Design and Analysis of Nonequilibrium Separation Processes

L. N. Sridhar, Carlos Maldonado, and Ana Maria Garcia
Dept. of Chemical Engineering, University of Puerto Rico, Mayaguez, PR 00681

Design and analysis of nonequilibrium separation process problem are discussed. Even though there have been published articles on the design and analysis of equilibrium separation process problems, these issues have not been addressed in great detail as far as nonequilibrium problems are concerned. Strategies are developed for drawing residue curve maps using mass-transfer model equations. In addition the multistage nonequilibrium separation process problem is rigorously analyzed and it is shown that, as in the single-stage case, any multiplicity that occurs is a result of the multiplicity that occurs here in the phase equilibrium calculations at the interface.

Introduction

The design aspect is first discussed where a brief background is presented of residue curve maps for equilibrium homogeneous systems. Our strategy is then presented for developing the similar kind of maps for nonequilibrium systems involving homogeneous mixtures without the use of efficiencies. In the second part of this article the analysis is developed for nonequilibrium systems focusing on the problem of solution-multiplicity thus extending the analysis of Sridhar et al. (2000) to multistage nonequilibrium separation process problems.

Residue Curve Maps

A residue curve map analysis predicts the composition path of the mixture in the still as the separation process takes place and, consequently, it is such analysis that is necessary to predict the composition changes in the still. A very good review of the development of the concept of nonreactive residue curve maps is presented by Widagdo and Seider (1996). Residue curve maps have been used since the early 1900s (Ostwald, 1990; Schreinmakers, 1901, 1903) for binary mixtures. Bushmakin and Kish (1957a,b) extended this approach to ternary mixtures while Zharov (1967, 1968a,b) extended their analysis to quaternary and multicomponent mixtures. Matusayama and Nishimura (1977) and Doherty and Perkins (1978a,b, 1979) applied residue curve map analysis to the separation of multicomponent homogeneous mixtures. We present a brief derivation of the residue curve map equation for equilibrium homogeneous systems (similar to Widagdo and Seider (1996)), before moving on to nonequilibrium systems.

Equilibrium residue curve maps

Consider L mols of a liquid, with composition x_i $(i = 1, \ldots, c)$ in a simple distillation still that is vaporized. The differential portion of this liquid ΔL is evaporated. The liquid phase now has a mol fraction $x_i + \Delta x_i$, while the vapor phase has a mol fraction y_i. The material balance equation can be written as

$$Lx_i = \Delta L y_i + (L - \Delta L)(x_i + \Delta x_i) \tag{1}$$

Simplification and taking the limit $\Delta L \rightarrow 0$ yields

$$\frac{dx_i}{(dL/L)} = (x_i - y_i) \tag{2}$$

Setting $(dL/L = dt)$, we have the residue curve map equation

$$\frac{dx_i}{(dt)} = (x_i - y_i) \tag{3}$$

Here x and y represent the liquid- and vapor-phase compositions and t is the dimensionless time. In order to determine

---

Correspondence concerning this article should be addressed to L. N. Sridhar.

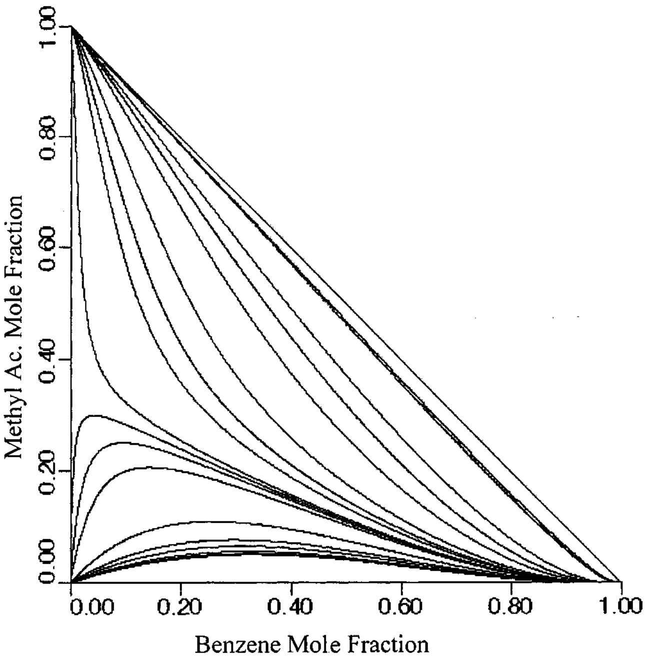

Figure 1. Residue for methyl Ac-benzene-chloroform created with equilibrium method.

the vapor-phase composition for a given liquid-phase composition one must solve the classic bubble point problem (commonly known as the BUBL-T) problem. The details of this problem and the method of solution are presented in various textbooks (Smith and VanNess, 1981; Henley and Seader; 1981). Very briefly, the variables involved are the vapor mol fractions $\{y_i\}$ and the temperature T. The equations involved are the c equilibrium equations

$$y_i - \kappa_i x_i = 0 \tag{4}$$

and the summation equation

$$\sum_{i=1}^{c} y_i - 1 = 0 \tag{5}$$

The equations are solved by Newton's method. Once the vapor composition is obtained, Eq. 3 can be integrated to obtain the residue curve.

Figure 1 shows an equilibrium residue curve map for the mixture methyl-acetate, choloroform, and benzene.

Nonequilibrium Model

In this section, we provide a brief description of the rate-based nonequilibrium model. The rate-based nonequilibrium model, originally developed by Krishnamurthy and Taylor (1985), was found to provide excellent simulation results for vapor liquid separation process problems as confirmed by Fair (1987), Seader (1988), Sivasubramanian and Boston (1988), and Ryan et al. (1994). Lao and Taylor (1994) have extended this work to multiple liquid phase problems, while Sridhar and Torres (1998, p. 2175) have incorporated a rigorous stability analysis in these problems.

While mass and energy balance and phase equilibrium relationships are found in equilibrium models, the difference between the equilibrium and nonequilibrium models lies in the manner that the equations are used. In equilibrium problems, the balance equations are written for the stage as a whole and the phases that exit the stage are in equilibrium with each other. For the nonequilibrium problem on the other hand, the material and energy balance equations are written for each phase allowing for mass and energy transfer across the boundaries. The temperature, pressure, and chemical potential are equal across the interface. It is shown by Krishnamurthy and Taylor (1985) that the addition of the material balance equations for both the phases results in the same material balance equation that one uses in the equilibrium-stage problem.

Sridhar and Torres (1998) were able to combine a numerical implementation of the tangent plane criterion as provided by Michelsen (1982), with the nonequilibrium model and were able to solve problems involving two and three liquid phases. In this work, they demonstrated (in the problem involving toluene, n-propanol, and water) that the tangent plane criterion, when combined with the nonequilibrium model, actually obtained the correct number of phases (two), while the equilibrium model incorrectly predicted three liquid phases. In the case of the problem involving nitromethane, 1-hexanol, and water they were able to show that both equilibrium and nonequilibrium models correctly predicted three liquid phases. Sridhar et al. (2000) rigorously showed that the nonequilibrium single-stage problem admitted a unique steady-state solution for some specifications and that any multiplicity in the nonequilibrium problem was a result of the multiplicity occurring in the interface phase equilibrium calculations.

Development of nonequilibrium residue curve maps

Baur et al. (1999) studied the influence of mass transfer on composition trajectories during distillation of mixtures with distillation boundaries. However, they use equilibrium residue curve maps for their study. Castillo and Towler (1998) use Murphree efficiencies to account for departures from equilibrium in residue curves for homogeneous mixtures. The residue curve map equation that they derive has the form

$$\frac{dx_i}{(dt)} = x_i E_i^{MV}(1 - \kappa_i) \tag{6}$$

where E_i^{MV} is the murphree efficiency and κ_i represents the K-value. However, as stated by Sawitowski (Taylor and Krishna, 1993), ".. The concept of plate efficiency of individual components in a multicomponent mixture is of doubtful validity and is retained only on account of its simplicity." We can avoid the use of efficiencies by directly solving the mass-transfer equations and can obtain the residue curve maps for the characterization of homogeneous azeotropic mixtures. We define an azeotrope in the traditional way (Sweitolawski, 1963; Widagdo and Seider, 1996) that the vapor resulting from the boiling of the liquid has the same composition of the liquid. For a nonequilibrium model, this implies that the bulk phase vapor and liquid compositions will be the same. We derive the nonequilibrium residue curve map equation as follows. Consider L mols of a liquid, with mol fraction x_i ($i = 1, \ldots, c$) in a simple distillation that is vaporized. The differentional portion of this liquid ΔL is evaporated. The liquid phase now has a mol fraction $x_i + \Delta x_i$ while the vapor phase has a mol fraction y_i. The evaporation can be modeled by a mass-transfer approach by writing a material balance for each of the phases as

$$L x_i = N_i^L + (L - \Delta L)(x_i + \Delta x_i) \tag{7}$$

and

$$N_i^L = V y_i \tag{8}$$

Adding Eqs. 7 and 8 and considering that $V = \Delta L$ by overall material balance, we take

$$L x_i = \Delta L y_i + (L - \Delta L)(x_i + \Delta x_i) \tag{9}$$

Simplification and taking the limit $\Delta L \to 0$ yields

$$\frac{dx_i}{(dL/L)} = (x_i - y_i) \tag{10}$$

Setting (dL/dt), we have the residue curve map equation

$$\frac{dx_i}{(dt)} = (x_i - y_i) \tag{11}$$

Here x and y represent the bulk-phase liquid and vapor-phase compositions, and t is the dimensionless time. The problem that we need to solve in order to integrate Eq. 11 is to find the bulk vapor phase given the liquid-phase bulk and interface compositions. In the next few sections we describe a method of solution for this problem.

Problem Statement

Given the bulk liquid-phase composition (x), in a three component mixture, the interface composition x^{int} and the pressure P, find:

- The bulk vapor phase composition y;
- The vapor-phase interface composition (y^{int});
- The temperature T; and
- The Fluxes N_1, N_2, N_3.

Variables in the Problem

- Vapor-phase interface composition (y_1^{int}, y_2^{int}, y_3^{int};
- bulk-phase vapor compositions (y_1, y_2);
- temperature (T); and
- fluxes (N_1, N_2, N_3).

The total number of variables is 9.

Equations used

The equations used are the three interface equilibrium equations

$$y_i^{\text{int}} - \kappa_i x_i^{\text{int}} = 0 \tag{12}$$

$i = 1, .. 3$

the *two* transfer-rate equations for the liquid phase

$$-N_1^L - N_t^L x_1^L - K_1^L\left(x_1^L - x_1^{\text{int}}\right) = 0 \tag{13}$$

$$N_2^L - N_t^L x_2^L - K_2^L\left(x_2^L - x_2^{\text{int}}\right) = 0 \tag{14}$$

the two transfer-rate equations for the vapor phase

$$N_1^L + N_t^L y_1^V - K_1^V\left(y_1^V - y_1^{\text{int}}\right) = 0 \tag{15}$$

and

$$-N_2^L + N_t^L y_2^V - K_2^V\left(y_2^V - y_2^{\text{int}}\right) = 0 \tag{16}$$

the energy continuity equation

$$N_1 \Delta H_1 + N_2 \Delta H_2 + N_3 \Delta H_3 = 0 \tag{17}$$

and the summation equation for the interface vapor mol fraction

$$\sum_{i=1}^{c} y_i^{\text{int}} - 1 = 0 \tag{18}$$

The interface flux material balances are taken care of in the transfer rate equations. The equations are assembled together and solved using Newton's method with finite difference derivatives.

At a singular point, the derivative (dx_i/dt) will be 0 and this implies that the bulk vapor and liquid phase compositions will be the same. This would be the bulk-phase azeotropic point or the nonequilibrium azeotropic point. It is shown that when we use this approach (and the given definition of the azeotrope) both the equilibrium (interface) and the nonequilibrium (bulk phase) azeotropes will coincide. In other words, x^L and y^V are equal at the same point when the interface compositions (x^{int} and y^{int}) are equal. In order to prove this we take the transfer rate equations for the liquid and vapor phases and the nonequilibrium and equilibrium azeotropic conditions yield

$$x_1^L = y_1^V \tag{19}$$

and

$$x_1^{\text{int}} = y_1^{\text{int}} \tag{20}$$

Substituting x_1^L for y_1^V and x_1^{int} for y_1^{int} in Eqs. 13 and 15 and adding them, we have

$$\left(K_1^L + K_1^V\right)\left(x_1^L - x_1^{\text{int}}\right) = 0 \tag{21}$$

Since molar density and the mass-transfer coefficients are positive, the only way that Eq. 21 can hold is if x_1^L and x_1^{int} are equal. Consequently, the bulk and the interface vapor compositions will also be equal. This implies that the nonequilibrium and equilibrium azeotropes will coincide. Figure 2a shows a residue curve map obtained by using this strategy for the mixture acetone chloroform and ethanol. Fig-

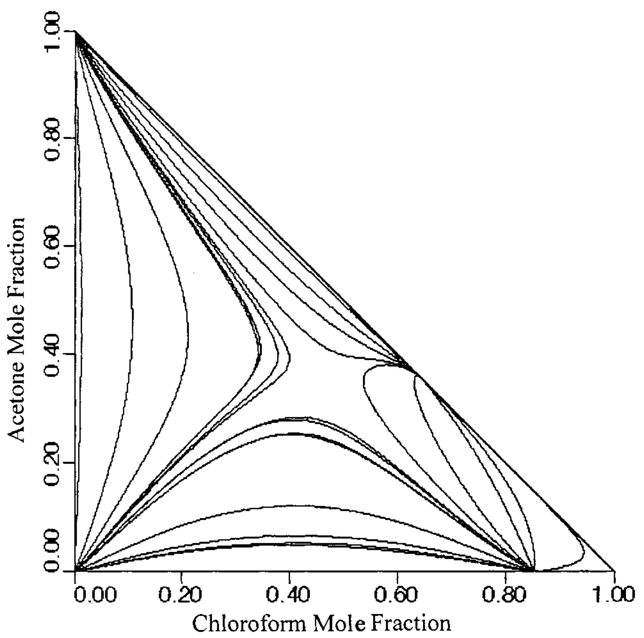

Figure 2a. Residue for acetone-chloroform-ethanol created with nonequilibrium method.

ure 2b shows a comparison between the residue curve maps for the equilibrium and nonequilibrium models. As can be seen in the figure, the nonequilibrium and the equilibrium azeotropes coincide, however, since the curvature of the residue curves in both the cases is different, the distillation boundaries can be different.

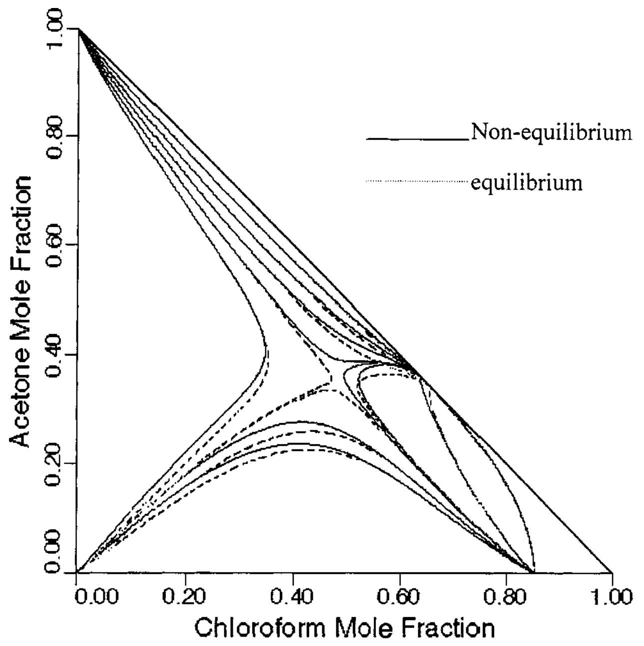

Figure 2b. Nonequilibrium vs. equilibrium residue curve maps for the mixture of acetone-chloroform-ethanol.

Analysis of Nonequilibrium Separation Problems

In the next few sections we present some analysis of multistage nonequilibrium separation processes. The problem that has triggered a lot of analysis in multistage separation problems is the determination of the cause(s) for the existence of solution multiplicities in these problems. Various analytical results were obtained by Rosenbrock (1960, 1962), Doherty and Perkins (1982), Lucia (1986), Sridhar and Lucia (1989, 1990), and Sridhar (1996, 1997). A brief review of the work on equilibrium staged solution multiplicities in separation processes is presented in the Appendix.

The first attempt to analyze the nonequilibrium problems was by Sridhar et al. (2000). In this work the results of Lucia (1986) were applied to the interface and a one-to-one correspondence between the bulk and the interface compositions was established thereby showing that any multiplicity occurring in the single-stage nonequilibrium problem was because of the multiplicity occurring in the equilibrium calculations at the interface. In the next few sections this approach is extended to multistage problems. We start with the simplest case possible (binary two-stage systems) and then extend the analysis to multistage and multicomponent systems. This approach will guarantee solution uniqueness for the specifications described in Sridhar and Lucia (1989) for binary mixtures, and Sridhar and Lucia (1990) and Sridhar (1997) for nonazeotropic multicomponent systems.

Analysis of two-stage binary nonequilibrium problems

In this section, we extend the analysis of the single-stage nonequilibrium problem to two stages. We denote the bulk liquid and vapor mol fractions of component i that exit stage j as x_{ij}^b and y_{ij}^b and the interface liquid and vapor mol fractions as x_{ij}^I and y_{ij}^I. As in the single-stage analysis of Sridhar et al. (2000), we start with binary mixtures and show that for every equilibrium two-stage problem there would be only one two-stage nonequilibrium problem. This would be achieved by demonstrating a one-to-one correspondence between the bulk and the interface compositions that exit both the stages. For a two-stage problem, the relevant compositions are x_{11}^b x_{12}^b y_{11}^b and y_{12}^b for the bulk phases and x_{11}^I x_{12}^I y_{11}^I and y_{12}^I. The Jacobian matrix J for the set of functions that connect the two sets of variables is given by

$$J = \begin{bmatrix} \frac{\partial x_{11}^b}{\partial x_{11}^I} & \frac{\partial x_{11}^b}{\partial x_{12}^I} & \frac{\partial x_{11}^b}{\partial y_{11}^I} & \frac{\partial x_{11}^b}{\partial y_{12}^I} \\ \frac{\partial x_{12}^b}{\partial x_{11}^I} & \frac{\partial x_{12}^b}{\partial x_{12}^I} & \frac{\partial x_{12}^b}{\partial y_{11}^I} & \frac{\partial x_{12}^b}{\partial y_{12}^I} \\ \frac{\partial y_{11}^b}{\partial x_{11}^I} & \frac{\partial y_{11}^b}{\partial x_{12}^I} & \frac{\partial y_{11}^b}{\partial y_{11}^I} & \frac{\partial y_{11}^b}{\partial y_{12}^I} \\ \frac{\partial y_{12}^b}{\partial x_{11}^I} & \frac{\partial y_{12}^b}{\partial x_{12}^I} & \frac{\partial y_{12}^b}{\partial y_{11}^I} & \frac{\partial y_{12}^b}{\partial y_{12}^I} \end{bmatrix} \qquad (22)$$

The expressions for the partial derivatives in the Jacobian matrix J can be obtained from the equations that constitute the two-stage nonequilibrium problem. Separate material balance equations are written for the vapor and liquid phases for each of the two stages. The liquid-phase material balance equations for stage I can be written as

$$L_1 x_{11}^b - F_{11}^L z_{11}^L + N_{11}^L a = 0 \tag{23}$$

The transfer rate equation involving the flux N_{11}^L is

$$N_{11}^L - N_{t1}^L x_{11}^b - K_1^L \left(x_{11}^b - x_{11}^I \right) = 0 \tag{24}$$

Substituting for N_{11}^L in Eq. 23, we take

$$\left(\frac{L_1}{a} + N_{t1} + K_1^L \right) x_{11}^b - \frac{F_{11} z_{11}^L}{a} - K_1^L x_{11}^I = 0 \tag{25}$$

or

$$x_{11}^b = \frac{F_{11}^L z_{11}^L}{\left(\dfrac{L_1}{a} + N_{t1} + K_1^L \right)} + \frac{K_1^L}{\left(\dfrac{L_1}{a} + N_{t1} + K_1^L \right)} x_{11}^I \tag{26}$$

This can be concisely written as

$$x_{11}^b = A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I \tag{27}$$

The corresponding equations for the second stage would be

$$L_2 x_{12}^b - L_1 x_{11}^b - F_{12}^L z_{12}^L + N_{12}^L a = 0 \tag{28}$$

where b represents the bulk phase and I represents the interface.

The occurrence of the term x_{11}^b in Eq. 28 is inconvenient in order to express the bulk phase compositions as a function of the interface compositions in the form

$$\left(x_{11}^b \right) = \phi_1 \left(x_{11}^I, x_{12}^I \right) \tag{29}$$

and

$$\left(x_{12}^b \right) = \phi_2 \left(x_{11}^I, x_{12}^I \right) \tag{30}$$

We can get around this problem by substituting for x_{11}^b from Eq. 27 and we get

$$L_2 x_{12}^b - L_1 \left(A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I \right) - F_{12}^L z_{12}^L + N_{12}^L a = 0 \tag{31}$$

The transfer-rate equation for the liquid phase for stage 2 is

$$N_{12}^L - N_{t2}^L x_{12}^b - K_1^L \left(x_{12}^b - x_{12}^I \right) = 0 \tag{32}$$

Substituting for the fluxes N_{12}^L in Eq. 31, we take

$$\begin{aligned} L_2 x_{12}^b - L_1 \left(A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I \right) - F_{12}^L z_{12}^L \\ + \left[N_{t2}^L x_{12}^b + K_1^L \left(x_{12}^b - x_{12}^I \right) \right] a = 0 \end{aligned} \tag{33}$$

or

$$x_{12}^b = A_{1211}^L z_{11}^L + A_{1212}^L z_{12}^L + B_{1211}^L x_{11}^I + B_{1212}^L x_{12}^I \tag{34}$$

The partial derivative $\partial x_{11}^b / \partial x_{11}^I$ can be obtained from Eq. 27 as

$$\frac{\partial x_{11}^b}{\partial x_{11}^I} = B_{1111}^L = \frac{K_1^L}{\left[(L_1/a) + K_1^L + N_{t1}^L \right]} \tag{35}$$

Similarly,

$$\frac{\partial x_{12}^b}{\partial x_{12}^I} = B_{1212}^L = \frac{K_2^L}{\left[(L_2/a) + K_2^L + N_{t2}^L \right]}. \tag{36}$$

The derivative $\partial x_{11}^b / \partial x_{12}^I = 0$ and so are the terms $\partial x_{ij}^b / \partial y_{kl}^I$ and $\partial y_{ij}^b / \partial x_{kl}^I$ because the material balance equations are written for each phase separately in the nonequilibrium model. The material balance equations for the vapor phase can be written as

$$V_1 y_{11}^b - F_{11}^V z_{11}^V + N_{11}^V a - V_2 y_{12}^b = 0 \tag{37}$$

for the first stage and

$$V_2 y_{12}^b - F_{12}^V z_{i2}^V + N_{12}^V a = 0 \tag{38}$$

for the second stage.

The transfer rate equations for the vapor phase for both stages are

$$N_{11}^V - N_{t1}^V y_{11}^b - K_1^v \left(y_{11}^b - y_{11}^I \right) = 0 \tag{39}$$

and

$$N_{12}^V - N_{t2}^V y_{12}^b - K_2^v \left(y_{12}^b - y_{12}^I \right) = 0 \tag{40}$$

Performing a similar analysis as in the liquid phase, we get the derivatives

$$\frac{\partial y_{11}^b}{\partial y_{11}^I} = \frac{K_1^V}{\left[(V_1/a) + K_1^V + N_{t1}^V \right]} \tag{41}$$

and

$$\frac{\partial y_{12}^b}{\partial y_{12}^I} = \frac{K_2^V}{\left[(V_2/a) + K_2^V + N_{t2}^V \right]} \tag{42}$$

The derivative $\partial y_{12}^b / \partial y_{11}^I = 0$ and this implies that the Jacobian matrix J would have the form

$$J = \begin{bmatrix} \dfrac{K_1^L}{\left[(L_1/a) + K_1^L + N_{t1}^L\right]} & 0 & 0 & 0 \\ \dfrac{\partial x_{12}^b}{\partial x_{11}^I} & \dfrac{K_2^L}{\left[(L_2/a) + K_2^L + N_{t2}^L\right]} & 0 & 0 \\ 0 & 0 & \dfrac{K_1^V}{\left[(V_1/a) + K_1^V + N_{t1}^V\right]} & \dfrac{\partial y_{11}^b}{\partial y_{12}^I} \\ 0 & 0 & 0 & \dfrac{K_2^V}{\left[(V_2/a) + K_2^V + N_{t2}^V\right]} \end{bmatrix} \tag{43}$$

The denominators in the expressions for the diagonal terms of J are always nonzero, because the mass-transfer coefficient K is positive and dominates the flux term N. This is because the mass-transfer coefficient is the *maximum* velocity at which a component can be transferred (Taylor and Krishna, 1993). Since the liquid and vapor molar flow rates are always positive, the denominator will always be positive.

The Jacobian matrix J can be concisely expressed as

$$J = \begin{bmatrix} J_L & 0 \\ 0 & J_V \end{bmatrix} \tag{44}$$

The block J_L is a lower triangular matrix, while the block J_V is an upper triangular matrix. The eigenvalues of both the blocks and, consequently, the eigenvalues of the Jacobian J, are the diagonal terms which are nonzero, and, consequently, J is nonsingular which implies that in a two-stage problem there exists a one-to-one correspondence between the bulk phase and the interface compositions. Therefore, any multiplicity in the nonequilibrium two-stage problem would be a result of the multiplicity that occurs in the interface equilibrium calculations.

Extension to Multistage Systems

For a three-stage problem, the Jacobian matrix J would have the form

$$J = \begin{bmatrix} \dfrac{\partial x_{11}^b}{\partial x_{11}^I} & \dfrac{\partial x_{11}^b}{\partial x_{12}^I} & \dfrac{\partial x_{11}^b}{\partial x_{13}^I} & \dfrac{\partial x_{11}^b}{\partial y_{11}^I} & \dfrac{\partial x_{11}^b}{\partial y_{12}^I} & \dfrac{\partial x_{11}^b}{\partial y_{13}^I} \\ \dfrac{\partial x_{12}^b}{\partial x_{11}^I} & \dfrac{\partial x_{12}^b}{\partial x_{12}^I} & \dfrac{\partial x_{12}^b}{\partial x_{13}^I} & \dfrac{\partial x_{12}^b}{\partial y_{11}^I} & \dfrac{\partial x_{12}^b}{\partial y_{12}^I} & \dfrac{\partial x_{12}^b}{\partial y_{13}^I} \\ \dfrac{\partial x_{13}^b}{\partial x_{11}^I} & \dfrac{\partial x_{13}^b}{\partial x_{12}^I} & \dfrac{\partial x_{13}^b}{\partial x_{13}^I} & \dfrac{\partial x_{13}^b}{\partial y_{11}^I} & \dfrac{\partial x_{13}^b}{\partial y_{12}^I} & \dfrac{\partial x_{13}^b}{\partial y_{13}^I} \\ \dfrac{\partial y_{11}^b}{\partial x_{11}^I} & \dfrac{\partial y_{11}^b}{\partial x_{12}^I} & \dfrac{\partial y_{11}^b}{\partial x_{13}^I} & \dfrac{\partial y_{11}^b}{\partial y_{11}^I} & \dfrac{\partial y_{11}^b}{\partial y_{12}^I} & \dfrac{\partial y_{11}^b}{\partial y_{13}^I} \\ \dfrac{\partial y_{12}^b}{\partial x_{11}^I} & \dfrac{\partial y_{12}^b}{\partial x_{12}^I} & \dfrac{\partial y_{12}^b}{\partial x_{13}^I} & \dfrac{\partial y_{12}^b}{\partial y_{11}^I} & \dfrac{\partial y_{12}^b}{\partial y_{12}^I} & \dfrac{\partial y_{12}^b}{\partial y_{13}^I} \\ \dfrac{\partial y_{13}^b}{\partial x_{11}^I} & \dfrac{\partial y_{13}^b}{\partial x_{12}^I} & \dfrac{\partial y_{13}^b}{\partial x_{13}^I} & \dfrac{\partial y_{13}^b}{\partial y_{11}^I} & \dfrac{\partial y_{13}^b}{\partial y_{12}^I} & \dfrac{\partial y_{13}^b}{\partial y_{13}^I} \end{bmatrix} \tag{45}$$

We write the material balance for the first stage as

$$L_1 x_{11}^b - F_{11}^L z_{11}^L + N_{11}^L a = 0 \tag{46}$$

while the equations for stages 2 and 3 can be written as

$$L_2 x_{12}^b - F_{12}^L z_{12}^L - L_1 x_{11}^b + N_{12}^L a = 0 \tag{47}$$

and

$$L_3 x_{13}^b - F_{13}^L z_{13}^L - L_2 x_{12}^b + N_{13}^L a = 0 \tag{48}$$

Again, in order to check for a one-to-one correspondence, we must be able to express the bulk and the interface equations in the form

$$\left(x_{11}^b\right) = \phi_1\left(x_{11}^I, x_{12}^I, x_{13}^I\right) \tag{49}$$

$$\left(x_{12}^b\right) = \phi_2\left(x_{11}^I, x_{12}^I, x_{13}^I\right) \tag{50}$$

and

$$\left(x_{13}^b\right) = \phi_3\left(x_{11}^I, x_{12}^I, x_{13}^I\right) \tag{51}$$

To facilitate this, we start by expressing x_{11}^b as a function of x_{11}^I in the form

$$x_{11}^b = \frac{F_{11}^L z_{11}^L}{\left(\dfrac{L_1}{a} + N_{t1} + K_1^L\right)} + \frac{K_1^L}{\left(\dfrac{L_1}{a} + N_{t1} + K_1^L\right)} x_{11}^I$$

This could be more concisely written as

$$x_{11}^b = A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I \tag{52}$$

This would result in

$$L_2 x_{12}^b - F_{12}^L z_{12}^L - L_1\left(A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I\right) + N_{12}^L a = 0 \tag{53}$$

Substituting for N_{12}^L we take

$$L_2 x_{12}^b - F_{12}^L z_{12}^L - L_1\left(A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I\right) + N_{t2}^L x_{12}^b + K_2^L\left(x_{12}^b - x_{12}^I\right) a = 0 \tag{54}$$

This equation can be concisely written as

$$x_{12}^b = A_{1211}^L z_{11}^L + A_{1212}^L z_{12}^L + B_{1211}^L x_{11}^I + B_{1212}^L x_{12}^I \tag{55}$$

Similarly

$$x_{13}^{b} = A_{1311}^{L} z_{11}^{L} + A_{1312}^{L} z_{12}^{L} + A_{1313}^{L} z_{13}^{L} + B_{1311}^{L} x_{11}^{I} + B_{1312}^{L} x_{12}^{I} + B_{1313}^{L} x_{13}^{I} \quad (56)$$

and the Jacobian matrix J has the form

$$J = \begin{bmatrix} J_L & 0 \\ 0 & J_V \end{bmatrix} \quad (57)$$

where J_L is a lower triangular matrix and J_V is an upper triangular matrix. The diagonal elements of J_L are

$$B_{1i1i}^{L} = \frac{K_i^L}{\left[(L_i/a) + K_i^L + N_{ti}^L \right]}$$

where $i = 1,2,3$. Similarly, the diagonal elements of J_V are

$$\frac{K_i^V}{\left[(V_i/a) + K_i^V + N_{ti}^V \right]}$$

The eigenvalues of the Jacobian matrix J are the diagonal terms which are nonzero and therefore the Jacobian matrix is nonsingular. This implies a one-to-one correspondence between the bulk and the interface compositions in the three-stage problem and, consequently, the multiplicity that occurs in a three-stage nonequilibrium problem will be a result of the multiplicity that occurs in the phase equilibrium calculations at the interface.

For a general problem of n_s stages, the liquid-phase material balance for any given stage k can be written as

$$L_k x_{1k}^{b} - \sum_{i=1}^{k} F_{1i}^{L} z_{1i}^{L} + \sum_{i=1}^{k} N_{1i}^{L} a = 0 \quad (58)$$

The transfer rate equations can be written as

$$N_{1i}^{L} - N_{1t}^{L} x_{1i}^{b} - K_{1i}^{L} \left(x_{1i}^{b} - x_{1i}^{L} \right) = 0 \quad (59)$$

for $i = 1,\ n_s$.

Substitution and differentiation would yield a Jacobian matrix similar to Eq. 57 where J_L and J_V are upper and lower triangular blocks and, consequently, the eigenvalues of the Jacobian matrix J are the diagonal terms which are

$$\frac{K_i^L}{\left[(L_i/a) + K_i^L + N_{ti}^L \right]}$$

where $i = 1,\ n_s$. The Jacobian matrix J is therefore nonsingular, and this implies a one-to-one correspondence between the bulk and the interface compositions for the binary multistage nonequilibrium problem. This also implies that any solution multiplicity in the binary multistage nonequilibrium problem occurs as a result of the multiplicity in the phase-equilibrium calculations at the interface.

Extension to ternary systems

The Jacobian matrix J for a two-stage ternary problem will be

$$J = \begin{bmatrix}
\frac{\partial x_{11}^{b}}{\partial x_{11}^{I}} & \frac{\partial x_{11}^{b}}{\partial x_{21}^{I}} & \frac{\partial x_{11}^{b}}{\partial x_{12}^{I}} & \frac{\partial x_{11}^{b}}{\partial x_{22}^{I}} & \frac{\partial x_{11}^{b}}{\partial y_{11}^{I}} & \frac{\partial x_{11}^{b}}{\partial y_{21}^{I}} & \frac{\partial x_{11}^{b}}{\partial y_{12}^{I}} & \frac{\partial x_{11}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial x_{21}^{b}}{\partial x_{11}^{I}} & \frac{\partial x_{21}^{b}}{\partial x_{21}^{I}} & \frac{\partial x_{21}^{b}}{\partial x_{12}^{I}} & \frac{\partial x_{21}^{b}}{\partial x_{22}^{I}} & \frac{\partial x_{21}^{b}}{\partial y_{11}^{I}} & \frac{\partial x_{21}^{b}}{\partial y_{21}^{I}} & \frac{\partial x_{21}^{b}}{\partial y_{12}^{I}} & \frac{\partial x_{21}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial x_{12}^{b}}{\partial x_{11}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{21}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{12}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{22}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{11}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{21}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{12}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial x_{22}^{b}}{\partial x_{11}^{I}} & \frac{\partial x_{22}^{b}}{\partial x_{21}^{I}} & \frac{\partial x_{22}^{b}}{\partial x_{12}^{I}} & \frac{\partial x_{22}^{b}}{\partial x_{22}^{I}} & \frac{\partial x_{22}^{b}}{\partial y_{11}^{I}} & \frac{\partial x_{22}^{b}}{\partial y_{21}^{I}} & \frac{\partial x_{22}^{b}}{\partial y_{12}^{I}} & \frac{\partial x_{22}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial y_{11}^{b}}{\partial x_{11}^{I}} & \frac{\partial y_{11}^{b}}{\partial x_{21}^{I}} & \frac{\partial y_{11}^{b}}{\partial x_{12}^{I}} & \frac{\partial y_{11}^{b}}{\partial x_{22}^{I}} & \frac{\partial y_{11}^{b}}{\partial y_{11}^{I}} & \frac{\partial y_{11}^{b}}{\partial y_{21}^{I}} & \frac{\partial y_{11}^{b}}{\partial y_{11}^{I}} & \frac{\partial y_{11}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial y_{21}^{b}}{\partial x_{11}^{I}} & \frac{\partial y_{21}^{b}}{\partial x_{21}^{I}} & \frac{\partial y_{21}^{b}}{\partial x_{12}^{I}} & \frac{\partial y_{21}^{b}}{\partial x_{22}^{I}} & \frac{\partial y_{21}^{b}}{\partial y_{11}^{I}} & \frac{\partial y_{21}^{b}}{\partial y_{21}^{I}} & \frac{\partial y_{21}^{b}}{\partial y_{12}^{I}} & \frac{\partial y_{21}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial x_{12}^{b}}{\partial x_{11}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{21}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{12}^{I}} & \frac{\partial x_{12}^{b}}{\partial x_{22}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{11}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{21}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{12}^{I}} & \frac{\partial x_{12}^{b}}{\partial y_{22}^{I}} \\
\frac{\partial y_{22}^{b}}{\partial x_{11}^{I}} & \frac{\partial y_{22}^{b}}{\partial x_{21}^{I}} & \frac{\partial y_{22}^{b}}{\partial x_{12}^{I}} & \frac{\partial y_{22}^{b}}{\partial x_{22}^{I}} & \frac{\partial y_{22}^{b}}{\partial y_{11}^{I}} & \frac{\partial y_{22}^{b}}{\partial y_{21}^{I}} & \frac{\partial y_{22}^{b}}{\partial y_{12}^{I}} & \frac{\partial y_{22}^{b}}{\partial y_{22}^{I}}
\end{bmatrix} \quad (60)$$

The terms $\partial x_{ij}^b/\partial y_{kl}^I$ and $\partial y_{ij}^b/\partial x_{kl}^I$ are 0 as separate material balance equations are written for both phases. Consequently, the Jacobian matrix can be concisely expressed in the form shown by Eq. 57. The component material balances for stages 1 and 2 can be written as

$$L_1 x_{i1}^b - F_1^L z_{i1}^L + N_{i1}^L a = 0 \tag{61}$$

and

$$L_2 x_{i2}^b - F_2^L z_{i2}^L - L_1 x_{i1}^b + N_{i2}^L a = 0 \tag{62}$$

where i is the component index 1,2. For a multicomponent system, both N_{11} and N_{21} depend on both x_{11} and x_{21}. Similarly, both N_{12} and N_{22} depend both on x_{12} and x_{22}. The transfer rate equations can be written as

$$N_{11}^L = N_{t1}^L x_{11}^b + K_{111}^L\left(x_{11}^b - x_{11}^I\right) + K_{121}^L\left(x_{21}^b - x_{21}^I\right) \tag{63}$$

$$N_{21}^L = N_{t1}^L x_{21}^b + K_{211}^L\left(x_{11}^b - x_{11}^I\right) + K_{221}^L\left(x_{21}^b - x_{21}^I\right) \tag{64}$$

Equation 61 can be written for component 1 and combined with Eq. 63 as

$$L_1 x_{11}^b - F_1^L z_{11}^L + \left[N_{t1}^L x_{11}^b + K_{111}^L\left(x_{11}^b - x_{11}^I\right) + K_{121}^L\left(x_{21}^b - x_{21}^I\right)\right] a = 0 \tag{65}$$

and

$$L_1 x_{21}^b - F_1^L z_{21}^L + \left[N_{t1}^L x_{21}^b + K_{211}^L\left(x_{11}^b - x_{11}^I\right) + K_{221}^L + \left(x_{21}^b - x_{21}^I\right)\right] a = 0 \tag{66}$$

Eliminating x_{21}^b from Eq. 65 and x_{11}^b from Eq. 66, we can write

$$x_{11}^b = A_{1111}^L z_{11}^L + B_{1111}^L x_{11}^I + B_{1121}^L x_{21}^I + A_{2121}^L z_{21}^L \tag{67}$$

and

$$x_{21}^b = A_{2121}^L z_{21}^L + B_{2111}^L x_{11}^I + B_{2121}^L x_{21}^I + A_{2111}^L z_{11}^L \tag{68}$$

The terms $\partial x_{11}^b/\partial x_{12}^I$, $\partial x_{11}^b/\partial x_{22}^I$, $\partial x_{21}^b/\partial x_{12}^I$, $\partial x_{21}^b/\partial x_{22}^I$ are 0. Consequently the block J_L has the form

$$J_L = \begin{bmatrix} J_{L_1} & 0 \\ A & J_{L_2} \end{bmatrix} \tag{69}$$

where

$$J_{L_1} = \begin{bmatrix} \dfrac{\partial x_{11}^b}{\partial x_{11}^I} & \dfrac{\partial x_{11}^b}{\partial x_{21}^I} \\ \dfrac{\partial x_{21}^b}{\partial x_{11}^I} & \dfrac{\partial x_{21}^b}{\partial x_{21}^I} \end{bmatrix} \tag{70}$$

The determinant of J_{L_1} is $B_{1111}^L B_{2121}^L - B_{2111}^L B_{1121}^L$ which is equal to

$$\left[\frac{K_{111}^L}{\left(K_{111}^L + N_{t1}^L + L_1/a\right)}\right]\left[\frac{K_{221}^L}{\left(K_{221}^L + N_{t1}^L + L_1/a\right)}\right] - \left[\frac{K_{121}^L}{\left(K_{121}^L + L_1/a\right)}\right]\left[\frac{K_{211}^L}{\left(K_{211}^L + L_1/a\right)}\right]$$

The diagonal terms of the matrix of the mass-transfer coefficients are greater than the nondiagonal terms, and consequently

$$K_{111}^L > K_{121}^L \tag{71}$$

and

$$K_{221}^L > K_{211}^L \tag{72}$$

This implies that

$$\frac{(L_1/a)}{\left(K_{111}^L\right)} + 1 < \frac{(L_1/a)}{\left(K_{121}^L\right)} + 1 \tag{73}$$

which leads to

$$\frac{K_{111}^L}{K_{111}^L + (L_1/a)} > \frac{K_{121}^L}{K_{121}^L + (L_1/a)} \tag{74}$$

The total flux N_{t1}^L is a very small number 10^{-5}–10^{-6} and, consequently

$$\frac{K_{111}^L}{K_{111}^L + N_{t1}^L + (L_1/a)} > \frac{K_{121}^L}{K_{121}^L + (L_1/a)} \tag{75}$$

Similarly,

$$\frac{K_{221}^L}{K_{221}^L + N_{t1}^L + (L_1/a)} > \frac{K_{211}^L}{K_{211}^L + (L_1/a)} \tag{76}$$

Consequently, the determinant of J_{L_1} is nonzero. Similarly, the determinant of J_{L_2} is nonzero. This implies that the determinant of J_L is nonzero and, in an identical fashion, the determinant of J_V is nonzero. This implies that, in a two-stage problem involving a ternary mixture, any multiplicity in the nonequilibrium problem would be a result of the multiplicity that occurs in the phase equilibrium calculations at the interface. This analysis can be easily extended to an n_s-stage column. For such a column, the matrix J would have the form given by Eq. 57, while J_L would have the form given by

$$J_L = \begin{bmatrix} J_{L_1} & 0 & 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & 0 \\ A_{21} & J_{L_2} & 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ A_{n_s 1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A_{n_s n_s - 1} & J_{L_{n_s}} \end{bmatrix} \tag{77}$$

Each of the diagonal blocks would have nonzero determinants, as shown in the two-stage case, and this would result in the nonsingularity of the matrix J_L. The matrix J_V would also be in an identical fashion nonsingular. Hence, the Jacobian matrix J would be nonsingular and therefore in the ternary problem there would be a one-to-one correspondence between the bulk and the interface compositions. Hence, any multiplicity in the ternary nonequilibrium problem would be a result of the multiplicities occurring in the equilibrium calculations at the interface.

Conclusion

A strategy has been developed for drawing residue curve maps by directly solving the mass-transfer model equations without the use of efficiencies. It is shown analytically and numerically that the azeotropes for the equilibrium and nonequilibrium problems coincide. A comparison between the equilibrium and nonequilibrium residue curves is made. The multistage nonequilibrium problem has been analyzed to show that all multiplicity in the nonequilibrium problem was because of the multiplicity that occurs in the phase equilibrium calculations at the interface. This is done by demonstrating a one-to-one corrrespondence between the bulk phase and the interface composition profiles.

Acknowledgment

This work was supported by NSF grant CTS-9903353 and NOAA grant NA17AE1625. Dr. Sridhar thanks Prof. Morari for providing the IMC multiplicity example.

Notation

a = interface area
A,B = coefficients
J = Jacobian matrix
K = mass-transfer coefficient
M = Murphree efficiency
L = liquid
N = flux
V = vapor
x = liquid mol fraction
y = vapor mol fraction
z = overall feed composition
κ = K-value

Superscripts

L = liquid
V = vapor

Subscripts

L = liquid
t = total
V = vapor

Literature Cited

Baur, R., R. Taylor, R. Krishna, and J. A. Copatti, "Influence of Mass Transfer in Distillation of Mixtures with a Distillation Boundary," *Chem. Eng. Res. Des.*, **77**, 561 (1999).

Bekiaris, N., G. A. Meski, C. M. Radu, and M. Morari, "Multiple Steady States in Homogeneous Azeotropic Distillation," *Ind. Eng., Chem. Res.*, **32**, 2023 (1993).

Bushmakin, I. N., and I. N. Kish, "Rectification Investigations of a Ternary System Having an Azeotrope of a Saddle-Point Type," *J. Appl. Chem, USSR*, **30**, 401 (1957a).

Bushmakin, I. N., and I. N. Kish, "Separating Lines of Distillation and Rectification in Ternary Systems," *J. Appl. Chem., USSR*, **30**, 595 (1957b).

Castillo, F. J. L., and G. P. Towler, "Influence of Multicomponent Mass Transfer on Homogeneous Azeotropic Distillation," *Chem. Eng. Sci.*, 963 (1998).

Doherty, M. F., and J. D. Perkins, "On the Dynamics of Distillation Processes: I. The Simple Distillation of Multicomponent Non-Reacting Homogeneous Liquid Mixtures," *Chem. Eng. Sci.*, **33**, 281 (1978a).

Doherty, M. F., and J. D. Perkins, "On the Dynamics of Distillation Processes: II. The Simple Distillation of Model Solutions," *Chem. Eng. Sci.*, **33**, 569 (1978b).

Doherty, M. F., and J. D. Perkins, "On the Dynamics of Distillation Processes: III. The Topological Structure of Ternary Residue Curve Maps," *Chem. Eng. Sci.*, **34**, 1401 (1979).

Doherty, M. F., and J. D. Perkins, "On the Dynamics of Distillation Processes: IV. Uniqueness and Stability of the Steady-State in Homogeneous Continuous Distillations," *Chem. Eng. Sci.*, **37**, 381 (1982).

Fair, J. R., "Distillation: Whither, Not Whether," *IChEME Symp. Ser., Distillation and Absorbtion*, No. 1045, A613 (1987).

Gani, R., and S. B. Jorgensen, "Multiplicity in Numerical Solution of Non-Linear Models: Separation Processes," *Comput. Chem. Eng.*, **18**, S55 (1994).

Gmehling, J., and U. Onken, *Vapor Liquid Equilibrium Data Collection, Organic Hydroxy Compounds, Alcohols*, Vol. 1, Part 2a, Dechema Frankfurt (1977).

Guttinger, T. E., "Multiple Steady States in Azeotropic and Reactive Distillation," PhD Thesis, ETH Zurich (1998).

Guttinger, T., C. Dorn, and M. Morari, "Experimental Study of Multiple Steady-States in Homogeneous Azeotropic Distillation," *Ind. Eng. Chem. Res.*, **36**, 794 (1997).

Henley, J. E., and J. D. Seader, *Equilibrium Staged Separation Processes in Chemical Engineering*, Wiley, New York (1981).

Kovach, J. W., III, and W. D. Seider, "Heterogeneous Azeotropic Distillation: Homotopy Continuation Methods," *Comput. Chem. Eng.*, **11**, 593 (1987).

Krishnamurthy, R., and R. Taylor, "A Non-Equilibrium Stage Model of Multicomponent Separation Processes," *AIChE J.*, **31**, 3 (1985).

Lao, M., and R. Taylor, "Modeling Mass Transfer in Three Phase Distillation," *I&EC Res.*, **33**, 2637 (1994).

Li, H., "Analysis of Equilibrium-Staged Separation Processes," PhD Thesis, Clarkson University, Potsdam, NY (1994).

Lucia, A., "Uniqueness of Solutions to Single-Stage Isobaric Flash Processes Involving Homogeneous Mixtures," *AIChE J.*, **32**, 1761 (1986).

Magnussen, Y., M. L. Michelsen, and Aa. Fredunslund, "Azeotropic Distillation using UNIFAC," *Instr. Chem. Eng. Symp. Ser.*, **56**, 4.2, -4.2,/19 (1979).

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

Ostwald, W., *Lehrbuch der Allgemeinen Chemie Engelman*, Leipzig, Germany (1900).

Ronsebrock, H. H., "A Lyapunov Function with Application to Some Nonlinear Physical Systems," *Automatica*, 31 (1962).

Rosenbrock, H. H., "A Theorem of Dynamic Conservation for Distillation," *Trans. Instn. Chem. Engrs.*, **38**, 279 (1960).

Ryan, J. M., C. L. Hsieh, and M. S. Sivasubramanian, "Predicting Misting and Bubbling in Towers," *Chem. Eng. Prog.*, **90**, 83 (Aug., 1994).

Schreinmakers, F. A. H., "Dampfdrucke im System: Benzol, Tetrachlorokolenstoff, und Athylalchohol," *Z. Phys. Chem.*, **47**, 257 (1903).

Schreinmakers, F. A. H., "Dampfdrucke im System: Wasser, Acetone and Phenol," *Z. Phys. Chem.*, **39**, 440 (1901).

Seader, J. D., "The Rate-Based Approach to Modeling Separations —A New Era," ASPENWORLD 88, Amsterdam, Netherlands (Nov., 1988).

Shewchuk, C. F., "Computation of Multiple Distillation Towers,"PhD Thesis, Univ. of Cambridge (1974).

Smith, J. M., and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, New York (1981).

Sridhar, L. N., and A. Lucia, "Analysis of Multicomponent Multistage Separation Processes-Fixed Temperature and Pressure Profiles," *Ind. Eng. Chem. Res.*, **19**, 1668 (1990).

Sridhar, L. N., and A. Lucia, "Analysis & Algorithms for Multistage Separation Processes," *Ind. Eng. Chem. Res.*, **28**, 793 (1989).

Sridhar, L. N., and M. Torres, "Stability Calculations for Nonequilibrium Separation Processes," *AIChE J.*, **44**, 2175 (1998).

Sridhar, L. N., "Analysis of Two-Stage Heterogeneous Separation Processes," *AIChE J.*, **42**, 2761 (1996).

Sridhar, L. N., "Multistage Standard Specification," *AIChE J.*, **43**, 5, 1369 (1997).

Sridhar, L. N., C. Maldonado, A. Garcia, and A. D. Frias, "Analysis of Single-Stage Non-Equilibrium Separation Process Problems," *AIChE J.*, **46**, 11, 2237 (2000).

Taylor, R., and R. Krishna, *Multicomponent Mass Transfer*, Wiley, New York (1993).

Widagdo, S., and W. D. Seider, "Azeotropic Distillation," *AIChE J.*, **42**(1), 96 (Jan. 1996).

Zharov, V. T., "Evaporation of Homogeneous Multicomponent Solutions: III. Behavior of Distillation Lines Near Singular Points," *Russ. J. Phys. Chem.*, **42**, 195 (1968b).

Zharov, V. T., "Free Evaporation of Homogeneous Multicomponent Solutions," *Russ. J. Phys. Chem.*, **41**, 1539 (1967).

Zharov, V. T., "Free Evaporation of Homogeneous Multicomponent Solutions: II. Four Component Systems," *Russ. J. Phys. Chem.*, **42**, 58 (1968a).

Appendix

The analytical work on multiple steady states in separation process problems is summarized. Shewchuk (1974) found two solutions to an azeotropic distillation and conjectured that this was because of faulty VLE data. Later, Magnussen et al. (1979), Kovach and Seider (1987), Venkataraman and Lucia (1988), Rovaglio and Doherty (1990) and Gani and Jorgensen (1994) confirmed that the multiplicity in the ethanol benzene water problem was legitimate. We refer to this class of multiplicities as legitimate model considered (LMC) multiplicities.

The first significant analytical work regarding the issue of the existence of multiple steady state was by Rosenbrock (1960, 1962) who showed that the equations describing any nonideal binary CMO distillation with nontheoretical plates and nonnegligible vapor holdup possesses a unique globally asymptotically stable singular point.

Doherty and Perkins (1982) addressed the problem of uniqueness and stability of the steady-state solutions in CMO

Table A1. Specifications and Flow Rates for Multistage VP Problem*

Stage	*F*	*V*	*P*	L
1	0.0	375.364	0.960	3.9572
2	0.0	375.364	0.960	379.3212
3	0.0	375.364	0.960	379.3212
4	0.0	375.364	0.960	379.3212
5	0.0	375.364	0.960	379.3212
6	0.0	375.364	0.960	379.3212
7	0.0	375.364	0.960	379.3212
8	0.0	375.364	0.960	379.3212
9	0.0	375.364	0.960	379.3212
10	0.0	375.364	0.960	379.3212
11	0.0	375.364	0.960	379.3212
12	72.4572	375.364	0.960	379.3212
13	0.0	375.364	0.960	306.864
14	0.0	375.364	0.960	306.864
15	0.0	375.364	0.960	306.864
16	0.0	375.364	0.960	306.864
17	0.0	375.364	0.960	306.864
18	0.0	375.364	0.960	306.864
19	0.0	375.364	0.960	306.864
20	0.0	375.364	0.960	306.864
21	0.0	375.364	0.960	306.864
22	0.0	375.364	0.960	306.864
23	0.0	375.364	0.960	306.864
24	0.0	68.500	0.960	306.864

*Stage: Stage number (partial reboiler = 24, total condenser = 1).
F = molar feed flow rate entering the tray.
V = molar vapor flow rate leaving the tray.
P = pressure (atm).
L = molar liquid flow rate leaving the tray.

Table A2. First Steady-State Solution of Multistage VP Problem*

Stage	x_1	x_2	y_1	y_2
1	2.6860600e-01	4.6397280e-01	7.4322729e-01	1.6315732e-01
2	7.3827588e-01	1.6629553e-01	8.5213116e-01	8.0627361e-02
3	8.4604364e-01	8.4626543e-02	8.8358540e-01	4.9752605e-02
4	8.7716974e-01	5.4073882e-02	8.9358859e-01	3.3623022e-02
5	8.8706857e-01	3.8112568e-02	8.9509364e-01	2.3892045e-02
6	8.8855792e-01	2.8483108e-02	8.9317821e-01	1.7660654e-02
7	8.8666248e-01	2.2316724e-02	8.9030497e-01	1.3605890e-02
8	8.8381921e-01	1.8304261e-02	8.8761495e-01	1.0979495e-02
9	8.8115725e-01	1.5705266e-02	8.8550284e-01	9.2977868e-03
10	8.7906717e-01	1.4041101e-02	8.8399320e-01	8.2334520e-03
11	8.7757328e-01	1.2987870e-02	8.8297280e-01	7.5660860e-03
12	8.7656353e-01	1.2327466e-02	8.8230645e-01	7.1503928e-03
13	8.8238405e-01	8.7188137e-03	8.8429368e-01	5.1237497e-03
14	8.8481488e-01	6.2397713e-03	8.8488101e-01	3.6813155e-03
15	8.8553331e-01	4.4753484e-03	8.8477674e-01	2.6389238e-03
16	8.8540577e-01	3.2002678e-03	8.8436872e-01	1.8823092e-03
17	8.8490667e-01	2.2747572e-03	8.8386762e-01	1.3337262e-03
18	8.8429371e-01	1.6037162e-03	8.8338073e-01	9.3736778e-04
19	8.8369814e-01	1.1188804e-03	8.8295547e-01	6.5219618e-04
20	8.8317794e-01	7.7005109e-04	8.8260613e-01	4.4784980e-04
21	8.8275063e-01	5.2008930e-04	8.8233033e-01	3.0193402e-04
22	8.8241326e-01	3.4160134e-04	8.8211846e-01	1.9804020e-04
23	8.8215409e-01	2.1451572e-04	8.8915884e-01	1.2423371e-04
24	8.8195884e-01	1.2423371e-04	8.8184031e-01	7.1892295e-05

*Stage: Stage number (partial reboiler = 24, total condenser = 1)
x_1 = molar liquid composition of component methanol
x_2 = molar liquid composition of component methyl butylyrate
x_3 = 1.0-x_10 − x_2 = molar liquid composition of component toluene
y_1 = molar vapor composition of component methanol
y_2 = molar vapor composition of component methyl butylrate
y_3 = 1.0-y_1-y_2 = molar vapor composition of component toluene

multistage columns involving binary mixtures. Using both a dynamic model and classical linear stability analysis, they showed that any distillation of this type has a unique and stable steady-state solution. Lucia (1986) rigorously established solution uniqueness for a single-stage isobaric flash process and showed solution uniqueness for a variety of specifications. Sridhar and Lucia (1989) extended the analysis to multistage separation process problems involving binary mixtures. Sridhar and Lucia (1990) showed solution uniqueness for a multistage multicomponent separations where the specification is the temperature profile in the column. Sridhar (1996) performed a similar analysis for two-stage separation process problem involving ternary mixtures and showed solution uniqueness for nonazeotropic homogeneous mixtures.

Sridhar (1997) extended this analysis to multistage separators and showed solution uniqueness for a multistage separation process problem involving nonazeotropic homogeneous mixtures and the standard specification of reflux ratio, bottoms flow rate, and the input heat duties to the intermediate stages. The vapor flow specification (VP) was first analyzed and then a one-to-one correspondence was established between the VP specification and the standard specification. In doing so the partial derivative of the input heat duty to stage j with respect to the vapor flow exiting stage $j+1$ was approximated as

$$\frac{\partial Q_j}{\partial V_{j+1}} = H^{L_j} - H^{V_{j+1}} \tag{A1}$$

Recently, Guttinger (1998) objected to this approximation. However, it was shown by Henley and Seader (1981) that this was the standard approximation used by equation tearing bubble-point algorithms and was effective in the solution of multistage separation process problems. Consequently, the objection of Guttinger (1998) is unimportant and all attempts to challenge the proof of Sridhar (1997) have been unsuccessful.

Guttinger et al. (1997) use the Wilson model to predict multiplicity for a multistage separation process problem involving the mixture methanol, toluene, and methyl-butyrate and justify the ∞/∞ analysis of Bekiaris et al. (1993). Li (1994) shows correctly that, at infinite reflux, column profiles do not generally coincide with residue curves, mass balance inconsistencies that lead to crossing tie lines can occur, and predictions of the ∞/∞ analysis cannot be generalized to finite columns. The Wilson coefficients for the mixture methanol, toluene, and methyl-butyrate (Guttinger et al., 1997) were obtained from two sources: the coefficients for the binary pair methanol-toluene were obtained from Gmehling and Onken (1977) while the coefficients for the binary pair involving methyl-butylrate were estimated using Aspen plus and data from UNIFAC with Dortmund corrections. Unfortunately, this arbitrary mixing of coefficients from different sources can lead to a faulty VLE model. We present results from their simulation and show plots where the liquid and vapor curves intersect thereby depicting spurious azeotropes. We believe that it is the faulty nature of this model that predicts the spurious multiplicity. The presence of the spurious azeotropes affects the trajectories of the residue curves in such a way

Table A3. Second Steady-State Solution of Multistage VP Problem*

Stage	x_1	x_2	y_1	y_2
1	1.5458410e-11	3.7801810e-01	3.4821173e-10	4.4230584e-01
2	3.4474038e-10	4.4163517e-01	7.1351111e-09	5.0693554e-01
3	7.0608367e-09	5.0559063e-01	1.3465258e-07	5.6933142e-01
4	1.3324800e-07	5.6733558e-01	2.3548955e-06	6.2723550e-01
5	2.3303287e-06	6.2463559e-01	3.8471409e-05	6.7903013e-01
6	3.8070063e-05	6.7588988e-01	5.9223453e-04	7.2357043e-01
7	5.8605616e-04	7.1996552e-01	8.6057219e-03	7.5540882e-01
8	8.5159442e-03	7.5147176e-01	1.0760091e-01	7.0742641e-01
9	1.0647838e-01	7.0398991e-01	5.6619790e-01	3.5030627e-01
10	5.6029114e-01	3.5059537e-01	8.1251830e-01	1.4252177e-01
11	8.0404185e-01	1.4497855e-01	8.7402925e-01	8.1470868e-02
12	8.6491110e-01	8.4564544e-02	8.9425396e-01	5.2916428e-02
13	8.9352248e-01	6.3592576e-02	9.0749858e-01	4.2627057e-02
14	9.0973587e-01	5.1006350e-02	9.1576639e-01	3.5606876e-02
15	9.1984928e-01	4.2419083e-02	9.2101654e-01	3.0361820e-02
16	9.2627140e-01	3.6003195e-02	9.2406663e-01	2.6142915e-02
17	9.3000234e-01	3.0842520e-02	9.2520988e-01	2.2521468e-02
18	9.3140079e-01	2.6412573e-02	9.2447728e-01	1.9231114e-02
19	9.3050466e-01	2.2387826e-02	9.2181612e-01	1.6109519e-02
20	9.2724946e-01	1.8569410e-02	9.1727912e-01	1.3084416e-02
21	9.2169969e-01	1.4869026e-02	9.1121022e-01	1.0173261e-02
22	9.1427604e-01	1.1308025e-02	9.0431106e-01	7.4681033e-03
23	9.0583681e-01	7.9990069e-03	8.9747603e-01	5.0897792e-03
24	8.9747603e-01	5.0897792e-03	8.9146989e-01	3.1281495e-03

*Stage: Stage number (partial reboiler = 24, total condenser = 1).
x_1 = molar liquid composition of component methanol
x_2 = molar liquid composition of component methyl butylrate
x_3 = 1.0-x_1-x_2 = molar liquid composition of component toluene
y_1: molar vapor composition of component methanol
y_2: molar vapor composition of component methyl butylrate
y_3 = 1.0-y_1-y_2 = molar vapor composition of component toluene

Table A4. Third Steady-State Solution of Multistage VP Problem

Stage	x_1	x_2	y_1	y_2
1	4.2505230e-20	1.1069800e-02	1.6959029e-18	1.4497629e-02
2	1.6786967e-18	1.4461867e-02	6.6566748e-17	1.8919807e-02
3	6.5872788e-17	1.8837913e-02	2.5915272e-15	2.4610810e-02
4	2.5644920e-15	2.4469546e-02	9.9873980e-14	3.1911611e-02
5	9.8832063e-14	3.1694183e-02	3.7996379e-12	4.1239704e-02
6	3.7599989e-12	4.0924962e-02	1.4220889e-10	5.3096457e-02
7	1.4072533e-10	5.2658021e-02	5.2140102e-09	6.8068350e-02
8	5.1596160e-09	6.7473722e-02	1.8632514e-07	8.6816925e-02
9	1.8438133e-07	8.6026707e-02	6.4510070e-06	1.1004992e-01
10	6.3837080e-06	1.0901733e-01	2.1487436e-04	1.3843845e-01
11	2.1263272e-04	1.3710970e-01	6.7907772e-03	1.7141652e-01
12	6.7199336e-03	1.6974373e-01	1.6962719e-01	1.7424179e-01
13	7.1524597e-03	2.0726888e-01	1.7006222e-01	2.1054552e-01
14	7.6846019e-03	2.5167654e-01	1.7058955e-01	2.5250339e-01
15	8.3296430e-03	3.0300050e-01	1.7124060e-01	2.9964885e-01
16	9.1260234e-03	3.6067005e-01	1.7250508e-01	3.5071508e-01
17	1.0672770e-02	4.2313558e-01	1.8266906e-01	3.9972492e-01
18	2.3105610e-02	4.8308569e-01	3.0455955e-01	3.8356508e-01
19	1.7220523e-01	4.6331856e-01	6.9688397e-01	1.7530540e-01
20	6.5210663e-01	2.0856991e-01	8.3290802e-01	8.8016151e-02
21	8.1849476e-01	1.0179544e-01	8.7371558e-01	5.6368834e-02
22	8.6841163e-01	6.3083624e-02	8.9079931e-01	3.8621835e-02
23	8.8930889e-01	4.1375035e-02	8.9747604e-01	2.6288139e-02
24	8.9747604e-01	2.6288139e-02	8.9804378e-01	1.6759723e-02

*Stage = stage number (partial reboiler = 24, total condenser = 1)
x_1 = molar liquid composition of component methanol
x_2 = molar liquid composition of component methyl butylrate
x_3 = 1.0-x_1-x_2 = molar liquid composition of component toluene
y_1 = molar vapor composition of component methanol
y_2 = molar vapor composition of component methyl butylrate
y_3 = 1.0-y_1-y_2 = molar vapor composition of component toluene

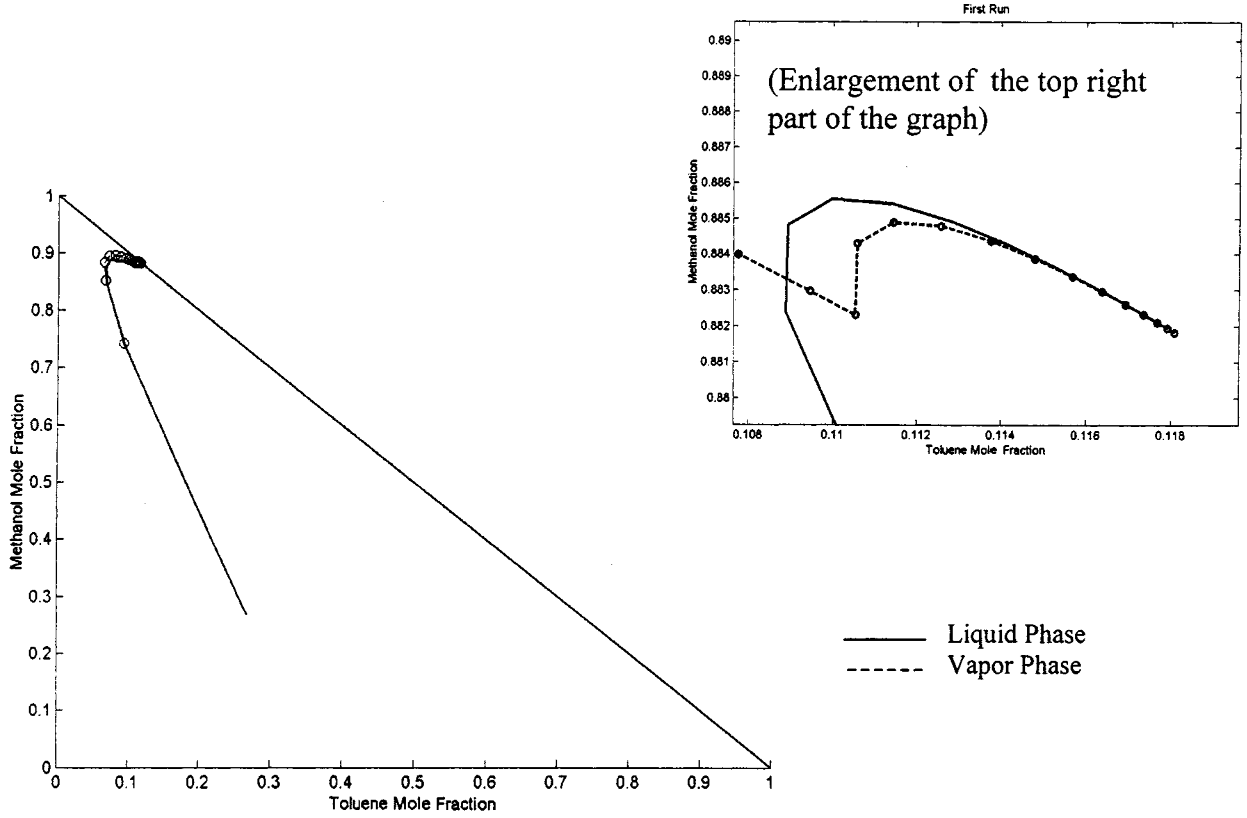

Figure A1. First spurious solution.

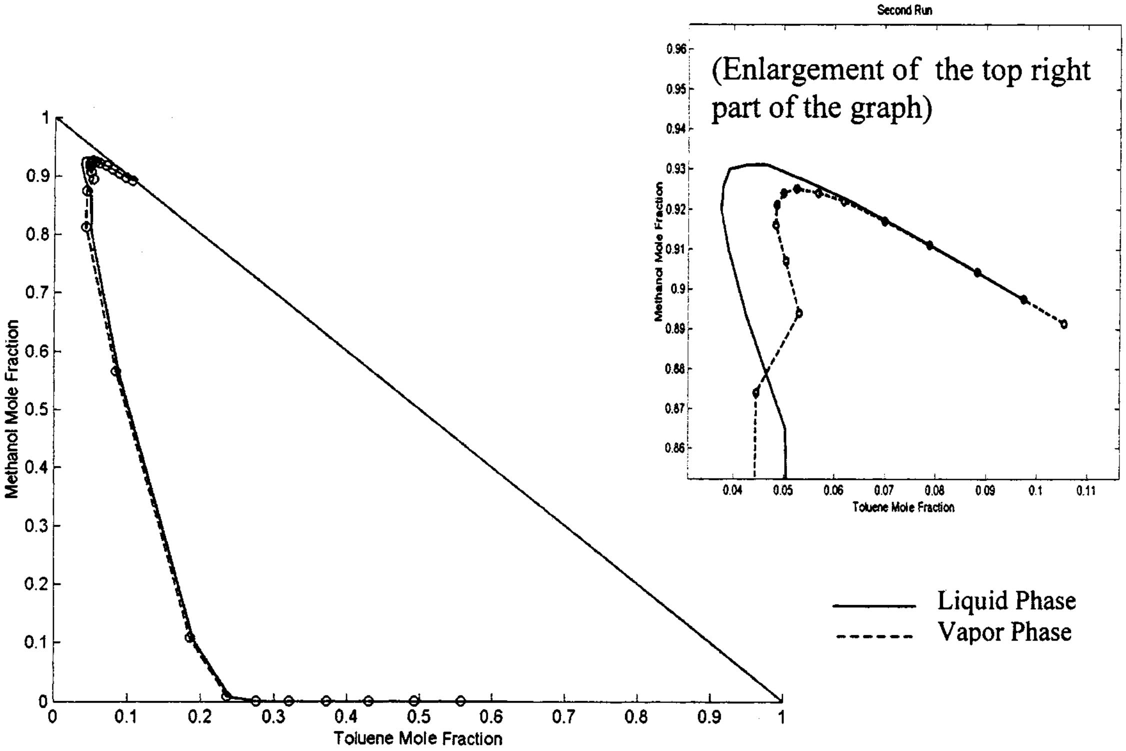

Figure A2. Second spurious solution.

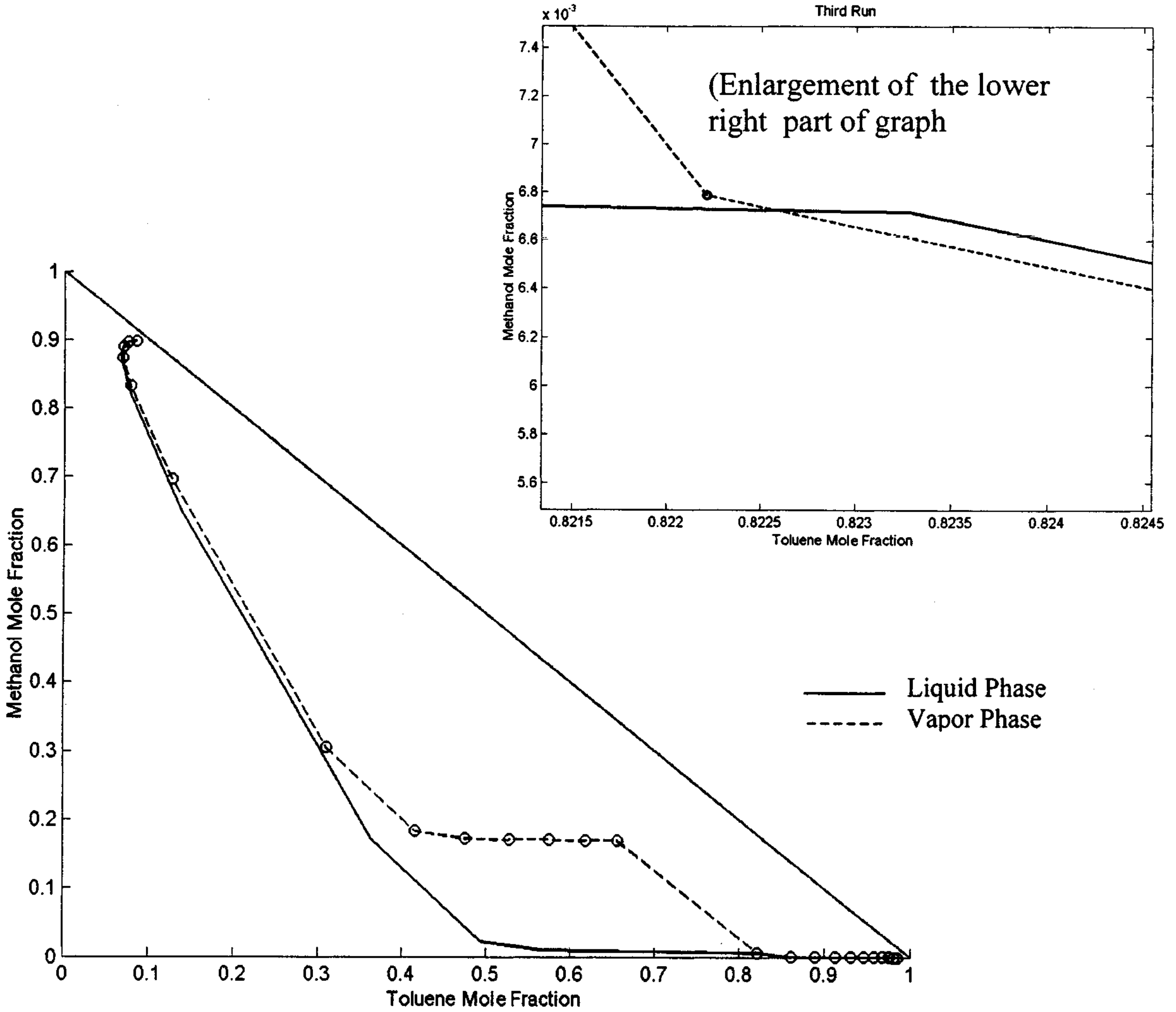

Figure A3. Third spurious solution.

that causes spurious multiplicities. Multiplicities which occur as a result of faulty VLE models can be misleading in trying to understand the cause(s) for their existence. We refer to this class of multiplicities as illegitimate model caused (IMC) multiplicities. Table A1 presents the input data for a multistage VP simulation presented by Guttinger and Morari. Tables A2, A3, and A4 contain the IMC-multiplicities for this problem obtained from a simulation presented by Guttinger and Morari. Figures A1, A2, and A3 show the plots of the liquid and vapor composition profiles for the three solutions. Note the intersection of the liquid and vapor composition profiles indicating the spurious azeotropes. The numerical results were obtained by Guttinger and Morari; all we did was to plot the data. The problem of solution multiplicities in staged separations has indeed come around a full circle. Shechuk (1974) found an LMC multiplicity and conjectured that the VLE model used may be faulty, while Guttinger et al. (1997) use faulty VLE models and produce IMC multiplicities.

Manuscript received Aug. 3, 2001, and revision received Dec. 4, 2001.