Separation Processes ChE 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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Liquid-liquid extraction (LLE)



[Flickr# 3453475667]

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} = concentration of A, the solute, in extract.
- 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
•
$$D_{A} = \frac{\mu_{R}^{0} - \mu_{E}^{0}}{RT} = \frac{\text{chemical potential difference}}{(R)(\text{temperature})}$$

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
 - Iimited 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

 $\leftarrow \text{ orders of magnitude greater}$

Equipment for LLE

- 1. Mixer-settlers
 - mix: impellers
 - mix: nozzles
 - mix: feeds meet directly in the pump
 - mix: geared-teeth devices
 - \blacktriangleright 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



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

Mixer-settlers

KnitMesh coalescer: consistency of "steel wool"



Horizontal gravity settling vessel



[Seader, 3ed, p302]

Spray columns: separation principle is gravity



Tray columns



- coalescence on each tray
- ▶ tray holes: ~ 3mm
- breaks gradient formation (axial dispersion)

Tray columns with mechanical agitation



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

Rotating devices



[Seader, 3ed, p 306]

- "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



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:

$$Fx_F + Sy_S = Ey_E + Rx_R$$

 $D = rac{y_E}{x_R}$

If
$$F = S = E = R$$
 and $y_s = 0$, then
only measure x_R :

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

- Capital letters refer to mass amounts
- ▶ $y_{\Box} \leftarrow$ refers to mass fractions in solvent layer

• $x_{\Box} \leftarrow$ 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



[Flickr# 3453475667]

Using a triangular phase diagrams



Lever rule



Mix P and Q

- mixture = K
 - $\frac{\mathsf{PK}}{\mathsf{KQ}} = \frac{\mathsf{amount Q}}{\mathsf{amount P}}$
- 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 *flexible* system?

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



Answer:

- due to solvent choice
- due to different temperatures
- due to pH modification, etc

Q1: Using the lever rule

Which is a more *flexible* system?

- 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



Which of C or S, when used as a solvent, will obtain a higher extract composition? Answer: 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?

Q3 *solution*: Using the lever rule



Composition of the mixture? Trick question: we need more information (e.g. amount of F and S must be given)

Q4: Going to equilibrium



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

Q4 solution: Going to equilibrium



What is the composition of the raffinate and extract? Use the tie lines [solid lines]; or interpolate between existing ones.

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?





(a) extract concentration increases: (A at E*) > (A at E): $y_{E^*} > y_E$ (b) solute recovery drops: (A at R*) > (A at R): $x_{R^*} > x_R$

Q6: Composition of the mixture, M?



Q6 solution: Composition of the mixture, M?



Answer: M = 350kg; $x_{M,A} = 0.17$; $x_{M,C} = 0.54$; $x_{M,S} = 0.29$

Q7: Composition of the 2 phases leaving in equilibrium?



Feed

Raffinate

Solvent

S = 100 kg

 $x_{S,A} = 0.0$

 $x_{5,5} = 1.0$

→E. Extract

Q7 solution: Composition of the 2 phases in equilibrium?



 $E_1 = 128$ kg; $x_{E_1,A} = 0.33$; $x_{E_1,C} = 0.06$; $x_{E_1,S} = 0.61$

Link units in series



[[]Richardson and Harker, p 723]

Q8: send raffinate from Q7 to second mixer-settler



Question: how much solvent should we use in the second stage?

Some theory: Two counter-current units



Just consider N = 2 stages for now. Steady state mass balance: $F + E_2 = E_1 + R_1$ $E_2 + R_2 = S + R_1$

Rearrange:

$$F - E_1 = R_1 - E_2$$
 $R_1 - E_2 = R_2 - S$

$$F - E_1 = R_1 - E_2 = R_2 - S = P$$

Note: each difference is equal to P (look on the flow sheet where those differences are).



Rearranging again:

$$F + P = E_1$$
$$R_1 + P = E_2$$
$$R_2 + P = S$$

Interpretation: *P* is a fictitious operating point on the ternary diagram

- P connects F and E₁
- P connects R_1 and E_2
- P connects R_2 and S



We require $x_{R2,A} = 0.05$ (solute concentration). What is $x_{E1,A}$?





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

 $x_{E1,A} \approx 0.38$ is found from an overall mass balance, through *M*.



Extrapolate through these lines until intersection at point P.



In stage 1: R_1 and E_1 leave in equilibrium and can be connected with a tie line.



Since we have point P and R_1 we can bring the line back and locate point E_2



The last unit in a cascade is a special case: we have R_2 , but we could have also calculated it from the tie line. Usually we have some overshoot or undershoot. Good agreement in this example.

In general: Counter-current units



 $F + E_2 = E_1 + R_1$ $E_2 + R_2 = E_3 + R_1$ $E_n + R_n = E_{n+1} + R_{n-1}$

Rearrange:

 $F - E_1 = R_1 - E_2$ $R_1 - E_2 = R_2 - E_3$ $R_{n-1} - E_n = R_n + E_{n+1}$

 $F - E_1 = R_1 - E_2 = \ldots = R_{n-1} - E_n = R_n + E_{n+1} = \ldots R_2 - S = P$

Notes:

1. each difference is equal to P (the difference between flows)

2. E_n and R_n are in equilibrium, leaving each stage [tie line]

Counter-current graphical solution



- We know F and S; connect with a line and locate "mixture" M
- Either specify E₁ or R_N (we will always know one of them)
- Connect a straight line through M passing through the one specified
- Find for the unspecified one [tie line]

- Connect S through R_N and extrapolate to P
- Connect E₁ through F and extrapolate to P
- Locate P by intersection of 2 lines
- In general: connect E_n and R_n via equilibrium tie lines

For practice



For practice



References

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- Uhlmann's Encyclopedia, "Liquid-Liquid Extraction", DOI:10.1002/14356007.b03_06.pub2