CHAPTER 8: LIQUID - LIQUID EXTRACTION

WITH TERNARY SYSTEMS

CARRIER + SOLUTE

SOLVENT + SOLUTE

CARRIER

SOLVENT

SOLUTE MISCEIBLE IN CARRIER + SOLVENT

CARRIER + SOLVENT IMMISCIBLE

AKA

EXTRACTION

SOLVENT EXTRACTION

LIQUID EXTRACTION
AROUND FOR A LONG TIME

- Au + Ag separation from Cu (Liq) (Pb (Liq) solvent)
- Aromatics + sulfur from Kerosene (Liquid SO₂ @ 10-20°F) (1930's)

MORE RECENT:

1) Temperature sensitive products
2) Higher purity (extract contaminants)
3) Better efficiency
4) Solvents with better selectivity

⇒ Use in cascade (like Chap. 5)
WHY EXTRACTION?

~ Ambient conditions

(CAVEAT — REGENERATION OF SOLVENT)
LOTS OF SOLVENT

Figure 8.1 Typical liquid–liquid extraction process.
How to contact two immiscible liquids?

1) One continuous phase
2) One dispersed phase

During contacting

Followed by phase separation,
(Aided by coalescence of dispersed phase + large density difference)

Activity correlations:

Ideal or non-ideal liquids?
(Hint: 2 liquid phases)

So, what do you suggest to determine $\gamma$?
So when pick extraction over distillation? (Not vs. other separation processes!)

1) Dissolved or complexed inorganics in organic or aqueous solution,

2) Dilute solution (odor, color)

3) High boiling component in waste stream ($ to evaporate water)

4) Heat sensitive solute ($ vs. vacuum distillation)

5) Chemical type vs. relative volatility

6) Close melting or close boiling liquids. (Take advantage of solubility differences)

7) Azeotropes,
**EXAMPLES IN INDUSTRY.**

<table>
<thead>
<tr>
<th>SOLUTE</th>
<th>CARRIER</th>
<th>SOLVENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>Water</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Butenes</td>
<td>Water</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Paraffins</td>
<td>Diethylene glycol</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Oil</td>
<td>Propane</td>
</tr>
<tr>
<td>Penicillin</td>
<td>Broth</td>
<td>Butyl acetate</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>Fish oil</td>
<td>Propane</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>Vegetable oil</td>
<td>Propane</td>
</tr>
</tbody>
</table>
EQUIPMENT:

A. MIXER-SETTLERS
   1. MIXING SECTION
   2. SETTLING SECTION
   ~ 80-90% of EQUILIBRIUM (EFFICIENCY)

Mixing-
   • IMPELLERS (NORMAL MIXING)
   • JET
   • INJECTORS
   • TURBULENCE IN NOZZLE

Settling
   ACHIEVED BY GRAVITY (IMPORTANCE OF DENSITY DIFFERENCE)
WHAT IF EMULSIFY?

→ COALESCE
  - MEMBRANES
  - MESH
  - ULTRASONIC
  - CHEMICAL TREATMENT (MESSY)

CAN ALSO SUPPLEMENT GRAVITY W/ CENTRIFUGAL FORCE.

☑️ SPRAY COLUMNS

CONVERSE
LIGHT CAN BE SPRAYED
- LARGE THROUGHPUT
- BACKMIXING (NOT A LOT OF STAGES)
- LOW COST

PACKED COLUMNS
LIKE FOR ABSORPTION
- PREFER CONTINUOUS PHASE TO WET PACKING
- NOT A LOT OF STAGES
- INTALOX SADDLES GOOD ... RASCHIG RINGS BAD (CAN SEPARATE PHASES)

PLATE COLUMNS
- STAGE WISE CONTACT
- SMALL TRAY SPACING
- GOOD EXTRACTION RATE
- CAN FLOOD (WEEPING NOT AS BIG OF PROBLEM)
E. Columns with Mechanical Agitation

- Used to improve dispersion when:
  1) Surface tension is high
  2) Density difference between carrier + solvent is low
  3) High liquid viscosity

How to agitate:

1) Packed + Trayed Columns
   - Pulse liquid flow
     (mechanical problems)

2) Axial rotating- agitators
   - Shear mixing- zones
   - Alternate w/ settling zones

See Figure 8.7 (Sender + Henley)
3) Reciprocating perforated plate
   (like a sieve tray moving up and down vertically)
   ⇒ Baffles used to minimize axial mixing (separate stages)

F Centrifugal extractors

⇒ low density difference
### Table 8.3 Advantages and Disadvantages of Different Extraction Equipment

<table>
<thead>
<tr>
<th>Class of Equipment</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixer-settlers</td>
<td>Good contacting</td>
<td>Large holdup</td>
</tr>
<tr>
<td></td>
<td>Handles wide flow ratio</td>
<td>High power costs</td>
</tr>
<tr>
<td></td>
<td>Low headroom</td>
<td>High investment</td>
</tr>
<tr>
<td></td>
<td>High efficiency</td>
<td>Large floor space</td>
</tr>
<tr>
<td></td>
<td>Many stages available</td>
<td>Interstage pumping may be required</td>
</tr>
<tr>
<td></td>
<td>Reliable scale-up</td>
<td></td>
</tr>
<tr>
<td>Continuous countercurrent</td>
<td>Low initial cost</td>
<td>Limited throughput with</td>
</tr>
<tr>
<td>contactors (no mechanical drive)</td>
<td>Low operating cost</td>
<td>small density difference</td>
</tr>
<tr>
<td></td>
<td>Simplest construction</td>
<td>Cannot handle high flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High headroom</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sometimes low efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficult scale-up</td>
</tr>
<tr>
<td>Continuous countercurrent</td>
<td>Good dispersion</td>
<td>Limited throughput with</td>
</tr>
<tr>
<td>contactors (mechanical agitation)</td>
<td>Reasonable cost</td>
<td>small density difference</td>
</tr>
<tr>
<td></td>
<td>Many stages possible</td>
<td>Cannot handle emulsifying</td>
</tr>
<tr>
<td></td>
<td>Relatively easy scale-up</td>
<td>systems</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cannot handle high flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ratio</td>
</tr>
<tr>
<td>Centrifugal extractors</td>
<td>Handles low density difference between phases</td>
<td>High initial costs</td>
</tr>
<tr>
<td></td>
<td>Low holdup volume</td>
<td>High operating cost</td>
</tr>
<tr>
<td></td>
<td>Short holdup time</td>
<td>High maintenance cost</td>
</tr>
<tr>
<td></td>
<td>Low space requirements</td>
<td>Limited number of stages</td>
</tr>
<tr>
<td></td>
<td>Small inventory of solvent</td>
<td>in single unit</td>
</tr>
</tbody>
</table>

*(Seader & Henley, p. 433)*

**Scheme for choosing extractor:**

**Fig. 8.8 (Seader & Henley)**

- **Small # Stages**  → **Mixer-settler**
- **Large # Stages**
  - High throughput
  - Large load range (flux)
  - Limited floor space  → **Rotating disk contactor**
GENERAL DESIGN CONSIDERATIONS:

CASCADE ARRANGEMENT

FEED → SOLVENT → RAFFINATE

SINGLE SECTION CASCADE
(SIMILAR TO ABSORPTION COLUMN)

⇒ Gives fractional recovery

SOLVENT → SR → SOLVENT

FREE EXTRACT

FEED

TWO-SECTION CASCADE
(SIMILAR TO DISTILLATION)

RAFFINATE ← SOLVENT

⇒ Can give very good recovery.
DUAL SOLVENT W/ TWO-SECTION CASCADE
(can also do without reflux)

More complex, but can give improved separation.

Factors that influence extraction:

1) Feed
   a) Flow rate
   b) Composition
   c) Temperature
   d) Pressure
2) STAGE CONFIGURATION (ONE OR TWO SECTION)
3) DEGREE OF RECOVERY
4) DEGREE OF FEED SEPARATION (2-SECTION)
5) CHOICE OF LIQUID SOLVENT (CRITICAL!)
6) OPERATING TEMPERATURE
7) OPERATING PRESSURE (SHOULD BE > $P_{\text{bubble}}$)
8) SOLVENT FLOW RATE
9) # OF EQUILIBRIUM STAGES
10) EMULSIFICATION & SCUM FORMATION
11) INTERFACIAL TENSION (AFFECTS DISPERSION & SETTLING)
12) PHASE-DENSITY DIFFERENCE
13) TYPE OF EXTRACTOR
14) EXTRACTOR SIZE & HORSEPOWER REQUIREMENT.

---

CHOICE OF SOLVENT IS CRITICAL!

=> THE IDEAL SOLVENT...
IDEAL SOLVENT:

1) HIGH SELECTIVITY FOR SOLUTE VS. CARRIER
   (MINIMIZE CARRIER RECOVERY REQUIREMENT)

2) HIGH SOLUTE SOLUBILITY
   (REDUCE SOLVENT/FEED RATIO)

3) LOW SOLUBILITY IN CARRIER

4) SOLUTE-SOLVENT HIGH TO EASE SOLUTE
   RECOVERY BY DISTILLATION

5) STABILITY (LIFETIME + RECYCLE)

6) INERT (MATERIALS OF CONSTRUCTION)

7) LOW VISCOSITY

8) NOT TOXIC / NON FLAMMABLE

9) LOW COST

10) MODERATE INTERFACIAL TENSION
    → TOO HIGH ⇒ HARD TO DISPERSE
     → TOO LOW ⇒ HARD TO PHASE SEPARATE
**Selectivity:** (Partition Coefficient) (From Thermodynamics)

At equilibrium,

\[(X_A)^I (Y_A)^I (P_a^{	ext{sat}})^I = (X_A)^II (Y_A)^II (P_a^{	ext{sat}})^II\]

Saturation pressure is a pure component property and \(P_i^{	ext{sat}} = f(T)\) only.

\[\Rightarrow (P_a^{	ext{sat}})^I = (P_a^{	ext{sat}})^II\]

Therefore,

\[(X_A)^I (Y_A)^I = (X_A)^II (Y_A)^II\]

Carrier phase Solvent phase

Partition coefficient is a "k" value. (Recall Chemcad)
\[ K_A = \frac{(X_A)_{\Pi}}{(X_A)_{\Omega}} = \frac{(\gamma_A)_{\Pi}}{\gamma_A)_{\Omega}} \]

where \( K_A \) is the partition coefficient or distribution coefficient for solute A between solvent S and carrier C.

**Phase I**: Raffinate rich in C

**Phase II**: Extract rich in S

Can also write distribution coefficients for the solvent + carrier:

\[ K_C = \frac{(X_C)_{\Pi}}{(X_C)_{\Omega}} = \frac{(\gamma_C)_{\Pi}}{\gamma_C)_{\Omega}} \]

\[ K_S = \frac{(X_S)_{\Pi}}{(X_S)_{\Omega}} = \frac{(\gamma_S)_{\Pi}}{\gamma_S)_{\Omega}} \]
The relative selectivity is a function of the $K$-values.

$$\beta_{Ac} = \frac{K_A}{K_C} = \frac{\frac{(x_A)^I}{(x_A)^{II}}}{\frac{(x_C)^I}{(x_C)^{II}}} = \frac{(\delta_A)^I}{(\delta_A)^{II}} = \frac{(\delta_C)^I}{(\delta_C)^{II}}$$

High $\beta_{Ac} \Rightarrow$

High conc. A in solvent
Low conc. C in solvent.

In general:

Want high $K_A$ (high capacity)

High $K_S$ \(\rightarrow\) to get clean solvent & carrier during recovery.

Low $K_C$

See Table 8.4

Seader & Henley

Low $\delta$
A likes S
PHASE DIAGRAMS FOR EXTRACTION.

At point M,

\[ X_C = 0.5 \quad , \quad X_S = 0.25 \quad , \quad X_A = 0.25 \]
WHEN USED FOR EXTRACTION...

P = PLAIT POINT (EQUAL COMPOSITIONS IN EACH LIQUID PHASE)
E = EXTRACT COMPOSITION
R = RAFFINATE COMPOSITION
$D \leq \text{miscibility limit}$
$C \geq \text{miscibility limit}$ 
For carrier in solvent and vice versa.

$Me \text{ total composition}$

Any composition on a tie line will equilibrate on respective E + R.

Outside of envelope, all three components miscible.

How to use for a single stage?

→ Example 4, 7a (p. 192, Sender & Henley)
EXAMPLE 4.7A  Calculate the composition of the equilibrium extract and raffinate phases produced when a 45% by weight glycol (B) - 55% water (A) solution is contacted with its own weight of pure furfural solvent (C) at 250°C and 101 kPa. Use the equilateral triangular diagram below to determine the composition of the water-glycol mixture obtained by removing all of the furfural from the extract.
**ASSUMPTIONS:**

**Basis:** 100 g of 45% glycerol-water feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>A</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>B</td>
</tr>
<tr>
<td>Furfural</td>
<td>C</td>
</tr>
</tbody>
</table>

\[ \Rightarrow \text{Feed (F)} \quad 55\,\text{g} \quad A \quad (\text{water}) \]

\[ 45\,\text{g} \quad B \quad (\text{glycerol}) \]

\[ \Rightarrow \text{Solvent (S)} \quad 100\,\text{g} \quad C \quad (\text{furfural}) \]

**MATERIAL BALANCE: (OVERALL)**

\[ M = S + F = E + R \]
Component balance on solvent ($i = c$)

\[ IN = OUT \ (\text{Just mixing}) \]

\[ F X_c^{(F)} + S X_c^{(S)} = (F + S) X_c^{(M)} \]

Mixture composition

Solve for \( \frac{F}{S} \)

\[ F (X_c^{(F)} - X_c^{(M)}) = S (X_c^{(M)} - X_c^{(S)}) \]

\[ \frac{F}{S} = \frac{X_c^{(M)} - X_c^{(S)}}{X_c^{(F)} - X_c^{(M)}} = \frac{X_c^{(S)} - X_c^{(M)}}{X_c^{(M)} - X_c^{(F)}} \]

\[ = \frac{F}{S} = \text{(slope) } S \]

(a straight line)

(And similar relationship from carrier balance)

Because \( F, S, \) and \( M \) are on a straight line, can use inverse lever rule.

\[ \frac{F}{S} = \frac{MS}{FM} \]
IN THIS CASE,

\[ F = S \]

\[ \therefore \frac{F}{S} = \frac{\overline{MS}}{\overline{FM}} = 1 \]

\[ X_c^{(s)} = 1 \]

\[ X_c^{(F)} = 0 \]

\[ \frac{1 - X_c^{(m)}}{X_c^{(m)} - 0} = 1 \]

\[ 1 - X_c^{(m)} = X_c^{(m)} \]

\[ 1 = 2X_c^{(m)} \Rightarrow X_c^{(m)} = 0.5 \]

Also, from component balance on carrier,

\[ 1 = 0 - X_A^{(m)} \]

\[ X_A^{(m)} - 0.55 = -X_A^{(m)} \]

\[ 2X_A^{(m)} = 0.55 \Rightarrow X_A^{(m)} = 0.275 \]

\[ \Rightarrow X_B^{(m)} = 0.225 \] 

\[ (\sum x_i^{(m)} = 1) \]
Can also get from phase diagram...

Figure 4.15 Solution to Example 4.7a.

How to get extract and raffinate compositions?

Follow tie line

E: \( X_A = 0.05 \), \( X_B = 0.29 \), \( X_C = 0.65 \)

R: \( X_A = 0.84 \), \( X_B = 0.09 \), \( X_C = 0.09 \)
CAN ALSO GET FLOW RATES OF E + R WITH INVERSE LEVER RULE:

\[ E = \frac{MR}{ER} \Rightarrow E = M \left( \frac{MR}{ER} \right) \]

(MEASURE MR + ER WITH RULER)

\[ F + S = M = E + R = 200 \text{ g} \]

\[ \Rightarrow E = 200 \text{ g} \left( \frac{MR}{ER} \right) = 200 \text{ g} \left( \frac{1.75''}{2.5''} \right) \]

\[ E = 140 \text{ g} \]

\[ \Rightarrow R = 60 \text{ g} \]

COMPOSITIONS FROM PHASE DIAGRAM.
Solvent-Free Extract?

Line through S+E when solvent conc \( \rightarrow 0 \)

\( (p+H) \)

\[
X_{H_2O} = 0.17 \\
X_{\text{glycol}} = 0.83
\]

(feed was \( X_{H_2O} = 0.55, X_{\text{glycol}} = 0.45 \))

\( \Rightarrow \) Multiple stages needed.

Could use cascade of single stages (same problem, different input)

or

Multiple stages in one unit (next time)
DIFFERENT TYPES OF PHASE BEHAVIOR:

Type I:
Solute and Solvent infinitely soluble

Advantages:
Good solvent capacity (concentrated in solute)

Disadvantage:
Solvent can't separate all feed compositions.

⇒ Usually prefer type I.

Type II:
Limited Solute/Solvent Solubility

Advantages:
Can separate any feed composition.

Disadvantage:
Low solvent capacity (need lots of solvent).
TEMPERATURE EFFECTS:

**LIMITED SOLUTE SOLUBILITY IN SOLVENT.**

**RAFFINATE & EXTRACT COMPOSITIONS IDENTICAL.**

**MOVING TO SOLUBILITY AT ALL COMPOSITIONS (NO SEPARATION).**

**SOLUTE + CARRIER MISCEABLE AT ALL TEMPS + COMPOSITIONS.**
Final note on dispersed phase:

Carrier or solvent can be the dispersed phase. However, usually carrier is dispersed. Why?

Rapid coalescence ⇒ easier to separate. However,
⇒ lower surface area ⇒ poor mass transfer

Need to concentrate solute at interface

Dispersed carrier          Dispersed solvent

Solute concentration highest in carrier, where is diffusion distance smallest?