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Liquid-liquid extraction (LLE)
References

► Schweitzer, “Handbook of Separation Techniques for Chemical Engineers”, chapter 1.9
► Richardson and Harker, “Chemical Engineering, Volume 2”, 5th edition, chapter 13
► Ghosh, “Principles of Bioseparation Engineering”, chapter 7
► Uhlmann’s Encyclopedia, “Liquid-Liquid Extraction”, DOI:10.1002/14356007.b03_06.pub2
Definitions

- **solute**: species we aim to recover (A) from the feed
- **feed or “feed solvent”**: one of the liquids in the system ("carrier")
- **solvent**: MSA (by convention: the “added” liquid)
- **extract**: solvent (not solute) mostly present in this layer.
  
  \[ y_{E,A} = \text{concentration of A, the solute, in extract.} \]

  We aim for the solute (A) to be mostly in the extract stream.

- **raffinate**: residual solute in this layer = \( x_{R,A} \)

- **distribution**: how the solute partitions itself = \( D_A = \frac{y_{E,A}}{x_{R,A}} \)

  - measure of affinity of solute
  
  \[
  \begin{align*}
  D_A &= \frac{\mu_R^0 - \mu_E^0}{RT} = \frac{\text{chemical potential difference}}{(R)(\text{temperature})}
  \end{align*}
  \]
Where/why LLE is used

Where?
- Bioseparations
- Nuclear (uranium recovery)
- Mining: nickel/cobalt; copper/iron
- Perfumes, fragrances and essential oils
- Fine and specialty chemicals
- Oil sands: extract bitumen away from water

Why?
- Temperature sensitive products
- High purity requirements
- High-boiling point species in low quantity
- Need to separate by species type (rather than relative volatility)
- Close-boiling points, but high solubility difference
- Azeotrope-forming mixtures
Extractor types: 3 major steps required

1. Mixing/contacting:
   - turbulent contact between liquid phases
   - small droplet dispersion in a continuous phase
     - which phase is dispersed?
   - mass-transfer between phases
   - limited by solute loading in solvent

2. Phase separation:
   - reverse of above mixing step
   - drops come together and coalesce
   - relies on density difference

3. Collection of phases leaving the unit
   - split the raffinate from the extract
What are we aiming for?

Main aims
- High recovery of solute overall (low $x_R$ and high $y_E$)
- Concentrated solute in extract (high $y_E$)

How to achieve this?
- Cocurrent mixer-settlers
- Cross-current mixer settlers
- Counter-current mixer-settlers in series
- High interfacial area during mixing
- Reduce mass-transfer resistance
- Promote mass transfer: aim is to move solute in feed to the solvent in extract stream
  - molecular diffusion
  - eddy diffusion
Co-, cross-, counter-current operations

[Hanson article, Chemical Engineering, posted to course website]
Some photos of equipment

[http://www.flickr.com/photos/51009184@N06/5062827346/]
Some photos of equipment
Equipment for LLE

1. Mixer-settlers (integrated unit)
   ▶ mix: impellers
   ▶ mix: nozzles
   ▶ mix: feeds meet directly in the pump
   ▶ mix: geared-teeth devices
   ▶ main aim: good contact; avoid droplets smaller than 2 \( \mu m \)
   ▶ settle: baffles, membranes
   ▶ settle: ultrasound
   ▶ settle: chemical treatment
   ▶ settle: centrifuges

2. Column-type units contain:
   ▶ (a) nothing or
   ▶ (b) trays and/or
   ▶ (c) packing and/or
   ▶ (d) pulsating and/or
   ▶ (e) agitation

3. Rotating devices

Important point: LLE is an equilibrium-limited separation (as opposed to rate-limited separations seen up to now).
Mixer-settlers

Common in mining industry: requirements

\[ \sim 40000 \text{ L/min flows} \]
Mixer-settlers

KnitMesh coalescer: consistency of “steel wool”

[Richardson and Harker, p 747]
Horizontal gravity settling vessel

[Seader, 3ed, p302]
Spray columns: separation principle is gravity

[Richardson and Harker, p 751]
Tray columns

- coalescence on each tray
- tray holes: $\sim 3\text{mm}$
- breaks gradient formation (axial dispersion)

[Richardson and Harker, p 749]
Tray columns with mechanical agitation

- shearing to create dispersion
- can have alternating layers of packing (coalescence)
- some column designs pulsate ⇑⇓

[Seader, 3ed, p302]
Rotating devices

“white” = lighter liquid
“grey” = heavier liquid

Used when foams and emulsions would easily form: i.e. gentle mass transfer.

Look up in your own time: centrifuge mixer-settlers
Linking up units (more on this later)

[Richardson and Harker, p 723]
Integration with downstream units

[Schweitzer, p 1-257]
Selecting a solvent

Schweitzer: “The choice of solvent for a LLE process can often have a more significant impact on the process economics than any other design decision that has to be made”.

Which properties of a solvent influence our aims with LLE?

- High distribution coefficient (selectivity) for solute
- Low distribution coefficient for carrier
- Reasonable volatility difference with solute and carrier
- Reasonable surface tension: easy to disperse and coalesce
- High density difference: separates rapidly by gravity
- Stability to maximize its reuse
- Inert to materials of construction
- Low viscosity: maximizes mass transfer
- Safe: non-toxic, non-flammable
- Cheap, and easily available
- Compatible with carrier and solute: avoid contamination
- Doesn’t foam, form emulsions, scum layers at interface
Calculating the distribution coefficient (in the lab only)

Mass balance:

\[ Fx_F + Sy_S = Ey_E + Rx_R \]

\[ D = \frac{y_E}{x_R} \]

If \( F = S = E = R \) and \( y_S = 0 \), then only measure \( x_R \):

\[ D = \frac{x_F}{x_R} - 1 \quad \text{← only in this special case} \]

- Capital letters refer to mass amounts
- \( y \) refers to mass fractions in solvent and extract layers
- \( x \) refers to mass fractions in carrier and raffinate layers

Once \( D \) is determined, we can obtain phase diagrams to understand how the process will operate.

Also: see Perry’s for many values of \( D \)
Triangular phase diagrams: from laboratory studies
Using a triangular phase diagrams

[http://www.youtube.com/watch?v=gGYHXhcKM5s]
Lever rule

Mix P and Q

- mixture = K

- \[ \frac{PK}{KQ} = \frac{\text{mass } Q}{\text{mass } P} \]

- The converse applies also: when a settled mixture separates into P and Q

- Applies anywhere: even in the miscible region
Q1: Using the lever rule

Which is a more flexible system: (a) or (b)?

- $S =$ pure solvent used
- $F =$ feed concentration point (more correctly it is $x_F$)

Answer: range of feed concentrations ($x_F$) is wider, i.e. more desirable, for (a). Difference between (a) and (b):

- due to solvent choice
- due to different temperatures
- due to pH modification, etc
Q2: Using the lever rule

Mix a feed stream, $F$, containing $C$ and $A$ (i.e. $x_F$) with a pure solvent stream $S$ (i.e. $y_S = 0$). Composition of the mixture?
Q2 solution: Using the lever rule

Composition of the mixture? *we need more information* (e.g. amount of *F* and *S* must be given to find point *M*)
Q3: Going to equilibrium

Let that mixture $M$ achieve equilibrium. What is the composition of the raffinate and extract?
What is the composition of the raffinate and extract? *Use the tie lines* [solid lines]; *or interpolate between existing ones.*
Q4: Altering flows

Recovery = fraction of solute recovered

For 1 stage

\[ 1 - \frac{(x_R)(R)}{(x_F)(F)} \]

Specifically

\[ 1 - \frac{(x_{R,A})(R)}{(x_{F,A})(F)} \]

Same system, but now lower solvent flow rate (to try save money!). What happens to (a) extract concentration and (b) solute recovery?
Q4 solution: Altering flows

Recovery = fraction of solute recovered

For 1 stage

\[ 1 - \frac{(x_R)(R)}{(x_F)(F)} \]

Specifically

\[ 1 - \frac{(x_{R,A})(R)}{(x_{F,A})(F)} \]

(a) extract concentration increases: (A at E*) > (A at E): \( y_{E*} > y_E \)

(b) solute recovery drops: (A at R*) > (A at R): \( x_{R*} > x_R \)
Q5: Composition of the mixture, $M$?

**Feed**
- $F = 250 \text{ kg}$
- $x_{F,A} = 0.24$
- $x_{F,C} = 0.76$
- $x_{F,S} = 0.00$

**Solvent**
- $S = 100 \text{ kg}$
- $x_{S,A} = 0.0$
- $x_{S,C} = 0.0$
- $x_{S,S} = 1.0$

**Answer:**
- $M = \ldots$
- $x_{M,A} = \ldots$
- $x_{M,C} = \ldots$
- $x_{M,S} = \ldots$
Q5 solution: Composition of the mixture, $M$?

Feed $F = 250 \text{ kg}$, $S = 100 \text{ kg}$

$x_{F,A} = 0.24$, $x_{S,A} = 0.0$

$x_{F,C} = 0.76$, $x_{S,C} = 0.0$

$x_{F,S} = 0.00$, $x_{S,S} = 1.0$

$M = F + S$

Answer: $M = 350 \text{ kg}$; $x_{M,A} = 0.17$; $x_{M,C} = 0.54$; $x_{M,S} = 0.29$
Q6: Composition of the 2 phases leaving in equilibrium?

Feed Solvent

$F = 250 \text{ kg}$  $S = 100 \text{ kg}$

$x_{F,A} = 0.24$  $x_{S,A} = 0.0$

$x_{F,C} = 0.76$  $x_{S,C} = 0.0$

$x_{F,S} = 0.00$  $x_{S,S} = 1.0$

$$R_1 =$$

$$E_1 =$$
Q6 solution: Composition of the 2 phases in equilibrium?

\[ M = E_1 + R_1 \]

\[ R_1 = 222 \text{ kg}; \quad x_{R_1,A} = 0.10; \quad x_{R_1,C} = 0.82; \quad x_{R_1,S} = 0.08 \]

\[ E_1 = 128 \text{ kg}; \quad y_{E_1,A} = 0.33; \quad y_{E_1,C} = 0.06; \quad y_{E_1,S} = 0.61 \]
Link units in *series*

[Introduce fresh solvent each time]

[Richardson and Harker, p 723]
Q7: send raffinate from Q6 to second mixer-settler

Question: how much solvent should we use in the second stage?
Q7 *solution*: send raffinate from Q6 to second mixer-settler

Compare extract:

Compare volumes:

**Answer**: equilibrium from point $B$ (most solvent), $C$, $D$ (least solvent) will each be different. Trade-off: higher extraction vs lower recovery
**Phase diagram: furfural, water, ethylene glycol**

**AIM**: to remove ethylene glycol (solute) from water (carrier) into solvent (furfural)

1. Calculate the mixture composition, \( M \)
2. Calculate the equilibrium compositions in \( E_1 \) and \( R_1 \)

**Note**: *extract* is defined as “the solvent-rich stream leaving the system”
Solution: Phase diagram: furfural, water, ethylene glycol

Feed Solvent
\[ F = 100 \text{ kg} \quad S = 200 \text{ kg} \]
\[ x_{F,A} = 0.45 \quad x_{S,A} = 0.0 \]
\[ x_{F,C} = 0.55 \quad x_{S,C} = 0.0 \]
\[ x_{F,S} = 0.00 \quad x_{S,S} = 1.0 \]

- A = ethylene glycol solute
- C = water (carrier)
- S = furfural solvent

\[
\begin{align*}
M &= 300 \text{ kg}; & x_{M,A} &= 0.15; & x_{M,C} &= 0.18; & x_{M,S} &= 0.67 \\
R_1 &= 82 \text{ kg}; & x_{R_1,A} &= 0.33; & x_{R_1,C} &= 0.57; & x_{R_1,S} &= 0.10 \\
E_1 &= 218 \text{ kg}; & y_{E_1,A} &= 0.09; & y_{E_1,C} &= 0.04; & y_{E_1,S} &= 0.87
\end{align*}
\]
Recap: Cross-flow arrangements

$N = 3$ in this illustration

- Recovery = fraction of solute recovered

$$1 - \frac{(x_{RN})(R_N)}{(x_F)(F)}$$

- Concentration of overall extract = solute leaving in each extract stream, divided by total extract flow rate

$$\frac{\sum_{n=1}^{N} (y_{E_n})(E_n)}{\sum_{n=1}^{N} E_n}$$
Review from last time
Review from last time
Review from last time
Cross-current vs counter-current

Cross-current ($N = 2$ stages)

- We combine multiple extract streams
- (Only 2 in illustration)
- In general: $y_{E_1} > y_{E_2} > \ldots$
- Fresh solvent added at each stage

Counter-current ($N = 2$ stages)

- “Re-use” the solvent, so
- Far lower solvent flows
- Recovery = $1 - \frac{(x_{R_N})(R_N)}{(x_F)(F)}$
- Concentration = $y_{E_1}$
- How many stages? What solvent flow?

You will have an assignment question to compare and contrast these two configurations
What we are aiming for

General approach:

1. Use ternary diagrams to determine operating lines
2. Estimate number of “theoretical plates” or “theoretical stages”
3. Convert “theoretical stages” to actual equipment size. E.g. assume we calculate that we need \( N \approx 6 \) theoretical stages.
   - does not mean we require 6 mixer-settlers (though we could do that, but costly)
   - it means we need a column which has equivalent operation of 6 counter-current mixer-settlers that fully reach equilibrium
   - at this point we resort to correlations and vendor assistance
   - vendors: provide \( \text{HETS} = \text{height equivalent to a theoretical stage} \)
   - use that to size the column

\[
\text{unit height (or size)} = \frac{\text{HETS} \times \text{number of theoretical stages}}{\text{stage efficiency}}
\]
For example

WINTRAY installed in BTX Operating Plant

Conventional RDC

WINTRAY® New Installation

Figure 2: Concept and Flow of WINTRAY System

[WINTRAY (Japanese company; newly patented design)]
Two *counter-current* units

*Reference for this section: Seader textbook, 3rd ed, p 312 to 324.*

Consider $N = 2$ stages for now. Steady state mass balance:

\[
F + E_2 = R_1 + E_1 \quad R_1 + S = R_2 + E_2
\]

Rearrange:

\[
F - E_1 = R_1 - E_2 \quad R_1 - E_2 = R_2 - S
\]

\[
(F - E_1) = (R_1 - E_2) = (R_2 - S) = P
\]

Note: each *difference* is equal to $P$ (look on the flow sheet above where those *differences* are).
Counter-current graphical solution: 2 units

Rearranging again:

\[ F = E_1 + P \]
\[ R_1 = E_2 + P \]
\[ R_2 = S + P \]

*Interpretation:*  
*P* is a fictitious operating point on the ternary diagram (from lever rule)  
- *F* is on the line that connects *E_1* and *P*  
- *R_1* is on the line that connects *E_2* and *P*  
- *R_2* is on the line that connects *S* and *P*
Counter-current graphical solution: 2 units

Step 1

Feed Solvent

\[ F = 250 \text{ kg} \]
\[ S = 100 \text{ kg} \]

\[ x_{F,A} = 0.24 \]
\[ x_{F,C} = 0.76 \]
\[ x_{F,S} = 0.00 \]

\[ x_{S,A} = 0.0 \]
\[ x_{S,C} = 0.0 \]
\[ x_{S,S} = 1.0 \]

Overall balance gives:

\[ M = S + F = E_1 + R_2 \]

For example, let's require \( x_{R_2,A} = 0.05 \) (solute concentration in raffinate).
Given an \( S \) flow rate, what is \( y_{E_1,A} \)? (concentration of solute in extract)
Counter-current graphical solution: 2 units

Step 2

Note: the line connecting \( E_1 \) to \( R_2 \) is not a tie line. We use the lever rule and an overall mass balance \((F + S = E_1 + R_2)\) to solve for all flows and compositions of \( F, S, E_1, \) and \( R_2 \).

\( y_{E_1,A} \approx 0.38 \) is found from an overall mass balance, through \( M \). Simply connect \( R_2 \) and \( M \) and project out to \( E_1 \)
Counter-current graphical solution: 2 units

Step 3

Recall:

\[ F = E_1 + P \]

\( F \) is on the line that connects \( E_1 \) and \( P \)

\[ R_2 = S + P \]

\( R_2 \) is on the line that connects \( S \) and \( P \)

Extrapolate through these lines until intersection at point \( P \).
**Step 4**

Once we have $E_1$, we can start: note that in stage 1 the $R_1$ and $E_1$ streams leave in equilibrium and can be connected with a tie line.
Counter-current graphical solution: 2 units

Step 5

Again recall:

\[ R_1 = E_2 + P \]

Since we have point \( P \) and \( R_1 \) we can bring the operating line back and locate point \( E_2 \).
The last unit in a cascade is a special case: we already know \( R_N = 2 \), but we could have also calculated it from the tie line with \( E_2 \). We aim for some overshoot of \( R_N \). (Good agreement in this example.)
In general: *Counter-current units*

\[ F + E_2 = E_1 + R_1 \quad E_2 + R_2 = E_3 + R_1 \quad E_n + R_n = E_{n+1} + R_{n-1} \]

Rearrange:

\[ F - E_1 = R_1 - E_2 \quad R_1 - E_2 = R_2 - E_3 \quad R_{n-1} - E_n = R_n - E_{n+1} \]

\[ (F - E_1) = (R_1 - E_2) = \ldots = (R_{n-1} - E_n) = (R_n - E_{n+1}) = \ldots = (R_N - S) = P \]

Notes:

1. each difference is equal to \( P \) (the difference between flows)
2. \( E_n \) and \( R_n \) are in equilibrium, leaving each stage [via tie line]
Counter-current graphical solution

1. We know $F$ and $S$; connect with a line and locate “mixture” $M$
2. Either specify $E_1$ or $R_N$ (we will always know one of them)
3. Connect a straight line through $M$ passing through the one specified
4. Solve for unspecified one [via tie line]
5. Connect $S$ through $R_N$ and extrapolate
6. Connect $E_1$ through $F$ and extrapolate; cross lines at $P$
7. Locate $P$ by intersection of 2 lines
8. In general: connect $E_n$ and $R_n$ via equilibrium tie lines
Tutorial-style question

Consider a system for which you have been given the ternary diagram (see next slides). \( A = \) solute, \( S = \) solvent (100% pure), \( C = \) carrier. The feed, \( F \) enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier.

1. Calculate the flow and composition of the extract and raffinate from:
   - 1st cross-current stage, using a pure solvent flow of 50 kg/hr.
   - 2nd cross-current stage, with an additional solvent flow of 50 kg/hr.

2. For the overall 2-stage cross-current system, find the:
   - overall recovery \([\text{answer: } \sim 93\%]\)
   - overall concentration of combined extract streams \([\text{answer: } \sim 21\%]\)

3. The objective now is to have a counter-current system so the raffinate leaving in the \( N^{th} \) stage, \( R_N \) has \( y_{R_N} = 0.025 \)
   - Show the construction on the ternary diagram for the number of equilibrium stages to achieve \( x_{R_N} = 0.025 \), given a solvent flow of 28 kg/hr.
   - Calculate the overall recovery and concentration of the extract stream.
   - Plot on the same axes the concentrations in the extract and raffinate streams.
Tutorial solution: step 1
Tutorial solution: step 2
Tutorial solution: step 3
Tutorial solution: step 4
Tutorial solution: step 5
Tutorial solution: step 6
Tutorial solution: concentration profile
For practice (A)
Recall:

\[ F + P = E_1 \]

\[ R_2 + P = S \]

**Thought experiment:** What is the minimal achievable \( E_1 \) concentration? *mentally move point \( M \) towards \( S \). What happens to \( P \) as solvent flow \( S \) is increased? Alternative explanation next.
Counter-current graphical solution: maximum solvent flow

Step 3(b)

Recall:

\[ F + P = E_1 \]
\[ R_2 + P = S \]

Subtle point: minimal achievable \( E_{1\text{min}} \) concentration:

- occurs at a certain \textit{maximum} solvent flow rate indicated by \( \circ \)
- note that \( R_2 \) is fixed (specified) in this example
Safety concerns

Liquid-liquid (solvent) extraction units safety concerns can be reduced by:

▶ using a high-flash point solvent
▶ avoid static electricity generation (sparking)
▶ slow liquid flow rates in pipes < 1 m/s to avoid static build-up
▶ use conductive piping, not plastics or rubbers
▶ feed organic phase from the bottom of tank, not the side, to avoid splashing
▶ avoid any areas for air pockets to form
▶ avoid generating mists of solvent
▶ electrical circuits must be rated explosion proof
▶ strict rules related to mobile electronics, welding, etc in the neighbourhood
▶ conduct full HAZOP and fire assessment
▶ do not allow trenches/dips for the solvent phase to accumulate, when spills occur

[Courtesy of “ALTA Solvent Extraction Short Course”, Alan Taylor]