Soft Nano Technology
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Lecture - 10
Sell Assembly of Surfactant Molecules

Welcome back. We have been discussing colloidal stability and we are nearly done with it. I will just highlight 2 specific cases; I mean there is with this colloidal stability. In fact, certain flow is associated.

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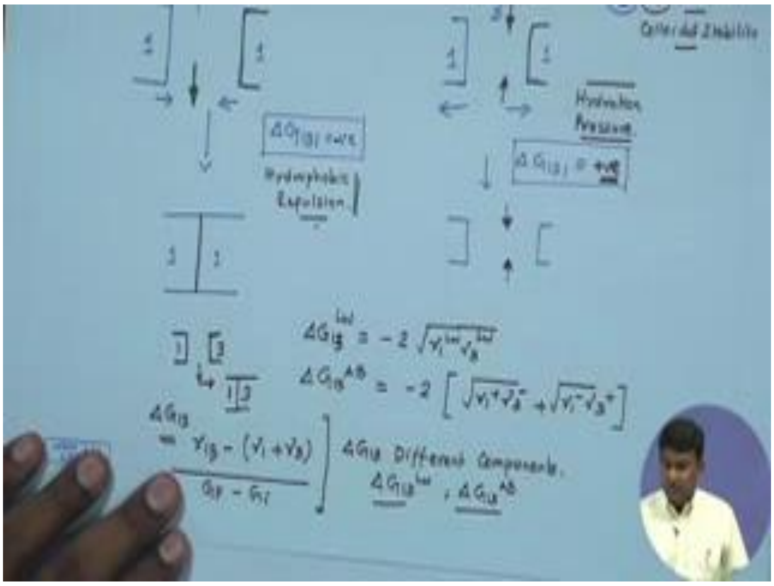

And before I move on to the topic of this particular lecture that is, self assembly of surfactant and molecules. I will just like to highlight that. So, now, it is a good recapitulation for all of you. So, you have 2 colloids of same material 1 in a liquid 3 and let us say that delta G 1 3 1 is negative.

This means that the colloids are going to head here. It is not going to be a stable colloid, which is fair enough and now you know that this possible either, you have both the colloids of the liquids are a polar or even one of them is a polar. You can also have this under a very special case of a yeah, these are the 2 conditions, also under a very special case of Monopolar liquid and Monopolar colloids, when both either both the positive components or both the negative components are 0, but what is important is, as the 2 colloids come in contact with each other, they actually squeeze out the liquid from the intermediate zone or the liquid that is between these 2 and this triggers a flow and this is known as Hydrophobic Repulsion.

On the other hand, if you have why it is called hydrophobic repulsion? Probably you can start thinking because 2 surfaces. So, we have already learned about what is Hydrophobicity? What is hydrophilicity? 2 surfaces, we lead here in water. Particularly, if this liquid is water, then it is called hydrophobic repulsion. Water of course, is a polar liquid. So, this is possible only when the colloids and the polar and polar colloids will have rather lower surface energies. So, the surfaces corresponding to them are going to be hydrophobic. They do not want water to spread on them.

Essentially what they will like is, they would like to cover themselves up with each other and squeeze away the water from them. So it is a very interesting case study. So, that is, why it is called the hydrophobic repulsion. If on the other hand the liquid is water and collides are stable. So, now, you know that this is possible, when this delta G 1 3 1 is positive this in fact, leads to an out ward motion of the 2 colloids because they are stable. They want to go away from each other; even if you forcibly bring them together they would like to go away from each other. So, what does that trigger? That in fact triggers an in wards flow of water or the liquid and this is known as hydration pressure.

This I thought that I will just tell you because all of you have done some course or the other on fluid dynamics and you see here based on the surface interactions. In fact, there is some flow that gets triggered. So, I mentioned that in the classical form of the Navier Stokes equation you really talked about the surface energy term, but here you see examples where, flow is a triggered due to surface effects. The other thing I just wanted to highlight, we now all understand and what is delta G 1 3. For example, it is something like, at least do not confuse it with these examples of 1 3 1, it is 1 3.

Very simple 2 surfaces 1 and 3 initially in air and vacuum coming in contact, that is it and one of the way, you can write it down is the final configuration. That is the G F minus G i, but if you look back in to the derivation that you have done. If you look back in to the derivation you have done, you also now know this delta G 1 3 has different components, which are primarily delta G 1 3 L w and delta G 1 3 A B and the individual component have these expressions.

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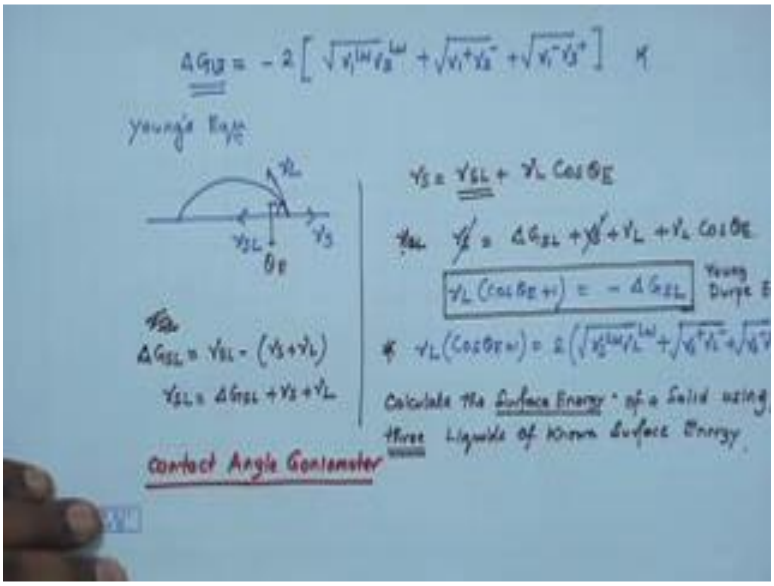

$$\Delta G_{13} = -2\left[\sqrt{\gamma_1^{LW}\gamma_3^{LW}} + \sqrt{\gamma_1^{+}\gamma_3^{-}} + \sqrt{\gamma_1^{-}\gamma_3^{+}}\right]$$

Young's Eqn

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_E$$

$$\cancel{\gamma_S} = \Delta G_{SL} + \cancel{\gamma_S} + \gamma_L + \gamma_L \cos\theta_E$$

$$\boxed{\gamma_L(\cos\theta_E + 1) = -\Delta G_{SL}}$$

Young Durpe E

$$\Delta G_{SL} = \gamma_{SL} - (\gamma_S + \gamma_L)$$

$$\gamma_{SL} = \Delta G_{SL} + \gamma_S + \gamma_L$$

$$\gamma_L(\cos\theta_E + 1) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S}\right.$$

Calculate the Surface Energy of a Solid using three Liquids of Known Surface Energy

Contact Angle Goniometer

You want to, if you would like to write the full expression of G 1 3, for a system where polar interactions are present. This is what you will get. Now with this, I will the reason why I wrote it is I will revisit the Young's equation at this time.

This is very well known now and you have gamma S is equal to gamma S L plus gamma L Cos theta E. This gamma S L, we now just pick up this gamma S L and we can write it down, get an expression following this particular expression, we just discussed and I mean we can write an expression like delta G S L is equal to gamma S L minus gamma S plus gamma L. It is, yes situation what you can thing that you had the pristine surface and you had the liquid somewhere and you simply bring them in contact. So, that is what is delta G S L.

If you substitute, 1 can get an expression for gamma S L in terms of delta G as delta G S L plus gamma S plus gamma L and this you can, if you substitute here, what you get is gamma S is equal to delta G S L plus gamma S plus gamma L plus gamma L Cos theta E. This in fact, cancels out and even if it cancels out, what you get is gamma L Cos theta E plus 1 is equal to minus delta G S L. You can in fact, take help of this equation now and simply substitute the expression of delta G S L, which will give you gamma L Cos theta E plus 1 is equal to 2.

This is now a very important expression. By the way, this particular form of Young's equation is known as the Young Durpe Equation even if you forget the names, I do not care about the (Refer Time: 09:03) details, but you can write the Young’s equation. This is nothing, but the Young’s equation written in these particular forms.

But this particular equation is very important because with this equation, in principle you can calculate the surface energy. I repeat surface energy of a solid using 3 liquids, why 3? This will be clear to you, 3 liquids of known surface energy. How does it work? You have a instrument available with us, which is known as the contact angle goniometer. I will just write it here.

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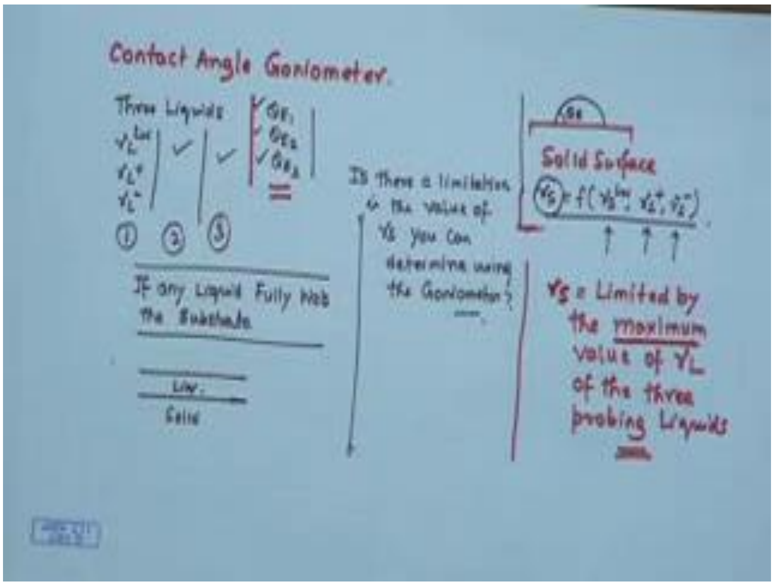
Contact Angle Goniometer.

Is there a limitation to the value of γ_S you can determine using the Goniometer?

If any Liquid Fully Wets the Substrate

$\gamma_S = f(\gamma_S^{LW}, \gamma_S^{+}, \gamma_S^{-})$

γ_S = Limited by the maximum value of γ_L of the three probing Liquids

Where, you can actually take a surface, solid surface and dispense a drop of any liquid and you can measure the theta. This is measurable. Its computer programmed you have a cameras you can measure it. Most people in fact, what they do? Is that they put a drop of water on a solid surface and based on that looking at the equilibrium contact angle they straight away comment whether the surface is hydrophobic or hydrophilic based on the convention of, what is this equilibrium contact angle, but there is more to that.

If you take a solid surface, its surface energy is gamma S and it is a function of gamma S L w gamma S plus and gamma S minus. If you can independently determine all these three parameters, there is no reason why you cannot calculate gamma S. So, what is typically done, you take 3 liquids remember, simultaneous algebraic equations 3 unknowns. So, there are you need 3 equations. So, you get 3 liquids they make 3 different contact angle. So, all the liquids will have. So, these 9 set of values is to be known. If you know them you get the theta E for liquid 1, liquid 2, liquid 3 these are known for that particular liquid.

You get 3 simultaneous equations and which you can solve, the simple 3 algebraic simultaneous equations, you can solve and you can get the 3 components and therefore, you can find out the surface energy of an unknown solid sample. This is very very effective. There is a limitation of course, of this technique and can you think. Is there a limitation in the value of gamma S, you can determine using the Goniometer? Well if the one of the mandatory requirements is that all the 3 liquids must make finite equilibrium contact angle because you need the values of theta E 1, theta E 2 theta E 3.

Therefore, if any liquid fully wets the substrate which is like this, complete weighting. Then you cannot use it and under what condition the liquid will start to fully wet the surface. The condition is if the surface energy of the solid is much higher than that of the liquid, there is a possibility that the contact angle will become very less and eventually will start to fully wet. So, one of the, one can impose a restriction by saying that the value of gamma S. This is important listen to it carefully maybe we can have a discussion or in the discussion forum I will comment on this.

The value of gamma is that you can measure is limited by the maximum value of gamma L of the 3 probing liquids. There are due to pinning and other conditions even a liquid on higher energy surface might exhibit a finite contact angle, but if you know that you are, the surface energy that you are going to calculate is lower than the surface energy of the liquids and you are guaranteed to have equilibrium contact angle, then your method works fine. Of course, the maximum value why? Because out of the 3 liquids, 1 will have the maximum value, the others will any way have lower values.

That is not going to be a problem and that is the maximum what you can measure. Think over it, this is an interesting aspect.

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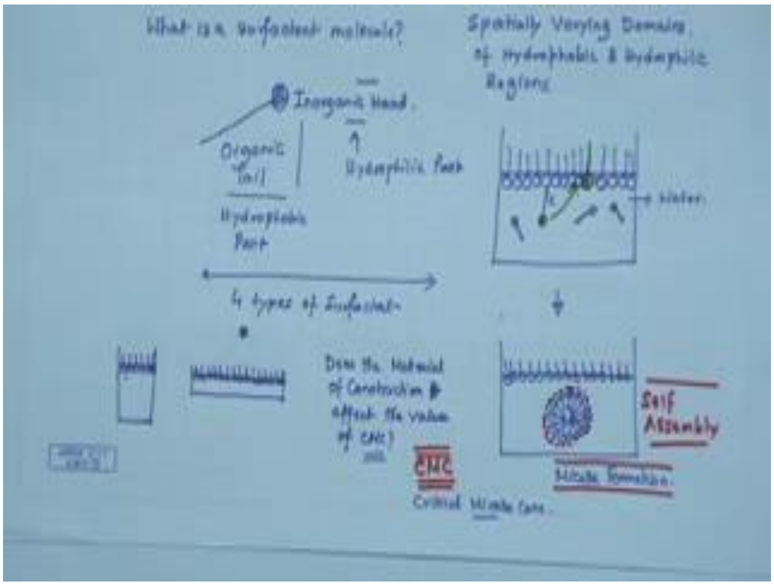

Now, we will quickly give you a very nice example of this so called surfactant and self assembly which is entirely related to hydrophobic and hydrophilic interaction. What is a surfactant molecule? I do not want to going to the detail chemistry of it. Name suggests it all; they are surface active molecules, but there are unique molecules which have spatially varying domains of hydrophobic and hydrophilic regions. Typically this is how a surfactant molecule looks like. You have an inorganic head and an organic tail. This organic tail is mostly hydro carbon. So, this is the hydrophobic part and this is the hydrophilic.

Now you know that hydrophilic part will like water, hydrophobic part will not like water etcetera. So, if you now take a container of water and let us say you put in 1 surfactant molecule indeed. Of course, there are classification; there are 4 type of surfactants, which are classified not very important for our context, they are known as cationic Surfactant, Anionic Surfactant just check it out in the net, you will get all the details. Non ionic surfactant depends on the nature of the head group. So, if the head group contains a positive charger; cationic surfactant, head group contains anionic group it is an anionic surfactant. A head group may not contain any charge. It is a non ionic surfactant or if the head group contains both the charges that is also possible it is known as a Zwitterionic surfactant.

Let us check out. But what is interesting for our case is that; if you have water and put 1 surfactant molecule, what happens is this part; the hydrophilic head likes to be in contact with water; however, the hydrophobic tail does not want to be in contact with water. So, how do you satisfy both of them? This is small molecule, this is water. So, the molecule can move depending on because you have seen because of hydration pressure or hydrophobic impulsion colloidal particles can move. They are not affected by gravity. So, what will happen is this molecule will migrate to the free surface and take a configuration like this. This way what happens, you see the hydrophilic head group is in contact with water.

It is satisfied and the hydrophobic tail is away from water. So, that is also satisfied. It is not coming in contact with water. So, of course, in real experiments you do not have ability of adding one surfactant at a time. So, you add lot of surfactant, you add some surfactant molecules and their first preferred location is going to be the free surface. So, they are going to migrate here, fine. What happens if you add excess amount of surfactant molecules? Excess in the sense there are the free surface is fully covered and you still have some surfactant molecules because they do not have now the space to migrate to the free surface.

They are forced to stay inside the liquid. So, what happens is under these circumstances. If the free surface is fully covered; so see for each of the molecules the hydrophobic tails is actually leading to significant amount of energy penalty or inter facial energy is rather high. They do not want to stay like that. So, what happens is these molecules sort of come together and form a spherical (Refer Time: 20:20) like this many of you might be, might have started to guess it. Yes, this is what is known as the Micelle formation.

What is a Micelle? You have it is a self assembly. Firstly, they organized by themselves. It is a self assembly process. It is a assembly of the surfactant molecules in such a way in spherical dome like fashion. So, that the outside surface so, the head groups are facing out ward. So, now, this sort of becomes, what is known as a Supramolecular assembly. It is not a single molecule, it is assemble of molecules, but water as a whole sees only the hydrophilic head groups. That is what is surrounding the outside and all the hydrophobic tails, which sort of do not have a preferred interaction towards affinity towards water, are sort of hidden beneath, this hydrophilic heads.

This is what is known as the Micelle formation; if you remember, while we were talking about the examples of different paradigms of nano fabrication. The second example I gave was a self assembly. And this is one of the classic examples of self assembly because the molecule assembles by them, because you do not have any mechanism to individually hold the molecules and assemble them and they assemble in a desired fashion. Here, what is the motivation for the formation of this type of an assembly? The motivation is in fact, to reduce inter facial energy penalty.

It forms and to water it is like a spherical ball, which has hydrophilic head and all the hydrophobic tails are sort of hidden below or behind this hydrophilic head groups. Few more examples or thought provoking questions one can ask; so the most classical one. Many of you probably know what is CMC; Critical Micelle Concentration of course, you need a certain concentration for the Micelle to form because if the concentration of the Micelle, of the surfactant molecules is very very less than the Micelle own form because as long as the free surface is free, the molecules will migrate there.

Even when the free surface is full and you have 2 less number of molecules, which are not enough to form a Micelle and cover all the tails nothing, no assembly will take place. There are also sort of gives you a feeling that, if you now take for the same system 2 containers, which are let us say like this. What it means is that? One is deep and shallow; the water volume is same, but the geometry is different. Are you going to get different values o CMC and my answer based on fundamentals would be; Yes, I am not very sure if you can physically measure the different using any instrument, but you see this because of the geometry of the vessel, this particular vessel is going to accommodate less number of surfactant molecules at the free surface.

Therefore, it will favor Micelle formation or favor early Micelle formation as compared to this one. This as higher surface area and therefore, it can accommodate larger number of surfactant molecules. One can also start thinking about does the material of construction favor or affect the value of CMC? Again I am not very sure because I am not a chemist. What can do? What is the accuracy with which you can measure CMC?

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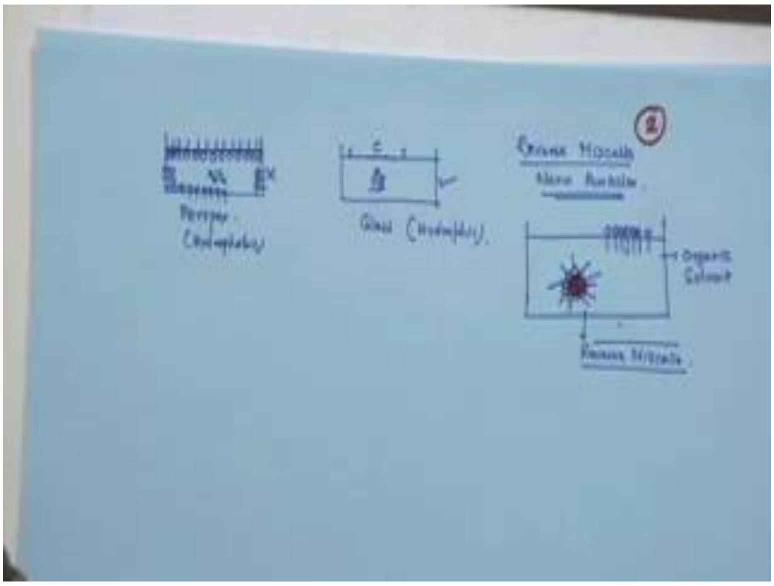

But in principle, if you take 2 containers of the same volume and one is let us say made of, let us say some plastic like perspex which is (Refer Time: 24:48) nothing else and one is let us say made of glass. Now glass is hydrophilic in fact, and this is hydrophobic.

When you add water, there is water therefore, the surface is in contact with water, but here the surface likes the water, here it does not like the water. So, when you add surfactant molecule of course, the first and the most preferred location for the surfactant molecules to go here is to the free interface, but I would expect that in this particular case a surfactant molecules preferred to add here to the surface. They will sort of act as hiding the hydrophobic wall container of the wall from water and then only Micelle formation will start. In this case the free surface gets filled up and then straight away Micelle formation starts.

Another important term, you might have come across is a reverse Micelle, which is a very very common technique for synthesis of nano particles. Reverse Micelles are almost know almost are sort of known as nano reactors. All you do is instead of water, you take an organic solvent where, the tails actually like and the head does not like because the head is hydrophilic. So, initially the interface gets populated like this and once the interface is filled up again, there is a Micelle like assembly, but the assembly is exactly the opposite orientation. Now the tails are facing out and the heads are sort of hidden.

This is sort of a reverse Micelle. The interesting thing is this, lot of literature on that and I do not want to talk about Micelle and reverse Micelle in this course. This is not the right course for that, but after todays discussion you can sort of look for yourself, but interesting thing is unlike a Micelle where, the core is filled up. Here the core is sort of hollow and that is why, this has sort of become a very very popular technique for synthesis of nano particles. You can have the reactants as dispersion and the Micelle can form the reverse Micelle can form around the acquets or what type of reactants you take and then you can have some reaction which triggers formation of you nano particles.

I will stop here and next class we will have a quick discussion on another aspects of surface tension, that is the Laplace pressure and I will try to do a quick recapitulation of whatever we have done so far and then we will move on to nano patterning.

Thank you.