Fundamentals and Applications of Supramolecular Chemistry
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Week 10
Lecture 46

W10L46_Supramolecular chemistry of surfactants

So, hello, everybody. Today we are going to discuss supramolecular chemistry in surfactants and amphiphiles, and eventually we will talk about supramolecular gelators. So, this is quite a wide area of interest on which we are now going to focus, specifically on a class of molecules that we refer to as amphiphiles.

And it is also important to realize that the molecular recognition events we will be talking about are mostly in the liquid state; that is, we will be looking at the assembly of molecules in the liquid state.

So, the liquid state, unlike the solid state, is also not very well characterized in terms of order. That means the order or arrangement of the molecules is not like that of the solid state, where the molecules are very tightly packed.

But what happens in the liquid now is that the molecules definitely have some random orientations, and they also tend to have a lot of flexibility in terms of molecular motion.

Still, in spite of this flexibility, because of the thermal energy associated with the molecules, they are free to move around in different regions of the liquid, but there also exist hydrogen bonds between specific functional groups of the liquid molecules.

So, liquids are also characterized by a certain range of ordering. However, the extent of ordering is much reduced compared to that of the solids.

The liquid state is a disordered collection of molecules that exhibit rapid motion. This is the first property or attribute of the liquid state. And the thermal energy in isotropic liquids is greater than the strength of the interactions, which are relatively smaller in magnitude.

So, because of these thermal events, and because thermal energy is associated with the collection of molecules in the liquid phase, they tend to exhibit random motion in different regions of the liquid, and these dynamic events are much stronger than the strength of the interactions between the molecules, which is much smaller in magnitude.

In spite of the fact that the molecules exhibit rapid motion and the thermal fluctuations in the system are of sufficiently large magnitude, the cooperative role of intermolecular interactions is still relevant in maintaining the condensed liquid phase.

So, we cannot ignore the overall role of intermolecular interactions in liquids, and they are also relevant for maintaining the condensed liquid phase. One such additional significance of the liquid phase is reflected in liquid crystals, which exhibit a certain degree of order in the arrangement of molecules in the bulk phase.

Now that means they do not have the extreme random-like motion associated with pure liquids. They do not have the absolutely frozen geometry that is characteristic of solids. But they exist in a phase that is intermediate between that of the solid and the liquid, and this is a special phase that exists.

They are referred to as liquid crystals, and they exhibit very different properties. We will talk about liquid crystals towards the later part of this week, and the presence of liquid crystals also characterizes the significance of the liquid state.

And, for example, we can also see that water, because of the extensive hydrogen bonding, exists at $P_0 = 1$ atmosphere and $T = 100$ degrees centigrade. Whereas in the case of hydrogen sulfide, the hydrogen bonds are quite weak; that is, we have the S-H...S versus O-H...O.

So, the S-H...S hydrogen bonds are quite weak, and the boiling point is -61 degrees centigrade, in spite of the high molar mass of H_2S. So, in principle, when the molecular weight is higher, the boiling point should also be higher, but in this case, because of the weak hydrogen bonds involving S-H...S, in the case of H_2S, that lowers the boiling point to -61 degrees centigrade.

So, the importance of liquid ordering is also relevant now, further in biological cell membranes. For example, we have bulky phospholipids, which are actually forced to order themselves in water, and this involves the combination of hydrophobic effects and the interactions between the solvent and the hydrophilic polar head, forming vesicles, which are cells that are vital to life.

So, the combination of the hydrophobic effects, and the interaction between the solvent, and the hydrophilic polar head, forms vesicles that is vital to life. And, for example, we have already seen that they play a very important role in biochemical transport, cellular signaling, and also protect the sensitive intracellular enzymes.

So, you see the relevance of this ordering of the liquid molecules now in biological cell membranes, and liquid crystals are relevant in LCDs.

Today we know that liquid crystal display technology is very popular and very important; therefore, this is a good application of liquid ordering, which is the formation of liquid crystals.

So, keeping this background in mind, let us now go to very specific arrangements: supramolecular arrangements of molecules that contain hydrophobic and hydrophilic sections. So, we can look at surfactants, for example, to start with. In the case of surfactants, it is a molecule that has two distinct zones. That is, it has a polar head, which can be negatively charged or positively charged.

Or it can have both negative and positive charges. That is zwitterionic. It has a non-polar hydrophobic tail, which is also a part of the surfactant. So, there are two distinct zones, and they both exhibit different solubilities.

So, the hydrophilic zone is water-soluble, and the hydrophobic zone, or the lipophilic zone, is soluble in organic solvents, and because of this dual behavior, they are referred to as amphiphiles.

Now, let us take some specific examples of these amphiphiles. For example, we can first take a very classic example, a very popular example of sodium dodecyl sulfate, SDS. And let us look at this structure.

We have got 12 carbons: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. We have got the hydrophobic part, and this is the hydrophilic part, or the one that interacts with the water molecules.

Similarly, we can also have phosphatidyl choline. The phosphatidyl choline, so we have this chain here. So, we again have this chain, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. So, we have this phosphatidyl chain, and again this is the lipophilic part, and this is the hydrophilic part. In this case, this can be aliphatic hydrocarbons, fluorocarbons, aryl rings, or other non-polar groups.

Whereas the polar part here can be sulfonated or phosphorylated, these are the polar groups, and based on the presence of the different hydrophilic and lipophilic parts, which is based on the functionality, there are four classes of surfactants. Number 1: Anionic surfactants like phospholipids and soaps; Number 2: cationic, which are quaternary ammonium salts; Number 3: amphoteric, which are betaines and zwitterionic in nature.

Let us take one particular example: $C_{19}H_{38}N_2O_3$. So, we have both the positive charges and negative charges in the same molecule. And finally we have got the non ionic fatty acids.

So, we have these kinds of species and these four classes of surfactants and now we would like to see how we actually investigate the interaction of these large chain-like molecules with the aqueous phase. So now we would like to see that you have now got the amphiphile and you have first dissolved in organic solvent, in which the amphiphile is soluble, and then you carefully pour this onto the surface of an aqueous medium.

So, you have an amphiphile, you have an organic solvent. You mix these two and then you pour this onto the surface of an aqueous medium. The organic solvent is then evaporating and the amphiphiles are then packed into a condensed monolayer.

So, what happens is that when you pour this mixture of the organic solvent and the amphiphile, in which the amphiphile is soluble, onto the surface of say, an aqueous phase, for example, water, the organic solvent starts evaporating and these hydrocarbon molecules or amphiphiles now start coming close to each other to eventually form a monolayer.

This is what leads to the formation of a monolayer and the thickness of this monolayer is one molecule thick. So now let us see how this particular process is achieved. So, we have a trough. And here we have put a movable barrier and here we have got, this is the movable barrier, this is the aqueous phase.

And on this you have poured the amphiphile plus the organic solvent. So, now, you see that the polar part is in contact with the water molecules, and the non-polar part is actually now exposed to the air interface.

So, at the interface of air and water, the hydrophobic part is now exposed to air, whereas the hydrophilic part is in contact with the water molecules. And we can now form this monolayer, another layer, at the back. So, in this way, you see that the molecules are now getting tightly packed.

So, you have this monolayer, and as you now move this barrier, the area which is available to the molecules is decreasing, and now the molecules come closer to each other, and they form this tightly packed monolayer on the surface of the water molecules.

And the pressure, which is created, can be measured, using a pressure sensor. That is a lateral pressure can be measured using a pressure sensor. So, now we see that the surface tension of clean water at room temperature is 72 milli Newton. Now what do the amphiphiles do.

The polar part of the amphiphiles actually forms strong hydrogen bonds with the water molecules. But now the non-polar parts, they are actually in air and there are very weak

interactions, between these non-polar parts, because the weak interaction between the non-polar parts, it reduces now the surface tension.

So, there is a drop in the surface tension, and it also decreases the pressure which is now present, and this change in the pressure can be now quantified as gamma pure water minus gamma surfactant which gives you the lateral pressure.

It is also important to characterize the arrangement of molecules on the surface. When you are slowly moving the barrier, and decreasing the surface area available to the molecules, then you have the formation of the monolayer.

It is a tightly packed layer. As the molecules come closer to each other, there are different thermodynamic processes, here which takes place. So, initially the molecules are free to move on the interface, but then the decrease of the available surface area, makes them come close to each other, and there exists an ordering of the nonpolar parts, of these hydrophobic molecules.

And we can now monitor the pressure pi as a function of the surface area of each molecule, and this gives rise to this kind of a curve, and this kink, characterizes a second order phase transition, and a finite discontinuity characterizes a first order phase transition, and this is the coexistence region.

So, you can now see very clearly, that as a function of pressure and surface area of each molecule, what are the thermodynamics associated with the processes that favor chain ordering in the liquid state which characterizes these surfactant-like molecules, when they order in a specific way at the water-air interface.

So, now this process is very important, and this is the process which actually is also the basis of the mode of action of soaps, which is able to remove the organic oils in water.

Because when you put this soap, then what happens is that the polar parts actually stick to the water molecules, the non-polar parts stick to the oil. And now when you wash it off, then the surfactant when it is getting removed, then the dirt is also being removed by sticking to the hydrophobic part.

And this is the mechanism or the mode of action of soap like action when you put these surfactants in water and these are also responsible for spreading, wetting of surfaces, including dispersion, and formation of emulsions, including frothing.

And the way in which these surfactant structures organize themselves in the liquid state can also change. They can exist in different kind of ordered structures.

So, the different ordered surfactant structures are: We can have a bilayer. So, this is a

bilayer. So, we can have a bilayer. We can have a monolayer; this is a monolayer.

Overall, this is a bilayer. We can have a micelle formation, where we can have the polar heads which are actually solvated by water, and we can also have the reverse micelle. You can also have the reverse micelle when you dissolve the surfactant in a non-polar solvent.

Then the non-polar parts or the lipophilic parts are actually stabilized by solvation by the non-polar solvent, and we can also have the formation of vesicles, where you can now have all my polar heads together and in between I will have the non- polar parts.

Okay, so you can see here, now this is a polar part, this is a polar part, in between we have got the non-polar part, so this forms a spherical arrangement which we call as vesicles. So, this kind of nice array of ordered surfactant structures can form when we actually dissolve surfactant molecules in water or in a non-polar solvent.

That they can, either form these bilayers, or they can form micelles, or they can form reverse micelles as well. So, in the next lecture we will now be looking at the phase diagram of these micelle-like structures and look into further investigations of these assemblies which are existing at the interface of air and water.

Thank you.