Heterogeneous Batch-Extractive Distillation of Minimum Boiling Azeotropic Mixtures

Ivonne Rodríguez Donis
Centro de Química Farmacéutica, 200 y 21 Atabey, Apdo. 16042, Playa, C. Habana, Cuba and Laboratoire de Génie Chimique UMR CNRS 5503, ENSIACET-UPS-CNRS, 118 Rte de Narbonne, 31077 Toulouse Cedex, France

Jhoany Acosta Esquijarosa
Centro de Química Farmacéutica, 200 y 21 Atabey, Apdo, 16042, Playa, C. Habana, Cuba

Vincent Gerbaud and Xavier Joulia
Laboratoire de Génie Chimique UMR CNRS 5503, ENSIACET-UPS-CNRS, 118 Rte de Narbonne, 31077 Toulouse Cedex, France

Following previous studies on heterogeneous batch azeotropic distillation, the use of heterogeneous entrainers for the separation of binary azeotropic mixtures by extractive distillation is evaluated. This process is well suited for systems where the entrainer forms a saddle heteregeneous azeotrope with any one of the original components, such systems being unsuitable for nonextractive heterogeneous batch-distillation processes. Process feasibility is assessed from the isovolatility curves and the volatility order diagram. It tells us whether the homogeneous original component or the heteroazeotrope is drawn at the column top and establishes the distillation tasks sequence using a batch-rectifying column. The theoretical insights are validated via rigourous simulation for the separation of the acetonitrile−water mixture with hexylamine or butyl acetate. Finally, the same method is applied for the theoretical analysis of a reported industrial example where water is used for the separation of a binary organic mixture, leading to a complex ternary system with several binary azeotropic points and a homogenous ternary azeotrope.

Introduction

Separating azeotropic mixtures or low relative volatility compounds in high-purity products is a task commonly encountered in the chemical industry. However, it cannot be performed using a conventional distillation process. When pressure-swing distillation is not economically appropriate, one often adds a selective entrainer to the original mixture. Such entrainers take advantage of the nonideality of a mixture involving components with different chemical structures. Indeed, technical and economical performance of extractive and azeotropic distillation relies on the effect of such entrainers. Entrainer selection for extractive distillation is tricky because many factors must be considered, such as the selectivity, solubility, boiling point, thermal stability, corrosion, toxicity, prices, and other chemical properties. Among these, selectivity and solubility are the primary factors because they enable us to alter in a convenient manner the relative volatility and the solubility of the original components in the entrainer. Because distillation is practically difficult or impossible when the relative volatility value nears unity (unity means that there is an azeotrope), the selectivity of an entrainer is defined by its ability to move away from unity the relative volatility between the original components A and B, which is defined according to Eq. 1

$$\alpha_{A,B} = \frac{\dfrac{y_A}{x_A}}{\dfrac{y_B}{x_B}} = \left(\frac{P_A^o}{P_B^o}\right) \cdot \left(\frac{\gamma_A}{\gamma_B}\right) \tag{1}$$

where components A and B are the low and high boiling temperatures, respectively, of the original component. The calculation of entrainers selectivity requires either liquid and

---

Correspondence concerning this article should be addressed to V. Gerbaud.

vapor equilibrium compositions or activity coefficients at a given entrainer concentration. Preliminary estimations of these variables can be obtained by simple experimental methods or by using suitable thermodynamic models. Indeed, phase equilibrium can be predicted using activity-coefficient models, or equations of state with binary interaction parameters regressed from binary or ternary equilibrium data, or using group-contribution approaches (Prausnitz et al., 1986; Fredenslund et al., 1975).

The effect of the entrainer on the relative volatility depends on interactions between entrainer and each original component in the liquid phase: molecules of different types repel or attract each other to some extent that depends on many factors (molecule size and conformation, charge distribution, intermolecular distance, hydrogen bonding formation, and so on). The natural relative volatility value, $\alpha_{A,B}$, will be moved away from unity if the entrainer interacts strongly with the low boiling temperature component A and weakly with the high boiling temperature component B. In fact, the entrainer should show a positive deviation from Raoult's law with component A without azeotrope formation and no or slight deviation with component B. Such an entrainer allows the separation of component A as distillate, whereas component B is retained in the still along with the entrainer. The opposite case is obtained if the entrainer is not chemically similar to component B. The first criterion has been largely used to choose homogeneous entrainers for the separation of minimum boiling azeotropes. A suitable entrainer is usually a high boiling component that forms a nonazeotropic mixture with the components to be separated. Extractive distillation with entrainers of this kind has been performed successfully in industrial columns (Perry et al., 1997).

Unfortunately, looking for a homogeneous entrainer with such properties is not an easy task: entrainers with high selectivity have shown a limited miscibility with at least one of the original components (Lee and Gentry, 1997; Lee, 1998), and are then qualified as heterogeneous entrainers. This is a logical result, because the dissimilar chemical structure between the entrainer and components A or B can commonly produce the formation of an azeotropic mixture and/or the appearance of a partial miscibility region among them. Then, the resulting ternary residue curve map does not provide a feasible scheme for the separation of the original mixture by a classic extractive distillation process. In this case, another auxiliary component called "cosolvent" must be blended with the entrainer to improve the miscibility in the resulting mixture without affecting its selectivity. This fact complicates the design of a new process.

In this article, we show that the presence of a heterogeneous azeotrope in the ternary system A-B-E is not a significant constraint for the selection of a suitable heterogeneous entrainer E. In the first part, we present the mechanism by which heterogeneous entrainers make the separation feasible from the analysis of the thermodynamic description of the ternary system. Knowing this information, we can establish the preliminary flow sheet of the heterogeneous batch extractive distillation process. Without intending to list exhaustively all feasible diagrams, we first illustrate the feasibility of the process with the separation of an acetonitrile−water mixture, with hexylamine or butyl acetate as heterogeneous entrainers. The corresponding [120] ternary system (Matsuyama and Nishimura, 1977) exhibits the simplest structure involving only two binary azeotropic points. Later, we analyze an industrial example where water is used as a feasible heterogeneous entrainer, which adds several binary azeotropic points and a homogenous ternary azeotrope to the resulting [222-m] ternary mixture. Many ternary systems involving a partial miscibility between two components (type I dual-liquid-region diagrams) and corresponding to the thermodynamic and topological properties of the diagrams we investigate have been reported (Gmehling et al., 1994). As we will explain below, the separation of the primary components by published batch processes would either require a complicated sequence of batch-distillation steps or even not be feasible by heterogeneous azeotropic distillation. Therefore, the heterogeneous batch extractive distillation process is an attractive alternative to be considered for the separation of these classes of ternary mixtures.

Theoretical insights established for the operation of heterogeneous extractive batch distillation are validated via simulations using the batch-process simulator ProSim Batch (ProSim S.A, 1991). The column model consists of the usual plate-by-plate MESH equations (material balance, equilibrium, summation of molar fractions, and heat balance), which are solved for the whole column, decanter included, and taking the liquid−liquid demixion into account. Numerical treatment of the differential algebraic equation (DAE) system and discrete events handling is performed with DISCo, a numerical package for hybrid systems with a DAE solver based on Gear's method (Sargousse et al., 1999). Isovolatility curves are computed in an excel spreadsheet with BibPhyAddIn (ProSim S.A, 1991).

Screening of Heterogeneous Entrainers for Extractive Batch Distillation

Several methods are available to determine which original component will be drawn as distillate at the batch-distillation column top and the minimum amount of entrainer to separate both components with the specified purity. The most recent method involves the determination of isovolatility curves $\alpha_{i,j} = 1$ (Laroche et al., 1992) that divide the ternary diagram into different regions in which the decreasing order of the component's volatility can be defined. Plotted on the residue curve map, the isovolatility curves gives the primary and essential information for the synthesis of extractive distillation processes: which component will be drawn as the distillate, the entrainer supply for a feasible separation, and the number of continuous distillation columns or batch-distillation tasks required for the separation of the original components and the entrainer recovery.

Laroche et al. (1992) addressed the screening of homogeneous entrainers for the separation of a minimum boiling azeotropic mixture with a light, intermediate, or heavy boiling entrainer by continuous extractive distillation. In all their cases, the entrainer forms no azeotrope with the original components. We apply this methodology to the separation of homogeneous minimum boiling temperature azeotropes by batch extractive distillation with heterogeneous entrainers, which forms a binary heterogeneous azeotrope between the entrainer and one of the original components. The entrainer is a high boiling temperature component and the heterogeneous azeotrope has an intermediate boiling temperature in the resulting ternary mixture. In contrast, the feasibility of a process involving a low boiling temperature or an intermediate boiling temperature entrainer is not addressed in this study. This will depend on the thermodynamics properties of each particular case: the ternary system should involve an unstable homogeneous ternary azeotrope, which imposes the stability of binary azeotropes as saddles. This mainly occurs with high boiling temperature entrainers and will be illustrated in the last part of this article.

Unlike in heterogeneous azeotropic batch distillation, where the unstable binary heteroazeotrope is obtained in the vapor overhead (Modla et al., 2001; Rodriguez-Donis et al., 2002), in heterogeneous extractive distillation, either the saddle miscible primary component (case 1) or the saddle binary heteroazeotrope (case 2) can be obtained in the vapor above the rectifying column thanks to the feed of the heterogeneous entrainer at some tray near the column top. For case 1, the process works in a way similar to homogeneous batch extractive distillation. For case 2, significant operation differences discussed below arise compared to the classic process. Notice that our study is limited to the separation of a minimum boiling binary azeotropic mixture, but a heterogeneous entrainer can also be used for the separation of binary mixtures with a low relative volatility and of maximum boiling binary azeotropic mixtures.

At first, we consider the simplest feasible ternary diagram, which has two binary azeotropes: the homogeneous minimum boiling azeotrope *AB* to be separated, and the heteroazeotrope between the entrainer *E* and either *A* or *B*. The resulting ternary diagram is divided by one unstable separatrix, and both primary components are located in different distillation regions (see Figure 1). The only unstable node is the original homogeneous azeotrope, and the separation of the original components is not possible by heterogeneous azeotropic distillation considering a rectifying column (Modla et al., 2001; Rodriguez-Donis et al., 2001). The entrainer vertex and the original immiscible component are the stable nodes in the ternary system. The separation of the original immiscible component is possible by heterogeneous azeotropic distillation using an inverted column as a first operating step where the entrainer is added along with the binary mixture in the reflux drum. This first step is over when the reflux drum trajectory reaches the unstable separatrix, inside the heterogeneous envelope, providing a liquid phase that belongs to another distillation region. Then, the separation of the original miscible component is possible using two additional batch-distillation steps when considering a rectifying or a stripping column. More details about the feasibility of the separation of minimum boiling azeotropic mixtures for similar ternary diagrams using this complex column sequence is reported in Rodriguez-Donis et al. (2001). This rather complicated three nonextractive batch tasks sequence makes the ternary system a suitable candidate to examine the feasibility of batch extractive heterogeneous distillation where the heterogeneous entrainer is added in some tray near the column top. Discriminating between process alternatives would require a more complete comparison, taking economical criteria as well as operating conditions and column availability into account.

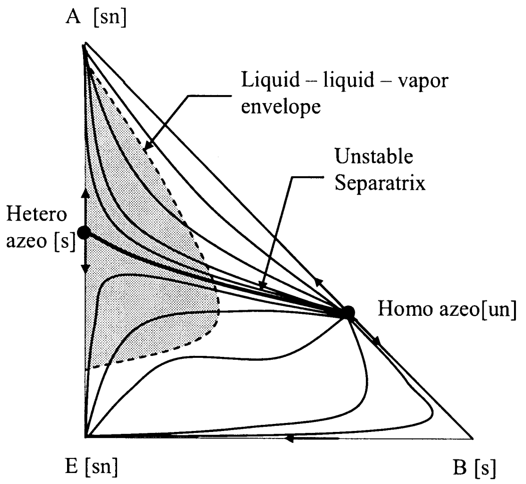


Figure 1. Residue curve map *ABE* for the ternary diagram [120].

An entrainer can lead to a ternary diagram with a heterogeneous region where the heteroazeotrope is a saddle if it exhibits the following thermodynamic behavior:

(1) The entrainer induces a strong positive deviation of Raoult's law with one original component (leading to the formation of a minimum boiling binary heterogeneous azeotrope).

(2) The entrainer forms an ideal binary mixture or it shows a negative deviation of Raoult's law without any azeotrope formation with the other key component.

If condition 1 holds for component *A* and condition 2 for component *B*, then the natural relative volatility is increased due to the addition of the heterogeneous entrainer. In the opposite case, the entrainer reduces the value of $\alpha_{A,B}$. In the first case, condition 1 could occur if the entrainer has an important polarity difference with component *A* and their boiling temperatures are close, whereas condition 2 can be satisfied under two criteria:

- The entrainer is selected from the same homologous chemical series as component *B*.
- The entrainer is chemically dissimilar from component *B*, but they have a high boiling temperature difference in order to avoid the formation of an azeotrope between them.

For the separation of aqueous–organic binary mixtures, many feasible entrainers could be found among those inducing a liquid–liquid phase split with water. For the separation of organic mixtures, water would often be a promising entrainer candidate.

Analysis of the feasibility of extractive distillation requires knowledge of the heterogeneous residue curve map and the calculation of an isovolatility curve for each binary mixture included in the ternary system. We analyze the feasibility of a heterogeneous extractive distillation process in a batch column taking the separation of acetonitrile–water mixture into consideration, which is a widely encountered waste stream in the separation of bioactive substances by liquid chromatography processes. Acetonitrile–water exhibits a minimum boiling azeotrope with a molar fraction of acetonitrile near 0.7 at 76.5°C under atmospheric pressure.

Because of the nonideal behavior occurring between water and many chemical compounds that often results in the formation of a heterogeneous azeotrope, it is not straightforward to find an entrainer that allows the separation of the miscible component (such as acetonitrile) as distillate. Therefore, one is looking for entrainers preferably selective for water so as to decrease the natural volatility between both original components.

Separation of Acetonitrile–Water by Heterogeneous Extractive Distillation in a Batch Rectifying Column

Choice of a suitable entrainer for the separation of acetonitrile – water, by heterogeneous extractive distillation

Table 1 shows the activity coefficients at infinite dilution in each other of acetonitrile and water, estimated by the NRTL model with the binary coefficients reported by Gmehling and Onken (1982) in the DECHEMA tables. Table 1 also includes the activity coefficients at infinite dilution of the two key components in several entrainers, as predicted by the UNIFAC activity-coefficient method. First, entrainers that belong to the same homologous series as acetonitrile are considered. Then, other entrainers are looked at in decreasing order of polarity as follows: amines > alcohols > esters > ketones > aromatics. Paraffins are disregarded because of the existence of some partial miscibility with acetonitrile that would lead to two immiscibility regions.

The results obtained in Table 1 match with the general feasible entrainer features described earlier. The use of high boiling temperature components of the same homologous series as acetonitrile strongly decreases the natural relative volatility of the mixture to be separated. On the other hand, the addition of an entrainer with a different chemical structure changes the natural relative volatility, depending on its polarity and the molecular interaction with each primary component. In fact, as seen by a value of $\gamma_1^\infty/\gamma_2^\infty > 1$, only hexylamine and heptylamine keep the acetonitrile as the most volatile component, which can be obtained as distillate, as in a conventional homogeneous extractive distillation. The addition of other heterogeneous entrainers has an effect similar to the one obtained for the components belonging to the acetonitrile's chemical family. Below we study in more detail the synthesis of heterogeneous batch extractive distillation for the two opposite alternatives, first considering the hexylamine as a representative of an increase of the natural acetonitrile–water relative volatility, and then we analyze the use of butyl acetate as a representative of a decrease in the relative volatility of acetonitrile–water. The key difference between the two cases is given by the fact that the isovolatility curve arrives at the homogeneous binary side (low boiling original component–entrainer) in the hexylamine case and at the heterogeneous binary side (high boiling original component–entrainer) in the butyl acetate case. Therefore, the low boiling original component will be obtained in the vapor overhead for the hexylamine case, but in the heteroazeotrope for the butyl acetate case. Table 1 also shows the value of x_P, which depends on the mixture thermodynamics, because it is the intersection point of the isovolatility curve on the binary side limited by the entrainer and one of the original components. Therefore, the influence of the entrainer on the $\gamma_1^\infty/\gamma_2^\infty$ ratio and on the x_P value is mainly determined by the molecular interaction between the key components and the selected entrainer. We have found that the obtained x_P values for heterogeneous entrainers are lower than those reported in previous works for homogeneous entrainers (Laroche et al., 1992; Lelkes et al., 1998). In general, homogeneous entrainers that provide a relative volatility value near to unity give a low x_P value. This is observed for the hexylamine and heptylamine entrainers despite the fact that the isovolatility curve reaches the binary side that contains no azeotropic point (case 1). However, for the heterogeneous entrainers, which can greatly reverse the normal relative volatility of the original components (case 2), all calculated x_P values in Table 1 are smaller than those normally reported for homogeneous systems. It seems that the presence of the binary heteroazeotrope on the binary side reached by the isovolatility curve affects the value of x_P because this point is always located between the heteroazeotrope and the high boiling temperature entrainer vertex. This particularity is not present in the homogeneous system where the isovolatility curve always arrives at the zeotropic binary side. Furthermore, Laroche et al. (1992) demonstrated via simulation for several ternary mixtures that the x_P value has an important influence on the performance of an extractive distillation process. In general, a larger fraction of the original component in x_P gives some evidence that the separation of the primary mixture is possible using a lower amount of the entrainer and minimum reflux ratio. All these features will be illustrated in more detail in the examples presented in the following sections.

Table 1. Comparison of Heterogenous Candidate Entrainers for the Separation of Acetonitrile (1) and Water (2)

Entrainer	Boiling Point (°C)	γ_1^∞	γ_2^∞	$\gamma_1^\infty/\gamma_2^\infty$	x_P
Acetonitrile (1)	80.1	—	11.21	1.60	—
Water (2)	100.0	7.00	—		—
Propionitrile	97.4	1.031	7.7818	0.13	0.4
Hexanenitrile	163.6	0.9769	4.7411	0.20	0.39
Hexylamine	132.7	2.9461	2.0914	1.41	0.45
Heptylamine	156.9	3.0050	2.3354	1.29	0.37
1 Pentanol	137.8	1.8358	3.0919	0.59	0.17
1 Hexanol	157.4	1.5888	2.8487	0.56	0.1
Butyl acetate	126	1.2068	5.1187	0.23	0.36
Pentyl acetate	148	1.1468	4.3947	0.26	0.35
2 Pentanone	102.3	1.1544	5.2339	0.22	0.38
2 Hexanone	127.7	1.1534	4.4418	0.26	0.37
Ethyl benzene	136.2	2.9310	16.11	0.18	0.18
Propyl benzene	159.2	2.64	10.717	0.25	0.17

Separation of acetonitrile – water with hexylamine

Figure 2 displays the ternary diagram for acetonitrile (A)–water (B)–hexylamine (E) with the isovolatility curves and the local volatility order of the three components in each subregion of the triangle. The isovolatility curves and the ternary liquid–liquid–vapor equilibrium envelope were calculated using the UNIFAC model. The possibility of applying an extractive distillation process to perform the separation of the original components is given by the analyses of the isovolatility curves in the ternary diagram $\alpha_{A,B}$, $\alpha_{A,E}$, and $\alpha_{B,E}$. In fact, the simplex is divided into three regions by the curves $\alpha_{A,B} = 1$ and $\alpha_{B,E} = 1$, whereas the acetonitrile is always more volatile than hexylamine ($\alpha_{A,E} > 1$). The curve $\alpha_{A,B} = 1$ di-

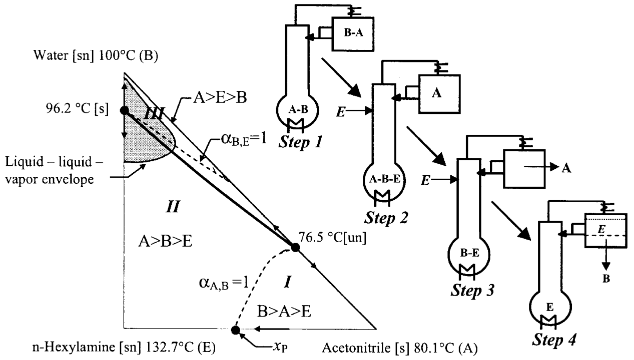


Figure 2. Isovolatility curves and volatility order diagram for acetonitrile–water–hexylamine; tasks sequence for the heterogeneous extractive batch-distillation process.

vides the triangle into regions I and II. In region I, water is the most volatile component, whereas in region II, it is acetonitrile. In both regions hexylamine is the high boiling component. In addition, the existence of the curve $\alpha_{B,B} = 1$ adds region III, where water is the high boiling component. The fact that the curve $\alpha_{A,B} = 1$ reaches the binary acetonitrile–hexylamine side tells us that, as in homogeneous batch distillation, acetonitrile will be drawn as distillate if the hexylamine is fed continuously in a tray near the top of the column. The minimum entrainer flow rate, F_{min}, is related to the position of the intersection point, x_P, of the curve $\alpha_{B,B} = 1$ on the binary acetonitrile–hexylamine side. Taking this preliminary thermodynamic information into account, the synthesis of the heterogeneous extractive distillation can be established with respect to the methodology devised by Yatim et al. (1993), Lang et al. (1994), and Lelkes et al. (1998), for a batch extractive homogeneous rectifying column. The only difference with the homogeneous entrainer process is the immiscibility gap defined by the presence of the binary heteroazeotrope.

Figure 2 shows the sequence of the batch-distillation steps needed to achieve the separation of the ternary mixture by heterogeneous extractive distillation in a batch-rectifying column. The separation of all components occurs in a way similar to those reported for homogeneous extractive distillation in the same configuration column (Lelkes et al., 1998):

Step 1. After the still is charged with the acetonitrile–water mixture, the column is operated at infinite reflux until the unstable homoazeotrope reaches the column top.

Step 2. Under infinite reflux operation, some entrainer is introduced continuously in a tray placed somewhere near the top of the column with a flow rate $F > F_{min}$. This operating condition determines the necessary and sufficient statement to make the process feasible, namely, connecting the extractive liquid profile at any still composition with the one existing in the rectifying section at the extractive stable node, S_n. Feeding the entrainer at infinite reflux produces the appearance of S_n, which is reached by all extractive profiles, and is also situated on the rectifying liquid profile given by a residue curve containing the specified distillate composition for the acetonitrile. This infinite reflux step is over when the homoazeotrope is replaced overhead by acetonitrile with a purity that is determined by the number of trays in the rectifying column section. Because acetonitrile is a saddle in the ternary system, for a given number of trays in the extractive section, there exist a maximum number of trays in the rectifying section that sets the highest reachable purity of this component in the distillate product. In the extractive section, an infinite number of trays provides the greatest concentration of acetonitrile in the distillate. However, this is impracticable in a real column, and a sharp separation between the original components is barely obtained by extractive distillation.

Step 3. The entrainer is still continuously fed, but a finite reflux ratio is set and high-purity acetonitrile is drawn as a distillate product. The use of a finite reflux ratio usually gives rise to the appearance of unfeasible regions. Therefore, the still path will not be able to reach the binary water–hexylamine side, and the recovery of acetonitrile is less than 100% (Lelkes et al., 1998). Hence, an intermediate cut is normally drawn from the column.

Step 4. Finally, one proceeds to the separation of the entrainer and of the heavy primary component remaining in the column. Then, the overhead vapor composition equals that of the heteroazeotropic, allowing the separation of a water-rich phase as distillate, while a hexylamine-rich phase is refluxed to the column and remains at the end of the process in both the decanter and the still.

The column operating conditions are reported in Table 2. The liquid–vapor equilibrium is estimated using the UNIFAC model. The simulation results of step 2 are shown in Figure 3: thanks to the feeding of hexylamine on the fifth tray from the top, the liquid composition in the reflux drum moves from the homogeneous acetonitrile–water azeotropic mixture toward the acetonitrile vertex. The feasibility is ensured because the extractive and the rectifying liquid profiles intersect at the final molar composition on the entrainer feed tray and the distillate acetonitrile fraction equals 0.973. This demonstrates that as with homogeneous extractive continuous distillation, the light original component *A* can be obtained as the distillate when the isovolatility curve $\alpha_{A,B} = 1$ reaches the binary side *A-E* according to the method developed by Laroche et al. (1992). In the opposite case, when the isovolatility curve $\alpha_{A,B} = 1$ reaches the heterogeneous binary side, the heteroazeotrope is drawn as the top product, as we

Table 2. Operating Conditions and Simulation Results for Step 2 of the Separation of Acetonitrile–Water Using *n*-Hexylamine by Heterogeneous Extractive Distillation in a Batch Rectifier

Operating Parameters	Values*
Initial charge (mol)	25
Composition of the initial charge	[0.65; 0.35; 0.0]
n-Hexylamine feed flow rate (mol/h)	21.5
n-Hexylamine feed composition	[0.0; 0.0; 1.0]
n-Hexylamine feed tray number	5
Total number of equilibrium stages (condenser and reboiler incl.)	32
Total column liquid holdup (mol)	1.62
Heat reboiler duty (W)	150
Operating pressure (atm)	1
Reflux ratio	Total

*Molar-composition vector order is [acetonitrile–water–*n*-hexylamine].

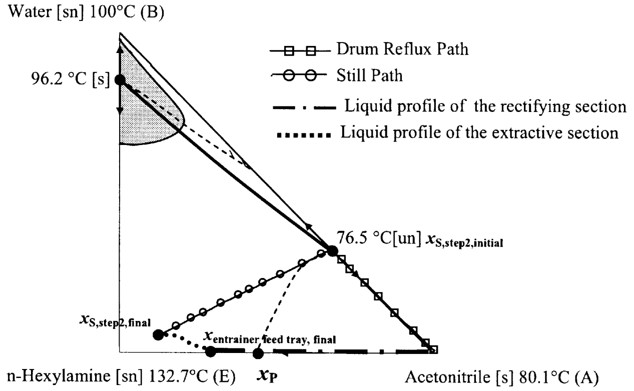


Figure 3. Simulation results of the operating step 2 for the separation of acetonitrile–water mixture with *n*-hexylamine.

will explain later. The main drawback of this process is the prohibitive consumption of the heterogeneous entrainer because of the small value of x_P, the composition of acetonitrile on the binary acetonitrile (A)–hexylamine (E) side. The composition of the entrainer feed tray, x_E, which links the liquid profile in both column sections, has to be placed between the hexylamine vertex and x_P. For that reason, a large amount of heterogeneous entrainer has to be added to the column to obtain an extractive liquid profile, joining the final still composition x_S with the rectifying liquid profile passing through the desired distillate composition. The low value of x_P restricts the feasible region to a zone of high hexylamine content. This problem could be overcome by using a middle-vessel column where the heterogeneous entrainer would be obtained as a bottom product and recycled to the feed tray above the middle vessel. In this case, water would remain with the hexylamine in the middle vessel at the end of the process, and this binary mixture could be separated in a further batch-distillation task where the binary heteroazeotrope would be drawn as vapor overhead and separated in a water-rich phase where purity will be set by the liquid–liquid split at the decanter temperature.

Separation of acetonitrile – water with butyl acetate

Figure 4 shows the isovolatility curve and the local volatility order between the three components for butyl acetate as heterogeneous entrainer. The ternary liquid–liquid–vapor equilibrium was predicted by using NRTL binary interaction coefficients estimated from recent experimental data of the ternary liquid–liquid–vapor mixture at the atmospheric pressure reported by Acosta-Esquijarosa et al. (2002). In this case, the ternary system involves all three isovolatility curves, defining four regions. In region I, water is the most volatile component, whereas it is acetonitrile in regions II and III, and butyl acetate in the little region IV. Whatever the region, the heteroazeotrope can be drawn overhead at the column top as vapor, because the curve $\alpha_{A,B} = 1$ reaches the heterogeneous binary-side water–butyl acetate. For the heterogeneous batch extractive process, the entrainer flow rate has to be higher than the minimum value defined by the position of x_P on the segment limited by the heteroazeotrope composition and the butyl acetate vertex.

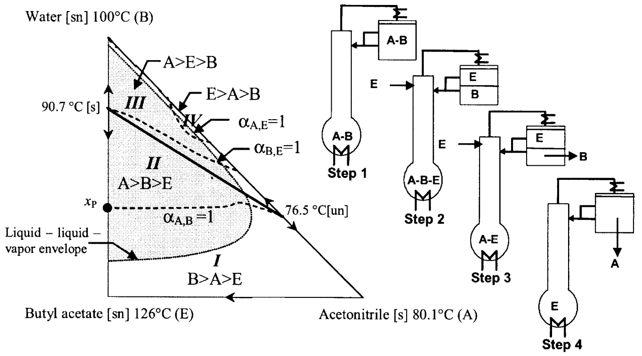


Figure 4. Isovolatility curves, volatility orders for the water–acetonitrile–butyl acetate system; tasks sequence for heterogeneous extractive batch-distillation process.

As in the hexylamine case, a feasible sequence of batch-rectifier tasks shown in Figure 4 can be defined to provide the separation of all components by heterogeneous extractive distillation. Step 1 is identical to the previous hexylamine case. In step 2 the heteroazeotrope takes the place of the unstable homoazeotrope thanks to the addition of butyl acetate at the top of the column under infinite reflux operation. This leads to a liquid–liquid phase split in the subcooled decanter, and the water-rich phase can be drawn as distillate during step 3, while the entrainer-rich phase is continuously refluxed to the column under a finite reflux ratio. After water is drained from the batch column, the separation of the binary mixture acetonitrile–butyl acetate remaining in the still and in the column can be performed as a conventional batch-distillation process.

To validate the relevant differences introduced by the use of the heterogeneous entrainer with the well-known homogeneous extractive batch distillation, the task sequence described in Figure 4 is validated through simulation. The liquid–liquid equilibrium in the decanter is estimated using the binary-coefficient values reported in the DECHEMA tables for the liquid–liquid equilibrium of the ternary mixture at 31°C (Sorensen and Arlt, 1979).

The process simulation proceeds as follow: initially, the azeotropic mixture is charged into the still and the column is operated at infinite reflux. The homogeneous acetonitrile–water azeotrope is obtained in the overhead vapor. When step 2 begins, pure butyl acetate is fed onto the first tray of the column top with the significant flow rate reported in Table 3. Simulation results of steps 2 and 3 are shown in Figure 5: the addition of butyl acetate at the column top produces the replacement of the original homogenous azeotropic mixture in the decanter by the heteroazeotrope, while the still path moves from its initial composition (acetonitrile–water azeotrope) toward the butyl acetate vertex. At the end of step 2, the liquid profile in the extractive section links the punctual still composition, x_S, with the stable node, S_n, located on the binary water–butyl acetate side. Besides, S_n lies on the same VLL tie line as the heteroazeotrope, giving a top vapor composition equal to that of the heteroazeotrope. The condensed vapor leads to a liquid–liquid split into the decanter, and the water-rich phase can be recovered as distillate in the subsequent operating step. It should be noted that unlike ho-

Table 3. Operating Conditions and Simulation Results for the Heterogeneous Extractive Distillation of Acetonitrile–Water using Butyl Acetate in a Batch Rectifier

Operating Parameters	Simulation Results*
Initial charge (mol)	12
Composition of initial charge	[0.6743; 0.3257; 0.0000]
Butyl acetate feed flow rate (mol/h)	21.5
Butyl acetate feed composition	[0.0; 0.0; 1.0]
Butyl acetate feed-tray number	1
Total number of equilibrium stages incl. decanter and reboiler	62
Total tray liquid holdup (mol)	0.22
Decanter liquid holdup (mol)	1.4
Decanter temperature (°C)	25
Heat reboiler duty (W)	150
Operating pressure (atm)	1
Reflux ratio	13.5–28
Distillate average composition (water-rich phase)	[0.0002; 0.9957; 0.0041]
Composition of entrainer-rich phase into decanter (end of step 3)	[0.0007; 0.0966; 0.9026]
Charge into reboiler at the end of step 3 (mol)	62.8
Liquid composition in the reboiler (end of step 3)	[0.0774; 0.005; 0.9176]
Total operation time step 2 + step 3 (h)	4.5

*Molar-composition vector order is [acetonitrile–water–butyl acetate].

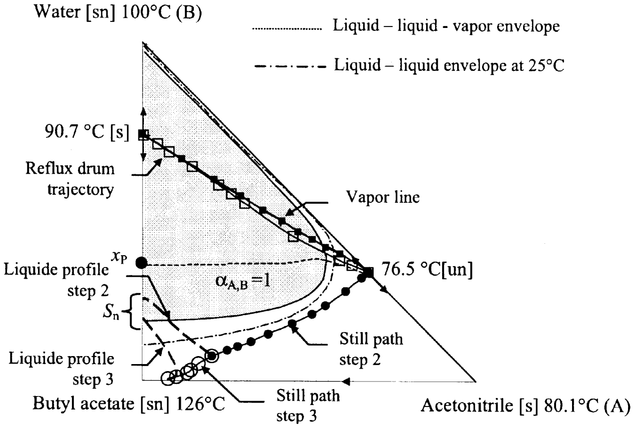


Figure 5. Simulation results of the separation of acetonitrile–water mixture with butyl acetate by heterogeneous extractive distillation in a batch rectifier.

mogeneous extractive batch distillation, and because of the specific properties of the VLL tie line overall liquid compositions that are in equilibrium with a unique vapor composition, the process is feasible without a rectifying section and the entrainer can be directly fed to the first tray in the column top. In homogeneous batch extractive distillation, a rectifying section would be needed to ensure that the overhead vapor composition is near the original light component. During step 3, the same entrainer flow rate as in step 2 is kept and one first establishes that 90% of the overall condensed vapor is refluxed at the top of the column, whereas the acetonitrile composition in the first top tray is lower than 0.005. When this latter condition is no longer accomplished, step 3 is continued, considering that 95% of condensed vapor is refluxed to the column top (this indeed increases the reflux and keeps the acetonitrile fraction on the first tray below 0.005, enabling it to reach the heteroazeotrope overhead). In both cases the remaining condensed vapor phase is sent to the decanter. In addition, an extra amount of entrainer-rich phase is also refluxed from the decanter and this amount is controlled by the fixed level of the organic phase into the decanter. This reflux policy assured that the heteroazeotrope is drawn during the whole process. The resulting reflux ratio during step 3 is shown in Table 3. Its value is large, but enables a molar purity of the aqueous distillate higher than 0.99 to be obtained. To maintain this purity with a lower reflux ratio would require a higher pure entrainer flow rate. Figure 5 shows that the still path during step 3 arrives at the binary acetonitrile–butyl acetate side, because water is removed as distillate (average molar purity of 0.9957). In the last operational step of the process, the remaining binary mixture acetonitrile and butyl acetate can be separated by conventional batch distillation.

Table 3 shows more simulation results, such as the duration of steps 2 and 3, the purity of the entrainer-rich phase in the decanter, the liquid holdup, and the composition in the still at the end of the process. As can be seen, the process operation is feasible but not very efficient: a large reflux ratio is required despite a significant entrainer flow rate (a ratio of total amount of entrainer to the initial mixture amount of 8.1). As a result, the final liquid amount in the reboiler is almost 5.2 times the initial charge. As in the hexylamine case, this inefficiency was predicted by the analysis of the isovolatility curves. It should be noted that steps 2 and 3 take place in the distillation region where the composition of butyl acetate is high. In fact, the interception of the still path at the end of step 3 occurs at the binary side at a point located very close to the butyl acetate vertex. As was shown by Lelkes et al. (1998), there is an opposite relationship between the minimum entrainer flow rate, $F_{\min}$, and the entrainer composition in x_P. In Table 1, the highest entrainer composition values of x_P (such as 0.45 for hexylamine, 0.4 for propionitrile, and 0.36 for butyl acetate) are lower than those reported for homogeneous entrainers (Laroche et al., 1992), and this implies that the heterogeneous batch extractive distillation process requires a large amount of entrainer. In batch distillation, such an economical drawback can be overcome by using a middle-vessel column, as was hinted earlier. On the other hand, it is not problematic for continuous distillation, because the flow sheet usually involves two columns and the entrainer can be recycled from the second recovery column to the first extractive column.

Feasibility Analysis of an Industrial Heterogeneous Batch Extractive Distillation Case

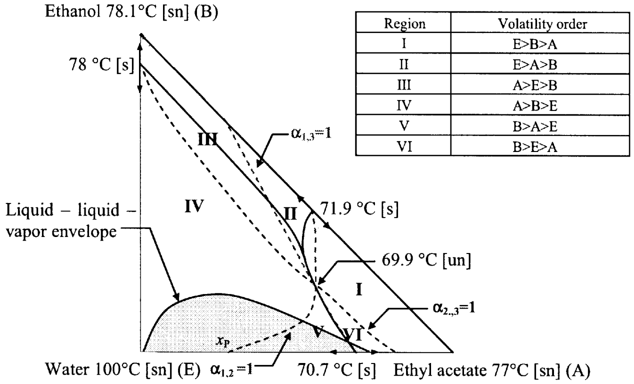
The two examples discussed earlier concerned a simple ternary diagram that can be used for the separation of a minimum boiling temperature azeotropic mixture by extractive batch distillation with a heterogeneous entrainer. In those cases, the heavy entrainer adds only an extra saddle binary heteroazeotrope. Köhler et al. (1995) reported the industrial separation by batch extractive heterogeneous distillation of two organic components using water as the heterogeneous entrainer. Water is a heavy entrainer that forms a heteroazeotrope with the light original component and a homogeneous azeotrope with the other primary component. Besides, the resulting ternary diagram exhibits an unstable ternary homogeneous azeotrope, forcing the topological stability of all three binary azeotropes to be saddles. The ternary diagram is divided into four basic distillation regions by three unstable separatrices. Köhler et al. (1995) demonstrated experimentally in an industrial batch-rectifying column that the saddle binary heteroazeotrope can be drawn as a vapor overhead by adding pure water at the column top. The performance of the process was improved by changing the water flow rate over time to maximize the amount of total distillate product with a fixed purity. They found that this operation is economically more advantageous than the traditional process involving a constant entrainer inlet flow.

As far as we know, the article by Köhler et al. (1995) is the first communication to describe the use of a heterogeneous entrainer for the separation of a nonideal mixture by extractive distillation. Experimental results were presented, but without any theoretical analysis of the performance of the process. In the following, we use the same method described earlier to explain the mechanism by which the process is feasible, knowing that ethyl acetate and ethanol are the original components of the mixture studied by Köhler et al. (1995) (Haverkamp, personal communication, 2002). Unlike the two previous examples, the heterogeneous entrainer, water, has a positive deviation from Raoult's law with both original components. However, a higher nonideality is shown with the ethyl acetate due to the partial miscibility between water and the light primary component that produces a binary heteroazeotrope under established conditions of temperature and pressure. Consequently, the addition of water to the original binary mixture produces a significant increase in the natural relative volatility between the primary components despite the existence of the homogeneous azeotrope ethanol–water. Table 4 contains the activity coefficients at infinite dilution of the two key components in its binary mixture, and also when one of them is replaced with water. The thermodynamic model NRTL was used with binary interaction coefficients reported in the DECHEMA tables (Gmehling and Onken, 1982) at atmospheric pressure.

Using the same computational tools, all isovolatility curves are calculated and shown in Figure 6. Because of the presence of the ternary azeotrope, each isovolatility curve starts at the corresponding binary azeotropic point, passes through the ternary azeotrope, and finishes at the opposite binary side. Now, the composition simplex is divided into six regions where the volatility order between all components can be established. Each region is limited by two isovolatility curves. In all regions located in the right side of the isovolatility curves the heavy component associated with each curve is the most volatile component. In the left region, the light component is the lightest. Based on this statement, the table included in Figure 6 gives the volatility order of the components in each region. Another important feature is due to the fact that the isovolatility curve $\alpha_{A,B}$ reaches the heterogeneous part of the ethyl acetate–water side (point x_P of molar composition of ethyl acetate equal to 0.3). Therefore, the heterogeneous batch extractive distillation process where water is fed at the top tray is feasible and will give the binary heterogeneous azeotrope as vapor overhead, as in the acetonitrile–water–butyl acetate example.

Table 4. Thermodynamic Properties of the Mixture Ethanol(1)-Ethylacetate (2)-Water (3)

Entrainer	Boiling Point (°C)	γ_1^∞	γ_2^∞	$\gamma_1^\infty/\gamma_2^\infty$	x_P
Ethanol (1)	78.1	—	2.3437	1.006	—
Ethyl acetate (2)	77	2.3567	—		—
Entrainer: water (3)	100.0	57.937	5.773	10.04	0.3



Region	Volatility order
I	E>B>A
II	E>A>B
III	A>E>B
IV	A>B>E
V	B>A>E
VI	B>E>A

Figure 6. Isovolatility curves, volatility orders for the ethyl acetate–ethanol–water system.

The sequence of batch-distillation tasks proposed by Köhler et al. (1995) for the separation of ethyl acetate–ethanol with water is similar to the sequence shown in Figure 4 for the ternary mixture acetonitrile–water–butyl acetate. Unfortunately, the authors did not provide a detailed description of the process and some operating conditions had to be inferred from some experimental results reported in their article: the initial charge F is located in region I with an approximated molar composition of ethyl acetate, ethanol, and water of 0.85, 0.12, and 0.03, respectively. Nothing is said about the starting condition of the column, but we suppose that the first step is a total conventional reflux operation. In addition, we also assume that a 20-tray column is sufficient to replace the ternary azeotrope by the binary heterogeneous azeotrope thanks to the addition of water at the first top column tray in step 2. Experimental results given in the article concern the variation in the water and distillate flow rates with time during step 3. No reflux ratio value used by the authors is given. The decanter temperature was reported to be equal to 30°C, and we suppose that the ethyl acetate purity in the distillate matches with the liquid–liquid equilibrium at this temperature value. In the article, step 3 finishes after operating for 22 h, after which it makes no economic sense for the prohibitively large water entrainer flow rate to recover the small amount of ethyl acetate remaining in the still. The ternary mixture obtained as a final residue in the reboiler is considered to be a waste stream of the process, and no further purification was recorded. In a supplementary step, the ethyl acetate–rich phase drawn out as distillate is recharged into the column to obtain this component with the required purity in the still.

Taking the operating conditions reported by the authors into account, we use the commercial simulator ProSim Batch (Prosim SA, 1991) to perform the separation in a batch-recti-

Table 5. Operating Conditions for the Heterogeneous Extractive Distillation of Ethyl Acetate–Ethanol Using Water in a Batch Rectifier

Operating Parameters	Simulation Results*
Initial charge (kg)	4,930
Composition of initial charge	[0.85; 0.12; 0.03]
Water feed flow rate (kg/h)	400
Water feed composition	[0.0; 0.0; 1.0]
Water feed-tray number	1
Total number of equilibrium stages (decanter and reboiler)	22
Total tray liquid holdup (kg)	200
Decanter liquid holdup (kg)	100
Decanter temperature (°C)	30
Heat reboiler duty (kW)	50
Operating pressure (atm)	1
Reflux ratio	0.1–2.4
Distillate average composition (ethyl acetate-rich phase)	[0.7343; 0.0029; 0.2628]
Recovery of ethyl acetate (%)	93.6
Composition of water-rich phase into decanter (end of step 3)	[0.0093; 0.0002; 0.9905]
Charge into reboiler at the end of step 3 (kg)	10179.1
Liquid composition in the reboiler (end of step 3)	[0.0036; 0.0129; 0.9835]
Operation time step 2 (h)	3.4
Operation time step 3 (h)	22

*Molar-composition vector order is [ethyl acetate–ethanol–water].

fying column. Table 5 contains the operating conditions. The initial charge amount is estimated from the total amount of distillate, its purity, and the composition of the original mixture (F in Figure 7). A constant water flow rate is assumed during the whole operation at the value defined by the authors. In addition, the liquid reflux to the column is composed of the water-rich phase only, and its amount is determined by the splitting ratio, ω, of the decanter heavy phase to the condensed overall liquid phase. Then we consider that both liquid-phase levels are constant in the decanter. Knowing the ω value and the initial distillate flow rate, we can estimate the vapor flow, and consequently the reboiler heat duty. All these operating conditions, along with the liquid holdup on the trays and the decanter, are defined to make feasible the separation of ethyl acetate as a distillate product during an operation time that matches the experimental value. The column is considered to be adiabatic and composed of 20 equilibrium stages.

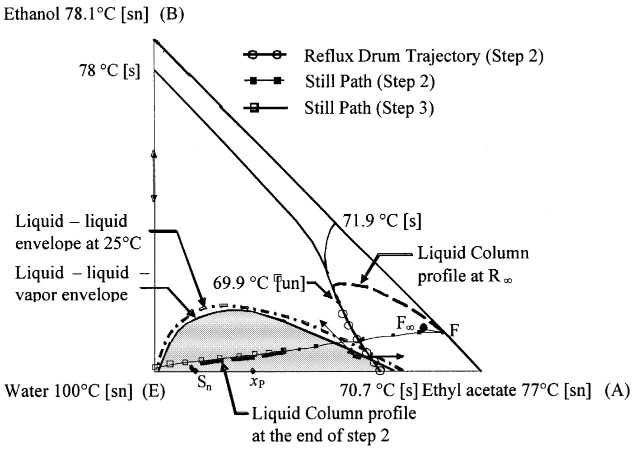


Figure 7. Simulation results of the separation of the ethanol–ethyl acetate mixture with water by heterogeneous extractive distillation in a batch rectifier.

Figure 7 displays the simulation results of the separation of the ethyl acetate–ethanol mixture with water by heterogeneous extractive batch distillation. The initial mixture F is charged in the still, and the operation is started under infinite reflux conditions. This gives a liquid column profile that links the liquid composition in the reboiler (F_∞) with the unstable ternary homogeneous azeotrope (Figure 7). In the subsequent step 2, water is fed to the first tray of the column, changing the relative volatility between both original components. After 3.4 h of operation, the composition of the binary heteroazeotrope is obtained in the liquid retained in the reflux drum. In addition, the still path follows a rectilinear direction determined by feeding the water to the column, and it crosses the unstable separatrix joining the ternary azeotrope and the heteroazeotrope. Unlike the previous example, the still path moves inside the heterogeneous liquid boiling envelope and all trays experience a liquid–liquid splitting. At the end of step 2, the liquid column profile connects the punctual still composition with the stable node, S_n, located on the heterogeneous binary ethyl acetate–water side. Therefore, the vapor above the composition is at the heteroazeotrope. It should be noted that all extractive liquid profiles lie in the heterogeneous region close the water vertex due to the small x_P value, and the liquid–liquid split even takes place in the still. However, the original authors did not report any operational problems during the execution of the process in the industrial column. Simulation results of step 3 are shown on Figure 7. In this case, water is also fed continuously at the top of the column, while the ethyl acetate–rich phase is drawn out as distillate product. Only the water–rich phase is refluxed at the column top, and the process runs under a low reflux ratio due to the small value of the liquid–liquid splitting ratio, ω, in the decanter. The still path traverses the heterogeneous boiling region, moves out of it, and finally reaches the binary homogeneous ethanol–water side close to the entrainer vertex. Table 5 shows the simulation results at the end of step 3. In the distillate, 93.6% of ethyl acetate is recovered with a molar purity determined by the liquid–liquid equilibrium at the decanter temperature. In general, the separation is feasible with a high entrainer consumption. Here, the final liquid amount in the reboiler is twice its initial value, and the ratio of total entrainer amount to the initial charge equals 2.1. Both parameters are lower than those obtained for the ternary acetonitrile–water–butyl acetate system, even though both cases exhibit similar x_P values. The difference between them is caused by the fact that water changes more significantly the relative volatility of the original binary mixture.

Conclusions

In this article, we have presented some evidence that an entrainer that induces a liquid–liquid split, and even forms a heteroazeotrope of intermediate boiling temperature, can provide a feasible alternative to the separation of minimum boiling azeotropic mixtures by batch extractive distillation. So far, homogeneous entrainers that do not form azeotropes with key components usually have been employed in an extractive distillation process. In addition, the use of heterogeneous entrainers has been restricted mainly to azeotropic distillation because of the existence of unstable heteroazeotropes. Based upon thermodynamic data, we have performed the synthesis of heterogeneous batch extractive distillation using the concepts of isovolatility in curves and local volatility in order to determine the key component to be drawn as distillate, the minimum amount of heterogeneous entrainer and the batch distillation tasks involved in the whole process. Because of the highly nonideal behavior of such systems, the entrainers mainly provide the separation of the primary heterogeneous component as a top product. The performance of the novel process was presented for the separation of two binary azeotropic mixtures using a heavy heterogeneous entrainer. The separation of the azeotropic mixture can be performed (1) by a process similar to those reported for homogeneous extractive distillation, or (2) by obtaining the heteroazeotrope as a vapor overhead. The feasibility of the second alternative was corroborated through rigorous simulation of the simplest ternary diagram that can be used for this process and by a published industrial example involving a ternary system with two binary homogeneous azeotropic mixtures, a binary heteroazeotrope, and a homogeneous ternary azeotrope. This new alternative increases the potential number of entrainers to be used in batch extractive distillation. However, this study has shown that a major drawback is the increased use of entrainers. Therefore, the study of this nonconventional extractive process in a middle-vessel column and its extension to the continuous distillation is a promising unexplored area.

Acknowledgment

This work is financially supported by the ALFA-Programme of the European Community. Its contribution was indeed highly appreciated, as is Dr. Hans Haverkamp's cooperation in giving us all the essential information about the industrial example.

Literature Cited

Acosta-Esquijarosa, J., A. Arce, E. Rodil, and A. Soto, "Thermodynamic Study on Binary and Ternary Mixture of Acetonitrile−Water−Butyl Acetate," *Fluid Phase Equilib.*, **203**, 83 (2002).

Fredenslund, A., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Non-Ideal Liquid Mixtures," *AIChE J.*, **21**, 1086 (1975).

Gmehling, J., and U. Onken. *Vapor−Liquid Equilibrium Data Collection. DECHEMA Chemistry Data Series*, Vol. 1 (12 parts), Dechema, Frankfurt am Main (1982).

Gmehling, J., J. Menke, J. Krafczyk, and K. Fischer, *Azeotropic Data*, VCH, Weinheim (1994).

Köhler, J., H. Haverkamp, and N. Schadler, "Discontinuous Rectification of Azeotropic Mixtures with Auxiliary Substances," *Chem. Ing. Tech.*, **67**(8), 967 (1995).

Lang P., H. Yatim, P. Moszkowicz, and M. Otterbein, "Batch Extractive Distillation Under Constant Reflux Ratio," *Comput. Chem. Eng.*, **18**, 1057 (1994).

Laroche, L., N. Bekiaris, H. W. Andersen, and M. Morari, "Homogeneous Azeotropic Distillation: Comparing Entrainers," *AIChE J.*, **38**, 1309 (1992).

Lee, F. M., and J. C. Gentry, "Don't Overlook Extractive Distillation," *Chem. Eng. Prog.*, **93**(10), 56 (1997).

Lee, F. M. "Extractive Distillation: Close-Boiling-Point," *Chem. Eng.*, **11**, 112 (1998).

Lelkes, Z., P. Lang, B. Benadda, and P. Moszkowicz, "Feasibility of Extractive Distillation in a Batch Rectifier," *AIChE J.*, **44**, 810 (1998).

Modla, G., P. Lang, and K. Molnar, "Batch Heteroazeotropic Rectification of a Low Relative Volatility Mixture Under Continuous Entrainer Feeding: Feasibility Studies," *CD-Rom Proc. World Congr. of Chemical Engineering*, Melbourne, Australia (2001).

Matsuyama, H., and H. Nishimura, "Topological and Thermodynamic Classification of Ternary Vapor−Liquid Equilibria," *J. Chem. Eng. Jpn.*, **10**(3), 181 (1977).

Perry, R. H., D. W. Green, and J. O. Maloney, *Perry's Chemical Engineer's Handbook*, 7th ed., McGraw-Hill, New York (1997).

Prausnitz, J. M., R. N. Lichtenhaler, and E. G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice Hall, Englewood Cliffs, NJ (1986).

ProSim, S.A., Reference Manual on http://www.prosim.net (1991).

Rodriguez-Donis, I., V. Gerbaud, and X. Joulia, "Entrainer Selection Rules for the Separation of Azeotropic and Close Boiling Temperature Mixtures by Heterogeneous Batch Distillation," *Ind. Chem. Eng. Res.*, **40**(22), 4935 (2001).

Rodriguez-Donis, I., V. Gerbaud, and X. Joulia, "Feasibility of Heterogeneous Batch Distillation," *AIChE J.*, **48**, 1168 (2002).

Sargousse, A., J. M. Lelann, X. Joulia, and L. Jourda, "D.I.S.C.o. : Un Nouvel Environnement de Simulation Orienté Objet," *Proc. MOSIM 99*, Annecy, France, p. 61 (1999).

Sorensen, J. M., and W. Arlt, *Liquid−Liquid Equilibrium Data Collection. DECHEMA Chemistry Data Series*, Frankfurt am Main (1979).

Yatim H., P. Moszkowicz, M. Otterbein, and P. Lang, "Dynamic Simulation of a Batch Extractive Distillation Process," *Comput. Chem. Eng.*, **17**, S57 (1993).

Manuscript received Feb. 7, 2003, and revision received May 7, 2003.