

Mass Transfer Operations II
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Lecture No. 10
Liquid-Liquid Extraction

Welcome to Mass Transfer Operations II course, today I will start discussing on this liquid-liquid extraction, the syllabus is as follows.

Syllabus

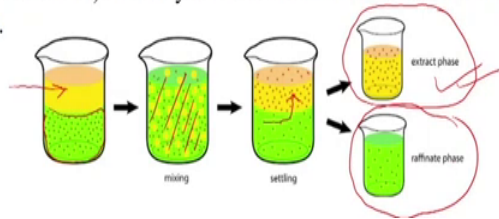
1. Introduction to liquid-liquid extraction; Liquid-liquid equilibria.
2. Effect of temperature on liquid-liquid equilibria.
3. Design calculation of single stage extraction.
4. Design calculation of multistage extraction.
5. Selection of extractors.

Introduction to liquid-liquid extraction; liquid-liquid equilibria. Then effect of temperature on liquid-liquid equilibria, design calculation of single stage extraction, design calculation of multistage extraction and finally selection of the extractors. Now we will be discussing on introduction to liquid-liquid extraction followed by these liquid-liquid equilibria.

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Liquid-Liquid Extraction (LLX)

- Liquid-liquid extraction (LLX) is a mass transfer operation in which a solution (feed: a mixture of solute and carrier liquid) is brought into intimate contact with a second immiscible or slightly miscible liquid (solvent) in order to achieve the transfer of solute(s) from the feed to the solvent.
- The solute rich phase is called the **extract**.
- The residual liquid (feed stream) that may have the little of the solute left in it is called the **raffinate**.



So, in the beginning we need to understand the process liquid-liquid extraction that is liquid-liquid extraction sometimes it is designated as LLX, it is mass transfer operation in which a solution containing this feed that is a mixture of solute and carrier solid is brought into intimate contact with a second immiscible or slightly miscible liquid in order to achieve the transfer of the solute or solutes from the feed to the extracting solvent. The solute rich phase is called the extract and the residual liquid that may have the little of the solute left in it is called raffinate. So if we say this one schematically say the feed is of these dots and with the we can say the carrier solvent it is initially there in the beaker.

And then second liquid actually is fed inside this beaker and it is mixed properly to get this homogeneous mixture and it is allowed for a long period of time so that the two liquids will be separated from each other due to this density difference and the solute or this we can say this one target component that is a dot now is distributed like this maximum amount of dot has gone to this extracting solvent and minimum amount of the solutes are present in the carrier solvent. And if it is allowed for a long period of time then it will be separated into two different liquid phases, this one is that we can say this one rich in the solute that we can say it is an extract phase and the raffinate means the exhaust phase where the we can say the small amount of the solute will be present.

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Extraction Mechanism

- Bringing the feed and the solvent into intimate contact by dispensing one phase into the other as droplets.
- Separation of extract and raffinate phase (different densities).
- Removal and recovery of the solute from the extract phase in a relatively pure form.
- Removal and recovery of solvent from each phase (by distillation usually).

Economics

- In a typical liquid-liquid extraction process, only about 15% of the capital cost goes towards the extractor and the remaining 85% goes towards distillation, other equipment of solvent recovery and product purification. Only 5% operating cost is required for extractor and remaining 95% towards solvent recovery.

Now this extraction mechanism, this is very simple mechanism that firstly we need to bring the feed and the extracting solvent into the intimate contact by dispensing one phase into the other as the droplets. Suppose in the beginning we have the feed with the solute and the carrier solvent and then we will be adding this extracting solvent into this feed and then we have to mix this properly so that it will be dispersed with the droplets. Now depending on the miscibility of the target component that is solute in the extracting solvent say these two will be separated into two different solutes will be moving from this carrier solvent to the extracting solvent. So now we can say the second step will be separation of the extract and the raffinate phases, so it is depended on the density difference between the two solvents.

Now we need to do the third step is that most important step that is removal and recovery of the solute from the extract phase in a relatively pure form, and the fourth one that is we can say this one the residual part that is removal and recovery of the solvent from each phases like this we can say this one from the extract phase as well as raffinate phase, so by distillation usually but there are so many other ways also.

Now if we talk about the economics of the extraction process, then it is very interesting also. In a typical liquid-liquid extraction process, only about 15 percent of the capital cost goes towards the extractor and the remaining 85 percent goes towards the distillation, or we can say this on other equipment of the solvent recovery and product purification. And in terms of we can say on cost, only 5 percent of the operating cost actually is required for extractor and remaining 95 percent towards the solvent recovery. So we can say from the economic point

of view the extraction is not stand-alone process, but it is dependent on other separation process, but if there is no other alternative other than extraction we need to go for that.

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Where extraction favours over distillation????

- ✓ The components to be separated have close boiling points. If the relative volatility is close to unity, number of trays in distillation will be large and extraction will be favoured.
- ✓ Separation of heat sensitive materials, such as antibiotics vitamins etc. (Penicillin ← butyl acetate).
- ✓ Recovery of non-volatile solutes, usually from aqueous solutions, in hydro metallurgy.
- ✓ Recovery of a solute from a very dilute solution.
- ✓ Removal of organics from aqueous streams – phenol from aqueous wastes.

So we will be discussing this one like where the extraction favours over distillation process? So there are so many, but here we are giving some examples like this the components to be separated have these close boiling points. So then distillation using distillation we cannot be separating these two components. If the relative volatility is also are close to unity then number of trays in the distillation column will be very large and then extraction will favour over this distillation process. Sometimes we can say this for heat sensitive material to be separated like antibiotics, vitamins, etcetera using this extraction process then we can say this one in distillation process.

Sometimes recovery of non-volatile solutes, usually from aqueous solutions in hydrometallurgy that is done by extraction process. And suppose for a very dilute solution there we cannot separate using this distillation process or any other processes, but there extraction process can efficiently separate the target components from the dilute solution. And some removal of the organics from the aqueous streams like phenols from aqueous wastes are done by extraction process where that cannot be separated by distillation process.

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Examples of Solvent Extraction

- Extraction of aromatics: Petroleum industry
BTX separation from petroleum fraction by furfural, sulpholane (T.H.Thiophene), NMP, Diethylene glycol, MEK, MIBK etc.
- Recovery and concentration of antibiotics:
Penicillin is produced by fermentation. The concentration in fermentation broth is 20 to 35 gm/L.
Recovery and concentration of penicillin is done using a solvent, such as, amyl acetate, butyl acetate or MIBK.

So few examples of the solvent extraction process we will be discussing here, then we will be going into the details of the extraction process. Like this first example is extraction of aromatics in petrochemical industry like this benzene, toluene, xylene, these are separated from petroleum fraction by furfural, sulpholane or NMP, Diethylene glycol, or Methyl ethyl ketone or Methyl Isobutyl Ketone, etc, these are all extracting solvents. And recovery and concentration of antibiotics like we can say penicillin, it is only recovered using this extraction process other than other mass transfer operations. Like the penicillin is produced by fermentation, we know this one from the fermentation broth we can separate this penicillin using this extraction process.

The concentration of penicillin in the fermentation broth ranges from 20 to 30 grams per litre. And the recovery and concentration of (peni peni) penicillin actually is done usually using solvent such as amyl acetate or butyl acetate or Methyl isobutyl ketone.

Liquid-liquid extraction (LLX) is a mass transfer operation in which a solution (feed: a mixture of solute and carrier liquid) is brought into intimate contact with a second immiscible or slightly miscible liquid (solvent) in order to achieve the transfer of solute from the solute to the solvent.

The solute rich phase is called the extract. The residual liquid (feed stream) that may have the little of the solute left in it is called the raffinate.

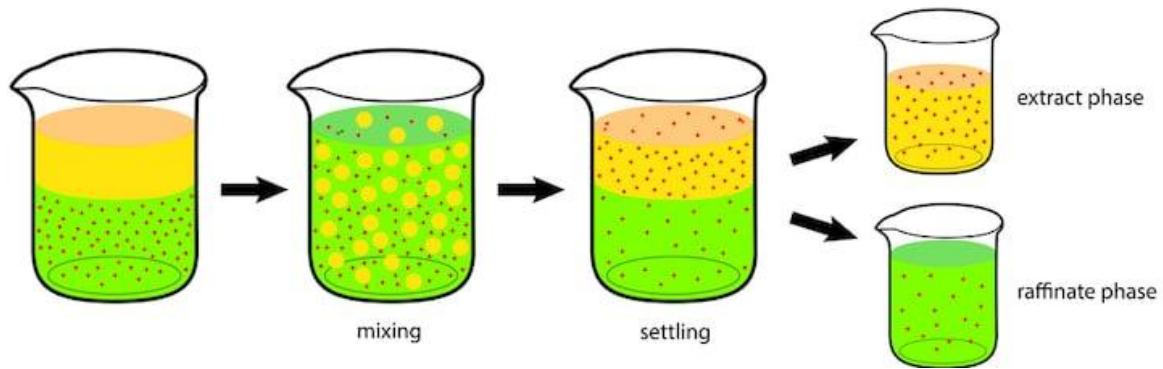


Figure 1

Extraction Mechanism

An extraction process generally involves **four major steps**:

- Bringing the feed and the solvent into intimate contact by dispensing one phase into the other as droplets.
- Separation of extract and raffinate phase (different densities).
- Removal and recovery of the solute from the extract phase in a relatively pure form.
- Removal and recovery of solvent from each phase (by distillation usually).

Economics

- In a typical liquid liquid extraction process, only about 15% of the capital cost goes towards the extractor and the remaining 85% goes towards distillation, other equipment of solvent recovery and product purification. Only 5% operating cost is required for extractor and remaining 95% towards solvent recovery.

Where extraction favours over distillation?

- The components to be separated have close boiling points. If the relative volatility is close to unity, number of trays in distillation will be large and extraction will be favoured.
- Separation of heat sensitive materials, such as antibiotics vitamins etc. (Penicillin $\leftarrow$ butyl acetate).

- 3) Recovery of non-volatile solutes, usually from aqueous solutions, in hydro metallurgy.
- 4) Recovery of a solute from a very dilute solution.
- 5) Removal of organics from aqueous streams – phenol from aqueous esters.

Example of solvent extraction

- 1) Extraction of aromatics : Petroleum industry

BTX separation from petroleum fraction by furfural, sulpholane (T.H.Thiophene), NMP, Diethylene glycol, MEK, MIBK etc.

- 2) Recovery and concentration of antibiotics : penicillin is produced by fermentation. The concentration in fermentation broth is 20 to 35 gm/ltr. Recovery and concentration of penicillin is done using a solvent such as amyl acetate, butyl acetate or MIBK.

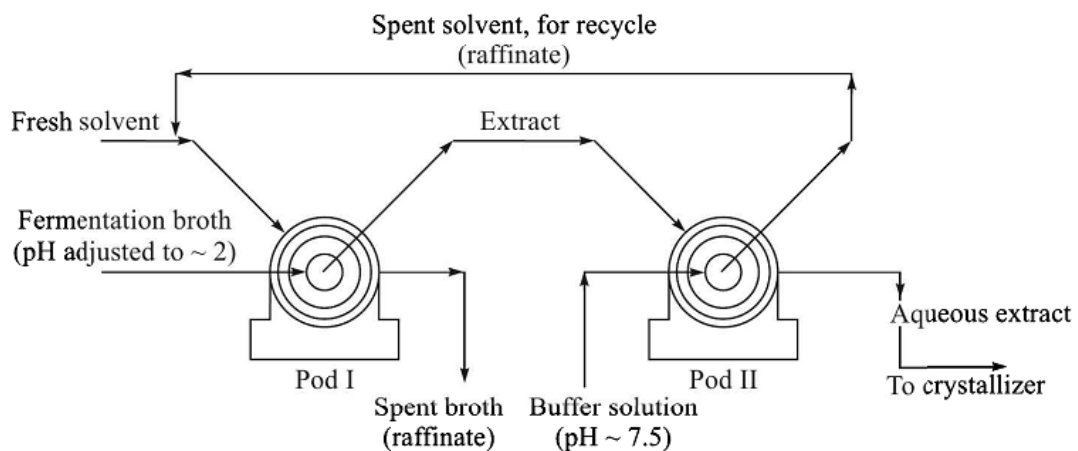


Figure 2: Flow sheet diagram for penicillin production.

At a pH of about 2, penicillin remains in the acid form and has a low solubility in water. But it is favourably transported to an organic solvent from aqueous fermentation broth because of a high distribution coefficient. A reversal of distribution coefficient occurs at a pH above 7.0. This pH dependent distribution of penicillin in the water ester pair is made use of to recover, purify and concentrate from broth. The experiments are carried out at 40°C.

3) Extraction of caprolactum :

It is used for manufacture of Nylon-6. It is synthesized from cyclohexane. (cyclohexane $\rightarrow$ cyclohexanol $\rightarrow$ cyclohexanone $\rightarrow$ cyclohexanone oxime $\rightarrow$ caprolactum). The last step of the process involves reaction of oxime with H_2SO_4 and forms caprolactum and $(\text{NH}_4)_2\text{SO}_4$. The reaction mixture separates into an organic rich phase ("lactum oil" containing 65 – 70% caprolactum). These two phases are fed at appropriate locations of a "Rotating disk contractor". Toluene is used as solvent phase. Caprolactum goes to the extract and $(\text{NH}_4)_2\text{SO}_4$ remains in the raffinate. These two streams are further treated to get caprolactum in a pure form and to recover the solvent and $(\text{NH}_4)_2\text{SO}_4$.

4) Other applications :

Food, Pharmaceuticals, Metallurgical, Environmental and Organic & Inorganic industries.

Liquid-Liquid equilibria (LLE)

A liquid-liquid extraction system contains at least three components – solute(C) , carrier liquid in the feed (A) and extracting solvent (B).

Classification of ternary systems

Three binary systems can be formed, A-B, B-C, C- A. Mutual miscibility behaviour of the component determines the nature of equilibrium diagram

Categories

- a) The carrier (A) and extracting solvent (B) are practically immiscible.
- b) The solute(C) is miscible with carrier (A) and solvent (B) in all proportions. $\rightarrow$ **Type I**
- c) The solute (C) is completely miscible with carrier (A) but both solute (C) and carrier (A) have limited miscibility with the solvent (B). $\rightarrow$ **Type II**

Equilateral triangular co-ordinates :

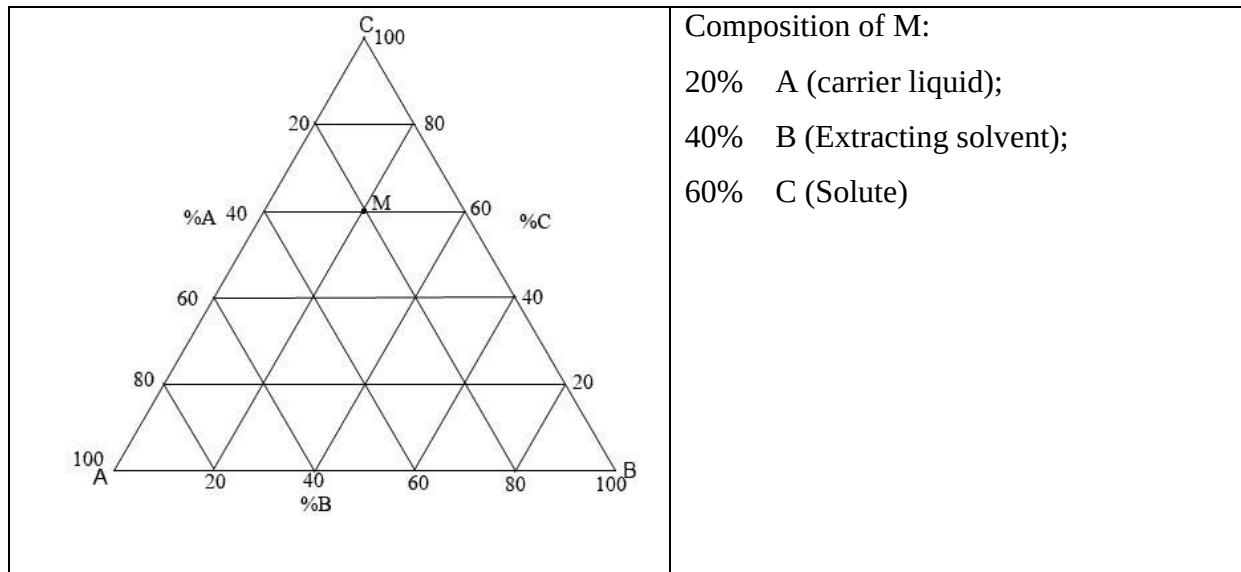


Figure 3: Equilateral triangular co-ordinates.

TYPE I

C is miscible with A and B: curve RPS is equilibrium diagram

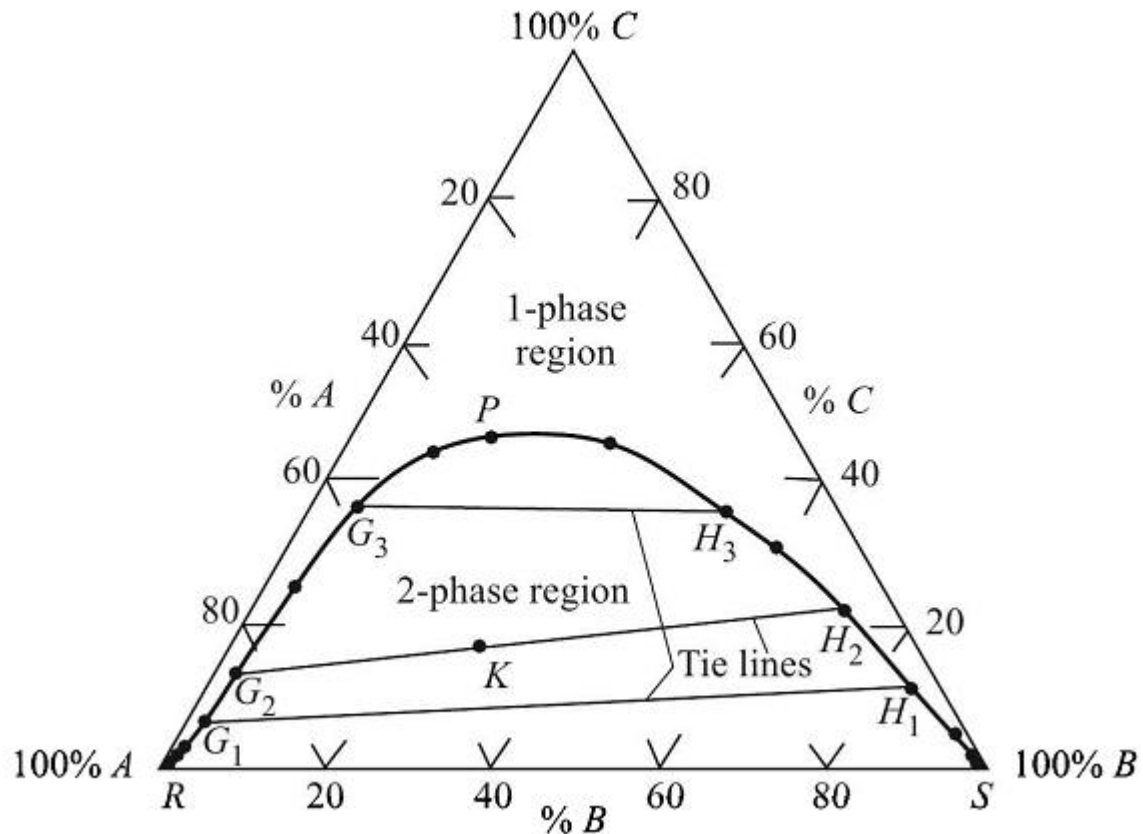


Figure 4: Liquid- Liquid equilibrium data.

Curve RPS is equilibrium diagram.

G_1 and $H_1 \rightarrow$ Two liquid phases in equilibrium

G_1 is rich in carrier (Raffinate)

H_1 is rich in solvent (Extract)

$G_1H_1 \rightarrow$ Tie line

** Point “P” demarcates the raffinate and extract sides of equilibrium curve and is called “**plait point**”. The type of curve RPS is called “binodal” because it has two arms RP and PS.

A liquid mixture having “overall composition” corresponding to a point K is a two phase mixture. Keep undisturbed it separates into two phases at equilibrium. The compositions are G_2 and H_2 . Amounts are given by “Lever arm rule”.

$$G_2/H_2 = KH_2/KG_2$$

TYPE II

A-B and B-C are partially miscible

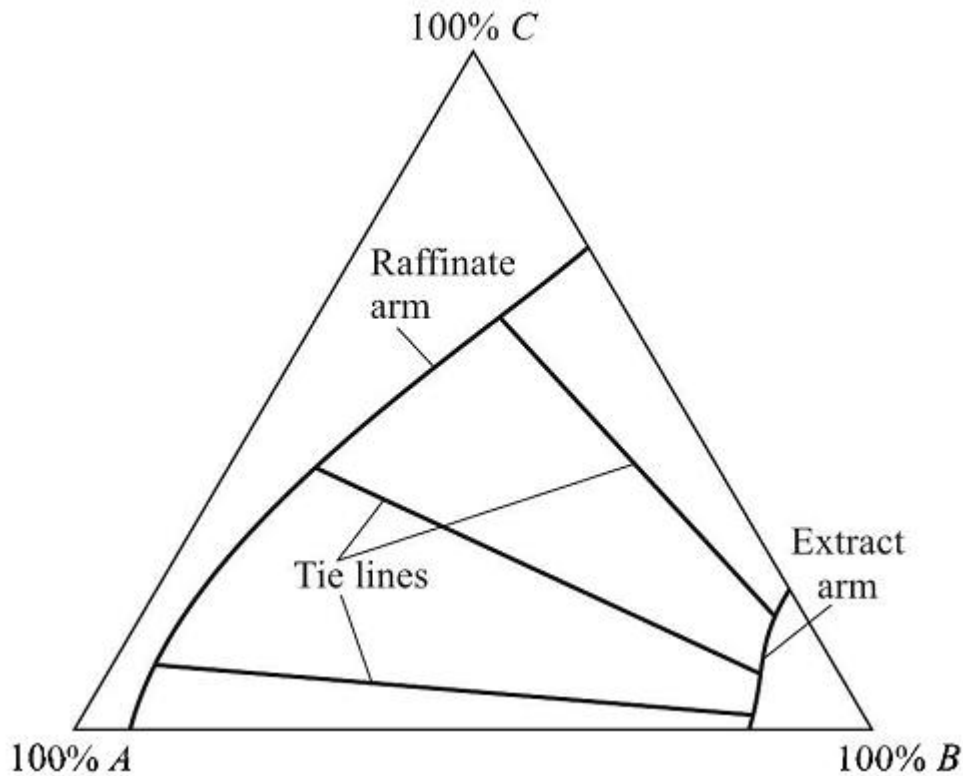


Figure 5: Liquid-Liquid equilibrium for Type-II system

The raffinate and the extract arm of the equilibrium diagram do not meet, so there is no “plait point”.

Right angled triangle diagram:

Mass fractions of the solute in the two phases (raffinate and extract) at equilibrium are plotted against the corresponding mass fractions of the solvent. Concentrations of the extract phase are denoted by y_A , y_B and y_C , and those of the raffinate are x_A , x_B and x_C . The raffinate arm PQ is obtained by plotting the set of points (x_B, x_C) ; the extract arm PR is obtained by plotting the set of points (y_B, y_C) . P is the “Plait point”. The point D_1 on the raffinate arm and D_2 on the extract arm represent compositions at equilibrium. D_1D_2 is tie line. The equilibrium diagram can also be drawn on the x_C - y_C plane.

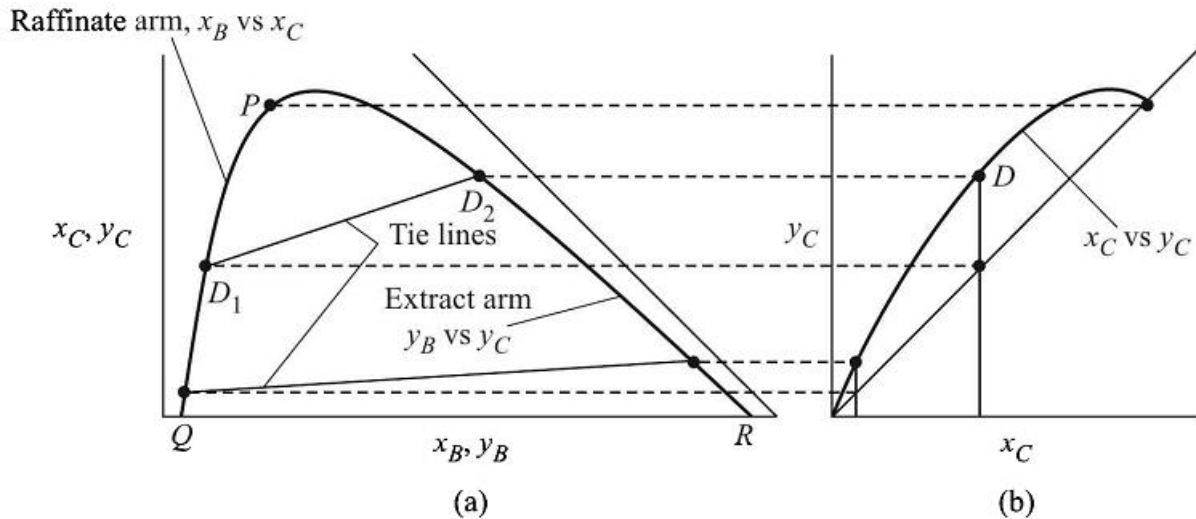


Figure 6: Right angled triangle diagram.

Equilibrium plot on solvent free basis:

In this presentation of LLE data, the mass ratios of solutes (X and Y) in the two phases are plotted vs the corresponding mass ratios (z or Z) of the solvent, on solvent free basis.

The quantities X, Y, z and Z are defined below:

$$X = x_C / (x_A + x_C), \quad z = x_B / (x_A + x_C) \longrightarrow \text{for raffinate}$$

$$Y = y_C / (y_A + y_C), \quad Z = y_B / (y_A + y_C) \longrightarrow \text{for extract}$$

x is the mass fraction of a component in raffinate.

y is the mass fraction of a component in extract.

The plot of X-z and Y-Z are called **Maloney-Schubert diagram** or **Janecke diagram**.

Janecke plot

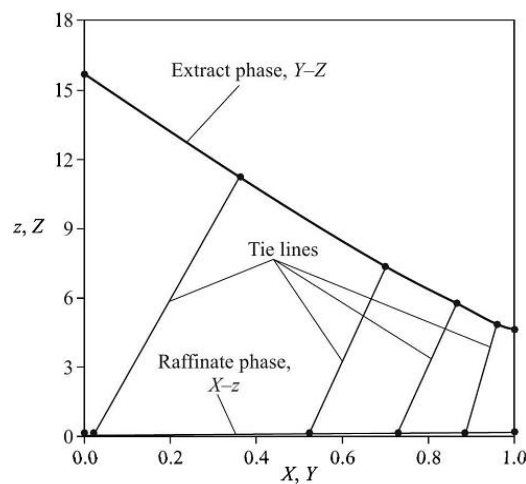
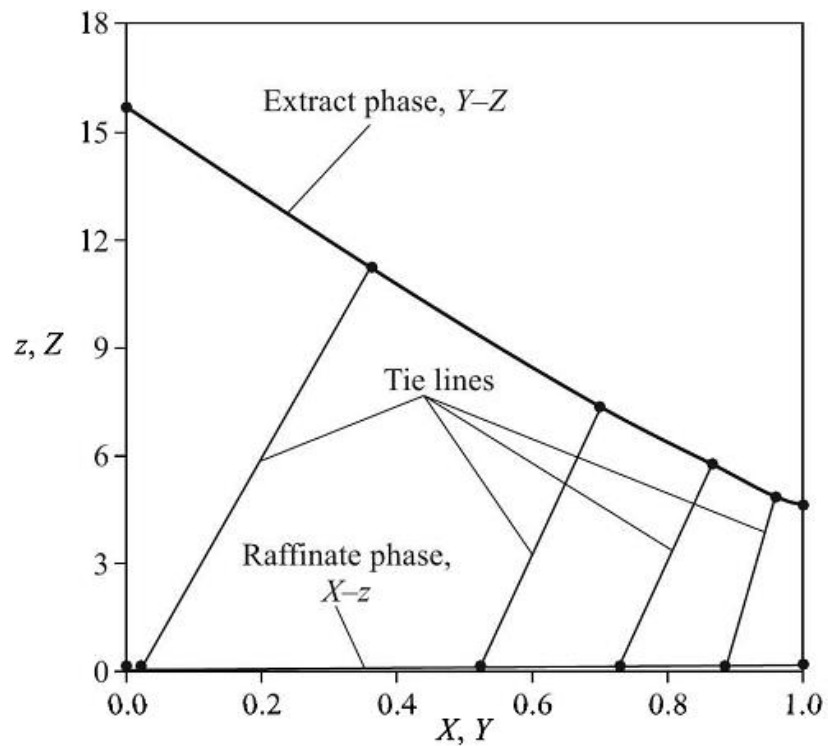


Figure 7: Janecke Plot

Problem 1: Draw the Janecke diagram for a liquid-liquid system using the following equilibrium data. Also show the tie lines in the diagram.

x_A	x_B	x_C	y_A	y_B	y_C
0.939	0.0601	0.0	0.06	0.94	0.0
0.7327	0.0654	0.0219	0.052	0.918	0.03
0.4402	0.0732	0.4866	0.036	0.88	0.084
0.246	0.09	0.664	0.0185	0.851	0.1305
0.103	0.1047	0.7923	0.0069	0.8276	0.1655
0.0	0.1103	0.8897	0.0	0.8246	0.1754

Solution:



$X = x_C / (x_A + x_C)$	$z = x_B / (x_A + x_C)$	$Y = y_C / (y_A + y_C)$	$Z = y_B / (y_A + y_C)$
0	0.064	0.0	15.67
0.29	0.067	0.366	11.2
0.525	0.079	0.7	7.33
0.73	0.099	0.876	5.71
0.885	0.117	0.96	4.8
1	0.124	1	4.7

So this is Janecke diagram.

So thank you. In the next class, we will be discussing about the effects of temperature on the liquid-liquid equilibria.