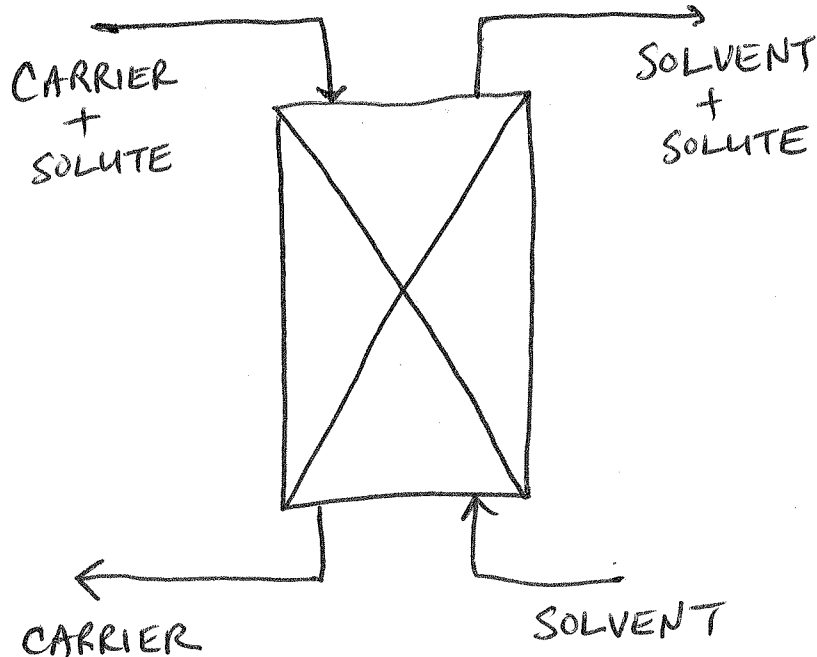


CHAPTER 8: LIQUID-LIQUID EXTRACTION
WITH TERNARY SYSTEMS



SOLUTE MISCIBLE IN CARRIER & SOLVENT

CARRIER & SOLVENT IMMISCIBLE.

AKA

EXTRACTION

SOLVENT EXTRACTION

LIQUID EXTRACTION

②

AROUND FOR A LONG TIME

- Au + Ag separation from Cu(Liq)
(Pb(Liq) solvent)
- Aromatics + sulfur from Kerosene
(Liquid SO_2 @ 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

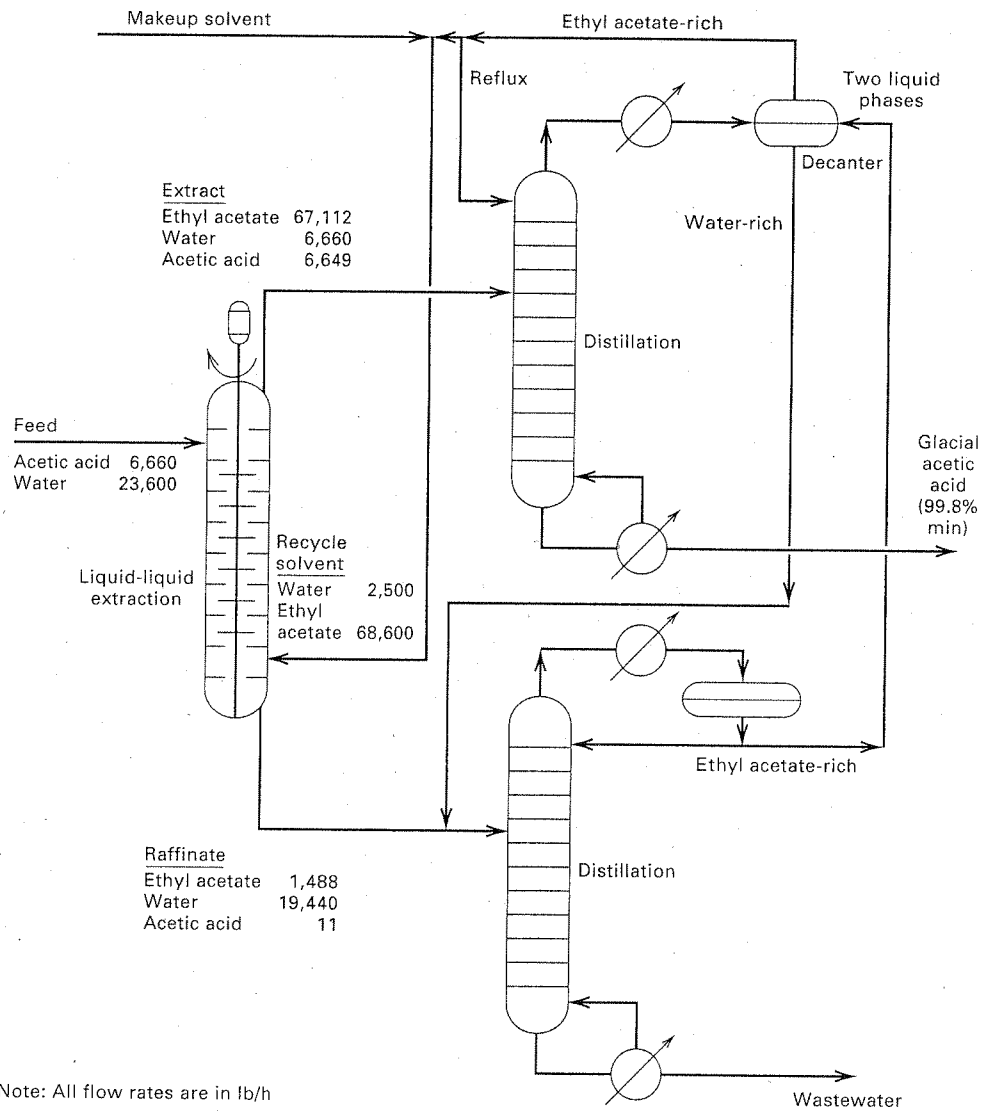


Figure 8.1 Typical liquid-liquid extraction process.

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 γ ?

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:

<u>SOLUTE</u>	<u>CARRIER</u>	<u>SOLVENT</u>
Acetic acid	Water	Ethyl acetate
Ammonia	Butenes	Water
	(poison)	
Aromatics	Paraffins	Diethylene glycol
Fatty acids	Oil	Propane
	(oxidants, spoils faster)	
Penicillin	Broth	Butyl acetate
Vitamin A	Fish oil	Propane
Vitamin E	Vegetable oil	Propane

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)

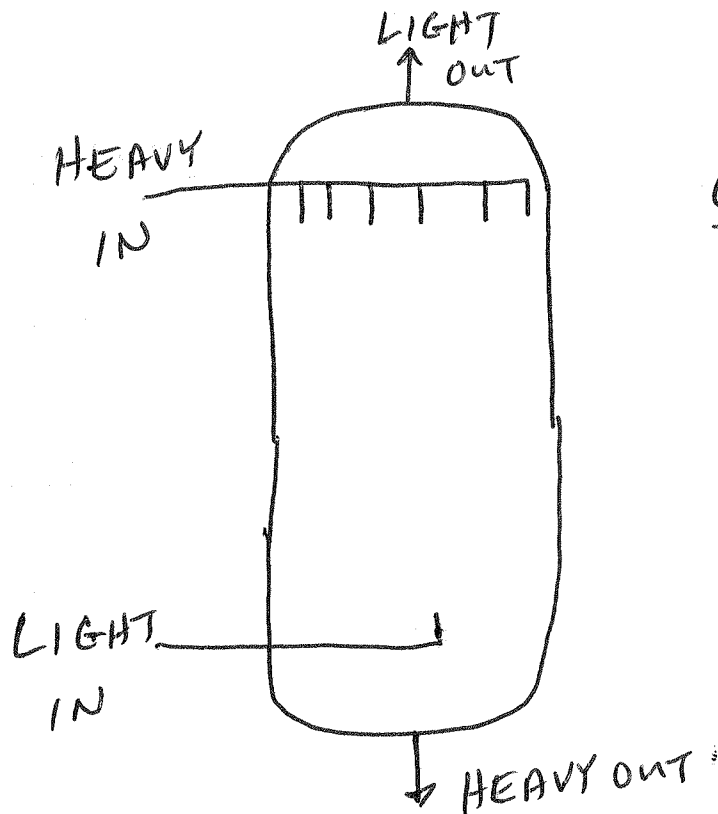
WHAT IF EMULSIFY?

→ COALESCE

- MEMBRANES
- MESH
- ULTRASOUND
- CHEMICAL TREATMENT (MESSY)

CAN ALSO SUPPLEMENT GRAVITY W/
CENTRIFUGAL FORCE.

[B] SPRAY COLUMNS



CONVERSE
LIGHT
CAN
BE SPRAYED

⇒ LARGE THROUGHPUT

⇒ BACKMIXING (NOT A LOT OF STAGES)

⇒ LOW COST

C 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)

D PLATE COLUMNS

⇒ STAGEWISE CONTACT

⇒ SMALL TRAY SPACING

⇒ GOOD EXTRACTION RATE

⇒ CAN FLOOD (WEEPING NOT ~~BA~~ 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

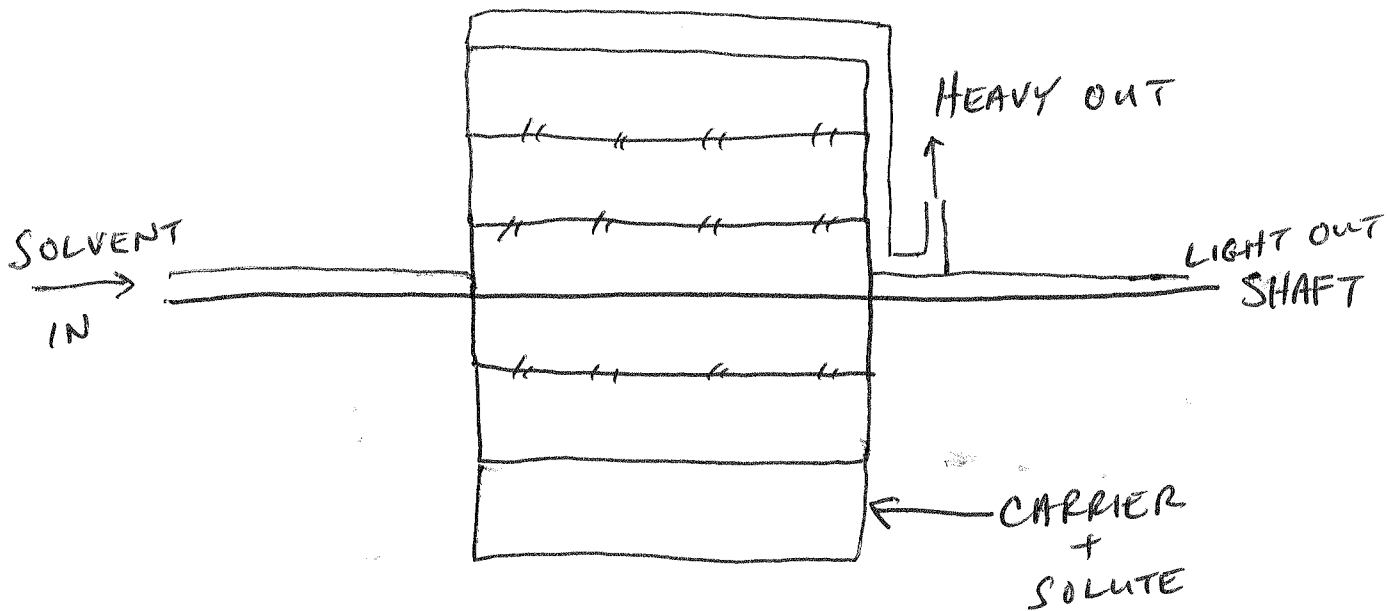
SEE FIGURE 8.7 (Seader + Henley)

3) RECIPROCATING PERFORATED PLATE

(LIKE A SIEVE TRAY MOVING UP & DOWN VERTICALLY)

⇒ BAFFLES USED ~~BA~~ TO MINIMIZE AXIAL MIXING (SEPARATE STAGES)

F CENTRIFUGAL EXTRACTORS



⇒ LOW DENSITY DIFFERENCE

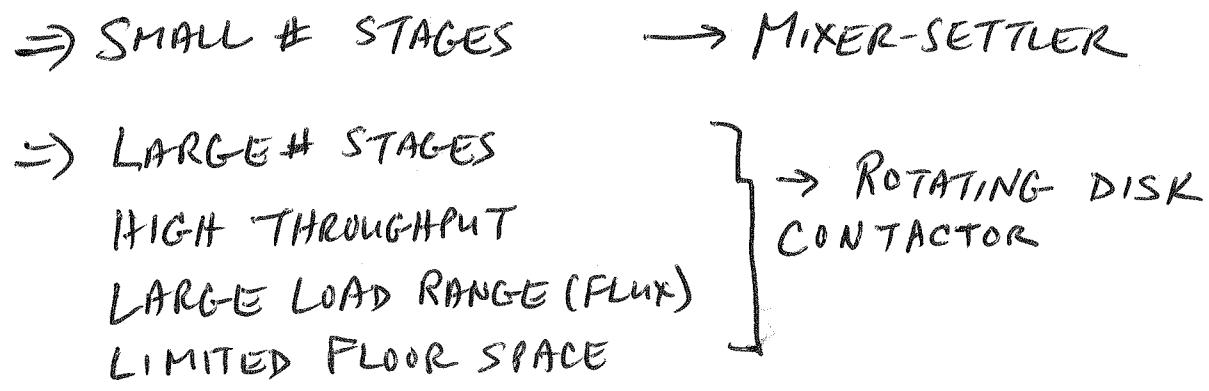
Table 8.3 Advantages and Disadvantages of Different Extraction Equipment

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

(SEADER + HENLEY, p. 433)

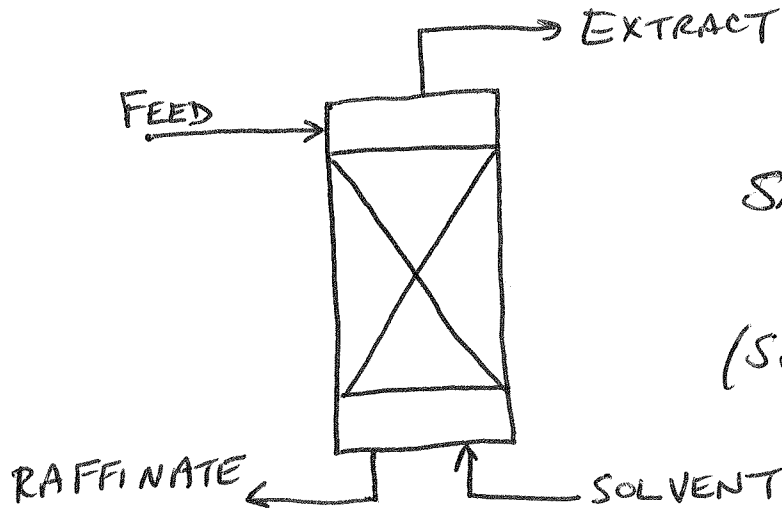
SCHEME FOR CHOOSING EXTRACTOR:

FIG. 8.8 (SEADER + HENLEY)



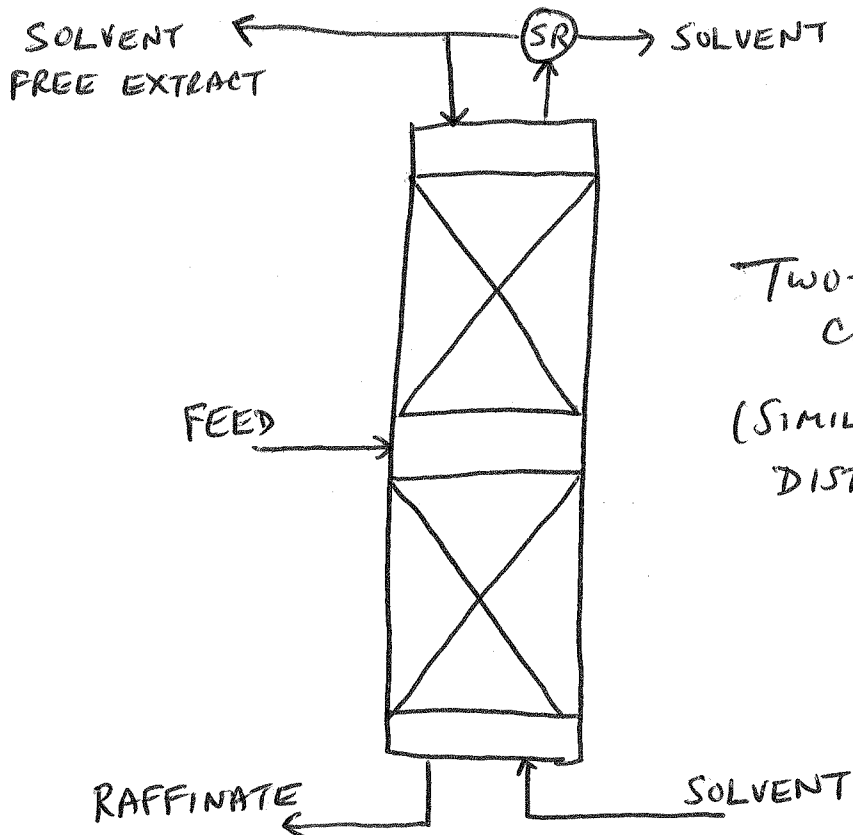
GENERAL DESIGN CONSIDERATIONS:

CASCADE ARRANGEMENT -



SINGLE SECTION
CASCADE
(SIMILAR TO ABSORPTION
COLUMN)

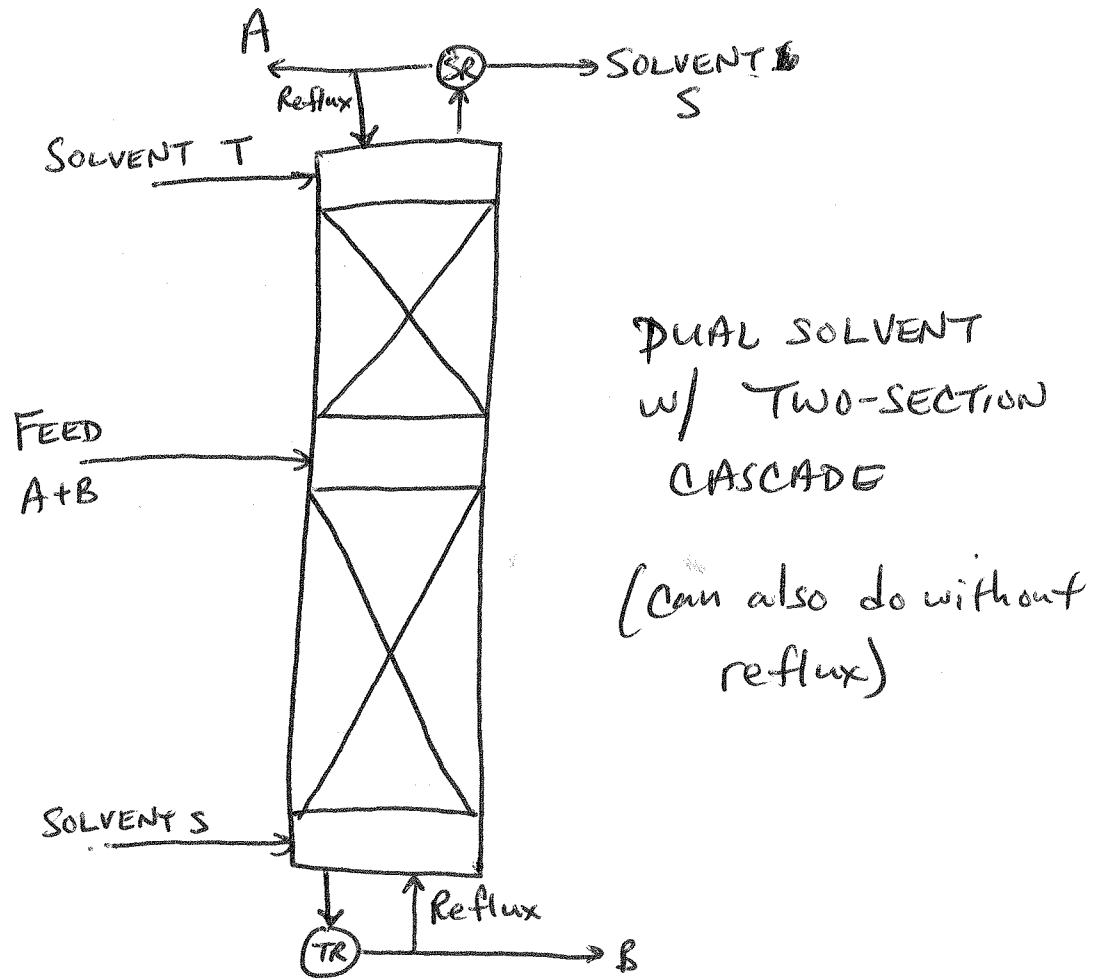
⇒ Gives fractional recovery



TWO-SECTION
CASCADE
(SIMILAR TO
DISTILLATION)

⇒ Can give very good recovery.

(2)



⇒ MORE COMPLEX, BUT CAN GIVE IMPROVED SEPARATION.

FACTORS THAT INFLUENCE EXTRACTION:

1) FEED

- a) FLOW RATE
- b) COMPOSITION
- c) TEMPERATURE
- d) PRESSURE

③

- 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) $\alpha_{\text{SOLUTE-SOLVENT}}$ 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,

$$(X_A)^I (\gamma_A)^I (P_A^{sat})^I = (X_A)^{II} (\gamma_A)^{II} (P_A^{sat})^{II}$$

SATURATION PRESSURE IS A PURE COMPONENT PROPERTY AND $P_i^{sat} = f(T)$ ONLY.

$$\Rightarrow (P_A^{sat})^I = (P_A^{sat})^{II}$$

THEREFORE,

$$\underbrace{(X_A)^I (\gamma_A)^I}_{\text{CARRIER PHASE}} = \underbrace{(X_A)^{II} (\gamma_A)^{II}}_{\text{SOLVENT PHASE}}$$

PARTITION COEFFICIENT IS A "K" VALUE.
(RECALL CHEMCAD)

⑦

$$K_A = \frac{(X_A)^{II}}{(X_A)^I} = \frac{(\gamma_A)^I}{(\gamma_A)^{II}}$$

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:

$$K_C = \frac{(X_C)^{II}}{(X_C)^I} = \frac{(\gamma_C)^I}{(\gamma_C)^{II}}$$

$$K_S = \frac{(X_S)^{II}}{(X_S)^I} = \frac{(\gamma_S)^I}{(\gamma_S)^{II}}$$

The relative SELECTIVITY is a function of the K-values.

$$\beta_{AC} = \frac{K_A}{K_C} = \frac{(x_A)^{II}/(x_A)^I}{(x_C)^{II}/(x_C)^I} = \frac{(\gamma_A)^I/(\gamma_A)^{II}}{(\gamma_C)^I/(\gamma_C)^{II}}$$

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

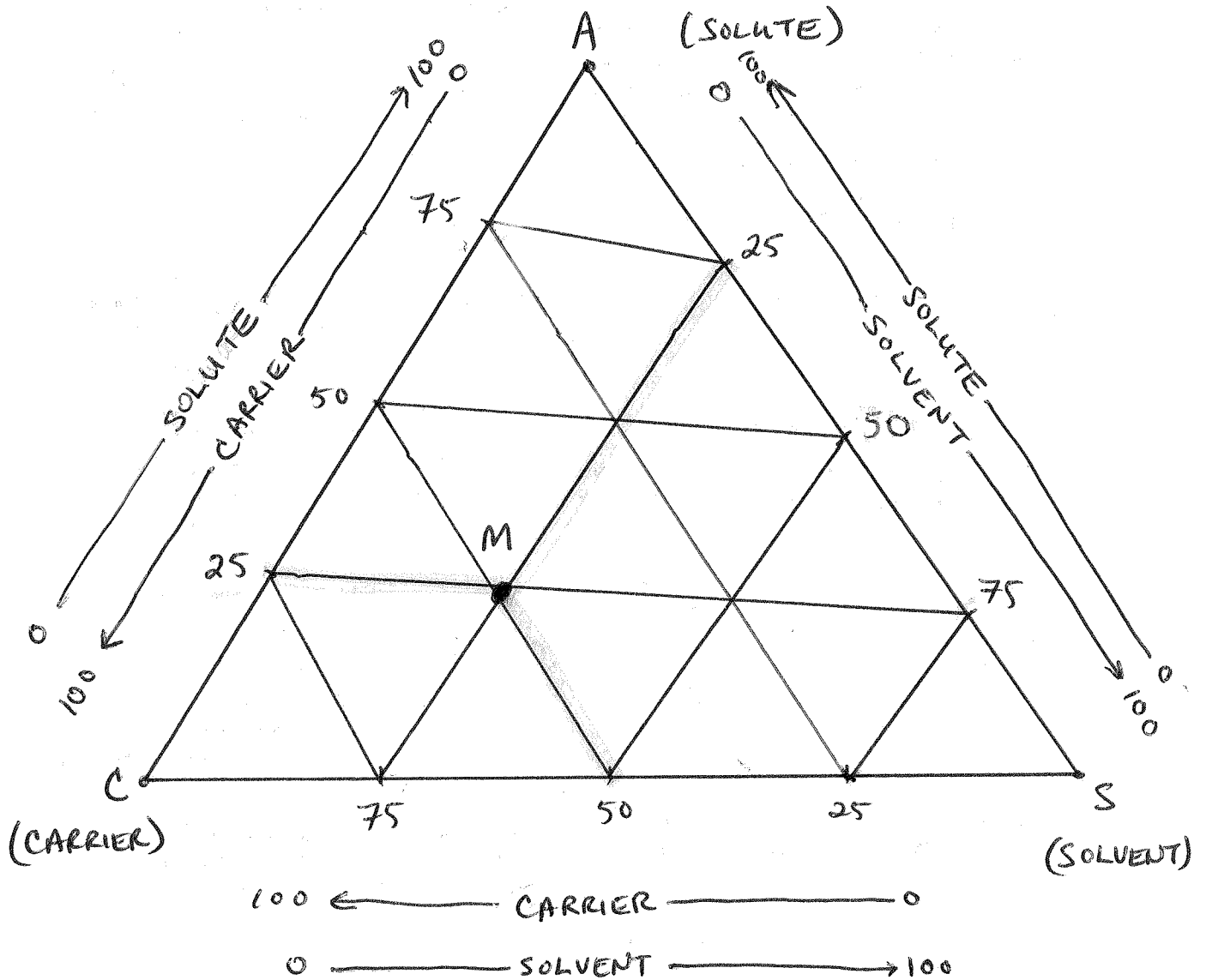
LOW K_C

} TO GET CLEAN SOLVENT & CARRIER DURING RECOVERY

SEE TABLE 8.4 SEADER & HENLEY. \rightarrow

LOW γ
A LIKES S

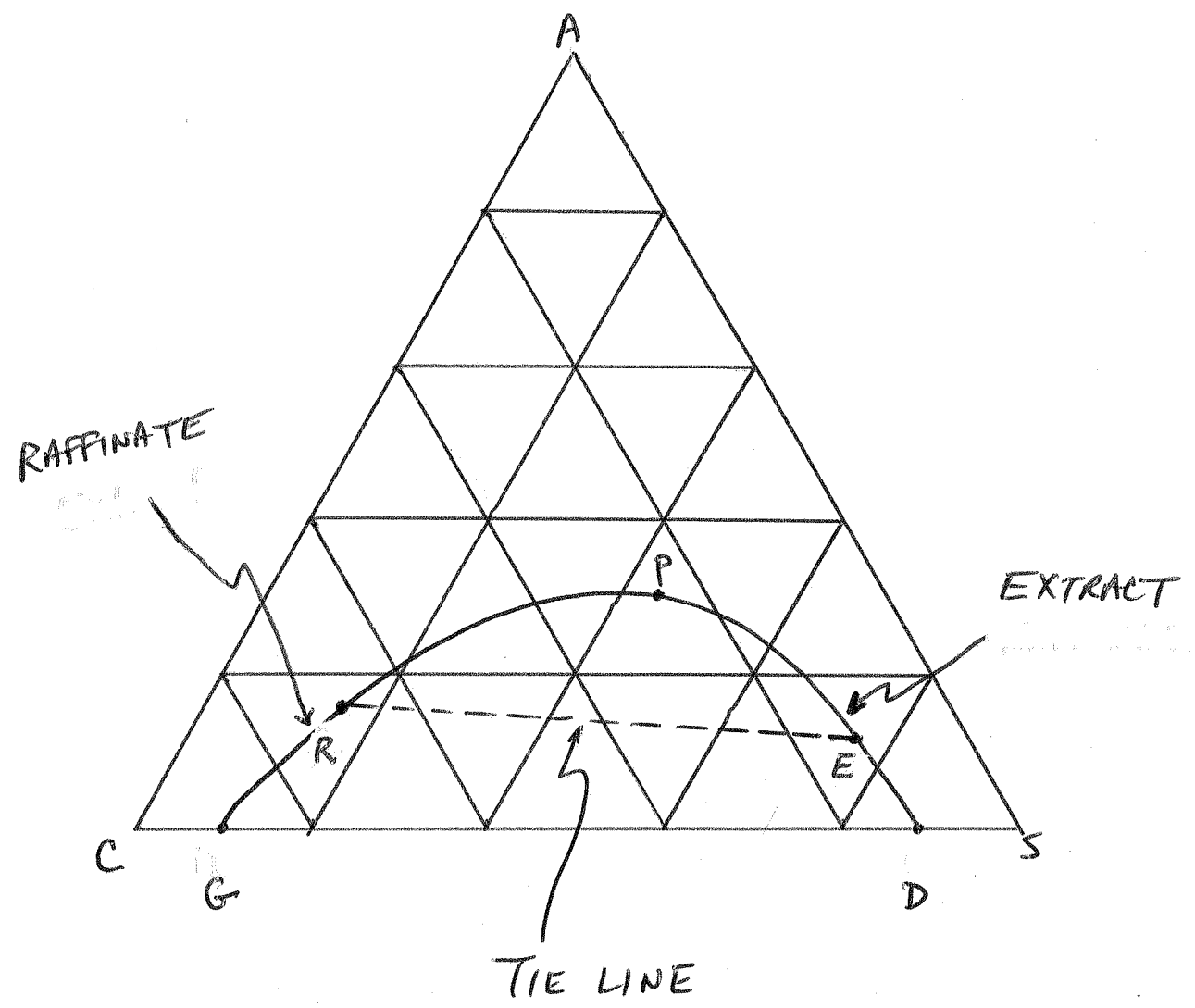
PHASE DIAGRAMS FOR EXTRACTION



At point M,

$$X_C = 0.5, \quad X_S = 0.25, \quad X_A = 0.25$$

WHEN USED FOR EXTRACTION...



P \equiv PLAIT POINT (EQUAL COMPOSITIONS IN EACH LIQUID PHASE)

E \equiv EXTRACT COMPOSITION

R \equiv RAFFINATE COMPOSITION

D ≡ MISCIBILITY LIMIT } FOR CARRIER IN
 G ≡ MISCIBILITY LIMIT } SOLVENT AND
 VICE VERSA.

M ≡ TOTAL COMPOSITION

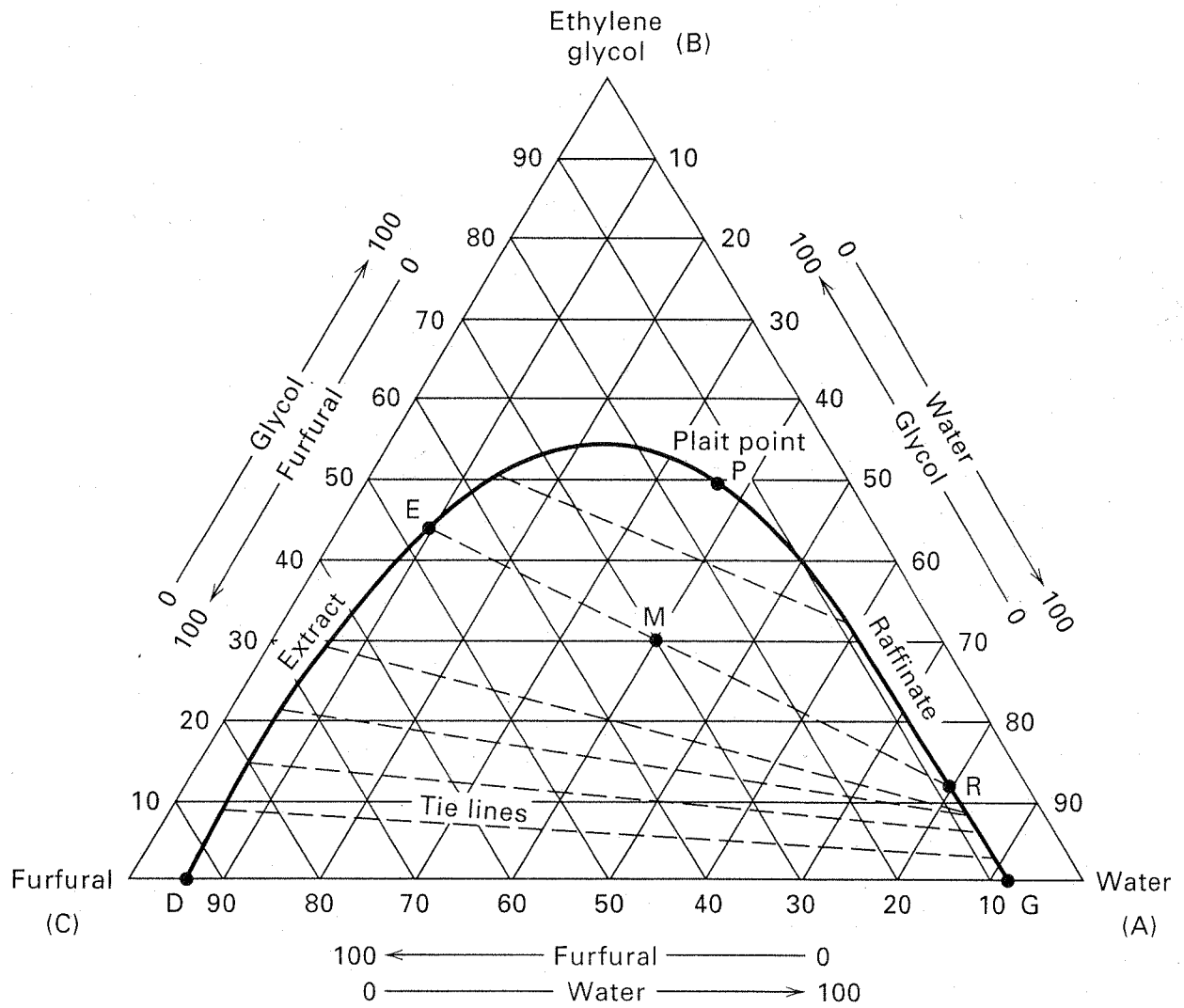
ANY COMPOSITION ON A TIE LINE WILL
 EQUILIBRATE ON RESPECTIVE E + R.

OUTSIDE OF ENVELOPE, ALL
 THREE COMPONENTS MISCIBLE.

How TO USE FOR A SINGLE
 STAGE?

→ EXAMPLE 4.7a (p. 192, Seader
 + 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 25°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?



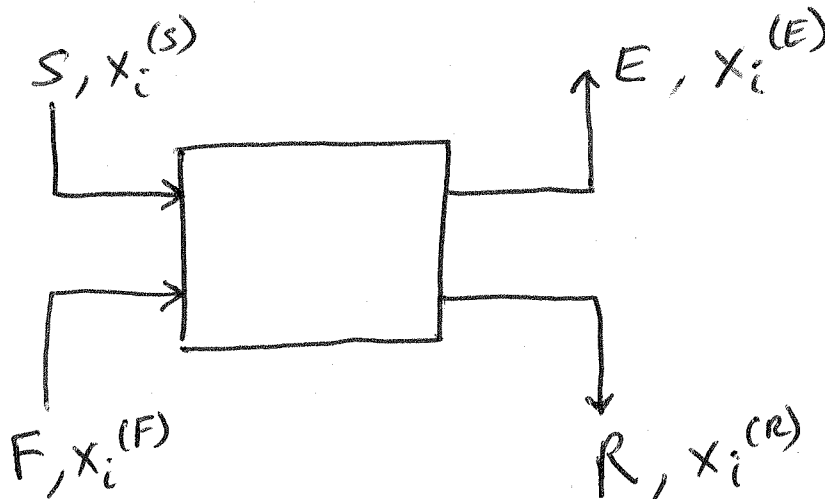
ASSUMPTIONS:

BASIS: 100 g of 45% glycol-water feed

SA	<u>Component</u>	<u>Symbol</u>
	Water	A
	Ethylene glycol	B
	Furfural	C

⇒ Feed (F) 55g A (water)
 45g B (glycol)

⇒ Solvent (S) 100g C (furfural)



MAT'L BALANCE: (OVERALL)

$$M = S + F = E + R$$

COMPONENT BALANCE ON SOLVENT (i=C)

IN = OUT (JUST MIXING)

$$F X_c^{(F)} + S X_c^{(S)} = (F+S) X_c^{(M)}$$

MIXTURE COMPOSITION

SOLVE FOR $\frac{F}{S}$

$$F(X_c^{(F)} - X_c^{(M)}) = S(X_c^{(M)} - X_c^{(S)})$$

$$\frac{F}{S} = \frac{X_c^{(M)} - X_c^{(S)}}{X_c^{(F)} - X_c^{(M)}} = \frac{X_c^{(S)} - X_c^{(M)}}{\underbrace{X_c^{(M)} - X_c^{(F)}}_{\text{slope}}}$$

$$\Rightarrow F = (\text{slope}) S$$

(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,

$$F=S$$

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

$$\left. \begin{array}{l} X_C^{(S)} = 1 \\ X_C^{(F)} = 0 \end{array} \right\} \frac{1 - X_C^{(M)}}{X_C^{(M)} - 0} = 1$$

$$1 - X_C^{(M)} = X_C^{(M)}$$

$$1 = 2X_C^{(M)} \Rightarrow \boxed{X_C^{(M)} = 0.5}$$

Also, from component balance on carrier,

$$1 = \frac{0 - X_A^{(M)}}{X_A^{(M)} - 0.55}$$

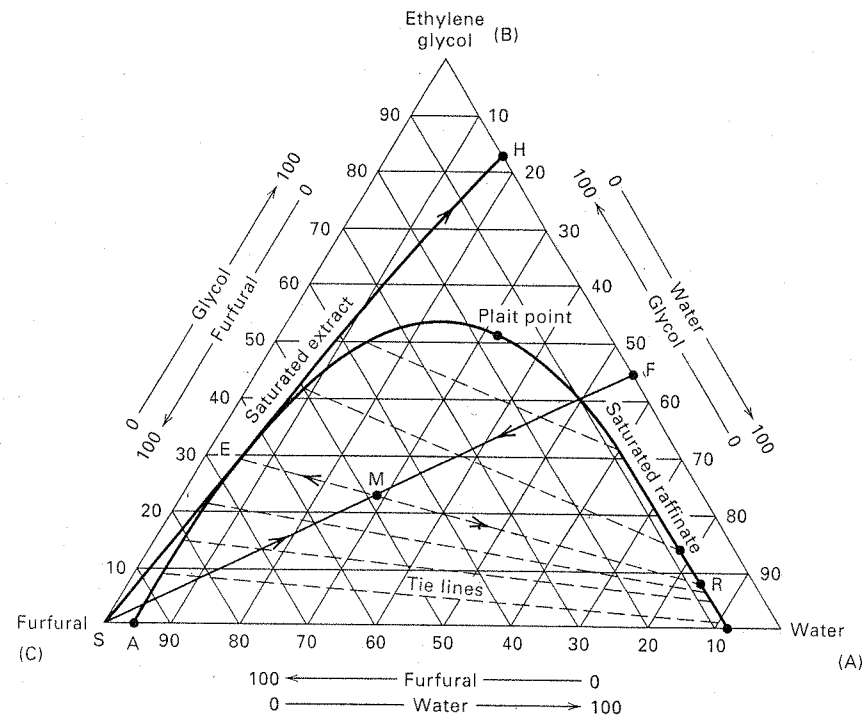
$$X_A^{(M)} - 0.55 = -X_A^{(M)}$$

$$2X_A^{(M)} = 0.55 \Rightarrow \boxed{X_A^{(M)} = 0.275}$$

$$\Rightarrow \boxed{X_B^{(M)} = 0.225}$$

$$(\sum X_i^{(M)} = 1)$$

CAN ALSO GET FROM PHASE DIAGRAM...



NOTE SLOPPY CONSTRUCTION

Figure 4.15 Solution to Example 4.7a.

SEADERT + HENLEY (p.192)

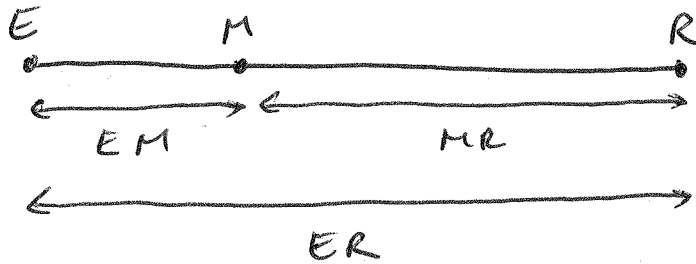
HOW TO GET EXTRACT + RAFFINATE COMPOSITIONS?

FOLLOW TIE LINE

E: $X_A = 0.05$ $X_B = 0.29$ $X_C = 0.665$

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:



+ $E + R = M$ (OVERALL MAT'L BALANCE)

$$\frac{E}{M} = \frac{\overline{MR}}{\overline{ER}} \Rightarrow E = M \left(\frac{\overline{MR}}{\overline{ER}} \right)$$

(MEASURE \overline{MR} + \overline{ER} WITH RULER)

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

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

$$E = 140 \text{ g}$$

$$\Rightarrow R = 60 \text{ g}$$

COMPOSITIONS FROM PHASE DIAGRAM.

SOLVENT-FREE EXTRACT?

LINE THROUGH S + E

WHEN SOLVENT CONC \rightarrow 0

(pt. H)

$$X_{H_2O} = 0.17$$

$$X_{Glycol} = 0.83$$

(feed was $X_{H_2O} = 0.55$, $X_{Glycol} = 0.45$)

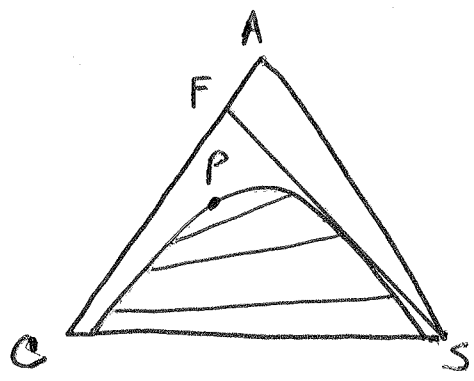
\Rightarrow MULTIPLE STAGES NEEDED.

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:

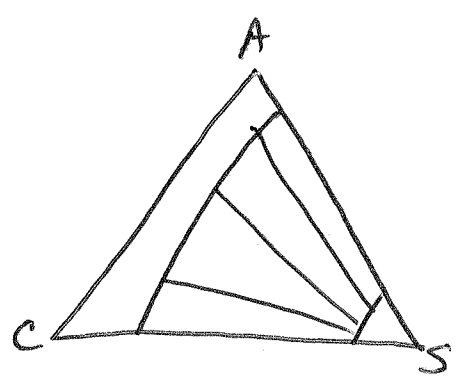
Solute and Solvent infinitely soluble

Advantages:

Good solvent capacity (concentrated in solute)

Disadvantage:

Solvent can't separate all feed compositions.



Type II:

Limited Solute/Solvent Solubility

Advantages:

Can separate any feed composition.

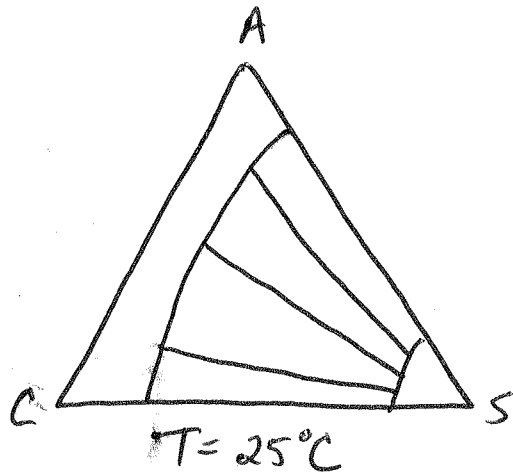
Disadvantage:

Low solvent capacity (need lots of solvent)

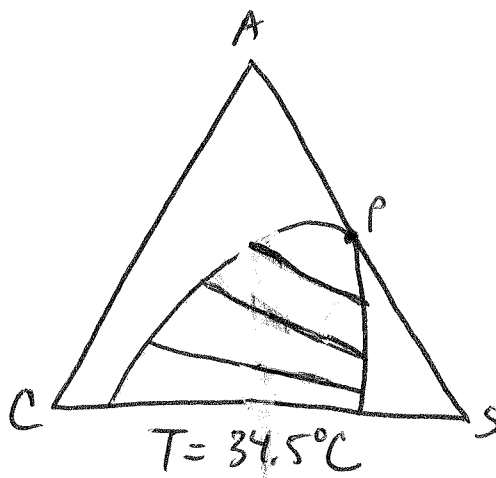
⇒ Usually prefer type I.

TEMPERATURE EFFECTS:

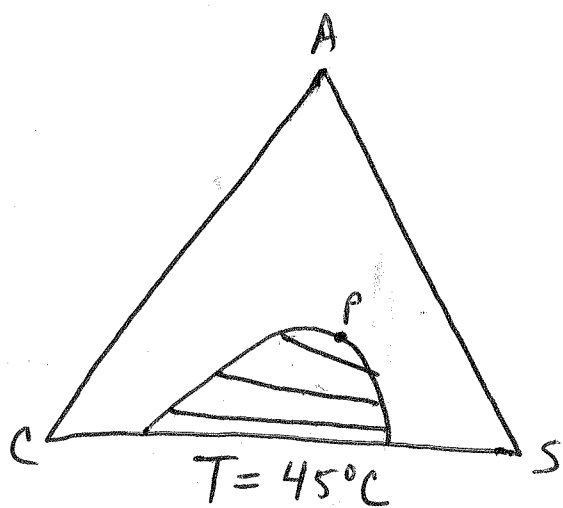
SOLUTE
+
CARRIER
MISCIBLE
AT
ALL TEMPS
+
COMPOSITIONS



LIMITED
SOLUTE
SOLUBILITY
IN SOLVENT.



RAFFINATE
+
EXTRACT
COMPOSITIONS
IDENTICAL



MOVING TO
SOLUBILITY
AT ALL
COMPOSITIONS
(NO SEPARATION)

FINAL NOTE ON DISPERSED PHASE:

CARRIER OR SOLVENT CAN BE THE DISPERSED PHASE. HOWEVER, USUALLY CARRIER IS DISPERSED. WHY?

RAPID COALESCENCE \Rightarrow EASIER TO SEPARATE.
HOWEVER,

\Rightarrow LOWER SURFACE AREA \Rightarrow POOR MASS TRANSFER

NEED TO CONCENTRATE SOLUTE AT INTERFACE

DISPERSED CARRIER

DISPERSED SOLVENT

SOLVENT

CARRIER



SOLUTE CONCENTRATION HIGHEST IN CARRIER.

WHERE IS DIFFUSION DISTANCE SMALLEST?