Extraction

Chemical Unit Operations II.

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Extraction

I. Liquid-liquid extraction (Solvent extraction)
II. Solid-liquid extraction (Leaching)
III. Supercritical fluid extraction
Liquid-liquid extraction

I. Applications

1. Hydrometallurgy
2. Inorganic processes
3. Petroleum industry
4. Pharmaceuticals
5. Waste waters
II. Liquid-liquid equilibrium

Binary systems

Curve: composition of saturated solutions of the two components.

Area **enclosed** by the curve: two phase region;
Area **outside** the curve: mixtures that are completely miscible.

**A, B**: composition of the phases in equilibrium.

Dashed line: **tie line**.

**UCST**: Upper Critical Solution Temperature.
**LCST**: Lower Critical Solution Temperature.
Binary systems

P=constant

Type I.

Type II.

Type III.

Type IV.
Ternary systems

\[ T = \text{constant} \]
\[ P = \text{constant} \]

A, B, C: pure components. Curve shown within the triangle: the boundary of the two phase region. Ternary solubility curve = binodal curve. Dashed line = tie line. 
P: plait point (limit of immiscibility).

**Type I.**: one partially miscible binary pair.
Ternary systems

Type II.: two partially miscible binary pairs.
III. Single stage extraction (batch extraction)

Theoretically ideal stage: where contact between phases is sufficiently intimate and maintained for a sufficient period of time that equilibrium is established.

Extract phase (E): solvent- rich phase
Raffinate phase (R): solvent-lean phase

III/1. Simple stirred tank

Equilibrium ratio for a simple ternary system:

\[ m = \frac{y}{x} \]

y: solute concentration in extract phase (wt%)
x: solute concentration in raffinate phase (wt%)
m: equilibrium ratio (distribution coefficient)
III/1. Simple stirred tank

Total material balance:
\[ m_{R_0} + m_{E_0} = m_{R_1} + m_{E_1} \]

Component balance for solute:
\[ m_{R_0} \times x_0 + m_{E_0} \times y_0 = m_{R_1} \times x_1 + m_{E_1} \times y_1 \]

- \( m_{R_0} \): mass of the initial solution (kg)
- \( m_{E_0} \): mass of the solvent (kg)
- \( m_{R_1} \): mass of the raffinate (kg)
- \( m_{E_1} \): mass of the extract (kg)
- \( x, y \): concentrations (wt%)
III/1. Simple stirred tank

If the solvent and diluent are immiscible and the concentration of solute is low:

\[ f = \frac{m_{E_0}}{m_{R_0}} = \frac{m_{E_1}}{m_{R_1}} = \text{constant} \]

\[ y_1 = m \times x_1 \rightarrow x_0 + f \times y_0 = x_1 + f \times y_1 = x_1 + f \times m \times x_1 \]

\[ E = \frac{m_{E_1} \times y_1}{m_{R_1} \times x_1} = f \times m \]

Extraction factor

If \( y_0 = 0 \) (neat solvent)

\[ x_1 = \frac{x_0}{1 + E} + \frac{E \times \left(\frac{y_0}{m}\right)}{1 + E} \]

\[ x_1 = \frac{x_0}{1 + E} \]
III/2. Multiple-extraction

The raffinate from the first stage is extracted with fresh solvent of the same composition in successive stages.

General solution (if neat solvent is used):

First stage

\[ x_1 = x_0 \cdot \frac{1}{1 + E} \]

Second stage

\[ x_2 = x_1 \cdot \frac{1}{1 + E} = x_0 \cdot \frac{1}{(1 + E)^2} \]

Third stage

\[ x_3 = x_2 \cdot \frac{1}{1 + E} = x_0 \cdot \frac{1}{(1 + E)^3} \]

n\textsuperscript{th} stage

\[ x_n = x_0 \cdot \frac{1}{(1 + E)^n} \]
If liquids are completely immisible or at least their solubility does not change over the range of concentration of distributed substance:

\[
y_1 = \frac{1}{f} \times (x_0 - x_1) + y_0
\]

\[
tg \alpha = -\frac{1}{f}; \text{ through } (x_0, y_0)
\]
III/2. Multiple-extraction

Final raffinate concentration.

\[ y_1 = \frac{1}{f} (x_0 - x_1) + y_0 \]

\[ \tan \alpha = -\frac{1}{f} \]
III/2. Multiple-extraction

Triangular diagram

- If \( f' \) and \( m' \) depend on the composition.

Material balance:

\[
m_{R_0} + m_{E_0} = m_{R_1} + m_{E_1}
\]

\[
m_{R_0} \cdot x_0 + m_{E_0} \cdot y_0 = m_{R_1} \cdot x_1 + m_{E_1} \cdot y_1
\]

\( x_{M_1} \): overall composition of the ternary mixture. \( M_1 \) point can be located by the lever-arm rule.

Calculation:

\[
x_{M_1} = \frac{m_{R_0} \cdot x_0 + m_{E_0} \cdot y_0}{m_{R_0} + m_{E_0}}
\]

\[
x_{M_1} = \frac{m_{R_1} \cdot x_1 + m_{E_1} \cdot y_1}{m_{R_1} + m_{E_1}}
\]
III/2. Multiple-extraction

Triangular diagram

Methods of calculation.
III/3. Continuous extraction

\[ \dot{m}_{E1} \quad y_1 \quad x_0 \quad \dot{m}_{R0} \]

\[ \begin{array}{c}
\dot{m}_{En} \\
y_n \\
x_{n-1} \\
\dot{m}_{Rn} \\
y_{n+1} \\
x_n \\
\dot{m}_{EN+1} \\
y_{N+1} \\
x_N
\end{array} \]

\[ \begin{array}{c}
\dot{m}_{En} : \text{extract mass flowrate leaving stage } n \text{ (kg/s)} \\
y_n : \text{solute concentration in } \dot{m}_{En} \text{ (mass fraction)} \\
\dot{m}_{Rn} : \text{raffinate flowrate leaving stage } n \text{ (kg/s)} \\
x_n : \text{solute concentration in } \dot{m}_{Rn} \text{ (mass fraction)} \\
N : \text{number of equilibrium stages (-)}
\end{array} \]
III/3. Continuous extraction

- If the solvent and diluent are completely immiscible and \( m \) is constant:

\[
\frac{x_N - \frac{y_{N+1}}{m}}{x_0 - \frac{y_{N+1}}{m}} = \frac{E - 1}{E^{N+1} - 1}
\]

\[
E = f \cdot m \quad \text{extraction fraction}
\]

\[
f = \frac{m_E}{m_R} \quad \text{flowrate ratio}
\]

If \( E = 1 \)

\[
\frac{x_N - \frac{y_{N+1}}{m}}{x_0 - \frac{y_{N+1}}{m}} = \frac{1}{N + 1} \quad \text{Kremser (1930)}
\]

- If the solvent and diluent are completely immiscible or at least their solubility does not change over the range of concentration of distributed substance: **McCabe-Thiele analysis**.

\[
\dot{m}_R \cdot x_{n-1} + \dot{m}_E \cdot y_{N+1} = \dot{m}_R \cdot x_N + \dot{m}_E \cdot y_n
\]

Raffinate and extraction rates are constant.

\[
y_n = \frac{1}{f} \cdot (x_{n-1} - x_N) + y_{N+1}
\]

Operating line
III/3. Continuous extraction

\[ y_n = \frac{1}{f} \cdot (x_{n-1} - x_N) + y_{N+1} \]

\[ \tan \alpha = 1/f; \text{ through } (x_N, y_{N+1}) \]
III/3. Continuous extraction

- If \( f \) changes only because of transfer of solute from raffinate phase to the extract phase the same diagram and method can be used.

\[
y = \frac{\text{solute}}{\text{solute} - \text{free solvent}} \\
x = \frac{\text{solute}}{\text{solute} - \text{free diluent}}
\]

New coordinate system.

Total flow rates:
- \( m_E \): solute-free extract (usually neat solvent)
- \( m_R \): solute-free raffinate (usually neat diluent)

- Triangular diagrams can be used for partially miscible systems!
- System of more than three components require computers for solution of their model equations.
IV. Selection of solvent in extraction

The proposed solvent must form a separate phase from the feed solution and should be able to extract the solute from the feed solution.

1. Distribution coefficient (m)
2. Solubility
3. Density ($\Delta \rho > 150 \text{ kg/m}^3$)
4. Interfacial tension
5. Viscosity
6. Chemical reactivity and stability
7. Vapour pressure
8. Flammability
9. Toxicity
10. Cost analysis
V. Equipment

1. Mixer-settler or a series of mixer-settlers
2. A column, which may be agitated or pulsed
3. Some other contactor such as a centrifugal device
V/1. Mixer-settler

The separating efficiency is proportional to the area of the phase interface.
V/1. Mixer-settler cascade

Large hold up volumes, long residence time, large physical size.
V/1. Mixer-settler cluster
V/1. Copper’s extraction in Mixer-settler
V/2. Columns without energy input

a.) Spray column

Simplicity
High throughput
Low cost

Application: little in industry.
b.) Packet columns

- The most purposes random packing;
- The packing should be wetted by the continuous phase.
c.) Sieve-Trey column

**Application**: in petroleum industry.
V/3. Columns with energy input
a.) Rotating Disc Contactor (RDC)

Application: in petroleum and chemical industries, waste water treatment.
b.) Oldshue-Rushton column (1952, USA)

http://www.separationprocesses.com/Extraction/SE_Chp03c.htm
Centrifugal Extractor (Podbielniak-Extractor)
Centrifugal extractor
(Podbielniak-Extractor)
Karr column
Karr column
Thank you for your attention!