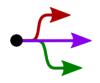
Separation Processes: **Liquid-liquid extraction**ChE 4M3



(c) Kevin Dunn, 2013

kevin.dunn@mcmaster.ca http://learnche.mcmaster.ca/4M3

Overall revision number: 256 (November 2013)

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

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Liquid-liquid extraction (LLE)

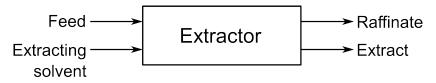


[Flickr# 3453475667]

References

- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", chapter 1.9
- Seader, Henley 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 and 12.6
- ▶ 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} = 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

$$D_{A} = \frac{\mu_{R}^{0} - \mu_{E}^{0}}{RT} = \frac{\text{chemical potential difference}}{(R)(\text{temperature})}$$

6

Where/why LLE is used

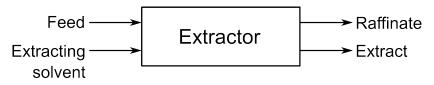
Where?

- 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)

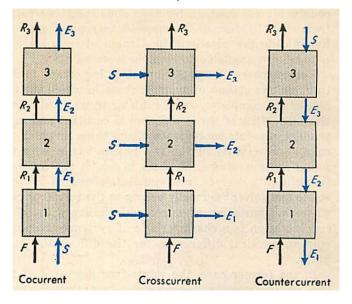
How to achieve this?

- 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

← microscopic movement

 \leftarrow orders of magnitude greater

Co-, cross-, counter-current operations



Some photos of equipment



Some photos of equipment

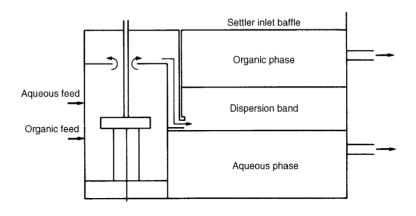


Equipment for LLE

- 1. Mixer-settlers (integrated unit)
 - mix: impellers
 - ▶ mix: nozzles
 - mix: feeds meet directly in the pump
 - mix: geared-teeth devices
 - \blacktriangleright main aim: good contact; avoid droplets smaller than 2 μ 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).

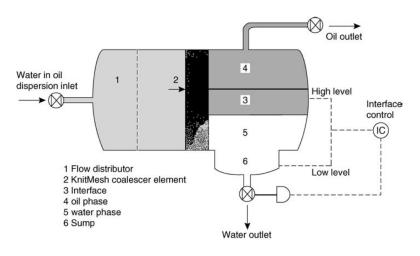
Mixer-settlers



<code>[Richardson and Harker, p 745]</code> Common in mining industry: requirements $\sim\!\!40000\ L/min$ flows

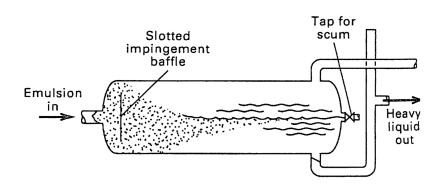
Mixer-settlers

KnitMesh coalescer: consistency of "steel wool"



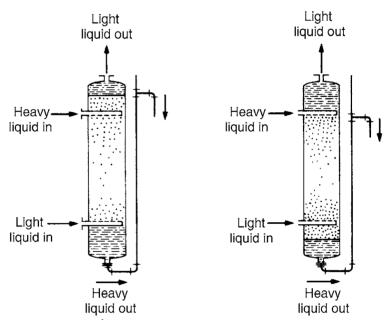
[Richardson and Harker, p 747]

Horizontal gravity settling vessel

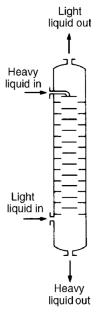


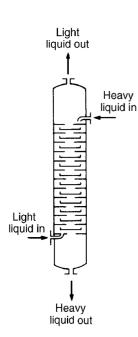
[Seader, 3ed, p302]

Spray columns: separation principle is gravity



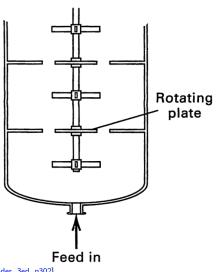
Tray columns





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

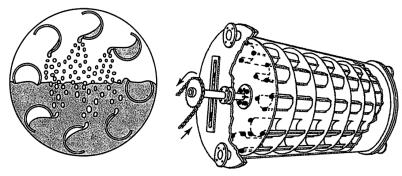
Tray columns with mechanical agitation



- shearing to create dispersion
- can have alternating layers of packing (coalescence)
- ▶ some column designs pulsate $\uparrow \Downarrow$

[Seader, 3ed, p302]

Rotating devices



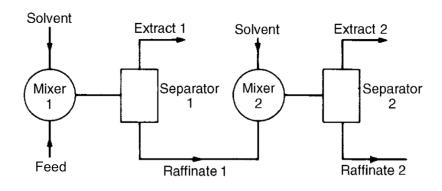
[Seader, 3ed, p 306]

- ▶ "white" = lighter liquid
- ▶ "grey" = heavier liquid

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

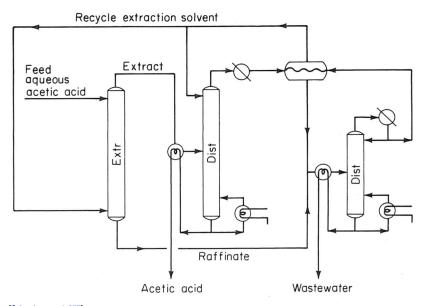
Look up in your own time: centrifuge mixer-settlers

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

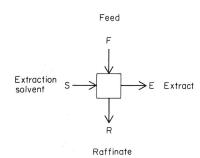
Calculating the distribution coefficient (in the lab only)

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 :

$$D = \frac{x_F}{x_R} - 1 \qquad \leftarrow \text{ only in this special case}$$



- Capital letters refer to mass amounts
- \triangleright y_{\square} \leftarrow refers to mass fractions in solvent and extract layers
- $\triangleright x_{\square} \leftarrow$ refers to mass fractions in carrier and raffinate layers

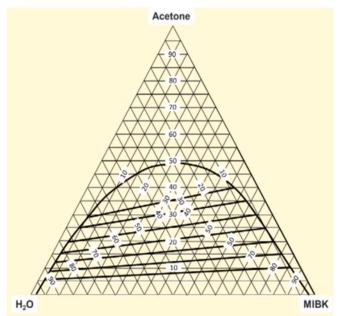
Once D is determined, we can obtain phase diagrams to understand how the process will operate.

Also: see Perry's for many values of D

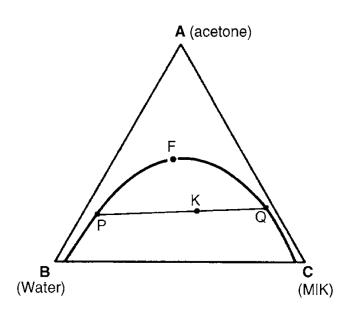
Triangular phase diagrams: from laboratory studies



Using a triangular phase diagrams



Lever rule



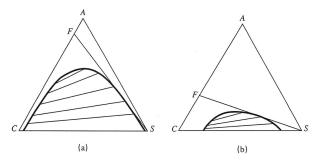
Mix P and Q

- ▶ mixture = K
- 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)?

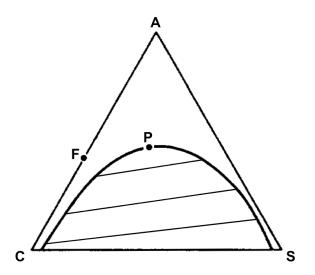
- ▶ S = pure solvent used
- ightharpoonup F = feed concentration point (more correctly it is x_F)



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

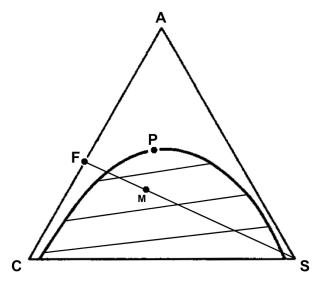
- due to solvent choice
- due to different temperatures
- ▶ due to pH modification, etc

Q2: Using the lever rule



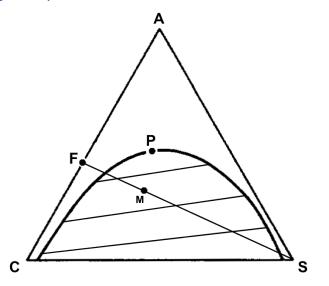
Mix a feed stream, F, containing C and A (i.e. x_F) with a pure solvent stream S (i.e. $y_S = 0$). Composition of the mixture?

Q2 *solution*: Using the lever rule



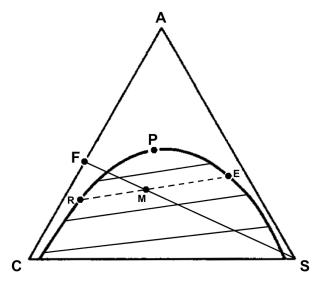
Composition of the mixture? we need more information (e.g. amount of F and S must be given to find point M)

Q3: Going to equilibrium



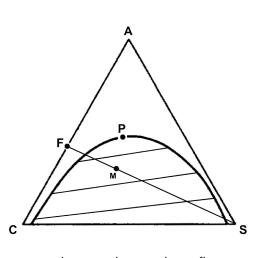
Let that mixture M achieve equilibrium. What is the composition of the raffinate and extract?

Q3 *solution*: Going to equilibrium



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

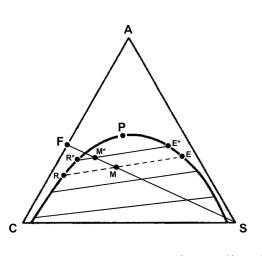
$$1-\frac{(x_R)(R)}{(x_F)(F)}$$

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

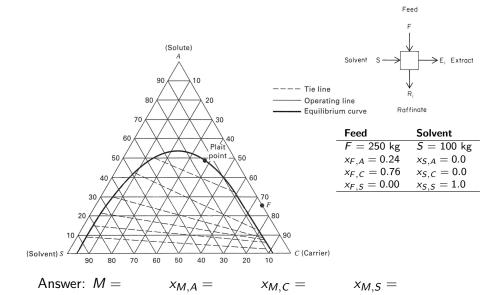
$$1 - \frac{(x_R)(R)}{(x_F)(F)}$$

Specifically

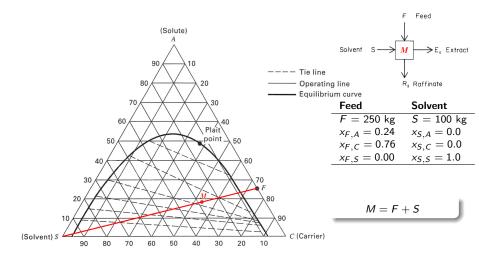
$$1 - \frac{(x_{R,A})(R)}{(x_{F,A})(F)}$$

- (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*?

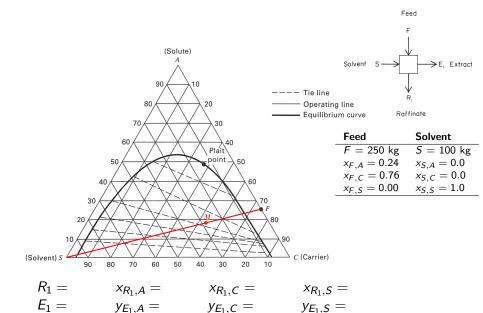


Q5 *solution*: Composition of the mixture, *M*?



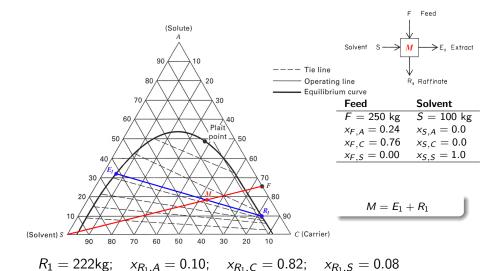
Answer: M = 350 kg; $x_{M,A} = 0.17$; $x_{M,C} = 0.54$; $x_{M,S} = 0.29$

Q6: Composition of the 2 phases leaving in equilibrium?



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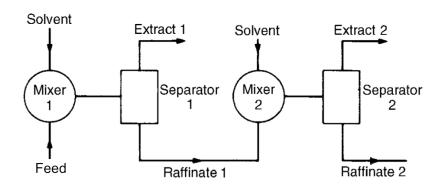
Q6 solution: Composition of the 2 phases in equilibrium?



 $E_1 = 128 \text{kg}; \quad y_{E_1,A} = 0.33; \quad y_{E_1,C} = 0.06; \quad y_{E_1,S} = 0.61$

38

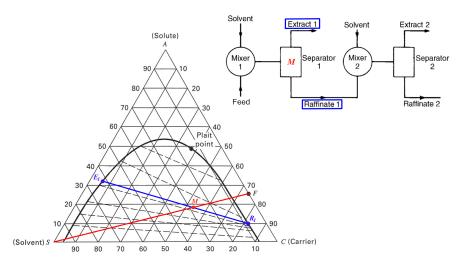
Link units in series



[Richardson and Harker, p 723]

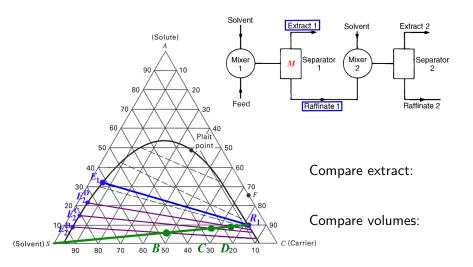
Introduce fresh solvent each time

Q7: send raffinate from Q6 to second mixer-settler



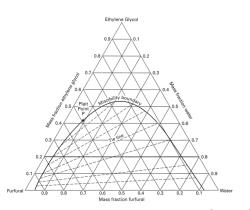
Question: how much solvent should we use in the second stage?

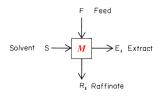
Q7 solution: send raffinate from Q6 to second mixer-settler



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





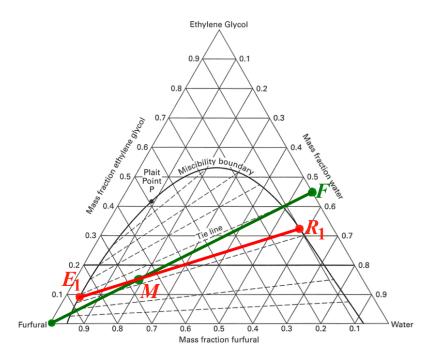
Feed	Solvent
F = 100 kg	S = 200 kg
$x_{F,A} = 0.45$	$x_{S,A} = 0.0$
$x_{F,C} = 0.55$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

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

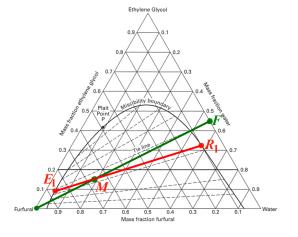
AIM: to remove ethylene glycol (solute) from water (carrier) into solvent (furfural)

- 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"



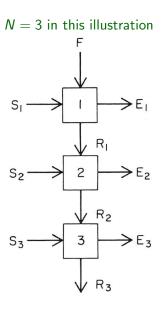
Solution: Phase diagram: furfural, water, ethylene glycol



Feed	Solvent
F = 100 kg	S = 200 kg
$x_{F,A} = 0.45$	$x_{S,A} = 0.0$
$x_{F,C} = 0.55$	$x_{S,C} = 0.0$
$x_{F,S} = 0.00$	$x_{S,S} = 1.0$

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

Recap: Cross-flow arrangements



Recovery = fraction of solute recovered

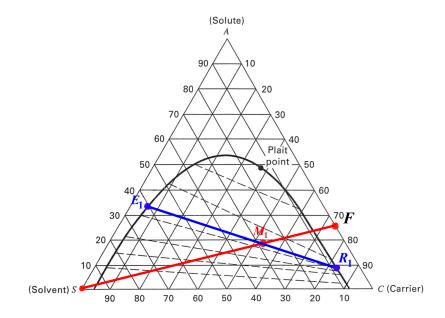
$$1-\frac{(x_{R_N})(R_N)}{(x_F)(F)}$$

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

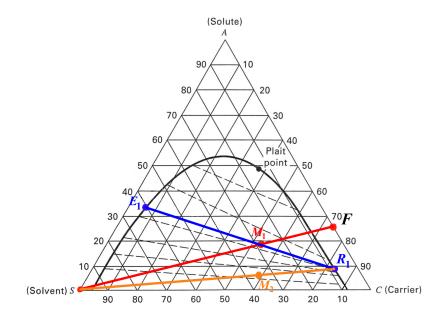
$$\frac{\sum_{n}^{N}(y_{E_{n}})(E_{n})}{\sum_{n}^{N}E_{n}}$$

[Schweitzer, p 1-263]

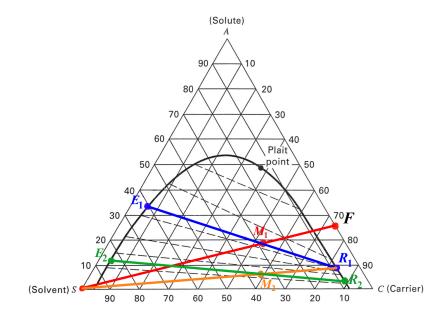
Review from last time



Review from last time



Review from last time

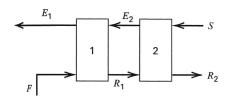


Cross-current vs counter-current

Cross-current (
$$N = 2$$
 stages)

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

Cross-current (N = 2 stages) Counter-current (N = 2 stages)



- "Re-use" the solvent, so
- Far lower solvent flows
- Recovery = $1 \frac{(x_{R_N})(R_N)}{(x_E)(F)}$
- \triangleright 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 HETS = height equivalent to a theoretical stage
 - use that to size the column
- unit height (or size) = $\frac{\mathsf{HETS} \times \mathsf{number} \ \mathsf{of} \ \mathsf{theoretical} \ \mathsf{stages}}{\mathsf{stage} \ \mathsf{efficiency}}$

For example

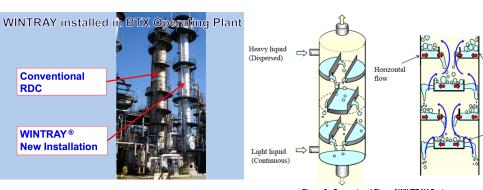
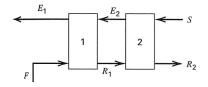


Figure 2: Concept and Flow of WINTRAY System

[WINTRAY (Japanese company; newly patented design)]

Two counter-current units

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



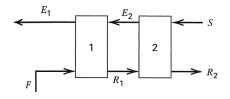
Consider N = 2 **stages** for now. Steady state mass balance:

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

Rearrange:

$$F - E_1 = R_1 - E_2$$
 $R_1 - E_2 = R_2 - S$
 $(F - E_1) = (R_1 - E_2) = (R_2 - S) = \boxed{P}$

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



Rearranging again:

$$F = E_1 + P$$

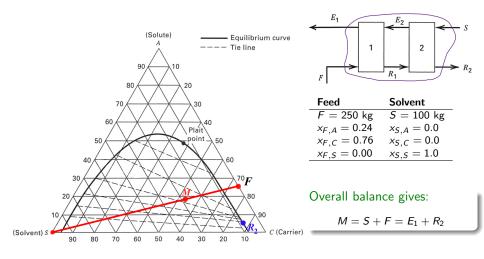
$$R_1 = E_2 + P$$

$$R_2 = S + P$$

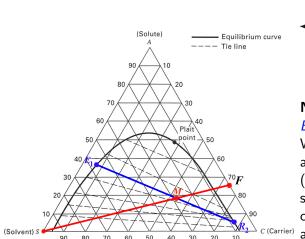
Interpretation: P is a fictitious operating point on the ternary diagram (from lever rule)

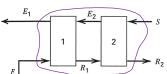
- \triangleright F is on the line that connects E_1 and P
- $ightharpoonup R_1$ is on the line that connects E_2 and P
- R₂ is on the line that connects S and P

Step 1



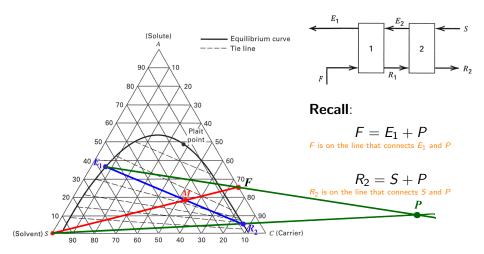
For example, let's require $x_{R_2,A} = 0.05$ (solute concentration in raffinate). Given an S flow rate, what is $y_{E_1,A}$? (concentration of solute in extract)



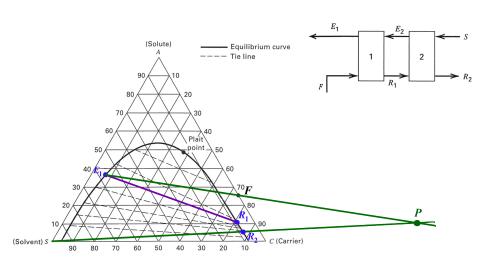


Note: the line connecting E_1 to R_2 is not a tie line. We use the lever rule and an overall mass balance $(F + S = E_1 + R_2)$ to solve for all flows and compositions of F, S, E_1 , and R_2 .

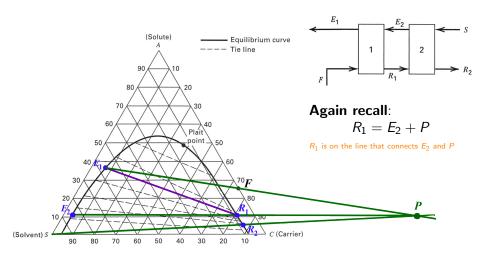
 $y_{E_1,A} \approx 0.38$ is found from an overall mass balance, through M. Simply connect R_2 and M and project out to E_1 .



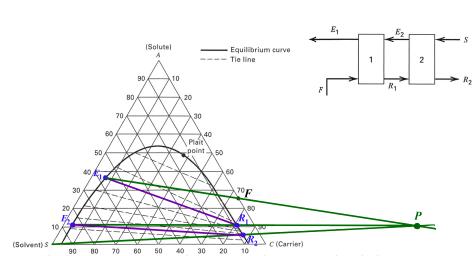
Extrapolate through these lines until intersection at point P.



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.

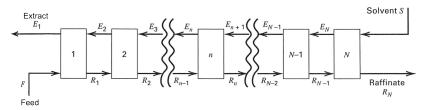


Since we have point P and R_1 we can bring the operating line back and locate point E_2



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



$$F+E_2=E_1+R_1$$

$$E_2 + R_2 = E_3 + R_1$$

$$E_n + R_n = E_{n+1} + R_{n-1}$$

Rearrange:

$$F-E_1=R_1-E_2$$

$$R_1-E_2=R_2-E_3$$

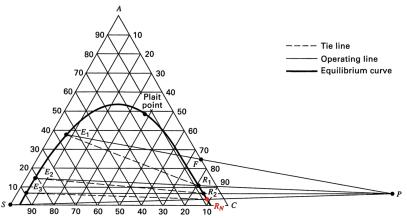
$$R_{n-1}-E_n = R_n-E_{n+1}$$

$$(F - E_1) = (R_1 - E_2) = \dots = (R_{n-1} - E_n) = (R_n - E_{n+1}) = \dots = (R_N - S) = \mathbf{P}$$

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



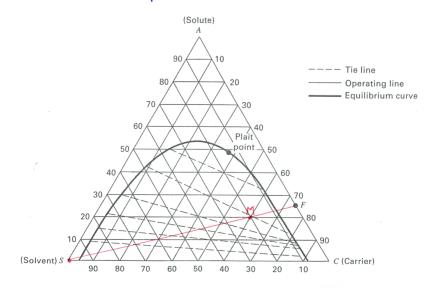
- 1. We know F and S; connect with a line and locate "mixture" M
- 2. Either specify E_1 or R_N (we will always know one of them)
- 3. Connect a straight line through *M* passing through the one specified
- 4. Solve for unspecified one [via tie line]

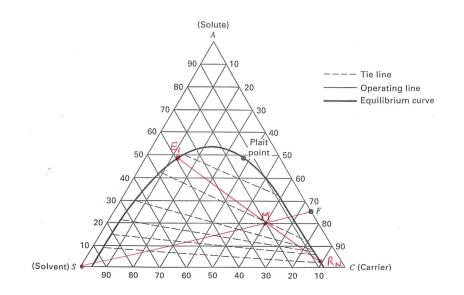
- 5. Connect S through R_N and extrapolate
- 6. Connect E_1 through F and extrapolate; cross lines at P
- 7. Locate *P* by intersection of 2 lines
- 8. In general: connect E_n and R_n via equilibrium tie lines

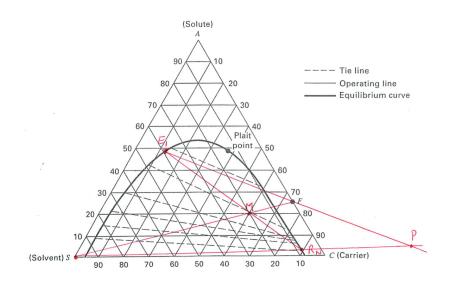
Tutorial-style question

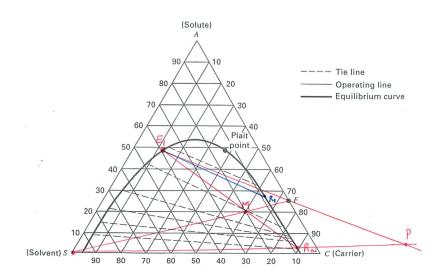
Consider a system for which you have been given the ternary diagram (see next slides). A = solute, S = solvent (100% pure), C = carrier. The feed, F enters at 112 kg/hr with composition of 25 wt% solute and 75 wt% carrier.

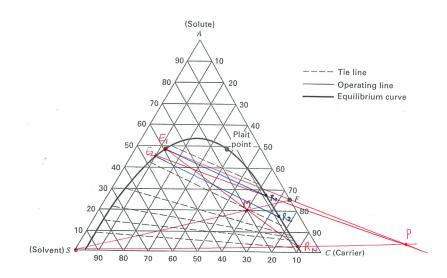
- 1. Calculate the flow and composition of the extract and raffinate from:
 - ▶ 1st cross-current stage, using a pure solvent flow of 50 kg/hr.
 - ▶ 2nd cross-current stage, with an additional solvent flow of 50 kg/hr.
- 2. For the overall 2-stage cross-current system, find the:
 - ▶ overall recovery [answer: ~93%]
 - ightharpoonup overall concentration of combined extract streams [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

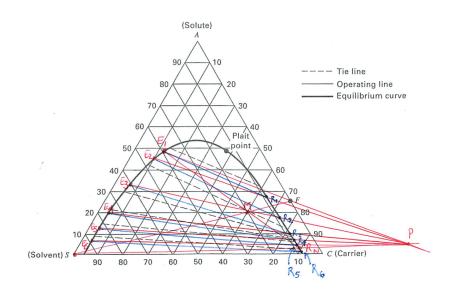




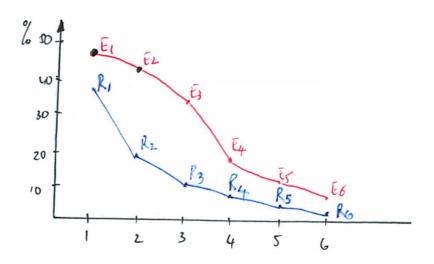




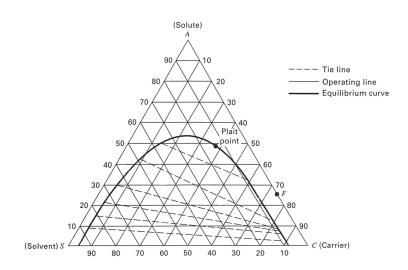




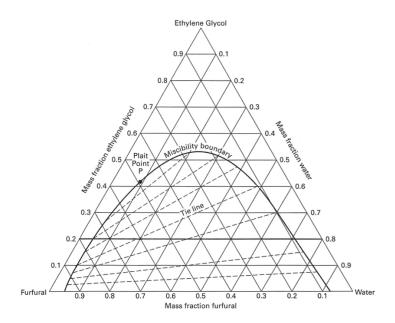
Tutorial solution: concentration profile

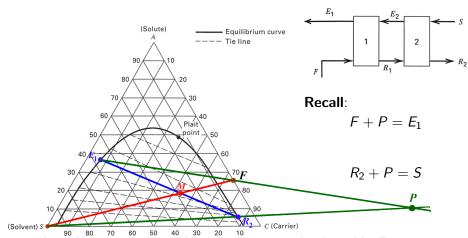


For practice (A)



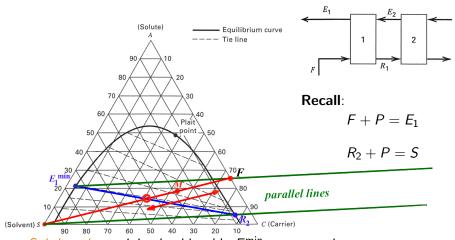
For practice (B)





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)



Subtle point: minimal achievable E_1^{\min} concentration:

- occurs at a certain maximum solvent flow rate indicated by O
- \triangleright 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