CHE 306
Stagewise Operations
Fall 2010

Extraction of Partially Miscible Systems

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All extraction systems are partially miscible to some extent

If partial miscibility is very low, one can use treatment for completely immiscible systems. Thus, one use the McCabe & Thiele analysis or Kremser equation

If partial miscibility is appreciable, one has to account for variable flow rates

For ternary systems: use a convenient stage-by-stage analysis

For multicomponent systems: use computer calculations
Consider a ternary system

Equilibrium between two liquid phases

\[ T_1 = T_{II} \]

\[ P_1 = P_{II} \]

Compositions of phases I & II are related
Consider a ternary system

Gibbs phase rule \[ F = C - P + 2 = 3 \]

T, P are fixed

Must specify one composition in either phases

All other compositions will be known
Figure 14-1. Equilibrium for water-chloroform-acetone at 25 °C and 1 atm.
### Table 14-1. Equilibrium data for the system water-chloroform-acetone at 1 atm and 25°C
(Alders, 1959; Perry and Green, 1997, p. 2-33)

<table>
<thead>
<tr>
<th>$x_D$ Water</th>
<th>$x_S$ Chloroform</th>
<th>$x_A$ Acetone</th>
<th>$y_D$ Water</th>
<th>$y_S$ Chloroform</th>
<th>$y_A$ Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.19</td>
<td>0.81</td>
<td>0.00</td>
<td>0.5</td>
<td>99.5</td>
<td>0.00</td>
</tr>
<tr>
<td>82.97</td>
<td>1.23</td>
<td>15.80</td>
<td>1.3</td>
<td>70.0</td>
<td>28.7</td>
</tr>
<tr>
<td>73.11</td>
<td>1.29</td>
<td>25.60</td>
<td>2.2</td>
<td>55.7</td>
<td>42.1</td>
</tr>
<tr>
<td>62.29</td>
<td>1.71</td>
<td>36.00</td>
<td>4.4</td>
<td>42.9</td>
<td>52.7</td>
</tr>
<tr>
<td>45.6</td>
<td>5.1</td>
<td>49.3</td>
<td>10.3</td>
<td>28.4</td>
<td>61.3</td>
</tr>
<tr>
<td>34.5</td>
<td>9.8</td>
<td>55.7</td>
<td>18.6</td>
<td>20.4</td>
<td>61.0</td>
</tr>
</tbody>
</table>
Solvent: chloroform
Diluent: water
Solute: acetone

**AEBRD**: solubility envelope
**AEB**: saturated extract line
**BRD**: saturated raffinate line
**B**: plait point
**ER**: tie line
Raffinate: diluent-rich phase

Extract: solvent-rich phase
Types I & II systems

**Figure 14-3.** Effect of temperature on equilibrium of methylcyclohexane-toluene-ammonia system from Fenske et al., AIChe Journal, 1, 335 (1955), copyright 1955, AIChe
Mixing operation

Figure 14-4. Mixing operation; A) equipment, B) triangular diagram
For a ternary system:

There are three independent mass balances

**overall** \[ F_1 + F_2 = M \]

**solute** \[ F_1 x_{A,F_1} + F_2 x_{A,F_2} = M x_{A,M} \]

**diluent** \[ F_1 x_{D,F_1} + F_2 x_{D,F_2} = M x_{D,M} \]
Coordinates of mixing point M

\[
\begin{align*}
xa,M & = \frac{F_1 x_{A,F_1} + F_2 x_{A,F_2}}{F_1 + F_2} \\
xd,M & = \frac{F_1 x_{D,F_1} + F_2 x_{D,F_2}}{F_1 + F_2}
\end{align*}
\]
$F_1$, $F_2$ and $M$ are collinear

slope from $M$ to $F_2 = \text{slope from } M \text{ to } F_1$

**Lever-arm rule**

\[
\frac{F_1}{F_2} = \frac{MF_2}{F_1M}
\]

**Alternative forms of lever arm rule**

\[
\frac{F_1}{M} = \frac{F_2M}{F_1F_2} \quad \text{and} \quad \frac{F_2}{M} = \frac{F_1M}{F_1F_2}
\]
Single-stage extractor

Batch extractor $\iff$ Single vessel equipped with mixer

Continuous single-stage extractor $\iff$ Requires a mixer and a steller
Feed & solvent: continuously fed to mixer

Raffinate & extract: continuously withdrawn from settler
Known variables: $S, F, y_{A,S}, y_{D,S}, x_{A,P}, x_{D,P}, T$ and $P$

Need to find: $E, R, y_{A,E}, y_{D,E}, x_{A,R}, x_{D,R}$

E and R are streams in equilibrium with each other
Calculation method

1/ plot S, F

2/ draw straight line between S and F

3/ use lever-arm rule to locate M

4/ construct tie line through point M

5/ find compositions of E and R streams

6/ find E/R using mass balances
Cross-flow extraction

Figure 14-8. Cross-flow extraction; A) cascade, B) solution of triangular diagram.
Contercurrent extraction cascades

Figure 14-9. Countercurrent extraction cascade
External Mass balances

Specified variables: T, P, flow rates and compositions of streams F and S, desired composition of solute in raffinate product (or percent removal)

Need to determine: number of equilibrium stages, flow rates and composition of outlet raffinate and extract streams
External mass balances

\[
E_0 + R_{N+1} = R_1 + E_N
\]

\[
E_0 y_{A,0} + R_{N+1} x_{A,N+1} = R_1 x_{A,1} + E_N y_{A,N}
\]

\[
E_0 y_{D,0} + R_{N+1} x_{D,N+1} = R_1 x_{D,1} + E_N y_{D,N}
\]
\( E_N \) and \( R_1 \) are on the saturated raffinate and extract curves, respectively

\[ \downarrow \]

Relationships between: \( y_{A,N} \) \( y_{D,N} \) and \( x_{A,1} \) \( x_{D,1} \)

5 equations need to be solved simultaneously for the 5 unknowns

\[ E_{N'} \ R_{1'} \ x_{D,1'} \ y_{A,N} \text{ and } y_{D,N} \]
Locate M

\[
x_{A,M} = \frac{E_0 y_{A,0} + R_{N+1} x_{A,N+1}}{E_0 + R_{N+1}}
\]

\[
x_{D,M} = \frac{E_0 y_{D,0} + R_{N+1} x_{D,N+1}}{E_0 + R_{N+1}}
\]
Figure 14-10. *External mass-balance calculation; A) mixer-separation representation, B) solution on triangular diagram*
Locate $R_1$  \( \xrightarrow{\text{Use known value of } x_{A,1}} \)  

Draw a straight line going through $M$ and $R_1$ 

Intersection with saturated extract curve: $E_N$ 

$R_1ME_N$ is not a tie line
Difference points & stage-by-stage calculations

Stage-by-stage calculations are made in order to determine:

- Number of stages
- Flow rates and compositions inside the cascade

External mass balances $\iff E_N, R_1, y_{A,N}$ and $y_{D,N}$
Known $R_1$

$R_1$ and $E_1$ are in equilibrium

Find $E_1$

$E_1$ and $R_2$ passing streams

4 unknowns: $x_{A,2}$, $x_{D,2}$, $E_1$ and $R_2$

3 mass balances around stage 1

$R_2$ is a saturated raffinate stream

Find $R_2$
Continue along the column until by repeating same procedure described to obtain $E_1$ and $R_2$

Stop when you reach raffinate specification (given by $x_{A,1}$)
Can use a graphical method:

Tie lines $\rightarrow$ equilibrium relationships

$x_{A,j}$ and $x_{D,j}$ relationships $\Rightarrow$ use saturated raffinate curve

Need a method to represent graphically mass balances
Mass balance around first stage

\[ E_0 - R_1 = E_1 - R_2 \]

Difference point:

\[ \Delta = E_0 - R_1 = \cdots = E_j - R_{j+1} = \cdots = E_N - R_{N+1} \]

constant
Net flow of solute and diluent is constant:

\[ \Delta x_{A,\Delta} = E_0 y_{A,0} - R_1 x_{A,1} = \cdots = E_j y_{A,j} - R_{j+1} x_{A,j+1} \]
\[ = \cdots = E_N y_{A,N} - R_{N+1} x_{A,N+1} \]

\[ \Delta x_{D,\Delta} = E_0 y_{D,0} - R_1 x_{D,1} = \cdots = E_j y_{D,j} - R_{j+1} x_{D,j+1} \]
\[ = \cdots = E_N y_{D,N} - R_{N+1} x_{D,N+1} \]

\[ \Delta, E_j, R_{j+1} \text{ are collinear} \]
Coordinates of difference point: \( \Delta \)

They can be negative

\[
x_{A,\Delta} = \frac{E_0y_{A,0} - R_1x_{A,1}}{\Delta} = \frac{E_Ny_{A,N} - R_{N+1}x_{A,N+1}}{\Delta}
\]

\[
x_{D,\Delta} = \frac{E_0y_{D,0} - R_1x_{D,1}}{\Delta} = \frac{E_Ny_{D,N} - R_{N+1}x_{D,N+1}}{\Delta}
\]
Graphical method

\[ R_1 \quad \Rightarrow \quad E_1 \]

Use tie line
Equilibrium relationship

\[ \Delta E_1 \quad \Rightarrow \quad R_2 \]

Use operating line
Mass balances

\[ R_2 \quad \Rightarrow \quad E_2 \]

\[ \Delta E_2 \quad \Rightarrow \quad R_3 \]
Graphical method consists of alternating between tie lines (equilibrium relationships) and operating lines (mass balances). 

Number of stages