane is the only entrainer to reduce the relative volatility α_{BE} when concentration of E is increased because α_{BE}^1 is lower than α_{BE}^0. That results in a ratio of relative volatility at infinite dilution of E, $\alpha_{AE}^1/\alpha_{BE}^1 = 2.09$, significantly larger than those for isobutylchloride ($\alpha_{AE}^1/\alpha_{BE}^1 = 1.436$), bromopropane ($\alpha_{AE}^1/\alpha_{BE}^1 = 1.326$), and 2-chlorobutane ($\alpha_{AE}^1/\alpha_{BE}^1 = 1.326$). That is why the univolatility line α_{AE} and the unidistribution line K_E for bromochloromethane have shapes different for bromochloromethane from the others entrainers. A bigger feasible region for separating A because of the position of the univolatility line α_{AE} and more favorable location of unidistribution line K_E is given by bromopropane and bromochloromethane.

5.3.2. Extractive Rectification Simulation Results Comparison. First, to validate further the choice of UNIFAC, Table 2

Table 2. Simulation Results for Separating Chloroform−Ethyl Acetate with Several Middle Boiling Entrainers

thermodynamic model	NRTL[a]	UNIFAC			
	sec-C_4H_9Cl ChemCad[a]	sec-C_4H_9Cl Batchcolumn	i-C_4H_9Cl Batchcolumn	C_3H_7Br Batchcolumn	CH_2BrCl Batchcolumn
$\bar{\alpha}_{AE}/\bar{\alpha}_{BE}$	1.57	1.69	1.68	1.55	1.71
$x_{ABD} = x_A/(x_A + x_B)$ in distillate	0.995	0.974	0.998	0.985	1
recovery yield %	91.96	92.9	94.2	86.9	95.7
max. still holdup (mol)	70.2	69.2	69.6	71.3	72.7
entrainer in distillate (mol)	54.13	55.8	55.8	56.1	52.2
entrainer in residue (mol)	35.87	34.2	34.2	33.9	37.8
amount of distillate (mol)	81.3	87.8	87.4	85.6	84.3

[a]Reference 15.

compares simulated results by Lelkes et al.[15] with Chemcad and NRTL and of this work, with ProSim BatchColumn. and UNIFAC. The rectification column features are identical, namely, 45 theoretical plates, heat duty of 1.5 kW, initial charge of 68 mol of an equimolar binary mixture chloroform− ethyl acetate, reflux ratio of $R = 20$, entrainer flow rate of 0.009 kmol/h to the boiler, and a distillation time of 10 h, giving a total amount of entrainer consumed of 90 mol. Data reported in Table 2 are very similar for both simulations in the case of 2-chlorobutane, except for the chloroform distillate purity, which is slightly inferior using UNIFAC. Besides, the A−B separating factor x_{ABD}; defined as $x_A/(x_A+x_B)$; is lower with UNIFAC because the distillate is more contaminated with ethyl acetate.

Second, for all four entrainers using UNIFAC as thermodynamic model and keeping the same simulation conditions as Lelkes et al.,[15] the simulated still and distillate paths, from x_{S0} to $x_{S,final}^{Ei}$ and from x_{D0}^{Ei} to $x_{D,final}^{Ei}$, obtained by batch column are displayed in Figure 16. The boundaries of the feasible region
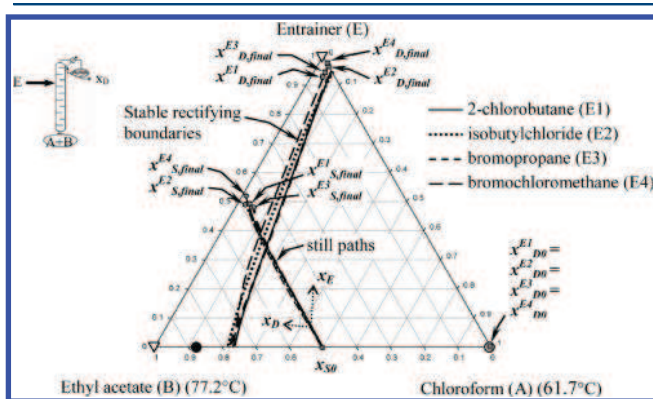

Figure 16. Simulated still path and distillate composition for four intermediate boiling entrainers for the separation of chloroform−ethyl acetate by using an extractive batch rectifier.

for the extractive liquid profiles for all entrainers are also shown in Figure 16 considering $R = 20$ and they are very similar.

By comparison of the process simulation results (Table 2), there is a strong correlation between, on one hand, the separating factor (x_{ABD}), the final distillate ($x_{D,final}^{E3}$), the final still composition ($x_{S,final}^{Ei}$), and the recovery yield and, on the other hand, the position of the univolatility lines (α_{AB}, α_{AE}) and the ratio $\bar{\alpha}_{AE}/\bar{\alpha}_{BE}$. A high value of $\bar{\alpha}_{AE}/\bar{\alpha}_{BE}$ indicates that the entrainer enhances the relative volatility between A and B. That is why bromochloromethane achieves the best separation results. Regarding the position of the line $\alpha_{AE} = 1$ that determines the size of the region AEB in which component A is the most volatile component, bromopropane and bromochloro-

methane are the most promising entrainers. Nevertheless, bromopropane provided the lowest separating factor (x_{ABD}) and recovery yield because it displays x_{PB} with the highest concentration of bromopropane. Hence, the region EBA (located on the left of $\alpha_{AE} = 1$ line) where chloroform (A) behaves as the least volatile component is the largest region compared with others entrainers. Moreover, the trajectory from α_{AE}^0 to α_{AE}^1 goes through a maximum value at $\alpha_{AE}^{0.5}$ and then decreases toward the apex of pure bromopropane giving a lower purity $x_{D,final}^{E3}$ by comparison with isobutylchloride and bromochloromethane.

As it can be noticed in Figure 16, the still path for the bromopropane reaches this region EBA sooner than other entrainers affecting quickly the purity of the distillate product. Position of α_{AB} and the variation range for α_{BE}^0 to α_{BE}^1 (closer to unity like $\bar{\alpha}_{BE}$) elucidate why the bromopropane has the lowest $\bar{\alpha}_{AE}/\bar{\alpha}_{BE}$ value.

6. CONCLUSIONS

Separation of minimum and maximum boiling temperature azeotropic mixtures by batch extractive distillation using an intermediate boiling entrainer has been studied by several authors in a rectifying and stripping column configuration. Like most of the papers devoted to the synthesis of batch extractive distillation, the feasibility of the separation has always been assessed by computing systematically the map of the liquid composition profiles inside each column section under a given reflux ratio and entrainer flow rate. However, those works have neglected or underestimated the importance of the location of the univolatility and unidistribution lines along with the classical residue curve analysis in those process syntheses.

The topological structure of the residue curve map containing a minimum or a maximum boiling temperature azeotropic mixture A−B with an intermediate entrainer E belongs to the single 1.0-1b Serafimov class. In this diagram, all three possible univolatility (α_{AB}, α_{BE}, and α_{AE}) and unidistribution lines (K_A, K_B, and K_E) can exist. They define volatility order regions and shape the residue curves, respectively, providing regions in which A is the most volatile component and B is the least volatile one. Moreover, both components A and B satisfy the general feasibility criterion for extractive batch distillation already validated in the literature for heavy and light entrainers. Existence of a residue curve moving along the edge A−E and B−E and following a decreasing and increasing temperature direction toward A and B apex into the regions wherein A (B) is the most (least) volatile component. As a result, an intermediate entrainer provides the possibility of separating A or B by extractive distillation using a batch rectifier or a batch stripper, respectively.

The ease of the recovery of A (B) in a batch rectifier (stripper) is influenced by the location of the univolatility lines α_{AE} (α_{BE}) and α_{AB} and the position of the unidistribution line K_E. Influence of these parameters on performance of extractive distillation were demonstrated via analysis of the separation of five minT azeotropic mixtures with a single intermediate boiling entrainer each time and one maxT azeotropic mixture considering four intermediate boiling entrainers. Predictions agree very well with the results obtained by rigorous simulation by using ProSim BatchColumn.

Bearing in mind these features, even if finding feasible intermediate entrainers is harder than heavy and light entrainers, a few thermodynamic calculations enable one to evaluate the interest and assess the feasibility of the separation of minimum and maximum boiling temperature azeotropes by using an intermediate boiling entrainer. That brings another alternative to process engineers, compared with the well-known use of heavy and light entrainers.

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Notes

The authors declare no competing financial interest.

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