Multiple Steady States in Distillation: Effect of VL(L)E Inaccuracies

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Output multiplicities in heterogeneous azeotropic distillation columns were studied. The accuracy of the thermodynamic description is a key factor that determines if multiplicities can be observed in numerical simulations. The descriptions used in the multiplicity-related literature are analyzed. The ∞/∞ analysis of Bekiaris et al. (1996) was used to check implications of inaccuracies in the reported thermodynamics on the existence of multiplicities in azeotropic distillation. On this basis, guidelines are derived concerning what features of thermodynamic descriptions need special attention for use in multiplicity prediction and simulation. Secondly, numerical studies on output multiplicities in heterogeneous azeotropic distillation in the literature were compared to the ∞/∞ predictions wherever possible. The ∞/∞ analysis was used to derive the relations between the reported multiplicities and to identify the physical phenomena causing them.

Introduction

Multiple steady states in distillation

Azeotropic distillation is one of the most widely used and important separation processes in the chemical and the specialty chemical industries. Among the surprising features of azeotropic distillation columns, multiple steady states were discovered. In the literature, the term *multiple steady states* is used to describe various, sometimes quite different situations.

Definition 1. By multiple steady states (MSS) in a distillation column we refer to **output multiplicities**, *that is, that a column of a given design exhibits different column profiles and, therefore, different product compositions at steady state for the same set of inputs (feed composition, flow rate and quality) and the same values of the operating parameters.* Note that this definition implies that the existence of MSS fundamentally depends on the column ''configuration,'' that is, on the selection of the operating parameters (hereafter denoted in square brackets). A mixture under consideration is called *homogeneous* if only one liquid phase exists throughout the composition space, and *heterogeneous* if two liquid phases exist for some compositions. For a given column design (number of stages, feed locations, column pressure, and type of condenser and reboiler), a given feed flow rate, composition, and quality (such as temperature), there are two operational degrees of freedom in a homogeneous two-product distillation column (Bekiaris et al., 1993). In the case of a heterogeneous two-product column, there is one additional degree of freedom, the decanter policy.

Moreover, a different type of multiplicity is of some importance in this work: *internal state multiplicities* are a type of multiplicity where more than one solution with identical product compositions exist for the same inputs and operating parameters. These solutions do only differ by the ''internal'' column profiles (excluding the products). Finally, by *parametric sensitivity*, we denote the familiar case where column profiles and products exhibit large differences in a very narrow interval of the operating parameters.

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So far, four physical phenomena have been found to give rise to output multiplicities in azeotropic distillation:

(1) Jacobsen and Skogestad (1991) reported two different types of multiplicities in binary distillation columns with ideal vapor-liquid-equilibrium (VLE):

(a) For constant molar overflow (CMO) and the $[L^M, V^N]$ configuration (note that the superscripts N and M denote molar or mass units of a flow rate), multiplicities can occur due to the nonlinear relationship between mass and molar flow rates (or volumetric and mass flow rates or heat duties and molar flow rates). This behavior is not expected for binary systems with configurations involving a product flow rate, such as $[D^M, V^N]$. Experimental studies have been reported by Kienle et al. (1995) and Koggersbøl et al. (1996).

(b) Multiplicities can further be caused by the presence of energy balances in the $[L^N, V^N]$ configuration of ideal binary columns (Jacobsen and Skogestad, 1991). Type 1a multiplicities have also been shown for more complex distillation systems such as in multicomponent azeotropic or reactive distillation (Güttinger and Morari; 1997, 1999).

(2a) This type of output multiplicities is caused by the underlying reactive or nonreactive VL(L)E and also occurs for CMO conditions. The existence of output multiplicities caused by the nonreactive VL(L)E was studied by Bekiaris et al. (1993) for homogeneous and by Bekiaris et al. (1996) for heterogeneous mixtures (∞/∞ analysis). These multiplicities have been verified experimentally for a ternary homogeneous and a heterogeneous system (Güttinger et al., 1997; Müller and Marquardt, 1997; Dorn et al., 1998).

Note that the forth type (2b) only occurs in reactive distillation (Güttinger and Morari, 1999).

Motivation and goals

This work mainly studies output multiplicities of type 2a in *heterogeneous* azeotropic distillation. Browsing through the literature, one can group the reports on MSS in heterogeneous columns into two basic categories.

On the one hand, many groups have reported numerical simulation results related to multiple steady states. In almost all these studies, however, the main focus was not multiplicity of steady states, but, for example, design, modeling, simulation, and/or operation of heterogeneous azeotropic columns. Frequently, the reports on the existence of multiplicities for heterogeneous systems of the same thermodynamic class are quite contradictory, sometimes even for identical mixtures. These contradictions will be traced back not to the use of erroneous methods, but to different assumptions and mainly, to differences or anomalies in the underlying thermodynamics.

On the other hand, there is the ∞/∞ analysis for heterogeneous azeotropic columns by Bekiaris et al. (1996). It provides a simple physical explanation as well as graphical prediction methods for the occurrence of type 2a multiplicities based solely on the vapor-liquid-liquid equilibrium (VLLE) of the heterogeneous mixture. However, Bekiaris and coworkers did not compare their results to the literature simulation results.

The implications of output multiplicities for distillation design, simulation, and operation are numerous and can be critical for design decisions (Bekiaris and Morari, 1996). Therefore, comparing the mentioned simulation and analytical results is very important. Consequently, this study has the following objectives: (1) to compare the reported simulation results where possible, or to point out why the results cannot be compared in a meaningful manner; (2) to identify the physical causes of the reported multiplicities by application of the ∞/∞ analysis and by comparing the simulation results to the ∞/∞ predictions where possible; (3) to suggest guidelines how MSS could best be investigated in heterogeneous azeotropic distillation by analysis, simulation and experiments. Importantly, *it is neither our aim to criticize any of the earlier studies*, nor to give a review on MSS in azeotropic distillation, for which the reader is referred to Güttinger (1998).

Selected literature reports on MSS in heterogeneous azeotropic distillation are briefly summarized. The main prediction tools and outcomes of the ∞/∞ analysis are reviewed, since they serve as a "standard for comparison" (directly comparing numerical results is often impossible). The vapor-liquid-liquid equilibrium (VLLE) of the heterogeneous mixture of ethanol(L), benzene(I) and water(H) is analyzed, that is, the available models and parameter sets. This mixture is referred to as the EWB system hereafter and was not only covered by most studies reported, but serves as an example to illustrate which features of thermodynamics need special care if one analyzes output multiplicities of type 2a in heterogeneous systems (caused by the VLLE). In a last part, the literature reports on output and state multiplicities are compared in detail.

Reported Multiplicities

The first reports on the existence of output multiplicities in distillation were published on the ternary EWB system. From simulations, Shewchuk (1974) stated: "It was also found that the dehydration tower converged to two different steady states depending on the starting guesses. Both of these solutions [...] satisfied the highly nonlinear equations." At that time, the phenomenon looked quite awkward and its existence was opposing the wide-spread belief that distillation models possess a globally asymptotically stable singular point. This belief was shown to be unjustified by Doherty and Perkins (1982). Shewchuk considered bad thermodynamic data to be responsible for his observation.

Next, Magnussen et al. (1979) studied the EWB system and presented simulation results that show the existence of three steady states (two of them stable and one unstable). They used a special column setup without phase splitter which will be described in detail later. Magnussen and coworkers report the liquid composition profiles of all three steady states to lie entirely in the single liquid-phase region (homogeneous profiles), only the overhead vapor forms two liquid phases after condensation. It is noteworthy that the multiplicities were observed with the UNIQUAC and NRTL activity coefficient models, but not using the Wilson model. This was the first indication that the existence of MSS depends on thermodynamic models and parameters. Magnussen et al.'s results triggered great interest in distillation multiplicities. The belief that heterogeneity of the mixture was a possible cause for such MSS directed the attention towards heterogeneous azeotropic distillation. Consequently, several simulation studies were published where multiplicities for the EWB mixture and other heterogeneous systems were reported.

Using a similar column as Magnussen and coworkers, and the NRTL activity coefficient model, Prokopakis et al. (1981) verified the three operating ''regimes'' of Magnussen et al. (1979) for the EWB mixture, but not steady-state multiplicity. For a mixture of isopropanol, water and cyclohexane, they reported two steady states for a specific case to be discussed in this work, which does not correspond to an ''open-loop'' output multiplicity as defined above.

Hereafter, simulation models started to directly include the decanter in the calculations, and the effect of closing the entrainer balance to multiplicities was studied. Prokopakis and Seider (1983a,b) again verified the three operating regimes of Magnussen et al. (1979) but not the multiplicity (UNIQUAC model). Kovach III and Seider (1987a,b) presented simulation (homotopy-continuation) and experimental results for the mixture secondary-butanol-water-disecondary-butyl ether. Although no multiplicities were found in the study, the authors located two steady states over a narrow range of the reflux ratios (parametric sensitivity). They conclude that the observations in the simulation are consistent with the experimentally observed erratic behavior of the distillation tower. By homotopy-continuation for the EWB mixture, five steady states were found for the same specifications for a column without a decanter and three steady states for a column with a decanter. Their results demonstrate the importance of considering the exact type of equipment for the prediction of heterogeneous MSS.

In the following years, more continuation studies were performed to examine output multiplicities: Venkataraman and Lucia (1988) studied the EWB column of Prokopakis and Seider (1983a) and found three steady states over a narrow range of the bottoms flow rate. Kingsley and Lucia (1988) showed for the same column that there is a minimum tray efficiency where the multiplicity disappears. However, these steady states were calculated ignoring the liquid-phase split on a tray. If the phase split is considered, all three profiles ''ultimately lead to the same heterogeneous solution'' and, thus, no heterogeneous multiplicities were shown. Widagdo et al. (1989) used the aqueous reflux ratio as a continuation parameter for the mixture secondary-butanol-water-disecondary-butyl ether, which was also studied by Kovach III and Seider (1987a,b). They found three steady states over a narrow range of aqueous reflux ratios—a multiplicity where the top tray exhibits a second liquid phase.

Cairns and Furzer (1990) study the multiplicities reported by Magnussen et al. (1979), but used the UNIFAC model to describe the liquid-phase behavior of the EWB mixture. The existence of three steady states (output multiplicities) was verified, but two of them were only obtained by ignoring the liquid-phase split on the column trays. Hence, Cairns and Furzer concluded that these two profiles are fictitious. Rovaglio and Doherty (1990) studied the EWB system in columns with and without a decanter, as well as for different sets of parameters and the UNIQUAC model. They found three steady states for all parameter sets (including those used by Magnussen et al. (1979) and Prokopakis and Seider (1983a,b)) through dynamic simulations.

Bossen et al. (1993) also studied the heterogeneous EWB mixture for a column with a decanter and for the UNIFAC model. The found output as well as state multiplicities, and their results are in good agreement with the results of Rovaglio and Doherty (1990). Rovaglio et al. (1993) verified the existence of MSS reported by various groups for the EWB system through dynamic simulations. They offered an explanation for the multiplicities reported by Rovaglio and Doherty (1990) based on the observation that the entrainer inventory in the stripping section is different for the three solutions reported. Although these steady states satisfy the convergence criteria applied, ''there may be small differences in the necessary makeup flow rates needed to keep these states constant and stable.'' Therefore, they concluded that (1) the three solutions are not real multiplicities, but one real (converged) solution and two ''pseudo'' solutions caused by insufficiently tight convergence criteria, and (2) that ''the problem of MSS seems to be associated with the numerical aspects related to the relative small amount of feed makeup.''

Müller and Marquardt (1997) performed experiments on a mixture of ethanol, water, and cyclohexane. They tracked two branches of stable solutions whose compositions compare favorably to the results obtained from the steady-state simulations. Moreover, they report dynamic measurements of the hysteresis behavior induced by the existence of MSS.

Sridhar (1996, 1997) studies the uniqueness of the steady state for zeotropic heterogeneous mixtures and some theoretical column specifications.

∞/∞ Analysis

Preliminaries

The ∞/∞ analysis for single nonreactive columns was formulated by Bekiaris et al. (1993) for homogeneous, and by Bekiaris et al. (1996) for heterogeneous mixtures. It is based on the limiting case of distillation columns with an infinite number of equilibrium stages (an infinite number of trays or infinite column length) operated at infinite internal flows (infinite reflux and boilup). This limiting case was introduced by Petlyuk and Avet'yan (1971) and is denoted as the ''∞/∞ case'' hereafter. Petlyuk and coworkers first used the ∞/∞ case for the prediction of output multiplicities for two classes of homogeneous mixtures (Petlyuk and Avet'yan, 1971; Petlyuk and Serafimov, 1983).

The attractiveness of the ∞/∞ case is based on the fact that it is possible to derive necessary and sufficient conditions for the feasibility of steady-state column profiles (Bekiaris et al., 1993, 1996). These conditions are based on two widely used tools: the simple distillation *residue curves* (Ostwald, 1900; Schreinemakers, 1901; Doherty and Perkins, 1978; Pham and Doherty, 1990) and the equilibrium *distillation lines* (Zharov, 1968; Zharov and Serafimov, 1975; Stichlmair et al., 1989). Refer to the review of Widagdo and Seider (1996) and to the literature mentioned for a detailed description of these tools and their application to column profiles.

In the diagrams presented hereafter, the lines are directed towards increasing temperature. The definitions of distillation regions, distillation boundaries, as well as the conventions of Bekiaris et al. (1996) are used throughout this work. Unless stated otherwise, we use the following convention to refer to a given mixture: L (I, H) corresponds to the component which has the lowest (intermediate, highest) boiling point. The locations of the feed, distillate, bottoms, reflux and overhead vapor in the composition triangle are denoted by *F*, *D*, *B*, *L* and *V*, respectively.

∞/∞ Predictions

In this section, the main results of the ∞/∞ analysis for heterogeneous azeotropic distillation columns are briefly summarized. These so-called "∞/∞ predictions" were developed by Bekiaris et al. (1996), and the reader interested in the details is referred to that article.

∞/∞ Bifurcation Analysis. Any heterogeneous two-product distillation column of given design with given feed composition, flow rate, and quality, as well as a given decanter policy, has two operational degrees of freedom. In the ∞/∞ case, however, the reflux is given to be infinite and, therefore, there is only one degree of freedom remaining. Hence, all feasible ∞/∞ column profiles can be parameterized with this single degree of freedom. Here, the molar distillate flow rate D^N is selected.

In order to find whether MSS can occur, that is, whether different column profiles correspond to the same value of D^N, all possible composition profiles are tracked in the composition simplex, starting from the column profile with $D^N = 0$ and ending at the profile with $D^N = F^N$ (the molar feed flow rate). That is, a continuation of solutions (bifurcation study) is performed using the distillate flow rate as the bifurcation parameter—a procedure which can be done using only graphical arguments. The resulting column profiles define the "continuation path."

Feasible Product Paths. Next, the feasible compositions of the column products have to be located for each of the profiles found, as described by Bekiaris et al. (1996), utilizing the information about the equipment at the top and the bottom of the column. The resulting paths of the product locations can be depicted in the composition space and will be denoted as the "product paths" hereafter.

Existence of Type 2a MSS. By plotting a product composition vs. the distillation flow rate, a bifurcation diagram is obtained (Figure 1). If the distillate is varying nonmonotonically along the continuation path as defined above, MSS will exist in the ∞/∞ case of a column and for the feed studied. The location of the limit (turning) points and the multiplicity interval (interval of the operating parameter where MSS exist) can be read from the bifurcation diagram.

Geometrical, Necessary and Sufficient, Multiplicity Condition. In general, the existence of MSS in the ∞/∞ case of a column with given feed can be determined by the geometrical, necessary, and sufficient multiplicity condition. By this, MSS are predicted based on the structural properties of the VL(L)E diagram; what is meant by structural properties is not necessarily the detailed VL(L)E description, but, in most cases, the character and location of the singular points, the location of boundaries, and of the two-liquid phase region for heterogeneous mixtures.

MSS Feed Region. Bekiaris et al. (1996) describe a graphical procedure to construct the region of feeds which will lead to MSS in the ∞/∞ case ("the MSS feed region") in great detail.

Bekiaris et al. (1996) further reported an infinite number of feasible ∞/∞ column profiles for the cases of heterogeneous tray columns without decanter and of heterogeneous tray and packed columns with decanter. There, the heterogeneity of the mixture allows for an infinite number of profiles connecting a pure component corner with a specific overhead vapor composition on the heterogeneous vapor line—and the profiles exhibit different top liquid compositions on the same tie line. Bekiaris and Morari (1996) extended the ∞/∞ predictions, which originally were developed for ternary mixtures, to cover systems with four components.

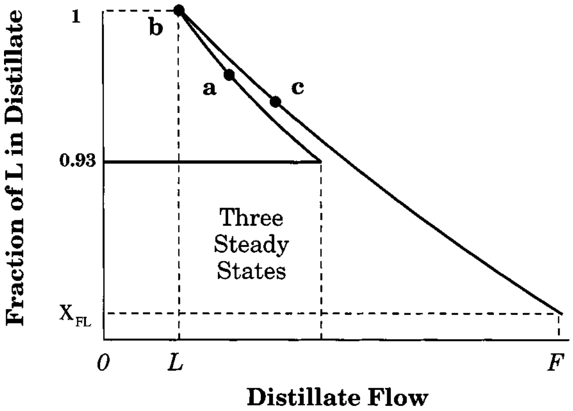

Figure 1. Example bifurcation diagram (001-class mixture according to the classification of Matsuyama and Nishimura (1977)) showing the light component mol fraction in the distillate as a function of the distillate flow.

The ∞/∞ case is the limiting case of high internal flows and a large number of equilibrium stages. Therefore, if the geometrical condition is fulfilled for a feed location, MSS will exist for some sufficiently large finite reflux and for a large, but finite, number of stages. However, the operating conditions where the multiplicities vanish cannot be predicted by the analysis. Nevertheless, MSS have been shown to exist at realistic operation conditions, that is, for small reflux flow rates, and experimentally (Güttinger et al., 1997; Müller and Marquardt, 1997). Even though the geometrical multiplicity condition is necessary and sufficient for output multiplicities in the ∞/∞ case, it is only sufficient for finite columns, that is, there may be multiplicities in finite columns which cannot be explained by the ∞/∞ analysis—for example, MSS caused by heat effects, type 1b (Jacobsen and Skogestad, 1991).

VLLE Predictions and Inaccuracies

Multiple steady states of type 2a are caused by the VL(L)-Equilibrium. Thus, it is important that the thermodynamic representation used for the prediction or simulation of a column adequately captures all major features which affect the existence of MSS (as existence and location of azeotropes or extent of the liquid-phase split, see the previous section). If there are inaccuracies in the representation, it is very well possible that multiplicities can be affected qualitatively and quantitatively. In the worst case, multiplicities predicted using one representation of thermodynamics could not exist in practice, or, one is surprised by problems caused by the presence of MSS even though the simulation did not provide evidence of their existence. Therefore, the thermodynamic mod-

Table 1. Antoine Coefficients for the Components, Ethanol, Benzene and Water (Gmehling and Onken, 1977)

Component	A_i	B_i	C_i
Ethanol	12.0455965	−3,667.705	−46.966
Benzene	09.2080465	−2,755.642	−53.989
Water	11.9514465	−3,984.923	−39.724

els and the parameter sets used play a critical role; likewise, the selection of adequate experimental data and the fitting methods applied to generate the thermodynamic parameter set.

In this section, frequently used representations of the VLLE of the mixture of ethanol, water, and benzene are studied. This mixture was not only used in the majority of the studies mentioned, but serves here as an example to derive general conclusions, which then can easily be applied to other systems as well. Moreover, the implications of the representations described hereafter on the existence of MSS are important to know when it comes to comparing multiplicities reported in the literature using these representations.

The calculations of the mixture's VLLE at atmospheric pressure were conducted with many different programs, including Aspen Plus (1995). Very good agreement between the results of the different programs was obtained. From experience reported in the literature for this mixture and from previous calculations (Bekiaris et al., 1996), the vapor phase can be assumed to behave ideally (following Dalton's Law). Therefore, the models for describing the liquid-phase nonidealities, that is, the activity coefficient model in our case, are of special importance in the VLLE calculations.

Here, liquid activity coefficients are computed by the modified UNIQUAC model, which is the most widely used in the articles reporting multiplicities. The model was taken from Prausnitz et al. (1986) (Eqs. 6.11-11−6.11-22 and 6.15-9−6.15-12). Note that the UNIQUAC binary parameters a_{ij} reported in this article are the ones used in Eq. 6.11-17 in Prausnitz et al. (1986) with unit K. If Aspen Plus (1995) is to be used for the VLLE calculations, the negative of the binary parameter values reported here must be provided.

Pure component vapor pressures are computed by the Antoine Equation

$$\ln\left(p_i^0\right) = A_i + \frac{B_i}{T + C_i} \tag{1}$$

where the temperature T is measured in Kelvin and the pressure in Pa. Table 1 contains the Antoine coefficients reported by Gmehling and Onken (1977) for the components ethanol, benzene, and water.

In the following, the different sets of UNIQUAC parameters used in the literature, their implications on the prediction of the VLLE, as well as on the existence of MSS (by means of the ∞/∞ predictions), are discussed.

Experimental azeotropic data

We start with the presentation of experimental evidence on the location and type of the azeotropes from the book of Gmehling et al. (1994). Table 2 summarizes the reports for the EWB mixture at atmospheric pressure. For the three binary azeotropes, the total number of literature references is listed together with the interval of molar compositions where the azeotropes are reported. There are 44 literature references all reporting a minimum-boiling, homogeneous azeotrope between ethanol and water. The most frequent value reported by 21 experimental studies was taken for the nominal composition (89.4 mol % ethanol), which is also consistent with Norman (1945). Next, there are 24 references reporting the ethanol-benzene azeotrope to be minimum-boiling and homogeneous. It is located at 44.9 mol % ethanol (13 references), a value also contained in Horsley (1973). The minimum-boiling benzene-water azeotrope is heterogeneous and located at 70.4 mol % benzene (in half of the eight references). Finally, there are four reports on the ternary EWB azeotrope, which all report a minimum-boiling heterogeneous azeotrope at the same composition shown in Table 2.

Therefore, the EWB mixture belongs to the 222-m class according to the classification of Matsuyama and Nishimura (1977), that is, there are three binary minimum-boiling saddle azeotropes and a ternary minimum-boiling heterogeneous node. In conclusion, there is a satisfactory amount of experimental evidence clearly reporting location and types of the four azeotropes of the EWB system.

Gmehling and Onken (1997)

Table 3 contains the pure component UNIQUAC parameters R_i, Q_i, and Q_i', and the UNIQUAC binary parameters a_{ij} in K for the mixture ethanol, water, and benzene from Gmehling and Onken (1977). Note that $Q_i' = Q$. In the multiplicities-related literature, this set of parameters was first reported by Prokopakis and Seider (1983b). The Gmehling and Onken (1977) *binary parameters* a_{ij} from Table 3 also appear in Widagdo et al. (1989) (multiplied with the gas constant $R = 1.98719$ cal/(mol K)). Note that the pure component UNIQUAC parameters in Table 1 of Widagdo et al. (1989) are *not* the parameters given by Gmehling and Onken (1977) (Table 3), but the ones by Prausnitz et al. (1980).

Table 4 shows the azeotropes predicted by this parameter set. The distillation line diagram and the two liquid-phase

Table 2. Experimental Data on the Location and Types of Azeotropes in the EWB System at 1 atm (Gmehling et al., 1994)

Mixture	Total Refs.	Interval Mol Fraction	No. of Refs.	Nominal Mol Fraction	Type
Ethanol-Water	44	0.890−0.905 E	21	0.894 E	min., homog.
Ehtanol-Benzene	24	0.438−0.464 E	13	0.449 E	min., homog.
Benzene-Water	08	0.700−0.705 B	04	0.704 B	min., heterog.
Ternary EWB			04	0.228 E 0.539 B	min., heterog.

Table 3. UNIQUAC Unary and Binary Parameters from Gmehling and Onken (1977) for the EWB Mixture

Unary Parameters			
Component	R_i	Q_i	Q'_i
Ethanol	2.1055	1.972	1.972
Benzene	3.1878	2.400	2.400
Water	0.9200	1.400	1.440

Binary Interaction Parameters		
Components		a_{ij} [K]
Ethanol	Benzene	−156.567
Benzene	Ethanol	850.609
Ethanol	Water	110.010
Water	Ethanol	200.054
Benzene	Water	1,072.790
Water	Benzene	428.452

boiling envelope are calculated with Aspen Plus (1995), and are shown in Figure 2. The three interior boundaries connecting the azeotropes cut the composition space into three distillation regions. All distillation lines start from the ternary azeotrope and end at one of the pure component corners. There are two major discrepancies listed below between the predictions in Table 4 and the experimental measurements from Table 2.

It is predicted that the binary mixture ethanol-benzene exhibits a region of immiscibility, and that the corresponding binary azeotrope is heterogeneous. The heterogeneous envelope is distorted and extends to the ethanol-benzene binary edge (Figure 2). This discrepancy was first reported by Prokopakis and Seider (1983b), who consequently abandoned the Gmehling and Onken (1977) parameters in favor of those by Prausnitz et al. (1980). Rovaglio and Doherty (1990) reconfirmed this erroneous prediction. In addition, the predicted composition of the ethanol-water azeotrope (69.83 mol% ethanol) is far from the "experimental interval" 89.0—90.5 mol %.

The distorted two liquid-phase envelope is also responsible for the occurrence of numerical errors in the calculation of the composition of the benzene-rich liquid phase using Aspen Plus (1995) (VLLE calculations), even though the lowest possible tolerance was used. The reason is that mixtures in a very wide region of the water-rich liquid phase (roughly, for mixtures on the heterogeneous envelope with benzene mol fractions between 0.02 and 0.45) are in equilibrium with (1) vapor compositions close to the ternary azeotrope and (2) benzene-rich liquid-phase compositions restricted to the binodal close to pure benzene (Figure 2). Therefore, the vapor line close to the ternary azeotrope and, consequently, the distillation line boundaries in the neighborhood of the ternary azeotrope cannot be calculated reliably.

Table 4. Predicted Azeotropes at 1 atm for the EWB Mixture Using UNIQUAC with Parameters from Gmehling and Onken (1977)

Azeotropes		
Mixture	Mol Fraction	Type
Ethanol-Water	**0.6983 E**	Homogeneous
Ethanol-Benzene	0.3771 B	**Heterogeneous**
Benzene-Water	0.7042 B	Heterogeneous
Ternary EWB	0.2525 E 0.5275 B	Heterogeneous

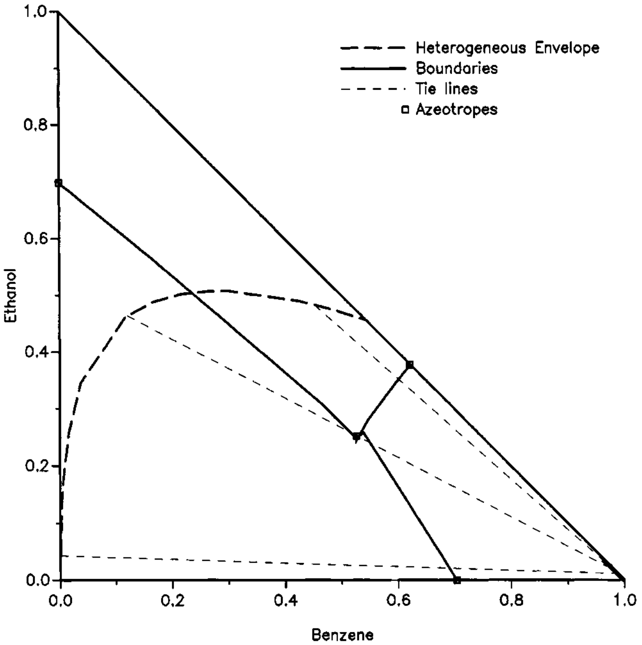

Figure 2. Computed distillation line diagram and LLE of the EWB mixture at 1 atm using the Gmehling and Onken (1977) UNIQUAC parameters (Table 3).

Because of the mentioned discrepancies in the VLLE predictions and the uncertainties regarding the VLLE calculations in a wide range of the two-liquid phase region, the ∞/∞ analysis will not be performed using the Gmehling and Onken (1977) parameter set for *columns without decanter*, where the exact shape of the vapor line plays a critical role (Bekiaris et al., 1996).

For *columns with decanter* and the decanter policy to remove a portion of the water-rich phase as distillate, while a mixture of the two liquid phases is used as reflux, the ∞/∞ analysis predicts output multiplicities. Three steady states are predicted for all feeds located in the shaded region of Figure 3 (the MSS feed region is established from the LI edge by straight connections to the two points on the envelope). The predictions are similar to the ones by Bekiaris et al. (1996) using another parameter set (described later). The former do not take into consideration the shape of the boundaries close to the ternary azeotrope because of the numerical errors. Instead, the ∞/∞ predictions are based on the simplification that each of the boundaries (T-X, T-Y and T-Z) does not cross a tie line more than once. Our computations show a violation close to the ternary azeotrope, which may be by the numerical errors mentioned. However, only minor, if any, changes are expected for the MSS feed region: there may exist more than three steady states for some feed compositions and some narrow range of product flow rates.

In conclusion, the parameter set of Gmehling and Onken (1977) should not be used in VLLE calculations, because it does not adequately describe the fundamental characteristics

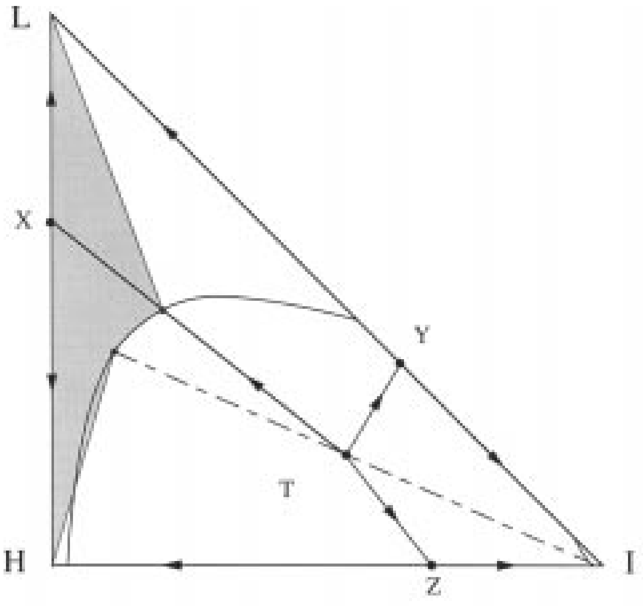

Figure 3. VLLE diagram of the EWB mixture using the Gmehling and Onken (1977) UNIQUAC parameters (Table 3).

Region of feeds leading to multiple steady states in the ∞/∞ case of a column with the decanter.

of the EWB mixture. Therefore, it is not possible to make reliable predictions on the existence of MSS, which should be robust against any inaccuracies and uncertainties as found for this parameter set.

Prausnitz et al. (1980)

Table 5 shows the UNIQUAC pure component and binary parameters by Prausnitz et al. (1980) for the EWB mixture. Note that $Q' \neq Q$. This set of parameters was first used by Prokopakis and Seider (1983b) and does not appear in Widagdo et al. (1989) (multiplied by the gas constant). Table 6 shows the azeotropes predicted by the Prausnitz et al. (1980) parameter set. This parameter set is widely used in the literature since the binary ethanol-benzene azeotrope is correctly predicted to be *homogeneous*, in contrast to the erroneous heterogeneous azeotrope resulting from Gmehling and Onken (1977).

Table 5. UNIQUAC Unary and Binary Parameters from Prausnitz et al. (1980) for the EWB Mixture

Unary Parameters			
Component	R_i	Q_i	Q'_i
Ethanol	2.11	1.97	0.92
Benzene	3.19	2.40	2.40
Water	0.92	1.40	1.00

Binary Interaction Parameters		
Components		a_{ij} [K]
Ethanol	Benzene	−149.34
Benzene	Ethanol	1131.13
Ethanol	Water	−163.72
Water	Ethanol	573.61
Benzene	Water	2057.42
Water	Benzene	115.13

Table 6. Predicted Azeotropes for the EWB Mixture at 1 atm Using UNIQUAC with Parameters from Prausnitz et al. (1980)

	Azeotropes	
Mixture	Mol Fraction	Type
Ethanol-Water	**No Azeotrope**	Homogeneous
Ethanol-Benzene	0.4284 E	Homogeneous
Benzene-Water	0.7050 B	Heterogeneous
Ternary EWB	0.2361 E 0.5589 B	Heterogeneous

Figure 4 shows the distillation line diagram and LLE computed using Aspen Plus (1995). There are only *two* binary minimum-boiling azeotropes in addition to the ternary heterogeneous azeotrope, and the ethanol-water azeotrope is missing. Consequently, there are two distillation regions, and two interior boundaries, and all distillation lines start from the ternary azeotrope and end at the pure water or benzene corners. The pure ethanol corner is a saddle singular point in this distillation line diagram.

This result is quite surprising, but becomes less unexpected, if one goes back to the "roots" and examines the sources used for the estimation of these parameters: the experimental data (Anderson and Prausnitz, 1978; Prausnitz et al., 1980, 1986). The objective of Prausnitz and coworkers was to derive a set of parameters that provide good prediction of the *liquid-liquid equilibrium* (LLE). More specifically, the parameter set they proposed (Table V-6, page 543 of Prausnitz et al. (1986)) is based on fitting the UNIQUAC model to the following experimental data: (1) ethanol-water isothermal

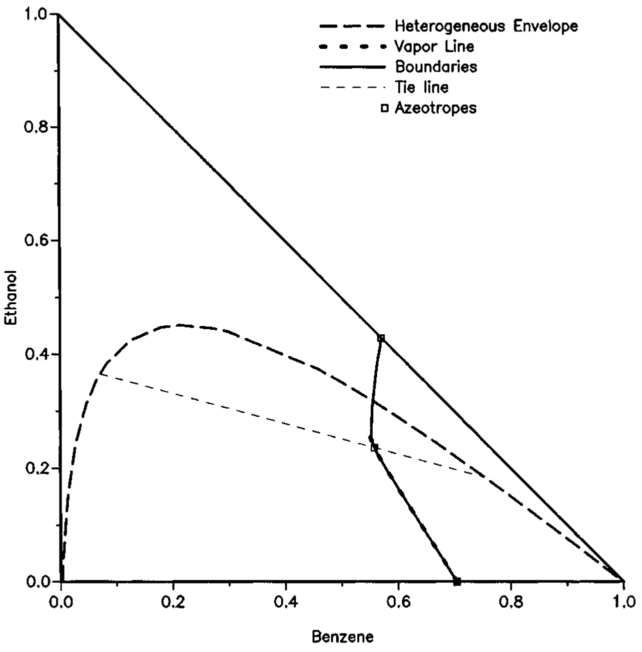

Figure 4. Computed distillation line diagram and LLE of the EWB mixture at 1 atm using the Prausnitz et al. (1980) UNIQUAC parameters (Table 5).

VLE data at 40°C; (2) ethanol-benzene isothermal VLE data at 45°C; (3) a single ternary tie line at 25°C. The predictions of the model with the parameter set resulting from the fit are tested by comparing the calculated results with more experimental data of tie lines at 25°C. Prausnitz et al. (1980) show that by including the single ternary tie line, the prediction of the LLE is improved at the cost of "a small loss of accuracy in the representation of the VLE for the two binary systems."

First, note that the experimental data were obtained 20−75°C away from VLLE temperatures at 1 atm. Therefore, using this parameter set for atmospheric VLLE calculations involves "extrapolation" of a highly nonlinear model, which requires extreme care. Secondly, the primary scope of Prausnitz and coworkers was the good prediction of the LLE at 25°C. Although a good description of the VLE is desirable, it was clearly of secondary importance. Using parameters obtained from a fit based on the binary VLE data (without the tie line), Figure 3 of Anderson and Prausnitz (1978) (or Figure 4−16 of Prausnitz et al. (1980)) shows a good agreement between predicted VLE and experimental data. By including the tie line for the fit, however, the resulting parameter set used by Prausnitz et al. (1980) does not predict an ethanol-water azeotrope at 40°C, a result which is consistent with our computations of the isothermal VLE using this parameter set. However, according to all three literature references listed in Gmehling et al. (1994), there exists a minimum-boiling azeotrope at 40°C.

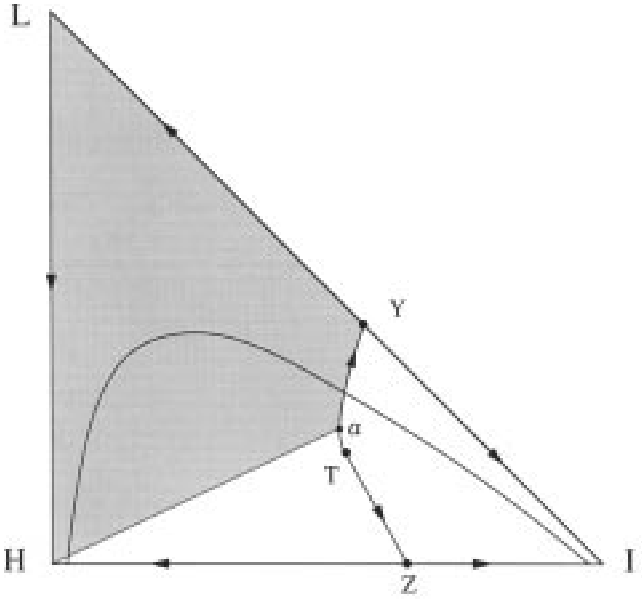

Figure 5. VLLE diagram of the EWB mixture using the Prausnitz et al. (1980) UNIQUAC parameters (Table 5).

Region of feeds leading to multiple steady states in the ∞/∞ case of a *Column without the decanter*.

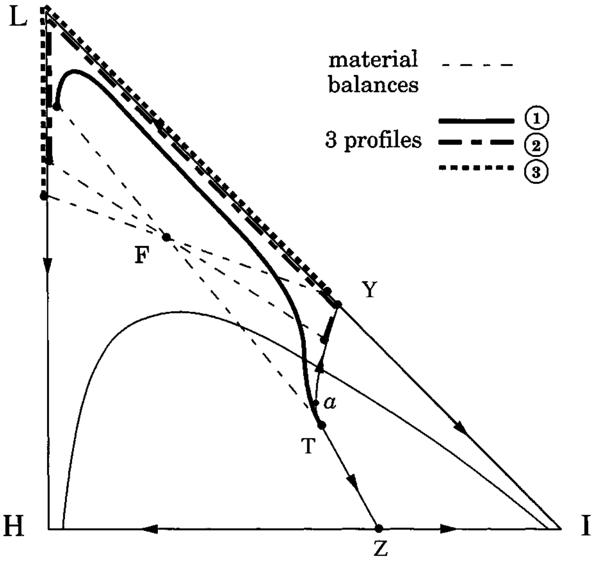

Figure 6. VLLE diagram of the EWB mixture using the Prausnitz et al. (1980) UNIQUAC parameters (Table 5).

Three steady-state profile with the same product flow rates in a *column without the decanter* (multiple steady states).

Therefore, based on the VLLE predictions shown in Figure 4, we conclude that the parameter set by Prausnitz et al. (1980) does not adequately describe the fundamental characteristics of the EWB mixture at atmospheric pressure and, thus, it should not be used in VLLE calculations (even though it is appropriate for the purpose it was obtained for: LLE calculations). However, since this set has been widely used in the literature and multiplicities have been reported using this set, ∞/∞ predictions will nevertheless be performed based on the distillation line diagram in Figure 4. Note that a somewhat distorted version of Figure 4 is used in the following for clarity: Figure 5.

For *columns without the decanter*, only the distillation line boundaries (TY and TZ in Figure 5) are needed for applying the ∞/∞ analysis. Point *a* in Figure 5 is defined as the point of the TY boundary where the tangent to the boundary is parallel to the LH edge. Note that two neighboring saddle singular points (azeotrope Y and pure ethanol L) exist in this diagram, which leads to the existence of MSS in this case, since the ∞/∞ geometrical condition is fulfilled for the path from *a* over Y and L to H (Bekiaris et al., 1996). The shaded region in Figure 5 (bounded by the mentioned path) reflects the feed composition region that leads to MSS. Note that these multiplicities do not exist if the diagram reflects the real EWB mixture including the ethanol-water (LI) azeotrope (the geometrical condition could not be fulfilled). Hence, the ∞/∞ analysis provides knowledge how a distillation experiment could be performed in order to test if a particular thermodynamic description corresponds to the real situation (Güttinger, 1998). Finally, Figure 6 illustrates *three* steady state profiles with the same distillate flow *D*.

For *columns with the decanter* and a decanter policy where a portion of the water-rich phase is taken as the distillate while a mixture of the liquid phases is used as reflux, the ∞/∞ analysis predicts homogeneous and heterogeneous multiplicities. In Figure 7 let *bc* be the tie line that passes through the ternary azeotrope *T*, *e* the point where the heterogeneous envelope intersects the boundary TY and *ed* the corresponding tie line. By application of the ∞/∞ geometrical condition, it is easy to show that the distillate flow rate decreases along the continuation path for distillate compositions located on the *bd* segment of the heterogeneous envelope, and bottoms

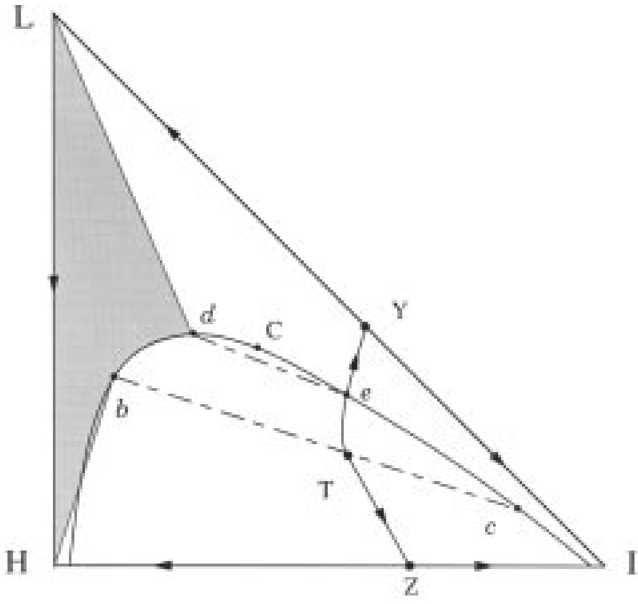

Figure 7. VLLE diagram of the EWB mixture-using the Prausnitz et al. (1980) UNIQUAC parameters (Table 5).

Region of feeds leading to two heterogeneous steady states in the ∞/∞ case of a *column with the decanter*.

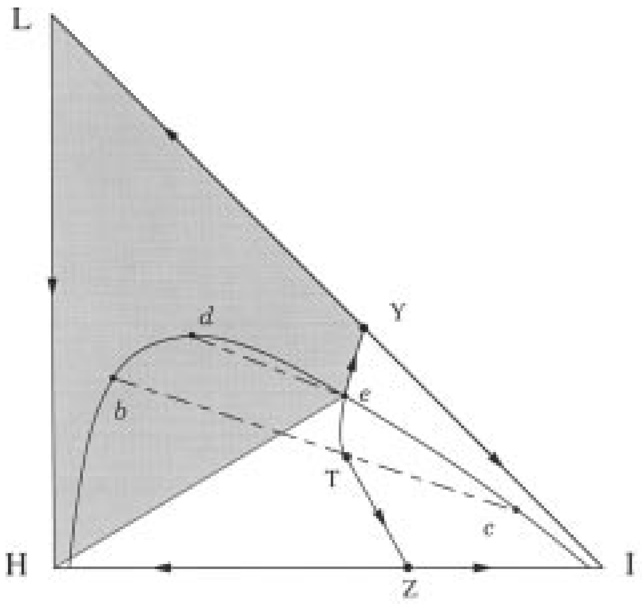

Figure 9. VLLE diagram of the EWB mixture using the Prausnitz et al. (1980) UNIQUAC parmeters (Table 5).

Region of feeds leading to *two homogeneous* steady states in the ∞/∞ case of a *column with the decanter*.

located at any point on the LH edge. The shaded region in Figure 7 depicts the feed composition region that leads to multiple (two) heterogeneous steady states (region bounded by L, H, *b* and *d*). Figure 8 illustrates two heterogeneous steady-state profiles with the same distillate flow rate *D*.

Note, though, that if the overhead vapor *V* of the column with decanter lies outside the two-liquid phase region, the column becomes identical to the column without decanter (since a single liquid phase exists in the decanter). Hence, the ∞/∞ predictions for columns without a decanter carry over to the columns with decanter if the distillate *D* is restricted to the single-liquid phase region. It is easy to show that for columns with decanter *two homogeneous* steady states are predicted for feeds located in the region enclosed by the straight lines YL, LH, He, and the *e*Y part of the boundary TY. The corresponding (homogeneous) MSS feed region is shaded in Figure 9 (H-*e*-Y-L), from which it is clear that it is part of the feed composition region that leads to three steady states for columns without a decanter, Figure 5. The two homogeneous profiles with the same distillate flow rate *D* for a column with decanter correspond to profiles 2 and 3 in Figure 6 of a column without a decanter. Note that column profiles analogous to profile 1 in Figure 6 are not feasible for columns with a decanter (*V* lies in the two-liquid phase region and according to the distillate policy, *D* must lie on the heterogeneous envelope).

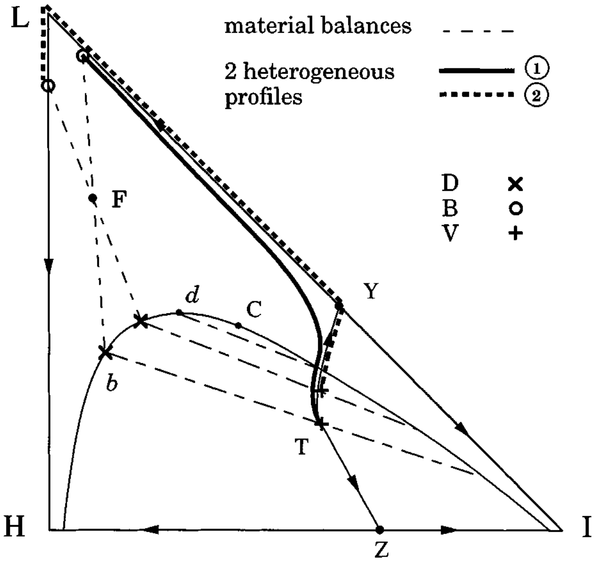

Figure 8. VLLE diagram of the EWB mixture using the Prausnitz et al. (1980) UNIQUAC parameters (Table 5).

Three-steady-state profile with the same product flow rates in a *column with the decanter* (multiple steady states).

For *columns with the decanter* and feeds in the intersection of the two feed regions shown in Figures 7 and 9, both heterogeneous and homogeneous multiplicities exist. However, this does not necessarily mean that for these feeds four steady states exist for the same distillate flow rate, because the heterogeneous and homogeneous distillate flow rate multiplicity intervals may not overlap, depending on the actual feed composition. Otherwise, two or three steady states exist for some interval(s) of the distillate flow rate.

Gmehling et al. (1981)

Gmehling et al. (1981) reported a new set of binary parameters in their update of the DECHEMA Chemistry Data Series on VLE. The pure component parameters are the same

Table 7. UNIQUAC Unary Parameters from Gmehling et al. (1981) for the EWB mixture

Binary Interaction Parameters		
Components		a_{ij} [K]
Ethanol	Benzene	-147.6769
Benzene	Ethanol	655.5251
Ethanol	Water	-10.8841
Water	Ethanol	91.1927
Benzene	Water	486.1731
Water	Benzene	388.7380

as the ones given by Gmehling and Onken (1977) in the upper part of Table 3. Table 7 lists the UNIQUAC binary parameter set from Gmehling et al. (1981) for the EWB mixture (converted to SI units, divided by the gas constant).

Table 8 shows the binary azeotropes predicted by the parameter set of Gmehling et al. (1981). Similarly to the set by Prausnitz et al. (1980), this set does not predict the ethanol-water azeotrope and, therefore, it does not adequately describe the EWB mixture and should not be used in VLLE calculations.

Some easy-to-make mistakes

In this section, curious phenomena are presented which result from a few easily made mistakes in using the parameters and models presented so far. Such mistakes lead to incorrect predictions which, amazingly enough, may look better (in some aspects) than the predictions with the correctly used parameters and models. Therefore, the predictions based on incorrect parameters and models may not alarm the user that some mistake was made, simply because these predictions are not worse than those from correct parameters and models.

One of these easily made mistakes is to mix up the units of the binary UNIQUAC parameters a_{ij}. Both cal/mol and K units are used in the literature and as defaults in commercial process simulators. Consider the case of the parameter set by Gmehling et al. (1981) where the values listed in the reference (in cal/mol) are not divided by R (to obtain K), and are used in the calculations as if their units were K. Table 9 shows the comparisons between the predicted binary azeotropes and the phase equilibria for the correctly and incorrectly used parameter set (note that the benzene-water azeotrope is not listed because predictions and experimental results are in very good agreement for both parameters sets).

As shown above, the correctly used parameter set does not predict the ethanol-water azeotrope, resulting in a fundamentally different distillation line diagram. For the incorrect parameter set, however, the ethanol-water binary azeotrope is predicted at 0.9131 mol fraction of ethanol, which is very close to the experimental range (0.890-0.905). Even though the ethanol-benzene azeotrope moved further away from the experimental range (0.438-0.464), the corresponding distillation line diagram is now qualitatively similar to the experimental one. From this example, it is clear that the predicted azeotropic information alone does not alarm the user that an incorrect parameter set is used. In contrast, the predictions using the correct set are more suspicious since the ethanol-water azeotrope is not predicted at all. However, the incorrect parameter set predicts a liquid-phase separation for the binary ethanol-benzene (similar to Figure 3), which contradicts the experimental observations.

Table 8. Predicted *Binary* Azeotropes for the EWB Mixture at 1 atm Using UNIQUAC with Parameters from Gmehling et al. (1981)

Azeotropes		
Mixture	Mol Fraction	Type
Ethanol-Water	**No Azeotrope**	Homogeneous
Ethanol-Benzene	0.3868 E	Homogeneous
Benzene-Water	0.6986 B	Heterogeneous

Table 9. Comparisons of Predicted Binary Azeotrope Composition and Types, as well as the Number of Liquid Phases for the Ethanol-Benzene Binary for Correctly and Incorrectly Used Parameter Sets at 1 atm

UNIQUAC Parameters	Ethanol-Water	Ethanol-Benzene	
	Azeotrope	Azeotrope	Binary
Gmehling et al. (1981) correct units of a_{ij}	**No azeotrope** homogeneous	0.3868 E homogeneous	Homogeneous
Gmehling et al. (1981) incorrect units* of a_{ij}	0.9131 E homogeneous	**0.2532 E** homogeneous	**Heterogeneous**
Prausnitz et al. (1980) correct values Q'	**No azeotrope** homogeneous	0.4284 E homogeneous	Homogeneous
Prausnitz et al. (1980) incorrect values* Q'	0.8754 E homogeneous	0.3953 E **heterogeneous**	**Heterogeneous**

*a_{ij} values as reported in Gmehling et al. (1981) with units assumed to be K instead of cal/mol.

†Q' values set equal to Q.

Another such mistake may happen when using sets with wrong values of Q or Q'. If the original UNIQUAC model were used instead of the modified UNIQUAC model, then one ignores that the Q' values are different from the Q values (setting Q' equal to Q), as shown here for the set by Prausnitz et al. (1980) in Table 5. Doing so is equivalent to using a mixed-source set of parameters, that is, using the binary UNIQUAC parameters by Prausnitz et al. (1980) and the pure component parameters by Gmehling and Onken (1977) (and, thus, erroneously forcing Q' to be equal to Q, compare Tables 3 and 5).

Table 9 shows the comparison between the predicted binary azeotropes and phase equilibria for the correctly and incorrectly used parameter set. Again, the incorrectly used parameter set predicts the ethanol-water azeotrope, which is missing using the set by Prausnitz et al. (1980), and a qualitatively correct distillation line diagram would be obtained. However, as before, liquid-phase separation including a heterogeneous azeotrope is predicted for the binary mixture ethanol—benzene (the VLLE and distillation line diagram are qualitatively similar to Figure 3). Therefore, it does not describe correctly the basic features of the mixture's VLLE.

Bekiaris et al. (1996)

The set of parameters by Bekiaris et al. (1996) consists of the pure component parameters from Gmehling and Onken (1977) (upper part of Table 3) and UNIQUAC binary parameters estimated from the UNIFAC model using the Aspen

Table 10. UNIQUAC Binary Parameters from Bekiaris et al. (1996) for the EWB Mixture

Binary Interaction Parameters		
Components		a_{ij} [K]
Ethanol	Benzene	−43.0334
Benzene	Ethanol	384.8920
Ethanol	Water	−32.9976
Water	Ethanol	203.8430
Benzene	Water	903.8000
Water	Benzene	362.3000

Plus (1995) property parameter estimation option. Table 10 contains the resulting binary parameters a_{ij} in K. Table 11 shows the azeotropes predicted by this parameter set, and Figure 10 shows the corresponding distillation line diagram and the LLE.

Note that the compositions of all three binary azeotropes lie in the experimental range (from Table 2) and have the correct type (homogeneous and heterogeneous). Moreover, the two-liquid phase region extends only to the benzene-water binary edge and the remaining two binaries are entirely homogeneous. One deviation is that the ternary azeotrope has a slightly higher ethanol composition than measured in the experiments (27 instead of 23 mol. %), that is, it is shifted toward pure ethanol in Figure 10. However, it is still heterogeneous as reported in the experiments. Nevertheless, this set captures the basic characteristics of the mixture's VLLE, in contrast to all the previously studied sets (Gmehling and Onken, 1977; Prausnitz et al., 1980; Gmehling et al., 1981).

Bekiaris et al. (1996) use the EWB mixture with the parameter set described here as an illustrative example throughout their study of multiplicities in heterogeneous azeotropic distillation. Refer to their article for the details regarding the ∞/∞ multiplicity predictions for various column designs. The main results are briefly summarized in the following.

For *columns without the decanter* (but, a total condenser), the existence of multiplicities critically depends on the location of the distillate path in the heterogeneous region and, consequently, in this case, the location of the vapor line and the column type (tray or packed) are of crucial importance. Note that we did not distinguish between tray and packed columns for the previously studied sets, because no qualitative difference was expected. The key feature that leads to multiplicities for tray columns is the geometry of the TX boundary in Figure 11 (which is replacing the computed distillation line diagram, Figure 10, for illustrative purposes). In the heterogeneous region, the TX boundary shows a "turn" from the left to the right (on the *ab* segment), that is, there are lines parallel to the LH edge which intersect the TX boundary more than once. This turn is caused by an analogous shape of the top end of the vapor line. Three steady states are predicted for tray columns with feeds in the shaded region of Figure 11 (with corners L, H, *a* and *b*), while a unique steady state exists for packed columns. Figure 12 illustrates three steady-state profiles with the same distillate flow rate D for a given feed F.

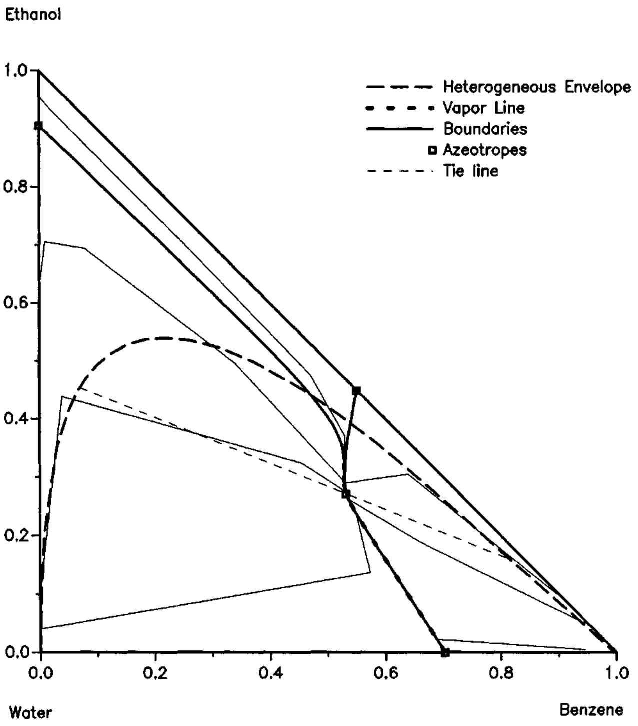

Figure 10. Computed distillation line diagram and VLLE of the EWB mixture at 1 atm using the Bekiaris et al. (1996) UNIQUAC parmeters (Table 10).

Table 11. Predicted Azeotropes for the EWB Mixture at 1 atm Using UNIQUAC with Parameters from Bekiaris et al. (1996)

Azeotropes		
Mixture	Mol Fraction	Type
Ethanol-Water	0.9053 E	Homogeneous
Ethanol-Benzene	0.4488 E	Homogeneous
Benzene-Water	0.7037 B	Heterogeneous
Ternary EWB	0.2712 E 0.5323 B	Heterogeneous

For *columns with the decanter* (where the distillate is a portion of the entrainer-poor phase only and a mixture of the two liquid phases is used as reflux), Bekiaris et al. (1996) concluded that the existence of MSS is generic for the whole heterogeneous mixture class, and, therefore, the presence of multiplicities does not critically depend on the some specific VLLE characteristic, as long as the basic qualitative structural properties of the VLLE diagram are preserved. Consequently, using tray or packed columns does not qualitatively affect the existence of MSS, although some minor quantitative differences are expected. In the following, the ∞/∞ predictions for packed columns are shown for illustrative purposes, because their column profiles in the heterogeneous region are better distinguished than for tray columns, where similar results hold.

Figure 13 shows a sketch of the residue curve boundaries, the heterogeneous envelope and one tie line. By applying the ∞/∞ geometrical condition, it is shown that the distillate flow rate decreases along the continuation path for distillate compositions located on the *ah* segment of the distillation path,

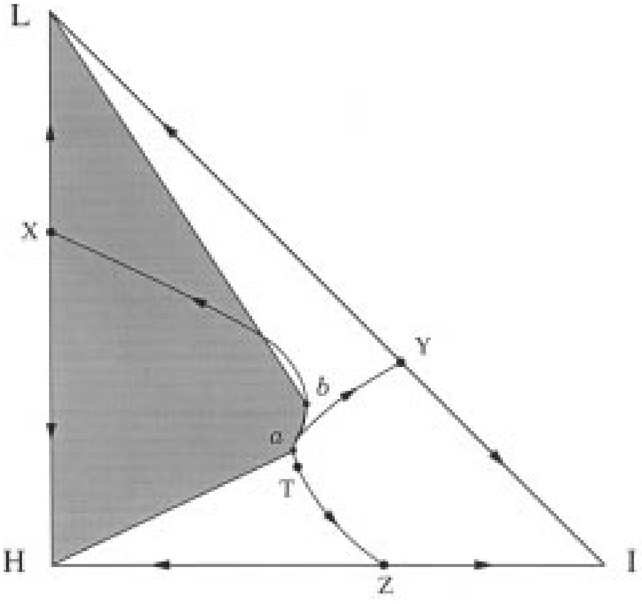

Figure 11. VLLE diagram (distillation line) of the EWB mixture using the Bekiaris et al. (1996) UNIQUAC parameters (Table 10).

Region of feeds leading to multiple steady states in the ∞/∞ case of a *tray column without decanter*.

and bottoms located at any point on the LH edge. Hence, the shaded region in Figure 13 (with corners L, H, *a* and *h*) depicts the feed composition region that leads to MSS in this case. Figure 14 illustrates three steady-state profiles (two heterogeneous and one homogeneous) with the same distillate flow rate *D*.

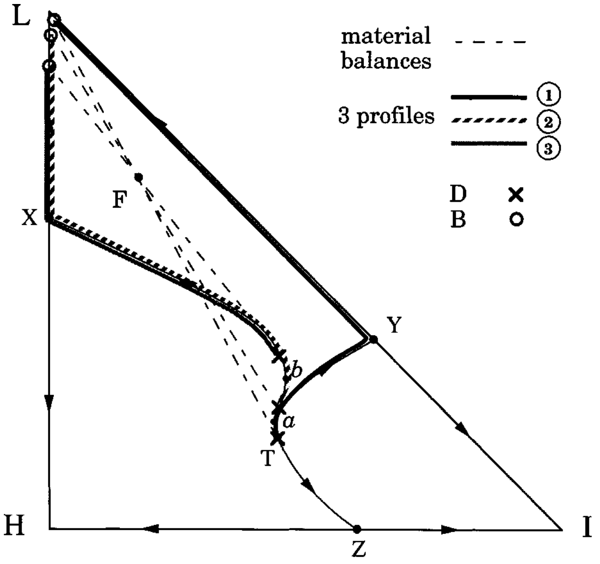

Figure 12. VLLE diagram (distillation line) of the EWB mixture using the Bekiaris et al. (1996) UNIQUAC parameters (Table 10).

Three steady-state profile with the same product flow rates in a *tray column without the decanter* (multiple steady states).

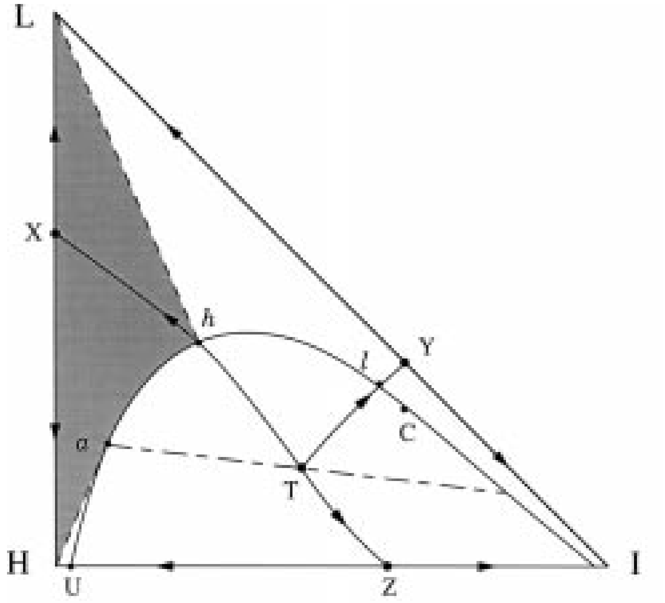

Figure 13. VLLE diagram (residue curve) of the EWB mixture using the Bekiaris et al. (1996) UNIQUAC parameters (Table 10) with all necessary information for the ∞/∞ predictions.

MSS feed region for *packed columns with the decanter*.

In summary, the parameter set by Bekiaris et al. (1996) captures the basic characteristics of the mixture's VLLE. Importantly, it was shown that some "details" of the VLLE may be critical for the existence of multiplicities in columns without decanter. In the following, we go one step further and make use of the main advantage of the ∞/∞ analysis over

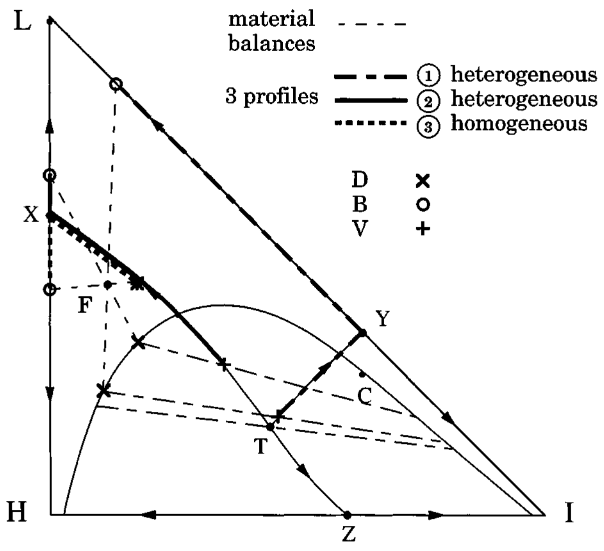

Figure 14. Distillation line diagram of the EWB mixture using the Bekiaris et al. (1996) UNIQUAC parameters (Table 10).

Three steady-state profile with the same product flow rates in a *packed column with the decanter* (multiple steady states).

numerical studies: that predictions can be obtained directly from experimental VL(L)E data (Bekiaris and Morari, 1996). Therefore, the available VLLE data for the EWB system are discussed in the next section.

Experimental VLLE data

Table 2 summarizes the experimentally observed azeotropes (at atmospheric pressure) based on the data by Gmehling et al. (1994), Horsley (1973), and Norman (1945). Figure 15 shows the location of the four azeotropes in the composition space, as well as the heterogeneous envelope, different tie lines, and the vapor line. Note that this figure contains all VLLE and LLE data (at atmospheric pressure) reported in Tables II and V by Norman (1945), although this data originate from different sources (discussed below).

Next, the experimental data are compared to the predictions using the set by Bekiaris et al. (1996). Despite the small deviation of the ternary azeotrope (from above), it can be seen that the experimental two-liquid phase region (Figure 15) is a bit smaller than the predicted one (Figure 10), and that the slopes of the experimental and predicted tie lines are different. The critical point predicted by the parameter set of Bekiaris et al. (1996) lies to the right of the TY boundary (point C illustrated in Figure 13); its benzene (I) mol fraction is approximately 0.6. The experimental critical point on the heterogeneous envelope in Figure 15 has a benzene mol fraction of approximately 0.2 (and, consequently, is on the left of the boundary that runs from the ternary azeotrope to the ethanol-water azeotrope).

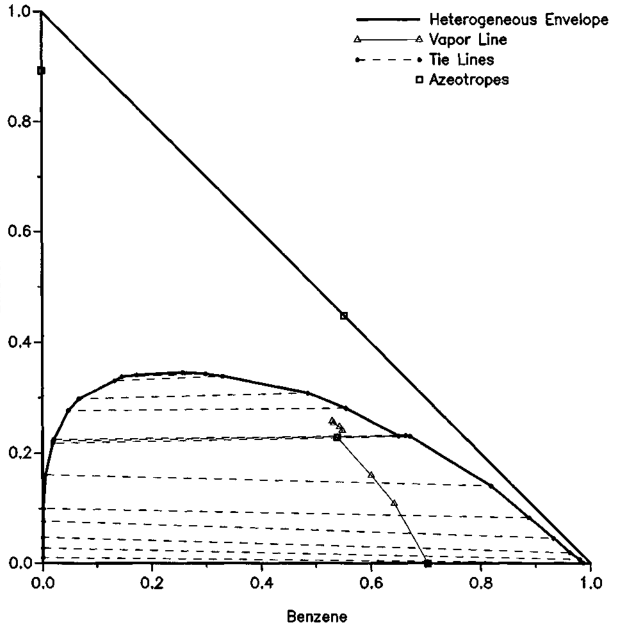

Figure 15. Experimentally reported azeotropes (Gmehling et al., 1994), as well as VLLE and LLE data (Norman, 1945) for the EWB mixture at atmospheric pressure.

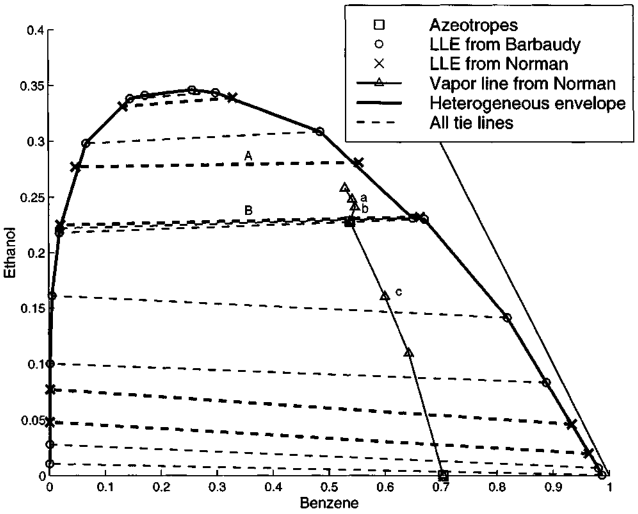

Figure 16. Experimental LLE data from Barbaudy (1927) and original VLLE data by Norman (1945) (both reported in Norman (1945) and also shown in Figure 15).

Azeotropes from Table 2 (all data at 1 atm).

Figure 16 shows a magnified view of the experimental VLLE data from Figure 15. Basically, it shows two different sets of data reported by Norman (1945) at atmospheric pressure: LLE data measured by Barbaudy (1927) (circles) and VLLE data measured by Norman (1945) (triangles for the vapor line and crosses for the tie lines). The apparent inconsistency in the tie lines close to the ternary azeotrope is due to small measurement errors and the different sources (the benzene-rich liquid-phase compositions between three measurement points with almost the same overall composition differ by a maximum 0.02 in the benzene mol fraction). Although the shape of the tie line at the ternary azeotrope is important, this small uncertainty is not expected to create any major problem in our analysis.

The situation is not as simple with the vapor line, though. All references in Gmehling et al. (1994) and also Norman (1945) and Horsley (1973) report the ternary azeotrope at the location shown in Figure 16 (and Table 2). The VLLE data measured by Norman (1945) (Table V in his article), however, do not seem consistent with this location of the ternary azeotrope. More specifically, the composition of the vapor in VLLE with liquids on the first tie line above the vapor line *A* is denoted by *a*. For liquid compositions on the topmost of the three tie lines around the ternary azeotrope, *B*, the vapor in VLLE is located at the third point from the top of the vapor line, *b*. Therefore, the aforementioned VLLE data in Table V of Norman (1945) indicates that the ternary azeotrope should lie between *a* and *b* on the vapor lie at component mol fractions of approximately 0.24–0.25 ethanol, 0.54–0.55 benzene, and 0.21 water. However, this is clearly inconsistent with all the experimental reports, which are shown in Figure 16 and listed in Table 2.

In many cases, such a discrepancy between experimental data would not be considered a serious problem. We have shown, though, that, for the EWB mixture, the shape of the vapor line close to the ternary azeotrope is critical for the existence of multiplicities in columns without a decanter. In the following, we for the first time predict MSS directly from the experimental data, discuss the implications of all these minor and major discrepancies in the data, and compare the resulting predictions with those obtained with the parameter set by Bekiaris et al. (1996).

∞/∞ analysis on the VLLE data

For *columns without the decanter*, it was shown that the key feature that leads to MSS for tray columns is the geometry of the TX boundary (see the illustration in Figure 11) in the heterogeneous region, and, in particular, the turn from the left to the right of the *ab* boundary segment, which is caused by an analogous turn of the top end of the vapor line.

First, we assume that all the experimental vapor line data points are correct and place the ternary azeotrope where the many literature references report it (Horsley, 1973; Gmehling et al., 1994), that is, we apply exactly the situation shown in Figure 16 with the vapor line containing the experimental points and the azeotropes. By this, we accept that there is a discrepancy in Table V of Norman (1945), probably due to some experimental errors. Then, the vapor line *shows a turn* just above the ternary azeotrope, as illustrated in Figure 11 and, hence, MSS exist in a ∞/∞ tray column without a decanter. This result is consistent with the ∞/∞ predictions based on the parameter set of Bekiaris et al. (1996). Some quantitative discrepancies in the multiplicity regions are obviously expected.

Secondly, it is assumed that the ternary azeotrope lies between *a* and *b* in Figure 16 (consistent with Table V of Norman (1945), but not with the experimental reports), and the experimentally reported ternary azeotrope is omitted from the vapor line (the line directly runs from *b* to *c*). Then, the vapor line *does not* show such a turn at its top end and, hence, no MSS exist in a ∞/∞ tray column without the decanter.

In conclusion, caused by the inconsistency of the reported data, we believe that it is not possible to draw safe conclusions regarding multiplicities for tray columns without decanter for the *real* EWB mixture. However, the knowledge from the ∞/∞ analysis again can be used to suggest experiments to clear up the correct location of the vapor line.

For *columns with the decanter* and a decanter policy where the distillate is a portion of the entrainer-poor phase only and a mixture of the two liquid phases is used as reflux, it was concluded that the existence of MSS is generic for the heterogeneous mixture class that EWB belongs to. Therefore, the presence of multiplicities does not critically depend on some specific VLLE characteristic, as long as the basic qualitative structural properties of the VLLE diagram are preserved. Since the qualitative structure of the experimental VLLE diagram (Figure 15 and 16) is identical to the distillation line and VLLE diagram is predicted using the UNIQUAC parameter set by Bekiaris et al. (1996) (Figure 10), the above statement also holds for the ∞/∞ predictions based on the experimental data and, hence, MSS exist in ∞/∞ packed or tray columns with decanter (for the policy above).

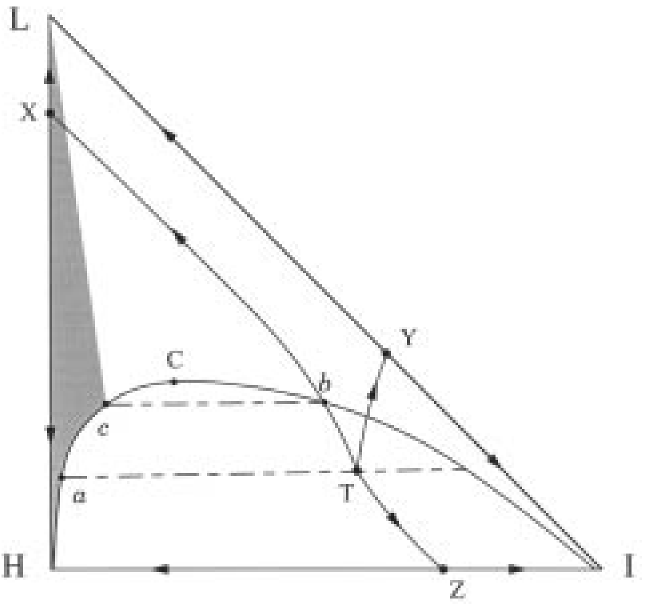

Figure 17. Figure 15 (experimental VLLE diagram) with the MSS feed region resulting from the ∞/∞ predictions.

The discrepancies between the experimental heterogeneous envelope and that predicted by Bekiaris et al. (1996) (including the tie lines and critical point) affect the predictions *quantitatively*. More specifically, the feed region that leads to multiplicities is affected because: (1) the experimental heterogeneous envelope is a bit smaller than the predicted one; (2) the experimental critical point lies to the left of the boundary that runs from the ternary azeotrope to the ethanol-water azeotrope. Note that the shape of the vapor line has essentially no effect for columns with decanter.

The first difference has no *qualitative* impact on the MSS feed region, that is, the feed region based on the experimental data would be analogous to the feed region shown in Figure 13 (just points *a* and *h* have different compositions). The difference in the location of the critical point has also a "qualitative" effect. The MSS feed region based on the experimental data cannot extend to the point of intersection of the heterogeneous envelope and the TX boundary (*h* in Figure 13), because this point is located to the right of the experimentally reported critical point (entrainer-rich phase). By application of the ∞/∞ multiplicity condition, the MSS feed region based on the experimental data only extends to point *c* in Figure 17, which is in LLE with the intersection point *b* of the heterogeneous envelope and the TX boundary. The resulting experimental-based MSS feed region *ac*LH is illustrated by shading in Figure 17.

One final note: the aforementioned differences between the predictions from the UNIQUAC model and the experimental data will obviously quantitatively affect other multiplicity-related issues such as the interval of the product flowrates where MSS exist for a given feed.

Discussion and Conclusions

In this section we discussed the VL(L)E predictions and inaccuracies of different sets of thermodynamic parameters used in the literature for the description of the EWB mixture. It was shown that *all* UNIQUAC parameter sets (Gmehling and Onken, 1977; Prausnitz et al., 1980; Gmehling et al., 1981) used in the distillation literature are inadequate both for capturing major features of the VLLE (ethanol-water azeotrope missing, two-liquid phases predicted where there is a single phase), and for multiplicity predictions. On the other hand, the set by Bekiaris et al. (1996) adequately describes the mixture's VLLE, although some discrepancies with experimental data exist.

Next, the ∞/∞ multiplicity prediction for the mentioned parameter sets were presented in addition to new ∞/∞ predictions, which are directly based on experimental VLLE data. In conclusion, the predictions based on the parameter set by Bekiaris et al. (1996) are in qualitative agreement with the ones from the experiments and, hence, they are most reliable to date to indicate what conditions lead to MSS in the distillation of the EWB mixture. Note that the actual study is limited to parameter sets used in the multiplicities related literature for the EWB mixture, and that there may be better representations of the VLLE of the mixture at other places.

More general, the analysis of the EWB mixture demonstrates how the ∞/∞ analysis can be used to bring out which features of the VL(L)E of a system are important down to the point where additional experiments are needed (such as for the vapor line of the EWB mixture) and where numerical tolerances need to be tightened (such as in the study of the parameter set of Gmehling and Onken (1977)).

From the discussions of the different parameter sets and the study of some easily made mistakes, we have seen that using parameters estimated from experimental data of a mixture does not necessarily mean that the resulting VL(L)E predictions adequately describe the real mixture's VL(L)E. It was also shown that parameters estimated from a group contribution method like UNIFAC are not always inferior in quality compared to parameters estimated from experimental data. For any use of VL(L)E models and parameter sets from literature, one needs to verify that:

- The experimental data used for fitting the parameters do cover the phenomena of interest (isothermal or isobaric VLE, LLE, or VLLE)
- The objective of the estimation (good LLE description, good VLE description, and so on) matches the actual purpose for which the parameters are used [as discussed for the set by Prausnitz et al. (1980)]
- A parameter set is *not* used without special attention to conditions not covered by the data (extrapolation of a highly nonlinear model)
- Parameters collected from different sources are consistent (see Güttinger and Morari (1996) on the inconsistent use of van Laar parameters by Bekiaris et al. (1993), even though the main results were not affected)
- The parameters are robust against numerical effects [as discussed for the set by Gmehling and Onken (1977)]
- Correct units and the correct VL(L)E model are used (see the easily made mistakes).

Comparison of Reported Multiplicities

This section studies in detail output multiplicities of type 2a reported in the literature for *finite heterogeneous* distillation columns. Even though the ∞/∞ geometrical condition is only sufficient for finite columns, that is, there may be type 1 multiplicities present which are not predicted, it is still interesting to compare the reported MSS with the ∞/∞ predictions presented in the section above.

However, precise comparisons are not always possible for the following reason: The amount and type of information provided by the respective authors about the computed multiplicities varies widely. It should be recognized that in many, if not all the articles reviewed, and, especially in the early ones, the reports on multiplicities are *not the primary goal* of the articles. Instead, new calculation algorithms, column design, dynamics studies, or new VL(L)E models (etc.) are the main topics of these articles and the reports on multiplicities are usually a side issue.

In the previous sections, the information required for the ∞/∞ prediction was discussed: the number and location of azeotropes, the location of distillation boundaries, the two-liquid-phase envelope, the vapor line, and some tie lines. Although many different VLLE models and parameter sets are used in the literature, if the above information were correctly reported in these articles, even just as graphical data, it would be sufficient for performing the ∞/∞ analysis. Obviously, since the presence of two liquid phases was conjectured early as a possible cause for multiplicities, the two-liquid-phase envelope and the tie lines are presented in a number of articles, whereas distillation boundaries are not expected to be seen in most of the articles studied. The location of the azeotropes, too, is not always shown.

Although the information required for the ∞/∞ multiplicity predictions is not always complete in these articles, the used VLLE model and parameter set are usually reported. Thus, the reported multiplicities in finite columns can be compared with the ∞/∞ predictions obtained in the previous section. For such a comparison, it is necessary to define the appropriate criteria. Bifurcation diagrams cannot be expected in all the articles reporting multiplicities and, hence, are not the criteria of choice here. Thus, the comparisons will be based on the location of the reported multiplicity composition profiles in the composition space, as well as on the composition of the feed and the products for the reported MSS.

Discrepancies between reported and ∞/∞ profiles can be due to effects of the finite internal flows or finite column length, or, in the case of finite columns, of the feed stage location, of subcooling, or because the equipment types (including the decanter policy) were not precisely described.

Shewchuk (1974)

Shewchuk first presented steady-state simulation results where the model of a heterogeneous distillation tower converged to *two* different steady-state solutions depending on the initial guesses. Since the author himself doubted the relevance of this result (he considered bad thermodynamic data to be responsible), the multiplicities were not reported in great detail. However, the column profiles shown seem to be very similar to the two stable profiles reported by Magnussen et al. (1979). Therefore, Shewchuk's (1974) multiplicities are very likely to be of the same type as the ones of Magnussen and coworkers which are discussed next.

Magnussen et al. (1979)

Magnussen et al. (1979) presented simulation results that show the existence of three steady states (two of them stable and one unstable) for the heterogeneous EWB mixture. In their calculations, constant molar overflow (CMO), constant atmospheric pressure, and ideal vapor phase were assumed. The column has 27 ideal stages including the reboiler (stage number 1) and is depicted in Figure 23 of Bekiaris et al. (1996). A mixture of 89 mol. % ethanol and 11 mol. % water is fed at stage 23 (feed F_1). The authors assumed that the distillate D is fed to a decanter which, however, is not included in the column calculation model. Instead of the benzene-rich phase from the decanter, a second stream F_2 is fed at the top of the column and compensates for the returned benzene-rich phase from the decanter and for the benzene makeup stream. The flow rates and compositions of both feeds are *fixed*. Magnussen et al. (1979) note that "the amount of azeotropic components [ethanol and water in the second feed] are specified according to experimentally observed LLE, and the amount of entrainer (benzene) is adjusted so as to produce the purest bottoms product." The column's design specifications are a fixed molar distillate flow rate and a fixed reflux ratio. Therefore, any multiplicities cannot be of type 1a and the specifications allow for comparisons to be made with ∞/∞ predictions for the same overall feed in a *column without the decanter*.

Moreover, Magnussen et al. (1979) studied three different models for the liquid-phase activity coefficients: Wilson, NRTL, and UNIQUAC. Note that the amount of benzene in F_2 is different for each of the models in order to produce the purest bottoms product (but is the same for all steady-states reported for the same model). A a result, output multiplicities were observed with the UNIQUAC and NRTL activity coefficient models, but a unique steady state was found with the Wilson equation model. The fact that the Wilson model cannot predict two liquid phases was recognized by Magnussen and coworkers who concluded from their simulations that the Wilson equation with the parameters used "is incapable of representing the system acceptably." Last, the only information reported about the NRTL multiplicities is that they are qualitatively similar to the ones obtained using UNIQUAC, which are the ones presented in detail and, therefore, the ones that will be compared with the ∞/∞ predictions.

Concerning the parameter sets used, Magnussen et al. (1979) state that "we have, in addition to UNIFAC, generated activity coefficients from the UNIQUAC, NRTL, and Wilson equations with parameters estimated from ternary VLE data (Gmehling and Onken, 1977)". We are grateful to one of the co-authors for the background information concerning the origin of those parameters. He recalls that Magnussen et al. (1979) used the regular unary parameters from Gmehling and Onken (1977) and binary interaction coefficients set to match the corresponding infinite dilution values as calculated from the UNIFAC table. Unfortunately, the specific values of these binary parameters are nonexistent today, 20 years later.

Note that, in some later publications, it was assumed that Magnussen et al. (1979) directly used the binary parameters reported by Gmehling and Onken (1977). Since this is not the case, it is obvious that we cannot compare the multiplicities reported by Magnussen et al. (1979) with ∞/∞ predictions based on unknown parameters. Therefore, we examine hereafter the compatibility of the reported multiplicities with the ∞/∞ predictions obtained for the parameter set of Bekiaris et al. (1996).

Specifically, it was shown that for a column without the decanter, MSS exist if the TX boundary (going from T to X) shows a turn (from the left to the right) as on the segment *ab* in Figure 11. In the following, the results by Magnussen et al. (1979) are discussed in detail to provide evidence which strongly suggests that the reported multiplicities (and probably also those by Shewchuk (1974)) are related to MSS in the ∞/∞ case. Note that this is not a proof since the UNIQUAC parameters that Magnussen and coworkers actually used are unknown.

Product Locations: Magnussen et al. (1979) present the molar compositions of the bottom products for the three solutions that they calculated (in their Figure 6). Using this and the feed information provided, the distillate compositions can be obtained from simple material balance calculations for the three steady states. The resulting compositions are shown in Table 12. Figure 18 qualitatively sketches the three steady-states material balances and the relative locations of the distillate, bottoms, and the feed in the composition space (the axes scales are distorted for illustrative purposes).

To understand the following comparison of the product locations reported by Magnussen et al. (1979) (Figure 18) with those obtained from the ∞/∞ predictions using the UNIQUAC parameter set of Bekiaris et al. (1996) in Figure 12, we treat the product locations of Magnussen's finite column as if they were obtained in a corresponding ∞/∞ column. Even though the feed and the axes scales in Figures 12 and 18 are different, the correspondence of the product locations of profiles 1, 2, and 3 from Figures 18 to those of profiles 1, 2 and 3 (respectively) in Figure 12 is obvious. Therefore, the profiles 2 and 3 in Figure 18 correspond to "type III" profiles in the ∞/∞ case, whose distillates lie on the TX boundary (and the bottoms on the LI edge; see Bekiaris et al. (1996) on the profile types). The bottom product of profile 1 in Figure 18, although close to both LH and LI, does not lie on any of the

Table 12. Overall Feed Composition as well as Distillate and Bottoms Compositions for the Three Steady States Reported by Magnussen et al. (1979) for the EWB Mixture

Component	Overall Feed*	Profile 1		Profile 2		Profile 3	
		D	B	D	B	D	B
Ethanol	0.6806	0.26507	0.99944	0.26864	0.9967	0.36207	0.925
Benzene	0.2313	0.53247	0.00026	0.53281	2.6×10^{-8}	0.53280	4×10^{-15}
Water	0.0881	0.20246	0.00030	0.19855	0.0033	0.10513	0.075

*F_1 consists of 89 mol/h ethanol and 11 mol/h water; F_2 consists of 9.9 mol/h ethanol, 1.8 mol/h water and 33.62 mol/h benzene.

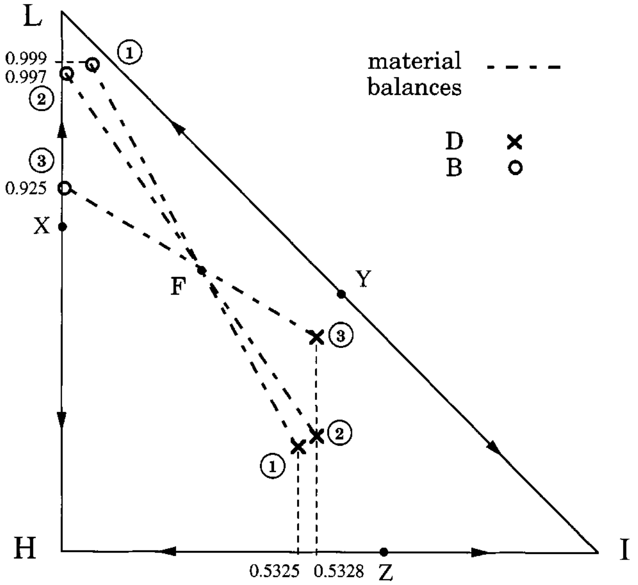

Figure 18. Product locations of the three steady-state profiles reported by Magnussen et al. (1979) for the EWB mixture.

two edges and, hence, it is treated as an interior point. Therefore, profile 1 must correspond to a "type I" ∞/∞ case column profile whose distillate would consequently be located at the ternary azeotrope T in Figure 18 (and, thus, on the TX boundary as well).

Because the distillates of profiles 1 to 3 must be located on the TX boundary in the ∞/∞ case (Figures 12 and 18), the shape of the TX boundary would have to be similar to one of the two shown in Figure 19, that is, T*b*′X or, for example, T*ab*X. In any case, TX exhibits a turn from the left to the right as predicted for the UNIQUAC parameter set by Bekiaris et al. (1996) on the *ab* segment in Figure 12 and, hence, output multiplicities exist in the ∞/∞ case of a column without a decanter.

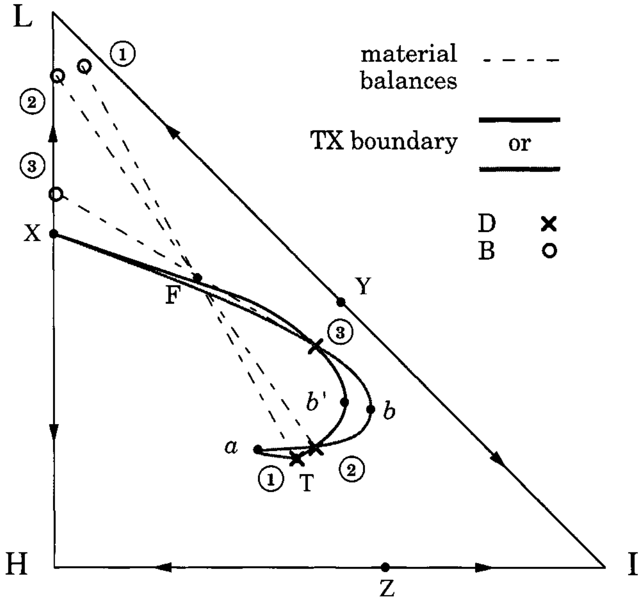

Figure 19. Possible TX boundaries consistent with the product locations reported by Magnussen et al. (1979) for the EWB mixture.

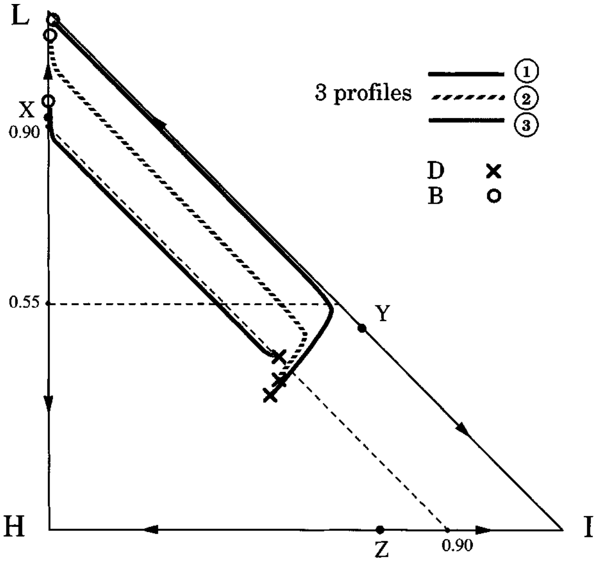

Figure 20. Composition profiles reported as MSS by Magnussen et al. (1979) for the EWB mixture.

Of course, in reality, the distillate products reported by Magnussen et al. (1979) do not exactly lie on the TX boundary because a finite, rather than a ∞/∞ column, is used. Nevertheless, the above discussion strongly suggests that the multiplicity observed by Magnussen et al. (1979) can be explained by the ∞/∞ analysis (multiplicity caused by the shape of the TX boundary).

Feed Location: Table 12 lists the composition of the overall feed of Magnussen et al. (1979), which belongs to the region of feeds that lead to MSS in the ∞/∞ case using the parameter set by Bekiaris et al. (1996), as illustrated in Figure 11. Even though the exact location of the MSS feed region depends on the specific VLLE model and parameters used by Magnussen and coworkers, it is clear that their overall feed lies in the general location predicted for the ∞/∞ case (close to the *b*L line in Figure 11).

Composition Profiles: Mangussen et al. (1979) provide the composition profiles of the three steady states they computed in Figure 6 of their article (as liquid-phase mol fractions vs. stage number). Based on this graphical information, the profiles are sketched in the composition triangle in Figure 20. The qualitative similarity of these finite case profiles with the ones predicted in the ∞/∞ case using the UNIQUAC parameter set by Bekiaris et al. (1996), which are shown in Figure 12, is obvious.

There are only two minor discrepancies between the two sets of profiles: The middle portion of profile 2 by Magnussen et al. (1979) is shifted "upwards", that is, it does not follow the TX boundary exactly, which may be caused by the finite value of the reflux in the column. Moreover, the part of profile 3 close to the top of the column exhibits a slight turn towards the LI (ethanol-benzene) edge. The latter may be caused by the second feed at the top of Magnussen's finite column, which consists of 74 mol. % benzene, 22 mol. % ethanol, and 4 mol. % water. It is known that in finite columns the feed location may affect the column profile, while in the ∞/∞ case, the location of the feeds does not affect the composition profile (Bekiaris et al. 1993). Except for these two minor discrepancies, which can be attributed to the finite column effects, the agreement is quite remarkable.

Stability of Steady States: Magnussen et al. (1979) performed transient calculations for the three solutions they computed and conclude that solutions 1 and 3 represent stable steady states, while solution 2 is unstable. Bekiaris et al. (1996) presented simulation results for the identical column, but using their UNIQUAC parameter set for the VLLE calculations. The computed bifurcation diagram (Figure 24 in their article) with the distillate flow rate as the bifurcation parameter agrees with the ∞/∞ predictions and the simulation results, and shows the same stability characteristics as reported by Magnussen and coworkers.

Multiplicity Region: Magnussen et al. (1979) presented some multiplicity region results (Figure 7 in their article), different from the interval of the product flow rate where multiplicities exist, which is used by Bekiaris and coworkers. Magnussen et al. (1979) keep constant the first feed F_1, the total flow of the second feed F_2, and the water flow of F_2, and vary the ethanol flow (and accordingly the benzene flow) of F_2. In other words, they present a bifurcation diagram with the overall feed composition (restricted to a line parallel to LI, as a detailed analysis of their procedure shows) as the bifurcation parameter. Note that the product flow rates are kept constant. By this, the authors show that three solutions exist in a narrow range of ethanol feed flows, which translates to an ethanol feed range of 67.70 to 68.07 mol. %. For higher ethanol contents in the overall feed, solution 3 exists, while at lower ethanol contents, only solution 1 exists.

Next, evidence is provided that this result is also in agreement with the ∞/∞ predictions. Since the original overall feed location used by Magnusssen et al. (1979) lies close to bL in Figure 11 and since the feed composition changes along a straight line parallel to the LI edge, at some point, the overall feed exits the MSS feed region (see Figure 11). The above conjecture is possible when the ethanol mol fraction in the feed is *decreased* and can explain why MSS vanish in this case. If the ethanol mol fraction is increased, however, the overall feed will always remain in the MSS feed region (Figure 11) and, hence, this does not seem to explain why the multiplicities vanish in the case of Magnussen et al. (1979).

Note, however, that the shaded region in Figure 11 depicts the feed compositions that lead to multiplicities in the ∞/∞ case for *some* range of the product flow rates, which is different for every feed composition. In contrast, Magnussen et al. (1979) keep the product flow rates fixed. Moreover, Figure 11 is based in the UNIQUAC parameters by Bekiaris et al. (1996). Using these parameters, Bekiaris et al. (1996) presented simulation results for the column by Magnussen et al. (1979), where the computed bifurcation diagram (Figure 24 in their article) shows a very narrow range of product flow rates (D between 63.06 and 63.68) for which three steady states exist (which is in agreement with the corresponding ∞/∞ predictions). The exact location and size of this interval of product flow rates where MSS exist depends on the feed composition. For small changes in the overall feed composition, the interval of the product flow rates where MSS exist shifts to higher (lower) distillate flow rates if the ethanol mol fraction in the feed is decreased (increased) along a line parallel to the LI edge. Because of the small size of the multiplicity interval, if the ethanol mol fraction in the overall feed is changed, even by a small amount (< 0.5 mol. %), the fixed distillate flow rate used by Magnussen et al. (1979) is easily located outside of the multiplicity interval, which is moving. Moreover, the ∞/∞ predictions show that if the ethanol content in the overall feed is decreased (increased), MSS will vanish and profile 1 (profile 3) will be the only solution (Bekiaris et al., 1996). This is in perfect agreement with the observations by Magnussen et al. (1979).

Liquid-Phase Miscibility: Magnussen et al. (1979) reported that "the liquid compositions on all stages were checked for miscibility, and it was verified that in all cases there is only one liquid phase." Although our calculations using the UNIQUAC parameter set by Bekiaris et al. (1996) do not agree with this, it is possible that this happens for some other set of parameters. Basically, the vapor line determines whether there will be a liquid-phase split on a tray of one of the (multiple) steady states. The vapor line follows the boundaries on the ZTa segment and on a part of the segment between the inflection points a and b in Figure 11.

Note that by the definition of the vapor line, there are two liquid phases on the top tray of the column if and only if the overhead vapor leaving that tray lies on the vapor line. For any other overhead vapor in the two-liquid phase region, the top tray of the column will exhibit a single liquid phase. As a result, Figure 11 shows that from the three multiplicity profiles as reported by Bekiaris et al. (1996), one is always homogeneous (overhead vapor on Xb), one is always heterogeneous (overhead vapor on Ta which is part of the vapor line), and the third one can be homogeneous or heterogeneous (depending on the exact location of the overhead vapor between a and b).

These results clearly do not agree with those by Magnussen et al. (1979). However, note that the UNIQUAC parameters used by Magnussen and coworkers are not exactly known, and it is possible that the vapor line follows a different path for these parameters. If it coincides only with a portion of the Ta part of the TX boundary, then three homogeneous steady states can be obtained.

Other Mixtures: Magnussen et al. (1979) observed a similar multiplicity for the ethanol(I)—water(H)—pentane(L) system, but no multiplicity was found for the toluene (H)—heptane(I)—2-butanone(L) system. The latter is a homogeneous mixture with one binary azeotrope between heptane and 2-butanone and belongs to the 100 class according to Matsuyama and Nishimura (1977). The ∞/∞ predictions show that, for this class, the absence of MSS is general (Bekiaris and Morari, 1996) and, thus, this result agrees with the observation by Magnussen et al. (1979).

The situation is not so simple for the ethanol(I)—water(H)—pentane(L) system, which is heterogeneous. Even though the entrainer, pentane, is lighter boiling than the two other components, the mixture's VLLE diagram is qualitatively similar to the one of the EWB mixture (both belong to the 222-m class). Since the parameters of this mixture are not known anymore, it is difficult to discuss the shape of the TX boundary, which determines the existence of MSS in a column without the decanter. Using Aspen Plus (1995) and the UNIFAC model to calculate a ternary residue curve diagram, the ∞/∞ analysis predicts that for this mixture, multiplicities can occur (in a packed column) and, thus, the observation of Magnussen et al. (1979) is not contradicted.

In conclusion, the discussion of the results by Magnussen et al. (1979) provides strong evidence that the multiplicities reported in that article are related to the ∞/∞ multiplicities of Bekiaris et al. (1996). The few minor discrepancies between the two can be attributed to the different UNIQUAC parameter sets used, and to the discrepancies between a finite column and the ∞/∞ limiting case. Still, the agreement is remarkable. The evidence presented here indicates that the multiplicities observed by Magnussen and coworkers do not result from some peculiarities in the UNIQUAC model (as proposed by the authors), but that they are caused by the same physical phenomena leading to MSS in the ∞/∞ case of a heterogeneous azeotropic distillation column, that is, they are type 2a multiplicities. Finally, since such type 2a multiplicities have been verified experimentally (Güttinger and Morari, 1997; Müller and Marquardt, 1997), the authors' conjecture that ''this exotic behavior and probably not take place in practice'' can be refuted.

Prokopakis et al. (1981)

Prokopakis et al. (1981) study the EWB mixture and the ternary mixture isopropanol—water—cyclohexane. For the column, it is assumed that the condensed overhead vapor is fed to a decanter which is not included in the column calculation model. Similarly to Magnussen et al. (1979), a second stream with fixed composition and flow rate is fed at the column top to compensate for the returned entrainer-rich phase from the decanter and the entrainer makeup stream. However, the separation scheme used in this article is slightly different from the one used by the previous authors: the total overhead vapor is considered to be the distillate of the column without the decanter, while Magnussen and coworkers returned a portion of the overhead vapor as a reflux back to the column. The NRTL activity coefficient model is used with parameters provided in the referenced literature. In the calculation model, enthalpy balances and a pressure drop along the column was considered.

For reasons already mentioned, the critical simulation results on multiplicities for the EWB mixture are not reported in detail, which makes the analysis difficult. In any case Prokopakis et al. (1981) were not able to verify the existence of MSS for this mixture. They observed, however, three regimes of column operation in terms of profile resemblance and product impurities distribution in the bottom product: Profiles where the stripping section contains (1) ethanol and benzene; (2) ethanol and neither (or minute quantities) of the other two components; (3) ethanol and water. The correspondence of these three regimes with the three steady states calculated by Magnussen et al. (1979) is not so clear (compare with Table 12). Despite conditions on the overall feed for the feasibility of the three regimes of profiles, which can be derived by the ∞/∞ analysis, there is no relation between these regimes and MSS in the ∞/∞ case of a column without the decanter.

Moreover, Prokopakis et al. (1981) considered one of the steady states calculated by Magnussen et al. (1979) to be infeasible because its overhead vapor composition does not lie in the two-liquid phase region (profile 3). Since similar comments appear in later articles, some clarification is needed. Profile 3 of Magnussen et al. (1979) is perfectly feasible for the column model for which it has been calculated, that is, a column without the decanter but two fixed feeds. However, if the decanter is included in the model, the second feed at the column top must be produced by mixing the entrainer-rich phase from the decanter with some benzene makeup stream. Since such material balance is not fulfilled for profile 3 of Magnussen et al. (1979), it is the *separation scheme* including the decanter that becomes infeasible. This shows that, in general, the decanter needs to be added to the model to get meaningful solutions for the separation scheme. In addition, generally, the existence of MSS in a column without the decanter *does not imply* that MSS exist in the same column with the decanter, and vice versa. From the ∞/∞ analysis, we know that, for example, if the TX boundary in Figure 11 is a straight line, a unique solution exists for a column without the decanter, while multiplicities exist for the same column with the decanter.

Next, Prokopakis et al. (1981) studied the mixture isopropanol—water—cyclohexane and reported *two* steady states for the same ''specifications'' in the column without the decanter. In these steady states, however, the entrainer (cyclohexane) flow rate in the boilup stream and the reflux flow rate and composition are held constant (specifications), while the product flow rates differ by much. Since, in practice, compositions of an internal column stream can only be specified by means by control, this case does not correspond to an ''open-loop'' output multiplicity as defined above. Hence, no comparison can be made with the ∞/∞ predictions. Simply, the two reported profiles show that there exist two sets of operating conditions for which the specified entrainer flow rate in the boilup can be achieved. Again, one of the solutions was considered ''infeasible'' for what has been explained above.

Prokopakis and Seider (1983a,b)

Prokopakis and Seider (1983b) presented a thorough study of the EWB mixture. The interaction parameters of the UNIQUAC sets by Gmehling and Onken (1977) and Prausnitz et al. (1980) are first used in this article. The authors detect the erroneous ethanol—benzene immiscibility predicted using the parameter set by Gmehling and Onken (1977), see Figure 2. Consequently, the parameter set by Prausnitz et al. (1980) was used in the simulations. Prokopakis and Seider, however, do not report that the ethanol-water azeotrope is missing using this set (see Figure 4), most likely, because their attention concerning the VL(L)E focused on the prediction of the two-liquid phase region and the heterogeneous ternary azeotrope. Nevertheless, the ∞/∞ analysis predicts MSS in the ∞/∞ case for a column with or without the decanter using this parameter set (see the corresponding section from above).

The main advance of the simulations performed by Prokopakis and Seider (1983b) compared with earlier studies is that they simulate the entire column sequence including in the model: energy balances, a subcooled decanter, and the overall material balance of the second, entrainer recovery column. However, since the authors are concerned about "infeasible" solutions (as in the previous section), the overhead vapor of the first column was constrained to be located in a narrow box in the two-liquid phase region in their calculation procedure. Some other constraints are also imposed, leading the authors to solve an optimization problem. As a result, Prokopakis and Seider (1983b) do not compute multiplicities, but present results about the three operating regimes of Prokopakis et al. (1981).

Because of the different solution strategy and the "constraints" used in this article, detailed comparisons with the ∞/∞ predictions cannot be made. Prokopakis and Seider (1983b) simulated a column with 27 trays similar to the one studied by Magnussen et al. (1979), but with the decanter and compare their results with those of Magnussen et al. (1979). In retrospect, from the results of the ∞/∞ analysis, it is clear that such comparisons cannot be made because MSS in a column without the decanter do not imply MSS in a column with the decanter as used here. Hence, the multiplicity profiles are different for columns with and without the decanter, also because of the use of two different sets of UNIQUAC parameters. Here, we can only examine the relation of the profiles calculated for the three regimes of Prokopakis and Seider (1983b) with the three steady-state profiles predicted for ∞/∞ columns with the decanter using the same UNIQUAC parameter set (Prausnitz et al., 1980), that is, profiles 1 and 2 in Figure 8 and profile 3 in Figure 6.

The regime 1 profile (Figure 9 in the article of Prokopakis and Seider) corresponds to the ∞/∞ profile 1 in Figure 8 (which happens to be similar to profile 1 by Magnussen et al.) —the ten bottom trays run along the ethanol—benzene edge. Similarly, for some intermediate trays of the regime 2 profile (Figure 10 in their article), water is eliminated and the profile runs along the ethanol-benzene edge towards pure ethanol. Since the main impurity in the bottom product, however, is water, this indicates that the profile turns around the ethanol corner and starts moving along the ethanol-water edge away from pure ethanol. Such a profile would correspond to profile 2 in Figure 8 as predicted by the ∞/∞ analysis. This profile is significantly different from profile 2 of Magnussen et al. (1979). Also, note that the definition of regime 2 by Prokopakis and Seider (1983b) implies a profile whose stripping trays run along the ethanol-water edge towards pure ethanol—this does not seem to agree with the actual profile presented in Figure 10 of their article.

Finally, Prokopakis and Seider's (1983b) attempts to simulate regime 3 failed because convergence could not be achieved subject to the constraints they imposed. The authors concluded that the third regime is infeasible, because they also considered infeasible a decanter where no phase separation takes place. However, we have shown that a third solution exists for columns with the decanter (profile 3 in Figure 6), where the liquid composition in the decanter lies in the single liquid-phase region. Hence, if one does not impose the (artificial) constraints, such a profile is feasible.

In a later article, Prokopakis and Seider (1983a) suggested that the profiles of regime 2 are unstable based on dynamic simulations showing that for a 60% feed flow disturbance, a regime 1 profile drifts through a regime 2 profile before finally reaching regime 3. The authors make a similar contention about the stability of one of the two isopropanol—water—cyclohexane profiles computed by Prokopakis et al. (1981). These arguments are not strong enough to "prove" the instability of these regimes and their relation to multiplicities (see Dorn et al. (1998) on experimental evidence of instability in columns with type 2a multiplicities).

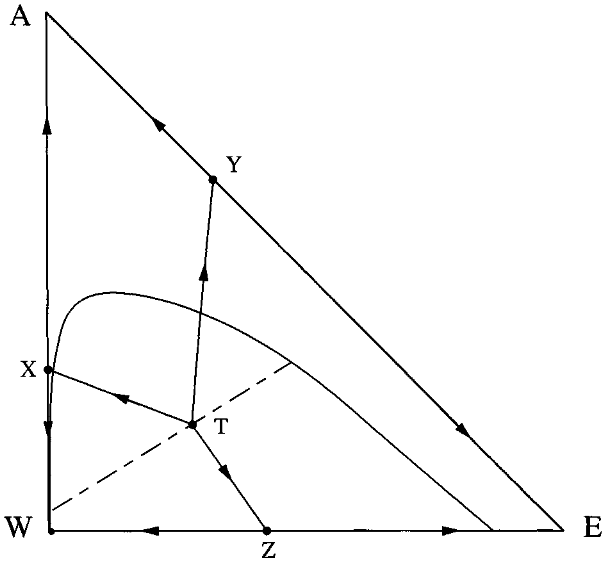

Figure 21. VLLE diagram of the mixture secondary butanol(A)-water(W)-disecondary butyl ether(E).

In conclusion, there are indications that the profiles calculated for regime 1 and 2 by Prokopakis and Seider (1983b) may correspond to the heterogeneous profiles 1 and 2 of the ∞/∞ predictions. Clearly, these indications are far fewer and weaker than those revealed in the comparisons with the result by Magnussen et al. (1979). There does not seem to exist a one-to-one relation between the three regimes, as defined by Prokopakis and Seider (1983b), and the multiplicities predicted in the ∞/∞ case of columns with decanter. This conclusion is similar to the one for columns without decanter and the regimes reported by Prokopakis et al. (1981).

Kovach III and Seider (1987a,b)

Kovach III and Seider (1987b) presented simulation and experimental results for a mixture of sec-butanol, water, and di-secondary butyl ether (mixed with butylenes and methyl-ethyl-ketone impurities). The properties of the VLLE of this mixture (shown in Figure 21) are similar to those of the EWB mixture (compare with Figure 14). There are some important differences, however. The secondary butanol-water azeotrope X is located closer to pure water (60 mol. % water), and the heterogeneous liquid envelope lies very close to the secondary butanol-water edge. Finally, the LLE tie lines, as shown in Figure 10 of Kovach III and Seider (1987b), have significantly different slopes from those of the EWB mixture.

Kovach III and Seider modeled a column with a subcooled decanter and used the reboiler heat duty, as well as the aqueous and organic reflux ratios as specifications. Note that in all articles previously discussed, there was no organic phase stream recovered as distillate (only water phase). In this case, there is organic phase in the distillate, and, as a result, the overall distillate composition does not lie on the heterogeneous liquid envelope, but inside the two-liquid phase region. Bekiaris et al. (1996) discussed the implications of such a decanter policy and demonstrated how it affects the product paths and the multiplicity predictions in the ∞/∞ case. Based on their study, conclusions regarding the existence of MSS for this mixture can be drawn on the basis of the mixture's VLLE diagram.

Kovach III and Seider (1987b) located two significantly different column profiles obtained by a very small change of the aqueous reflux ratio (Figure 9 in their article, profiles I and F). The authors find that this parametric sensitivity is consistent with the experimentally observed erratic behavior of the column. No multiplicity was found, however. The stripping section of profile I follows the entrainer-alcohol edge, while the stripping section of profile F runs along the water-alcohol edge. This is very similar to the observed "regimes" by Prokopakis and Seider (1983b). This type of profile "shifting" for small parameter changes is not necessarily related to multiplicities since it appears for mixtures that do not exhibit MSS (parametric sensitivity). Because of the shape of the two-liquid phase region (close to the water-alcohol edge), a single liquid phase on all trays is computed for profile I, while two liquid phases exist on 70% of the trays for profile F. The fraction of organic phase in the distillate is small for both profiles (≈ 0.03).

Although a detailed distillation line diagram is not at hand, one can predict based on the VLLE information from Figure 21 that for small fractions of organic phase in the distillate, MSS exist in the ∞/∞ case of a column with the decanter for feeds in a narrow area close to the alcohol-water edge, as is the case for the feed used by Kovach III and Seider (1987b). The ∞/∞ predictions are expected to be similar to those shown in Figure 14 for the EWB mixture, except that the homogeneous profile 3 may possibly not exist, and so the number of steady states is only two instead of three. Thus, ∞/∞ multiplicities seem to exist for the column by Kovach III and Seider (1987b), but a more detailed study of the distillation line diagram is required for a definitive conclusion since the column specifications are quite different. This is beyond the scope of this article. Anyhow, the two profiles computed by Kovach III and Seider (1987b) resemble the ∞/∞ profiles for type 2a multiplicities.

In another article, Kovach III and Seider (1987a) presented simulation results using homotopy-continuation for a column separating the EWB mixture. The column is similar to the one studied by Prokopakis et al. (1981), that is, the condenser and the decanter are not included in the model and a second stream (with fixed flow rate and composition) is fed at the top of the column. The specifications are the same as in Kovach III and Seider (1987b) and the boil-up molar flow rate is used as the continuation parameter. Note that as in Prokopakis et al. (1981), the separation scheme used is slightly different from the one by Magnussen et al. (1979). The UNIQUAC parameter set by Prausnitz et al. (1980) is used for the VLLE calculations. The column model includes enthalpy balances and considers pressure drop along the column.

In their Figure 6, Kovach III and Seider (1987a) locate five steady states for the same boilup molar flow rate. Since the authors specify the molar boilup with a fixed molar reflux (an $[L/D, V]$ configuration), and since they include heat balances in their model, only type 1b multiplicities can occur in addition to type 2a. Therefore, theoretically, more than three steady states are possible if the intervals of the operating parameters where MSS exist overlap. Since profiles I and II in Kovach III and Seider (1987a) have the same product flow rate and the same product compositions, they correspond to an internal state multiplicity as defined earlier (the only difference is the location of the composition front). Even though profiles IV and V are also similar to I and II on many trays, their composition front is located at the bottom of the column, resulting in different bottoms compositions (output multiplicities). The stripping section parts of the four profiles I-IV lie on the ethanol-benzene edge. Profile III is different from the other four since its stripping profile follows the ethanol-water edge (output multiplicities). Unfortunately, a comparison of the above five steady states with the three steady states shown in Figure 6 for an ∞/∞ column without the decanter and with the parameter set by Prausnitz et al. (1980) does not provide any significant indication of some correspondence or relationship between the two results. This can be explained by the fact that: (a) multiplicities may be of different types; (b) MSS depend on the actual column configuration. The $[L/D, V]$ configuration used by Kovach III and Seider (1987a) is significantly different from a configuration involving a molar *product* flow rate as used in the ∞/∞ analysis.

Finally, when the decanter is included in the model, only three steady states result.

Lucia and coworkers

Venkataraman and Lucia (1988) perform continuation studies for a 42-stage EWB column using the bottoms flow rate as the continuation parameter and a given reflux ratio. The decanter is not included in the model and a second stream is fed at the top of the column. A partial condenser is used, ideal stages are assumed, and pressure drop along the column is considered. Moreover, the UNIQUAC parameter set by Prausnitz et al. (1980) was used to describe the liquid phase, and the B-truncated virial equation of state for the vapor phase. The assumption of a nonideal vapor phase is not expected to have a large impact on the structure of the distillation line diagram, but some differences compared to Figure 4 may exist. Venkataraman and Lucia (1988) computed three steady states over a narrow range of bottoms flow rates, where a single liquid phase exists on all trays (output multiplicities). In the following, these results are compared to the ∞/∞ predictions for a column without the decanter and the Prausnitz et al. (1980) parameter set.

The three profiles that Venkataraman and Lucia (1988) computed are shown in Figure 3 of their article and the corresponding bifurcation diagrams in Figure 4. There are qualitative similarities between these bifurcation diagrams, the ones computed by Bekiaris et al. (1996) for the column by Magnussen et al. (1979) (Figure 24 in the Bekiaris article), and the ∞/∞ predictions without the decanter (Figure 8 in the Bekiaris article). The shapes of the bifurcation diagrams are very similar and the solution multiplicity occurs over a narrow range of the bifurcation parameter (distillate or bottoms flow rates). There are differences, too. Since the overall feed locations are different for the two studies and, since the calculations of the bifurcation diagrams are based on two different sets of UNIQUAC parameters, it is not surprising that the location of the limit (turning) points is different (Venkataraman and Lucia, 1988; Bekiaris et al., 1996). Moreover, Venkataraman and Lucia (1988) compute a single liquid phase on all the trays similar to the results by Magnussen et al. (1979). This issue was already discussed in the section on the results by Magnussen et al. (1979).

Kingsley and Lucia (1988) extended the results by Venkataraman and Lucia (1988) by studying the effect of the Murphree tray efficiency η of the top four trays of the column. For $\eta = 1$, the authors compute a single liquid phase on all the trays, while the overhead vapor composition lies in the heterogeneous region. As expected, for small enough η, and as long as the overhead vapor composition still lies in the heterogeneous region, the composition differences between these trays decrease and, as a result, two liquid phases will exist on one or more of the trays at the top of the column.

Kingsley and Lucia (1988) performed the above column simulations by ignoring the existence of a second liquid phase on the trays (''homogeneous'' solutions). Note that these solutions are *not homogeneous*, as defined above, since the liquid compositions of some trays are located in the heterogeneous region. To avoid any confusion, we refer to these solutions as *two-phase solutions*, that is, calculated using a VLE instead of a VLLE algorithm. Unfortunately, a two-phase solution with some trays heterogeneous has no physical meaning, because the equilibrium calculations on the trays with liquid composition in the heterogeneous region have to take into account the existence of the second liquid phase (VLLE calculations are required). The significant impact of doing VLE instead of VLLE calculations, as well as the potential for incorrect conclusion, has been discussed by Pham and Doherty (1990).

Figure 2 of Kingsley and Lucia (1988) shows the ethanol mol fraction in the bottoms as a function of the tray efficiency on the top four trays and of the bottoms flow rate (two-phase solutions). Three steady states exist over a narrow range of the bottoms flow rate for columns with a tray efficiency of the top four trays larger than 0.447. Next, Kingsley and Lucia (1988) use these two-phase solutions as starting points for a VLLE calculation to obtain meaningful heterogeneous solutions. Figure 4 of Kingsley and Lucia (1988) shows the composite ''two-phase computed'' and ''true heterogeneous solution'' bifurcation diagram. As explained above, the two-phase ''homogeneous'' solutions change to heterogeneous ones as the tray efficiency decreases below some critical value η_{het}.

Again, three steady states exist over a narrow range of the bottoms flow rate for columns with tray efficiency of the top four trays larger than some critical value η^*. For columns with tray efficiency less than this critical value, a unique steady state exists for the whole range of bottoms flows. The value η^*, although not explicitly mentioned in the article, is reported to be larger than 0.447 (the value for the two-phase solutions). However, as the tray efficiency decreases, multiplicities vanish before the onset of the three-phase behavior on the top trays is reached, that is, $\eta^* > \eta_{\text{het}}$. Therefore, Kingsley and Lucia (1988) do not find multiple heterogeneous solutions, although the starting points for their calculations (the two-phase solutions) exhibit multiplicity. Note that Bekiaris et al. (1996) provided a physical explanation of the influence of the Murphree tray efficiency by studying the relationship between tray columns with efficiencies and packed columns.

Widagdo et al. (1989)

Widagdo et al. (1989) used the aqueous reflux ratio as a bifurcation parameter for the mixture sec-butanol-water-di-secondary butyl ether, which was also studied by Kovach III and Seider. They found three steady states over a narrow range of aqueous reflux ratios when a second liquid phase exists on the top tray. In all three solutions, the top tray temperature is almost unchanged and ''the compositions and flow rates of the distillate and bottoms are not significantly altered as the aqueous reflux varies.'' The temperatures of the trays below the top tray are the only difference between the three solutions represented in the article (with a maximum temperature difference on the second tray). This may seem unusual at first, but it is possible if the top tray composition moves along (or very close to) a tie line in the heterogeneous region as the aqueous reflux ratio changes. Since the top tray compositions then lie on the same tie line, the top tray temperature remains unchanged (by the VLLE), but the temperature and composition of the tray below can change. The effect of this change propagates down the column, but its impact decreases the further we move away from the top. Hence, the effect of the temperature change is more profound on the tray below the top tray, which agrees with the computations by Widagdo et al. (1989).

The phenomenon described above resembles a situation first reported by Bekiaris et al. (1996), where in the ∞/∞ case of a column with the decanter, internal state multiplicities are obtained for different top tray compositions on the same tie line and the bottoms at the stable node (Figure 20 in that article). It has not been studied in detail what happens in this situation if a finite column is considered. However, output multiplicities are not expected and, thus, the argumentation above may not explain the multiplicities that Widagdo et al. (1989) reported.

Next, Widagdo et al. (1989) study eight column configurations with different number of trays and feed locations. The multiplicity is observed in one of them, but not in any of the other configurations (including the one with the largest number of trays). The reboiler heat duty and the organic phase reflux ratio are the column specifications in these calculations, while the aqueous phase reflux ratio is the bifurcation parameter. Even though a detailed ∞/∞ analysis of this mixture and the column specification would be possible, it is beyond the scope of this article.

Finally, Widagdo et al. (1989) performed a bifurcation analysis of a single-stage column, which shows a unique solution.

Cairns and Furzer (1990)

Cairns and Furzer (1990) present a study of the impact of the thermodynamic model and parameters on the calculated three-phase region of numerous heterogeneous mixtures, and compare the results of simulations including a VLLE algorithm to those of simulations where the liquid-phase splitting is ignored.

Cairns and Furzer (1990) also study the multiplicities reported by Magnussen et al. (1979), directly using the UNIFAC model to describe the liquid-phase behavior of the EWB mixture. By ignoring the liquid-phase split to the column trays, three solutions are calculated by varying the initial profile estimate in the calculation (output multiplicities). The authors show that two of the three solutions are ''fictitious'' since the top trays lie in heterogeneous region. The remaining third solution is also the only solution when the simulations included the phase-splitting (VLLE) algorithm. A single liquid phase exists on all trays of this solution and, thus, no real multiplicities were obtained.

The authors also report two solutions for the mixture ethanol-water-isooctane. One solution is again obtained by ignoring the liquid-phase splitting, and it is shown to be fictitious. In summary, Cairns and Furzer (1990) demonstrated that erroneous solutions can result when ignoring the liquid-phase split, but they do not compute MSS with the corrected algorithms.

Rovaglio and coworkers (1990, 1991, 1993)

Rovaglio and Doherty (1990) studied the EWB mixture in a 27-tray column with and without the decanter using different UNIQUAC parameter sets. For a column without the decanter, the UNIQUAC parameter set by Gmehling and Onken (1977) (the authors recognized the erroneous prediction of the two-phase region), and a column design, as well as operating conditions identical to those used by Magnussen et al. (1979), Rovaglio and Doherty reported that their results are in agreement with those obtained by Magnussen and coworkers.

More details are presented for a column where the decanter is included in the model: Figure 5 in the article by Rovaglio and Doherty (1990) shows three solutions. It is interesting how the authors compute these three solutions. Starting from one steady-state solution (first profile), a temporary disturbance in the feed flow rate is imposed and the transient behavior of the column is calculated by dynamic simulation. With all operating conditions at the original value, the authors identify a stationary point (second, ''unstable'' profile) through which the column profile goes before settling to a new steady state (third profile). A steady-state solver is used to verify that all three profiles satisfy the convergence criteria, and are steady-state solutions of the model. The profiles of the three solutions follow different paths in the composition triangle and all have some trays located in the two-liquid-phase region. Even if the liquid-phase split is ignored on the trays (but not in the decanter), three solutions are calculated. Finally, Rovaglio and Doherty (1990) vary the reflux ratio and calculate three solutions over a large range of reflux ratios.

Using the same simulation approach, three solutions are calculated for a column design similar to Prokopakis and Seider (1983a) and using the parameter set of Prausnitz et al. (1980), without reporting that one azeotrope is missing. Here, the starting point of the dynamic simulations is not a steady state and no disturbance is imposed. Nevertheless, the column goes through two intermediate stationary points (two ''unstable'' profiles) before settling down (''stable'' profile). From the existence of two unstable solutions, Rovaglio and Doherty (1990) conclude that more than three steady states exist for this column. This is consistent with the fact that Kovach III and Seider (1987a) reported five steady states.

However, in this second calculation, the profiles of the three solutions follow approximately the same path in the composition triangle and approach the pure ethanol corner along the benzene-ethanol edge. This difference from the profiles calculated above for the design by Magnussen et al. (1979) can be explained by the different UNIQUAC parameter sets used (the parameter set by Prausnitz et al. (1980) does not predict the ethanol-water azeotrope, see Figure 8).

The most significant difference between the three profiles calculated for the column design by Prokopakis and Seider (1983a) is the position of the composition and temperature front in the column. Finally, in all three solutions, only the decanter exhibits a liquid-phase split, while all trays are homogeneous. Rovaglio et al. (1991) showed that the above three solutions persist (using the parameter set by Prausnitz et al. (1980)), even when the entrainer recovery column and the benzene recycle stream are included in the model. They further show that by increasing the entrainer makeup flow, the three solutions move closer to each other until they collapse into one.

Rovalgio et al. (1993) offer an explanation for the multiple solutions reported by Rovaglio and Doherty (1990). They use dynamic simulations and a trick to show that the three solutions reported by Rovaglio and Doherty (1990) do not correspond to *exactly* the same makeup flow (see Rovaglio et al. (1993) for more information on their procedure). With this, the authors demonstrated that although the three solutions satisfy the convergence criteria (of the steady-state simulator), ''there may be small differences in the necessary makeup flow rates needed to keep these states constant and stable.'' In addition, the residuals of the global material balance of two of the solutions obtained by Rovaglio and Doherty (1990) (along the transient of the dynamic simulation) can dynamically force the column to move slowly, with a time constant of 30 h, towards the final [third] solution.'' Therefore, Rovaglio et al. (1993) conclude that the three solutions are not real MSS, but one real (converged) solution, and two pseudo solutions caused by insufficiently tight convergence criteria. These results are convincing since the residuals of the global material balance of the third solution are significantly smaller than those of the other two ''pseudo'' solutions. This seems reasonable if one considers how the two ''pseudo'' solutions were obtained originally (as stationary, but not real, converged solutions in a dynamic simulation).

Rovaglio et al. (1993) performed a similar analysis for the three regimes reported by Prokopakis and Seider (1983b), and for one of the profiles computed by Cairns and Furzer (1990). They conclude that ''small differences in the convergence criteria can drive the column to different solutions'' (or better ''pseudo'' solutions). The evidence presented regarding these profiles, however, is not very strong. It shows that the residuals are relatively large but it is not clear whether a more accurately converged solution would deviate from these profiles.

The final conclusion of Rovaglio et al. (1993) is that "the problem of multiple steady states seems to be associated with the numerical aspects related to the relative small amount of feed makeup." Indeed, for this type of column calculations, accurate and careful convergence checks are needed to avoid this type of erroneous or inconclusive results. The authors' conjecture that the entire phenomenon of MSS seems to be associated with computational (numerical) aspects, however, this is not true in retrospective. The physical explanation of the existence of multiplicities provided by the ∞/∞ analysis, the numerous homogeneous and heterogeneous simulation examples presented, and, finally, the experimental verification (Güttinger et al., 1997; Müller and Marquardt, 1997) leave no doubt that MSS of type 2a exist in azeotropic distillation.

Bossen et al. (1993); Gani and Jørgensen (1994)

Bossen et al. (1993) also studied the heterogeneous EWB mixture for a column including the decanter using the UNIFAC model. In one of four steady states they found, the whole profile, as well as the decanter compositions, lie in the homogeneous region. The products of the remaining three profiles have exactly the same product compositions and flow rates. The only difference between these three profiles is the location of the front of sharp ethanol-benzene composition change (internal state multiplicities). Since these three profiles are in very good agreement with the results of Rovaglio and Doherty (1990), which were obtained for UNIQUAC, it is highly probable that the convergence criteria applied in this study were not tight enough and, thus, only two of the four steady states might be real and converged (Rovaglio et al., 1993).

Gani and Jørgensen (1994) calculated as many as ten solutions for the EWB column above. However, they do not indicate their convergence tolerance, thus not porviding sufficient evidence that the solutions were fully converged. Therefore, the conjecture made for the previous study applies equally to this work and possibly no multiplicities have been found.

Müller and Marquardt (1997)

In their work, Müller and Marquardt (1997) apply the procedure (analysis, simulation and experimental strategy) reported by Güttinger and Morari (1997) to the heterogeneous mixture of ethanol, water, and cyclohexane (instead of a homogeneous mixture). First, the ∞/∞ analysis for heterogeneous mixtures was applied to predict the existence of MSS caused by the VLLE (Bekiaris et al., 1996). In comparing the MSS interval for volumetric and molar specification of the distillate flow rate, it can be seen that singularities in the input relationship cause the MSS interval to be smaller (Jacobsen and Skogestad, 1991), but still significant enough to be measured on a volumetric basis. In the experimental part, Müller and Marquardt tracked the two stable solution branches whose compositions favorably compare to the results obtained from the steady-state simulations. The unstable branch was not measured due to operational problems in the decanter. Moreover, they report dynamic measurements of the hystersis behavior induced by the existence of MSS.

Sridhar (1997)

In spite of all the experimental evidence for multiplicities to exist also in homogeneous mixtures (Kienle et al., 1995; Koggersbøl et al., 1996; Güttinger et al., 1997; Dorn et al., 1998), there are still "proofs" in the literature that MSS do not exist.

Conclusions

In the first part of this article, it was shown that extreme care needs to be taken towards the thermodynamic model and parameters used for the simulation of heterogeneous azeotropic distillation columns, because the existence of multiplicities is very sensitive to the thermodynamic description in many, or even most, cases. Expecially, the sources of the experimental data, the estimation procedures applied, and the range of applicability of models and parameters need attention beyond routine application.

The ∞/∞ analysis of Bekiaris et al. (1993, 1996) can directly operate on the experimental VL(L)E data and, if the thermodynamic model and parameters are completely reported, provides an understanding of the implications of a mixture's VL(L)E properties for the steady-state behavior of a distillation column. The ∞/∞ predictions indicate where a thermodynamic description is inadequate down to the point where it can suggest experiments for the refinement of such a description.

From the discussion of the literature reports on mulplicities, it can be concluded that while numerical analysis is necessary, it is almost useless without the ∞/∞ analysis. Sensitivity studies of whatever type cannot provide any of the information the ∞/∞ analysis can. The prediction methods of Bekiaris et al. (1993, 1996) are most reliable to date to indicate what conditions will lead to output multiplicities.

This article was not aimed to criticize literature reports which were mostly not focused on the existence of multiplicities. It's good to provide guidelines for future numerical work on multiple steady states.

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Notation

p_i^0 = pure component vapor pressures
Q_c, Q_r = condenser and reboiler heat duties

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