Fundamentals and Applications of Supramolecular Chemistry

Deepak Chopra
Department of Chemistry
IISER Bhopal

Week 10
Lecture 47

W10L47_Properties, Structures and Phase Diagram of Surfactants

So, hello, everybody.

So, now let us continue our discussion from where we left off in the last lecture. In the last lecture, we talked about the formation of a monolayer at the interface of water and air, and we also looked at the formation of such stable thermodynamic assemblies at the air-water interface, which results in the formation of a monolayer.

And we also realized that the addition of these surfactant molecules actually decreases the surface tension at the air-water interface. The process of solubilization of these surfactant molecules can now take place, and that is also responsible for the action of soap, including spreading, wetting, and formation of emulsions.

And the formation of all these events, as well as their existence, is governed by the interaction of the surfactant and the lowering of the surface tension of the air-water interface.

Then we realized further that when we increase the concentration of the surfactant molecules in aqueous solution, different kinds of assemblies start to form. And we looked at the presence of bilayer micelles, reverse micelles, and then vesicles. So, now let us go more deeply into this discussion.

So, to start with, when we begin with a small concentration of the surfactant molecule, we have the formation of these monolayers, where the non-polar parts, the hydrophobic parts, interact with each other, and the polar parts actually stick to each other because of the hydrogen bonding interactions between the polar parts of the molecule.

So, the polar parts come close to each other, and the non-polar parts—the hydrophobic parts, the lipophilic parts—are sideways. So, they form this monolayer. Now, this monolayer can arrange to give a bilayer, where again the tails—this is the tail part—and this is the head part—interact with the tail of the next monolayer, such that it increases the hydrophobic interaction between the tail portions.

And the hydrophilic portions are now exposed to water because we are considering water as a medium in which we are dissolving the surfactant molecule. So, this forms a bilayer, and now the stacking of these bilayers gives rise to a lamellar phase.

So, you have a bilayer, you have the water molecules, you have the polar parts, and the non-polar parts in between. Now, the stacking of these bilayers will give you the lamellar phase, and this is a very organized phase.

So, you see now that the surfactant molecules are getting very well organized into definite discrete structures, starting from bilayers to lamellar phases. The thickness of the monolayer, as we saw, is equal to the dimension of the molecule, which is one molecule thick. When you have a bilayer, this layer is actually twice the length of the molecule.

This way, we can determine the thickness of the layer. We can also have the formation of micelles. Now these are different kinds of arrangements, where, as we increase the concentration of the surfactant, they start actually assuming a spherical kind of shape, where the polar heads, the hydrophilic groups, are exposed to water, and the non-polar heads are actually contained inside the core.

So, essentially, micelles can be represented as tiny drops of oil in water. And then we can also look at the formation of reverse micelles, which takes place in organic solvents.

So, when you dissolve the surfactant in organic solvents, the non-polar parts, the hydrophobic parts, are solvated by the non-polar solvent molecules, and the polar part is deeply buried inside. They actually interact with each other because of their like polar nature, and the non-polar parts create the outer covering, which leads to the formation of reverse micelles.

Following this, there is also the formation of vesicles, and what happens in the case of vesicles is that you have these bilayers now, and they can coil completely to form a more spherical structure. So, when they coil, we now have two distinct polar regions.

There is a polar region inside the cavity, and then there is also a polar region in the exterior, and in between, we have got a non-polar region.

So, this is a vesicle and can now be thought of as a biological cell where you can transport nutrients and ions from the outer extracellular part to the intracellular part via these bilayers. This is kind of mimicking that of a biological cell, although this is a very simplified version of it.

So, we have two distinct polar parts, and in between, we have the non-polar part, which gives rise to these vesicles. We can look a little bit more carefully at the spherical

micelles, and in this regard, we can take examples of anionic micelles, with stabilization by cations. So, for example, we can have this anionic micelle, where these are the negatively charged groups, and then we have the cations, which are shown in red.

Because of the strong electrostatic interactions that exist between the cation and the anion, the cationic sheet is also present. So, we have the hydrophobic part, and this is the hydrophilic part, and we now have different layers here that are present.

So, the hydrophobic core is around 1 to 3 nm, and we have the Stern layer, which is 0.1 to 0.3 nanometers. And then we have the Gouy-Chapman layer, which is 10 to 100 nm. So, in the Gouy-Chapman layer, we have these cations and anions arranged. The hydrophobic part is 1 to 3 nm, and we have the Stern layer, which is 0.1 to 0.3 nm thick. It should be kept in mind that the formation of micelles only takes place at a certain concentration.

So, the concentration at which micelle formation takes place is called the critical micelle concentration; this is also referred to as CMC. You can actually determine the CMC for a particular surfactant molecule because there is a change in properties when micelles form. And that particular concentration at which these micelles form, which is called the CMC, can be determined with a lot of precision, because there is an abrupt change in the density, conductivity, surface tension, and osmotic pressure for a given surfactant-water mixture.

So, there is a sudden change in these properties and that allows us to determine the CMC, very accurately. The second thing is that the CMC, the value of the critical micellar concentration, depends upon the nature of the side chain or the hydrophobic part. So, the CMC is strongly affected by this side chain; if you have a branched side chain, then the CMC increases.

Why? Because when you have branching of the side chain or the non-polar part, it is very difficult to pack the molecules, as efficient packing will lead to the involvement of severe sterics. Therefore, in order to achieve a packed structure, where you have strong hydrophobic interactions and a high packing density, which means in a lesser volume, you need to pack a large number of surfactant molecules.

So, to achieve this particular configuration is difficult, and that results in an increase in the critical micellar concentration. Because it is difficult to create the micelle core, having a long alkyl or aryl chain decreases the CMC, as it enhances the van der Waals interactions between the nonpolar parts. For example, in the case of SDS, sodium dodecyl sulfate, at 20 degrees centigrade, when the concentration of CMC is 8.1 moles per dm^3, it is observed that 162 monomer units on average form the micelle. Similarly, if you take Me(CH2)11-(O-CH2-O-CH2)6-OH.

If you take this particular surfactant molecule, the CMC is only 0.1 moles per dm^3, which is very, very low. So, with low concentration, you are able to achieve micelle formation, and also because these have long aliphatic side chains, they are able to assemble or contain a larger number of these monomer units. Approximately 400 monomer units are present.

Also, it has been observed that the formation of micelles is more favored in the case of non-polar surfactant molecules because when you have polar or charged surfactant molecules, there exist electrostatic repulsions.

And because there are electrostatic repulsions between the side groups, it tends to destabilize the micelle formation, so when the destabilization happens, the cation is already there to counter this destabilization, and therefore there is a competition between the repulsion and the attractive forces.

So, the process of assembling these surfactant molecules is difficult for the ionic surfactants because of the electrostatic repulsion present in the Stern layer. However, when you have the uncharged ionic groups, they are not charged; thus, this electrostatic repulsion is not present, and therefore, the formation of the micelle takes place in a very favorable fashion.

And now the next thing that we would like to investigate with respect to micelles is the formation of the phase diagram, which discusses the different kinds of structures that are formed as you increase the concentration of the surfactant.

Now, before that, I also wanted to tell you further that you have now seen the formation of vesicles, reverse micelles, and reverse micelles are actually tiny drops of water in oil.

Micelles, you have seen bilayers, and now the stacking of bilayers gives rise to the lamellar phase, and you have another possibility. Now, that is when you have these micelles.

These micelles can now stack in a particular direction to form the cylindrical phase, resulting in the formation of these higher-dimensional structures. For example, the micelle is a 0D structure. Now, you have the propagation of the spherical micelles—a tube-like formation takes place, and a cylindrical tube forms.

This is the cylindrical phase, and then the stacking of the cylinders will give rise to the hexagonal phase. So, these are the new phases of the ordered types, which are formed at much higher concentrations of the surfactant molecule, and they are forming different kinds of ordered structures.

And it is important to see these different phases that exist in the case of the surfactant molecules when they self-assemble in a solution. So, you can also have the cylindrical phase and the stacking of the cylinders to give you the hexagonal phase.

Now, I have drawn here for you the temperature versus concentration phase diagram and let us start with the low concentration. At low concentrations, you see the amphiphiles are actually free to move around in the solution. You see that they are swimming around in the solution; they exist as free amphiphiles.

And the moment you start increasing the concentration, at a particular concentration, which we call the CMC, the formation of the ordered aggregate starts taking place. So, now we have crossed from the region of free amphiphiles to the micellar solution, where there is the existence of micelles.

And depending on the local environment, the concentration can vary, as you can see that these species can exist over a range of concentrations and also over a range of temperatures.

So, temperature and concentration are the two important parameters that govern the micelle structure. We can have spherical aggregates, and then the spherical aggregates can also form cylindrical aggregates, as we saw.

As you can see again, the cubic phase exists at a particular temperature. However, at slightly higher temperatures, the cubic phase gets disrupted and gives rise to the spherical or cylindrical phases. Lowering the temperature can give you the cubic phase.

As you further increase the concentration, ordering again takes place, and these cylinders, as I told you, stack together to give you the hexagonal phase. So, you have the stacking that takes place to give you the hexagonal phase, and this is now a 2-D structure, from 0D to 1D. Now the 2-D hexagonal phase has been formed at a concentration range between 30 and 50 percent, and if you further increase the concentration, you will get the lamellar phase, which is formed here, and eventually, at even higher concentrations, we will get the inverted phase.

The inverted phase now corresponds to the reverse hexagonal phase, and eventually, it will lead to the formation of the reverse micelles. So, we see now, very interestingly, that we start from the spherical structure, then we go to the cylindrical structure, which is an elongated cylindrical structure.

Then we go to the hexagonal, then we go to the lamellar, then we go to the reverse hexagonal, then to the reverse micelle. And also, keep in mind that when you lower the temperature of the solution, you will obviously get a very highly ordered phase called the

crystalline phase. But the path of self-assembly starts from spherical to cylindrical to hexagonal to lamellar, to reverse phase or the inverted phase, which is reverse hexagonal, and then to the reverse micelle.

So, this ordering takes place in solution and leads to the formation of different phases, and the structures formed by the surfactants depend on the molecular structure of the individual amphiphiles and the nature of the packing. The nature of the compactness is dependent upon the critical packing parameter, which we define as gamma.

This is according to the Israelachvili theory, and it defines the critical packing parameter to be equal to V/AL, where V is the volume of the hydrophobic chain of the surfactant, A is the cross-sectional area of the hydrophilic group, and L is the length of the hydrocarbon chain. And this is what gives it the desired packing efficiency.

To start with, if we have a small hydrocarbon chain, it is referred to as a cone-like amphiphile; as we increase the length of the hydrocarbon chain, it starts with the cone-like character, then becomes a little bit cylindrical, and eventually becomes cylindrical. If we form the inverted or reverse micelle, then there is an inversion in the shape as well.

So, let us look at this arrangement. We have a polar head group, and we have a small non-polar part. This is the cone amphiphile; it is characterized by a small value of V/A.L. Why? Because, the volume of the nonpolar part, essentially the volume of the cone, is small, compared to the product of A and L. Then, it slightly acquires some cylindrical character, and this happens in the case of the hexagonal phase.

And in the case of the lamellar phase, it is more like a cylindrical phase; it is more like the other lamellar phase, and then we can have the reverse hexagonal phase. So, this is in order of increasing V to AL ratio. So, the increasing V to AL ratio indicates that the cylindrical shape is actually for the lamellar phase. So, we have the cone-shaped amphiphile, then we have the hexagonal phase, we have the lamellar phase, and then we have the reverse hexagonal. And as you can see now, if the shape is cone-shaped, you have a smaller size hydrocarbon, and you are able to pack the amphiphile better.

So you get a much higher packing density of the amphiphile when you have a small hydrocarbon chain. As the size of the hydrocarbon chain increases, it becomes more difficult to pack it, into a more efficient arrangement, and that depends on the ratio of V to AL. Now keeping this in mind, what are the applications of the formation of these kinds of vesicles?

We have the bilayers, and these are important components of surfactant chemistry. So, we have realized that these are important, and so what is a bilayer? It is an extended sheet-like structure, and lamellar, as we saw, is a stacking of the bilayers.

Now what is important is how we can look at this process of formation of these bilayers and vesicles.

So, to start with, what we can do is take a dry lipid film, okay? So, we have this substrate and the dry lipid. How do you form the dry lipid film? You have a solution of the powdered lipid, and through the evaporation process, you get the dry lipid film, and then you soak it in water.

When you soak it in water, it will swell up to give rise to the formation of these layers of the films. Now the next thing is what we can do with these layers: can we make them into vesicles, or can we make them into higher order structures, and so on and so forth? So that can be done. Using different procedures, we have to impart agitation to these layers.

What happens when you do the agitation? For example, when you now do agitation, these layers will actually start coming out. These layers will start coming out, and the layers will fragment and curl upon themselves. So, the layers can actually curl upon themselves, and this can give rise to multilamellar vesicles.

These are the multilamellar vesicles, and they are around 300 to 5000 nm in thickness. And now, we can also, when we have got these multilamellar vesicles, do extrusion, which is mechanical extrusion; in the process of mechanical extrusion, what do we do? The liquid suspension is forced through a polycarbonate film of defined pore size, and this will give rise to the LUVs, that is, the large uni-lamellar vesicles, LUVs.

So, these essentially look as follows, and then these will give you, as for the LUVs, a much larger one. So, these actually now combine to give you the LUVs, where when you do a sonication, which is supposed to homogenize the solution, it will lead to the formation of small unilamellar vesicles, that will be like these.

These are the small unilamellar vesicles, and these are called SUVs. So, you have the LUVs, the SUVs, and the MLUs. The size for these LUVs is 100 to 300 nm, and for the SUVs, it is 20 to 100 nm.

So, this tells you that we are now able to create different kinds of vesicles. We can have, depending on the agitation you provide to the medium, as the layers start peeling off, and then the layers can actually curl around themselves, and when they curl upon themselves, they will form these multilaminar vesicles.

Then the multilaminar vesicles, depending on mechanical extrusion or sonication, will yield large unilamellar vesicles or small unilamellar vesicles. So, now all these vesicles, which are being formed, have interesting applications. For example, now the ionophore mechanism, which we have discussed, happens via these vesicles in biological cells.

So, with this, we come to the conclusion of this particular lecture, where we have looked at the surfactant properties, surfactant self-assembly, and some of the relevance of the formation of vesicles, the phase diagram, and the factors that affect the formation of these different ordered structures in surfactant molecules, and so on and so forth.

And now, in the next lecture, we will take up more case studies related to surfactant species as well.

Thank you.