Keywords: Polymer chain, surfactants, micelles, packing parameter

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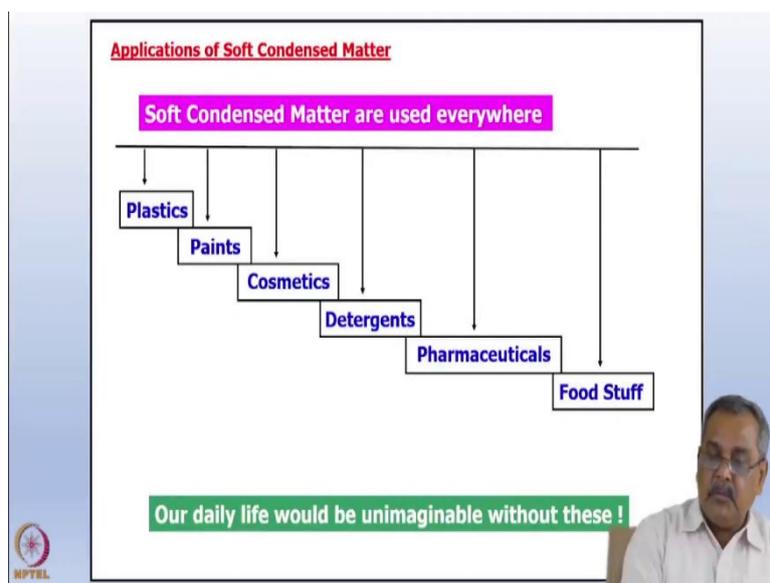
Briefly, I will tell you that why this is so interesting, because when you talk about soft condensed matter, it covers a wide range from plastics to paints to cosmetics, detergents to pharmaceutical to food stuff, almost a huge chunk of things that we use in our daily life and understanding their structure is important.
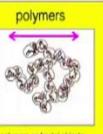
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And possibly the first time soft condensed matter world was used or came into prominence was the work by de Gennes and in his 1991 Nobel Prize, he mentioned about soft condensed matters and are also known as the Complex Fluids.

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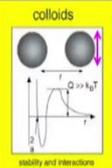
In this first instrument that I talk to you about, which is slit-based system, a large number of soft condensed matter with inhomogeneities in 1 to 50 nm scale was studied by small angle neutron scattering. And I will try to demonstrate some of the examples of the work done. It is huge in volume so, far as the materials being studied. But just to give you a taste, I have chosen a few examples. An interesting example is a polymer chain,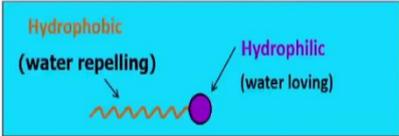 that can bend, can twist, and in a medium it can either roll up or can open up and becoming either a coil or a rod and can move like a snake inside a medium. All these have to do with their utility in a particular application.

And people are interested to know how they coil up what is their radius of gyration, do they coil or do they open up? All these questions are asked and these can be answered by using small angle neutron scattering.

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I take an example of surfactants. Surfactants are very interesting amphiphilic molecule that have got a hydrophobic tail group and a hydrophilic head group [or vice versa]. So, basically, if I may give a simplistic picture, it has got a tail by showing it like this, I mean, the tail is not really a rigid tail, as in inorganic chemistry. But it is flexible and it has got a hydrophilic headgroup. Typically, they comprise heads and tails. When you put the surfactants molecule in a solution, or in aqueous media, generally they try to sit on the surface, because the tails

would not like to go inside the water. But the fact is that when you keep increasing the concentration of surfactants on the surface, then surfactant to surfactant interaction will not allow them to go beyond a certain concentration to remain on the surface.

So, above a certain critical concentration, they do an interesting thing, they start forming this kind of globules, where the head groups are on the surface, and the tail groups are inside. These structures are known as micelles. So, that is how they hide their tails from the water. And this is a very, very interesting thing. I can just mention one thing, that the detergents we use routinely, there the dirts are oily. So, the dirts are oily and the detergents will have these surfactants. When the surfactants have this oily dirt in the water medium, they form this kind of structure on the dirt and removes it from the cloth and throws it out. So, this one is a very simple example that I am telling you. But this is a million-dollar detergent industry for that matter.

This is the nature of micells. And I have just given you examples of some of the micelles like CTAB micelle. It is cationic means it has got a head group which is having a negative charge. They can also have heads that are anionic or positive charge, nonionic and Zwitterionic that are double charges. So, there are various kinds of surfactants.

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Different structures of surfactant aggregates

spherical micelle | cylindrical micelle

in water

bilayer | vesicle

And as I told you just now, the micelles are the clusters of the surfactant molecules in aqueous solution. So, the hydrophobic part goes inside and the hydrophilic part remains outside and these are typically about 50 Å. The shape and size of these micelles are very important for various applications.

Micelles formation is basically known as a self-association process. So, they look like tiny microbes, possibly they are chemical microbes, but they associate with each other because they want to minimize the energy. Most of the self assemblies always come from the fact that every assembly tries to minimize its energy. Here, the interaction between the tail and water must be giving positive energy.

So, it is better to hide the tails from the water. And that is why this surfactant is formed so that the energy is minimum. These are large soft objects, by soft I mean, a micelle is unlike a hard, let us say cannonball. This is a soft, squishy ball. You can squeeze it, you can change the shape of it. And the dynamics of micelles in the solution will be slow.

Typically, timescales are milliseconds to fractions of milliseconds, and not like the atomic and molecular dynamics, which happens in femtosecond. Here is a schematic which shows how the micelles will form when you increase the density.

And these are the various kinds of micelles that can form, they can form spheres which I showed is the simplest thing. When you keep increasing the density of surfactants more and more then sphere no more a possibility, because then sphere head groups will start repelling specially with the charge, they will keep repelling then they like to go to this kind of

confirmation, which is cylindrical or they can even form bilayers or vesicles which are multilayers. Vesicles are basically, these micelles where one headgroup looks inside. It is like a tokamak or like a medu wada, you can say. This has got a geometry where you can even have spherical vesicles which have multi layered structures. You can see, the micelles are drawn here and there is one inside another inside another. There are multi-layers, and they can be like this, or they can be vesicles like this.

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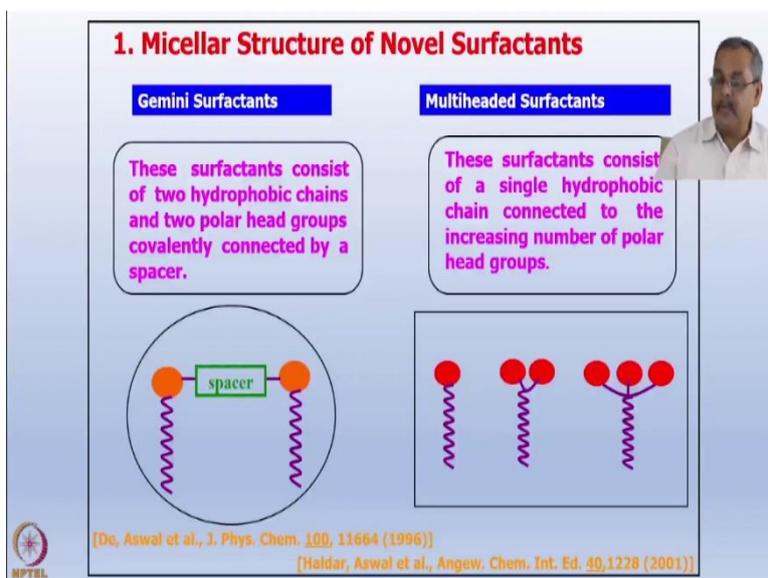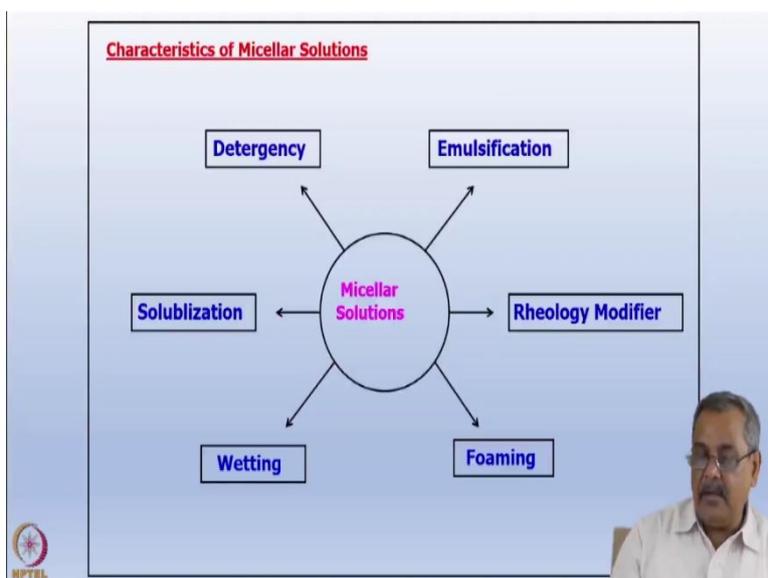
Micelles are used in various cases, viz. in detergents, in emulsification, in solubilization, in wetting, in foaming applications etc. I will just give a short example. I will stop for the time being and I will come back with more examples on other systems. Here is a micellar structure I am showing you, the tail group and the head group. I have taken an example from a novel

micelle where instead of one head group, there are two micelles that are attached by a spacer group. This is a multi headed surfactant where one tail group has got multiple head groups. What we study is that when I put them in aqueous solution, how they form structures and when the structures break.

This is is of interest, not only to the chemists and physicists but also to the industry, because depending upon how the micelles formed, how big the micelles are, their applications become important and relevant.

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Gemini surfactant has very unusual properties. The Gemini surfactants, were made in IISc, Bangalore. I just want to share with you some empirical results. You can see that micelles have

got a head group, which has got an area (a) and the tail group has a length, l. And there is a packing parameter (P) given by, $P = \dfrac{V}{al}$ where V is the surfactant volume.

The spherical micelles are formed when this packing parameter $<1/3$ which I have showed you earlier. If $1/3<P<1/2$ then it forms a cylindrical micelle. When $1/2<P<1$ it forms vesicles. This can be shown even from calculations and from simulations without experiment. There are bilayers when P is equal to 1 and reverse micelles when $P > 1$.

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I just take one or two more examples. This is a flexible versus rigid spacer. The spacer which I showed here, that can be a rigid group such as a Benzoic group, or it can be something like a polymer chain which is flexible.

In the example shown here you can see these are flexible long chains $(CH_2)_m$. Interestingly, from the experiment that we could do in the small angle machine here, we found that the slope of the curve [Intensity vs. Q] changes drastically depending on the length of this flexible chain group. It follows a $(1/Q)^2$, $1/Q$ or $(1/Q)^0$, for m equal to 3,4 and 5, respectively.

But in case of rigid head groups, we have a peak here. I showed you earlier that the intensity (I) is proportional to $P(Q)$ and $S(Q)$ that is structure factor as well as form factor. Here, it forms multilamellar vesicles and you can find out vesicle to vesicle distance from the peak's Q value using $2\pi/Q$ relationship and here it is 31 Å.
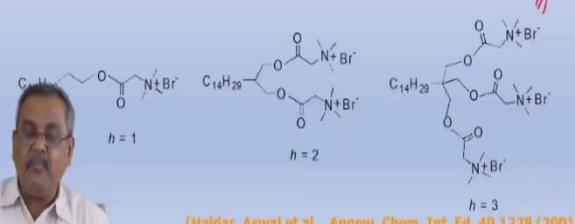
We can find out the coordination numbers from r small angle neutron scattering. We can also find out the geometry in solution from a millimolar micellar solution with different lengths of head groups. This is a very interesting experiment that was done on the slit based small angle neutron scattering machine.

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Before I complete today, I wanted to discuss with you a few more examples. This is about multi headed surfactants. Now, multi micelles are forming because the competition of two opposing forces that are the hydrophobic attraction between the tails and the electrostatic repulsion between the head groups which limits the size of a micelle.

Basically, the tails they are hydrophobic, and they want to hide from the water. So, they will be going inside. When I form of multi-headed micelle, it has got a greater number of tails. So, they like to come together, they will like to bunch together, because there is a hydrophobic attraction between them.

At the same time, because this is a multi headed micelle, you can see there is a charge on the head group, and then the charge on the head group will repel each other. So, there are two competing forces, the tails they like to bunch together and the heads they want to move away from each other. The balance between these two forces, will dictate what is going to be the geometry of the micelle using multi headed surfactants.
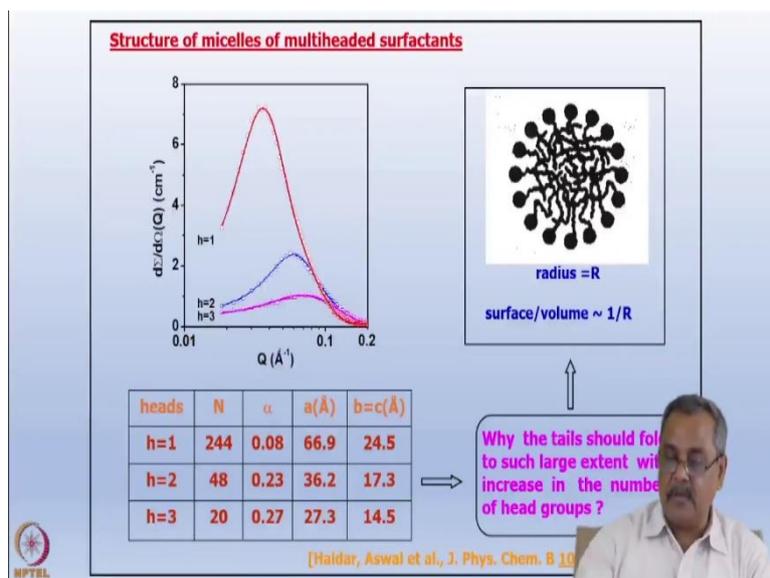
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Schematic representation of multiheaded surfactant micelles

h = 1

h = 2   h = 3
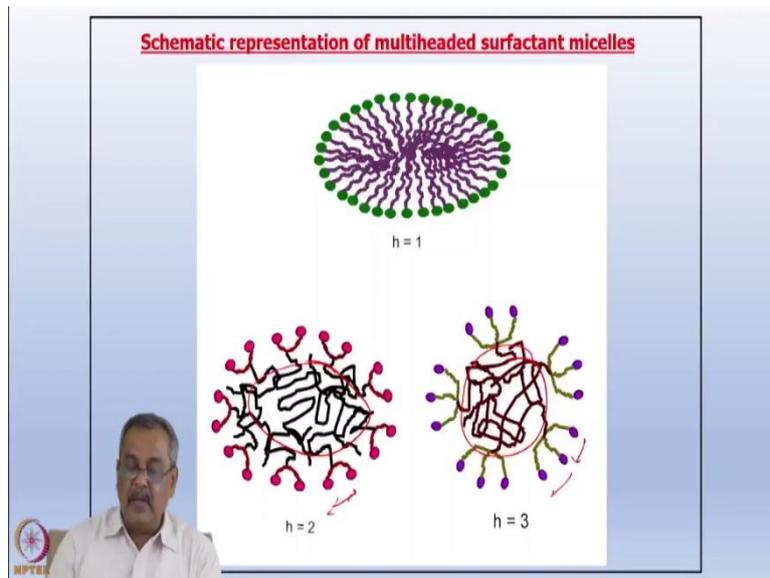
This is just a schematic. You can see that when the head group is 1 it is a very simplistic picture. Actually, you form spheres. When you have two head groups or three head groups, then you can see tails tend to tangle because the head groups like to maintain the distance between them.

There is lots of tangling, but this will give very, very different small angle neutron scattering signals. And you can actually find out what is happening when you put such multi headed surfactant inside an aqueous medium.

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Structure of micelles of multiheaded surfactants

radius =R

surface/volume ~ 1/R

heads	N	α	a(Å)	b=c(Å)
h=1	244	0.08	66.9	24.5
h=2	48	0.23	36.2	17.3
h=3	20	0.27	27.3	14.5

Why the tails should fol to such large extent wit increase in the numbe of head groups?

[Haidar, Aswal et al., J. Phys. Chem. B 10

I have just used one very interesting example. You can see that the structure of micelles of multihead surfactants. I have used, $h = 1$, 2 and 3. This is the data. Interestingly, as you go to

larger and larger number of head groups, surely the repulsion takes place, but you can see that combinatorial number goes down drastically from 244 to 20.

Basically, they form a prolate ellipsoid in this case, and you can see that the semi major axis drastically reduces when you go from 1 to 3, the number of head groups and the tails they really tangle and fold to such a large extent because there is attraction between them that there is no repulsion. That is what these experimental result dictates.

This completes a part of my discussion on small angle neutron scattering. I will use few more examples, data obtained on the slit based geometry and at least few examples on the double crystal based medium resolution SANS in the next lecture before I draw a curtain on small angle neutron scattering and move on to other mesoscopic techniques in my lecture. Thank you.