Liquid – Liquid Extraction

Processos de Separação

LEQB

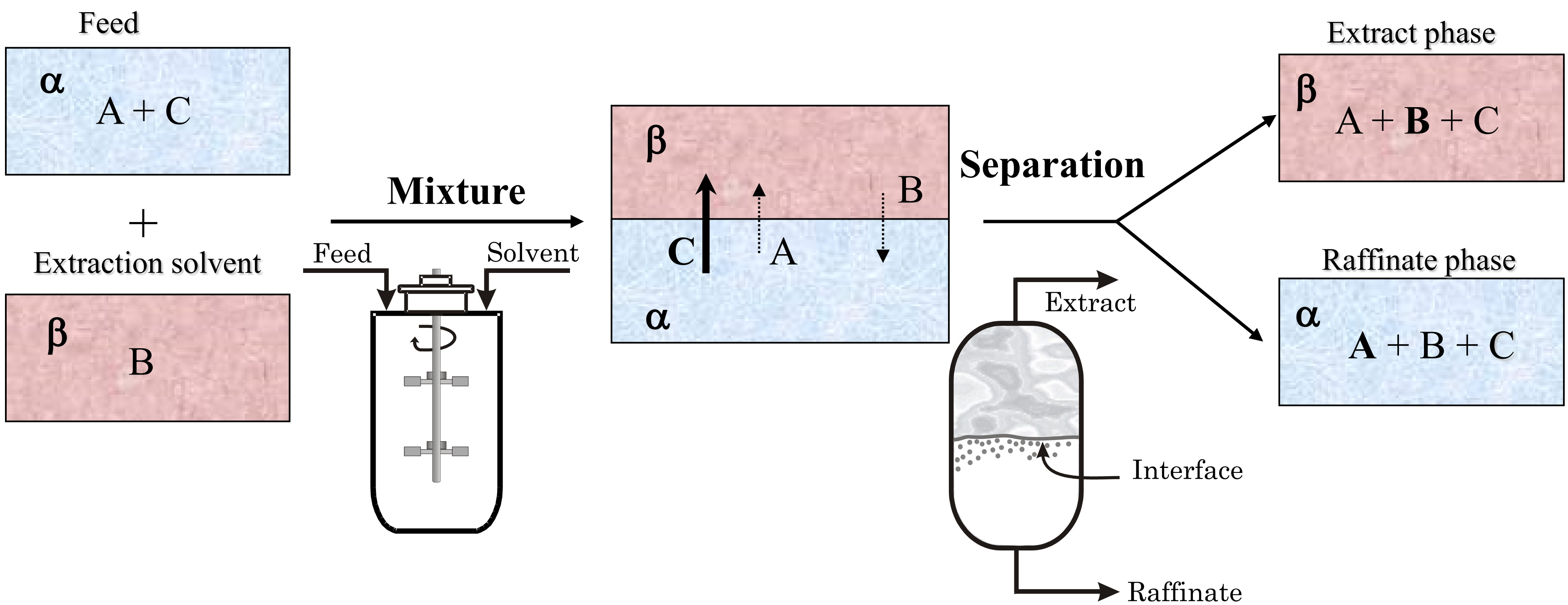
2023/2024

Liquid - Liquid Extraction

Separation of the components of a **liquid** mixture by contact with a **liquid** solvent

Substances from the original solution are distributed **differently** between the two liquid phases

How is it operated?



Solubility of n-hexane in water (25 ºC): 12 mg/L (ppm)

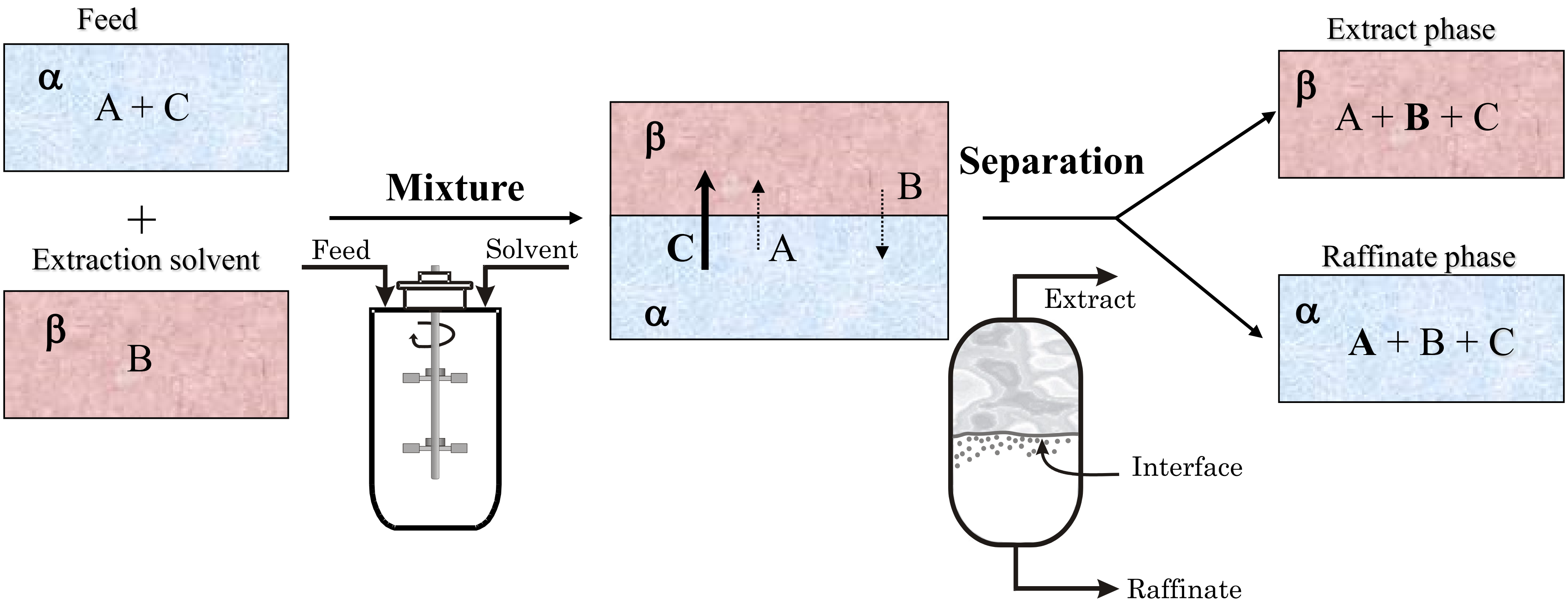
Solubility of water in n-hexane (25 ºC): 90 mg/L (ppm)

Polak & Lu. Can. J. Chem. 51, 4018 (1973)

A: Water (diluent)

C: Acetone (solute)

B: *n*-Hexane (solvent)



Objective ⇨ $m_C|_{\text{Phase } \beta} >> m_C|_{\text{Phase } \alpha}$

A: Water (diluent)

C: Acetone (solute)

B: *n*-Hexane (solvent)

greater complexity of the process!

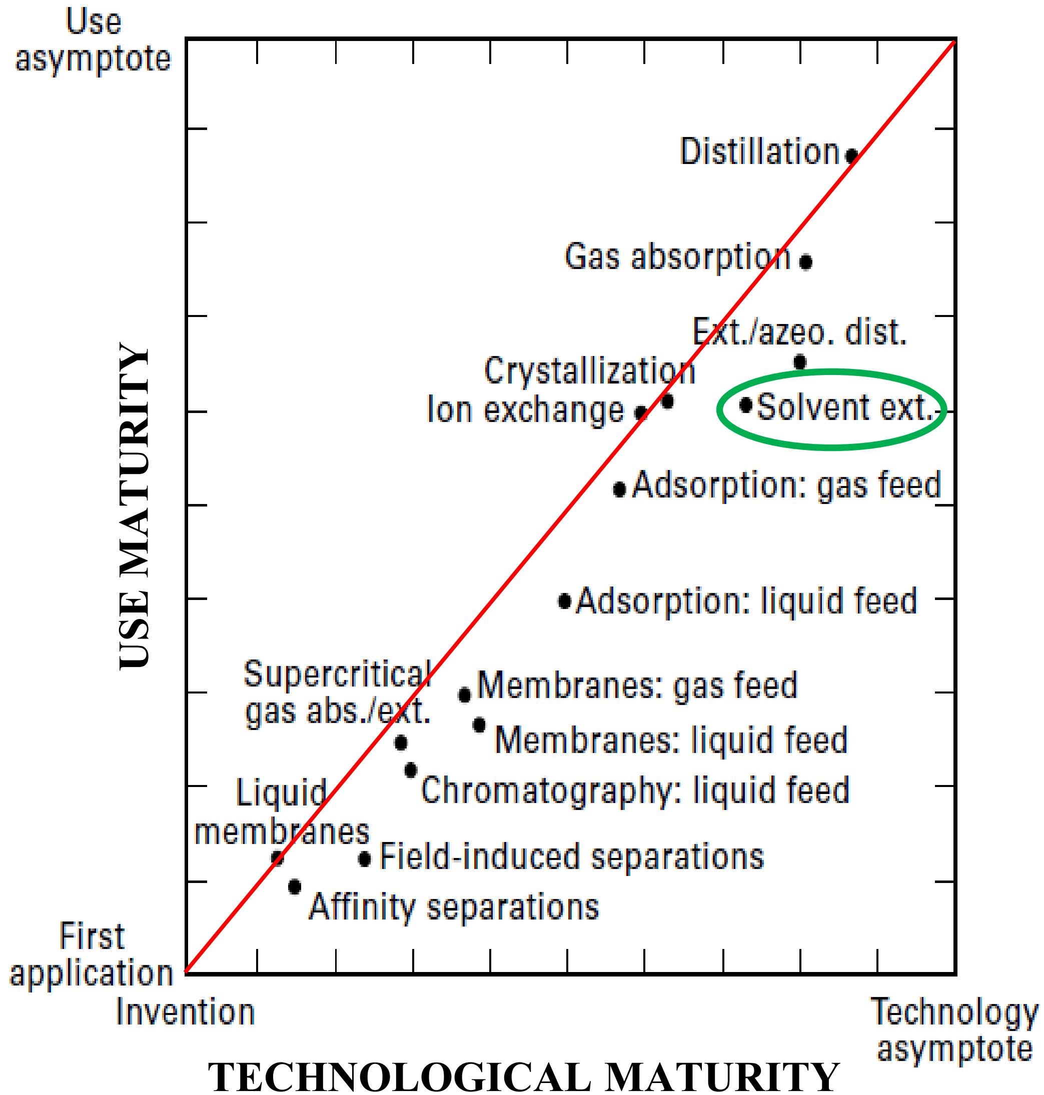
$n_{initial} = 2 \rightarrow n_{final} = 3$

APPLICATION FIELDS

- Competition with other operations (distillation)
    - Dilute aqueous solutions
    - Substances that degrade thermally
    - Mixtures with similar volatilities (separation by distillation is very difficult in such cases)

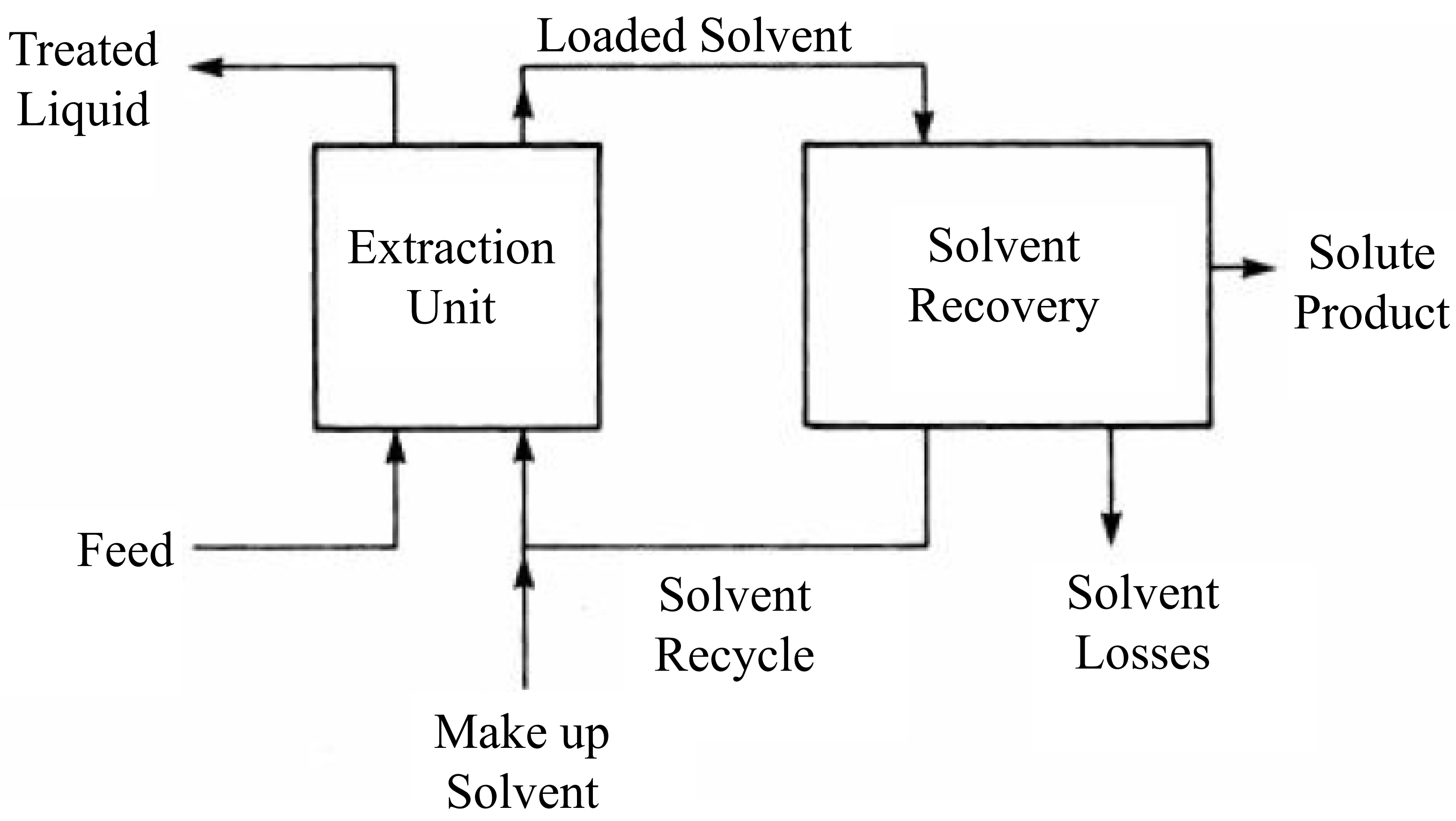
Limitations

- Thermodynamic equilibrium
  - ➢ more complex models (involving activity coefficients, γ)
  - ➢ need for experimental data
- Less technologically mature process than distillation
  - ➢ more complex mass transport process (all the substances partition between the two liquid phases)
- Need to use solvents that ensure simultaneously a good performance, economic and environmental sustainability, and proper safety conditions

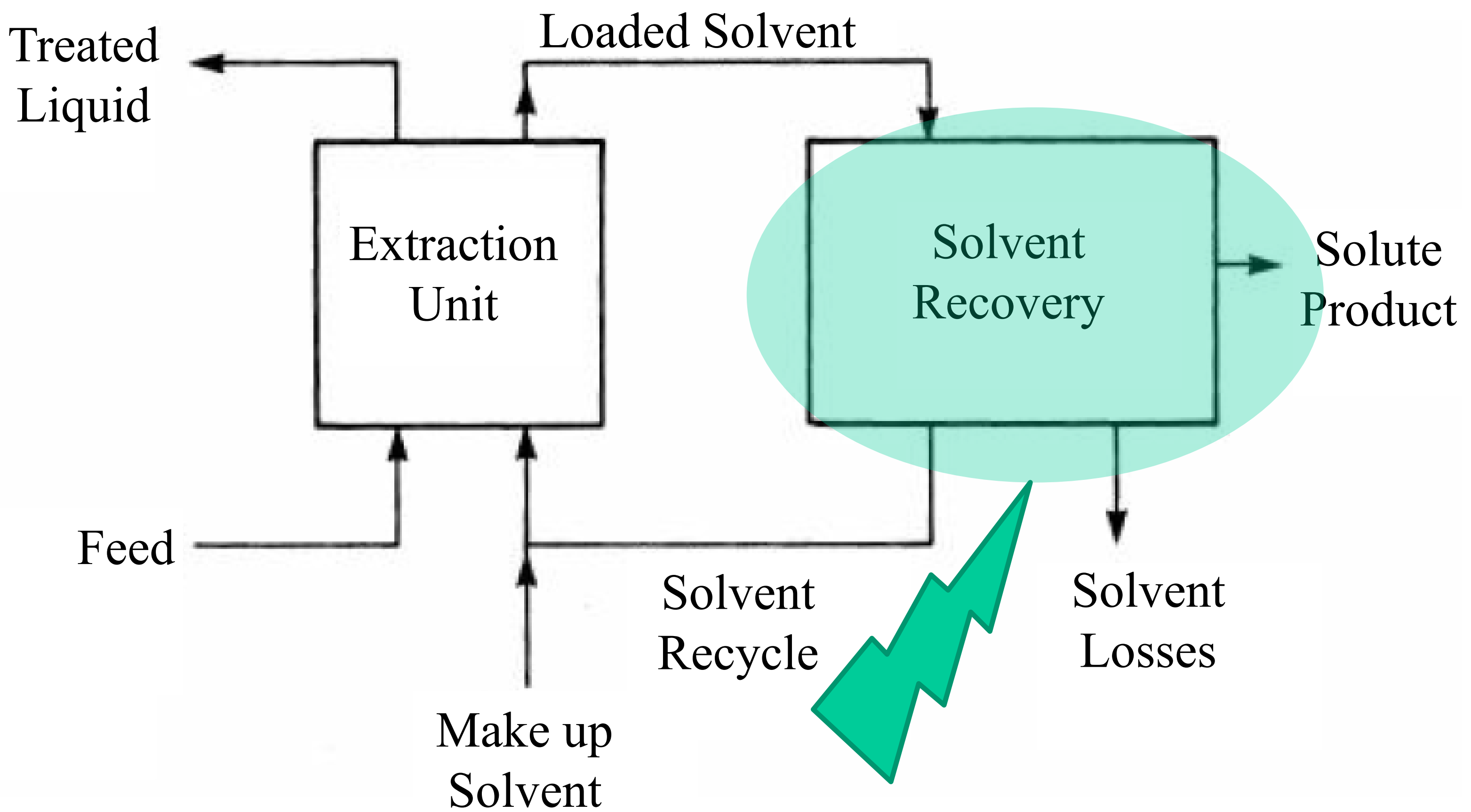


Keller, G.E., II, AIChE Monogr. Ser, 83(17) (1987)

More elaborate process: Two steps minimum!

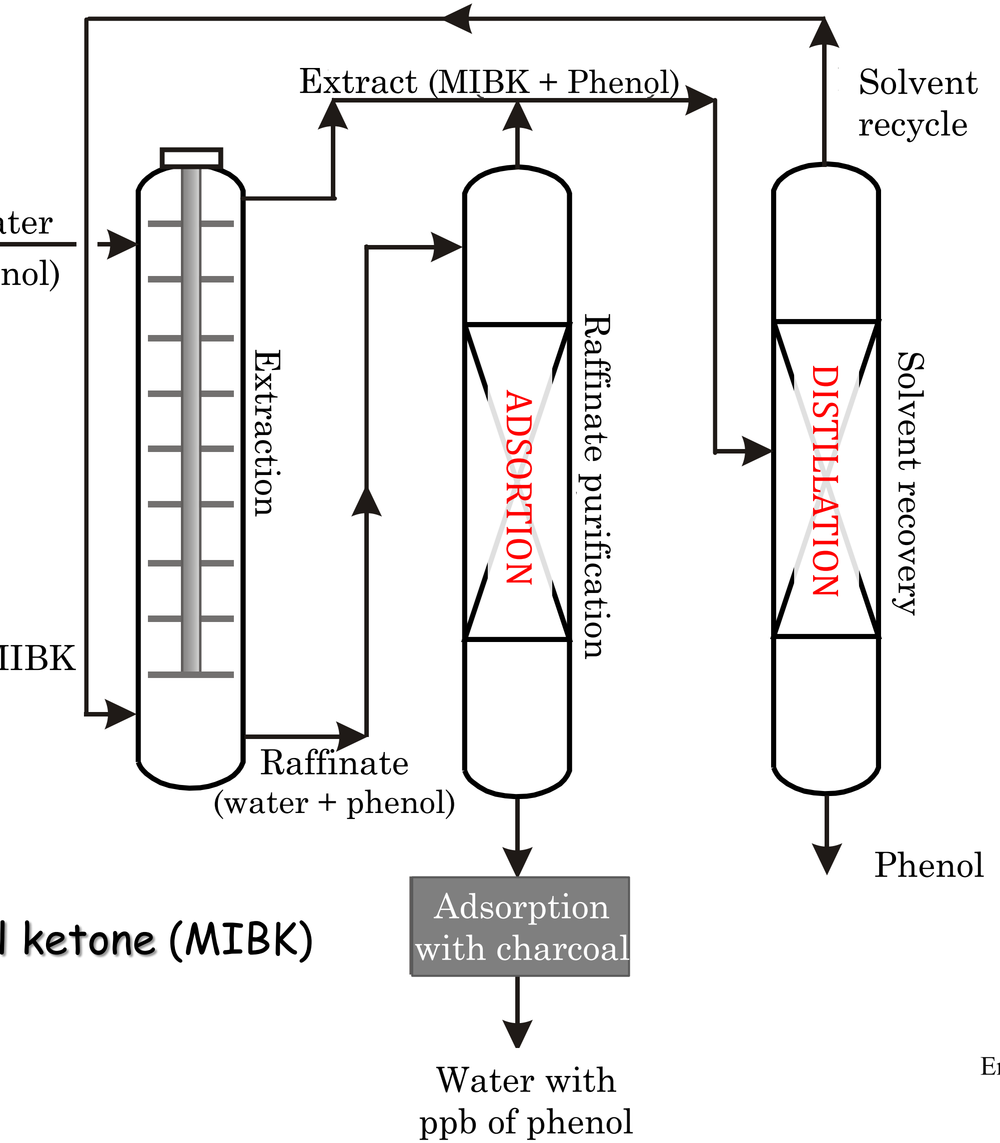


Commonly used solvents: organic compounds (toxic…)

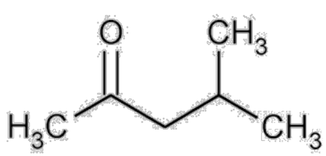


Environmental problems

Wastewater purification process containing phenol



Solvent: **methyl isobutyl ketone** (MIBK)



NOMENCLATURE

Compounds

A – Diluent (Water)

B – Solvent (*n*-Hexane)

C – Solute (Acetone)

Streams

E – extract phase stream

R – raffinate phase stream

S – solvent stream (B)

F – feed stream (A + C)

NOMENCLATURE

Compositions (molar or mass units)

x : fraction of solute C in the raffinate phase

y : fraction of solute C in the extract phase

$$\boxed{x, y = \frac{m_C}{(m_A + m_B + m_C)}}$$

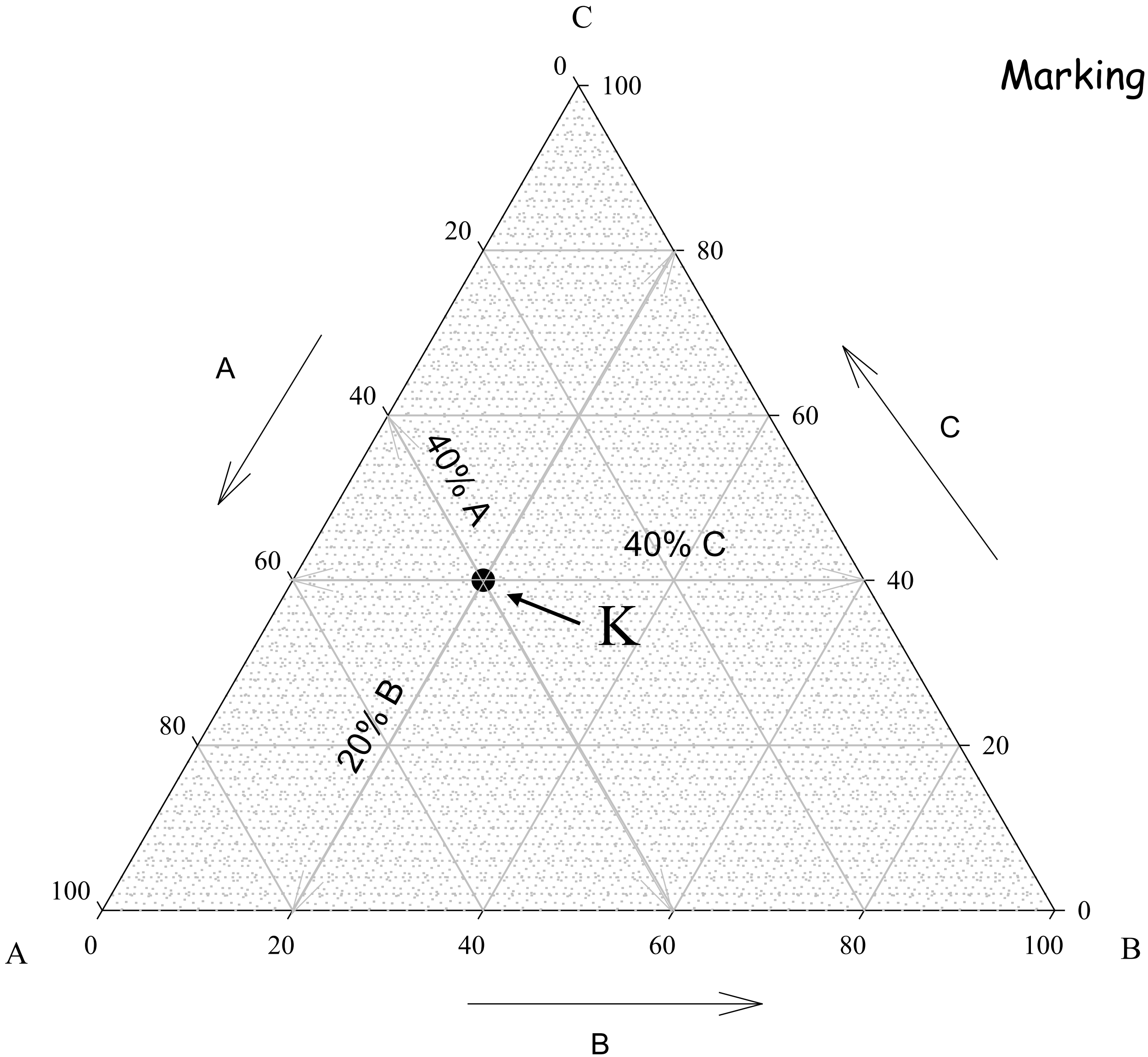
x' $= \frac{x}{1-x}$: ratio of solute C in the raffinate phase

y' $= \frac{y}{1-y}$: ratio of solute C in the extract phase

$$\boxed{x', y' = \frac{m_C}{(m_A + m_B)}}$$

A – Diluent
B – Solvent
C – Solute

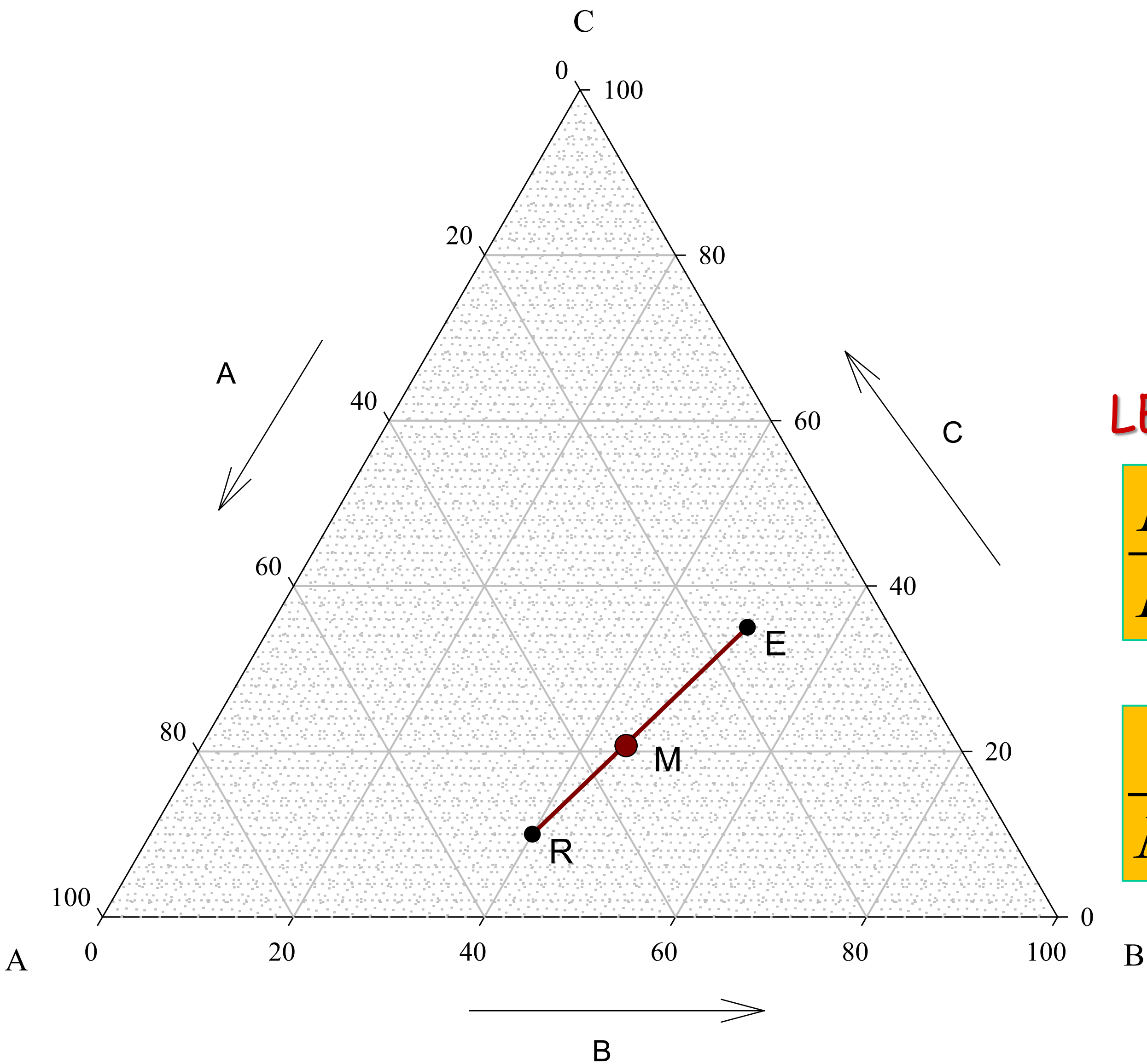
Graphic representation – Ternary Diagram

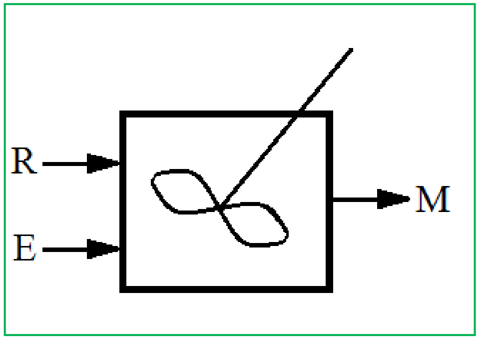


Marking a point - example

K : 40% C
40% A
20% B

Mixing operation - Calculations





$$R + E = M$$

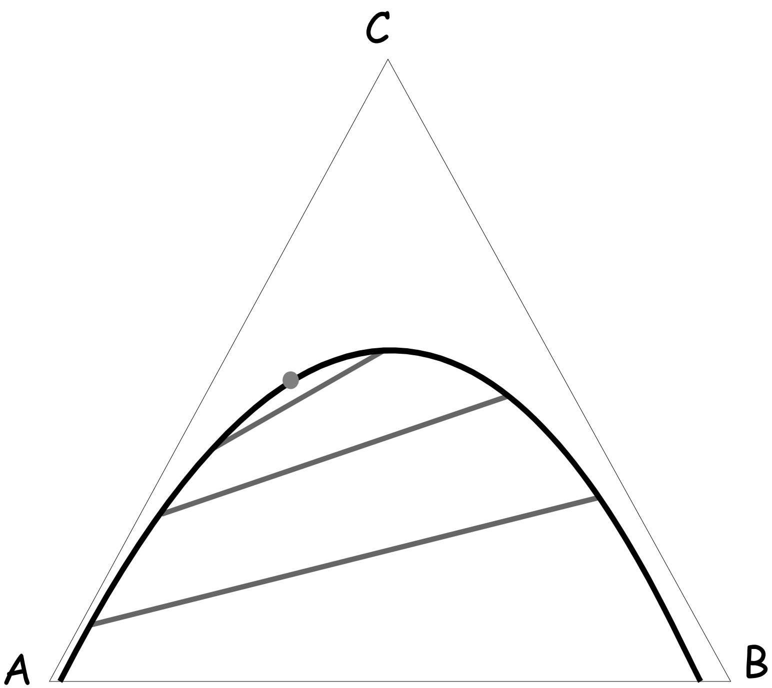
LEVEL-ARM RULE

$$\frac{R}{E} = \frac{\overline{ME}}{\overline{RM}} = \frac{x_M - y_E}{x_R - x_M}$$

$$\frac{R}{M} = \frac{\overline{ME}}{\overline{RE}} = \frac{x_M - y_E}{x_R - y_E}$$

Thermodynamic equilibrium of Liquid - Liquid Systems

❑ 1 PAIR <u>PARTIALLY</u> MISCIBLE



examples:
- water (A) + acetone (C) + *n*-hexane (B)
- water (A) + acetic acid (C) + isopropyl ether (B)

A – Diluent
B – Solvent
C – Solute

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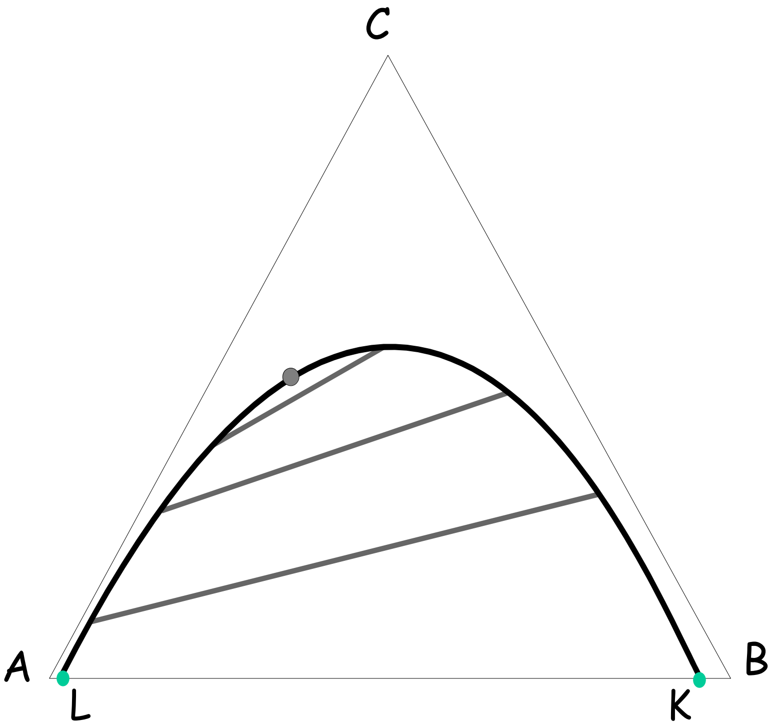

L – solubility of B in A
K – solubility of A in B

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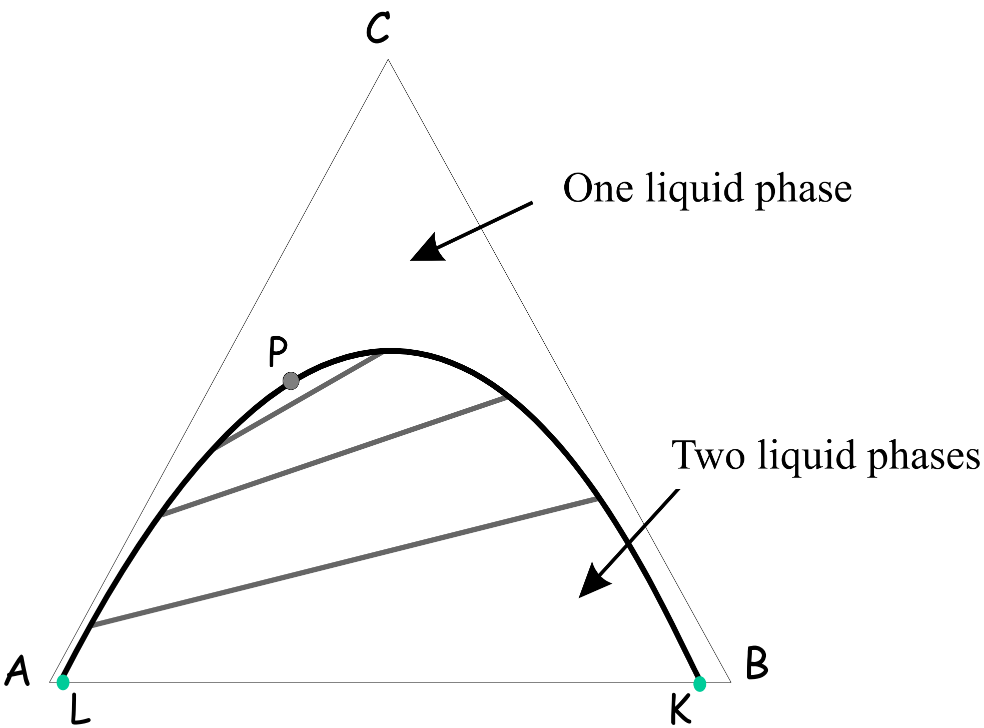

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LPK – **binodal curve**
outside: one phase
inside: two phases in equilibrium

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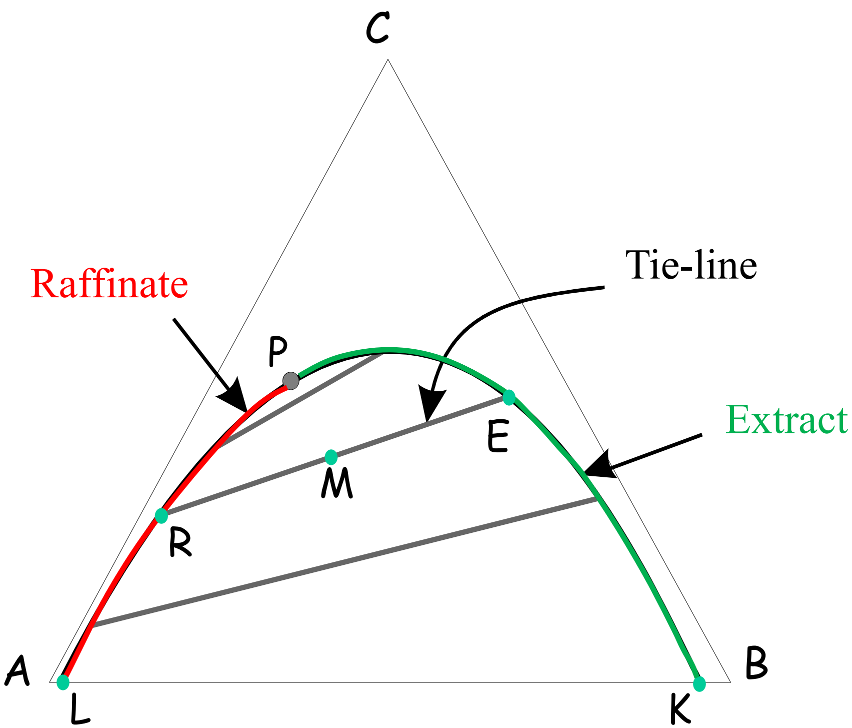

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LPK – binodal curve
outside: one phase
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Extract curve: $\overline{KEP}$
Raffinate curve: $\overline{LRP}$

RME – **tie-line** (*Linha de união*)

P – Plait point (*Ponto de enlace*)

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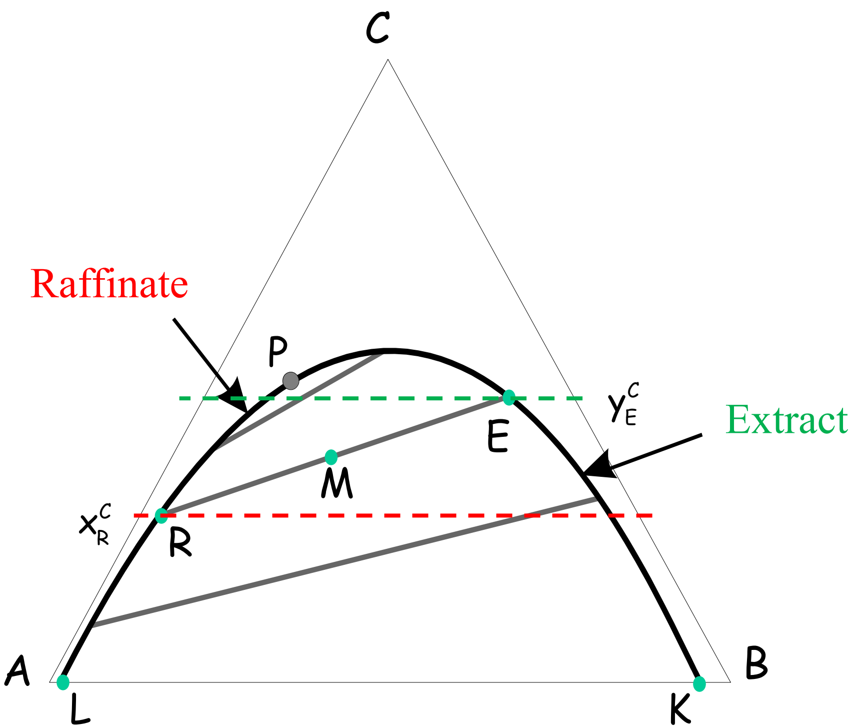

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$y_E^C > x_R^C$ => C partitions more to the extract phase

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Thermodynamic equilibrium of Liquid - Liquid Systems

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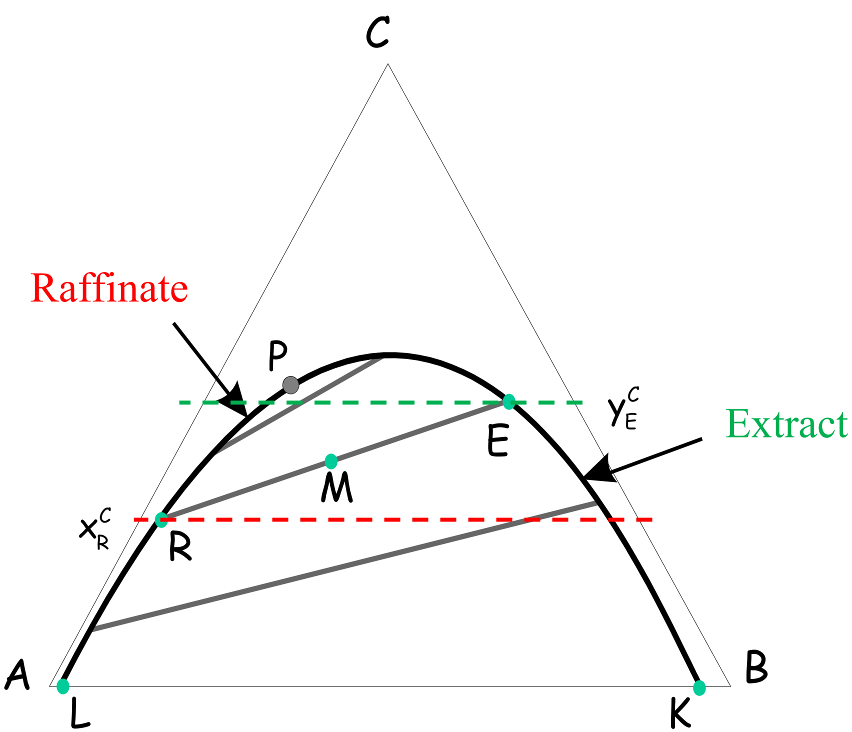

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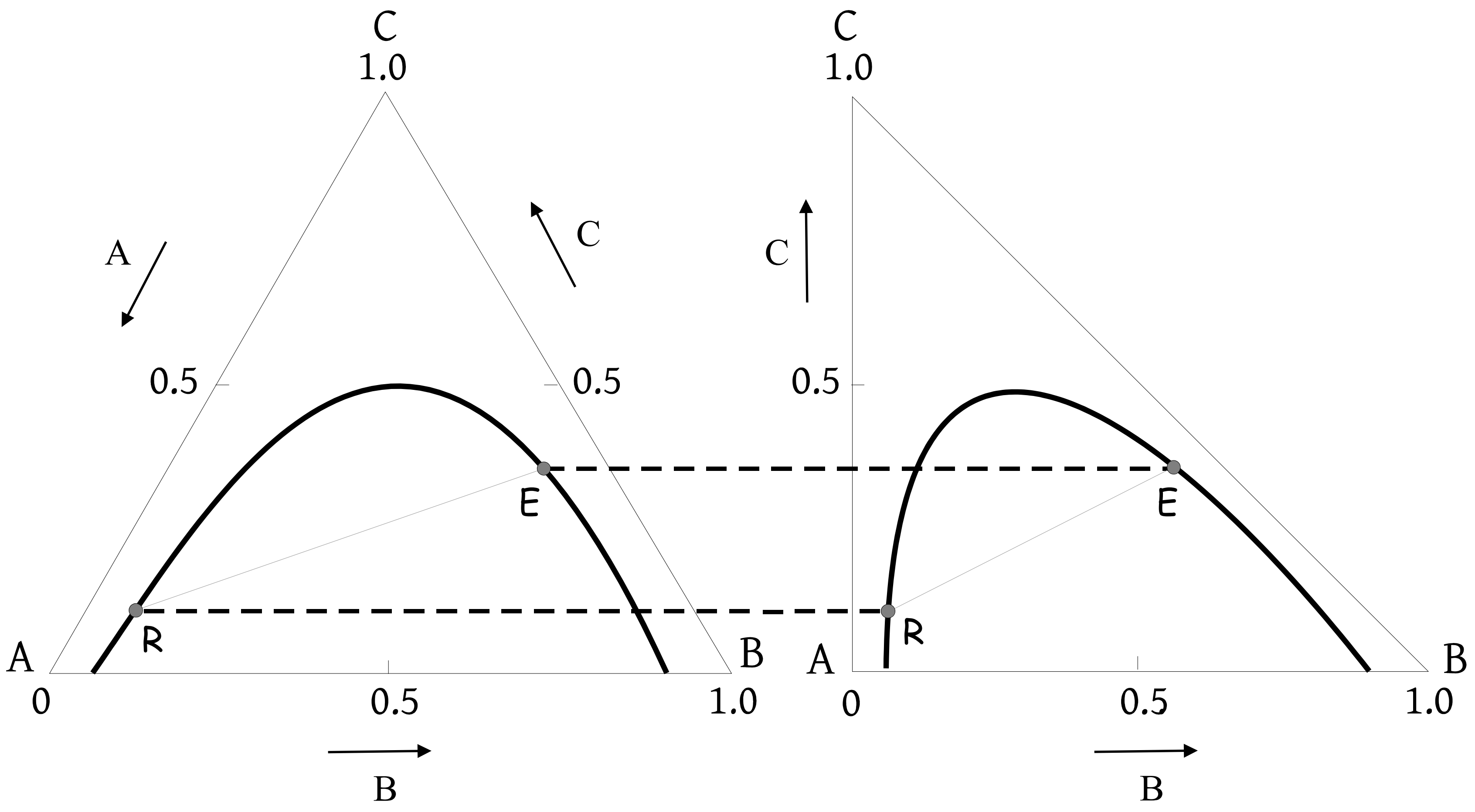
$y_E^C > x_R^C$ => C partitions more to the extract phase

$$K_{D,C} = y_E^C / x_R^C$$ (Distribution coefficient)

$K_{D,C} > 1$ => tie-lines with positive slope

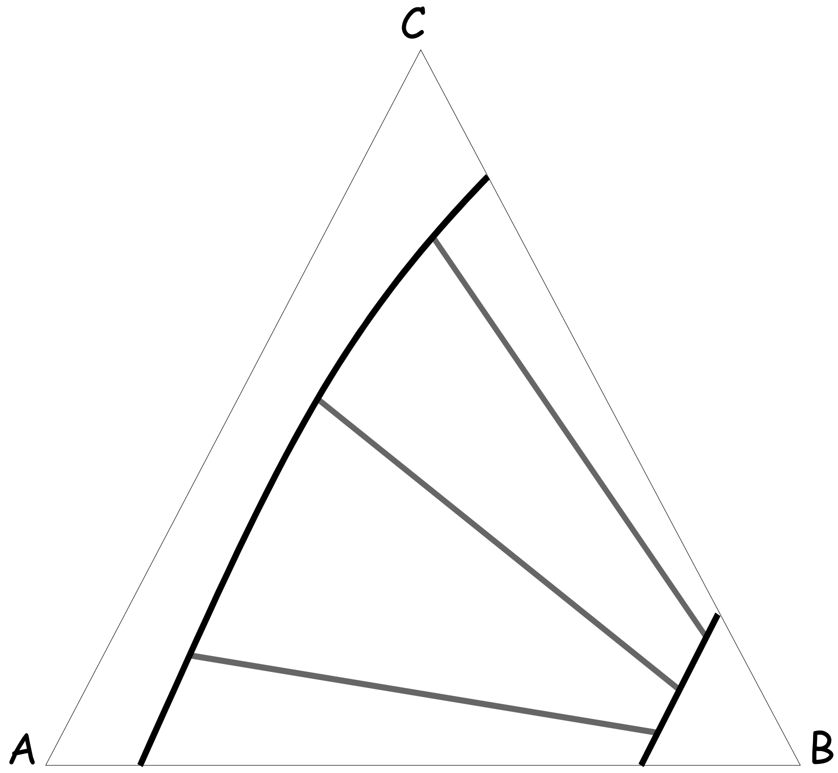
$K_{D,C} < 1$ => tie-lines with negative slope

Right triangular diagram (*Diagrama Rectangular*)



Thermodynamic equilibrium of Liquid - Liquid Systems

❑ 2 PAIRS <u>PARTIALLY</u> MISCIBLE



examples:
- Chlorobenzene (A) + water (B) + methyl-ethyl-ketone (C)
- Heptane (A) + aniline (B) + methylcyclohexane (C)
- Ethylbenzene (A) + dietilenoglicol (B) + styrene (C)

A – Diluent
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Thermodynamic equilibrium of Liquid - Liquid Systems

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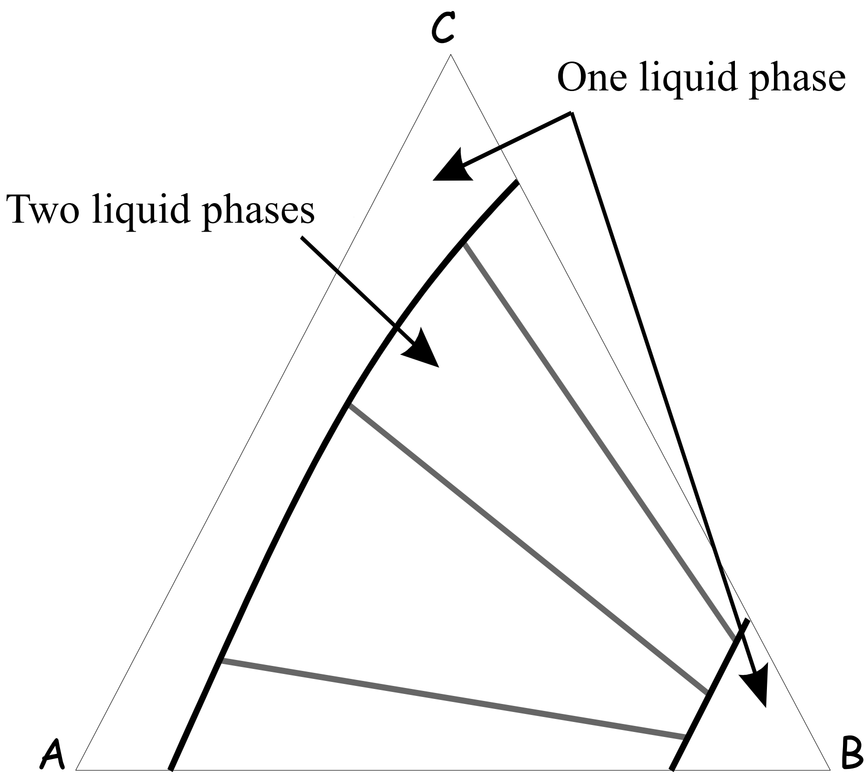

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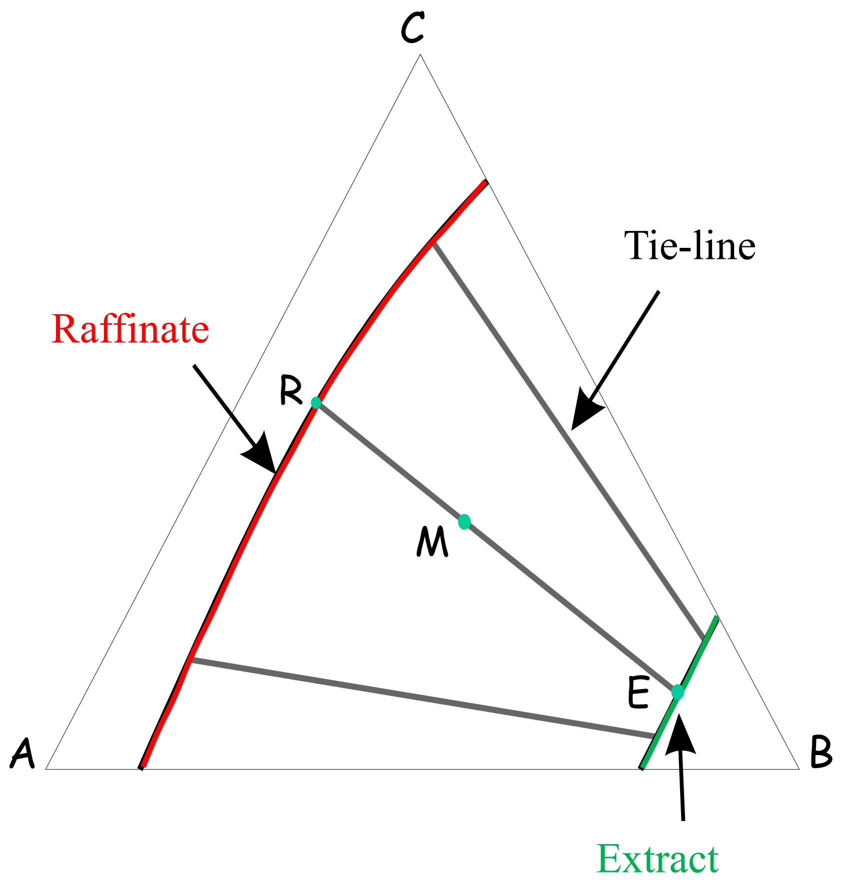

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Thermodynamic equilibrium of Liquid - Liquid Systems

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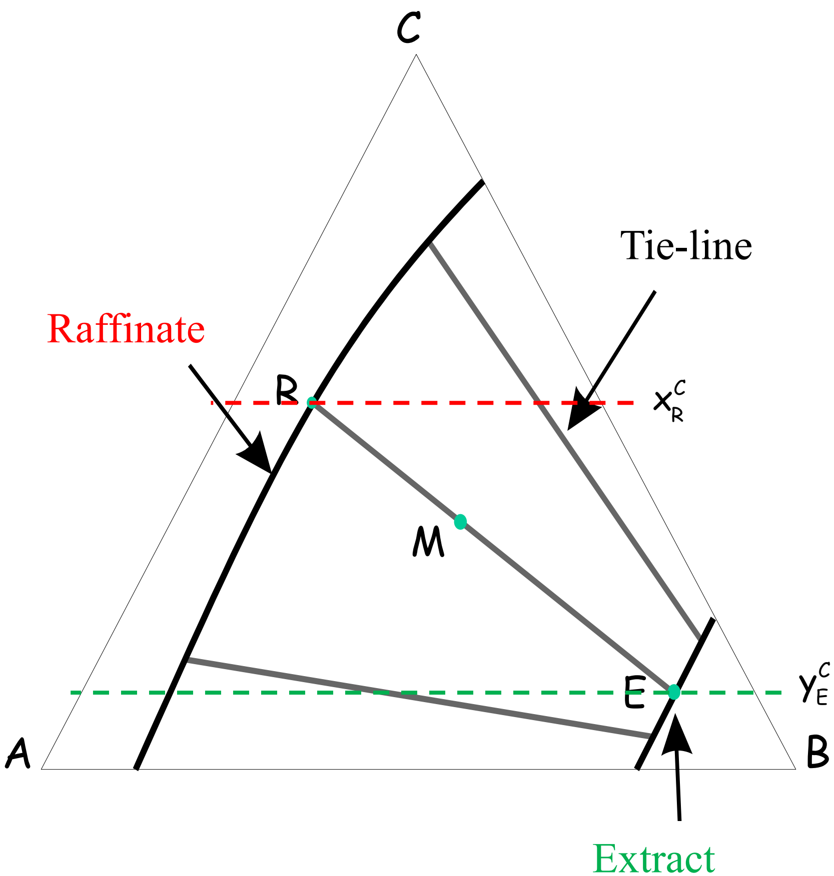


$y_E^C < x_R^C$

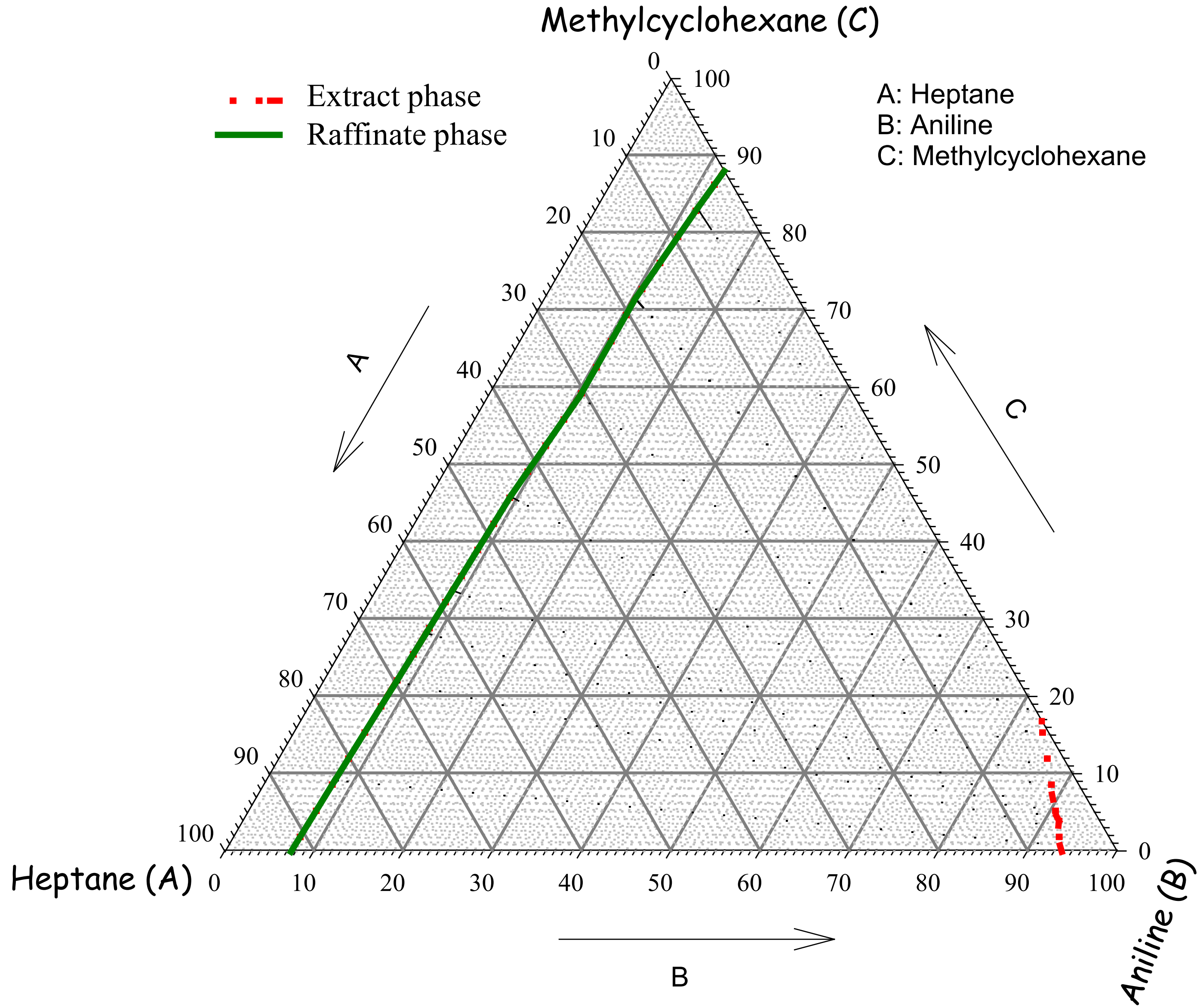
⬇

C is distributed more in the raffinate phase

☞ Impossible the separation?

A - Diluent
B - Solvent
C - Solute

System Heptane-Aniline-Methylcyclohexane



A – Diluent

B – Solvent

C – Solute

System Heptane-Aniline-Methylcyclohexane

R :

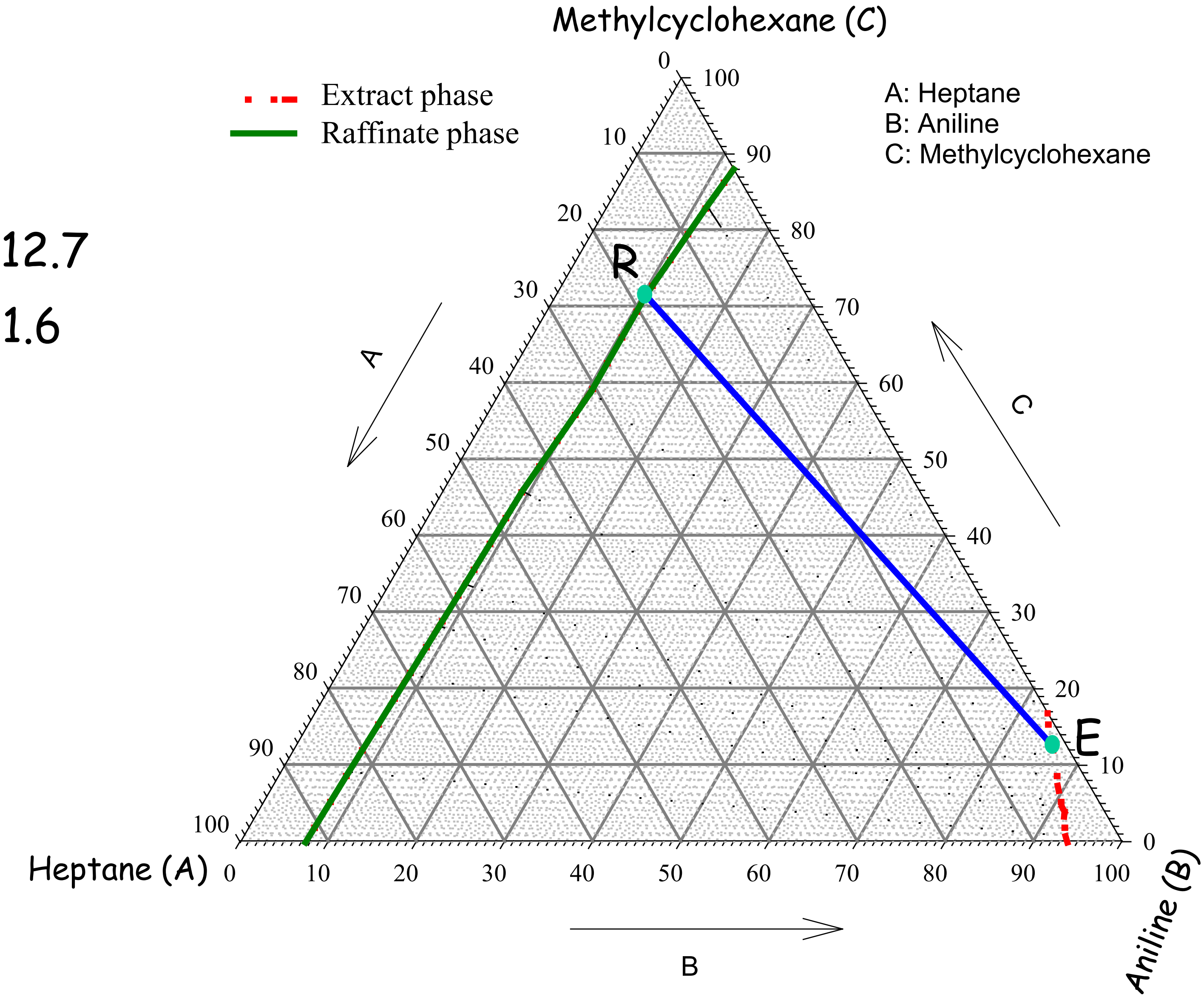
$x_R^C = 71.6$

$x_R^A = 18.2$

E :

$y_E^C = 12.7$

$y_E^A = 1.6$



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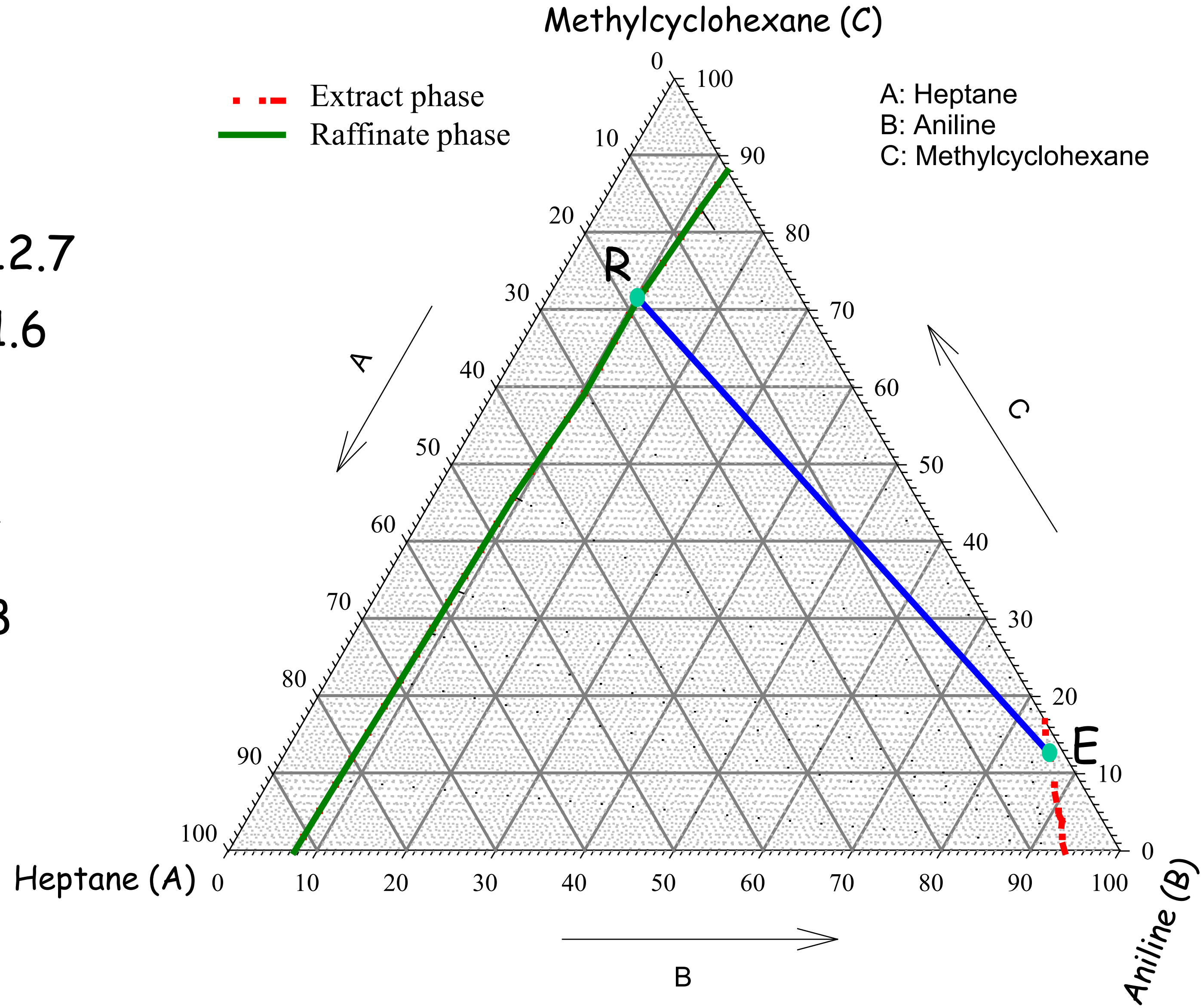
$y_E^A = 1.6$

$$K_{D,C} = y_E^C / x_R^C = 0.177$$

$$K_{D,A} = y_E^A / x_R^A = 0.088$$



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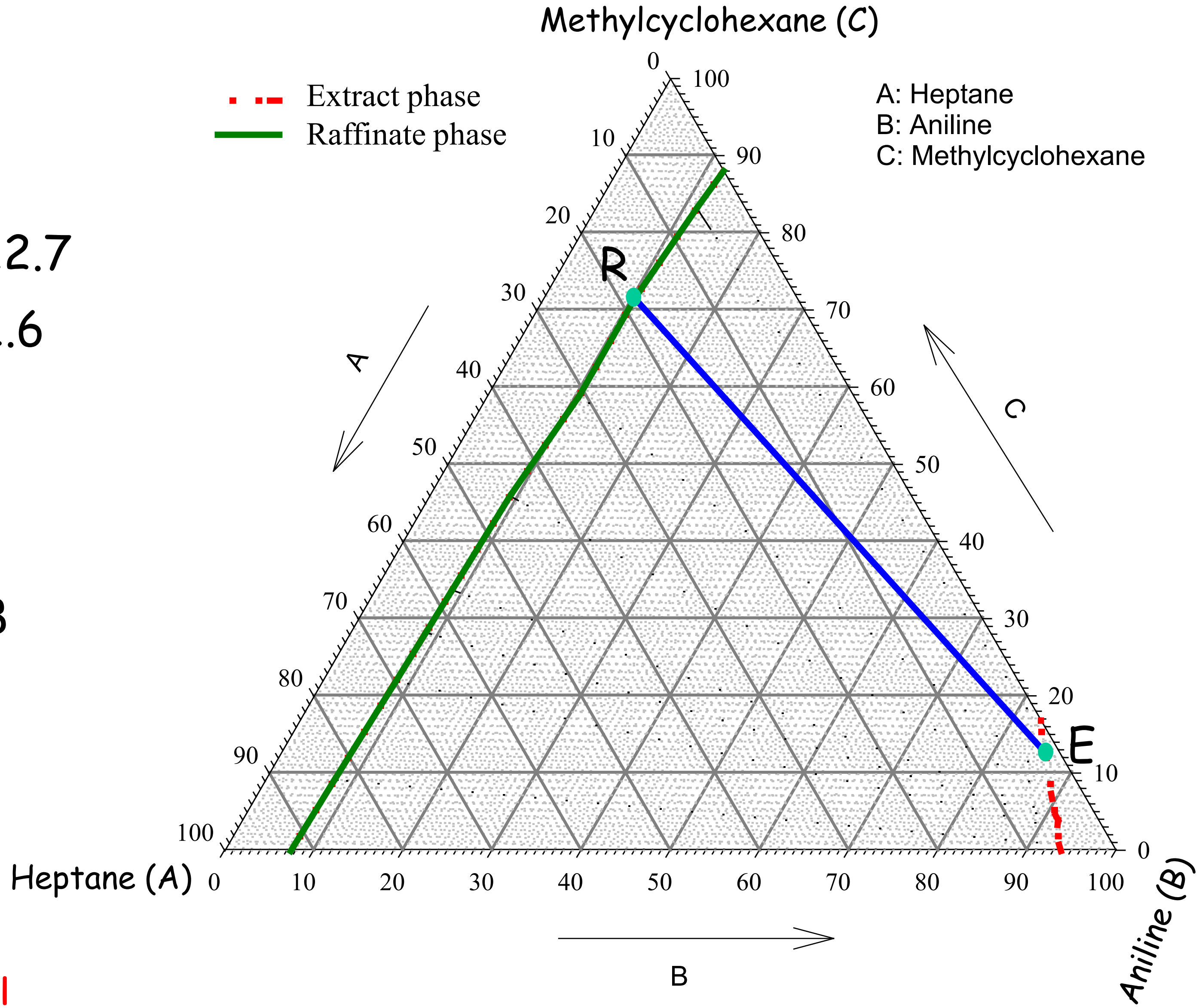
$K_{D,C} = y_E^C / x_R^C = 0.177$

$K_{D,A} = y_E^A / x_R^A = 0.088$

$\Rightarrow K_{D,C} > K_{D,A}$

$\therefore$ Extract rich in C!



Selection criteria when choosing a Solvent

1. Selectivity

Must be ≠ 1

$$\boxed{\beta = \frac{K_{D,C}}{K_{D,A}} = \frac{y_E^C / x_R^C}{y_E^A / x_R^A}}$$

$\beta > 1 \Rightarrow$ separation occurs!

$\beta = 1 \Rightarrow$ no separation!

2. Distribution coefficient

Preferable to be > 1

$$\boxed{K_{D,C} = y_E^C / x_R^C}$$

- Not necessary to be > 1
- > K_D => less solvent loss

3. Solvent recovery

Must be easy → usually by **distillation**

4. Solvents immiscibility

Solvent and diluent should be **immiscible** as possible

5. Density

There must be an appreciable **difference in densities** between the two liquid phases for separation to occur

6. Chemical reactivity

The solvent should be **chemically stable and inert** with respect to the other components of the system and the material

7. viscosity, vapor pressure and freezing point

It should have **low values** to facilitate handling and storage of the solvent

8. Risks

The solvent should be **neither toxic nor flammable**

9. Price

The cost of the solvent should be low

10. Green chemistry

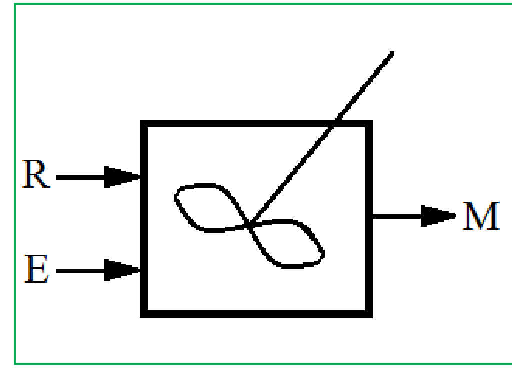
Environmental concerns → "green" solvents, environmentally friendly

=> Elimination of chlorinated solvents; less use of hydrocarbons

=> ALTERNATIVE SOLVENTS!

- ✓ Ionic liquids
- ✓ Supercritical fluids
- ✓ Eutectic solvents

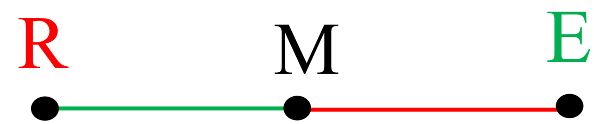
LEVEL-ARM RULE



B.M. global

B.M. partial to C

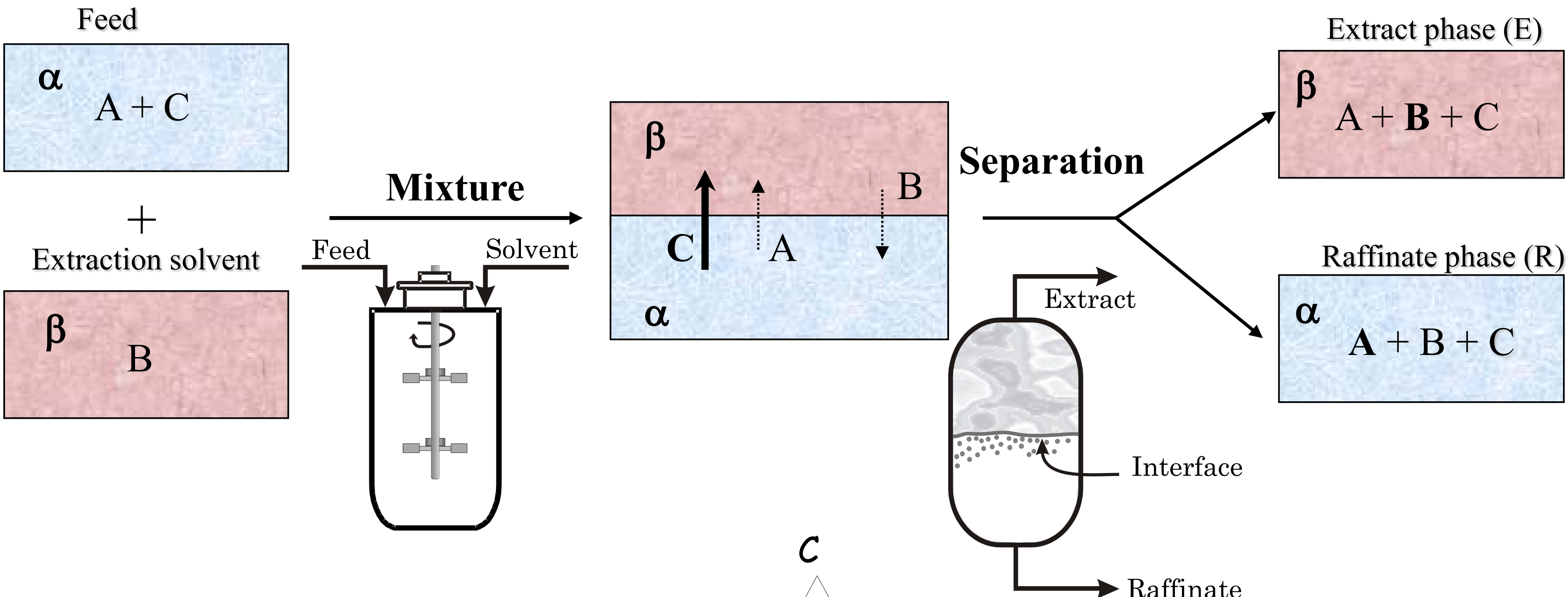
$$\begin{cases} R + E = M \\ Rx_R + Ey_E = Mx_M \end{cases}$$

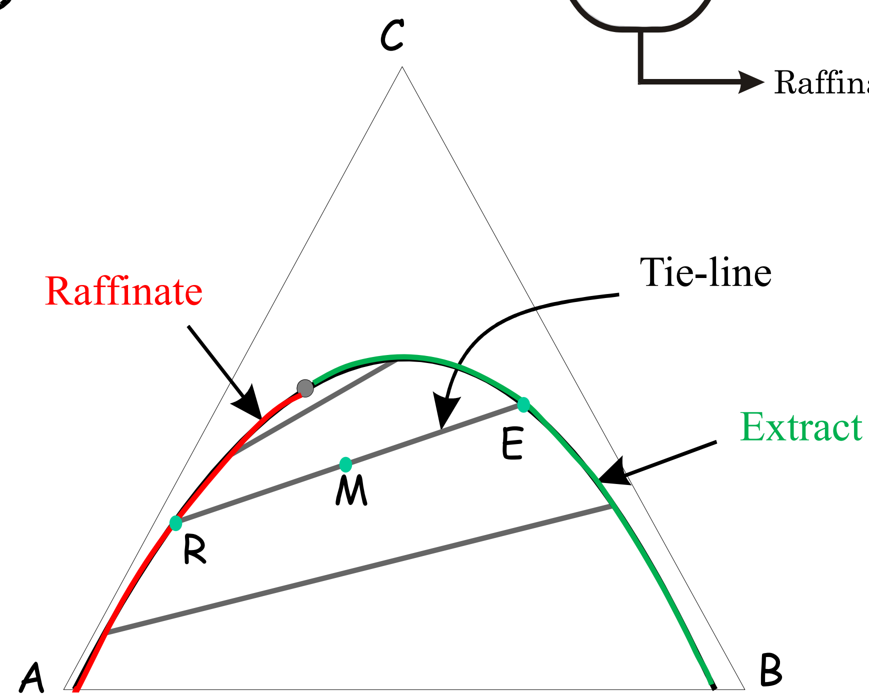


$$Rx_R + Ey_E = (R + E)x_M$$

$$R(x_R - x_M) = E(x_M - y_E)$$

$$\frac{R}{E} = \frac{x_M - y_E}{x_R - x_M} = \frac{\overline{ME}}{\overline{RM}}$$





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