

Fundamentals and Applications of Supramolecular Chemistry
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Week 05
Lecture 21

W5L21_Host Guest Complexation in Clathrates, Properties of Gas Hydrates

So, hello everybody, now we are entering the new week, week 5, and this week we will be discussing an interesting set of compounds, particularly concerning the solid state, and now we will be focusing our discussion on host-guest interactions in compounds that form clathrates.

So, clathrates are a new class of chemical entities, and the formation of clathrates is particularly relevant in the solid state because now what happens is that we have the host molecule, which is not an individual molecule. It is not necessary for the host to engage individually with the guest.

But what is more important is that the host forms a three-dimensional lattice or a three-dimensional crystal structure; that is, it corresponds to a solid state where the host molecules are arranged in a periodic fashion.

And now this host framework either generates voids in the crystal structure into which I can include gas molecules, for example, solvents or other organic molecules, or drug molecules, etc.

And I can also have the host, which has different crystalline arrangements, and this phenomenon by which a host molecule or any compound can exist in different crystalline arrangements is referred to as polymorphism.

So, we are now going to enter into the field of solid-state inclusion complexes, solid-state clathrates, the formation of different crystalline forms of a given substance, which we refer to as polymorphism, solid-state phenomena, crystal engineering, hydrogen bonding topology, how the hydrogen-bonded frameworks form crystalline structures, and some of their applications.

So, this week is going to be a very interesting learning experience in which we will talk more about crystalline solids and host-guest complexation behavior in solid-state compounds.

So, now we can look at these different aspects of solid-state arrangements of the host molecules in the presence of the guest molecules where it is not a prerequisite for the host molecule to interact specifically with the guest.

So, what are the properties of clathrate? So, in a clathrate, the host molecule H is usually crystalline; it is a crystalline compound.

The host molecule is the entire (usually crystalline) solid, and the guest binding cavity need not be an intrinsic property of the individual host molecules. So, when we are going to have a guest, it will specifically look for a cavity, and the cavity need not necessarily come from the host molecule; that is, it need not necessarily be the intrinsic host cavity.

But the cavity can be created by the three-dimensional arrangement of the host molecules to form a three-dimensional solid, which we call a crystal, and that cavity which is created can now include a guest; hence, this need not be an intrinsic property of the individual host molecule.

Number 2, the composition of the clathrates need not be stoichiometric. There are voids present in the crystalline lattice created by the host molecules.

It is not necessary that all the voids be occupied; most of the voids will be occupied, but some will be statistically unoccupied, and that will result in the composition of the clathrate being non-stoichiometric.

So, it is not necessary for the composition of the clathrate to be stoichiometric, and this can happen because it is not necessary for all the voids in the crystal to be filled with gas. So, we can have clathrates that are non-stoichiometric; this is because it is not necessary for all the voids to be filled with the gas.

So, keeping these two prerequisites in mind, and knowing that the parent molecule, that is the host, can actually create its own structure, which can create a cavity that does not necessarily create a cavity, depending upon whether it creates one, the guest binding molecules can go and occupy the voids that are present in the crystal structure of the host molecule. Now, let us look at these aspects of clathrate formation in a more general sense.

So, to start with, we have a host molecule, which is cavity-free, and this host molecule, which does not have any guest included, does not have any cavity, forms a particular crystalline arrangement, and is called apohost.

It is called apohost, and normally this apohost is bulky; it is a rigid structure and a very strong structure; you cannot disrupt the crystalline lattice easily. So, it is bulky and rigid, and it contains specific functional groups that can hydrogen-bond with the guest molecules.

So, it is necessary that we have some specifics here in terms of the functional groups that are present on the apohost, such that they can form strong hydrogen bonds with the guest and form these clathrates. Now, this is a solid, and we will now add the guest molecules.

We are considering the guest molecules to be liquid; needless to say, you can always have a solid host, plus a guest that is a solid, liquid, or gas, which is in equilibrium with the host-guest complex, and the resulting host-guest complex is a solid.

So, the guest can be a solid, liquid, or gas to start with; my host is a solid-state structure, and this can form a host-guest complex, which is a resulting solid and has a high degree of crystallinity.

So, when we mix these guest molecules with the cavity-free apohost, we have solvation. Now we know that they are all swimming around here. So, we now have the apohost, which is being solvated by the liquid guest molecules, and then what can happen is that it can crystallize, containing the guest molecules.

So, now you can see a very nice three-dimensional structure is formed where the arrangement of the apohost molecules, as you can see here, is different from the cavity-free one.

So, this is the one that now contains the guest molecules, along with the host molecules, and it forms a crystalline framework or a crystalline structure where the guest molecules go and occupy the voids created by the host molecules.

So, the host and the guest together create this three-dimensional structure. Now what can happen is that once we get this host-guest complex, we can try to remove the guest molecule and see what happens to the host structure.

Either the host structure will remain the same, which means the crystallinity of the host structure is maintained, or when you remove the guest molecules, the crystallinity can decrease, there can be a loss of crystallinity, and the structure can collapse, which means the host structure will lose its parent arrangement; the entire three-dimensional structure will collapse.

This is another thing that can happen, and the third thing that can happen is that when you remove some of the solvent molecules, some of the solvent molecules still remain, and that creates another phase. So, we can have another phase.

For example, let us call this the beta phase, and the cavity-free one is called the alpha phase. So now we can consider the possibility of a third phase for this host-guest complex. Let us look at all three possibilities.

So, first of all, when you have the removal of G molecules, which means the guest molecules, you can get back the alpha phase, which is the apohost, plus the solvent molecules with the guest molecules, which are actually liquid in nature, will be released into the bulk. The next thing is that we can remove the guest molecules from the structure. So now you see the apo host is formed again. This is a new apo host; this is a new structure, which is actually a different crystalline arrangement than that of the alpha phase. We call this the beta 0 phase.

Again, this is an apo host, but this arrangement is different from the previous arrangement. So, when you bring in the guest molecules, there is a change in the crystalline arrangement of the apohost, and now when you remove the guest molecules, it will have a different structure corresponding to a different arrangement of the apohost.

So, essentially this apohost or this particular beta 0 phase is derived from the beta phase by the simple removal of the guest molecules. And you can have a gamma phase, which is formed when you remove some of the solvent molecules. Now, when you remove some of the solvent molecules, you will have a different arrangement.

Let us see that arrangement. So, you will have the solvent molecule sitting here, the guest molecule sitting here, then you will again have the guest molecule sitting here, and you will again have the guest molecule sitting here, but you will have no guest molecules sitting between these.

So, you see this particular arrangement essentially happens because now what you have done is remove some of the solvent molecules, and therefore these two chains come close to each other and pack themselves in a way to maximize the van der Waals interactions.

Therefore, we now get a new phase, the gamma phase, where some of the voids have been filled, where some of the voids have lost the solvent molecules, and a structural rearrangement has taken place to give you a new phase that we call the gamma phase.

So, you can have cases where the parent host structure generates voids, and all the voids are filled up; you can have the removal of all the guest molecules, and then all the voids are present; that is called the apo host.

We can also have partial removal of the solvent molecules and then some rearrangement in the structure to maximize close packing and minimize the voids, while the voids that were already occupied still have the guest molecules, giving you a gamma phase.

So, all these possibilities exist when you have the formation of clathrates, and today in the literature, there are a large number of examples where a large number of compounds have been made that actually crystallize first.

Now the purpose of forming the solid state is important because the individual host-guest interactions are not strong enough to enhance the binding. Additionally, because the overall binding is weak, these interactions are effectively between more non-polar hosts and non-polar guests.

So, what we do is that we now essentially form the crystal structure because there is a network of hydrogen bonds that actually makes the solid, and then the guest molecules that are in the liquid state can come and crystallize along with the host molecules in the three-dimensional structure.

So, we will be looking at examples pertaining to these clathrates, and in this regard, we will first look at clathrate hydrates, where essentially, we have now got the formation of a hydrate structure, and the hydrate here refers to the water molecule.

So, water molecules here form a three-dimensional structure, and here it is the entire three-dimensional structure that serves as a host. And these water molecules are strongly hydrogen-bonded, and the overall cavity created by the three-dimensional structure of the water molecules can now include different kinds of guest molecules.

In this case, molecules can be as simple as hydrogen, chlorine, bromine, iodine, hydrogen sulfide, HCN, chloroform, carbon tetrachloride, carbon disulfide, nitric oxide, carbon monoxide, carbon dioxide, alkanes, and so on and so forth. So, all the spectrum of molecules can now be included as guests.

So, water here, to start with, via extensive hydrogen bonding, forms a three-dimensional structure; we have the O-H...O hydrogen bonds, which form a 3D structure that is the host lattice, and the voids, or cavities, which are created can now be filled with small non-polar guest molecules.

For example, we can have chlorine, bromine, iodine, HCl, hydrogen, carbon monoxide, carbon dioxide, carbon sulfide, NO, etc., plus, and very importantly, alkanes also.

Small-sized alkanes, for example, methane, ethane, propane, and butane. So, the entire spectrum of very small molecules can now be included in the host structure, which is formed by extensive hydrogen bonding of the water molecules.

So, we call these clathrate hydrates, and they were first discovered in 1810. So, I would like to give you some background on the history of the formation of clathrate hydrates, and then we will go to the structure and other related properties of these clathrate hydrates.

And when you have the formation of these clathrate hydrates, the structural property for the formation of clathrate hydrates is that there does not exist strong hydrogen bonding or

dipole-dipole interactions between the host lattice and the guest molecules. This does not take place; there is not a strong association between them.

So, the first hydrate species was actually an aqueous solution of chlorine, which gave a solid compound of composition $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, and this was first discovered by Sir Humphrey Davy in 1810. So, this was first discovered by Sir Humphrey Davy, and the composition was confirmed by Michael Faraday, a very famous scientist, in 1823. So, once the compound was discovered, the composition was confirmed by Michael Faraday, and it was found to be $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.

Following this, a lot of research went into the formation of these gas hydrates. We call these gas hydrates because Cl_2 is a gas, and water is a liquid, and water forms a structure into which we have voids, in which chlorine molecules can go and now occupy the voids created by the host lattice.

Following this, SO_2 , which is sulfur dioxide, has been used as a guest molecule and complexed with hydrates to form inclusion complexes, and this was done by D. LaRivet in 1829, followed by bromine as a guest molecule, the aqueous solution of which gives the clathrate hydrate, discovered by Alexeyev in 1876. So, Alexeyev discovered this in 1876.

And finally, the most important discovery happened when alkanes, such as methane, formed gas hydrates, which were discovered by Willard in 1888. Followed by the inclusion of noble gases by de Forend in 1923. So, there were a large number of discoveries that were made with respect to the formation of these gas hydrates.

And the most important discovery turned out to be the combination of compounds formed by alkanes with these water molecules, and this turned out to be a very significant discovery. And before we go further into why this discovery is important, I would like to now mention that these solid-state clathrates are formed under very specific conditions of temperature and pressure.

They are clathrates of the solid-state type, formed under very specific conditions of temperature and pressure. Particularly, these are formed under low temperature conditions. The next most important property of these gas hydrates, which distinguishes them from the solvent molecule, for example, the solvent molecule here is water.

So, water has its own set of properties: it is a liquid at room temperature, and below 0 degrees Celsius, it freezes to ice. So, the properties of this gas hydrate are very different from the properties of ice, and one such important property is the melting point of these clathrates.

It has been found that the melting point of these is 31.5 degrees centigrade, above the melting point of the hexagonal form of ice. Now, ice you know when it is formed depending on the pressure and the temperature of the system, can form different types of polymorphs. In other words, you can have different crystalline arrangements of the water molecules in the ice structure. And in this case, we are referring to the hexagonal form of ice whose melting point is 0 degrees, and the melting point of these clathrates is actually 31.5 degrees.

That means these clathrates, which are actually the inclusion complexes of different non-polar species with water, are very, very stable; they are thermally very stable, and they melt at much higher temperatures compared to the temperature at which ice melts, and this is a very, very practical problem.

Now, why is this a practical problem? Because when alkanes, for example, methane, ethane, propane, and butane, these kinds of gases or natural gases are being transported, they are transported via pipelines from one place to another in cold conditions at low temperatures.

These block the transport of gases by forming clathrates or gas hydrates. So, now you see, you have a pipeline, and you are going to transport methane or these hydrocarbons. Now, when the outside temperature is very, very cold and you have moisture or water present inside these tubes.

Then what happens is that water combines with this methane to form gas hydrates, solid state structures, and now these essentially fill up the entire pipeline. So, this forms a solid inclusion complex.

So, methane plus water forms this solid-state inclusion complex, where water has a parent structure and methane is included in the voids created by the structure of water, and these essentially have a very high melting point. That means, even when the temperature goes up to 10 degrees, 15 degrees, or 20 degrees.

Outside, these blockages, which are formed from solid-state inclusion compounds, have completely blocked the passage of methane through these pipelines because these gases have to be transported from one place to another under the seabed, and that process does not take place.

Now, once the blockage takes place and gases cannot be transported, these blocks have to be removed. These blocks have to be removed, and it has also been observed that now, when you take these gas hydrates and apply high temperature, these gas hydrates burn.

What is essentially burning in this is, say you have these gas hydrates, and when you apply high temperature, you will see methane gas coming out and water being converted into vapor.

So, both water converts to vapor and methane gas is being expelled, and this gas formation takes place, leading to the conversion of the solid-state hydrates and the solid-state inclusion complexes into the corresponding gases. And this is a million-dollar problem in the industry because what happens is that these pipelines can burst.

Because if the gas hydrates are not removed, then the pressure builds up inside these pipelines, which can lead to the bursting of pipelines, and this can actually be quite devastating. This can lead to severe losses because gases are being transported, and these have applications.

So, this is a serious problem: the formation of gas hydrates, and the remedy to this gas hydrate problem is that you can remove the gas hydrates, as I said, by applying high temperature, or that is by warming up, or by putting a reagent that absorbs water or moisture; therefore, the methane gas will be released.

That is one way of doing it, and the second way is to add kinetic and thermodynamic inhibitors that do not permit the formation of these clathrates. So, we can add an inhibitor that prevents the formation of hydrate-like or clathrate-type structures.

So, you see that the formation of gas hydrates, or particularly inclusion complexes with methane, ethane, and others, is a serious problem. This has to be treated, and it is one of the very important applications of these gas hydrates.

Now, what we will look at in the next lecture is the structures of these gas hydrates, and depending on the size of the void created in the structure of the gas hydrate, we can have different compositions of these gas hydrates and different kinds of molecules in terms of the guests of different sizes that can be filled in the voids created by the structure of the gas hydrates.

Thank you.