Neutron Scattering for Condensed Matter Studies
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Week 7: Lecture 20 A

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I will continue with the examples from SANS studies. First, what has been done in Dhruva, but I will also use examples from other sources. In these examples, I tried to mix length scales as well as materials, because both of them are of interest to various people. One started from microscopic structure and we are now moving on to mesoscopic structure. Mesoscopic structure in various materials is of interest to various groups of researchers and also to various industries. In last lecture, I discussed with you some examples of micelles forming using surfactant molecules. I will continue a little bit with that. I will also talk about polymers.

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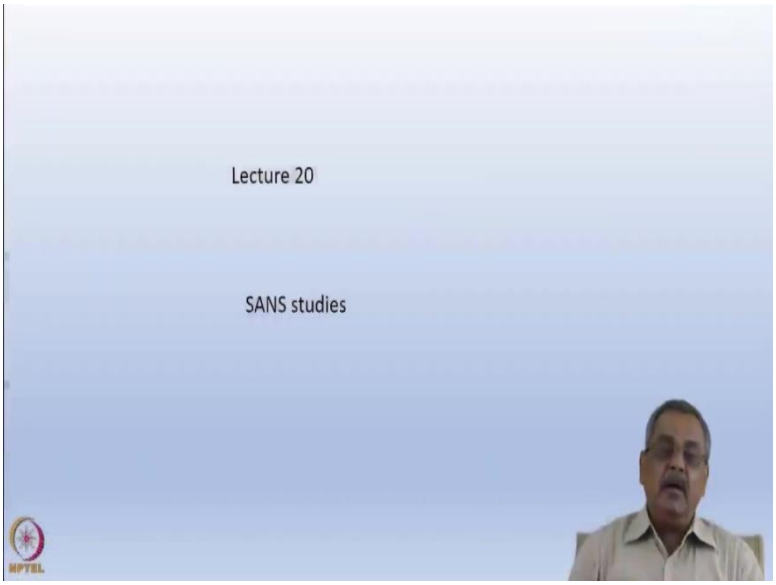

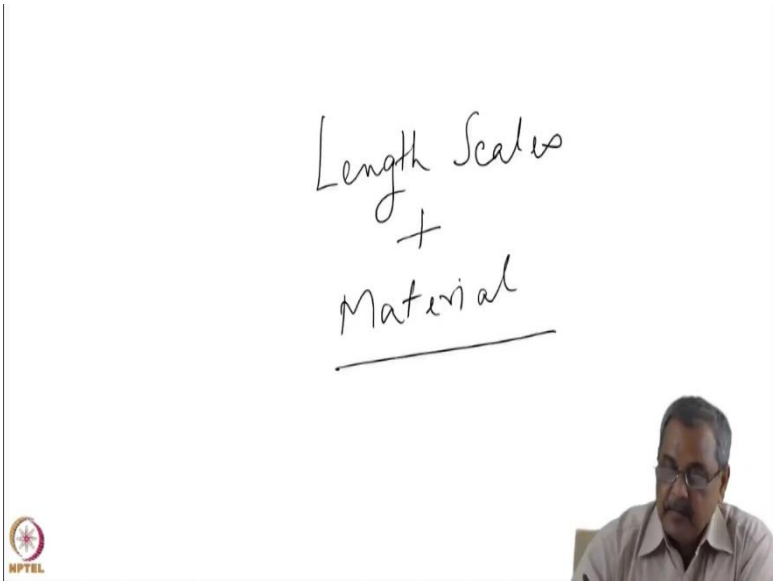

I will also talk about a very interesting subject known as vortex lattice in superconductors. So, in these lectures, I will mix up length scales and materials, because SANS technique is of interest for materials and I will try to cover a range of materials, so that you will get a flavor of what can be done using SANS techniques.

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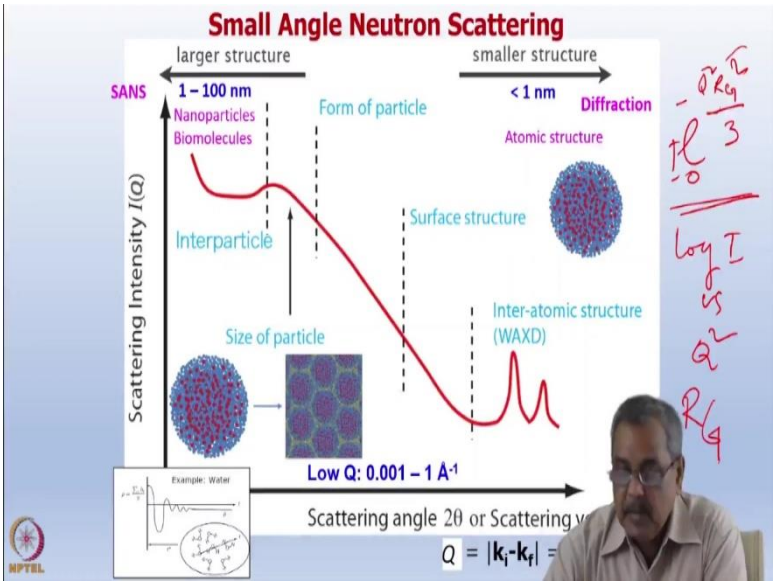

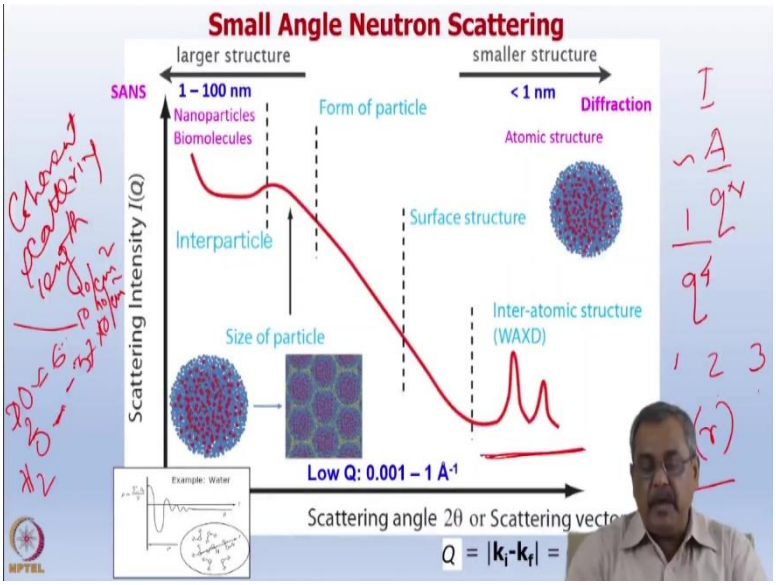

I will repeat with this figure on small angle neutron scattering. As I told you earlier with a little derivation that in the low Q range you have Guinier law $I_0 e^{-\frac{Q^2 R_G^2}{3}}$ for intensity. So, log of intensity *vs* Q^2 should be a straight line. Of course, this depends if it is a spherical sample with a mean R_G^2. If it is not then it can deviate from straight line. Such low Q plots can give me the values of R_G in the Guinier region. In the Porod region, when you go to larger Q then the intensity is given by A/q^N where A is some constant. Depending on the fractal dimension (N) of the material that you are using SANS gives surface structure. And here, it is q^4 law for perfectly spherical smooth surfaces.

But it can be other powers of q if you are using fractal materials and I will show you as an example from fractal material what we get. I have also talked to you that fractals are materials which does not have integral dimensions. Instead of 1, 2, 3 like 1 dimensional, 2 dimensional and 3 dimensional objects, fractal objects can have dimension between 1 and between 2, for 2 and 3. And why? Because the way they are embedded in space as I showed you, as you reduce the length scales, the number of scales required do not go as an integer power law.

I took the example as 1 dimensional fractal and the coastline of India and showed you that as you go to shorter and shorter length scale, the length become longer and longer faster than a an integral power law. Also, in higher angles of the small angle scattering, you can get structure of the nano size inhomogeneities that you are studying. So, interatomic structure will give intensity similar to Bragg peak or more precisely similar to what you saw in liquid and amorphous systems. You will get peaks that will tell you an average inter-inhomogeneity distance.

And of course, the *x* axis is *Q* vector in all our structure work and I must mention at this point before I miss it that in all this structural work, we are considering coherent scattering cross section and not incoherent scattering, because incoherent scattering cross section does not help me to get $g(r)$ or inter particle correlations. But incoherent scattering cross section can help in studying dynamics. I will come to that later. But when I am talking about all the structure work, I will be talking about coherent scattering length. Please remember this.

I also showed you that in case of small angle neutron scattering you can make mixtures of D_2O which has got scattering length density (SLD) approximately 6×10^{10} cm^{-2} and H_2O with SLD 0.57×10^{10} cm^{-2}. By mixing D_2O and H_2O, we can make a contrast with respect to the particle that you want to study to desirable values and we can sort of lighten up different parts of a particle. SANS gives broad kind of information that we get in a broad range of *Q* values.

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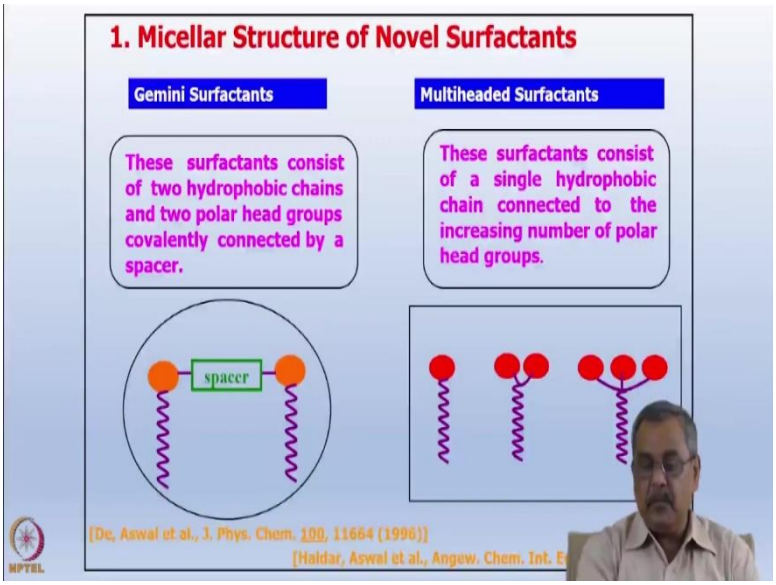

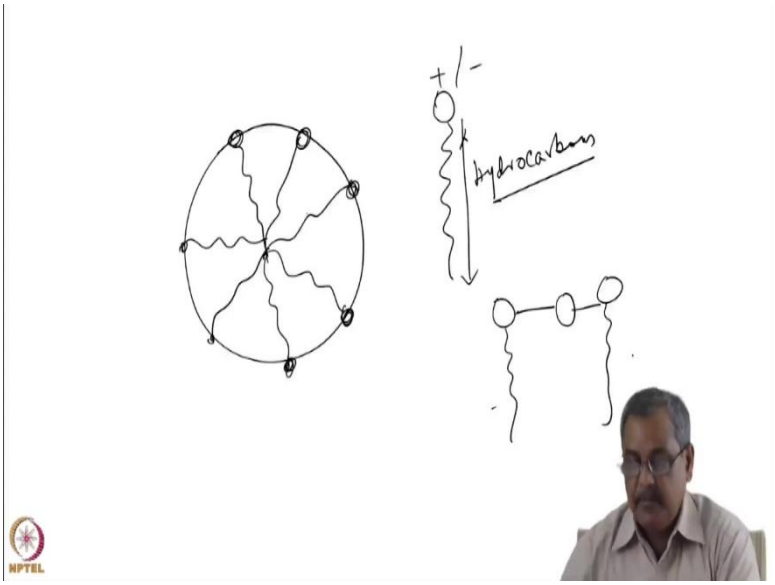

I have chosen few examples. I showed you micellar structures earlier. Now, firstly, I will be talking about something called Gemini surfactants, very interesting as this simple sketch shows that micelles were having a head group which can be a cationic, anionic or neutral and a large tail group of hydrocarbons. This large head group is generally positive or negative and like to face the water whereas, the tail group which is made of hydrocarbon chains will be hydrophobic and then I discussed with you that in the simplest case they will form a sphere with the heads looking outward and the tails looking inward. Micelles are very important component in various chemical industries.

Now, I am going one step ahead from this kind of single head group surfactants. These are designed by a specialist group at IISC Bangalore. The SANS experiments were done at Dhruva. These are called Gemini surfactants which has got two head groups connected by a chain. This is a micelle with multiple head groups and multiple tails. In this case there is a spacer layer and there are two head groups. Now, the question was asked that how do they combine to form a structure in a solvent something like a micelle.

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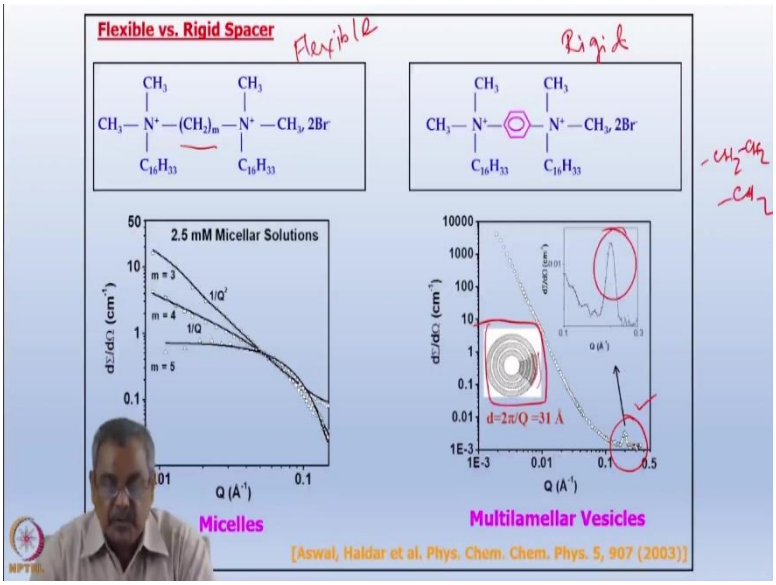

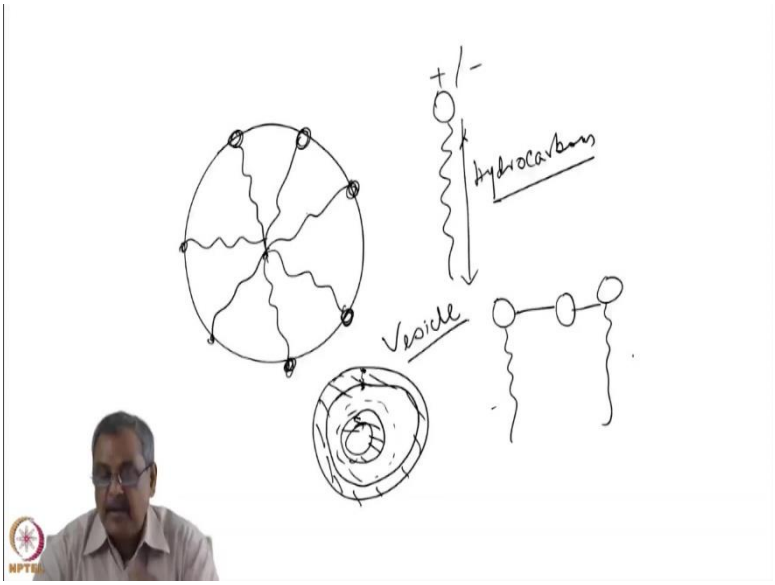

Studies used either a flexible chain, here the flexible chain is the chain of $(CH_2)_m$ where m is number of chain length. This is flexible because you can bend it. Another one we discussed was the benzoic ring as spacer group which is not flexible but rigid. We formed micelle using surfactants with two kinds of spacers and see the difference in the small angle data. In the $d\Sigma/d\Omega$ $vs.Q$ plot for flexible spacer we can see that there is $1/Q$ dependence if m = 4, $1/Q^2$ dependence if m = 3 and there is 0 slope at low Q for m = 5. This is the confirmation of the surfactant when it forms Micelle is changing because it can bend.

This gives us a lot of flexibility in forming structures, when playing with the length of the head group and that is evident from the low Q data. At the same time whenever the spacer group is rigid, we have a structure which is vesicular. A vesicle is basically a micelle but with bilayers.

There can be bilayers or there can be more number of layers. In our case of bilayers actually, it can be like this: the head groups of the micelle come here in the present case, because there are multiple head groups so, two of them will be there let me just be clearer about it.

You may understand that bilayer means, there are two surfactant layers. This is an inner layer. So, these structures will have the micelle stacked up and this is called a vesicle. And here, in this vesicle you will have two head groups coming together and in between you have got gap where the solvent goes in the vesicle. And in case of rigid spacer layer, we find that vesicle structure is preferred. This is a structure which is preferred unlike a flexible chain connecting the two head groups.

And this vesicle structure, what I am talking about, is shown as over here. These are the head groups forming the surface layers here and in between the tails are there in this vesicle. There is an inter particle distance because this is a circle inside circle inside circle inform of shells. We have what is a first layer then second layer then third layer. You have got a small coherent structure peak due to average interparticle distance.

We have multilamellar vesicle where it is one sphere inside another inside another and you can find out the, shell thickness from this small peak that we see around 0.1 to 0.5 $Å^{-1}$ in this SANS data. This is one example. This is a very fine work with the Gemini surfactants. And their structured in the micelle were studied using small angle neutron scattering. Similar studies are possible if anyone is interested in the structure of this kind of inhomogeneity in a solution.

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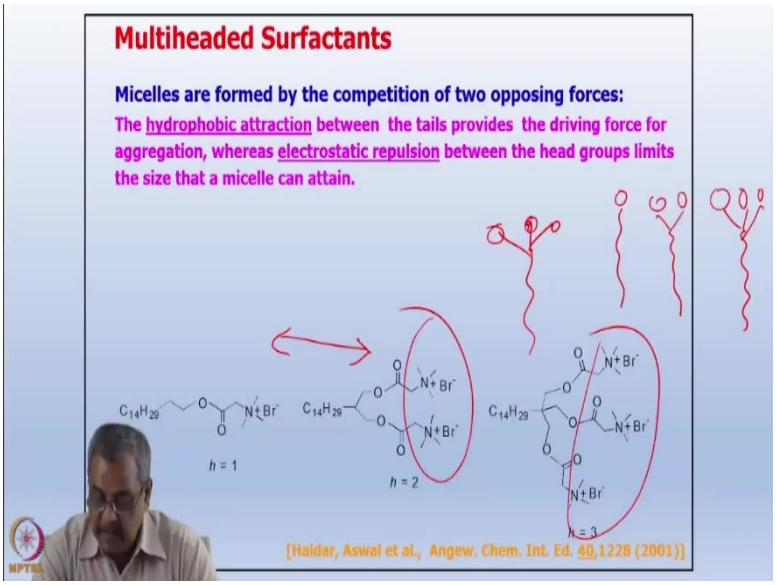

Then I can talk about multi headed surfactants. The previous examples had two surfactants connected by a chain. But here it is a single tail and there are multiple head groups, the tail here is $C_{14}H_{29}$. It is a long tail, but you have got now two head groups.

So, we can make such surfactant molecules where the hydrophobic tail is one but connect to multiple head groups. I am simplifying it for your understanding. There are multiple head groups here. I can have one head group or two head groups or even three head groups. And let us see what we get when we try to form micelle structure with such micelles.

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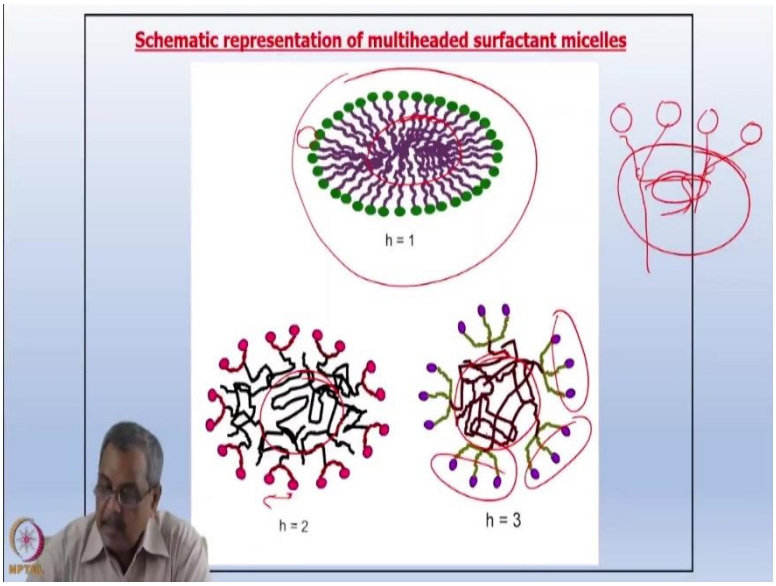

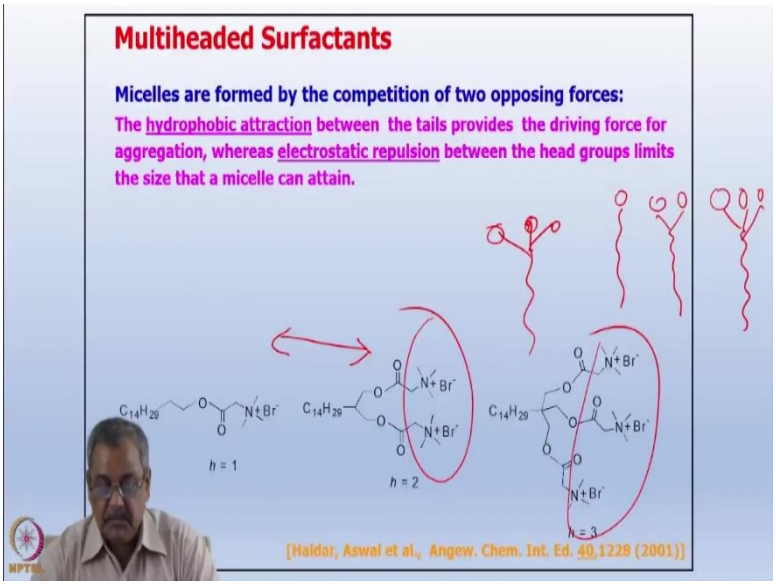

This is a schematic of the structure that it might form. It is shown in two dimensions. In reality it will be in three dimensions. So, when you have $h = 1$ the tails are stretched and you can see depending on the tail length with twice the tail length as diameter you have got a circular structure., In case of three dimension it will be a spherical structure. But when you have $h = 2$, I am showing a micelle with 2 head groups, you can see the 2 head groups are repelling each other. Because the head groups are of same charge, they are repelling each other. When they repel each other, then this association is difficult to form because they will try to get away from each other. The tails will have hydrophobic interaction which will tell them to be close to each other.

So, head groups try to get apart and the tail groups try to come together and the tails also start folding. If these two head groups have to be away, but the tails are there now these tails they try to come close to each other. So, they to bend and get entangled inside the micelles.

And this entanglement increases as you increase the number of head groups. So, the coordination number of surfactants, forming micelles decreases and the entanglement increases, because they have to fill up this space and not allow any water to come in at the same time the repulsion between the head groups have to be respected.

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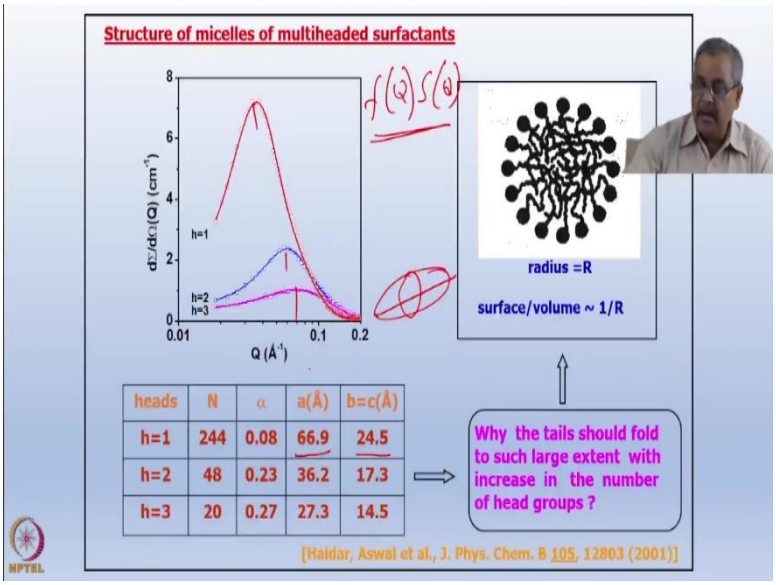

And the data I show you here. This is the small angel neutron scattering data. It has got two parts one is the form factor part; one is the structure factor part. The structure factor gives us the inter particle distance and the peak comes from there. Now, you can see as the peak is moving out, that means the size of micelles and the inter-particle distance is becoming smaller. So, that means with increasing number of head groups, the micelles become smaller. That is one indication because the peak is moving outward.

Also, while fitting this law, we can find out the coordination number of such surfactants in a micelle under the assumption this is a prolate spheroid we find that for h = 1 the coordination number is 244, for h = 2 the coordination number is 48 as I mentioned to you earlier and for h = 3 the coordination number is 20. Also, you can see the *a* (semi-major axis) and *b* (semi-minor axis) values indicate this forms a prolate spheroid with $b = c$. You can see under the assumption that the Micelle takes a prolate spheroid shape, we find the parameters for the prolate spheroid in Å.

I wanted to point it out to you that I am dealing with length scales which are much larger than crystallographic length scales, but am able to predict inter particle distance like I did in case of atomic liquids and molecular liquids. I am able to find out the inter particle distances from SANS. I can find out the particle size by fitting the models for a prolate spheroid. So, this is a finding in SANS where I can predict the shape of the particles and also their inter particle distance in an experiment. This was also an example from what we did at Dhruva SANS instrument.

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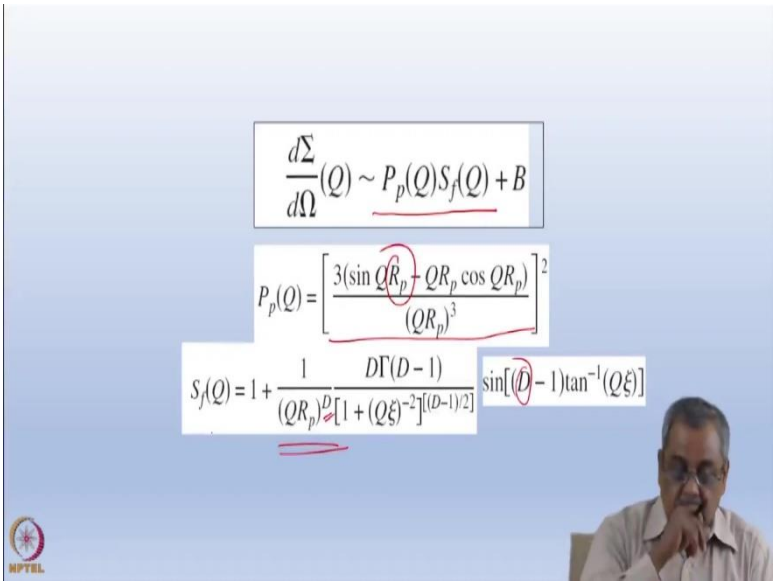

Now, I will go ahead with the example of surfactant and protein interaction. Now again, I just briefly mention that $P(Q)$ is a form factor and $S(Q)$ is the structure factor where you have the dimension D the fractal dimension of the inhomogeneity. Do not pay too much attention in this expression except the fact that you have a form factor and a structure factor part here. The form factor I have derived earlier for a sphere and Rp is the radius of gyration for a spherical particle. This expression gives me the structure factor as a power of D, where D is the dimension, it can be fractal dimension for the objects. So, these are two things we must pay attention to in this expression.

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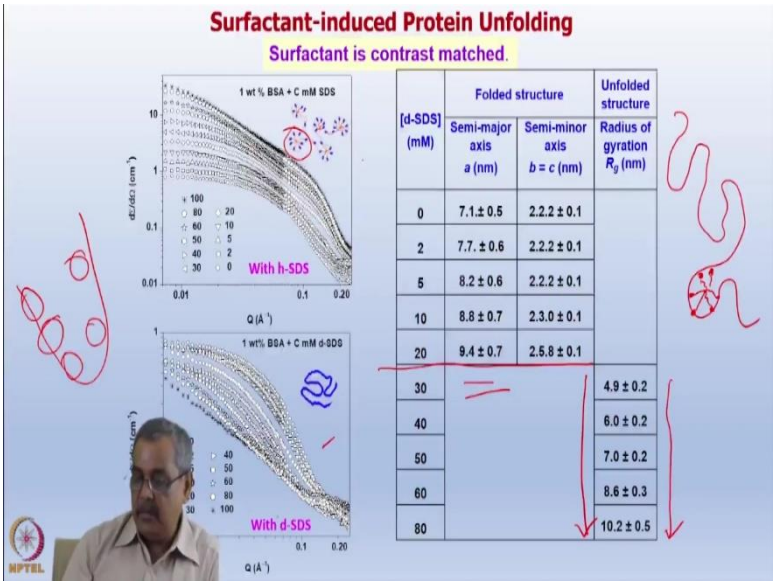
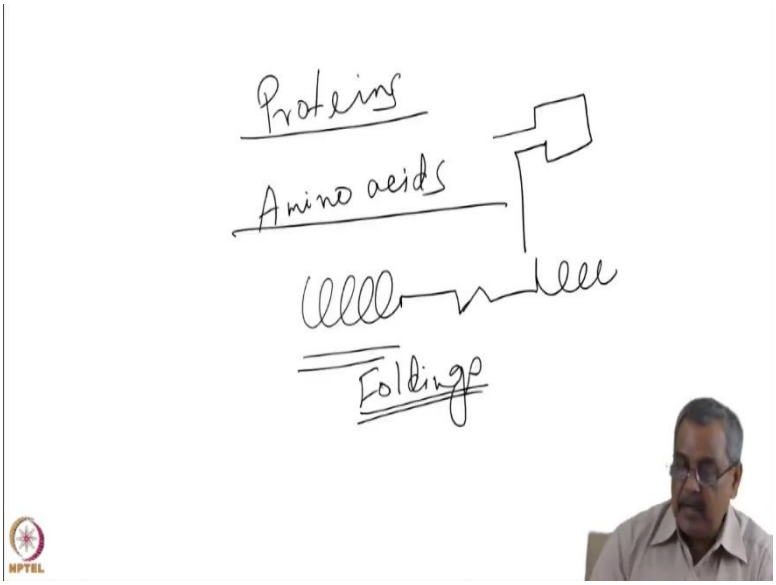


[d-SDS] (mM)	Folded structure		Unfolded structure
	Semi-major axis a (nm)	Semi-minor axis $b = c$ (nm)	Radius of gyration R_g (nm)
0	7.1 ± 0.5	2.2.2 ± 0.1	
2	7.7. ± 0.6	2.2.2 ± 0.1	
5	8.2 ± 0.6	2.2.2 ± 0.1	
10	8.8 ± 0.7	2.3.0 ± 0.1	
20	9.4 ± 0.7	2.5.8 ± 0.1	
30	=		4.9 ± 0.2
40			6.0 ± 0.2
50			7.0 ± 0.2
60			8.6 ± 0.3
80			10.2 ± 0.5



I am now talking about surfactant induced protein unfolding. Proteins are important for many of the functions in our body and proteins are made of amino acids. The list of amino acids, is limited. But with various combination of amino acids, the proteins, they form helixes and beta sheets as they fold. The protein folding is an important aspect of proteins activity, The proteins are made of alpha helixes and beta sheets. So, you have parts of the protein which will be possibly be sheets like this and also there are helixes. And they fold up in its local environment, in whichever environment we are putting them.

Depending on the environment, protein folding changes, and proteins' activity also changes because it has lots of charge sites. Now, in this example, the interaction between protein and surfactants have been studied in a solution. I give you this as an example. This is bovine serum albumin, which is a protein. SDS is a micelle and there is interaction between the two and you can see that when we add this SDS to the solution, this background changes the protein.

And there are these small spots where inside because of the charge on the protein. We have this kind of micelles. This is a very interesting system interesting biologically and also chemically because the proteins are interacting with the micelle that has been formed using SDS surfactants and with a percentage of BSA and SDS in solution, these results show that the structure of the micelle changes.

And again, in this experiment, the protein we call it our necklace and the bead arrangement show the micelles. So, as if the protein for the background, the chain of the necklace and this micelle are forming beads on those in a very, very simplistic modelling .and you can see that in these experiments we do contrast matching, so that you can see the protein or you can see

the micelle formed with the SDS surfactants. By contrast matching the background which is a H_2O and D_2O mixture and also by using hydrogenated SDS and deuterated SDS, we can observe various components. So, what we find here is that, with the SDS concentration in milli molar range, you can see that the structure of the micelle changes. The structural difference is not too large, they are almost similar, but marginally different. But you can find out. When protein unfolds along with the micelle, then there is a drastic drop in the radius of gyration of the micelle, but with unfolding the radius of gyration increases. So, this is one interesting aspect of protein and surfactant interaction in a solution and the study was done using small angle neutron scattering. I used examples from organic chemistry and also from biology, so it can really integrate studies in this whole range of materials when you are okay with the length scale that you can study. You can see these micelles have 70 to 90 Å size semi major axis, semi-minor axis around 20 Å. This is a folded structure. When it is unfolded you get a radius of gyration that indicates that the micelle arrangement is becoming larger. Unfolding depends on the strength of the SDS surfactant.

So, up to 20 millimolar concentration, the structure remains folded the protein remains folded and beyond this concentration the protein starts unfolding from this point onwards and we have found out the radius of gyration of the micelle in this unfolded protein structure. We have done the experiment with 1 wt% of BSA protein which is bovine serum albumin and with hydrogenated and deuterated SDS micelle. This experiment was also done on the slit and velocity selector based small angle neutron scattering machine in Dhruva.

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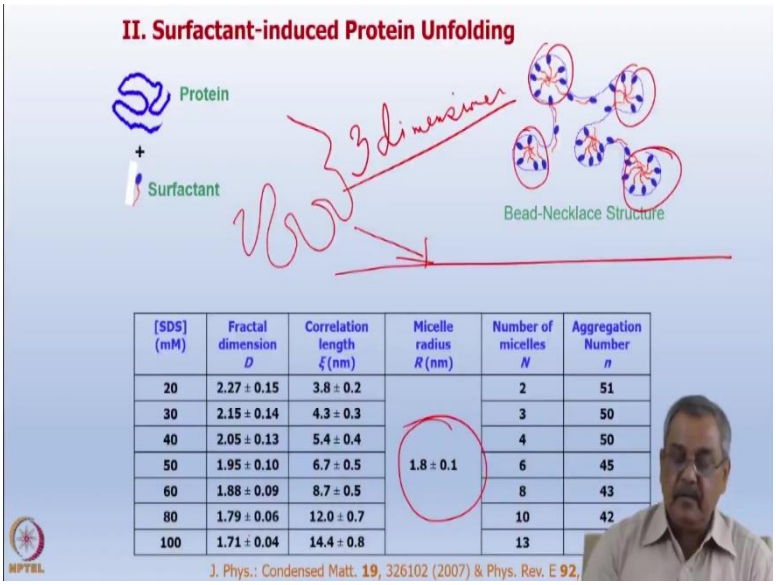

And, this is the comparative statement of bead and necklace structure for protein and the SDS surfactant of various concentration and the fractal dimensions. As we go to as they go to higher and higher concentration of SDS micelle, as the chain becomes more and more linear, you can see the fractal dimension reduces. Actually, the fractal dimension should have been 3, for a 3-dimensional object, but it is never so. Starting from 20 millimolar concentration when the fractal dimensions is 2.27, it keeps reducing at higher concentrations.

So, as this structure becomes more and more linear, you can see the fractal dimension goes towards 1 but it is not 1, it is 1.71. So, fractal dimension is 2.27 to start with which is just away from 3-dimensional structure and goes to an almost linear value (1.77) and of course, the micelle radius remains almost fixed. This is the micelle radii, which are sitting in pockets in the unfolded chain. The unfolding is like the coastline of India that I discussed with you earlier.

This protein can be unfolding like this. And then from there it might become more and more linear. When it goes to more and more linear values, then you can see the fractal dimension changes, because now how the surfactants attach to the background protein structure dictates how the fractal dimension will be coming out. And also, the number of micelle and the aggregation number changes. So, here I complete my discussion on what we did on surfactants and protein unfolding.

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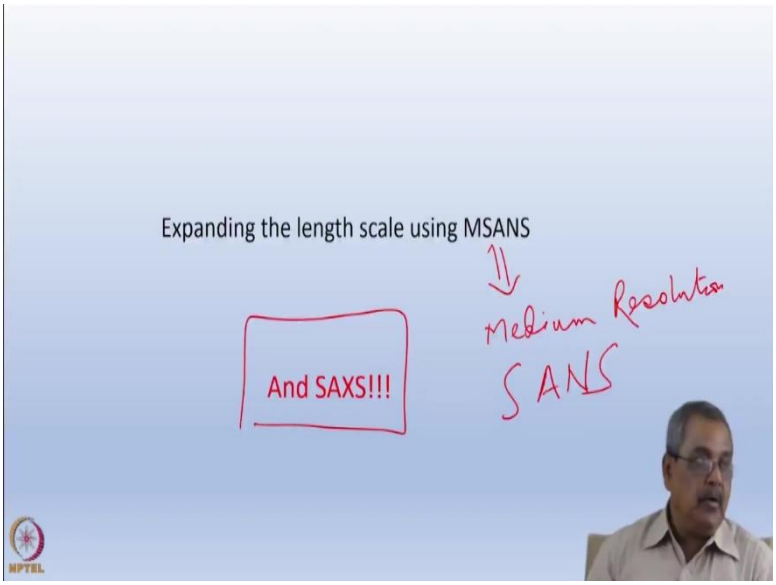

Now, the question is that can we can expand the length scale of the inhomogeneity using MSANS, which is medium resolution SANS? We can also add a small angle X-ray scattering or SAXS machine with SANS. These are a very interesting complementary tools that you can have data from SANS and SAXS. You can have data from SAXS if your sample allows it, since not that all the samples will allow you to get small angle X ray scattering data.

The example that I used so far are deuterated or hydrogenated samples and they cannot be used for small angle X ray scattering. So, I will be using some examples where MSANS and small angel X ray scattering has been added to get data over larger *Q*-range in the next module In next part of the talk.