Mass transfer effects in distillation
Springer, P.A.M.

Citation for published version (APA):

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Chapter 6

Ternary homogeneous azeotropic systems

6.1 Introduction

There is considerable industrial interest in the design and optimization of homogeneous and heterogeneous azeotropic distillation. This interest stems from the large number of industrial columns in operation and the potential of developing improved separation schemes so as to minimize energy consumption. Residue curve maps are commonly used in developing separation flow schemes (Stichlmair & Fair, 1998; Doherty & Malone, 2001 and Widagdo & Seider, 1996). The residue curve map is usually divided into separate regions by simple distillation region boundaries that act as impassable barriers to the residue curves in each of the regions. The existence, location and curvature of distillation boundaries are very important in the synthesis of distillation column sequences (Stichlmair & Fair, 1998; Doherty & Malone, 2001; Widagdo & Seider, 1996; Li et al., 1999; Knapp & Doherty, 1992; Foucher & Doherty, 1991; Knapp & Doherty, 1990; Pham & Doherty, 1990; Julka & Doherty, 1990; Barbosa & Doherty, 1988; Fidkowski et al., 1993; Levy et al., 1985; Wahnschafft et al., 1994; Wahnschafft et al., 1992; Doherty & Caldarola, 1985; Van Dongen & Doherty, 1985; Pelkonen et al., 1997; Castillo et al., 1998 and Rev, 1992).

Levy et al. (1985) have put forward the following two “rules” in continuous azeotropic distillations:

1. If the simple distillation boundary is perfectly linear, then the steady-state composition profile in a continuous distillation column cannot cross the boundary from either side.

2. If the simple distillation boundary is curved, then the steady-state composition profile in a continuous distillation column cannot cross the boundary from the concave side but may cross the boundary from the convex side when moving from the product compositions inward.

Consider, for example, the system methanol – isopropanol – water; the residue curve map for this system, calculated using the NRTL parameters taken from the literature (Gmehling & Onken, 1977) and specified in Table 6.1 (also Table 3.3) is shown in Fig. 6.1(a). A straight-line distillation boundary connects the binary isopropanol-water azeotrope with pure methanol and divides the composition space into two regions. According to Rule (1), the column composition trajectories cannot cross this straight line distillation boundary, whichever side the feed is located. For either of the two feed locations, F1 and F2 in Fig. 6.1(a), boundary crossing is therefore forbidden.

For the system acetone - chloroform - methanol we have three binary and one ternary azeotrope dividing the composition space into four regions by means of four distillation boundaries, that are all curved; see the residue curve map shown in Fig. 6.1(b) calculated using the NRTL parameters listed in Table 6.1. According to Rule (2), the column trajectory obtained for operation with the feed located on the concave side of a boundary, with say
composition indicated by F1 is able to cross that boundary. This has been demonstrated experimentally by Li et al. (1999). Conversely, if the feed is located on the convex side, with say composition indicated by F2 the boundary cannot be crossed (Levy et al., 1985).

Most of the published literature simulation studies on the possibilities of crossing of distillation boundaries use the equilibrium (EQ) stage model. There is evidence in the published literature that experimentally measured composition profiles in distillation columns are better simulated with nonequilibrium (NEQ) stage models, in which proper account is taken of mass transfer in either fluid phase by use of the rigorous Maxwell-Stefan diffusion equations, rather than with simpler models that assume equal component efficiencies (Wesselingh & Krishna, 2000; Krishnamurthy & Taylor, 1985; Taylor et al., 1994; Taylor & Krishna, 1993; Krishna & Wesselingh, 1997; Baur et al., 1999; Springer & Krishna, 2001; Pelkonen et al., 1997; Pelkonen et al., 2001 and Springer et al., 2002). Pelkonen et al. (1997) performed total reflux experiments with the system methanol-2-propanol-water in a packed distillation column and showed that if the composition at the top of the column is located on the distillation boundary (i.e. the line connecting pure methanol with the methanol-2-propanol binary azeotrope) the experimentally measured composition profiles end up with a reboiler composition that is rich in water. The measured composition trajectories can be simulated very well using a nonequilibrium (NEQ) stage model incorporating the Maxwell-Stefan diffusion equations. On the other hand, an equilibrium (EQ) stage model (i.e. a model in which the component efficiencies are each taken to 100%) predicts that the reboiler compositions corresponds to pure isopropanol. The simulation results of Baur et al. (1999) show that the differences in the component efficiencies cause the deviation in the NEQ and EQ column trajectories. Pelkonen et al. (1997 and 2001) also performed similar experiments with the quaternary system acetone-methanol-isopropanol-water, with the composition near the top of the column chosen to lie on the distillation boundary and obtained the same dramatic differences between the predictions of the NEQ and EQ models. The NEQ model predictions were in accord with the experiments.
The experimental results of Pelkonen et al. (1997) raise the question whether the observed dramatic differences between NEQ and EQ model predictions are also obtained when the starting compositions are not located precisely on the distillation boundary but on either side of it.

The major objective of this chapter is to demonstrate that differences in the component efficiencies in ternary homogeneous azeotropic distillation can cause column trajectories to cross slightly curved distillation boundaries and even straight-line distillation boundaries, provided that the “starting” compositions are located within a finite region of compositions on one side of the distillation boundary. Furthermore, it will be shown that such boundary crossing phenomena can be predicted by the NEQ model, but not by EQ stage models that assume equal component efficiencies since the EQ distillation trajectories must necessarily follow the residue curve lines for total reflux operations (Stichlmair & Fair, 1999).

To verify the above stated, several experiments were performed with three different ‘homogeneous’ ternary azeotropic mixtures; Water-Ethanol-Acetone, Water-Ethanol-Methanol and Water-Ethanol-Methylacetate. The residue curve maps for these three systems, calculated with NRTL parameters listed in Table 6.1, are shown in Fig. 6.2(a-e).

### Table 6.1

*NRTL parameters for ternary mixtures at 101.3 kPa (Gmehling & Onken, 1977). These parameters are used along with \( G_j = \exp(-\alpha_j / T_j) \) and \( T_j = T_j / T \).

<table>
<thead>
<tr>
<th>Ternary systems</th>
<th>Component ( i )</th>
<th>Component ( j )</th>
<th>( B_{ij} / [K] )</th>
<th>( B_{ji} / [K] )</th>
<th>( \alpha_{ij} / [-] )</th>
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<tr>
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<tr>
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<td>-182.605</td>
<td>0.297</td>
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</tr>
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<td>284.8969</td>
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Fig. 6.2(a). Residue curve map for the Water (1) – Ethanol (2) – Acetone (3) system, showing a straight-line distillation boundary and a binary minimum boiling azeotrope between water and ethanol. (b) Zoomed-in version of Fig. 6.2(a). (c) Residue curve map for the Water (1) – Ethanol (2) – Methanol (3) system, showing a curved distillation boundary and a binary minimum boiling azeotrope between water and ethanol. (d) Zoomed-in version of Fig. 6.2(c). (e) Residue curve map for the Water (1) – Ethanol (2) – Methylacetate (3) system, showing a curved distillation boundary and two binary azeotropes between water – ethanol and water - methylacetate. (f) Zoomed-in version of Fig. 6.2(e).

The first system (Fig. 6.2(a-b)) shows a binary minimum boiling azeotrope between water and ethanol; an almost straight distillation boundary connects the azeotrope with pure acetone. The second system (Fig. 6.2(c-d)) shows a binary minimum boiling azeotrope between water and ethanol; a slightly curved distillation boundary connects the azeotrope with pure methanol. The third system (Fig. 6.2(e-f)) shows two binary azeotropes between the water-
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ethanol and water-methylacetae mixtures; a slightly (more towards the water-methylacetae azeotrope) curved distillation boundary connects the two azeotropes. For high water compositions there is a small region of partial miscibility. However, our experimental work was restricted to water mole fraction below 0.2 and thus was within the province of the homogeneous region in all cases. Therefore, this system is categorized in this Chapter for homogenous systems and not in chapter 8 in which heterogeneous azeotropic systems will be discussed.

6.2 Water (1) – Ethanol (2) – Acetone (3)

The experiments were carried out in the laboratory-scale distillation column supplied by Schott Nederland B.V. analog to the way in which the experiments for the binaries were carried out. The complete description of the experimental procedure and experimental set-up is described in detail in Chapter 3.

Further down in this chapter, the experiments for the water-ethanol-acetone system will be compared with simulation results obtained by using an EQ stage model and a rigorous NEQ stage model. The NEQ stage model development related to our experimental set-up and operation conditions is also described in an earlier stage in Chapter 4.

As can be read in the “simulation strategy” in Chapter 4, one specific vapour (or liquid) composition from the experimentally obtained composition profile, is needed as an input (starting) composition for the simulation runs. For the water-ethanol-acetone system, this starting composition is chosen to be equal to the vapor composition leaving stage 2 and thus entering the condenser (indicated by a large open circle in all plots).

6.2.1 Experimental results for the Water-Ethanol-Acetone system

The experimentally determined composition trajectories for a set of 9 experiments are shown in Fig. 6.3 (next page), along with the residue curve map. At total reflux the composition of the vapor leaving any given stage equals the composition of the liquid arriving at that stage from above. Therefore, the 8 vapor and 4 liquid composition samples can be combined when plotting the composition trajectories. In Fig. 6.3 the vapor samples are denoted by open circles and the liquid samples by open squares. In experiments T2-03, T2-06 and T2-10 the column trajectories were all located on the left side of the distillation boundary (indicated by the thick line). All the remaining 6 experiments clearly exhibit boundary crossing phenomena. We also note that the experimental data points cut across the residue curves to the right at a sharp angle. In all the experiments, excepting T2-18, there was no acetone present in the reboiler liquid. In the experiment T2-18, the acetone content in the initial charge to the system was high and this resulted in a finite acetone content in the reboiler.

Clearly, boundary crossing phenomena is not in conformity with the assumption of thermodynamic phase equilibrium, which underlies the residue curve maps; this is evidenced by the fact that the experimental trajectories do not follow the residue curve map. In order to understand, and rationalize, the boundary crossing phenomena we developed a rigorous nonequilibrium (NEQ) stage model, see Chapter 4. In the next section, this advanced NEQ stage model and a standard EQ model will be compared with each other and used for the simulation of our experiments with the Water-Ethanol-Acetone system.
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Fig. 6.3. Experimental results (open circles for vapor and open squares for liquid samples) showing the column composition trajectories for the Water (1) – Ethanol (2) – Acetone (3) system. Also shown are the simulation results showing the trajectories calculated by the equilibrium (EQ) stage model and the nonequilibrium (NEQ) stage model, along with the residue curve map. The large open circles represent the experimental composition specified in the simulations. In the NEQ model simulations, a bubble size \( d_b = 4.5 \) mm was chosen.
6.2.2 Comparison of EQ and NEQ simulations with experiments

All experiments were simulated with the EQ stage model and the rigorous NEQ stage model. Let us consider one of the experiments (T2-26) in some detail. Fig. 6.4(a) compares the EQ model with the experimental results. The large open circle represents the vapor composition leaving stage 2 and entering the condenser; this is specified in the simulations. We note that while the experimental points cross the distillation boundary, the EQ column trajectory does not and remains on the left side of this boundary. The EQ trajectory closely follows the residue curve map, shown in Fig. 6.2(a-b). A further point to note is that while the experimental results show that proceeding down the column (in the direction of the reboiler) the compositions get richer in water, the EQ simulations predict that these trays get progressively richer in ethanol. The NEQ model simulations require specification of the bubble diameter, see Chapter 4. For a range of bubble diameters 3 – 5.5 mm, the NEQ trajectories have been plotted in Fig. 6.4(b). For $d_b = 3$ mm, the NEQ trajectory remains to the left of the distillation boundary and does not cross it. Decreasing the bubble diameter has the effect of increasing the mass transfer coefficient (see Eq. (4.18) and Eq. (4.19)) and makes the NEQ model tend towards the EQ model. To match the EQ trajectory, the bubble size has to be 1.5 mm, or smaller. Conversely, increasing the bubble diameter, decreases the mass transfer coefficient and the NEQ trajectories move away from the EQ trajectory. For $d_b = 4.5$, 5 and 5.5 mm, all three NEQ trajectories cross the distillation boundary. The best agreement with the experiments is obtained with $d_b = 4.5$ mm.

Let us consider the experimental run T2-18, for which the simulations were carried out by specifying the vapor compositions leaving the reboiler; see Fig. 6.5. We see from Fig. 6.5(a) that the EQ model does not cross the boundary and remains to the right side of it (Note: we now start of from the right side of the boundary since we specify the vapor compositions leaving the reboiler). Simulations for the NEQ model with varying bubble diameters are
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Fig. 6.5. Simulation results compared with the experimental data (open circles for vapor and open squares for liquid samples) for run T2-18 (Water-ethanol-acetone system). (a) Here the EQ model is compared with experimental results. (b) The NEQ model, for varying bubble diameters, is compared with experimental results. The large open circle is the specified composition for the simulations; this corresponds to the vapor composition leaving the reboiler (12).

shown in Fig. 6.5(b). As in the case of T2-26, for \( d_b = 3 \text{ mm} \), the NEQ trajectory remains to the right of the distillation boundary and does not cross it. For \( d_b = 4.5, 5 \text{ and } 5 \text{ mm} \), all three NEQ trajectories cross the boundary. The best agreement with the experiments is again obtained with \( d_b = 4.5 \text{ mm} \).

The simulation results for the EQ and NEQ model, with \( d_b = 4.5 \text{ mm} \), for all the experimental runs are shown in Fig. 6.3, along with the experimental results.

Consider the runs T2-03, T2-06 and T2-10. For all these runs no boundary crossing is observed experimentally; see Fig. 6.3(a-c). Both EQ and NEQ models do not anticipate boundary crossing. The EQ model follows the trajectory dictated by the residue curve map, whereas the NEQ model has a tendency to cut across to the right of the residue curve. The predictions of the NEQ model are superior to that of the EQ model and in much better agreement with the experimentally measured composition trajectories. This tendency of the experiments to cut across to the right of the residue curves is strongly evident for run T2-10; here the NEQ model does a very good job of predicting the column trajectory.

Consider the runs T2-14, T2-18, T2-26, T2-27, T2-28, and T2-29 in Fig. 6.3(d-i). For all these runs we experience boundary crossing and the NEQ model successfully anticipates this phenomenon. In all the cases the EQ model fails to cross the boundary and the EQ trajectory remains on one side of the boundary. For all these runs the experimental results show that proceeding down the column (in the direction of the reboiler) the compositions get richer in water. The EQ simulations starting from the top tray (stage 2) predict that these trays get progressively richer in ethanol; this is qualitatively different to the experimental observations.
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6.3 Water (1) – Ethanol (2) – Methanol (3)

The experiments for the homogeneous azeotropic mixture water-ethanol-methanol were carried out in the laboratory scale distillation column supplied by Schott Nederland B.V. according to the experimental set-up and procedure as described in Chapter 3. For the simulations, the NEQ stage model as described in Chapter 4 and an EQ stage model were used. The specified “input” composition for the simulations was chosen to be equal to the vapour composition leaving stage 4 from the experimentally obtained composition profiles (indicated by the large open circle in each plot).

6.3.1 Experimental results for Water-Ethanol-Methanol system

The experimentally determined composition trajectories for a set of 9 experiments are shown in Fig. 6.6 (next page), along with the residue curve map. Also here holds that at total reflux the composition of the vapor leaving any given stage equals the composition of the liquid arriving at that stage from above and thus the 9 vapor and 4 liquid composition samples are plotted in one single plot. In Fig. 6.6 the vapor samples are denoted by open circles and the liquid samples by open squares. In experiments T4-01, T4-06, T4-08 and T4-11 the column trajectories were all located on the left side of the distillation boundary (indicated by the thick line). All the remaining five experiments clearly exhibit boundary crossing phenomena.

6.3.2 Comparison of EQ and NEQ simulations with experiments

All experiments for the water-ethanol-methanol system were simulated with the EQ stage model and the rigorous NEQ stage model as well. Let us consider one of the experiments (T4-13) in some detail. Fig. 6.7(a) compares the EQ model with the experimental results. The large open circle represents the vapor composition leaving stage 4; this is specified in the simulations. We note that while the experimental points cross the distillation boundary, the EQ column trajectory does not and remains on the left side of the boundary. The EQ trajectory closely follows the residue curve map, shown in Fig. 6.2(c-d). Also for this system, a point to note is that while the experimental results show that proceeding down the column (in the direction of the reboiler) the compositions get richer in water, the EQ simulations predict that these trays get progressively richer in ethanol. The NEQ model simulations require specification of the bubble diameter. For a range of bubble diameters 3 – 5.5 mm, the NEQ trajectories have been plotted in Fig. 6.7(b). Only for \( d_b = 4.5, 5 \) and 5.5 mm, all NEQ trajectories cross the boundary. The best agreement with the experiments is obtained with \( d_b = 5.0 \) mm.

The simulation results for the EQ and NEQ model, with \( d_b = 5.0 \) mm, for all the experimental runs are shown in Fig. 6.6, along with the experimental results. Consider the runs T4-01, T4-06, T4-08 and T4-11. For all these runs no boundary crossing is observed experimentally; see Fig. 6.6(a-d). Both EQ and NEQ models do not anticipate boundary crossing. The EQ model follows the trajectory dictated by the residue curve map, whereas the NEQ model has a tendency to cut across to the right of the residue curve. The predictions of the NEQ model are superior to that of the EQ model and in much better agreement with the experimentally measured composition trajectories. This tendency of the experiments to cut across to the right of the residue curves is strongly evident for run T4-01,
Fig. 6.6. Experimental results (open circles for vapor and open squares for liquid samples) showing the column composition trajectories for the Water (1) – Ethanol (2) – Methanol (3) system. Also shown are the simulation results showing the trajectories calculated by the equilibrium (EQ) stage model and the nonequilibrium (NEQ) stage model, along with the residue curve map. The large open circles represent the experimental composition specified in the simulations. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.
T4-06 and T4-08; here the NEQ model does a very good job of predicting the column trajectory.

Consider the runs T4-13, T4-17, T4-22, T4-23 and T4-24 in Fig. 6.6(e-i). For all these runs we experience boundary crossing and the NEQ model successfully anticipates this phenomenon. In all the cases the EQ model fails to cross the boundary and the EQ trajectory remains on one side of the boundary. For all these runs the experimental results show that proceeding down the column (in the direction of the reboiler) the compositions get richer in water. The EQ simulations predict that these trays get progressively richer in ethanol; this is qualitatively different to the experimental observations.

Fig. 6.7. Simulation results compared with the experimental data (open circles for vapor and open squares for liquid samples) for run T4-13 (Water-ethanol-methanol system). (a) Here the EQ model is compared with experimental results. (b) The NEQ model, for varying bubble diameters, is compared with experimental results. The large open circle is the specified composition for the simulations; this corresponds to the vapor composition leaving stage 4.
6.4 Water (1) – Ethanol (2) – Methylacetate (3)

The experiments for the heterogeneous azeotropic mixture water-ethanol-methylacetate were carried out in the laboratory scale distillation column supplied by Schott Nederland B.V. as well. The complete description of the experimental set-up and procedure is written down in Chapter 3. For the simulations, the NEQ stage model as described in Chapter 4 and an EQ stage model were used. The specified “input” composition for the simulations was chosen to be equal to the experimental vapour composition leaving stage 4 again (indicated by the large open circle in each plot).

As mentioned in the introduction of this chapter, the system water-ethanol-methylacetate shows a small region of partial miscibility for high water compositions. Since our experimental work was restricted to water mole fraction below 0.2 and thus within the province of the homogeneous region in all cases, this system is categorized in this chapter and not in Chapter 8 that will deal with other heterogeneous azeotropic systems.

6.4.1 Experimental results for the Water-Ethanol-Methylacetate system

The experimentally determined composition trajectories for a set of 9 experiments are shown in Fig. 6.8 (next page), along with the residue curve map. Again, the 8 vapour and 4 liquid composition samples are combined within the plot of the composition trajectories, since for total reflux operation at steady state, the composition of the vapour leaving any given stage equals the composition of the liquid arriving at that stage from above.

In Fig. 6.8 the vapour samples are denoted by open circles and the liquid samples by open squares. The large open circles in Fig. 6.8 represent the input compositions in the simulations. In experiments T3-03, T3-04, T3-10 and T3-11 the column trajectories were all located on the left side of the distillation boundary (indicated by the thick line). All the remaining 5 experiments clearly exhibit boundary crossing phenomena. We also note that the experimental data points cut across the residue curves to the right at a sharp angle. In all the experiments there was practically no methylacetate present in the reboiler liquid.

Also based on the experiments with the Water-Ethanol-Methylacetate system, it can be concluded that boundary crossing phenomena is not in conformity with the assumption of thermodynamic phase equilibrium, which underlies the residue curve maps (Stichlmair & Fair, 1998); this is evidenced by the fact that the experimental trajectories for the Water-Ethanol-Methylacetate system do not follow the residue curve map.

In the next section, the NEQ stage model (developed in Chapter 4), a standard EQ model and our experiments with the Water-Ethanol-Methylacetate system will be compared with each other and discussed.

6.4.2 Comparison of EQ and NEQ simulations with experiments

All experiments were simulated with the EQ stage model and the rigorous NEQ stage model. Let us consider one of the experiments (T3-23) in some detail again. Fig. 6.9(a) compares the EQ model with the experimental results. The large open circle represents the vapour composition leaving stage 4; this is specified in the simulations. We note that while the experimental points cross the distillation boundary, the EQ column trajectory does not and
Fig. 6.8. Experimental results (open circles for vapor and open squares for liquid samples) showing the column composition trajectories for the Water (1) – Ethanol (2) – Methylacetate (3) system. Also shown are the simulation results showing the trajectories calculated by the equilibrium (EQ) stage model and the nonequilibrium (NEQ) stage model, along with the residue curve map. The large open circles represent the experimental composition specified in the simulations. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.
remains on the left side of the boundary. The EQ trajectory closely follows the residue curve map, shown in Fig. 6.2(e-f). A further point to note is that while the experimental results show that proceeding down the column (in the direction of the reboiler) the compositions get richer in water, the EQ simulations predict that these trays get progressively richer in ethanol. The NEQ model simulations require specification of the bubble diameter. For a range of bubble diameters 3 – 5.5 mm, the NEQ trajectories have been plotted in Fig. 6.9(b). For \( d_b = 3 \) mm, the NEQ trajectory remains to the left of the distillation boundary and does not cross it. As we know, decreasing the bubble diameter has the effect of increasing the mass transfer coefficient (see Eq (4.18) and Eq (4.19)) and makes the NEQ model tend towards the EQ model. To match the EQ trajectory, the bubble size has to be around 1.5 mm. Conversely, increasing the bubble diameter, decreases the mass transfer coefficient and the NEQ trajectories move away from the EQ trajectory. For \( d_b = 4.5, 5 \) and 5.5 mm, all three NEQ trajectories cross the boundary. The best agreement with the experiments for the Water-Ethanol-Methylacetate system is obtained with \( d_b = 5.0 \) mm.

The simulation results for the EQ and NEQ model, with \( d_b = 5.0 \) mm, for all the experimental runs are shown in Fig. 6.8, along with the experimental results. Consider the runs T3-03, T3-04, T3-10 and T3-11. For all these runs no boundary crossing is observed experimentally; see Fig. 6.8(a-d). Both EQ and NEQ models do not anticipate boundary crossing. The EQ model follows the trajectory dictated by the residue curve map, whereas the NEQ model has a tendency to cut across to the right of the residue curve. The predictions of the NEQ model are superior to that of the EQ model and are in much better agreement with the experimentally measured composition trajectories. This tendency of the experiments to cut across to the right of the residue curves is strongly evident for run T3-10 and T3-11; here the NEQ model does a very good job of predicting the column trajectory. Consider the runs T3-18, T3-20, T3-21, T3-23 and T3-25 in Fig. 6.8(e-i). For all these runs we experience boundary crossing and the NEQ model successfully anticipates this phenomenon. In all the cases the EQ model fails to cross the boundary and the EQ trajectory remains on one side of the boundary.

![Simulation results compared with the experimental data](image)
6.5 Fitting of the bubble diameter

In order to show that the choices of the bubble diameter $d_b$ is not merely a “convenient fit” of our ternary experiments for the Water-Ethanol-Acetone, Water-Ethanol-Methanol and Water-Ethanol-Methylacetate systems, we also carried out experiments with several binary mixtures, see Chapter 5. Since not all of the investigated binary mixtures are of importance for the homogenous ternary systems discussed in this chapter, I will only restrict to those who are partly involved in the ternary mixtures just mentioned above or to be dealt with later on in this chapter. Hence, to mention are a set of eight experiments with the binary mixture Water-Ethanol, sets of four experiments with the binary mixtures Water-Methanol, Water-Isopropanol and Methanol-Isopropanol and finally two experiments with the Water-Methylacetate binary mixture. All the experiments with the several binary mixtures were carried out in the same experimental set-up as described in Chapter 3. The experimentally measured column (vapour) composition trajectories for these specific binaries are shown in Fig. 6.10(a-f) (next page), along with the NEQ model predictions taking $d_b = 4.5$ mm and 5.0 mm (Note: a more detailed discussion of the binary experiments can be found in Chapter 5). The NEQ simulations were carried out by specifying the vapour composition leaving the reboiler (stage 12); as we proceed up the column we approach the azeotropic compositions. From Fig. 6.10, we see that the NEQ simulations describe the experimental column trajectories very well for all binaries by using a 4.5 mm bubble diameter as well as by using a 5.0 mm bubble diameter. From Chapter 5, we already learned that the differences between a 4.5 mm or 5.0 mm bubble are tough to distinguish; one fixed bubble-diameter ($d_b$) could predict composition profiles within a certain margin just below the experimental column trajectory, whereas the other bubble-diameter ($d_b'$) predicts composition profiles within a similar margin just above the experimental column trajectory. Hence, only when the bubble-diameter is changed by 1 or more millimeters, it will (in general) display worth-mentioning differences, see also the various figures in Chapter 5 or for instance Fig. 6.4(b), Fig. 6.5(b), Fig. 6.7(b) and Fig. 6.9(b) in which NEQ simulation profiles are plotted with various bubble-diameters; along with the experimental results of the concerning ternary azeotropic system discussed.

Outlined, the NEQ simulations for the binary systems support our NEQ simulations for the ternary azeotropic systems studied in this Chapter.
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Fig. 6.10. Experimental results showing the vapor column composition trajectories for five different binary systems. Also shown are the simulation results showing the trajectories calculated by the NEQ stage model. For each binary, the experimental vapor composition leaving the reboiler is specified in the simulations. In the NEQ model simulations, a bubble size $d_b = 4.5 \text{ mm}$ (solid line) and $5.0 \text{ mm}$ (dotted line) were chosen.
Chapter 6

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6.6 Component Murphree efficiencies in ternary distillation

We may conclude from the foregoing results for the various homogeneous ternary azeotropic mixtures that the divergent behavior of the observed column composition trajectories for total reflux operations (closed system) in relation to what might be expected according to the textbooks (following the residue curve lines), are caused by multicomponent mass transfer effects. In short, the boundary crossing phenomenon is caused by multicomponent mass transfer effects. To explain this in some detail we consider again run T2-26 from the Water-Ethanol-Acetone system, run T4-13 from the Water-Ethanol-Methanol system and T3-23 from the Water-Ethanol-Methylacetate system. The values of the binary pair vapor diffusivities, $D_{y,ij}$, for those three ternary mixtures are specified respectively in Table 6.2(a), 6.2(b) and 6.2(c) for one single stage, along with the corresponding liquid phase coefficients. The estimated values of the Fourier numbers are calculated using

$$F_0 = \frac{4 D_{y,ij} \tau_v}{d_s^2}$$

and also given in Table 6.2(a), 6.2(b) and 6.2(c), along with the values of the surface tension ($\sigma$) and liquid density ($\rho_L$) that are needed in order to estimate the single bubble rise velocity ($V_b$) and thus the vapor residence time ($\tau_v$) using Eq. (4.10) and Eq. (4.9), see Chapter 4. The vapour phase diffusivities of the three binary pairs in each ternary system are estimated using the Fuller-Schettler-Giddings equation; details of the estimation procedure are to be found in Kooijman & Taylor (2001). This book also specifies the estimation methods for liquid phase diffusivities, densities and surface tension. From Table 6.2(a-c), we see that the $F_0$-values exceed 0.06 in all cases, justifying the use of Eq. (4.18) for estimation of the vapor phase mass transfer coefficients $k_{y,ij}$ of the binary pairs in the mixture; the $k_{y,ij}$ have an unity-power dependence on the vapor diffusivities $D_{y,ij}$. By evaluating the individual contributions of the liquid and vapor phases in Eq. (4.11) it can be verified that the mass transfer resistance is predominantly in the vapor phase. The liquid phase resistance contributes less than 10% of the total resistance; this conclusion was found to be valid for all the experimental runs carried out in this study for the Water-Ethanol-Acetone, Water-Ethanol-Methanol and Water-Ethanol-Methylacetate system.

Table 6.2(a)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Values for stage 6 of experiments T2-26 for the Water (1) – Ethanol (2) – Acetone (3) system obtained by NEQ model simulations (bubble diameter = 4.3 mm).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{y,ij}$</td>
<td>$[10^{-6} \text{ m}^2/\text{s}]$</td>
<td>21.0, 18.2, 9.07</td>
</tr>
<tr>
<td>$D_{x,ij}$</td>
<td>$[10^{-9} \text{ m}^2/\text{s}]$</td>
<td>5.95, 4.42, 3.01</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$[10^{-2} \text{ N/m}]$</td>
<td>3.46</td>
</tr>
<tr>
<td>$\rho_L$</td>
<td>$[\text{kg/m}^3]$</td>
<td>773</td>
</tr>
<tr>
<td>$V_b$</td>
<td>$[\text{m/s}]$</td>
<td>0.205</td>
</tr>
<tr>
<td>$\tau_v$</td>
<td>$[\text{s}]$</td>
<td>0.0449</td>
</tr>
<tr>
<td>$F_0_{ij}$</td>
<td>[-]</td>
<td>0.186, 0.162, 0.08</td>
</tr>
</tbody>
</table>
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Table 6.2(b)
Physical and transport properties for stage 6 of experiments T4-13 for the Water (1) – Ethanol (2) – Methanol (3) system obtained by NEQ model simulations (bubble diameter = 5.0 mm).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>i-j pair</th>
<th>1-2 pair</th>
<th>1-3 pair</th>
<th>2-3 pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{y,ij}$</td>
<td>$[10^{-6} \text{ m}^2/\text{s}]$</td>
<td>21.2</td>
<td>27.4</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>$D_{x,ij}$</td>
<td>$[10^{-9} \text{ m}^2/\text{s}]$</td>
<td>6.17</td>
<td>5.61</td>
<td>4.09</td>
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</tr>
<tr>
<td>$\sigma$</td>
<td>$[10^{-2} \text{ N/m}]$</td>
<td>3.402</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>$[\text{kg/m}^3]$</td>
<td>769</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_b$</td>
<td>$[\text{m/s}]$</td>
<td>0.206</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_v$</td>
<td>$[\text{s}]$</td>
<td>0.0448</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fo_{ij}$</td>
<td>[-]</td>
<td>0.152</td>
<td>0.196</td>
<td>0.098</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2(c)
Physical and transport properties for stage 6 of experiments T3-23 for the Water (1) – Ethanol (2) – Methylacetate (3) system obtained by NEQ model simulations (bubble diameter = 5.0 mm).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>i-j pair</th>
<th>1-2 pair</th>
<th>1-3 pair</th>
<th>2-3 pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{y,ij}$</td>
<td>$[10^{-6} \text{ m}^2/\text{s}]$</td>
<td>20.4</td>
<td>16.7</td>
<td>8.14</td>
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<tr>
<td>$D_{x,ij}$</td>
<td>$[10^{-9} \text{ m}^2/\text{s}]$</td>
<td>6.06</td>
<td>4.95</td>
<td>3.10</td>
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</tr>
<tr>
<td>$\sigma$</td>
<td>$[10^{-2} \text{ N/m}]$</td>
<td>3.073</td>
<td></td>
<td></td>
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<td>$\rho_b$</td>
<td>$[\text{kg/m}^3]$</td>
<td>826</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_b$</td>
<td>$[\text{m/s}]$</td>
<td>0.199</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_v$</td>
<td>$[\text{s}]$</td>
<td>0.0463</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fo_{ij}$</td>
<td>[-]</td>
<td>0.151</td>
<td>0.124</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

To understand the phenomena of boundary crossing, we consider the component Murphree stage efficiencies, defined by

$$E_i = \frac{y_{i,L} - y_{i,E}}{y_{i}^* - y_{i,E}^*}, \quad i = 1, 2, 3$$

(6.2)

For the EQ model the component efficiencies are all equal to unity. For the NEQ model the component efficiencies will, in general, differ from one another. To illustrate this, we present the calculations of $E_i$ for run T2-26, T4-13 and T3-23 in respectively Fig. 6.11(a), 6.12(a) and 6.13(a) obtained from NEQ simulations with a bubble diameter of 4.5 mm for the Water-Ethanol-Acetone system and 5.0 mm for the Water-Ethanol-Methanol and Water-Ethanol-Methylacetate system. It is clear that the component Murphree efficiencies are all different from one another and vary from stage to stage. The origin of the differences in $E_i$ can be traced to the differences in the binary pair vapor diffusivities, $D_{y,12}$, $D_{y,13}$ and $D_{y,23}$ (Table 6.2(a-c)). We note that the coefficient $D_{y,23}$ for all three mixtures is about half of the other coefficients. The difference between binary pair diffusivities cause the component efficiency values to be different from one another. Let us consider the component efficiencies for the Water-Ethanol-Acetone system in some more detail, see Fig. 6.11(a) The variation of the ethanol efficiency is particularly “strange” in that on stage 9 the value is close to zero whereas on stage 10 the component efficiency exceeds unity. The reason for the strange behaviour of the ethanol efficiency is to be found in the driving force (denominator term in
Eq. (6.2)) which is shown in Fig. 6.11(b); the driving force changes sign between stages 9 and 10 and the magnitude of the driving force is therefore vanishingly small on stages 9 and 10. The transfer of ethanol on these trays is dictated by the transfer of the other two components (Water and Acetone) because of coupling effects which are properly accounted for in the Maxwell-Stefan formulation (Krishna & Wesselingh, 1997; Wesselingh & Krishna, 2000 and Taylor & Krishna, 1993). For binary mixtures component efficiencies are bounded and lie between zero and unity; for mixtures with three or more components, component efficiencies are unbounded and can assume values ranging from $-\infty$ to $+\infty$. If the binary $D_{ij}$ were close to one another, the differences in the component efficiencies would be negligible. Differences in the component efficiencies cause the actual composition trajectory followed on any given stage $(y_i - y_{iE})$ to deviate from the trajectory dictated by the equilibrium vector $(y_i - y_{iE})$.

Fig. 6.12(a). Component efficiencies for the experiment T4-13 of the Water-Ethanol-Methanol system and (b) the driving forces for Ethanol at each stage, calculated by the NEQ stage model. In the NEQ model simulations, a bubble size $d_b = 5.0 \text{ mm}$ was chosen.
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Fig. 6.13(a). Component efficiencies for the experiment T3-23 of the Water-Ethanol-Methylacetate system and (b) the driving forces for Ethanol at each stage, calculated by the NEQ stage model. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.

For various vapor compositions entering any given stage, we have plotted in Fig. 6.14(a) the actual composition vector $(y_i, L - y_{LE})$, calculated from the NEQ model (taking bubble diameter of 4.5 mm) along with the equilibrium vector $(y_i^* - y_{LE})$ for the Water-Ethanol-Acetone system. The angle between the NEQ trajectory (continuous line) and the EQ trajectory (dashed line) increases when the differences in the component efficiencies increase. If all the component efficiencies were equal to one another, the NEQ and EQ trajectories would coincide.

Fig. 6.14(a). Calculated direction vectors for the Water-Ethanol-Acetone system using the EQ stage model (100% efficiency for all components, denoted by the dashed lines) and the NEQ stage model (denoted by the continuous lines). In the NEQ model simulations, a bubble size $d_b = 4.5$ mm was chosen. (b) All starting compositions within the gray shaded region will cross the distillation boundary to the right of this boundary.
We see from Fig. 6.14(a), that the NEQ trajectory has a tendency to cut across to the right of the EQ trajectory, precisely as has been observed in the experiments (cf. Fig. 6.3). It is this tendency to cut towards the right of the composition space that causes boundary crossing. By performing several NEQ simulations with various starting compositions of the vapor entering the condenser we can determine the region within which the column trajectories will cross the distillation boundary and end up with reboiler compositions in the right region of the distillation boundary. This boundary crossing region is shown as the grey shaded area in Fig. 6.14(b). It can be verified that the starting compositions for the three runs T2-03, T2-06 and T2-10 for the Water-Ethanol-Acetone system lie to the left of the grey shaded region; no boundary crossing is therefore observed for these runs, see Fig. 6.3. For the remainder of the experiments with this particular ternary mixture, the starting compositions (vapor compositions leaving stage 2 and thus entering the condenser) lie within the shaded region; boundary crossing is observed for all these six runs, see Fig. 6.3. Similar graphs like Fig. 6.14(a-b) are also produced for the Water-Ethanol-Methanol and Water-Ethanol-Methylacetate system in respectively Fig. 6.15(a-b) and Fig. 6.16(a-b). For the latter two systems, a bubble diameter of 5.0 mm was used for the calculations with the NEQ stage model.

![Fig. 6.15(a). Calculated direction vectors for the Water-Ethanol-Methanol system using the EQ stage model (100% efficiency for all components, denoted by the dashed lines) and the NEQ stage model (denoted by the continuous lines). In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen. (b) All starting compositions within the gray shaded region will cross the distillation boundary to the right of this boundary.](image)
6.7 Simulated ternary azeotropic systems

Besides the three ternary mixtures for which the experimental and simulation results are discussed in detail above, additional simulations were executed with other ternary systems as well. Noteworthy results for two additional mixtures will be presented in short below. The simulation strategy used for these simulations was the same as the one used for all the other binary and ternary system discussed before, see Chapter 4. Also the same rigorous NEQ stage model was used as developed in Chapter 4 and an EQ stage-model with equal component efficiencies for all components.

6.7.1 Methanol (1) – Isopropanol (2) – Water (3)

Let us consider the system: methanol (1) – isopropanol (2) – water (3) that has one binary azeotrope, as indicated in Fig. 6.17(a). We note that the boundary is very nearly a straight line. According to literature guidelines (Levy et al., 1985) it is not possible to cross a straight-line boundary. But these remarks regarding boundary crossing are based on the use of the EQ stage model. In order to see whether the introduction of mass transfer resistance has an influence on the column composition trajectories (a boundary crossing phenomenon) for this homogeneous ternary azeotropic system, we carried out the simulations with both EQ and NEQ stage models for a 12-stage column operating at total reflux. The feed composition was chosen to be $x_1 = 0.8$, $x_2 = 0.15$ which is located in the top region above the distillation boundary, see Fig. 6.1(a) and fixed on stage 1 (condenser). The EQ (cross-hair markers) and NEQ (open square markers) composition trajectories are seen to follow completely different composition trajectories; see Fig. 6.17(b). The NEQ model predicts that the bottom product composition corresponds to (nearly) pure water whereas the EQ model predicts the bottom product to consist of (nearly) pure iso-propanol. Those predictions by both models show
Fig. 6.17(a). Residue curves for the Methanol (1) – Isopropanol (2) – Water (3) system. (b) and (c) compare EQ and NEQ distillation trajectories, showing the same simulation drawn to different scale. For all feed compositions located in the gray shaded region in (d), boundary crossing is observed.

qualitatively big differences. Fig. 6.17(c), drawn to a different scale, clearly shows that the NEQ model crosses the (straight) distillation boundary. To understand the phenomena of boundary crossing and the reason behind the different trajectories followed by the EQ and NEQ stage model, we consider the component Murphree stage efficiencies again (Eq. (6.2)), calculated on the basis of the multicomponent mass transfer theory presented in Chapter 4.

We note that the component efficiencies of the individual components are all significantly different, see Fig. 6.18(b). These differences are to be traced to the differences in the vapour diffusivities of the binary pairs in the mixture (the interphase mass transfer process is controlled by vapour phase transport). For the component of intermediate volatility, isopropanol, we note that the Murphree point efficiency shows a strong variation along the column. On stage 6 the efficiency is low (about 40%) and on the stage 7 this value increases to about 90%. The reason for this strong variation is to be found in the driving force of isopropanol which approaches vanishingly small values on stages 6 and 7; see Fig. 6.18(a).
The transfer of isopropanol is strongly dictated by the transfer of the other two species, water and methanol. We performed several simulations with the different feed compositions lying above the distillation boundary. For all feed compositions located in the dark shaded region shown in Fig. 6.17(d) we observed that the NEQ model predicts that the straight line distillation boundary will be crossed.
6.7.2 Water (1) – Methanol (2) – Methylacetate (3)

Consider the system: water (1) – methanol (2) – methylacetate (3) for which a (homogeneous) part of the residue curve map is shown in Fig. 6.19(a). The system also contains a region of liquid-liquid phase splitting towards the right hand side of the triangular diagram; this region is avoided in our analysis).

![Residue Curve Lines](image)

**Fig. 6.19(a).** Residue curves for the Water (1) – Methanol (2) – Methylacetate (3) system. (b) A comparison of the EQ and NEQ column composition trajectories. The column is operated at total reflux with no feed and product streams. The initial liquid composition for simulations is $x_1 = 0.44, x_2 = 0.2$ and fixed on stage 1.

This system has two binary azeotropes and the distillation boundary is curved. Fig. 6.19(b) compares EQ and NEQ distillation trajectories in a 12-stage column for total reflux operation with the liquid composition leaving the condenser taken to be $x_1 = 0.044, x_2 = 0.2$. The feed is located on the concave side of the distillation boundary. We find that the EQ and NEQ column trajectories move in different directions away from the condenser downwards; see Fig. 6.19(b). The EQ model predicts that the column gets progressively richer in methylacetate as we move down to the reboiler. The NEQ model, on the other hand, anticipates that the column gets progressively richer in water. Furthermore, we note that the NEQ trajectory crosses the distillation boundary. The difference in the EQ and NEQ column trajectories can be traced to the differences in the Murphree efficiencies of the three components, shown in Fig. 6.20(b) (next page). The differences in the component efficiencies can be traced to the differences in the values of the diffusivities of the binary pairs in the vapour phase (the transfer resistance in the liquid phase is negligible). The efficiency of methylacetate assumes a value below zero on stage 7 and is higher than 100% on stage 8. This strange variation of the methylacetate component efficiency is to be attributed to its component driving force which changes sign between stages 7 and 8; see Fig. 6.20(a). On stages 7 and 8 the transfer of methylacetate is dictated by the transfer of the other two components in the mixture due to multicomponent coupling effects (Taylor & Krishna, 1993).
Fig. 6.20(a). Component driving forces and (b) Murphree component efficiencies for the Water (1) – Methanol (2) – Methylacetate (3) system. The values correspond to the total reflux simulation for which the initial liquid composition is $x_1 = 0.44$, $x_2 = 0.2$ and fixed on stage 1.
6.8 Conclusions

The following major conclusions can be drawn from the work presented in this chapter.

- The measured composition trajectories during distillation of the systems Water-Ethanol-Acetone, Water-Ethanol-Methanol and Water-Ethanol-Methylacetate (three different mixtures) under total reflux conditions in a bubble cap distillation column clearly demonstrate that crossing of a distillation boundary is possible. Even when the boundary is a straight-line (as is the case for the Water-Ethanol-Acetone mixture), this phenomenon will be observed, provided that the measured profiles are located within a certain region from the distillation boundary.

- An NEQ stage model is able to model the experimental results. The experimental results agree very well with the developed model (Chapter 4). The NEQ model correctly anticipates boundary crossing.

- An EQ stage model fails to anticipate boundary crossing in any experiment with any examined mixture. The EQ model provides a much poorer representation of the column composition trajectories and do not agree qualitatively with the experimental results. While the experimentally measured trajectory shows that the column gets progressively richer in water as we proceed down to the reboiler, the EQ trajectory predicts that the column gets progressively richer in ethanol, see Fig. 6.3, Fig. 6.6 and Fig. 6.8.

- The differences in the NEQ and EQ trajectories emanates from differences in the component Murphree efficiencies, which in turn can be traced to differences in the binary vapour phase diffusivities $D_{y,ij}$.

Further based on the merely simulated ternary azeotropic systems, we see again that the EQ and NEQ models may predict completely different composition trajectories.

- For the Methanol-Isopropanol-Water, the NEQ model has shown to be capable of crossing straight-line distillation boundaries (as with the Water-Ethanol-Acetone system was proven by experiments and simulations as well). In order to remind, in the literature it is remarked that straight-line distillation boundaries cannot be crossed; this conclusion is restricted in its applicability to EQ models.

- For the system Water-Methanol-Methylacetate, with the feed located on the concave side of a curved distillation boundary, the NEQ model trajectories are seen to be capable of crossing the boundary. The EQ model, in sharp contrast does not anticipate this crossing phenomenon.

Those simulations demonstrate that the literature guidelines regarding boundary crossing do not have general validity.

The overall conclusion to be drawn from this work is that for reliable simulation of distillation of azeotropic systems exhibiting a distillation boundary, we must adopt a rigorous NEQ stage model. In a theoretical simulation study, Castillo & Towler (1998) have shown how the differences in the EQ and NEQ distillation column trajectories could be exploited by the engineer in order to obtain process designs that could not be contemplated if mass transfer effects were ignored, and that some designs based solely on EQ models become infeasible when mass transfer is considered.