Separation Processes
ChE 4M3
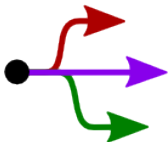
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http://learnche.mcmaster.ca/4M3

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We appreciate:

- ▶ if you let us know about **any errors** in the slides
- ▶ **any suggestions to improve the notes**

All of the above can be done by writing to
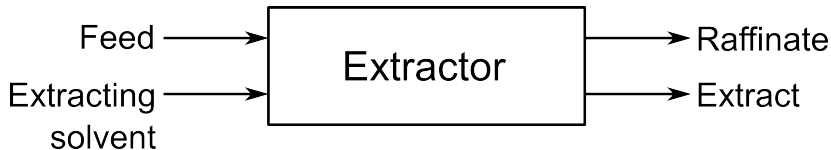
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If reporting errors/updates, please quote the current revision number: 87

Liquid-liquid extraction (LLE)

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: solute mostly present in this layer $= y_A$
- ▶ raffinate: residual solute in this layer $= x_A$
- ▶ distribution: how the solute partitions itself $= D_A = \dfrac{y_A}{x_A} = \dfrac{y_E}{x_R}$

  - ▶ measure of affinity of solute
  - ▶ $D_A = \dfrac{\mu_R^0 - \mu_E^0}{RT} = \dfrac{\text{chemical potential difference}}{(R)(\text{temperature})}$

Where/why LLE is used

Where?

- ▶ Bioseparations
- ▶ Nuclear (uranium recovery)
- ▶ Mining: nickel/cobalt; copper/iron
- ▶ Perfumes, fragrances and essential oils
- ▶ Fine and specialty chemicals

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
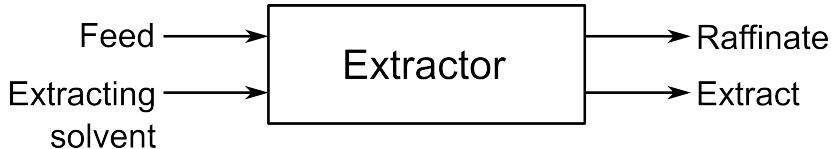
1. Mixing/contacting:
   - turbulent contact between liquid phases
   - small droplet dispersion in a continuous phase
     - which phase is dispersed?
   - mass-transfer between phases
   - limited by solute loading in solvent
2. Phase separation:
   - reverse of mixing step
   - drops coalesce
   - relies on density difference
3. Collection of phases leaving the unit

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?

- Counter-current mixer-settlers in series
- High interfacial area during mixing
- Reduce mass-transfer resistance
- Promote mass transfer
  - molecular diffusion
  - eddy diffusion $\leftarrow$ orders of magnitude greater

Equipment for LLE

1. Mixer-settlers
   - mix: impellers
   - mix: nozzles
   - mix: feeds meet directly in the pump
   - mix: geared-teeth devices
   - main aim: good contact; avoid droplets smaller than 2 μm
   - settle: baffles, membranes
   - settle: ultrasound
   - settle: chemical treatment
   - settle: centrifuges
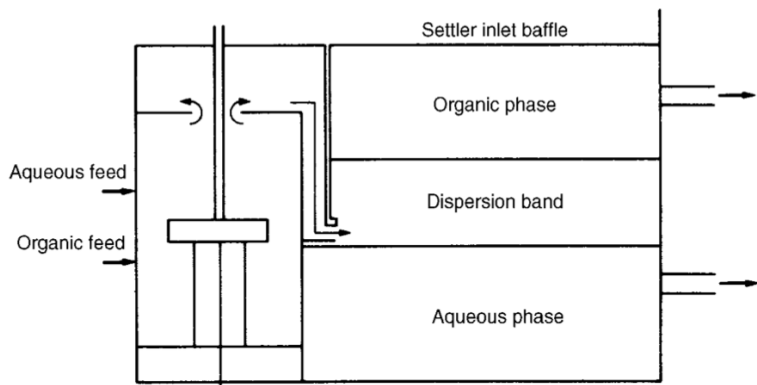2. Columns with:
   - (a) nothing or
   - (b) trays and/or
   - (c) packing and/or
   - (d) pulsating and/or
   - (e) agitation
3. Rotating devices

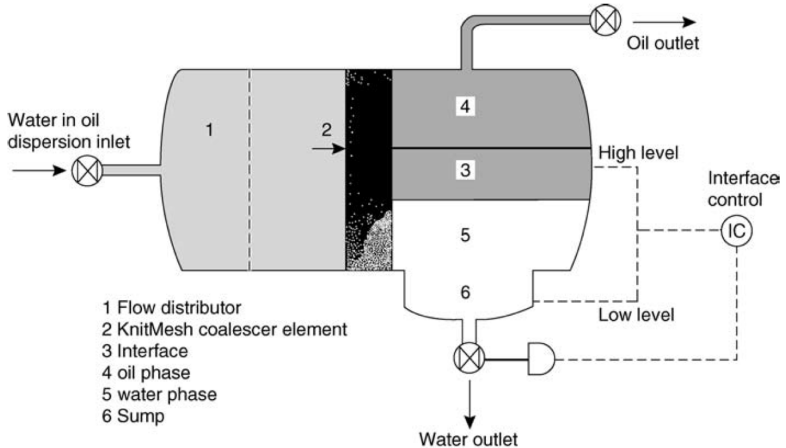Important point: LLE is an equilibrium-limited separation (as opposed to rate limited separations seen up to now).

Mixer-settlers

Settler inlet baffle

Organic phase

Dispersion band

Aqueous phase

Aqueous feed

Organic feed

[Richardson and Harker, p 745] Common in mining industry: requirements ~40000 L/min flows

Mixer-settlers

KnitMesh coalescer: consistency of "steel wool"

Water in oil dispersion inlet

Oil outlet

High level

Interface control

IC

Low level

Water outlet

1 Flow distributor
2 KnitMesh coalescer element
3 Interface
4 oil phase
5 water phase
6 Sump

[Richardson and Harker, p 747]

Horizontal gravity settling vessel

Slotted impingement baffle

Tap for scum

Emulsion in

Heavy liquid out
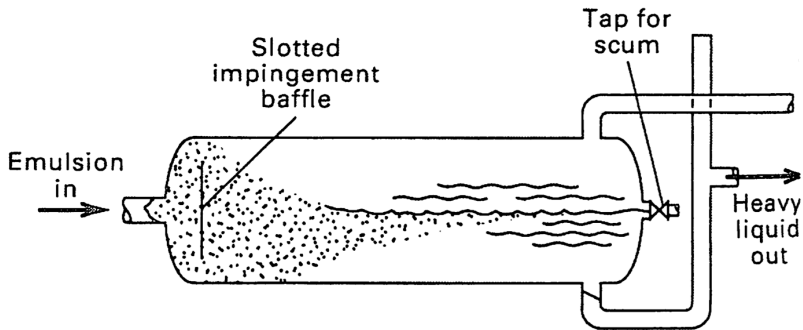
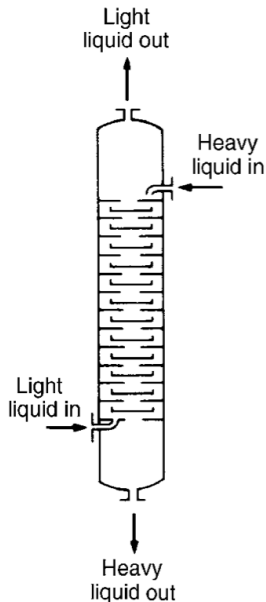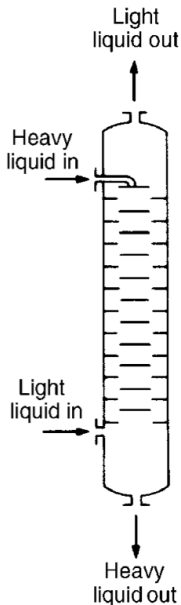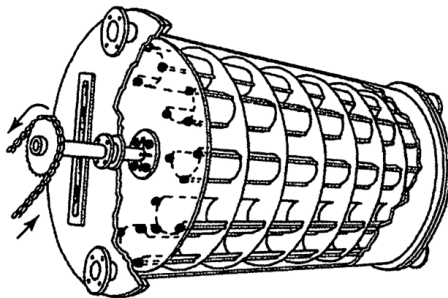[Seader, 3ed, p302]

Spray columns: separation principle is gravity
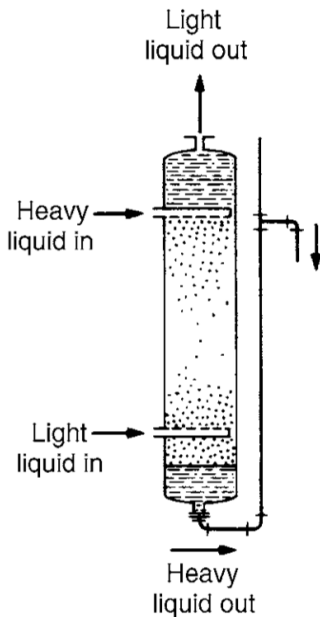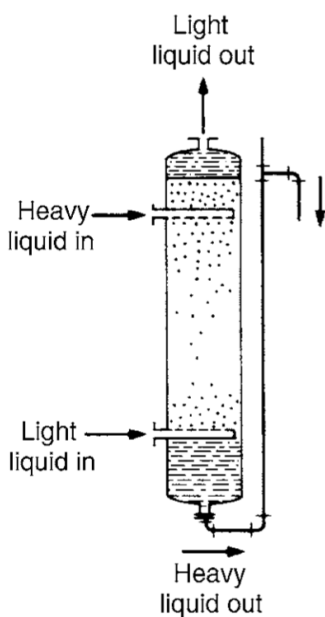
Tray columns

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

[Richardson and Harker, p 749]

Rotating devices
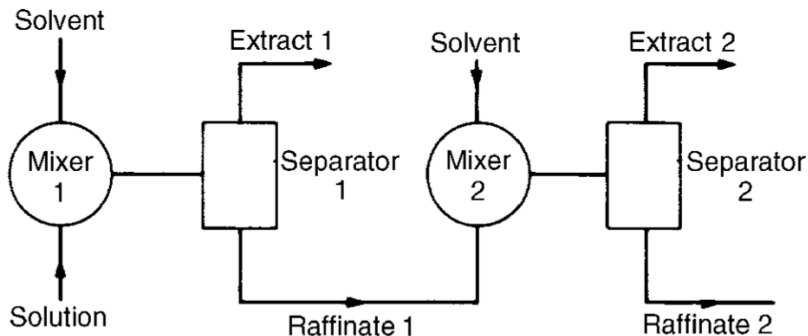
- ▶ "white" = lighter liquid
- ▶ "grey" = heavier liquid
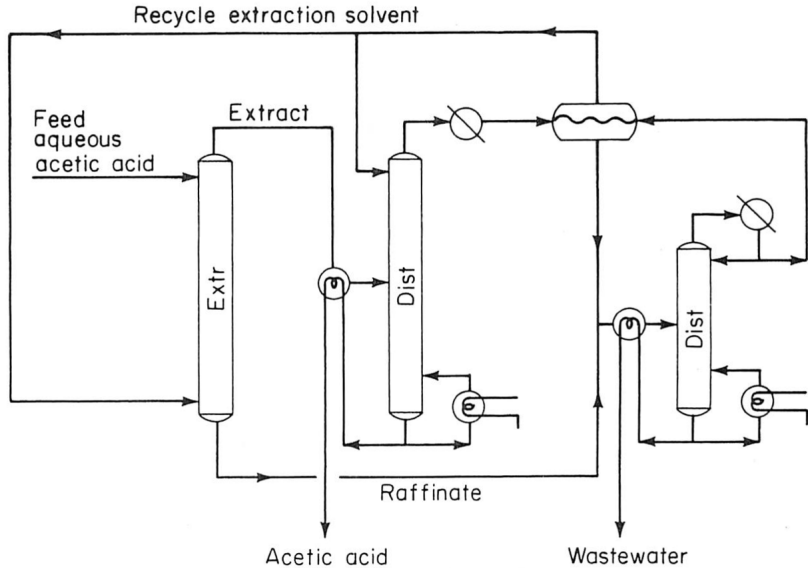
Used when foams and emulsions would easily form: i.e. gentle mass transfer.

Linking up units (more on this later)

[Richardson and Harker, p 723]

Integration with downstream units

[Schweitzer, p 1-257]

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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
-
-
-
-
-
-
-
-
-
-
-

Calculating the distribution coefficient

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:

$$D = \frac{x_F}{x_R} - 1$$

Feed

Extraction solvent $S \rightarrow$ $\rightarrow E$ Extract

R

Raffinate

- ▶ Capital letters refer to mass amounts
- ▶ $y_\square$ ← refers to mass fractions in solvent layer
- ▶ $x_\square$ ← refers to mass fractions in carrier and extract layers

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

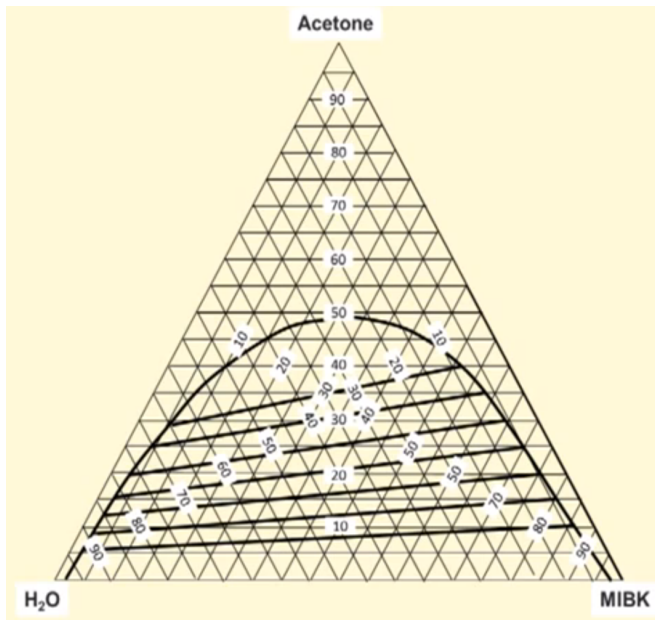Also: see Perry's for many values of D
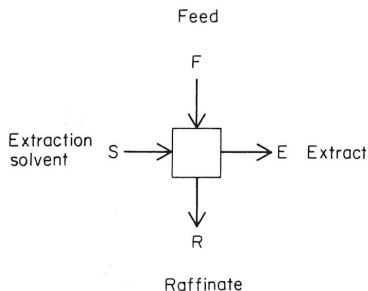
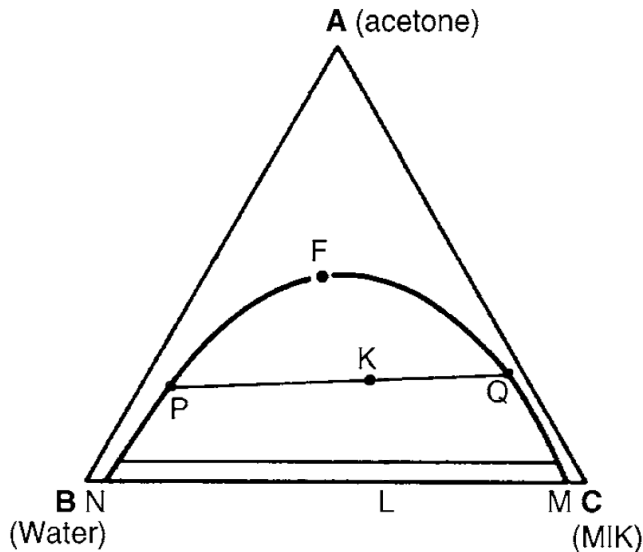# Triangular phase diagrams: from laboratory studies

Using a triangular phase diagrams
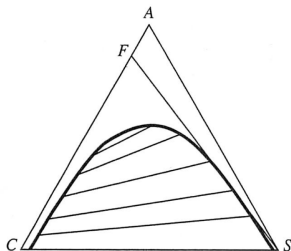
Lever rule

Mix P and Q

- mixture $=$ K

- $\dfrac{PK}{KQ} = \dfrac{\text{amount Q}}{\text{amount P}}$

- The converse applies also: when separating a settled mixture

- Applies anywhere: even in the miscible region

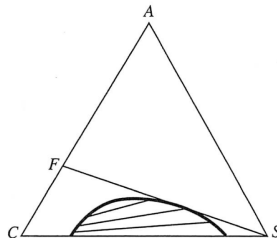# Q1: Using the lever rule

Which is a more or effective system?

- ▶ S = pure solvent used
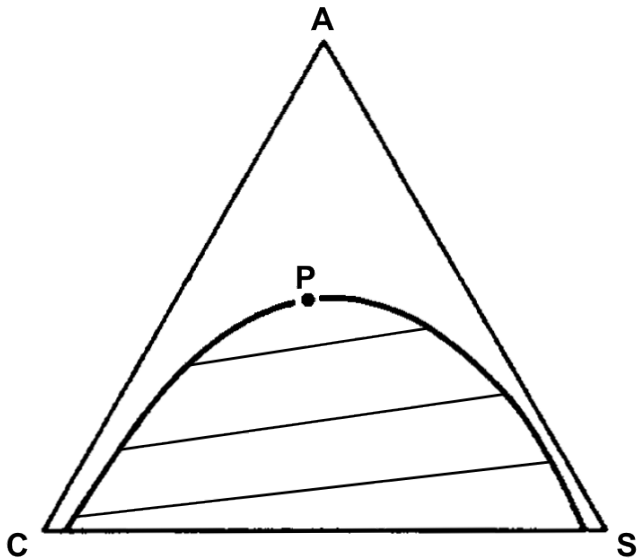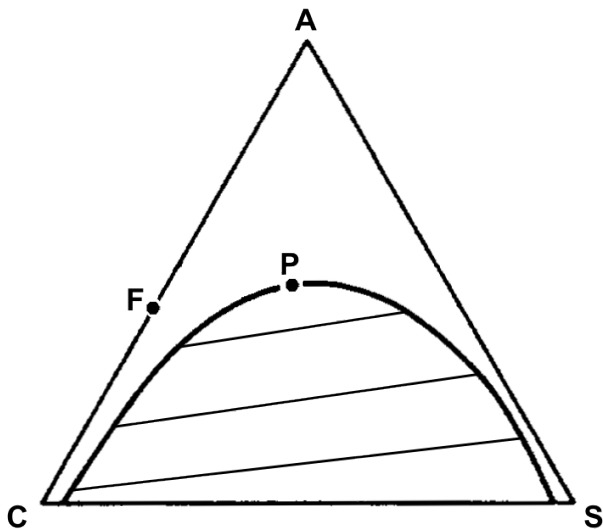- ▶ F = feed concentration

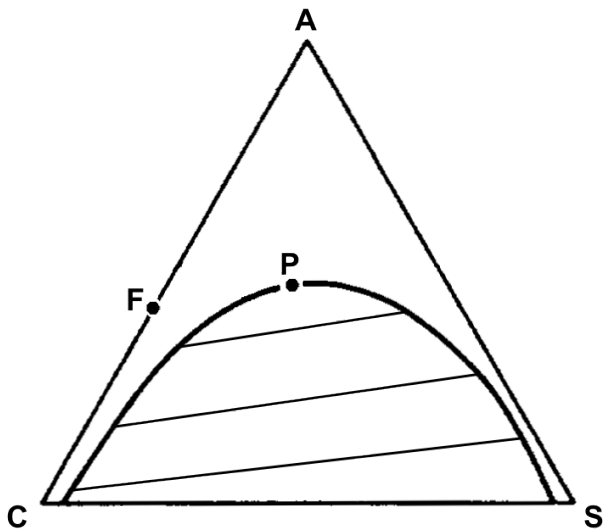(a) (b)

Answer:

Q2: Using the lever rule

Which is a more effective as a solvent: C or S ?
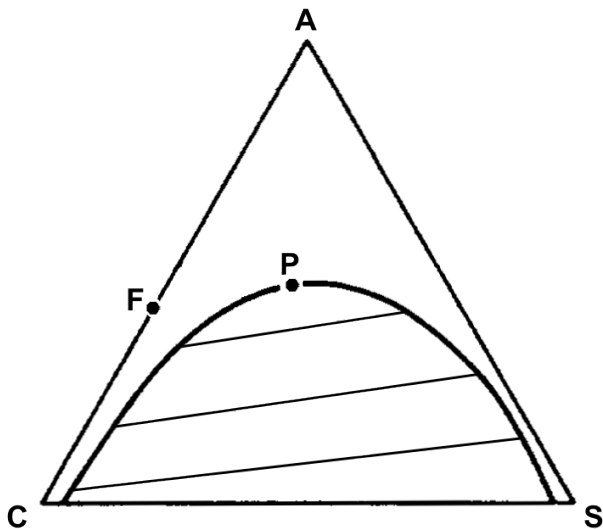
Q3: Using the lever rule

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?

Q4: Going to equilibrium

Let that mixture M achieve equilibrium. What is the composition of the raffinate and extract?

Q5: Altering flows

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

References

- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 1.9
- Seader, Henly and Roper, "Separation Process Principles", 3rd edition, chapter 8
- Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 13
- Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 12.5
- Ghosh, "Principles of Bioseparation Engineering", chapter 7
- Uhlmann's Encyclopedia, "Liquid-Liquid Extraction", DOI:10.1002/14356007.b03_06.pub2