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

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Chapter 7

Quaternary homogeneous azeotropic systems

7.1 Introduction

There is some evidence in the published literature that experimentally measured composition profiles in distillation columns are better simulated with models based on the rigorous Maxwell-Stefan diffusion equations than with simpler models that assume equal component efficiencies (Taylor & Krishna, 1993; Krishna & Wesselingh, 1997; Baur et al., 1999; Springer & Krishna, 2001; Pelkonen et al., 1997 and 2001 and Springer et al., 2002). Of particular interest and significance are the experimental measurements of Pelkonen et al. (1997 and 2001) and Springer et al. (2002). Pelkonen et al. (1997) performed total reflux experiments with the system methanol-isopropanol-water in a packed distillation column and showed that if the composition at the top of the column is located on the distillation boundary, the experimentally measured composition profiles end up with a reboiler composition that is rich in water, whereas the EQ model predicts that the reboiler composition corresponds to pure isopropanol. The NEQ model is able to describe the experimentally observed profile quite well. Similar dramatic differences between the predictions of the EQ and NEQ models were also obtained for the quaternary system acetone-methanol-isopropanol-water when the composition near the top of the column is chosen to lie on the distillation boundary (see also introduction Chapter 6).

The experimental results of Springer et al. (2002) (Chapter 6) with the ternary azeotropic system ethanol-water-acetone in a bubble cap tray column show that even straight line boundaries can be crossed; this boundary crossing phenomena is anticipated by the NEQ model but not by the EQ model. The same phenomena was also observed for other ternary homogeneous mixtures for which the distillation boundaries are slightly curved. In chapter 6, the experimental results and verifications of the necessity to use a NEQ stage model in describing trajectories during azeotropic distillation for two more mixtures are discussed; water-ethanol-methanol and water-ethanol-methylacetate (Springer et al., 2002).

The major objective of this paper is to extend the earlier work presented in chapter 5 and chapter 6 (Springer et al., 2002) and to demonstrate that for quaternary azeotropic distillation in a tray column, distillation boundaries (which are surfaces dividing the composition space into two regions) can be crossed as well, provided that the starting compositions are located within a finite region of compositions on one side of the boundary. Furthermore, it will be shown that such boundary crossing phenomena can be predicted by the NEQ models, incorporating the Maxwell-Stefan equations, and can be attributed to differences in component Murphree efficiencies. Clearly, the EQ models will be incapable of anticipating boundary crossing effects since the EQ distillation trajectories must necessarily follow the residue curve lines for total reflux operations (Stichlmair & Fair, 1998 and Doherty & Malone, 2001).
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Table 7.1  
The NRTL parameters for the quaternary mixture water (1) - ethanol (2) - methanol (3) - acetone (4) at 101.3 kPa (Gmehling & Onken, 1977). These parameters are used along with $G_i = \exp(-\alpha_{ij}T_{ij})$ and $T_{ij} = B_{ij}/T$

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<th>Quaternary system (homogeneous)</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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<td>-182.6052</td>
<td>0.297</td>
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</tr>
<tr>
<td>Water</td>
<td>Acetone</td>
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<td>330.4768</td>
<td>0.5103</td>
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<tr>
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<td>73.413</td>
<td>-79.1718</td>
<td>0.3029</td>
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</tr>
<tr>
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<td>22.83319</td>
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<tr>
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<td>Acetone</td>
<td>97.78178</td>
<td>107.83</td>
<td>0.3008</td>
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</tbody>
</table>

To verify the boundary crossing phenomena, we performed experiments with the quaternary system: water (1) - ethanol (2) - methanol (3) - acetone (4) in a bubble cap tray distillation column. The vapour-liquid equilibrium was determined using NRTL parameters taken from (Gmehling & Onken, 1977) and listed in Table 7.1 (and Table 3.3). The distillation boundary forms a surface connecting the ethanol-water azeotrope with pure methanol and pure acetone. The distillation boundary (surface) is shown in Fig. 7.1(a-b-c) (See next page), that represent three different views of the quaternary composition space. Consider Fig. 7.1(a-b), the three dimensional composition space is viewed from two different sides; Fig. 7.1(a) shows the component methanol in front whereas Fig. 7.1(b) shows the component acetone in front. If only the front of these two projections is considered (the component at the back is set to zero), the projections of the ternary systems: water-ethanol-methanol (Fig. 7.1(d)) and water-ethanol-acetone (Fig. 7.1(e)) remain respectively with their own distillation boundaries (called: the “methanol boundary” in Fig. 7.1(d) and the “acetone boundary” in Fig. 7.1(e)). In Fig. 7.1(f), the two distillation boundaries (Fig. 7.1(d-e)) are combined together with all the “pseudo distillation boundary-lines” that lie in between (represented by the gray shaded region); only when a point is located below this shaded region, you can be sure that the point is actually lying below the distillation boundary surface. Fig. 7.1(g) shows the same graph as Fig. 7.1(f), but with a different axis-arrangement.

7.2 Quaternary system: Water (1) – Ethanol (2) – Methanol (3) – Acetone (4)

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 and ternaries were carried out. The complete description of the experimental procedure and experimental set-up is described in detail in Chapter 3.

After the experimental results are discussed, they will be compared with the simulation results obtained from an EQ stage model (using equal component efficiencies on all stages) and from the rigorous NEQ stage model as developed and described in detail in the earlier Chapter 4.

The vapour composition, taken from the experimental column trajectory, for the specification of the input (starting) composition for the performance of the simulation runs is the vapour composition leaving stage 4 (indicated by a large open circle in all plots). The simulated composition profile (with both models) of the total reflux run is forced to pass through this specified composition (see Chapter 4).
Fig. 7.1(a-b-c). Three dimensional residue curve space for the Water (1) - Ethanol (2) - Methanol (3) - Acetone (4) quaternary system, showing an almost plane distillation boundary-surface with its corners at pure methanol, pure acetone and the binary azeotrope between water-ethanol. (d) Front view projection of Fig. 7.1(a) with the methanol component in front, showing the ternary "methanol boundary". (e) Front view projection of Fig. 7.1(b) with the acetone component in front, showing the ternary "acetone boundary". (f-g) Combination of the two ternary boundaries from Fig. 7.1(d-e) together with all the "pseudo distillation boundary lines" that lie in between (represented by the gray shaded region).
7.2.1 Experimental results for the Water – Ethanol – Methanol – Acetone system

The experimentally determined composition trajectories for a set of 6 experiments are presented in Fig. 7.2(a-f) (next pages) in three different projections for each single experiment. The first two projections of Fig. 7.2(a-f) are similar to the projections shown in Fig. 7.1(d) and Fig. 7.1(e). The third projection is obtained when looked at the distillation boundary surface from above with the component ethanol at the rear (as in Fig. 7.1(c)). This projection does not give any information concerning a possible boundary crossing, but does show from another point of view the differences between the trajectories predicted by the EQ model versus NEQ model (discussed and developed in Chapter 4). 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 9 vapor and 4 liquid composition samples can be combined when plotting the composition trajectories. In Fig. 7.2, the vapor samples are denoted by open circles and the liquid samples by open squares. In experiment Q1, the column trajectory was located completely below the distillation boundary surface, which corresponds to the left of the ternary distillation boundaries in Fig. 7.2(a1) and Fig. 7.2(a2) (indicated by a thick line). All the remaining five experiments, Q2 to Q6, clearly exhibit boundary crossing phenomena. In these experiments both the “methanol” and “acetone” boundaries are crossed. Clearly, boundary crossing phenomena is not in conformity with the assumption of thermodynamic phase equilibrium; this is evidenced by the fact that the experimental trajectories do not agree with the constraints, enforced by the distillation boundary (surface). In order to understand, and rationalize, the boundary crossing phenomena we developed the rigorous nonequilibrium (NEQ) stage model (Chapter 4). The next section deals with the comparison of the simulation results from the EQ stage model and the developed NEQ stage model with the experimental results for the Water-Ethanol-Methanol-Acetone mixture.

7.2.2 Comparison of EQ and NEQ simulations with experiments

All 6 quaternary experiments, Q1 to Q6, were simulated with both the EQ stage model and the rigorous NEQ stage model. Let us consider one of the experiments, Q6, in some detail. Fig. 7.3(a) (See page 77) compares the EQ model with the experimental results. The large open circle represents the vapour composition leaving stage 4; the specified “input” composition for in the simulations. We note that while the experimental points cross the distillation boundary (grey colored surface), the EQ column trajectory does not and remains below the boundary surface. 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. The NEQ simulations were carried out for a range of bubble diameters in the 3 – 5.5 mm range. We know from Eq. (4.18) and Eq. (4.19) that the mass transfer coefficient gets bigger when the bubble diameter is smaller. This implies that for very small bubble diameters, the NEQ model will predict similar composition trajectories as the EQ stage model. To match the EQ model profiles, a bubble diameter of around 1.5 mm or smaller has to be specified. Conversely, increasing the bubble diameter, decreases the mass transfer coefficient and the NEQ trajectories move away from the EQ trajectory. The best agreement with the experiments for our quaternary system is obtained with \( d_b = 5.0 \) mm. The simulation result for the NEQ
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![Diagram of experimental results for run Q1-Q3 with simulation results showing trajectories calculated by the EQ model and the NEQ model. The large open circle represents the composition used as input specification in the simulations. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.]

Fig. 7.2(a-c). Experimental results for run Q1-Q3 (open circles for vapor and open squares for liquid samples) showing the column composition trajectories for the Water (1) – Ethanol (2) – Methanol (3) – Acetone (4) system in three different front view projections. Also shown are the simulation results showing the trajectories calculated by the EQ model and the NEQ model. The large open circle represents the composition used as input specification in the simulations. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.
Fig. 7.2(d-f). Experimental results for run Q4-Q6 (open circles for vapor and open squares for liquid samples) showing the column composition trajectories for the Water (1) – Ethanol (2) – Methanol (3) – Acetone (4) system in three different front view projections. Also shown are the simulation results showing the trajectories calculated by the EQ model and the NEQ model. The large open circle represents the composition used as input specification in the simulations. In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.
model, with $d_b = 5.0 \text{ mm}$, is plotted for the experimental run Q6 in Fig. 7.3(b). The NEQ trajectory is in very good agreement with the experiment results and is able to reproduce the boundary crossing observed.

The simulation results for the EQ and NEQ model (with $d_b = 5.0 \text{ mm}$) for all the six experimental runs are shown in Fig. 7.2(a-f) in three different projections, along with the experimental results.

Consider the run Q1. For this run no boundary crossing is observed experimentally; see Fig. 7.2(a1-3). Both EQ and NEQ models do not anticipate boundary crossing, although 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.

Consider the runs Q2 up to and including Q6 in Fig. 7.2. For all these runs we experience boundary crossing; in the experiments both the “methanol” and “acetone” boundaries are crossed. The NEQ model successfully anticipates the crossing of the “methanol” and “acetone” boundaries. In all the cases the EQ model fails to cross the “acetone” boundary. For run Q2, the EQ model fails to cross the “methanol” boundary as well. (Note: the EQ model never goes through the boundary surface, whereas the experimental profile and the NEQ stage model do cross the boundary surface for these last five runs; this would be visually observable when all these runs were plotted in three dimensional plots like in Fig. 7.3). 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. 7.3(a)](image_url)

**Fig. 7.3(a).** EQ model and (b) NEQ model simulation results compared with the experimental data (open circles for vapor and open squares for liquid samples) for run Q6 (water-ethanol-methanol-acetone system). The large open circle represents the specified composition for the simulations; this corresponds to the vapor composition leaving stage 4.
7.3 Verification of the choice of the bubble size

In order to verify and to demonstrate that the choice of a 5.0 mm bubble size is not just a convenient fit of the quaternary experimental results, we only have to recall the NEQ model simulations for our (of importance) binary and ternary azeotropic systems. In order to call to mind, we performed experiments with the ternary mixture water-ethanol-methanol. The experimental results for a set of nine runs are shown in Fig. 6.6 (Chapter 6). All experiments were simulated with the EQ stage model and the rigorous NEQ stage model, taking $d_b = 5.0$ mm. The large open circle in Fig. 6.6 represents the vapor composition leaving stage 4; this is specified in the simulations as ‘input’ composition/parameter.

Consider the runs T4-01, T4-06, T4-08 and T4-11. For all these runs no boundary crossing is observed experimentally. 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 with $d_b = 5.0$ mm are superior to that of the EQ model and in much better agreement with the experimentally measured composition trajectories. Consider the runs T4-13, T4-17, T4-22, T4-23 and T4-24 in Fig. 6.6. For all these runs we experience boundary crossing and the NEQ model with a $d_b = 5.0$ mm 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. A second graph in chapter 6 (Fig. 6.7(b)) shows that for various bubble-diameters (in a range from 3-5.5 mm), the NEQ stage model simulations are in the best agreement with the experimental results when a bubble-size of $d_b = 5.0$ mm is chosen. Since the water-ethanol-methanol system is a part of the quaternary system, this result is a fair support for the use of a 5.0 mm bubble-diameter for the quaternary system as well.

We also performed experiments with a set of eight runs with the binary mixture water-ethanol and a set of four experiments with the binary mixture water-methanol (both involved in the quaternary mixture). Note: all the experiments with the two binaries and the ternary just mentioned above 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. 7.4(a-c), along with the NEQ model predictions taking $d_b = 5.0$ mm. (Note: Those results are also plotted in Fig. 6.10(a-c) and further discussed in Chapter 5). The NEQ simulations for the binaries were carried out by specifying the vapour composition leaving the reboiler (stage 12); as we proceed up the column we approach the azeotropes.

From Fig. 7.4(a-d), we see that the NEQ simulations using a 5.0 mm bubble-diameter describe the experimental column trajectories very well for the two binaries and the ternary water-ethanol-methanol (one more plotted in Fig. 7.4(d)). Since equal bubble-sizes (5.0 mm) turned out to be best fitting the experiments for the foregoing binaries and ternary, it is not surprisingly that a 5.0 mm bubble-diameter is also best used for our quaternary system. Nevertheless, it is not more than fair to remind that the Water-Ethanol-Acetone system (also part of the quaternary) was best simulated with a 4.5 mm bubble-diameter instead of a 5.0 mm bubble-size. Yet, it has already been mentioned before (concerning Fig. 6.10(a-f)) that the differences between a 4.5 and 5.0 mm bubble is not that extreme. Besides, the fact that our quaternary mixture is better simulated with a 5.0 mm bubble-size could perhaps be explained by the fact that the amounts of acetone in the experimental profiles are much lower than for instance the amounts of methanol, not to mention the amounts of ethanol and water. Therefore, one could argue that the NEQ simulation results for the ternary mixture water-
Fig. 7.4. Experimental results, showing the vapor column composition trajectories for (a-b) the binaries Water (1) – Ethanol (2), (c) Water (1) – Methanol (2) and (d) the ternary Water (1) – Ethanol (2) – Methanol (3). Also shown are the simulation results showing the trajectories calculated by the nonequilibrium (NEQ) stage model. For each binary, the experimental vapor composition leaving the reboiler is specified in the simulations. For the ternary system, the vapor composition leaving stage 4 is specified. In the NEQ model simulations, a bubble size $d_b = 5.0 \text{ mm}$ (solid line) was chosen.

Ethanol-methanol, best simulated with a bubble-size $d_b = 5.0 \text{ mm}$, reckon more than the results for the ternary mixture water-ethanol-acetone.
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7.4 Component Murphree efficiency in quaternary distillation

As was the case for the ternary azeotropic system, we may conclude for the quaternary system as well that boundary crossing (surface break through) is caused by multicomponent mass transfer effects. To explain this, we consider again one specific run “Q6”. The values of the binary pair vapor diffusivities, \( D_{y,ij} \) for water (1) – ethanol (2) – methanol (3) – acetone (4) are specified in Table 7.2 for stage 6, along with the corresponding liquid phase coefficients and the matrix of vapour phase transfer units \([NTU_y]\) and liquid phase transfer units \([NTU_x]\). The estimated values of the Fourier numbers calculated using

\[
Fo_y = \frac{4 D_{y,ij} \tau_y}{d_b^2}
\]  

are also given in Table 7.2 for stage 6, 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 \((\tau_v)\). From Table 7.2, we see that the Fourier values exceed 0.06 in all cases, justifying the use of Eq. (4.18) for estimation of the vapor phase mass transfer coefficients \(\kappa_{y,ij}\) of the binary pairs in the mixture; the \(\kappa_{y,ij}\) 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 again. The liquid phase resistance contributes less than 10% of the total resistance; this conclusion was found to be valid for all the 6 experimental runs carried out with this quaternary mixture.

Table 7.2
Physical and transport properties for stage 6 of experiment Q6 for the Water (1) – Ethanol (2) – Methanol (3) – Acetone (4) system obtained by NEQ model simulations (bubble diameter = 5.0 mm).

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<th>Parameter</th>
<th>units</th>
<th>1-2 pair</th>
<th>1-3 pair</th>
<th>1-4 pair</th>
<th>2-3 pair</th>
<th>2-4 pair</th>
<th>3-4 pair</th>
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<tr>
<td>(D_{y,ij})</td>
<td>(10^{-5} \text{ m}^2/\text{s})</td>
<td>2.1</td>
<td>2.72</td>
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<td>(D_{x,ij})</td>
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<td>(\sigma)</td>
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<tr>
<td>(\rho_l)</td>
<td>([\text{kg/m}^3])</td>
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<td>(V_b)</td>
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<td></td>
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<tr>
<td>(\tau_v)</td>
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<td>0.1308</td>
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<td>0.0848</td>
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</table>
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(a) Component Murphree efficiencies

(b) Methanol driving force

Fig. 7.5(a). Murphree component efficiencies along the column for experiment Q6 (water-ethanol-methanol-acetone system) calculated by the NEQ stage model using a bubble size (d_b) of 5.0 mm. (b) Methanol driving force along the column.

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

\[ E_i = \frac{y_{i,L} - y_{i,E}}{y_i* - y_{i,E}}, \quad i=1,2,3,4 \]

(7.2)

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, which is illustrated for run Q6 in Fig. 7.5(a). It is clear that the component Murphree efficiencies are all different from one another and vary from stage to stage. In particular we note that the methanol efficiency is negative on stage 3. The reason for the negative methanol efficiency is that its constituent driving force is vanishingly small on stage 3 (see Fig. 7.5(b)) and therefore its transfer is dictated by the movement of the other three components in the mixture. The origin of the differences in \( E_i \) can be traced to the differences in the binary pair vapor diffusivities \( D_{y_{ij}} \). If the binary \( D_{y_{ij}} \) were close to one another, the differences in the component efficiencies would be negligible. As we saw for the investigated three ternary systems, the differences in the component efficiencies are also causing the actual composition trajectory followed on any stage \( (y_{i,E}, y_{i,L}) \) to deviate from the trajectory dictated by the equilibrium vector \( (y_i*, y_{i,E}) \) for the examined quaternary system. Several actual composition vectors, calculated by the NEQ stage model using a 5.0 mm bubble-diameter, along with equilibrium vectors are plotted for various vapour compositions entering any given stage in two different ways, see Fig. 7.6(a-b). 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.
We see from Fig. 7.6(a-b), 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. 7.2). It is this tendency to cut towards the right of the composition space that causes boundary “surface” crossing.

**Fig. 7.6(a-b).** Calculated direction vectors using the EQ stage model (100% efficiency for all components, denoted by the dashed lines) and the NEQ stage model (denoted by the solid lines). In the NEQ model simulations, a bubble size $d_b = 5.0$ mm was chosen.
7.5 Conclusions

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

- The experimentally measured composition trajectories during the distillation of the quaternary mixture water – ethanol – methanol – acetone, under total reflux in a laboratory-scale bubble cap distillation column demonstrate that crossing of a distillation surface (boundary) is possible.
- The NEQ stage model, in which proper account is taken of mass transfer in either fluid phase by use of the rigorous Maxwell-Stefan diffusion equations, is able to model the experimental results. The experimental results agree very well with the developed model in which a bubble of 5.0 mm in diameter is chosen. The NEQ stage model correctly anticipates boundary crossing in the quaternary mixture. The choice (fit) of a bubble-size \( db = 5.0 \) mm is confirmed by experiments with the binaries water - ethanol and water - methanol and the ternary mixture water - ethanol - methanol. By the latter too, boundary crossing is observed in several experiments and described by the NEQ stage model.
- An EQ stage model, which assumes equal component efficiencies for all components, fails to anticipate boundary (surface) crossing in any experiment.
- The differences in the NEQ and EQ trajectories emanates from differences in the component Murphree efficiencies. These in turn can be traced to differences in the binary pair vapour phase diffusivities \( D_{y,ij} \).

Earlier conclusions drawn after the study on homogeneous ternary azeotropic mixtures in chapter 6 are strengthened by the work on quaternary azeotropic systems in this chapter. In case a distillation boundary exhibit, the engineer should be aware that for reliable simulation of distillation, it is better to adopt a rigorous NEQ stage model. Like on one hand, it can turn out that some designs, initially considered to be possible purely based on EQ stage models, become infeasible when mass transfer effects are considered. On the other hand the opposite might also occur that 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.