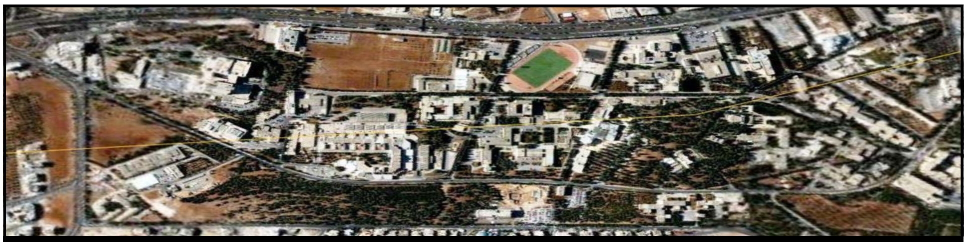

Chemical Engineering Thermodynamics II (0905323)
11-Liquid-Liquid Equilibria (LLE)

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Concepts

- Due to certain stability conditions, some mixtures will split into two (or more) liquid phases e.g., oil and water.
- The equilibrium criteria is the same regardless of the type of phases we have i.e., equality of the fugacities of each species in every phase.

$$\bar{f}_i^{\,I}(T,P,\mathbf{x}^I) = \bar{f}_i^{\,II}(T,P,\mathbf{x}^{II})$$

$$x_i^I \gamma_i^I f_i^I = x_i^{II} \gamma_i^{II} f_i^{II}$$

- If each pure species can exist as a liquid at the given T, then the two phase fugacities are equal for each species

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}$$

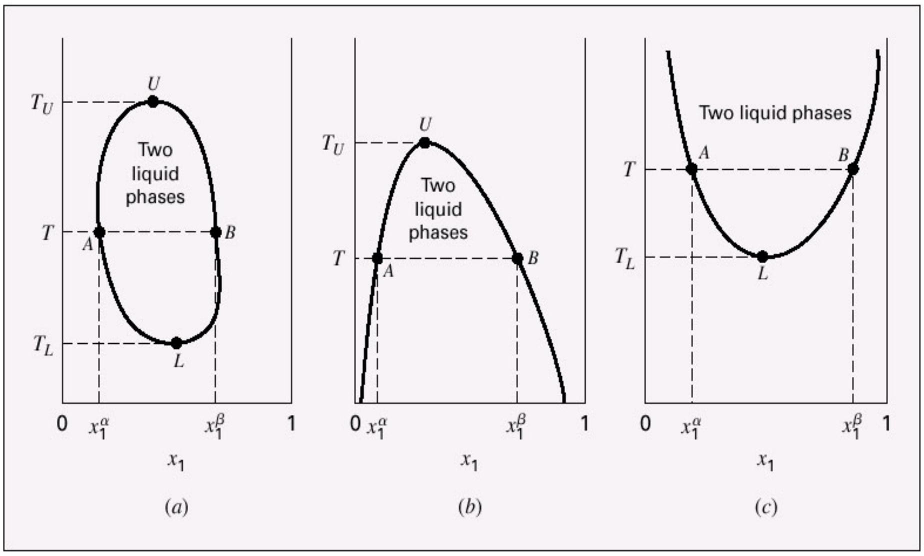
- In this treatment we are concerned with cases that P has negligible or no effect on the activity coefficients and binary systems.

- This equilibrium condition can be utilized to
  - determine solubility of materials with each other if we have a proper model for the activity coefficients,
  - determine the parameters of an activity coefficient model if we make an experimental determination of solubility
- This is achieved using the following equations

$$x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II}$$
$$x_2^I \gamma_2^I = (1 - x_1^I)\gamma_2^I = (1 - x_1^{II})\gamma_2^{II} = x_2^{II} \gamma_2^{II}$$

Representation of Binary LLE Data

- LLE data are usually plotted in a solubility diagram.
  - Solubility diagram are plots of temperature versus the composition of the two phases.
  - Tie lines are the lines connecting the two phases giving their equilibrium compositions



Island: featuring both upper and lower critical (consolute) temperatures	An upper critical (consolute) temperatures	A lower critical (consolute) temperatures

Distribution Coefficient

- When a component "**the solute**" is distributed between two liquid phases we define the distribution coefficient as:

$$K = \frac{\text{Concentration of solute in phase I}}{\text{Concentration of solute in phase II}}$$

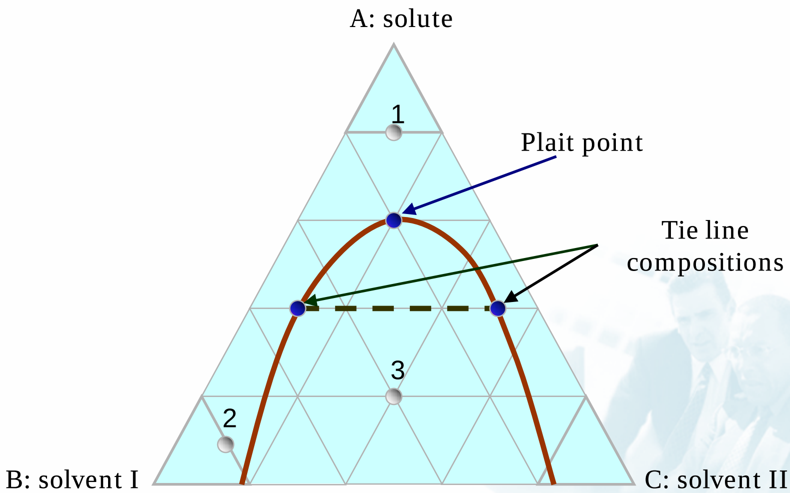
- Equilibrium conditions dictate that

$$K_i = \frac{x_i^I}{x_i^{II}} = \frac{\gamma_i^{II}}{\gamma_i^I}$$

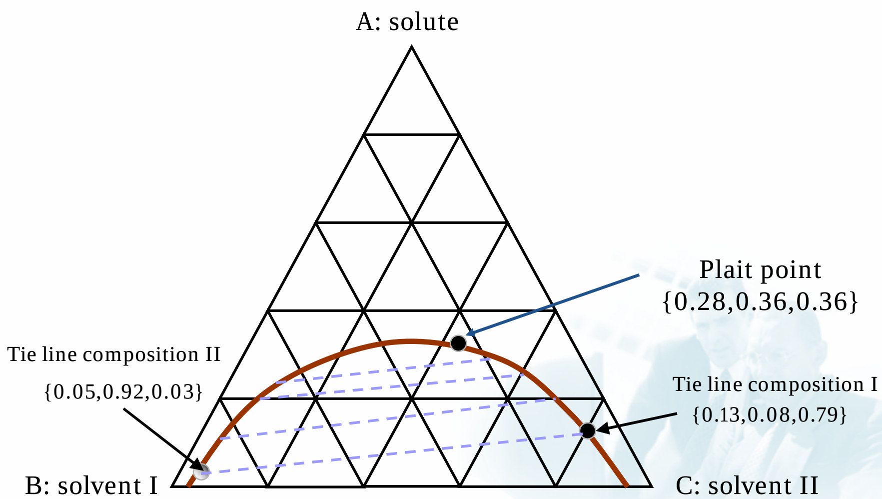
Representation of Ternary LLE Data

- The majority of LLE data deals with ternary mixtures (solvent I-Solute-Solvent II).
  - Usually plotted on a ternary diagram.
  - The ternary diagram are "a smart way" to escape from plotting three dimensional graphs.
  - LLE data takes many shapes depending on the system under study.

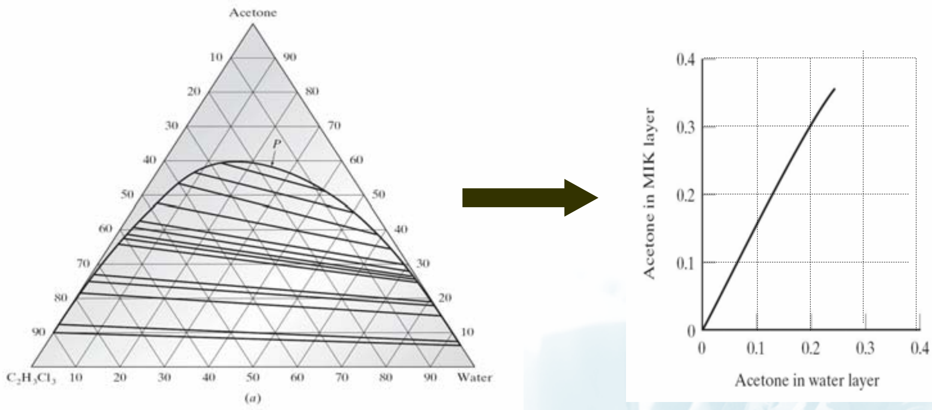
Reading Ternary Diagrams

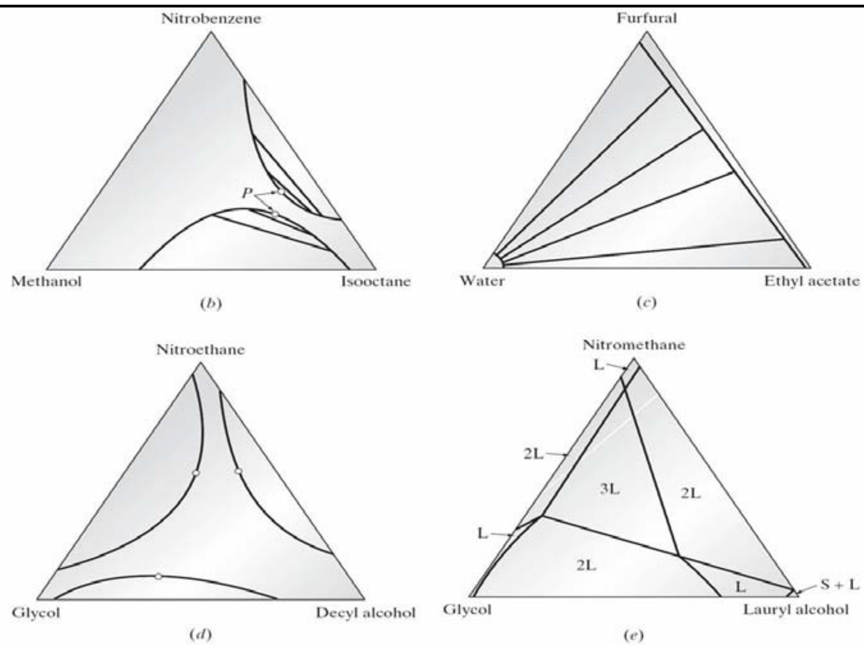


Reading Ternary Diagrams



Distribution Coefficients





Systems with more than Two Liquid Phases