Interfacial Engineering

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Lecture-16

Shapes of micelles, critical micelle concentration (CMC); critical packing parameter (CPP)

Aggregation number; Thermodynamics of micelle formation; Micellization; CPP

Welcome back.

So, in today's video lecture, we will start Module 3. So from now onwards we will look at module 3. So mainly in module 3, we will cover several aspects about the surfactants and micelles. We will talk about, what is surfactant and what is micelles, okay? We will also cover some of the important topics like, what is known as critical micellar concentration, what is packing factor, okay? Why, you know, micelles assume a certain shape, right? We look at what is the change in Gibbs free energy of micellization at the standard reference state. We will look at what is the HLB guidelines one has to follow if you want to you know use the surfactants for various applications like detergent applications and emulsion applications and then we will look at you know adsorption isotherm right So we have got you know so many topics to be covered under the module 3 and in today's video lecture we are going to you know to look at the overview of surfactant and micelles right let's begin.

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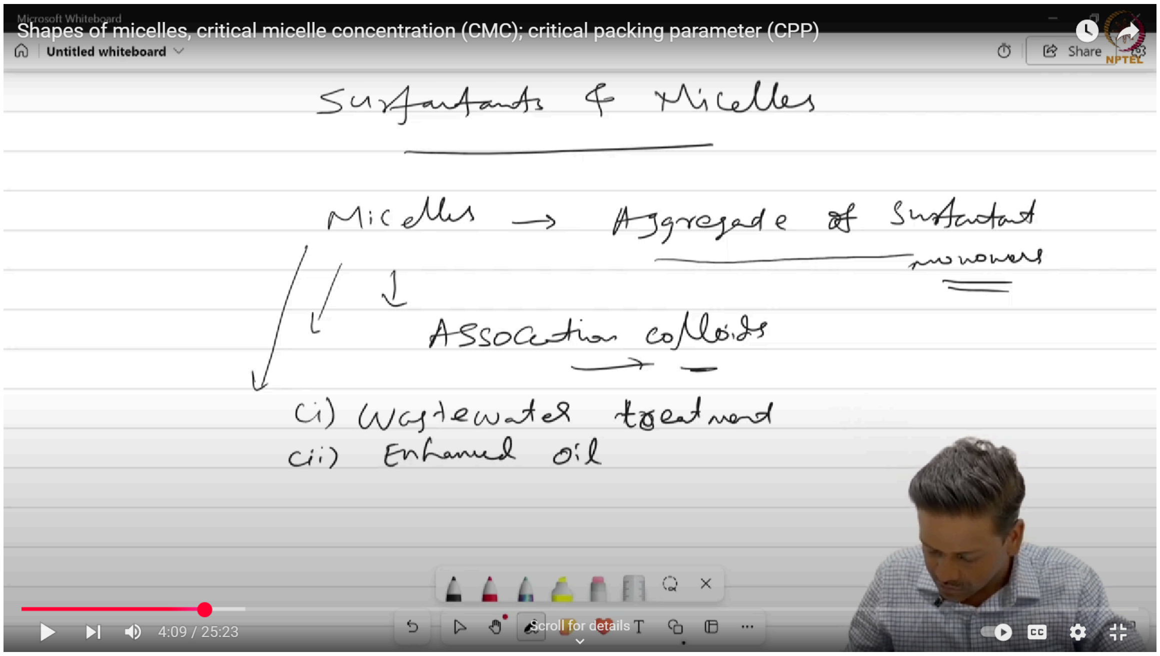

So we will start from the overview of you know surfactants and micelles. Micelles mean they are an aggregate of surfactants right okay. I can say monomer let's say individual surfactant right so it is nothing but aggregation of you know surfactant molecules right so sometimes often you know people also regard micelles as association colloids okay because why this is also referred to as colloids because the size of the micelle usually ranges up to a few hundred nanometers, right? And, you know, because of those characteristics, people also call micelles association colloids, okay? Micelles can also be treated as colloids, right? Right. So, we will look at today's lecture, are different types of surfactants, and their applications.

We will also try to cover some of the naturally occurring surfactants. So, before we begin, we will also see what is the application of micelles. Micelles are used in many applications. If you want me to list few maybe you can say that it is also used in wastewater treatment okay or you can also say enhanced oil recovery right. All right. Yeah. So now we will look at the, you know, the surfactant itself. Right.

First.

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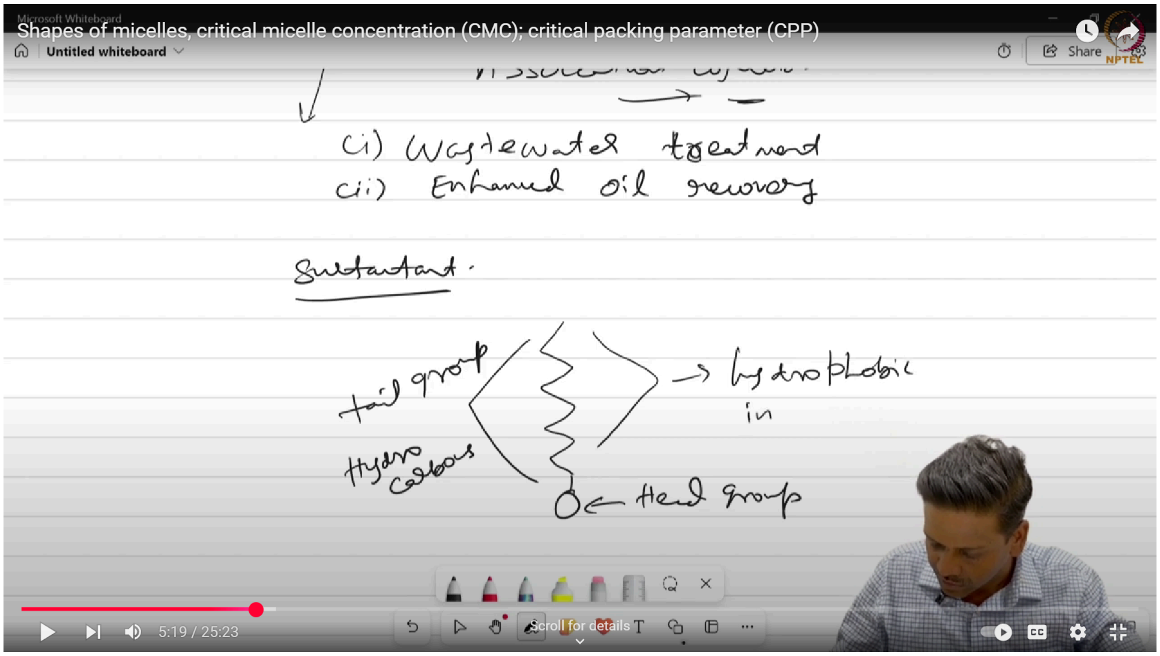

So, surfactant is usually, you know, an amphiphilic compound. It has got, you know, two parts. Okay. One is the head group, which is hydrophilic and you have a tail group that is usually constituted by hydrocarbons okay? So, we also call this tail group as backbone of surfactant and usually this tail group you know is hydrophobic right? Alright. There are different types of surfactants, you know, you would encounter, you know, a surfactant with two head, two tail group or a surfactant with two head group, right, like zwitter-ionic surfactant, okay, or Gemini surfactant.

So there are different types of surfactant depending on the application, one would have to look at and explore, right, right.

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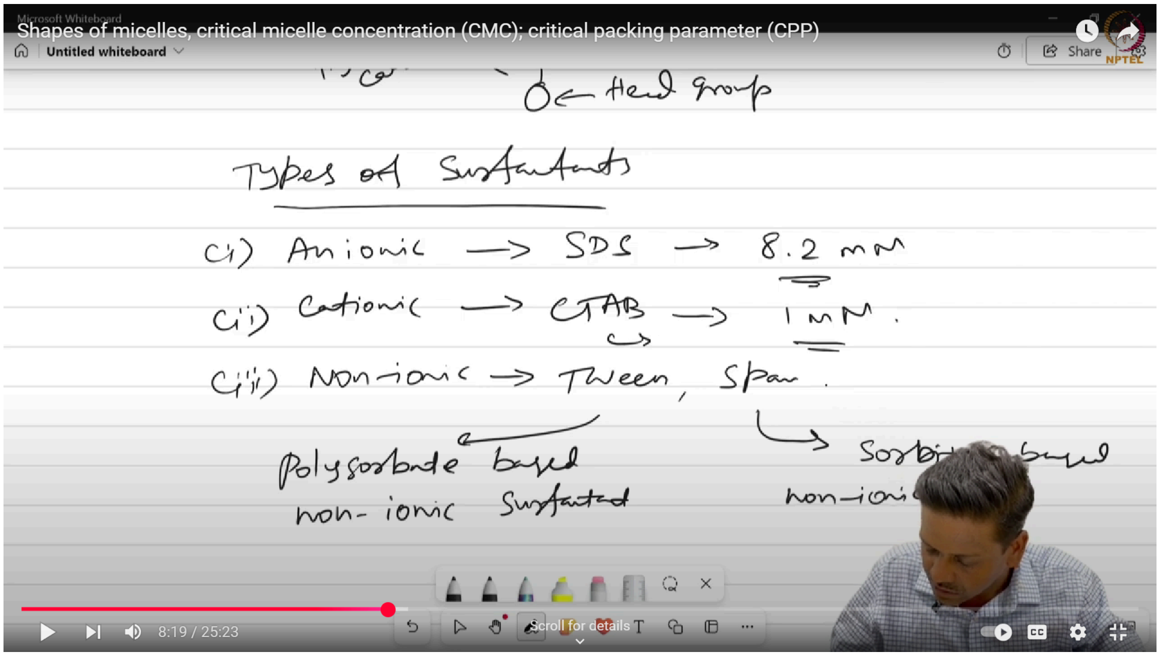

So let's talk about different types of surfactants, okay? Okay, when we talk about different types of surfactants, let's have a broad classification, right? So, you know, we can say that anionic surfactant, so the first one to, you know, to be included in the list is anionic surfactant. You can give an example let's say SDS right usually the CMC for SDS is 8.2 millimolars okay right SDS is sodium dodecyl sulfate okay and the next one is cationic surfactant okay one good example that people often use is CTAB, this is nothing but cetyl-trimethylammonium bromide. Okay, which is basically a quaternary ammonium salt. It has good antiseptic properties. So, you would find this in a medical application mainly. The CMC of this is usually 1 millimolar. Last but not least is non-ionic. This one doesn't belong to cationic or anionic. There are some commercially available non-ionic surfactants. If I can name a few, I can say what is known as tween or span. So tween is usually a polysorbate-based non-ionic surfactant. And span is usually sorbiton-based, right? Usually sorbitan-based non-ionic surfactant, okay?

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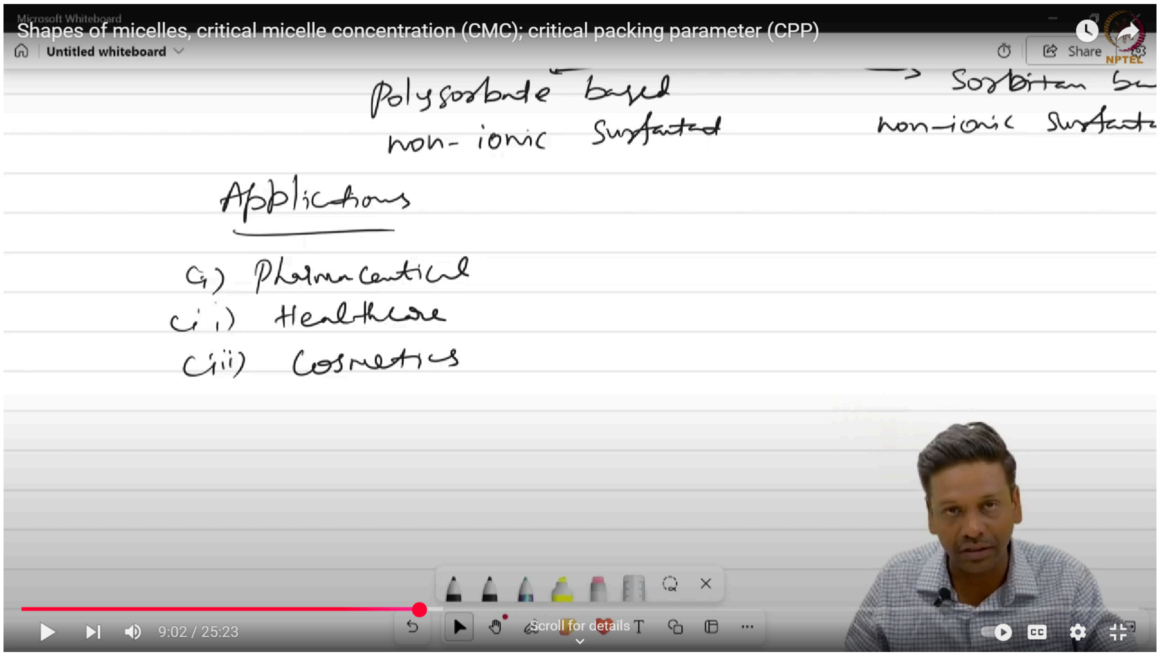

So, we can list a few applications of, you know, the surfactant. You would find many applications in many industries again let's say you know pharma industries right or you can say healthcare or you can say mainly in cosmetics also, right? So these are, so one can list several applications, but these are, you know, mostly, I mean, widely used, right? Surfactants are widely used in these industries, right? Okay.

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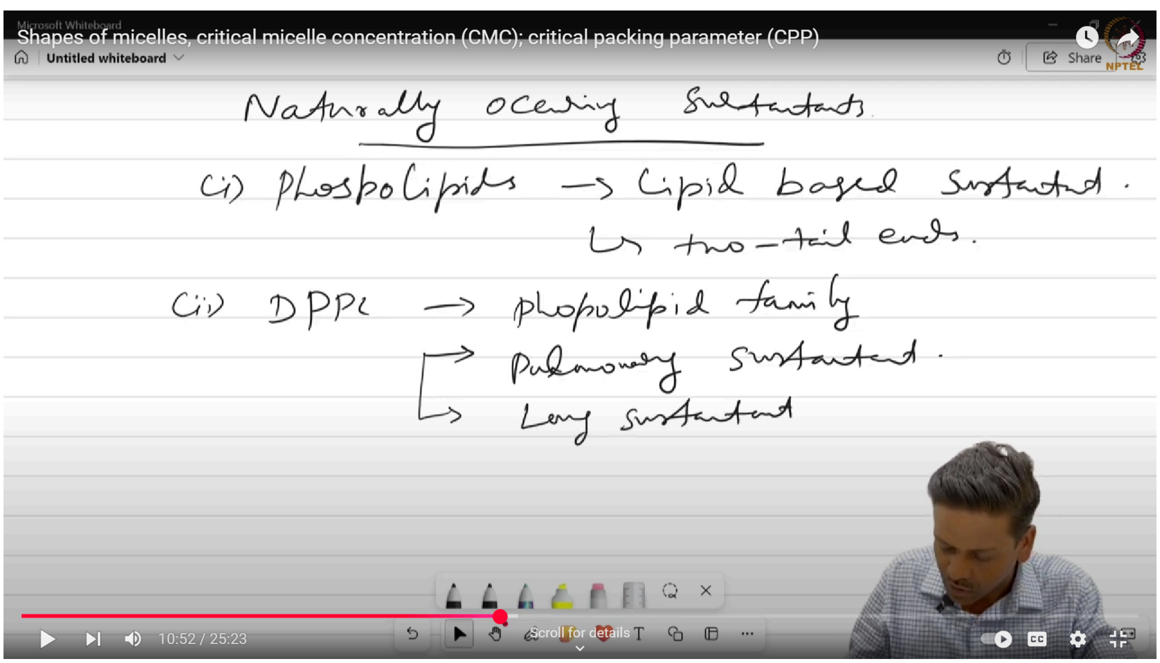

So now we can look at some of the naturally occurring surfactants, okay? These are not made synthetically, right? These are available by nature, right? I mean, these surfactants exist in nature, right? Say, for example, I can give a good example of phospholipids, right? This is usually a lipid-based surfactant. It contains two tails usually, right? So, the next one is what is known as DPPC, okay? So, this is usually, again, a phospholipid-based only family, phospholipid family. This is also regarded as a Pulmonary surfactant. Because this is the main constituent of the pulmonary tract, and it is also called the lung surfactant. Why this DPPC-type surfactant is a main constituent of the pulmonary tract because this is naturally formed so this helps reduce the surface tension at the liquid gas interface right in the pulmonary tract which means that it reduces the work of breathing and makes breathing a lot easier. So, there are several naturally occurring surfactants. One can give several examples, but I just want to list a few in the interest of time. So now what we will do is we will look at the phase diagram of surfactant. And we will look at, you know, the packing factor, packing consideration, right? Why does a micelle, you know, have to assume a specific shape, right? Right.And those aspects we will see now. Okay. Yeah.

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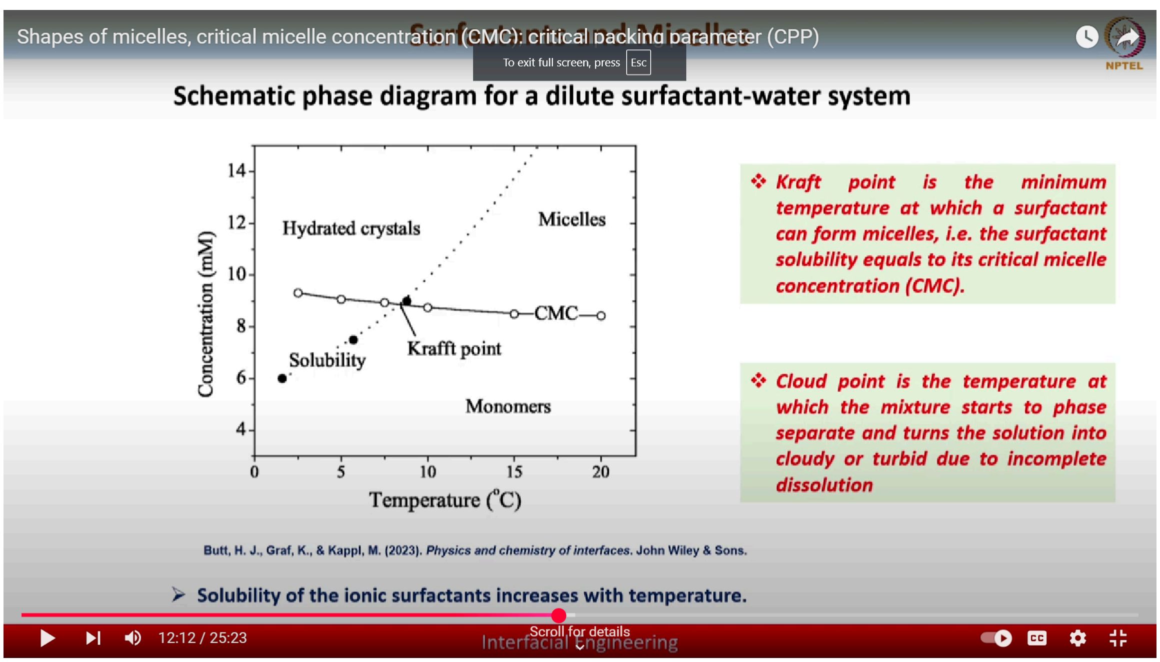

So now let's look at the phase diagram of surfactant right dilute surfactant water system you can see in this phase diagram there are three different states right one is the monomer state, micelle state, hydrated crystal state, and apart from this you would also need to know what is known as Krafft point, cloud point which we will cover now so what is very important is the operating line you know which you will be operating right for example if you want to synthesize micelles you should also know how to control if it modulates not only the concentration but also the temperature because even though above the CMC line, you can make micelles, what is so important is you should be always above the Krafft point, right? If you are above the Krafft point and above the CMC line, only then the micelles are favorable, right? So if you're going from monomer to micelles, you should know that two parameters. One is the Krafft point and as well and the other one is the CMC right so if you are even if you are above the CMC and if you are not above the Krafft point micelle states you cannot attain and the other one you may be above the CMC line but you are below the Krafft point so one would achieve the hydrated crystals, right? So in this state, what will happen is the surfactant will precipitate out in the form of hydrated crystals. So, one should avoid this point if you are keen on making the micelles. So monomer state, even though you are, you know, above the crap point, but if you are below the CMC line, you would surely get the you know, monomer state. So. you cannot achieve this conversion from monomer to micelle state. This phase diagram is very, very important so that you know what are the operating parameters. One has to fix the temperature and concentration if you are interested in making one of these others I mean achieving one of these states right so there is something called Krafft point as you know just now we described Krafft point is the minimum temperature at which a surfactant can form micelles right so above which the surfactant can form micelles. At the same time, the cloud point is the extreme limit, the maximum point. Even though you are above the Krafft point, if you are above the cloud point, what will happen is the surfactant, the micelles will precipitate out from the solution, right? So, I mean, it will make the sample turbid.The solution will turn into you know cloudy or turbid okay one has to avoid this situation by knowing the cloud point of the sample right yeah.

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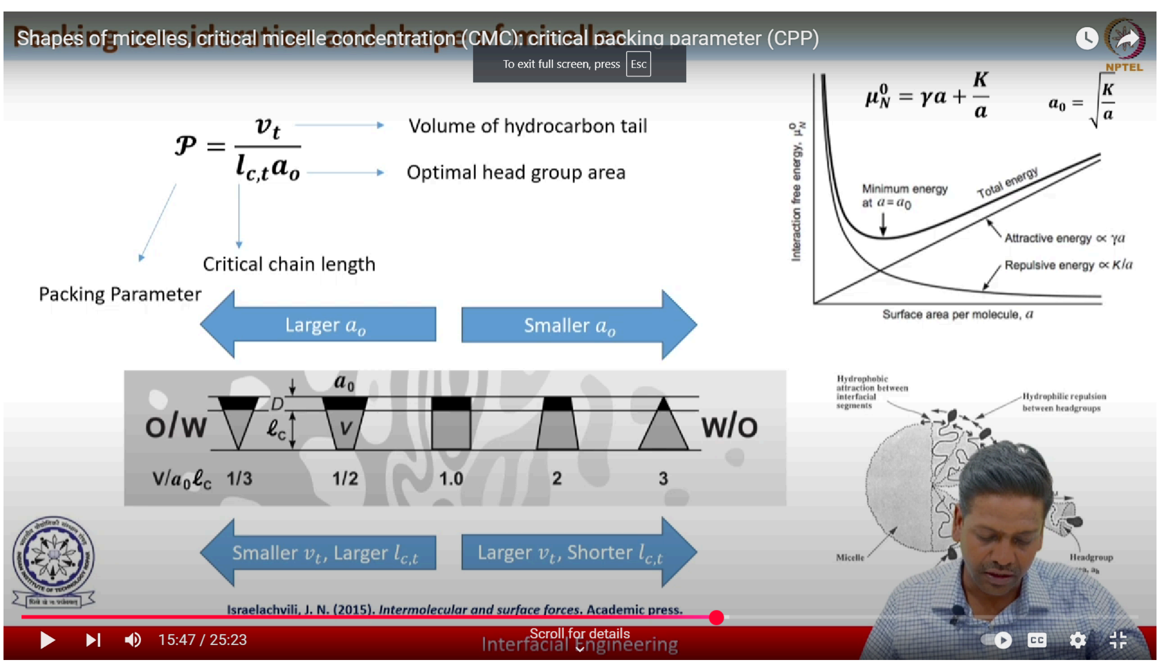

So now we'll look at the packing consideration and the shape of micelles. As you know, the formation of the micelle itself is nothing but a self-assembly or self-organization of the surfactant molecules. So surfactants can assume a different shape, different equilibrium shape, from spherical to cylindrical okay, and a lamellar and several of them but what decides them to assume a particular shape is a question that we are asking okay there is something called the packing guideline or packing factor it is just a guideline but it tells us that let's say if you have got some particular packing factor what one can understand is that this micelle will only assume a particular shape which corresponds to this particular packing factor. For example, if your packing factor is less than 1 by 3 or equal to 1 by 3 you can say that this micelle will only assume a spherical shape, or if it is let's say can similar way you can also do this exercise to know if you let's say if you want to know whether apart from the spherical shape if it forms a cylindrical shape, for that also you can use this guideline, right, whether it assumes spherical shape or cylindrical shape.

Now what decides or what dictates the surfactant to assume a certain shape is because that comes from the fundamental nature of the surfactant or fundamental shape or structure that they assume, right, at the individual surfactant level itself. For example, you can say that this surfactant, assume into or put them into a cone-like shape right uh in this zigzag when they uh you know uh uh accept this zigzag path line right when they accept this zigzag path or orientation, they will assume a cone-like uh shape you know that when you pack this cone right compactly one would get the spherical shape, right? So, the question that we are asking is what decides this shape is a couple of parameters. I mean, a few parameters that decide. One is the head group, the optimal head group area, okay? Let's say if the optimal head group area becomes larger and larger, one would walk in this direction. That means you will go from a cylinder to a truncated cone to cone. Whereas if the head group area becomes smaller and smaller, one would walk in the opposite direction, which means that you will get an inverse truncated cone or inverse cone. In this zone, if you are moving, you will most likely stabilize oil in water immersion. In this zone, if you are moving, you will most likely stabilize water in oil immersion. Okay so similar is the case with the other operating parameters like you know the volume of the tail and chain critical chain length and volume of the tail and critical chain length right right so what decides the surfactant choose the optimal head group area that is based on the minimal energy configuration, for example, this head group of surfactant usually contains some functional groups like let's say carboxylic acid group amino group right so this head group when they come each other we are very close to each other there will be a repulsion right whereas the tail group that contributes to the hydrophobic interaction and when the tail group comes closer, there will be a hydrophobic attraction. There will be attraction between the two. So there has to be the right balance between the repulsive force and the attractive force. At some point, when attractive force and repulsive force meet each other, right? There will be a minimum energy, you know, the system will attain a minimum energy and that happens exactly at this point. That is nothing but the optimal head group area. Okay so at this optimal head group area like you know at minimum energy configuration it will assume a certain fundamental structure or shape and that's how they will assume the if they assume a cone-like shape fundamentally then they will assume spherical shape when it forms micelles okay when it assumes truncated cone-like shape, then they will assume, you know, most likely, or when they assume cylindrical shape fundamentally, then they will assume cylindrical micelles. So, in this way, one would get, you know, micelles with different shapes, okay?And if you want to get more insight into these topics, you can refer to the book authored by Israelachvilli on intermolecular and surface forces.

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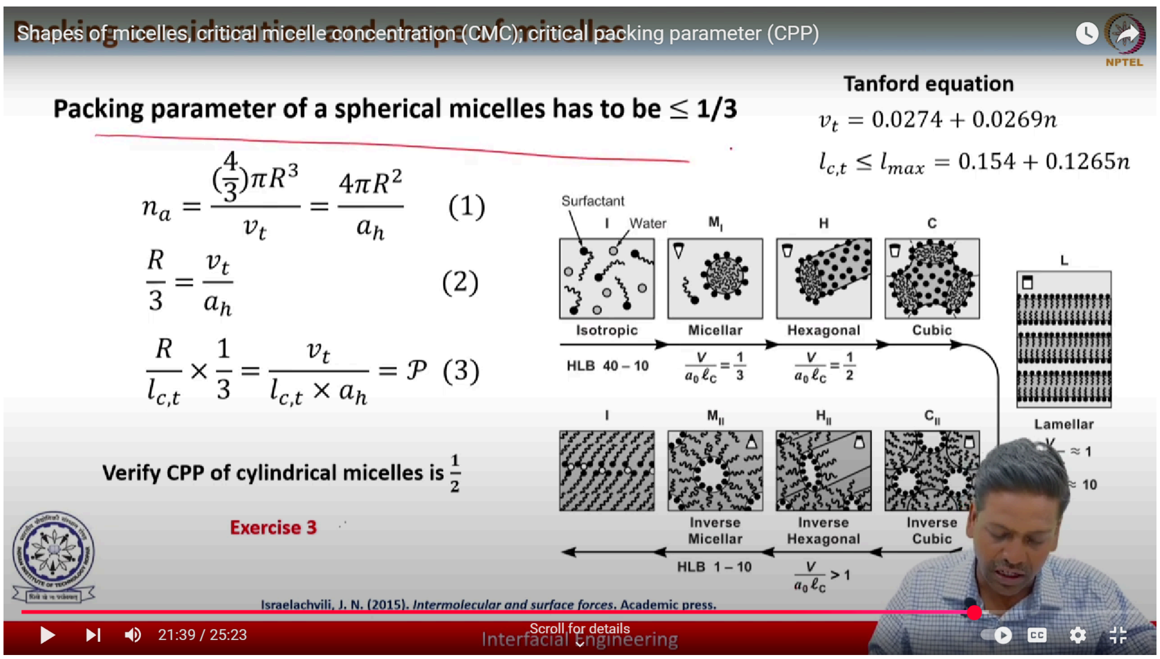

Now we can see how this packing parameter can be calculated. It's a number balance. So, what one can do is you have on the left-hand side the volume of the surfactant. Right here r refers to the radius of the micelle which is measured up to the apex of the cone so it goes from one end that is tip of the cone to the apex of the cone and this one is measured up to the the volume which is considered up to the apex of the cone right from the tip of the cone.So the ratio of these two should give the number. This comes from the volume basis whereas the similar way if I do surface area basis like the radius of the here the radius constitutes the head group constitutes the surface area and when you divide the surface area with the area of the head group one would get the number but these two number has to balance each other So in this way, you would get this ratio, right? But what we want to do is we want to forcibly introduce this parameter that is called chain length so that this becomes a dimensionless quantity. In this way, if you are on both sides, if you introduce this chain length, one would get this packing factor, right? And you see this packing factor has to be less than or equal to 1 by 3 because here the radius is measured from the tip of the cone to the apex of the cone whereas the chain length is Critical chain length, since they assume zigzag, you know, path, and at the liquid core, right, they will assume, you know, extended, you know, conformation, right? So, in any case, this LCT, critical chain length, will be either greater than, I mean, always greater than or equal to the radius of the micelles, right? Depending on the configuration of the surfactant. In this way, one can say surely that the packing factor will always be less than or equal to 1 by 3. So similar exercise, you can do it yourself, you know, to know what is the packing factor for cylindrical micelles, right? You can check that this is 1 by 2, right? Now, there is something called the Tanford equation, which is again a kind of empirical equation, which is based on the number of, you know carbon atoms present in the chain so you can use some time to understand what is the volume of the tail right and what it's critical chain length right if these data are not given one can use this Tanford equation to calculate this you know parameters as well now what I have shown here is the micelles with different shape and all corresponds to packing factor right different packing factor you can verify yourself for these micelles I mean for these micelles with the different shape right. So, we will stop here will continue from the next lecture.

Thank you