Soft Nano Technology

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Lecture – 09

Components of Surface Tension – 2

We were discussing the different components of surface and interface tension. And now we have reached a stage where, we know that when we are considering the interactions. Fundamentally when we are considering the interactions between two dissimilar molecules or a similar molecule the interaction we are considering is based on Van Der Waals interaction as well as polar interaction and those gets manifested in terms of surface and inter facial tension, which also has components of Van Der Waals interaction as well as polar interaction.

We first talked about the how to mathematically obtain an expression for the magnitude of the Van Der Waals interaction between two molecules, of this similar materials provided the interaction, the self interaction of molecules v 1 1 and v 2 2 are known and we came up with a formula that v 1 2 l w.

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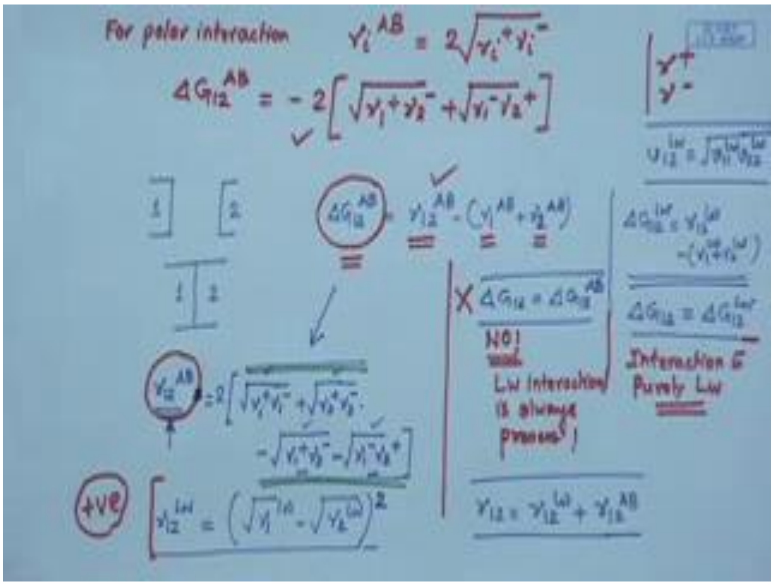

Is given as under root of v 1 1 L w and v 2 2 l w. Then we looked into certain cases and we realized of very interesting thing that, only by considering Van Der Waals interactions that is when we talk about considering different terms which is fine when considering

Van Der Waals interactions you. In fact, cannot explain colloidal stability, we have seen that because two surfaces or I just physically put this as statement in a different way to similar polar colloidal objects in a polar liquid medium. We have seen that they will always come in contacts.

Colloidal stability cannot be explained. So, we now realize that in order to have colloidal stability, when a stable colloid it is important to have additional interactions and the second interaction that we told that, we will consider will be the polar interactions. We started to define the again terms that can consider, that can mathematically represent the polar interaction and we defined two terms.

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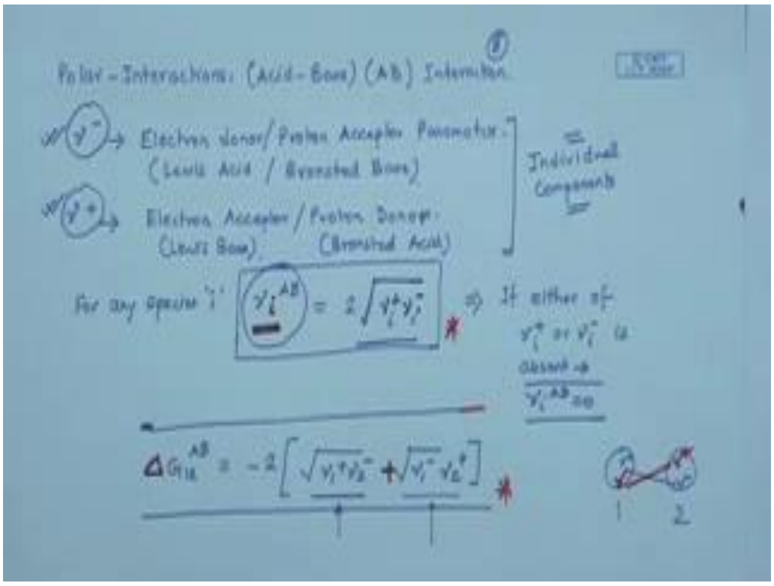

Polar-Interactions: (Acid-Base) (AB) Interaction

γ^- → Electron donor/Proton Acceptor Parameter. (Lewis Acid / Bronsted Base)

γ^+ → Electron Acceptor / Proton Donor. (Lewis Base) (Bronsted Acid)

= Individual Components

For any species 'i' $\boxed{\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-}}$ * ⇒ If either of γ_i^+ or γ_i^- is absent → $\gamma_i^{AB} = 0$

$$\Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right] *$$

Essentially the electron donor or the proton acceptor parameter gamma minus and the conjugate parameter that is electron acceptor or the proton donor term and these terms are for every component. It is not inter facial term; it is for individual components or in other words, they are the constituents of the polar component of surface tension of a material i. So, these are the individual constituents of the polar component of surface tension of a material i and how they are related is based on some sort of a geometric mean, multiplied by 2. Further we note that for polar interactions, delta G 1 2 A B that is the polar component of delta G between two dissimilar surfaces.

Only the polar component is given by this particular relation. Where, it is essentially addition of the two cross interactions, which is half years because we already argued that in order to have a polar interaction you need to have opposite polarity and if you have an opposite polarity in the neighboring molecules. Let us say this is 1 and this is 2. Of course, the class component of this is going to interact with the minus components of this, leading to attraction and similarly the minus components of this is going to attract the or interact with the plus component of 2 and that is exactly what you see because this delta G 1 2 also corresponds to when they come in contact and it is some sort of an additive, addition of the 2 cross interactions.

Based on this understanding, we continue our discussion on the polar component of surface and inter facial tension.

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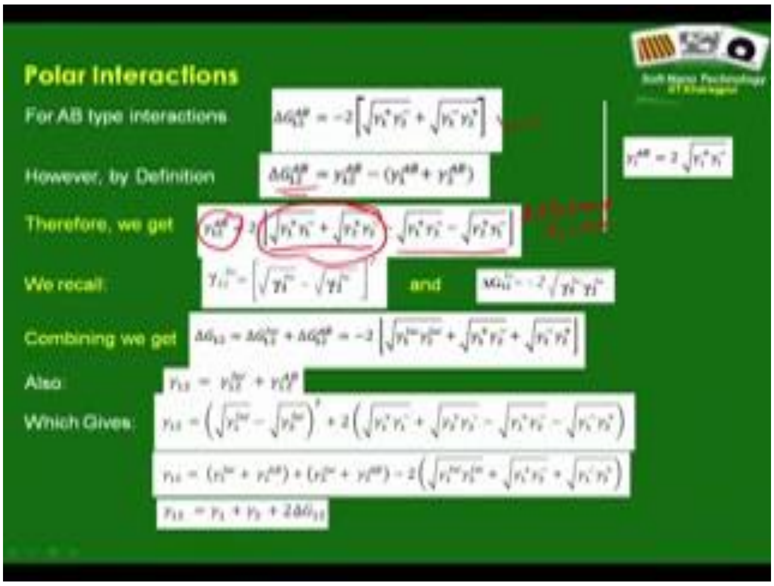

Polar Interactions

For AB type interactions $\Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right]$

However, by Definition $\Delta G_{12}^{AB} = \gamma_{12}^{AB} - (\gamma_1^{AB} + \gamma_2^{AB})$

$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-}$

Therefore, we get $\gamma_{12}^{AB} = 2\left[\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right]$

We recall: $\gamma_{12}^{LW} = \left[\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right]^2$ and $\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

Combining we get $\Delta G_{12} = \Delta G_{12}^{LW} + \Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right]$

Also: $\gamma_{12} = \gamma_{12}^{LW} + \gamma_{12}^{AB}$

Which Gives: $\gamma_{12} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right)$

$\gamma_{12} = (\gamma_1^{LW} + \gamma_1^{AB}) + (\gamma_2^{LW} + \gamma_2^{AB}) - 2\left(\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right)$

$\gamma_{12} = \gamma_1 + \gamma_2 + 2\Delta G_{12}$

What do you seen on your screen? We have already discussed all those things. So, this is what, which was discussed and we can also rewrite G 1 2 considering the same old picture. This is very similar to what we had written in the earlier case, as delta G 1 2 L w as gamma 1 2 L w minus gamma 1 plus gamma 2. Here I would like to make a statement and one to sort of some initiates, some bit of thought, in your mind. While considering the Van Der Waals interactions, delta G 1 2 is equal to delta G 1 2 l w.

My question is can we write that, while considering the polar interaction? That we consider only a system where, we have polar interaction and the answer is a big emphatic no. Why? Because I have been telling this to you thing for a while and I thing now all of you understand and based on this particular discussion for next 2 minutes, you will understand if even better way that you can have situations where, the interaction is only Van Der Waals, but if you have a system which is polar where, there is polar interactions; please do not forget that L w interactions is always present.

This statement is not correct, but you can individually looking to the term delta G 1 2 A B, that gives you sort of the free energy change, due to addition to of a two surfaces which have polarity. What is the contribution of the polar components of the surface and inter facial tension? Therefore, what we you can combine this one and this one and what you get is this particular formula. Please do not try to remember or mug it up, you can very easily derive it. It looks a little cumbersome, but it is very simple. What you get? This is the polar component of inter facial tension.

I will just write in order to compare the expression of the Van Der Waals component of inter facial tension because ultimately your gamma 1 2 is going to be, gamma 1 2 L w plus gamma 1 2 A B and here you note something interesting. We have already seen, that this term is going to be positive no matter what is the magnitude of gamma 1 and gamma 2 l w; however, here you see that gamma 1 2 A B can be positive or negative and it depends on the numerical values of this individual components because these all come under, under root. So, individually all these terms are positive and since all these terms are positive, now one in facts needs to look or in other words gamma 1 2 A B is going to be positive, if the total cohesive polar interaction because this is inter facial tension of 1, this is inter facial tension of 2.

This is polar interactions, but between the gamma plus and gamma minus of similar objects this is within 1 and this is within 2 and this is the adhesive interactions, that is the polar interaction between dissimilar objects. So, if the cohesive interaction the strength of cohesive interaction exceeds the strength of adhesive interaction, adhesive interaction is combination of these two terms, cohesive interaction of these two terms. You can so identify that in the transparency and as I promised this will be made available to you.

This is the cohesive terms and this is the adhesive terms and depending on the strength. If the strength of the cohesive terms is higher than the strength of the adhesive terms. Then you also have gamma 1 A B as positive, but if the strength of the adhesive term is stronger or higher than this, then gamma 1 2 A B can be negative right. You can have a situation theoretically that, gamma 1 2 A B negative, but again gamma 1 2 is positive and that will depend on the relative magnitudes of the polar and Van Der Waals component of inter facial tension. Why a negative value of gamma 1 2 L w is going to be important for us is simply.

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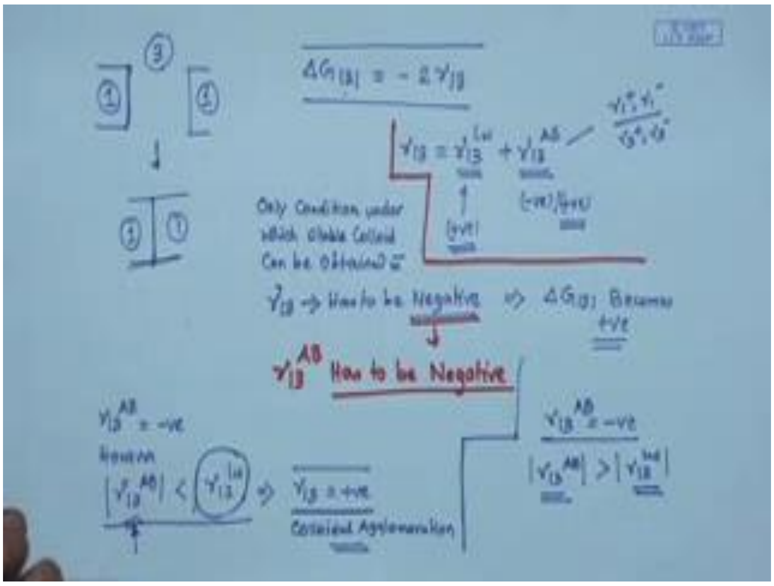

We are look into the problem of two colloidal particles of same material 1, trying to come in to contact within a liquid medium 3 because the change in the free energy or we can write is of gamma delta G 1 3 1 these two objectives of 1 coming, initially they are dispersed in liquid 3 and then they are coming in contact and you can find it out the expression. You can do it yourself, the expression turns out to be minus 2 gamma 1 3.

Now if we consider a system where we have both polar and Van Der Waals interactions, this 1 3 L w is going to have two terms and here we actually have expressions for both the terms, just 1 2 we just replaced it with 1 3, which is fine as more of (Refer Time: 11:48) a difference and here you can see that this term is always going to be positive and this term depending on the relative magnitudes of the four constituent terms. What are the four constituent terms? Gamma 1 plus gamma 1 minus gamma 3 plus gamma 3 minus they can be a positive or negative.

Now, if both are positive, no point the colloid is again the unstable because both the terms are positive, this is positive delta g 1 3 1 is negative and therefore, their addition is guaranteed. So, that is not an exciting situation. Though the only way, can be obtained is gamma 1 3 as a whole has to be negative because if it is negative, only then delta G 1 3

1will become positive and therefore, what would it mean? That the two surface, the two colloids of 1 will thermodynamically will no longer be favored to come in contact.

Only condition for a colloidal stability is gamma 1 3 has to be negative which would imply that delta G 1 3 1 becomes positive and now we are look considering all the concepts we have built slowly. How this can be negative? So, necessary condition for this to be negative is of course, gamma 1 3 A B has to be negative and now you also understand under what condition this is? This is possible, when the adhesive polar interaction, the adhesive part of the polar interaction, the adhesive component of the polar interaction exceeds the cohesive component of polar interaction.

So that only, this condition we will make gamma 1 3 A B negative, but there is some additional condition this can be negative, but if its numerical value is lower than the magnitude of gamma 1 3 l w, I repeat this is negative. Let us, consider a situation is negative. However, gamma 1 3 A B, the numerical value is lower than gamma 1 3 l w. What would that lead to? That will lead to this to be positive, so this because this is anyway positive. So, this again leads to colloidal agglomeration, but there is a difference. So, what is important in this particular case? Is the colloid will agglomerate but you have competition.

The Van Der Waals force is responsible for the Van Der Waals components of inter facial energy is responsible for their agglomeration, but the polar component is trying to oppose that, but numerically the strength of the Van Der Waals force is stronger and therefore they agglomerate.

The only condition under which you can obtain a stable colloid, is you need to have a negative inter facial value of gamma 1 3 arising out of the polar interaction and numerically this has to exceed the value of gamma 1 3 l w, which will always prefer addition of the colloidal particles in air as well as in a liquid medium. So, that is sort of what we wanted to discuss about the individual components of the surface tension.

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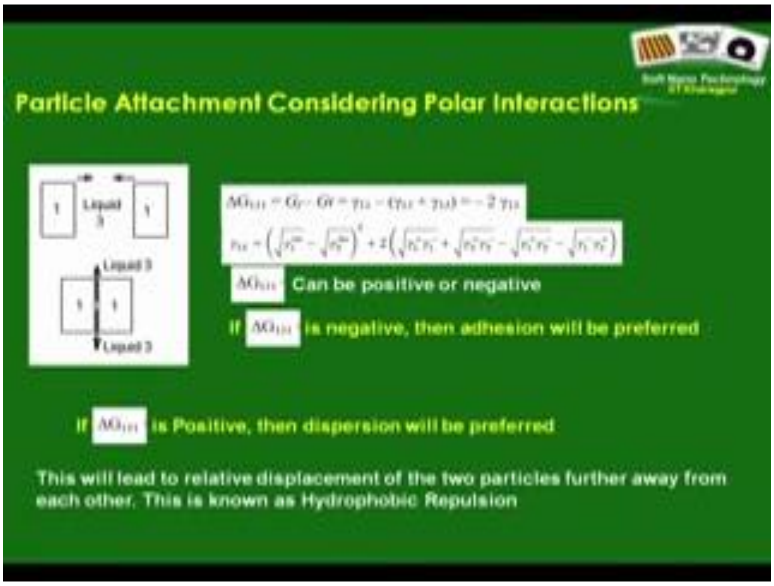

Particle Attachment Considering Polar Interactions

$$\Delta G_{131} = G_f - G_i = \gamma_{11} - (\gamma_{13} + \gamma_{13}) = -2\gamma_{13}$$

$$\gamma_{13} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2 + 2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-} - \sqrt{\gamma_1^+\gamma_3^-} - \sqrt{\gamma_1^-\gamma_3^+}\right)$$

ΔG_{131} Can be positive or negative

If ΔG_{131} is negative, then adhesion will be preferred

If ΔG_{131} is Positive, then dispersion will be preferred

This will lead to relative displacement of the two particles further away from each other. This is known as Hydrophobic Repulsion

There are certain additional interesting observations that one can make, one of them is.

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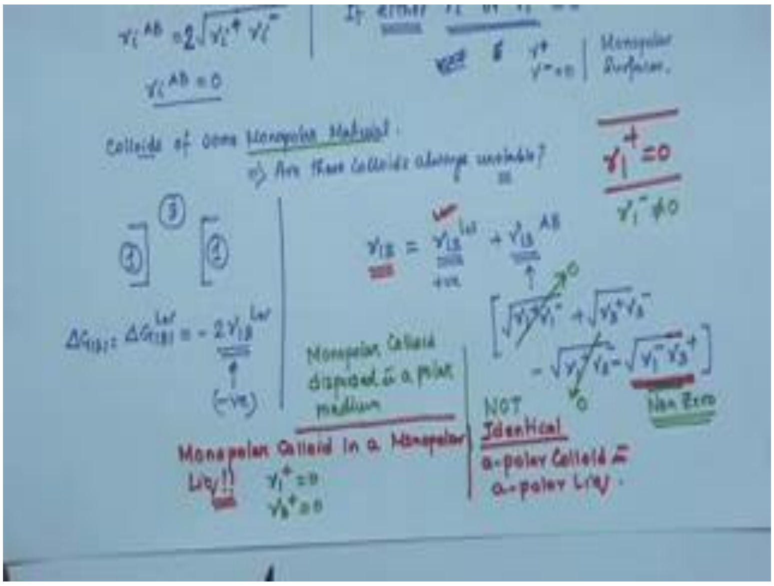

If you look at the expression for gamma i A B and what did we consider? We considered that, it is sort of a geometric mean of gamma i plus and gamma i minus sorry I am just missing out; it has a pre factor 2. It is not very important. One of the consequences that we in fact, discussed was if either gamma i plus or gamma i minus is equal to 0; either is very important in gamma i A B is equal to 0. So, this is very interesting.

You tend to apparently feel that, when you talk about the surface tension, you calculate the surface tension of this material there is no effect of the polar component; which is correct. There are lots of surfaces or materials which either has and which actually sort of obeys this condition. There are many surfaces where for example, gamma plus is non 0, but gamma minus is 0 or the opposite is also true and these are in fact, called Monopolar surfaces. So, if I straight away ask you that you have let us say colloids of some Monopolar material. So, do they always are here? So, are these type of colloids always unstable?

Is the question clear? We are seeing that, if one of the components is 0, then there is no effect of the polar component of surface energy for a specific material and in this case we are asking, what I am asking? Like what we have observed for purely a polar substance, this is what we got. This is always negative, this term is always negative, and therefore colloids are never stable. So, for Monopolar colloids is it the same situation? Well please do not jump on to conclusion because when we are considering a colloidal dispersion even with the Monopolar colloid, this gamma 1 3 term. In fact, contains gamma 1 3 L w and gamma 1 3 A B and there is no need to discuss gamma 1 3 l w, further it is always positive, but please be careful this gamma 1 3 A B. In fact, contains these terms and that is very interesting. Let us say, let us assume that gamma 1 plus is 0.

What it means? That indeed this term is 0, that also means that gamma 1 minus is non 0, this term is 0. This term is also 0; however, this term is non zero. So, the situation of, if you have a Monopolar colloid is dispersed in a polar medium is not similar, to an a polar colloid in a polar liquid why? Because indeed you do not have any contribution coming in terms of total surface energy of this material 1 due to the polar interaction, but due to the cross interaction, the adhesive interaction in a polar liquid. This term will be non zero and depending again on the magnitudes, this term in principle at least mathematically has the possibility, that this term numerically exceeds this term and therefore, gamma 1 3can become negative and the moment gamma 1 3 becomes negative delta G 1 3 1 would become positive and that would lead to a stable colloid.

This is possible one can, further two is the question. What happens? You have a Monopolar colloid in a Monopolar liquid and again do not jump into the conclusion. Please try to find out, what are the terms that are present? Well if it turns out that gamma 1 plus is 0 and gamma 3 plus is also 0 then of course, all the terms are non zeros. So there is actually no contribution of gamma 1 3 A B, it will tend to 0. Why? It is very obvious.

Look at the expression gamma 1 plus makes this term and this term 0, gamma 3 plus makes this term and this term 0.

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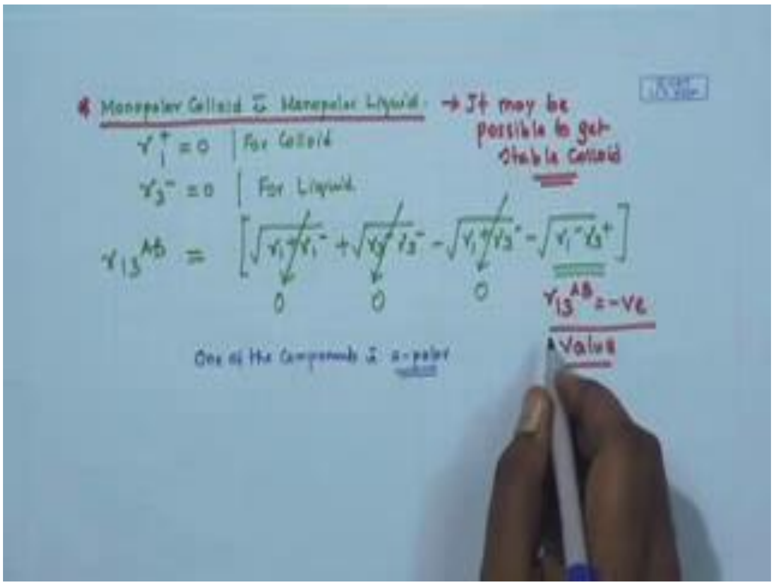

Monopolar Colloid ī Monopolar Liquid → It may be possible to get stable Colloid

$\gamma_1^+ = 0$ | For Colloid

$\gamma_3^- = 0$ | For Liquid

$$\gamma_{13}^{AB} = \left[\underbrace{\cancel{\sqrt{\gamma_1^+\gamma_1^-}}}_{0} + \underbrace{\cancel{\sqrt{\gamma_3^+\gamma_3^-}}}_{0} - \underbrace{\cancel{\sqrt{\gamma_1^+\gamma_3^-}}}_{0} - \sqrt{\gamma_1^-\gamma_3^+}\right]$$

$\gamma_{13}^{AB} = -ve$ Value

One of the Components ī a-polar

However, continuing with the discussion of the same case, Monopolar colloid in Monopolar liquid. If you have a situation that, for the colloid let us say gamma 1 plus is 0 and for the liquid, let us say gamma 3 minus is 0 or it can be vice versa also. Then again in this expression, I will quickly write down the expression again for your understanding. This is the term corresponding to gamma 1 3 A B and you will again find that well, this term does not contribute, this term does not contribute; however, there can be one term, there is one term which is non zero. So, again in principle, this term contributes. So, gamma 1 3 A B will indeed have a negative value and depending on its relative magnitude of gamma 1 3 A B with gamma 1 3 L w again, you can in theoretically at least get a positive value of delta G 1 3 1. So, even under this condition, it may be possible to get stable colloid.

We now have had a very pretty nice picture of this so called colloidal stability. We looked into several conditions one thing, one condition that sort of unconditionally leads to unstable colloid is, if you have a polar colloid, in a polar liquid. It has to be unstable it will definitely, the particles will definitely agglomerate. On the other hand, if you have a polar liquid and a polar colloid well, there are possibilities and you have to look into the individual numbers.

There will be polar interactions and you have to look into the relative strength of the adhesive and the cohesive interactions and you may achieve stability and you can also have Monopolar colloid and a polar liquid or a Monopolar colloid and a Monopolar liquid medium and under appropriate condition. Even in those cases, it is possible to have some sort of stability coming out. One question I will leave for you, is that if you have a polar liquid, a polar colloid in a polar liquid, how that is going to contribute? So, if you have a polar colloid, what it means is that gamma 1 plus is 0, gamma 1 minus is 0 and that. In fact, you can see for yourself that the cohesive terms, the adhesive terms which can lead to a negative value they actually do not work out. So, it is gone.

If 1 of the components is a polar, the cohesive interaction goes to, the adhesive interaction goes to 0. A polar means that gamma 1 plus gamma 1 minus both are going to be 0 or gamma 3 plus gamma 3 minus both are going to be 0 and therefore, in principle theoretically you cannot explain colloidal stability.

With that I will stop and there are certain additional aspects associated with this, when the colloids are coming in contact. I will discuss that and move on to one very fascinating thing that is a surfactant molecule in the next lecture.

Thank you.