Principles and Practices of Process Equipment and Plant Design

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Module - 02
Lecture - 07
Phase Equilibrium (Contd.)

In this particular class, we will continue with our Phase Equilibrium discussions. We had already discussed the vapor-liquid equilibrium and the solubility curves. The next operation is liquid-solid adsorption and gas-solid adsorption, and liquid-liquid equilibrium conditions.

In the first class on phase equilibrium what we had discussed that the units in which we express the concentration. Usually while in the gas phase, it is expressed in terms of partial pressure, in the same way for the liquid phase it can be expressed either in terms of mole fraction or in terms of mole ratio.

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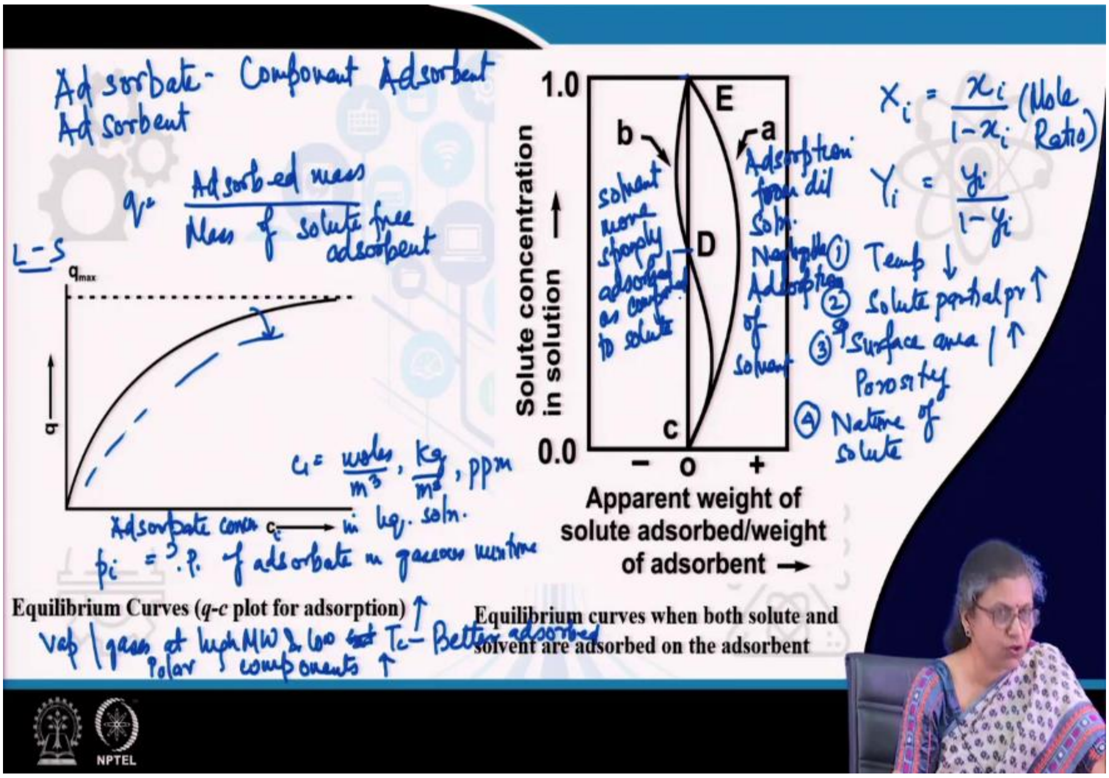

Equilibrium Curves (*q-c* plot for adsorption) ↑

Vap / gases at high MW & low Tc – Better adsorbed
Polar components ↑

Equilibrium curves when both solute and solvent are adsorbed on the adsorbent

I had forgotten to mention in the previous class that apart from mole fraction there are also cases where we adopt the mole ratio.

What is the mole ratio? The mole ratio is normally expressed in terms of capital letters. So, X_i equals to the moles of the component "i" in terms of this solute-free solvent or this in terms of this solute-free mixture.

$$X_i = \frac{x_i}{1 - x_i}$$

Where Xi represents the mole ratio in the liquid phase.

In the same way, if you are dealing with the gas phase and the liquid phase or vapor-liquid equilibrium.

$$Y_i = \frac{y_i}{1 - y_i}$$

Where Yi represents the mole ratio in the gas phase.

Instead of expressing equilibrium data in x-y data format, we can also represent the equilibrium in terms of capital X and capital Y data. These are known as the mole ratio.

The advantage of using capital X_i and capital Y_i is that this very often leads to your linear plots and that is quite advantageous for us. Anyhow now coming back to adsorption. In the case of the gas-solid equilibrium condition, we express the y axis in terms of q where q represents the adsorbed mass divided by the mass of solute free adsorbent.

$$q = \frac{Adsorbed\ mass}{Mass\ of\ solute\ free\ adsorbent}$$

Now, before I start the adsorption equilibrium, I would like to mention the difference between adsorbate and adsorbent.

Adsorbate: Component which is adsorbed by another component;

Adsorbent: It helps in adsoption of the component (adsorbate);

The component which is adsorbed that component is known as adsorbate; that means, the component which is adsorbed and the solute which adsorbs this component that is known as adsorbent. This is the component that absorbs and what does it adsorb, it adsorbs the adsorbate.

In this case, q can be expressed as follow:

$$q = \frac{adsorbed\ mass\ of\ the\ adsorbate}{mass\ of\ solute\ free\ adsorbent}$$

The Y-X axis has been shown for liquid-solid adsorption (L-S). So, therefore, it is shown in terms of q versus c, where this particular concentration can be expressed in therms of $c_{i.}$ This ci can be expressed in mole/m^3 or kg/m^3 or may in ppm.

For gas-liquid adsorption, adsorbate concentration can be expressed p_i. Where p_i is the partial pressure of the adsorbate in the gaseous mixture.

The equilibrium curve q vs c is a general type of graph in the case of adsorption. The concentration may be expressed as per convenience but the trend of the curve will like as shown in the graph. Now let us discuss the effect of the different measurable parameters on the adsorption curve. Say, for example, temperature, what do you expect to happen when suppose with an increase of temperature, how do you think that this particular curve is going to change?

Again, I would like to remind you adsorption is an exothermic process, it is accompanied by the release of heat. Just like I had told you about absorption. So, therefore, if it is accompanied by the release of heat. From Vant Hoff's law, we know that for higher temperatures adsorption decreases. So, for higher temperatures the adsorbate loading or q decreases. Provided the partial pressure of the solute in case of gas adsorption is constant and similarly, the solute concentration in a liquid solution is constant. So, with an increase in temperature, we find that q decreases at a constant p. We will get the same trends of curve but the highest value q_{max} will be less at higher temperatures.

What about the partial pressure of the solute? For liquid-solid adsorption, this should not matter, but for gas-solid adsorption quite naturally when we go for higher pressure, it increases the loading at a constant temperature. So, if the temperature is kept constant as we go for higher pressure, the loading increases. So, first, we discuss the effect of temperature. So, we find that with temperature adsorbate loading decreases. Then solute partial pressure, as we increase, it increases adsorbate loading. This solute partial pressure can be increased by increasing the amount of solute in the gas phase and or in any particular way if we can increase the solute partial pressure, it increases.

There is one other thing also which is important in adsorption, which did not occur in vapor-liquid equilibrium or your solubility curves is the specific surface area. We need to remember that adsorption is a surface phenomenon.

So, if we increase the specific surface area or if we increase the porosity of the medium, naturally the total area available for adsorption increases, and so naturally whenever we go for higher porosity it ensues a higher specific surface area. So, therefore, larger adsorption capacity per unit weight of the adsorbent, or in other words, this also increases q.

The next thing is which again influences this particular adsorption curve is the nature of the solute. How does the nature of the solute influence the adsorption of this particular adsorption curve if you can tell me? We find out that for vapors and gases with high molecular weight, and low critical temperature (Tc), these are more readily adsorbed, or they are better adsorbed. Comparatively, we find that permanent gases are less readily adsorbed. The same way polar molecules are better adsorbed. So, therefore, vapor or gases at the high molecular weight and low Tc, are better as adsorbed. Permanent gases are less readily absorbed and also polar components are also much better adsorbed. So, they also give a higher adsorbent loading and this explains why water is much more readily absorbed as compared to hydrocarbons etc.

I have already mentioned that more or less the q versus your concentration curve, where it is usually concentration the liquid phase and the partial pressure in the gas phase. So, for this particular curve, it's more or less has the same characteristics. The only thing is that for the liquid-solid case it is not influenced by this solute partial pressure, otherwise more or less it's the same.

But there is something very interesting when we talk about liquid-solid adsorption. If we start with the fresh adsorbent and we started what happens even if we start with some particular very inert solvent also. Under that condition also initially some amount of solvent gets occluded into the pores of the adsorbent.

Now, the moment some amount of solvent goes and gets adsorbed, quite naturally the C_i increases. It appears, which is evident from this particular portion (right side curve, b portion) of the curve, that your q becomes negative under such a particular condition.

Therefore, under these conditions, we must consider the apparent weight of the solute adsorbed per weight of the adsorbent.

Now the curve which I have drawn in this particular case. For, “curve a”, that denotes adsorption from dilute solution where the solvent is negligibly adsorbed. Now, this is the curve that normally happens. So, for this particular curve, we find that this is the curve that we would expect. But when we find that the solvent is appreciably adsorbed, under that case we have a “curve b” something of this sort, where this particular part D, under this condition the solvent is more strongly adsorbed as compared to the solute. So, therefore, we get a curve something of this sort over a certain range of conditions. So, therefore, this particular thing has to be kept in mind when we are dealing with liquid-solid adsorption cases.

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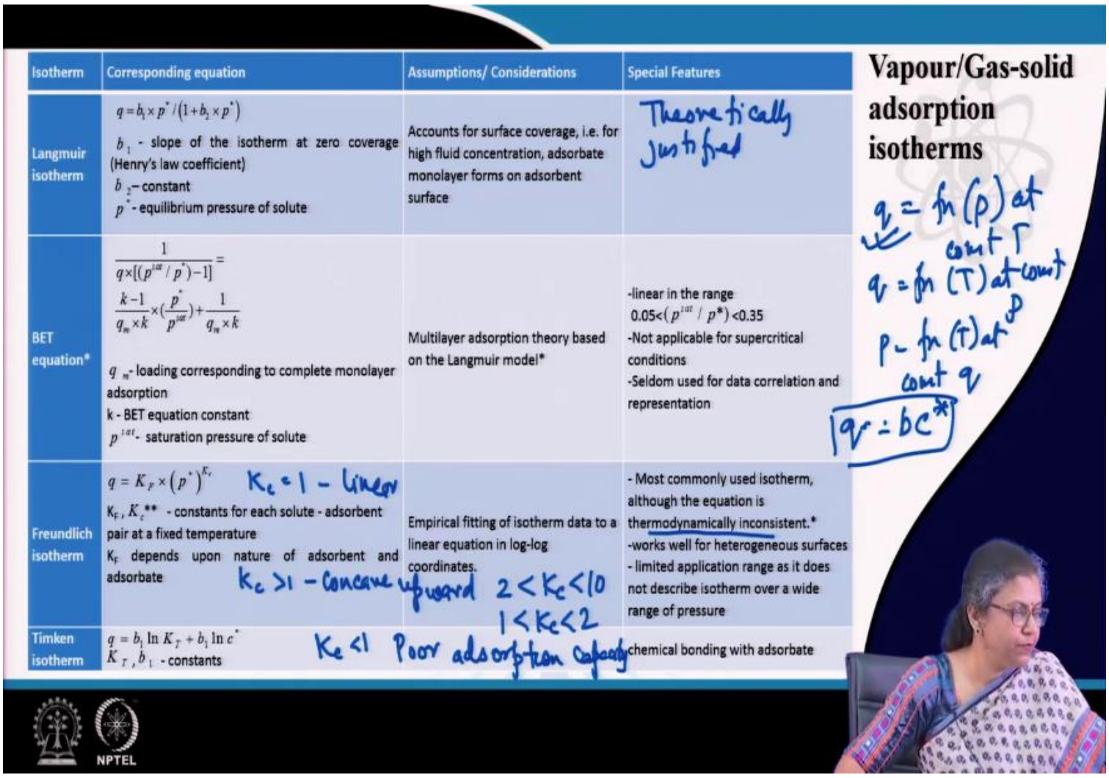

Vapour/Gas-solid adsorption isotherms

Isotherm	Corresponding equation	Assumptions/ Considerations	Special Features
Langmuir isotherm	$q = b_1 \times p^* / (1 + b_2 \times p^*)$ b_1 - slope of the isotherm at zero coverage (Henry's law coefficient) b_2 – constant p^* - equilibrium pressure of solute	Accounts for surface coverage, i.e. for high fluid concentration, adsorbate monolayer forms on adsorbent surface	Theoretically justified
BET equation*	$\frac{1}{q \times [(p^{sat}/p^*) - 1]} =$ $\frac{k-1}{q_m \times k} \times (\frac{p^*}{p^{sat}}) + \frac{1}{q_m \times k}$ q_m - loading corresponding to complete monolayer adsorption k - BET equation constant p^{sat} - saturation pressure of solute	Multilayer adsorption theory based on the Langmuir model*	-linear in the range $0.05 < (p^{sat} / p^*) < 0.35$ -Not applicable for supercritical conditions -Seldom used for data correlation and representation
Freundlich isotherm	$q = K_F \times (p^*)^{K_c}$ $K_c = 1$ - linear K_F, K_c** - constants for each solute - adsorbent pair at a fixed temperature K_F depends upon nature of adsorbent and adsorbate $K_c > 1$ - Concave upward $2 < K_c < 10$ $1 < K_c < 2$	Empirical fitting of isotherm data to a linear equation in log-log coordinates.	- Most commonly used isotherm, although the equation is thermodynamically inconsistent.* -works well for heterogeneous surfaces - limited application range as it does not describe isotherm over a wide range of pressure
Timken isotherm	$q = b_1 \ln K_T + b_1 \ln c^*$ K_T, b_1 - constants $K_c < 1$ Poor adsorption capacity		chemical bonding with adsorbate

$q = fn(p)$ at const T

$q = fn(T)$ at const p

$p = fn(T)$ at const q

$\boxed{q = bc^*}$

Well, for the adsorption if you see that just like there are equations which are available to generate vapor-liquid, and gas solubility data. In the same way, we find that there are equations, which are available to express q in terms of p and T.

Now, remember one thing that normally these things are expressed in terms of isotherms. So, therefore, we find that for most of the cases we express the adsorption in terms of isotherms or other words. Usually, we express them in terms of q as a function of p at constant T.

Expressing q as a function of T or expressing q as a, at constant p or maybe expressing p as a function of T at constant q which is known as isostere. So, therefore, more than these two this is much more common, and therefore, we find that there are a large number of equations, which are available for expressing adsorption isotherm.

$$q = f_n(p) \ at\ constant\ T, which\ is\ called\ isotherm$$

$$q = f_n(T) at\ constant\ p, which\ is\ called\ isobar$$

$$p = f_n(T)\ at\ q, which\ is\ called\ isostere$$

All these available equations, stem out from Henry’s law sort of an equation which tells q is equals to say some particular constant say b or a or whatever into c*. So, this is the basic equation.

$$q = bc^*$$

This equation is the simplest adsorption isotherm. From this particular equation, this is modified to account for the actual situation and there are a good number of equations. The assumptions for the different equations are all written. Although the Freundlich equation is much more used. It is the most commonly used equation, but it is thermodynamically inconsistent. In the case of, Langmuir equation, although it is not so much used, this is theoretically justified.

Why do we call that the Freundlich equation is thermodynamically inconsistent? Because it does not have a finite Henry’s law constant. So, therefore, this is thermodynamically inconsistent, but this equation is the most commonly used.

In the Freundlich equation,

- When Kc =1, under that condition, the isotherm is linear,
- When Kc>1, under that condition, isotherm is concave upward and indicate good adsorption capacity,
- Normally, 2<Kc<10, indicate good adsorption capability,
- 1<Kc<2 denotes moderately difficult adsorption capability,
- Kc<1 shows very poor adsorption capability,

Therefore, if we would like to select an adsorbent, we would like to ensure that the Kc value is greater than 2. In that particular case, it represents that the adsorption is going to be effective in this particular case. We do not select any particular absorbent which yields Kc which is less than 1.

Well so with these things said we have discussed adsorption.

The next thing is liquid-liquid extraction. In liquid-liquid extraction what do we have?

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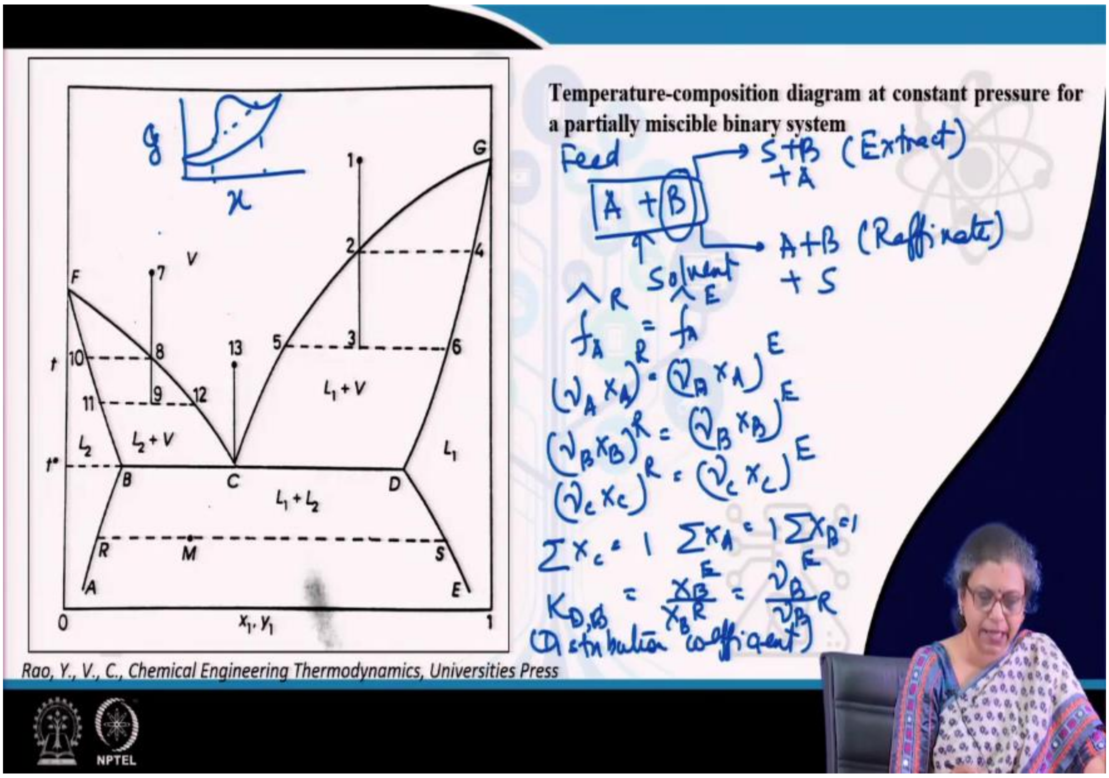

Temperature-composition diagram at constant pressure for a partially miscible binary system

S+B (Extract) +A

A+B (Raffinate) + S

$\hat{f}_A^R = \hat{f}_A^E$

$(\gamma_A x_A)^R = (\gamma_A x_A)^E$

$(\gamma_B x_B)^R = (\gamma_B x_B)^E$

$(\gamma_C x_C)^R = (\gamma_C x_C)^E$

$\sum x_C = 1$ $\sum x_A = 1$ $\sum x_B = 1$

$K_{D,B} = \frac{x_B^E}{x_B^R} = \frac{\gamma_B^E}{\gamma_B^R}$

(Distribution coefficient)

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

For liquid-liquid extraction cases, we introduce one particular liquid into another particular liquid mixture. Say we have a mixture of saying A and B, what do we add here? In this particular liquid mixture say we add some particular solvent S. What do we expect? Maybe we would like to remove B from A.

So, therefore, from here what do we expect to get? We would expect to get a mixture of S and B, which is known as the extract phase which has been extracted. There will be having some amount of B, which is remaining in A and this is known as the raffinate. But along with this, there is something more that we should remember when we are dealing with liquid-liquid extraction cases.

No matter whatever solvent you use even if the solvent (S) and the basic solvent (A) in the feed even if they are chemically extremely difficult, there will always be some amount of miscibility between these two solvents. So, therefore, we will find that no matter whatever solvent you select, we will find that in the extract phase there will be some amount of A, in the raffinate phase, there will be some amount of S.

So, therefore, in this particular case what do we find? We find that we were dealing with such particular situations where we found that more or less only one component was diffusing. We could assume that suppose it is air ammonia and water, the air does not dissolve in water. Even for vapor-liquid equilibrium, we had assumed that for the two phases some components were diffusing here, some components which were diffusing in the other direction. So, for a binary mixture, either the t-x can vary and we can find out p-y or maybe the t-y varies we can find out p-x etcetera.

But in this particular case, we find that both the phases have got all the three components that are available in this particular case. Therefore, at equilibrium, the fugacity of A in the raffinate phase should be equal to the fugacity A in the extract phase. In other words, $\gamma_{A*}X_A$ in the raffinate phase should be equal to $\gamma_{A*}X_A$ in the extract phase. Similarly, we can say that $\gamma_{B*}X_B$ in the raffinate phase should be equal to $\gamma_{B*}X_B$ in the extract phase.

$$\hat{f}_A^R = \hat{f}_A^E$$

$$(\gamma_A X_A)^R = (\gamma_A X_A)^E$$

$$(\gamma_B X_B)^R = (\gamma_B X_B)^E$$

$$(\gamma_C X_C)^R = (\gamma_C X_C)^E$$

Since we are dealing with two liquid solutions, there is every chance that both of them are going to be non-ideal. So, therefore, gammas are extremely important in this particular case. Therefore, the process of finding out gammas is the same. But in most cases, we have to include the gammas in the phase equilibrium equations written down for liquid-liquid extraction cases.

So, therefore, these are the equilibrium relationships coupled up with the fact that sigma X_C should be equal to 1, sigma X_A should be equal to 1, and sigma X_B also should be equal to 1. So, therefore, in this particular case the K factor or the equilibrium ratio that we have talked about. In this particular case, it is generally denoted as the distribution coefficient, which is say x_i in the extract phase by the x_i in the raffinate phase.

Which is naturally gamma i, say i mean in this particular case if B is the component which gives you gamma B in the extract phase divided by gamma B in the raffinate phase. Once you can find out K_D for component B. You can also find out alpha and you can find out the expression of alpha.

$$\sum x_C = 1\,;\ \sum x_A = 1\,;\ \sum x_B = 1$$

$$Distribution\ coefficient, K_{D,B} = \frac{{x_B}^E}{{x_B}^R} = \frac{{\gamma_B}^E}{{\gamma_B}^R}$$

When we are performing the liquid-liquid extraction, we are operating in ABCDE zone. This particular zone as you can see this is a typical liquid-liquid extraction curve.

We find that in this particular zone when one particular liquid is in a very small proportion then they are miscible in L 2 liquids are miscible. When say for example, the component the liquid 1 is in a very small proportion. So, therefore, when L1 is in a very small proportion they are miscible in all proportions.

When L 2 is in a very small proportion, then also they are miscible in all proportions. Over some particular range. Say for example, we have started with pure liquid L 2 and then we start adding L1 there. Gradually we find that there is one particular zone where we find that the Gibbs free energy of this solution is higher than the Gibbs free energy of the two components taken separately.

If we can draw the Gibbs free energy, say the molar Gibbs free energy as a function of X, we find that in a miscible system, the Gibbs free energy over some range is higher. So, for this particular range, we find that the two solutions they would prefer to be separated than being in a solution.

So, therefore, and remember one thing that liquid-liquid equilibrium is influenced by temperature, but it is independent of pressure. So, we always would like to operate this at a higher and higher pressure to ensure that this range, the existence of two liquids are can be extended over a larger range of composition and we do not enter the vapor range.

Suppose by saying any chance we reduce the pressure then, in that case, we find that the vapor-liquid equilibrium sets in, but I will not be going into the details of all this. I would just like to mention that whenever we perform liquid-liquid extraction, we would like to operate in this particular zone. As I have said that during liquid-liquid extractions since all the components, even if it is a binary mixture all the components are available in both phases.

Normally, the liquid that we add is known as a solvent. The original solution is a feed, and what has been extracted is the extract which majorly comprises of S and a very small amount of A. Something which is remaining which majorly comprises of A, some amount of B, which has not been extracted, some small amount of S.

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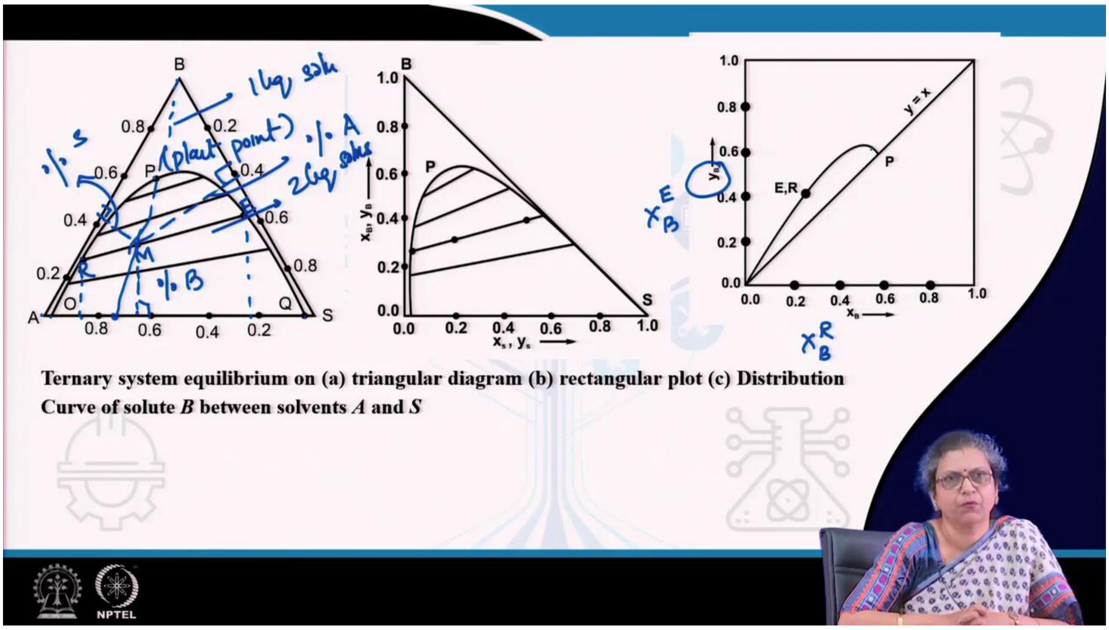

Ternary system equilibrium on (a) triangular diagram (b) rectangular plot (c) Distribution Curve of solute *B* between solvents *A* and *S*

Therefore, since all of these are the compositions of all of these variables. Therefore, to express liquid-liquid equilibrium data, what we have, we refer to ternary plots to find to rather than to depict the composition of all the three components on a 2D plot.

Now, what is this ternary plot in very briefly if I can mention this? This particular ternary plot if you find this is represented in an equilateral triangle. Where all the spices refer to the pure component. So, this refers to 100 percent A, 100 percent B. A and B were the original solution to which we had given S. They are maybe of the equilateral triangle that refers to or that corresponds to the composition of the solution A B, which was our original feed solution.

As we move from A to B, we find that the proportion of B increases, and the proportion of A decreases. When we add S in the A and B mixture, what will happen? From this particular straight line joining A and B, we enter inside the triangle. We enter into this particular portion (the curve portion inside the equilateral triangle) which is the three components system. Same way if you refer to this particular arm BS, this gives you the composition of the solution of B and S, and the same way arm AS gives you the composition of the solution of A and S.

Inside this (the curve portion inside the equilateral triangle) all three components are present. You will find that moment you add S, the composition immediately shifts from this straight line inside the triangle right. When it shifts here, all three phases are present. Now since the solubility of S in A is very less. So, therefore, we find that the curve rather there is some particular equilibrium curve established between A and S.

Now, the more they are insoluble the closer will be these points to the two particular apices. And if they are less soluble then they will be more removed from the apices. Now we find that this corresponds to the solution of S in A and this corresponds to a solution of A in S. We find that just like I had shown in the previous figure in the same way we find that there is a range, where this A and S are immiscible. Same thing I show here also that there is a range where A and S are immiscible

So, when you and outside this range, we have A B and S miscible in all proportions, and therefore, we have one liquid solution here and we have two liquid solutions here. So, that automatically tells you that if you want to perform the liquid-liquid extraction you need to perform it within this particular dome.

Suppose say, for example, you have this was the composition you have of the A B solution, you have added S and now suppose the composition has is at M. So, therefore, the overall composition of the A-B-S mixture is at M, which separates into the raffinate phase, composition corresponding to this and the extract phase with the composition or rather with the proportion of S corresponding to this.

So, therefore, this particular line represents the raffinate and extract composition in equilibrium to the overall composition of the liquid mixture, this is known as a tie line. And you will observe that in this particular case you find that these tie lines are not parallel. Usually, the slope in an upward direction. They gradually become smaller and smaller till finally, it reduces to the point. This point is known as the plate point. Beyond this is the limiting condition for this immiscible zone. Remember one thing, this is rarely at the center or rather these two curves are the meet symmetrically and this is usually at one side and this gives you the limit of immiscibility in this particular case.

Since this is an equilateral triangle, so quite naturally we know that in an equilateral triangle this sum, from this particular point if we drop say perpendiculars to the three sides then the sum of these perpendiculars is equal to the sum of the or other is equal to the altitude.

So, therefore, if we take the altitude as 100 percent of the entire composition, then we find that this length corresponds to the percentage of B. This particular length corresponds to the percentage of S. This particular length corresponds to the percentage of A in this particular case.

And also from B if you drop a. Sorry it became if you drop a line here then you find that this corresponds to the proportion of A and S in the solution. As we move along this line the proportion of A and S remains constant, it's only B that is added up, and that changes the overall composition of the mixture.

Now, rather than this, there is another much more convenient way of expressing the ternary system equilibrium, where we can express the compositions on a rectangular plot or in a right-angle triangle, where we find that the composition of component B in the raffinate and the extract phase is denoted by the Y-axis, the composition of S in the raffinate and the extract phase is denoted in the X-axis. By difference from these, we find out the composition of A.

In this case also the same thing we can show the two-phase zone and the single-phase zone and your tie lines everything can be shown, and corresponding to the two ends of the tie lines, just as we have drawn in t-x-y, P-x-y in all plots. In this case, we can also plot the proportion of B in the extract phase normally that is shown as Y_B.

If you can also be denoted as X_B in the extract phase and the proportion of B in the raffinate phase. By convention, the raffinate phase composition is denoted by X and the extract phase composition is denoted by Y. So, therefore, in this sort of an X-Y plot, if we plot the endpoints of the tie line, we can get an equilibrium curve. Here you have to remember since B is preferentially extracted by S and so, therefore, the curve lies above the Y equals to the X line.

So, therefore, in short, we have discussed the different equilibrium curves, the vapor-liquid equilibrium, the gas solubility, the isotherms for adsorption, and the ternary plot for liquid-liquid extraction.

So, from these, I wanted to give you an idea regarding the different equilibrium representations, how they are represented. There are mathematical equations available, there are also plots, there can be tables also available the entire thing has originated from thermodynamic equilibrium, which states that at equilibrium the chemical potential of each component in the different phases should be identical.

In other words, the fugacity of each component in the different phases should be identical. Based on that we can express the equilibrium data, either in terms of your plots or in terms of K. The K values are usually used for ideal solutions, and they are very frequently used in hydrocarbon industries because mostly those solutions are the hydrocarbons. They form the members of a homologous series. So they form ideal solutions.

Very frequently they are expressed in terms of alpha, which gives you the relative ease of separation. And just like we have equilibrium ratios or the K values for distillation, we have distribution coefficient for the liquid-liquid extraction cases.

Just like p-x-y, t-x-y, x-y are important for distillation. Your p_i versus x_i curves is important for adsorption. q versus c_i or q versus p_i curves are important for liquid-solid adsorption and gas-solid adsorption respectively. The ternary plots are important for liquid-liquid extraction.

So, with this, we complete the discussions on phase equilibrium which governs the interface mass transfer, and from the next class, we start discussing individual processes. So, we plan to start with distillation and then proceed to the other operations or the other mass transfer operations, whose brief introduction has already been provided to you in the introductory lecture on mass transfer operations.

Thank you very much.