Mass transfer effects in distillation
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Chapter 4

NEQ model development

4.1 Homogeneous azeotropic systems

The development of the NEQ stage model follows the ideas and concepts developed earlier by Taylor, Krishna and others and described in earlier publications (Krishna & Wesselingh, 1997; Wesselingh & Krishna, 2000; Taylor & Krishna, 1993; Krishnanmurthy & Taylor, 1985; Taylor et al., 1994; Baur et al., 1999). The building blocks of the NEQ model are material balances, energy balances, equilibrium relations, and mass and energy transfer models.

We focus first on the material balances and estimation of mass transfer coefficients. Consider first a single stage j pictured in Fig. 4.1.

Fig. 4.1. Schematic of the bubble froth regime on a tray
All our experiments were carried out in the bubbly froth regime. Visual observations of tray operation (photographs are available at our website: http://ct-cr4.chem.uva.nl/distillation) showed that the bubbles were roughly of uniform size and shape. In our model development we assume that the bubbles rise through the liquid in a plug flow manner. Furthermore, we assume that the liquid phase is well-mixed. The steady state component molar balance for n-component distillation in tray columns is given by the (n-1)-dimensional matrix relation

\[ V_b \frac{d(y)}{dh} = [K_{oj}] (y^* - y)a' \]  

(4.1)

where \(a'\) is the interfacial area per unit volume of the dispersed bubble phase and \(V_b\) is the bubble rise velocity. Eq. (4.1) can be re-written in terms of the overall number of transfer units for the vapour phase, [\(NTU_{oV}\)]:

\[ \frac{d(y)}{d\xi} = [NTU_{oV}] (y^* - y), \]  

(4.2)

where \(\xi = h/h_f\) is the dimensional distance along the froth and [\(NTU_{oV}\)] is defined as:

\[ [NTU_{oV}] = \int_0^{h_f} [K_{oj}] a'/V_b \] dh  

(4.3)

Carrying out the integration, assuming that the matrix of overall mass transfer coefficients [\(K_{oj}\)] does not vary along the froth height, we obtain

\[ [NTU_{oV}] = \int_0^{h_f} [K_{oj}] a'/V_b = [K_{oj}] a' \frac{h_f}{V_b}, \]  

(4.4)

Assuming that the [\(NTU_{oV}\)] on a single stage is constant, Eq. (4.2) can be integrated using the boundary conditions

\[ \xi = 0 \text{ (inlet to tray)} \rightarrow (y) = (y_{j+1}) \]

\[ \xi = 1 \text{ (outlet to tray)} \rightarrow (y) = (y_j) \]  

(4.5)

to obtain the compositions leaving the distillation stage; detailed derivations are available in Taylor & Krishna (1993):

\[ (y^* - y_j) = \exp[-[NTU_{oV}](y^* - y_{j+1})] \]  

(4.6)

Introducing the matrix \([Q] = \exp[-[NTU_{oV}]]\), we may re-write Eq. (4.6) in the form

\[ (y_j - y_{j+1}) = ([I] - [Q])(y^* - y_{j+1}), \]  

(4.7)

where \([I]\) is the identity matrix. The limiting case of the EQ stage model is obtained when the mass transfer coefficients in either fluid phase attain large values; \([Q]\) reduces in this case to the null matrix and the compositions leaving the tray \((y_j)\) are equal to \((y^*)\), in equilibrium with the liquid leaving the tray. We follow the procedure of Kooijman & Taylor (1995) for the implementation of Eq. (4.7) in the stage-to-stage calculation.
Estimation of interfacial areas and mass transfer coefficients:

From Eq. (4.4), we see that \([NTU_{Oy}]\) can be calculated from knowledge of \([K_{Oy}]\), the interfacial area per unit volume of vapour \(a'\) and the vapour phase residence time \(\tau_v\).

In our model we assume all the bubbles to be spherical in shape with a diameter \(d_b\). The interfacial area per unit volume of vapour \(a'\) is therefore given by:

\[
a' = \frac{6}{d_b} \tag{4.8}
\]

The vapour residence time is determined by:

\[
\tau_v = \frac{h_f}{V_b} \tag{4.9}
\]

where \(h_f\) is the height of dispersion (froth). The height of the dispersion on the tray is taken to be the height of the downcomer tube above the tray floor, i.e. 9.2 mm as seen in Fig. 3.3 (see Chapter 3). This is a good approximation; any uncertainties in the value of \(h_f\) will be reflected in the choice of the bubble size. The bubble rise velocity \(V_b\) is estimated using the Mendelson equation (Mendelson, 1967), recommended by Krishna et al. (1999):

\[
V_b = \left[ \frac{2\sigma}{\rho_f d_b} + \frac{g d_b}{2} \right]^{1/2} \tag{4.10}
\]

The overall matrix of mass transfer coefficients \([K_{Oy}]\) is given by the addition of resistances formula:

\[
[K_{Oy}]^{-1} = [k_y]^{-1} + \frac{C_y}{C_x} [K_{eq}] [k_x]^{-1}, \tag{4.11}
\]

in which \([K_{eq}]\) represents the diagonal matrix of \(K\)-values and \([k_y]\) and \([k_x]\) are the partial transfer coefficient matrices for the vapour and liquid phases respectively.

Let us consider the matrix of the multicomponent vapour mass transfer coefficient \([k_y]\). The \((n-1)^2\) elements \(k_{y,ij}\) can be estimated from the mass transfer coefficients of the constituent binary pairs, \(\kappa_{y,ij}\) by making use of the Maxwell-Stefan formulation; the final result for a ternary system is:

\[
\begin{align*}
\kappa_{y,11} &= \kappa_{y,13}(y_1\kappa_{y,23} + (1-y_1)\kappa_{y,12})/S \\
\kappa_{y,12} &= y_1\kappa_{y,13}(\kappa_{y,13} - \kappa_{y,12})/S \\
\kappa_{y,21} &= y_2\kappa_{y,13}(\kappa_{y,13} - \kappa_{y,12})/S \\
\kappa_{y,22} &= \kappa_{y,23}(y_2\kappa_{y,13} + (1-y_2)\kappa_{y,12})/S \\
\end{align*} \tag{4.12}
\]

where

\[
S = y_1\kappa_{y,23} + y_2\kappa_{y,13} + y_3\kappa_{y,12} \tag{4.13}
\]
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Or written in a more general form for a n-component system:

\[
[k_y] = [R_y]^{-1}
\]  (4.14)

where the elements of the matrix of inverse mass transfer coefficients \([R_y]\) is given by:

\[
R_{y,ii} = \frac{y_j}{\kappa^*_{y,ii}} + \sum_{k=1, k\neq i}^{n} \frac{y_j}{\kappa^*_{y,ki}}; \quad R_{y,ij} = -y_j \left( \frac{1}{\kappa^*_{y,ij}} - \frac{1}{\kappa^*_{y,ii}} \right) \quad i = 1, 2, ..., (n-1)
\]  (4.15)

For each of the binary pairs in the mixture, the \(\kappa_{y,ij}\) can be estimated from the following equation for instationary diffusion within a spherical bubble (Taylor & Krishna, 1993):

\[
Sh_{ij} = \frac{\kappa_{y,ij} d_b}{D_{y,ij}} = \frac{2}{3} \pi^2 \left\{ \sum_{m=1}^{\infty} \exp\left\{-m^2 \pi^2 Fo_{y,j} \right\} \right\} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left\{-m^2 \pi^2 Fo_{y,j} \right\}
\]  (4.16)

with \(ij = \) every possible binary pair; …for a ternary: \(ij = 12, 13, 23\).

For Fourier numbers \(Fo_{y,j} = 4D_{y,ij} \tau_{y,j} / d_b^2\) larger than about 0.06, the Sherwood number reduces to the asymptotic value:

\[
Sh_{ij} = \frac{2 \pi^2}{3} \approx 6.58
\]  (4.17)

For this steady-state limit, the binary vapour mass transfer coefficients are given by:

\[
\kappa_{y,ij} = \frac{2 \pi^2 D_{y,ij}}{3 d_b}
\]  (4.18)

Eq. (4.18) leads to the important conclusion that \(\kappa_{y,ij}\) would have an unity-power dependence on the vapour diffusivity \(D_{y,ij}\), which is in sharp contrast with the square-root dependence for small values of \(Fo\), small vapour phase residence times.

The matrix of the multicomponent liquid mass transfer coefficient \([k_y]\) can be obtained analogously to Eqs (4.12) and (4.13) or to Eqs (4.14) and (4.15). The binary liquid mass transfer coefficient \(\kappa_{x,ij}\) can be obtained from the penetration model:

\[
\kappa_{x,ij} = \frac{2 \pi^2 \sqrt{D_{x,ij}}}{\pi \tau_c}
\]  (4.19)

where the contact time of the liquid with gas bubbles, \(\tau_c\) is given by:

\[
\tau_c = \frac{d_b}{V_b}
\]  (4.20)

In the above set of model equations, the only unknown parameter is the bubble diameter \(d_b\). Once the bubble diameter is set, the system of equations can be solved. Substituting Eq. (4.11) in Eq. (4.4) gives us the \([NTU_{0,y}]\), required for calculation of the \([Q]\) matrix in Eq. (4.7).
The material balance relations outlined above need to be solved along with the enthalpy balance relations, as described in Chapter 14 of Taylor & Krishna (1993). The required heat transfer coefficients in the vapour phase are calculated from the heat transfer analog of Eq. (4.16) for the vapour phase Nusselt number. Similarly, the liquid phase heat transfer coefficient is obtained by the application of the penetration model to the liquid phase, analogous to Eq. (4.19).

The entire set of material and energy balance equations, along with the interphase mass and energy transfer rate relations are then incorporated into a rigorous stage-to-stage model as described in Chapter 14 of Taylor & Krishna (1993). This chapter contains more exhaustive details of this model including sample calculations for binary and ternary mixtures.

### 4.2 Heterogeneous azeotropic systems

To be able to handle heterogeneous azeotropic systems as well, we extend the NEQ model developed earlier (Springer et al., 2002) in order to cater for liquid-liquid phase splitting on some or all of the trays. Visual observations of tray operation clearly showed which stages were still in the homogeneous region and which stages entered the heterogeneous region. The appearance of two liquids on a stage was visually indicated by a “milky” emulsion; consisting of a continuous phase (phase Lc) in which a second liquid phase (phase Ld) is dispersed, as pictured in Fig. 4.2.

**Fig. 4.2. Schematic of the bubble froth regime on a tray with two liquid phases**

![Schematic of the bubble froth regime on a tray with two liquid phases](image)
Our experimental results with the heterogeneous systems water-ethanol-cyclohexane and water-acetone-toluene (to be discussed in chapter 8.2) were conducted in composition regions poorer in water, and from consideration of the phase flows we concluded that the continuous liquid phase in the trays exhibiting phase splitting (in all experiments for both systems) was the “organic” phase and the dispersed phase was the “aqueous” phase. We therefore have to reckon with two interphase transfer processes: (1) dispersed aqueous phase (Ld) to continuous organic phase (Lc) and (2) continuous organic liquid phase (Lc) to vapour (V); these transfer processes are pictured in Fig. 4.3.

![Diagram of three-phase distillation](image)

**Fig. 4.3. Schematic showing the four transfer resistances for three phase distillation**
All our experiments were carried out in the bubbly froth regime. We assume the bubbles to be uniform in size and having a diameter $d_b$. In this context reference must be made to the paper by Mehlhorn et al. (1996) who showed that a two bubble class model would be more appropriate; our approach of using an effective bubble diameter must be viewed as a first approximation. For the trays on which we have liquid-liquid phase splitting the liquid droplets are also assumed to be uniform in size, having a diameter $d_l$. Examination of the liquid-liquid emulsion phase under a microscope show that the aqueous phase droplet sizes to have diameters in the $10 - 30 \mu m$ range. In publications order to quantify the transfer processes, pictured in Fig. 4.3, we extend the treatment in earlier by Taylor, Krishna and others (Baur et al., 1999; Krishna & Wesselingh, 1997; Krishnamurthy & Taylor, 1985a; 1985b; 1985c; Springer et al., 2002; Taylor et al., 1994; Taylor & Krishna, 1993 and Wesselingh & Krishna, 2000) to three-phase dispersions. There are four transport resistances to reckon with. The transfer coefficients inside the rigid bubbles and within the aqueous phase droplets can be estimated from taking the corresponding Sherwood numbers to equal $2\pi^2/3$ by extending the ideas of Springer et al. (2002). For estimating the transfer coefficients in the continuous organic liquid phase surrounding the droplets, we take a conservative estimate of the $Sh = 2$. The estimation of the transfer coefficients in the continuous liquid phase surrounding the bubble follows the penetration model:

$$\kappa_{ij}^{le,b} = 2\sqrt{\frac{D_{ij}^{le}}{\pi t_b}}$$

(4.21)

where the contact time of the continuous liquid phase with gas bubbles, $t_b$, is given by:

$$t_b = \frac{d_b}{V_b}$$

(4.22)

The bubble rise velocity $V_b$ is estimated using the Mendelson equation (Mendelson, 1967), recommended by Krishna et al. (1999):

$$V_b = \sqrt{\frac{2\sigma^{le} + g d_b}{\rho^{le} d_b}}$$

(4.23)

The calculation method of the transfer coefficients $\kappa_{ij}$ for all the four transfer resistances is summarized in Fig. 4.3. The transfer coefficients are different for each of the three binary pairs 1-2, 1-3, and 2-3 in the ternary mixture. The binary pair $\kappa_{ij}$ is obtained by substituting the appropriate binary pair M-S diffusivity $D_{ij}$, in the fluid phase under consideration, into the relations presented in Fig. 4.3. The four transfer coefficient matrices $[\kappa^V]$, $[\kappa^{le,b}]$, $[\kappa^{le,d}]$ and $[\kappa^{ld}]$ can then be calculated from Eq. (4.12) and Eq. (4.13) by using the appropriate values of the bulk fluid phase compositions $x_i$ and binary pair $\kappa_{ij}$.

The flux entering the vapour bubble can be expressed in terms of an overall matrix of mass transfer coefficients

$$(N) = c_i^v [K^{ov}] [y_i^* - y]$$

(4.24)

where $y_i^*$ is the composition of the vapour in equilibrium with the continuous liquid phase.
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From the continuity relations for interphase mass transfer, the following expression can be derived for the overall transfer coefficient matrix \([K^{ON}]\):

\[
\begin{align*}
[K^{ON}]^{-1} &= [k^F]^{-1} + \frac{c_i^V}{c_i^{LC}} [K^{VLC}_{eq}][k^{LC,L}]^{-1} \\
&\quad + \frac{c_i^V}{c_i^{LC}} \frac{a_h}{a_d} [K^{VLC}_{eq}][k^{LC,L}]^{-1} + \frac{c_i^V}{c_i^{LC}} \frac{a_h}{a_d} [K^{VLC}_{eq}][k^{LC,L}]^{-1} \\
&= \sum_{j=1}^{3} [K^{VLC}_{eq}][k^{LC,L}]^{-1} + \sum_{j=1}^{3} \frac{c_i^V}{c_i^{LC}} \frac{a_h}{a_d} [K^{VLC}_{eq}][k^{LC,L}]^{-1} \\
\end{align*}
\]

The \([K^{VLC}_{eq}]\) and \([k^{LC,L}]^{-1}\) are diagonal K-value matrices with elements

\[
K^{VLC}_{eq} = \begin{pmatrix} \frac{y_{LC}}{x_{LC}} \end{pmatrix}; \quad K^{LC,L} = \begin{pmatrix} \frac{x_{LC}}{x_{LC}} \end{pmatrix}; \quad i = 1, 2
\]

The K-values defined in Eq. (4.26) are used only for the estimation of the overall mass transfer coefficients following Eq. (4.25); for the estimation of the vapour-liquid-liquid equilibria, use is made of the rigorous NRTL equations.

The values of the \(\kappa_i\) in the liquid phases for our experimental heterogeneous systems have the same order of magnitudes (see Table 8.2; Chapter 8) and therefore the elements of matrices \([k^{LC,L}]^{-1}\), \([k^{LC,L}]^{-1}\) and \([k^{LC,L}]^{-1}\) will be of the same order of magnitude. The contribution of the last two resistances on the right member of Eq. (4.25) will be negligible compared to the contributions of the first two terms, because the ratios \(c_i^V a_h / c_i^{LC} a_d\) and \(c_i^V a_h / c_i^{LC} a_d\) have very low values for the chosen values of the bubble diameter (2.5 mm) and drop diameter (10 \(\mu m\)) for our investigated heterogeneous mixtures (see Table 8.2; Chapter 8). Put another way, the two liquid phases can be assumed to be in equilibrium with each other; this is the assumption made also by the Eckert & Vanek (2001) in the development of their NEQ model for three phase distillation. This also implies that the precise knowledge of the droplet diameter is unnecessary.

The next step in the model development is to integrate the flux expression for interphase transfer along the height of dispersion on the tray. This goes analog as described in the earlier part above for the homogeneous azeotropic systems; following Eq. (4.1) to Eq. (4.7). However, it should be noted that in the estimation of the bubble rise velocity, the properties of the continuous organic phase (Lc) are used; as can be seen in Eq. (4.23). Furthermore, the \([NTU^{ON}]\) is now given by substituting Eq. (4.25) in Eq. (4.4). the \([NTU^{ON}]\) is required for calculation of the \([Q]\) matrix in Eq. (4.7).
4.3 Simulation strategies

Simulations of the total reflux experimental runs were carried out using both the equilibrium (EQ) stage model and the rigorous nonequilibrium stage (NEQ) model developed above. The operating pressure for all experiments was 101.3 kPa and the ideal gas law was used. Activity coefficients were calculated using the NRTL interaction parameters, specified in Table 3.3, and the vapour pressures were calculated using the Antoine equations. The vapour phase was assumed to be thermodynamically ideal. The column consists of 12 stages, including the total condenser (stage 1) and partial reboiler (stage 12). The reflux flow rate (0.006 mol/s) and the bottom flow rate (0.0 mol/s) were used for specifying the column-operations. Since the mass and heat transfer coefficients are independent on the internal flows, the composition and temperature profiles are not dependent on the precise value of the specified reflux flow rate.

Since the column is operated at total reflux, the reflux flow rate determined the inner flow rates of vapour and liquid phases on each stage. Simulation of total reflux operations is “complicated” by the fact that there is no feed to the column at steady-state. To overcome this problem we specify one of the experimentally determined compositions of the streams leaving or entering a stage as input parameter. The simulated composition profile of the total reflux run is forced to pass through this specified composition. The “input” compositions are indicated by large open circles when the experimental results will be compared with simulations for each system/mixture to be investigated; see the figures in question in Chapter 5, 6, 7 and 8. The entire set of equations system was solved numerically by using the Newton’s method (Krishnamurthy & Taylor, 1985 and Taylor et al., 1994). The NEQ implementation is available in the software program ChemSep, developed by Taylor and others (Taylor & Krishna, 1993; Krishnamurthy & Taylor, 1985; Taylor et al., 1994 and Baur et al., 1999). Detailed information on ChemSep is available at http://www.chemsep.org and in the recent book by Kooijman & Taylor (2001); this book contains details of all thermodynamics and mass transfer models for tray columns that have been implemented into the software.