Nano structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 2
Lecture - 5
Synthetic Methodologies (Contd)

Welcome back to this nano structured materials course, where we are discussing the synthesis, properties, self assembly and applications. We have finished module 1 in which we had two lectures and in module 2, we had two lectures earlier. Module 2 is on synthetic methodologies and in that, the first two lectures that we have concluded was based on the sol-gel methodology. In sol-gel methodology, we showed how you can make nano structured materials of various porosities, starting from a colloidal sol or a polymeric sol and then convert it into a gel, and then into the nano structured material.

It can be made in a film or as a monolith or as porous interconnected structure. Today is the third lecture in this module 2, and this lecture and the next lecture will be on another method of making nano structured materials. This particular methodology is called the microemulsion technique and we would be discussing in detail: what are microemulsions? How we can stabilize them, how we can use them to make different kinds of nano materials? And also how we can control the size and shape of various nano structures?

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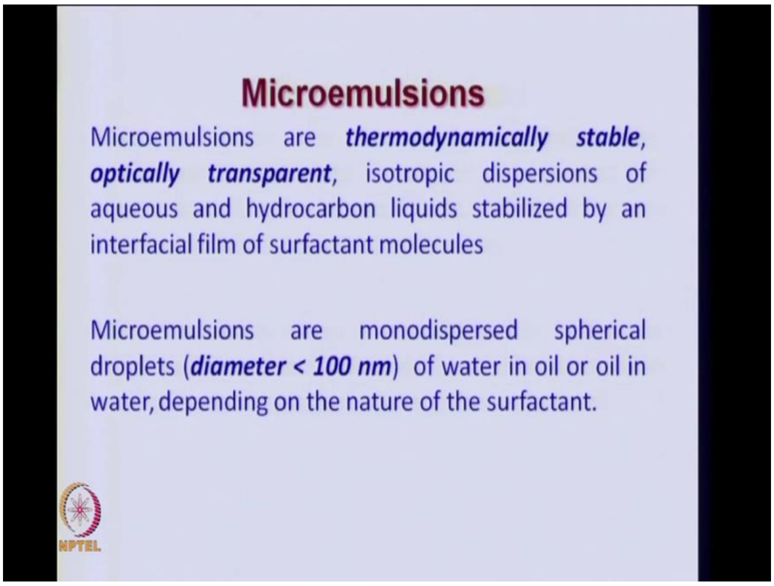

Microemulsions

Microemulsions are ***thermodynamically stable***, ***optically transparent***, isotropic dispersions of aqueous and hydrocarbon liquids stabilized by an interfacial film of surfactant molecules

Microemulsions are monodispersed spherical droplets (***diameter < 100 nm***) of water in oil or oil in water, depending on the nature of the surfactant.

What are microemulsions? Microemulsions are thermodynamically stable, optically transparent isotropic dispersions of aqueous and hydrocarbon liquids. Hydrocarbon means non aqueous medium and these dispersion of aqueous and hydrocarbon liquid is stabilized by an interfacial film of surfactant molecules. What we have introduced here is, we have mixture of an aqueous or a water based solution and hydrocarbon liquid, like an oil, which is a non aqueous medium. Normally, the aqueous and the non aqueous will not mix, but how to make them mix, is through a film of surfactant molecules. This surfactant molecules are normally having a hydrophilic head and a hydrophobic tail, like soap molecules which you use in your daily life

The surfactant molecules have this tendency that; part of the molecule can be immersed in a water or aqua system and part of the molecule likes to be in the non aqueous medium. So, when there is a film by layer or two liquids, having an interface like oil and water, then when you add the surfactant molecules, they would like to be at the interfacial region. So, these surfactant molecules, which are at the interface of the aqueous and the nonaqueous medium, can arrange themselves in various forms. One of the forms by which the surfactants aggregate is like a sphere.

When you forms spheres which are monodispersed, then you can get microemulsion droplets and these droplets can have either water or oil, with diameters of around 100 or less than 100 nanometers. We can control them. That depends on the nature of the surfactant, and of course the amount of water and solvent, etc. So, microemulsions are monodispersed spherical droplets of water in oil or oil in water. Of course, we can also have microemulsions with certain different type of organization of the surfactants.

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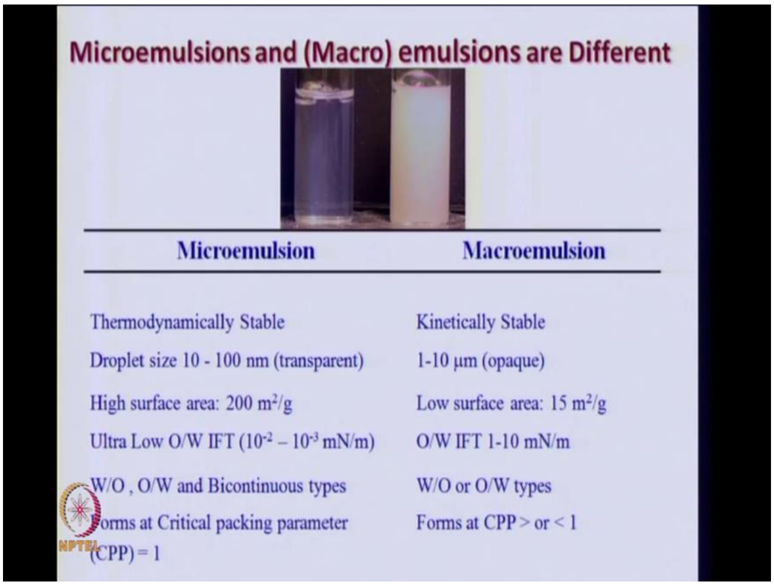

Microemulsions and (Macro) emulsions are Different

Microemulsion	Macroemulsion
Thermodynamically Stable	Kinetically Stable
Droplet size 10 - 100 nm (transparent)	1-10 µm (opaque)
High surface area: 200 m^2/g	Low surface area: 15 m^2/g
Ultra Low O/W IFT ($10^{-2} – 10^{-3}$ mN/m)	O/W IFT 1-10 mN/m
W/O , O/W and Bicontinuous types	W/O or O/W types
Forms at Critical packing parameter (CPP) = 1	Forms at CPP > or < 1

Microemulsions and macroemulsions are two different things. What is a microemulsion? A microemulsion as we just mentioned, is a transparent solution and is thermodynamically stable. If you see on the left, this is a transparent system where you can see through this solution. This is a microemulsion, whereas the macroemulsion is opaque and you cannot see through that. The other properties of a microemulsion is the size of the droplet. That means, what is the size of the surfactant aggregates in which the water or oil is present; that size is of the order of 10 to 100 nanometers. It has high surface area and ultra low interfacial tension. IFT is the interfacial tension between the oil and the water phase. This is of the order of 10 to the power minus 2 to 10 to the power minus 3 million newton’s per meter.

You can form water in oil, that means very small amount of water droplets surrounded by oil and having at the interface of water and oil surfactants. That is called a water in oil microemulsion or you can have oil in water microemulsion, where the content of oil is very less, and this is present within these spheres. You can also have bicontinuous type of microemulsions. Normally, microemulsion will form at a critical packing parameter or cpp of 1. On the other hand, macroemulsions are kinetically stable; they are not thermodynamically stable. They form large droplets of 1 to 10 micron in size.

That is why, their solutions are not transparent; they are opaque. They have low surface area of 15 meter square per gram and normally they will form the oil and water interface, will have a interfacial tension, which is much a higher; some thousand time or ten thousand times higher than present in microemulsions. That is of the order of one to ten mille newton's per meter, whereas in microemulsions, it is 10 to the power minus 2 to 10 to the power minus three mille newton per meter. There is a large difference in the interfacial tension present at the interface in a microemulsion and a macroemulsion.

That is why, macroemulsions, because of this large interfacial tension are not thermodynamically stable and they are kinetically stable. You can get both water in oil as well as oil in water type of macroemulsions, but it is difficult you cannot get the bicontinuous type of systems, which you can get in the microemulsions. Then the formation of macroemulsion occurs at a critical packing parameter when it is greater than or less than 1, not when it is equal to one.

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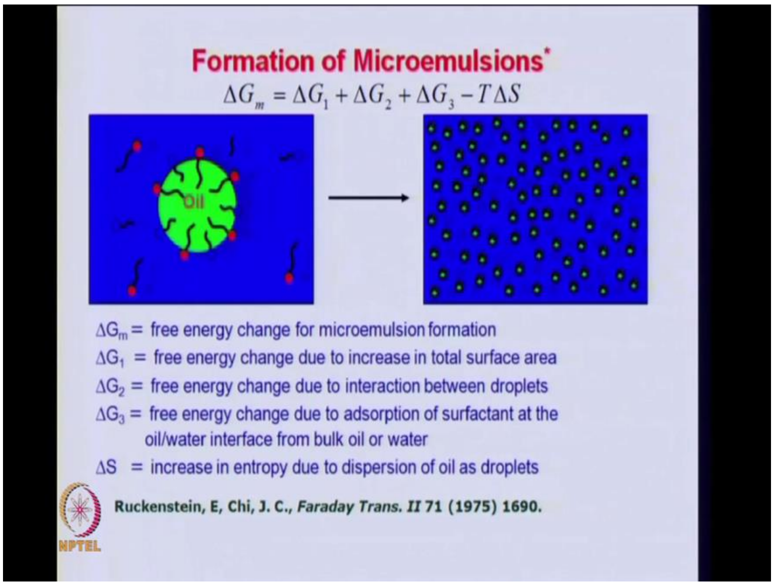

Formation of Microemulsions*

$$\Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3 - T\Delta S$$

ΔG_m = free energy change for microemulsion formation

ΔG_1 = free energy change due to increase in total surface area

ΔG_2 = free energy change due to interaction between droplets

ΔG_3 = free energy change due to adsorption of surfactant at the oil/water interface from bulk oil or water

ΔS = increase in entropy due to dispersion of oil as droplets

Ruckenstein, E, Chi, J. C., *Faraday Trans. II* 71 (1975) 1690.

The thermodynamics of the formation of microemulsions can be explained by writing the free energy terms. The delta Gm is the free energy change for the formation of the microemulsion. That is equal to the formation of free energy change due to the change or increase in total surface area. When the microemulsion is forming you are having a change in surface area and this delta G1 is a term, which relates that the energy to the enhancement in the surface area. Delta G2 is the free energy change due to the interaction between the droplets. As these droplets are forming, they are interacting that brings about free energy change which is given by delta G2. Delta G3 is the free energy change due to adsorption of the surfactant at the oil water interface. So, these three free energy changes are additive.

Then you have an increase in entropy because you are dispersing the oil as droplets. So, the increase in entropy is because you are disturbing the order of water. This enhanced disorder leads to an increase in the entropy. That will bring about a term, which is minus t delta s, where delta s relates to the increase in entropy due to the formation of the droplets, which breaks the order and creates disorder in the water medium.

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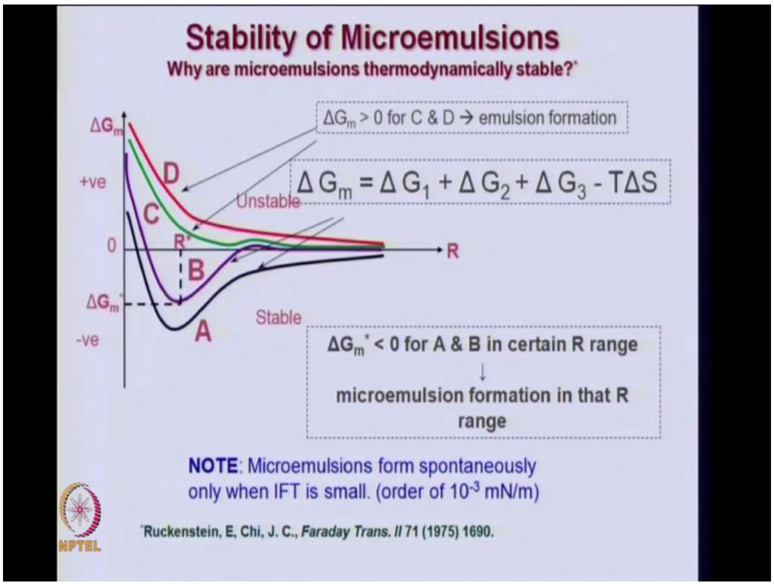

Stability of Microemulsions

Why are microemulsions thermodynamically stable?*

$\Delta G_m > 0$ for C & D → emulsion formation

$$\Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3 - T\Delta S$$

$\Delta G_m^* < 0$ for A & B in certain R range

↓

microemulsion formation in that R range

NOTE: Microemulsions form spontaneously only when IFT is small. (order of 10^{-3} mN/m)

*Ruckenstein, E, Chi, J. C., *Faraday Trans. II* 71 (1975) 1690.

If you present these things graphically, the delta G for the formation of the microemulsion if you see that this is greater than 0 for emulsion. Emulsions are unstable and hence you see that the delta Gm is always positive. It becomes increasingly positive as you come to small distances, whereas for stable microemulsions, you will have a minimum in the delta G of the formation of microemulsion. This will be the distance at which the minimum free energy occurs, will give you the size of the microemulsions. So, delta Gm star less than 0 for the formation of a microemulsion in a particular range of r.

So, whenever the microemulsions forming spontaneously, it can only do that when the interfacial tension is very small.

That is what we mentioned earlier, that the interfacial tension is small of the order of 10 to the power minus three million newton per meter, around that order the microemulsions formed. If the interfacial tension is large, then it will not lead to stable microemulsions.

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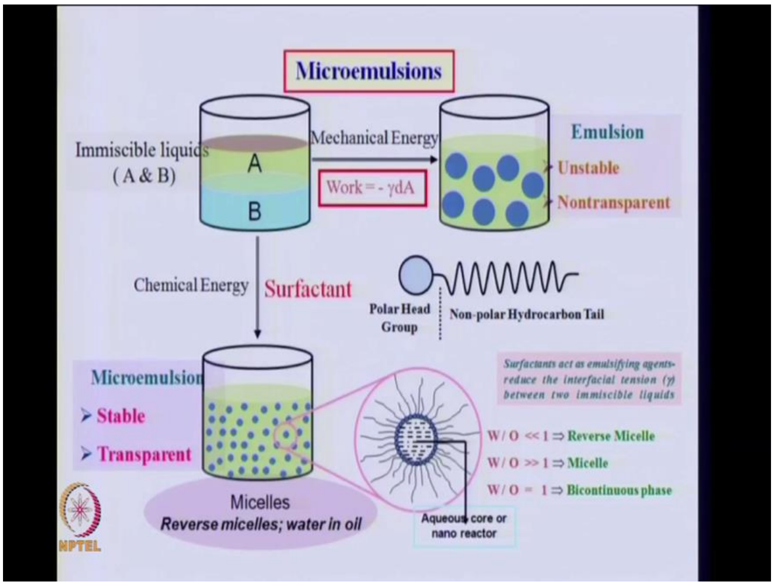

Microemulsions

Immiscible liquids (A & B)

A

B

Mechanical Energy

Work = - γdA

Emulsion

Unstable

Nontransparent

Chemical Energy

Surfactant

Polar Head Group

Non-polar Hydrocarbon Tail

Microemulsion

- Stable
- Transparent

Micelles

Reverse micelles; water in oil

Surfactants act as emulsifying agents- reduce the interfacial tension (γ) between two immiscible liquids

W / O << 1 ⇒ Reverse Micelle

W / O >> 1 ⇒ Micelle

W / O = 1 ⇒ Bicontinuous phase

Aqueous core or nano reactor

Again to discuss or show you pictorially what is happening, you have these two liquids. One you can consider the aqueous phase and the other is the nonaqueous phase. The two are immiscible, like oil and water and you will have an interface, where the oil and water meet. If you shake them giving mechanical energy, you can mix them. But that is only stable for a short small time; that is kinetically stable, if you give some mechanical energy. That is typically an emulsion. It is unstable and it is not transparent.

However, if you want to make a stable microemulsion, which is transparent, you add surfactant. Surfactant, basically are these kind of molecules, which has a polar head group and a non polar hydrocarbon tail. So, when you add these kind of molecules in this system, this polar head group will go into the aqueous layer and the non polar hydrocarbon tail will go and sit in the oil layer. It will be lying at the interface. But when you increase the concentration of such molecules, then you can get some surfactant assemblies like that.

Within the solution, you will get these small spheres, which are basically this kind of surfactant assemblies, where these molecules have come together in the form of a sphere. You can see the polar head groups are pointing inwards and the hydrocarbon tails are pointing out wards. So, this is a particular spherical aggregate of surfactants, where you have a hydrophilic head groups pointing inwards. So, this will be like water or aqueous medium to be inside because, the head groups are hydrophilic and they are polar head groups and the chains outside are hydrophobic. So, the oil medium will stay outside.

Inside this solution, now you will have many such spheres which you cannot see through your naked eye. This will be transparent, but if you look under or use some technique, you can find this organization of spheres and the water, one of the medium say the b is water, will be present inside these spheres. Only the oil medium will be outside. So, such a spherical aggregate of surfactants in this microemulsion is typically called a reverse micelle. So, reverse micelle is a microemulsion, where you have the water and oil. The water content is much less than the oil content and the water are trapped within these spheres.

Then you get reverse micelles, if you have the other system. Suppose, these spheres had these tail groups inside and the polar head groups are outside, then water would be in the medium outside and oil would be inside. In that case it is called a micelle. When the water and oil is nearly same concentration then you may get a bicontinuous phase. So, typically you get a microemulsion, where you have got these surfactant aggregates and one of the liquids is trapped within this sphere and other liquid stays outside the sphere. This gives you a transparent solution. This is what the basic structure of a micelle or a reverse micelle, which has got spherical aggregates of surfactants. This particular geometry can help you control the synthesis of nanostructures by controlling the diameter of these nanostructures.

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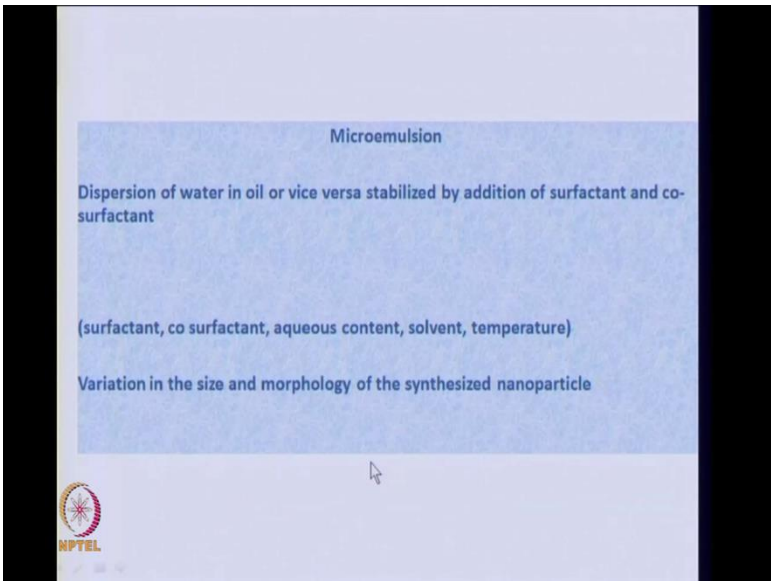

Microemulsion

Dispersion of water in oil or vice versa stabilized by addition of surfactant and co-surfactant

(surfactant, co surfactant, aqueous content, solvent, temperature)

Variation in the size and morphology of the synthesized nanoparticle

We can now define microemulsion as dispersion of water in oil or vice versa, that means; oil in water which is stabilized by addition of surfactant and co surfactant. We have introduced the surfactant before. A co surfactant helps the surfactant reduce the interfacial tension between the water or aqueous medium and the nonaqueous medium. Both surfactant and co surfactant are basically helping, stabilize the immiscible system by lowering the interfacial tension. Co surfactants normally are, some long chain alcohols or amines, and we will discuss about them. So, to form a microemulsion you can vary the surfactant, co surfactant, the water content, the solvent on the oil phase or the nonaqueous medium and the temperature. All these will affect the size and the morphology of the surfactant aggregate and hence, any synthesis of nanoparticle will be affected by the variation in the size and morphology.

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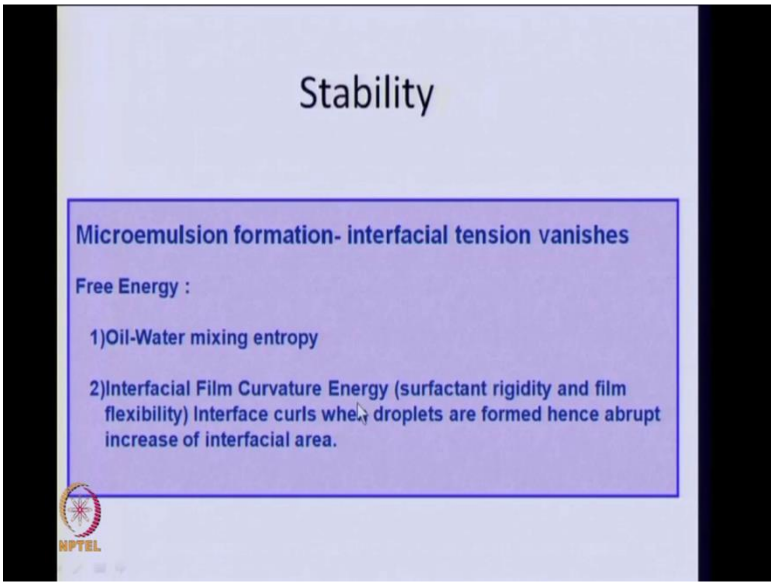

Stability

Microemulsion formation- interfacial tension vanishes

Free Energy :

1)Oil-Water mixing entropy

2)Interfacial Film Curvature Energy (surfactant rigidity and film flexibility) Interface curls when droplets are formed hence abrupt increase of interfacial area.

The stability of the microemulsions is basically, due to the decrease in the interfacial tension and the free energy is related; the free energy of formation of the microemulsion is related to the oil water mixing entropy and the interfacial film curvature energy. These are two things which contribute to the free energy. The interfacial curvature energy is related to the surfactant rigidity and film flexibility. So, the interface curls when droplets are formed and hence, there is an increase in the interfacial area. That is related to the free energy term due to surface area.

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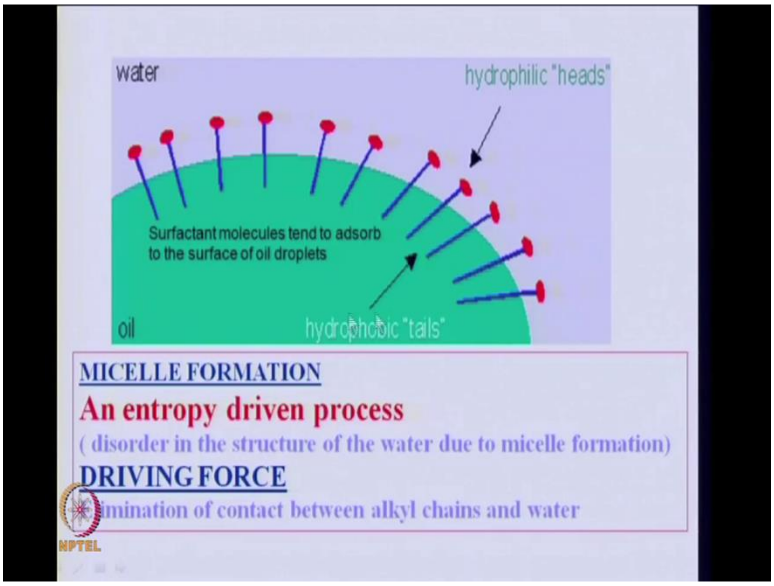

MICELLE FORMATION

An entropy driven process

(disorder in the structure of the water due to micelle formation)

DRIVING FORCE

imination of contact between alkyl chains and water

You can look at the picture that you have this kind of droplet, where the surfactant molecule tends to adsorb. In this case, if this is the head group which is polar then the hydrophobic tail will be going into the oil droplet or the nonaqueous medium and the polar head groups will be in the aqueous medium or wherever there is water. This is the normal structure of reverse micelle or water. Sorry. This is the structure of a micelle where oil is inside and water is outside. This is also called an oil in water microemulsion. In general, micelle formation is an entropy driven process as mentioned earlier. It creates whenever you form these micelles of this order of aggregate or surfactant molecules. There is a disorder in the structure of the water due to the micelle formation. The driving force is that the alkyl chains want to be away from the aqueous solution. It tries to eliminate the contact between the alkyl chains and water, and that leads to the formation of these micelles. So, that is the driving force.

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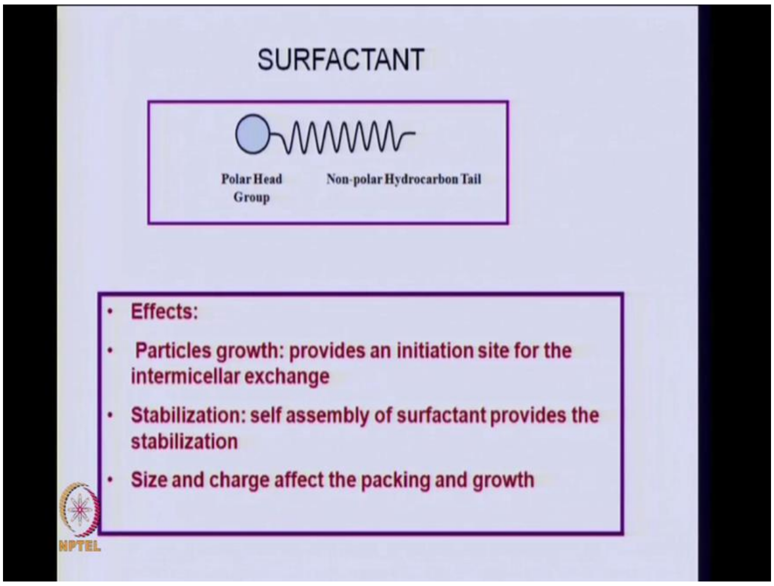

SURFACTANT

- Effects:
- Particles growth: provides an initiation site for the intermicellar exchange
- Stabilization: self assembly of surfactant provides the stabilization
- Size and charge affect the packing and growth

This we have discussed little bit earlier. This is a surfactant molecule which has a polar head group, and it has a nonpolar hydrocarbon tail. We can control the size of the polar head group. We can change the charge on the polar head group. It can have many types of charges: positive, negative, neutral. You can have many kinds of these hydrocarbon tails, very long tails. We can have two tails and we can have three tails. You can design many kinds of surfactant molecules. What is the affect of these surfactant molecules? It affects the growth of the particle, since it provides an initiation site for the intermicellar exchange. It stabilizes through the self assembly of these surfactant molecules. The size and charge of these polar head groups and tails affect the packing and growth of the nanoparticles, which will be synthesized within these spheres, which may be in micelles or reverse micelles.

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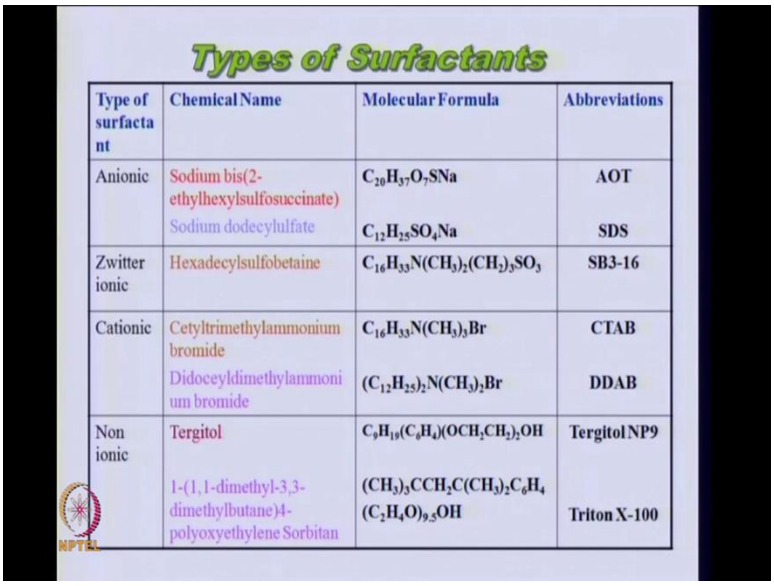

Types of Surfactants

Type of surfactant	Chemical Name	Molecular Formula	Abbreviations
Anionic	Sodium bis(2-ethylhexylsulfosuccinate) Sodium dodecylulfate	$C_{20}H_{37}O_7SNa$ $C_{12}H_{25}SO_4Na$	AOT SDS
Zwitter ionic	Hexadecylsulfobetaine	$C_{16}H_{33}N(CH_3)_2(CH_2)_3SO_3$	SB3-16
Cationic	Cetyltrimethylammonium bromide Didoceyldimethylammonium bromide	$C_{16}H_{33}N(CH_3)_3Br$ $(C_{12}H_{25})_2N(CH_3)_2Br$	CTAB DDAB
Non ionic	Tergitol 1-(1,1-dimethyl-3,3-dimethylbutane)4-polyoxyethylene Sorbitan	$C_9H_{19}(C_6H_4)(OCH_2CH_2)_9OH$ $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(C_2H_4O)_{9.5}OH$	Tergitol NP9 Triton X-100

There are varieties of surfactants. For example, you can have anionic surfactants, for example, is SDS in short, which is a sodium dodecyl sulfate or you can have with the molecular formula given here. You can have something which is called sodium bis (2-ethylhexylsulfosuccinate) and that formula is given here. Its commercial name is AOT, very common surfactant. These as you see will have a negative head group. If you dissociate this sodium iron, there will be a negative charge on the head group of this molecule. Both these are anionic surfactants, because they will have a negative head group when this molecule is dissolved in water. AOT and SDS are both anionic surfactants.

You can have zwitter ionic surfactants, like SB3-16, which is hexadecyl sulfobetaine, this is the formula. You can have cationic surfactants like CTAB. This is one of the most popular cationic surfactants, where you have the 16 carbon chains, it is cetyl trimethyl ammonium bromide. You can see that is a cetyl, the sixteen carbon chain and your trimethyl group and you have a bromide. Once you dissolve this aqueous medium, the bromide iron will ionize and remaining one positive charge will be on this nitrogen. You will have cationic surfactant. So, CTAB is the cationic surfactant. Similarly, you can have DDAB, where you have a 12 carbon chain, again a bromide. There will be a positive ion on the nitrogen when this molecule dissociates in water.

You can have anionic zwitter ionic. That means, both positive and negative charges in this system; positive on the nitrogen and negative on this side. And you can have nonionic surfactants, but with the polar head group. For example, you have tergitol NP9, this is the commercial name very commonly used. And then triton X-100, this is another commercial name with this kind of molecule. In these cases, as you see there is a ether linkage here. That gives the polarity, although there is no charge on the head group, but it is a polar molecule and these are nonionic surfactants.

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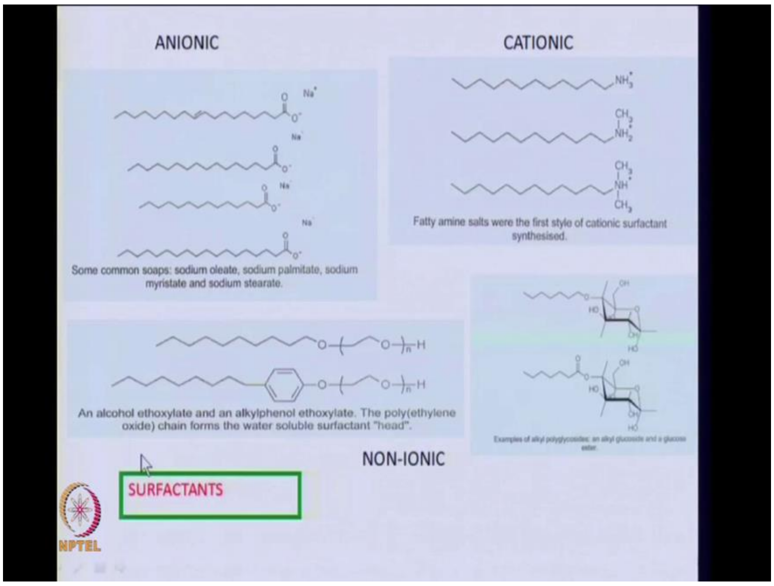

ANIONIC

CATIONIC

Some common soaps: sodium oleate, sodium palmitate, sodium myristate and sodium stearate.

Fatty amine salts were the first style of cationic surfactant synthesised.

An alcohol ethoxylate and an alkylphenol ethoxylate. The poly(ethylene oxide) chain forms the water soluble surfactant "head".

Examples of alkyl polyglycosides: an alkyl glucoside and a glucose ester.

NON-IONIC

SURFACTANTS

This is an example of anionic surfactants and you can see these are the negative charge on the head group, and this is the hydrocarbon chain. You can have cationic surfactants, where you have this positive charge on the nitrogen and you have hydrophobic tail. This is the hydrophilic or polar head group. This is the hydrophobic chain. You can have nonionic surfactants like this molecule, where you have a head group which is nonionic, but it has some affinity for water. This is the hydrocarbon chain which has affinity for oil or nonaqueous medium. You can also have surfactants like this, which is an alkyl glycoside and a glucose ester, where make together an alkyl glycoside, and a glucose ester make this alkyl polyglycoside which is acting like a surfactant. Because, it has a hydrocarbon or a non aqueous loving tail, and you have a polar head group uncharged. It has some polarity. So, there is a variety of surfactants which is available.

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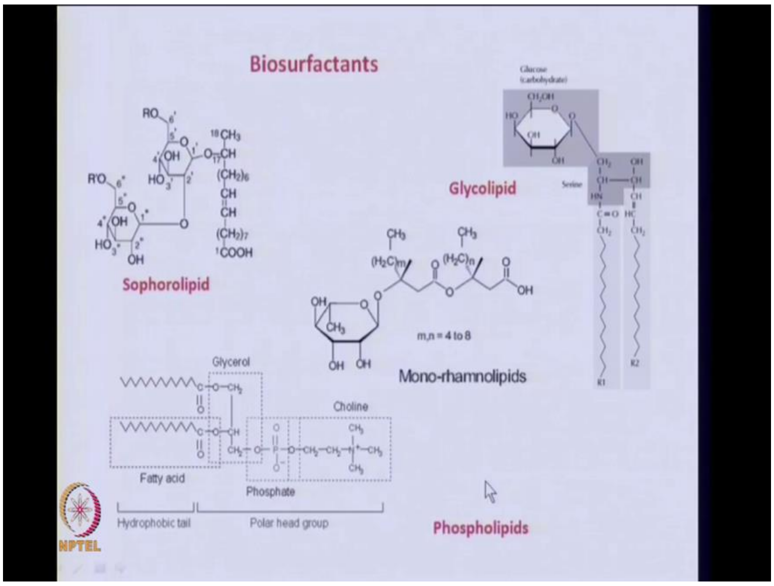

Biosurfactants

You can also have biosurfactants. That means: surfactants which are known in nature. These are some complex molecules. This is called sophorolipid and these are glycolipid. There are several such molecules which are available in nature. So, surfactants like this are useful if you want to do anything in pharmaceutical industry or the food industry, where biodegradable molecules are more important. So, these kinds of surfactants can be used for applications in those kinds of industries. You can have phospholipids like this which are very well known, where you have this hydrophobic tail and then you have a polar head group, which is acting here. These are neutral surfactants, and also they are biosurfactants, so neutral biosurfactants.

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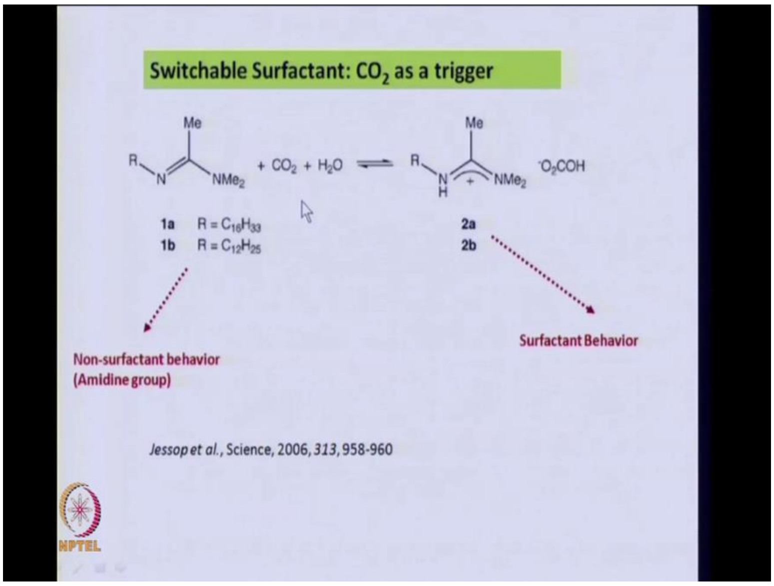

Switchable Surfactant: CO_2 as a trigger

1a R = $C_{16}H_{33}$
1b R = $C_{12}H_{25}$

2a
2b

Non-surfactant behavior
(Amidine group)

Surfactant Behavior

Jessop et al., Science, 2006, *313*, 958-960

You can have interesting surfactants which you can design. For example, this is a surfactant molecule, which does not behave like a surfactant as such. But when you have pass carbon dioxide through the solution, then it becomes ionic and then it behaves like a surfactant. That means: it can then aggregate, if you put it in sufficient quantity in a solution containing water and oil, then it can give rise to spherical aggregates or different shapes of aggregates, like a micelles or reverse micelles, depending on the concentration of carbon dioxide. So, carbon dioxide triggers this molecule, which is not a surfactant here, but in the presence of carbon dioxide, becomes a surfactant. So, such surfactants are called switchable surfactants.

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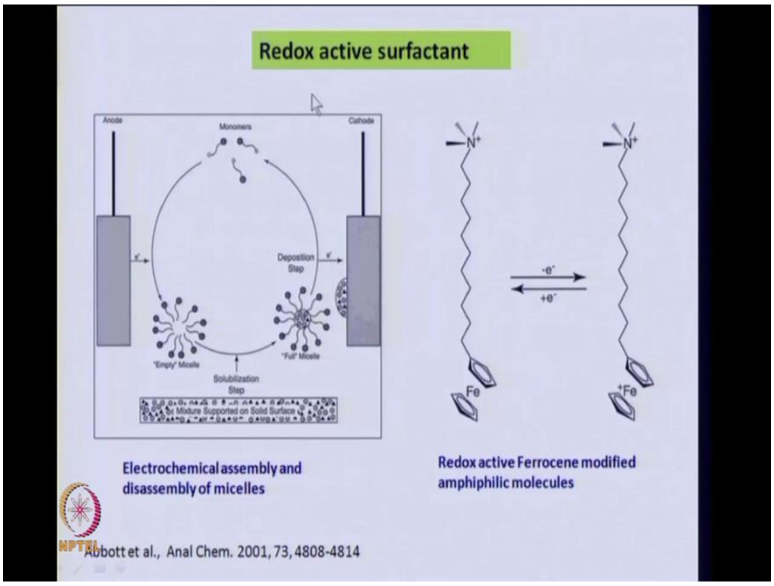

Redox active surfactant

Electrochemical assembly and disassembly of micelles

Redox active Ferrocene modified amphiphilic molecules

Abbott et al., Anal Chem. 2001, 73, 4808-4814

You can have redox active surfactant. For example: there is a surfactant which is like a monomer. That means, it is not organized in any shape. They are all loose. The molecules are separate. But when it takes up an electron: if you give some electrons from an electrode, it picks up electrons. If it does that then it starts aggregating. It becomes like an empty micelle. The hydrocarbon chains are inside and the polar head groups are outside. Of course, there is nothing inside right now. This is an empty micelle, but if there is some oil; suppose, at the next stage you introduce some oil, nonaqueous solvent, then these micelles can take up those oil and then they will become filled micelles.

Then if you remove an electron, this aggregate structure will be destroyed and this will open up and the solvent will go and stick there, whatever is there. They will then again be monomers. So, from monomers to spherical geometry of the surfactant aggregates in the presence of electron, takes up some oil and then gives out an electron to breakup, and leaves the oil, and again you can cycle these monomers. This monomer to surfactant aggregate through either reduction and then opening up of the micelle through the oxidation, this kind of redox active surfactants are also known.

This is an example, where you have used electrochemical assembly and disassembly of surfactants. You can do the similar thing in molecules which contain say ferrocene. Ferrocene is this iron, with 2 cyclopentyl groups. The other side is a chain with some trialkylamine and this is a hydrophobic chain. If you take out an electron then you can change this ferrocene to ferrocenium iron. So, there is a positive charge. Because, one electron has been removed and if you add an electron to this, then you get back this ferrocene derivative. So, you can go back and forth by removing electrons or by adding electrons and these are again redox active amphiphilic molecule. Amphiphiles are basically, again surfactants. Anything amphiphile means that it has a a possibility of adhering to hydrophilic, as well as hydrophobic moieties. So, any surfactant is an amphiphile.

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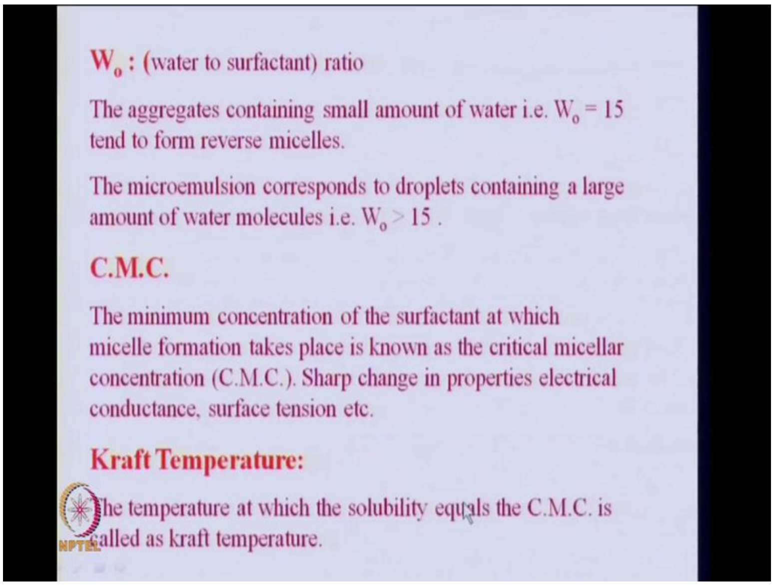

W_0 : (water to surfactant) ratio

The aggregates containing small amount of water i.e. $W_0 = 15$ tend to form reverse micelles.

The microemulsion corresponds to droplets containing a large amount of water molecules i.e. $W_0 > 15$.

C.M.C.

The minimum concentration of the surfactant at which micelle formation takes place is known as the critical micellar concentration (C.M.C.). Sharp change in properties electrical conductance, surface tension etc.

Kraft Temperature:

The temperature at which the solubility equals the C.M.C. is called as kraft temperature.

There are certain terms which are used in microemulsions, surfactants and reverse micelles, etc. One is, what is called the W naught parameter, which is related to the ratio of concentration of water is to surfactant. So, how much water is there to the respective surfactant. For example, you can have aggregates containing small amount of water is W naught equal to 15. They tend to form reverse micelles. Whenever you have microemulsion with W naught greater than 15, you can get lot of water. Basically, what we are saying is, as we are increasing W naught, you are adding more water in the system. So, water is to surfactant ratio is given by W naught. You have another term called the C.M.C. which is called the critical micellar concentration, and this is the minimum concentration of the surfactant at which the aggregation of surfactants to a micellar structure will take place. That is called the C.M.C. or critical micellar concentration.

For different systems the C.M.C. is different. If you choose a surfactant A, with water and say, solvent like hexane, you will have some critical micellar concentration C.M.C. If you change surfactant A to surfactant B, keeping water and the solvent same, you will have a different C.M.C. So, the C.M.C. depends on the kind of surfactant you are using and the kind of solvent you are using, etc. At the C.M.C., when the surfactant aggregation takes place, there is a sudden change in the properties of the micro emulsion or the system. These changes in properties can be studied easily if you study the viscosity or these lights catering or conductance or surface tension. Many of these properties will change sharply at the critical micellar concentration.

It is easy to determine what is the concentration of the surfactant at which the micelle forms. There is another term which is used, which is called the craft temperature. This is the temperature at which the solubility equals the C.M.C. And that temperature is called the craft temperature. These are certain terms which are used regularly in the study of microemulsions, surfactants, nanoparticles synthesis of surfactants using surfactants and microemulsions. One has to understand these terms because, you have to change these parameters optimally to get the right kind of surfactant aggregates, which will help you control ultimately the size and shape of the nanoparticles, which you want to synthesize within these surfactant aggregates.

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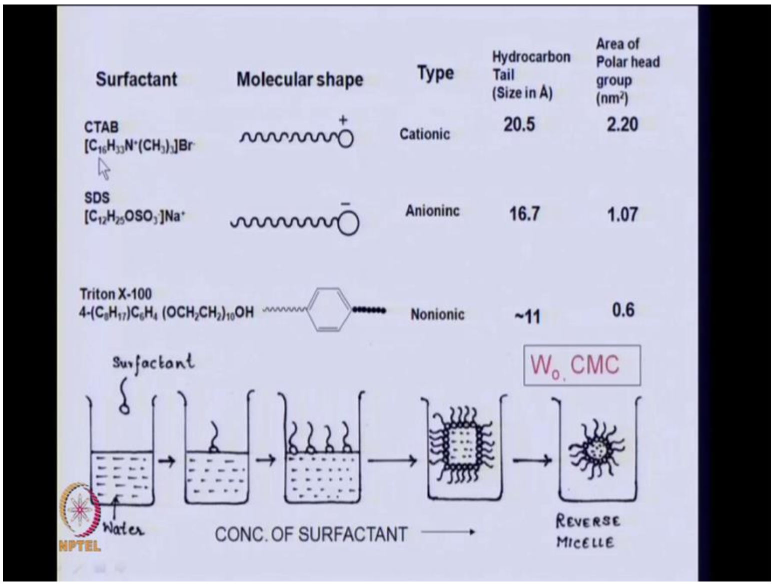

Surfactant	Molecular shape	Type	Hydrocarbon Tail (Size in Å)	Area of Polar head group (nm²)
CTAB $[C_{16}H_{33}N^{+}(CH_3)_3]Br^{-}$		Cationic	20.5	2.20
SDS $[C_{12}H_{25}OSO_3^{-}]Na^{+}$		Anioninc	16.7	1.07
Triton X-100 $4\text{-}(C_8H_{17})C_6H_4\ (OCH_2CH_2)_{10}OH$		Nonionic	~11	0.6

W_o, CMC

Here, we show you if you have a surfactant like CTAB, which is a cationic surfactant, and has a polar head group at this trialkylamine side. There is a long hydrocarbon; 16 carbon chain, which is the hydrophobic chain. There you can find out what is the typical hydrocarbon tail length and it will have a typical head group area. So, this head group area and the tail length are very important, in understanding what kind of aggregate these surfactants will make.

As you change the surfactant from CTAB to SDS, which is an anionic surfactant to triton X-100, which is a neutral surfactant. You go from cationic to anionic and to a non ionic surfactants. If you vary the dimensions, you see here, the length of the tail is 20.5 angstrom, whereas, in this case with this 12 carbon chain, the length is smaller. Obviously, this is 12 carbons and this is 16 carbon chain. So, the length will be smaller. In this case, it is 16.7 and in this triton X-100, it is 11 angstrom. You can vary the length. Similarly, you can vary the area of this head group. Here, as you see the head group area is very small in the nonionic surfactant, whereas, in these cases, the head group area in the cationic surfactant CTAB is much larger. These will affect the type of geometry and the critical micellar concentration at which the surfactant aggregates will form. If you start; what happens when you start adding surfactants to water? You have water and you are adding a surfactant molecule. Initially, the surfactants stays at the interface. You have water and oil or some other medium, which does not dissolve; which is immiscible in water. Then the surfactant molecules try to remain at the interface with the polar head groups on the side of the hydrophilic liquid, which is water.

The tails point towards the liquid, which is hydrophobic. After a certain concentration, that means: after you have added 4, 10, 20, certain number of molecules of surfactants, these surfactants tend to aggregate. When they tend to aggregate they take the water within their aggregate because, the head groups want to be immersed in the hydrophilic part of the system. And outside you have the oil remaining. So, this is typically how, as you vary the concentration, the surfactant molecules aglumerate in a particular manner and they solubilize the water inside. This is a typical formation of a reverse micelle. So, what is the W naught value?, what is the C.M.C?, those things are important to design the typical surfactant aggregates, that you want in a particular system.

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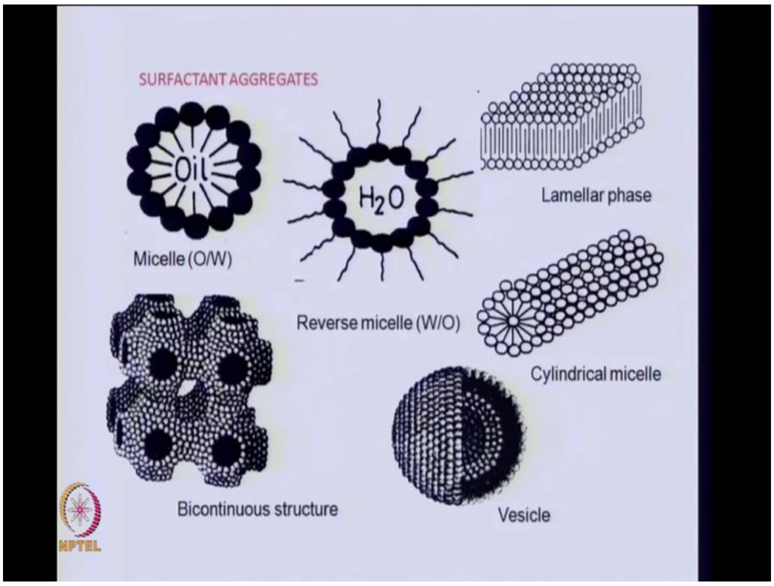

SURFACTANT AGGREGATES

You can get, not only these kinds of spheres; spherical aggregates of surfactant like, this is the reverse micelle or water in oil; water will be inside and oil will be outside. Because, the polar head groups are inside. This the micelle, where you have the hydrocarbon or hydrophobic tails inside and the polar head groups outside.

This is the micelle which will trap the oil medium. These are reverse micelle which will trap the aqueous medium. These are spherical aggregates of surfactants, but you can get also other type of structures like, this is a lamellar phase, where you have this polar head groups on one plane like this, and the tails are inside. There is another layer of polar molecule whose tails are inside. So, there is a tail-tail. These are hydrophobic tails which like each other, and they arrange themselves in the lamellar phases. You can have cylindrical micelles, where you have this hydrophobic tails, pointing inside. On the surface of the cylinder, you have all the hydrophilic or polar molecules on the outside.

Similarly, you can have vesicles like these, which is like one layer inside another layer. The vesicles are known in our living systems also. In living bodies, we have vesicles. These are typical bicontinuous structures which we set, can also be present in microemulsions. You can have different types of structures of these surfactant aggregates, which are controlled by concentration of surfactant; oil, water and the type of these individual chemical entities.

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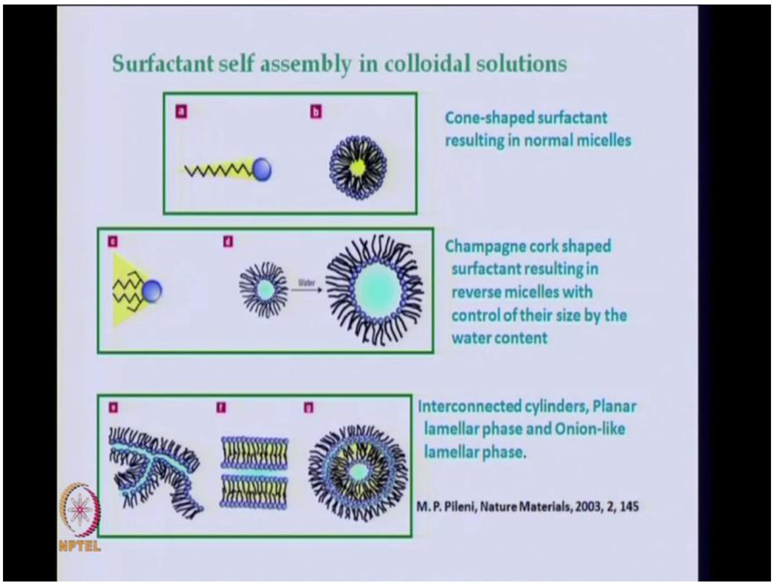

Surfactant self assembly in colloidal solutions

Cone-shaped surfactant resulting in normal micelles

Champagne cork shaped surfactant resulting in reverse micelles with control of their size by the water content

Interconnected cylinders, Planar lamellar phase and Onion-like lamellar phase.

M. P. Pileni, Nature Materials, 2003, 2, 145

These are some other shapes, which are different. Here, you can see a cone shaped surfactant which results in a normal micelle. If you have this kind of a a surfactant, where you see you have a polar head group and you have 3 or 4 different tails, and that forms what is called the cork shaped surfactant, which is again a reverse micelle. Here it is of course, a micelle. Typically if you have 2 or 3 hydrophobic tails, then invariably, they lead to reverse micellar organization, where you can have aqueous medium inside. In the micelles, you can have nonaqueous medium inside. You can have more complicated structures, which are interconnected cylinders like this, or planar lamellar structures or onion like structures. That means, there is 1 reverse micelle here, and then there is another organization of surfactant molecules, such that you have 2 polar head groups interacting with each other here. These are called onion like structures. So, variety of surfactant aggregates are possible, which self assemble themselves under certain conditions in colloidal solutions.

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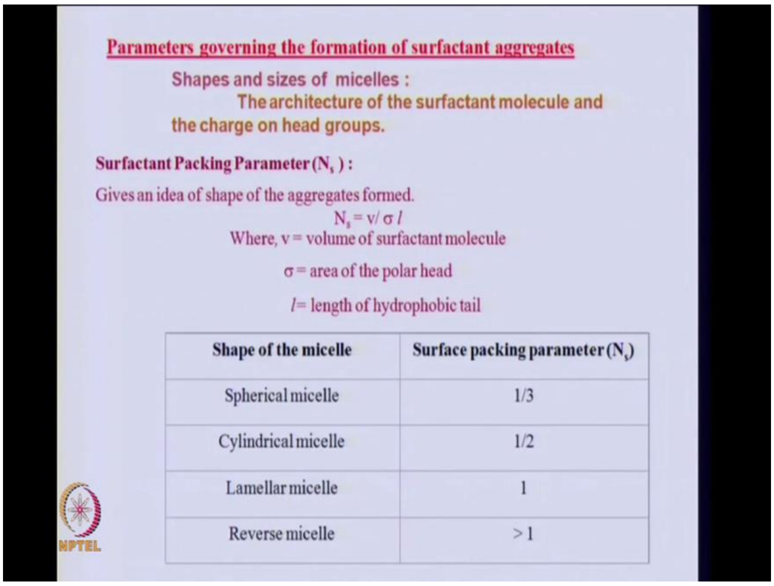

Parameters governing the formation of surfactant aggregates

Shapes and sizes of micelles :
The architecture of the surfactant molecule and the charge on head groups.

Surfactant Packing Parameter (N_s) :

Gives an idea of shape of the aggregates formed.

$N_s = v/\sigma l$

Where, v = volume of surfactant molecule

σ = area of the polar head

l = length of hydrophobic tail

Shape of the micelle	Surface packing parameter (N_s)
Spherical micelle	1/3
Cylindrical micelle	1/2
Lamellar micelle	1
Reverse micelle	> 1

There are certain parameters, which govern, which depend on the length of the hydrophobic chain, and the area of the head group, etc. There is a parameter which is called the surfactant packing parameter Ns, which is related to the volume of the surfactant molecule, divided by the area of the polar head group, which is multiplied by the length of the hydrophobic tail. Typically, if you do proper calculations of these numbers, you will find that most of the time, you will get spherical micelles.

If this Ns value of the surfactant packing parameter is 1 by 3, or you will get cylindrical micelles when it is 1 by 2, you will get lamellar micelles when it is 1, and you may get reverse micelles when it is greater than 1. In this equation, all these parameters; length of the hydrophobic tail, the area of the polar head group, the volume of the surfactant molecule, all come into the picture which ultimately, can be put together as one parameter and which gives you guide, to what kind of shape you will finally end up with, when you use different types of surfactant molecules, which have different lengths and different area of the head group.

Typically, when you want to synthesize nanostructured materials using this microemulsions, you can start with thinking that you want to make spherical particles, is the simplest and you start with reverse micelles as nonreactors.

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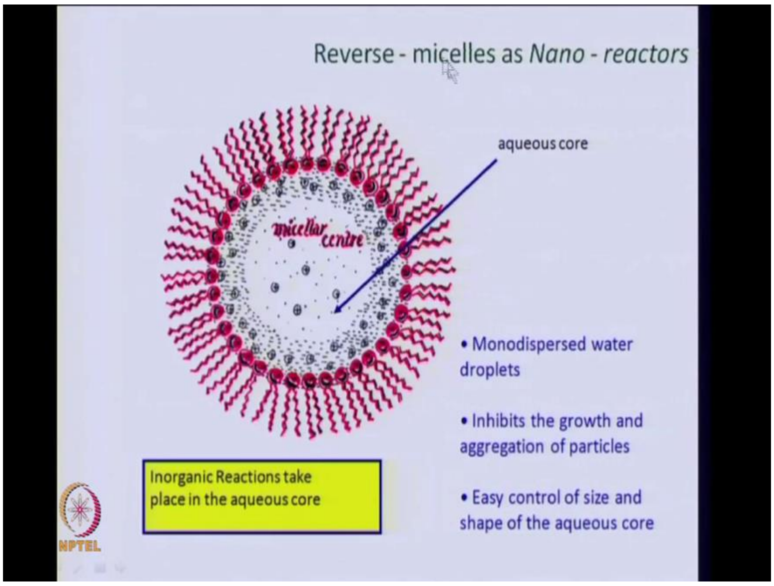

Reverse - micelles as *Nano - reactors*

- Monodispersed water droplets
- Inhibits the growth and aggregation of particles
- Easy control of size and shape of the aqueous core

Inorganic Reactions take place in the aqueous core

Why we call them as nonreactors because, these moiety where there is an aqueous medium there and you will be synthesizing the particles within this. So, this whole thing is like a reactor. The only thing is, this diameter is in nano dimensions; it may be 5 nanometers or 10 nanometers. This kind of surfactant aggregates with aqueous solution inside, can be treated as nonreactors. This the aqueous core, where you can do your reactions to give rise to inorganic particles. Of course, if you want to use nonreactors to synthesize organic particles then you will have to use micelles, and not reverse micelles. Because, in a reverse micelle you can only do synthesis with metal ions which get into the aqueous medium. For organic systems, this part has to be a nonaqueous medium. So, you have to use micelle, where the hydrophobic tails should be pointing inwards. Here, the hydrophobic tails are pointing outwards.

The polar head groups are pointing inside. Inorganic solids are nanoparticles, can be formed within this reverse micellar core. Using these, you can get monodispersed water droplets which leads to small particles because, it inhibits the growth and aggregation of particles. It is easy to control the size and shape of the particle because, you can control the size and shape of the aqueous core.

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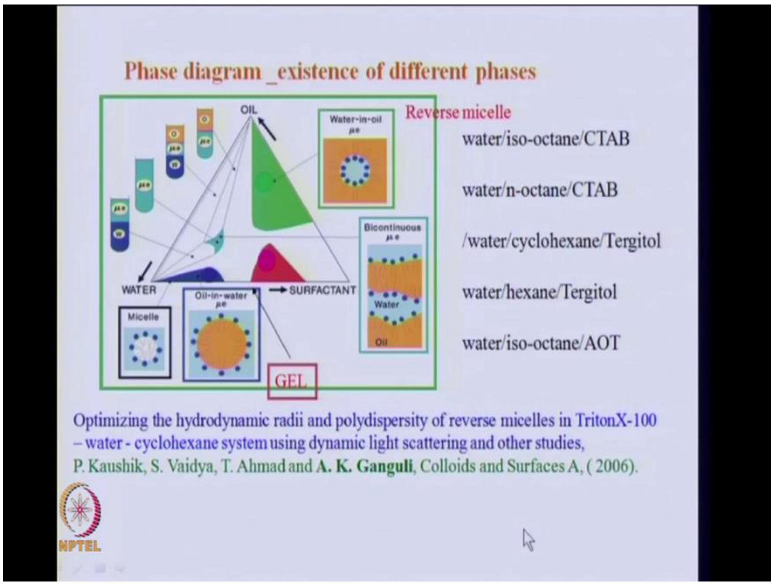

Phase diagram _existence of different phases

water/iso-octane/CTAB

water/n-octane/CTAB

/water/cyclohexane/Tergitol

water/hexane/Tergitol

water/iso-octane/AOT

Optimizing the hydrodynamic radii and polydispersity of reverse micelles in TritonX-100 – water - cyclohexane system using dynamic light scattering and other studies,
P. Kaushik, S. Vaidya, T. Ahmad and **A. K. Ganguli**, Colloids and Surfaces A, (2006).

When you have this kind of system of microemulsion, the understanding of the phase diagram is very important. Because, you have water, you have a nonaqueous medium and you have a surfactant. This is called a ternary phase diagram. Within this ternary phase diagram, some composition will lead to microemulsions. Some composition will lead to micelle type of microemulsions, some of which are called oil in water microemulsion or in some other area, typically, where you have got less water, you are away from water; these regions you will get water in oil microemulsion. Of course, you can also get gels in certain regions of the phase diagram. So, what this phase diagram tells you; what should be the composition of your microemulsion system in order to get reverse micelles or micelles.

To understand this phase diagram is very important, because you have to choose your system properly. If you want to synthesize a material, in a particular surfactant oil medium, you have to know its phase diagram. Because you want to know what is the composition of the oil water surfactant, which you need to choose. These are some typical examples: water isooctane is the nonaqueous medium; CTAB is a surfactant. There are different types of phase diagrams you can generate. Some phase diagrams are known in the literature; some you have to find out whenever you want to work. So, this kind of a ternary phase diagram is very important to know.

However, if you add a co surfactant then you have, not only water surfactant and oil. You also have a fourth component, which is a co surfactant. So, you will have to draw or understand a quaternary phase diagram, which is still more complex.

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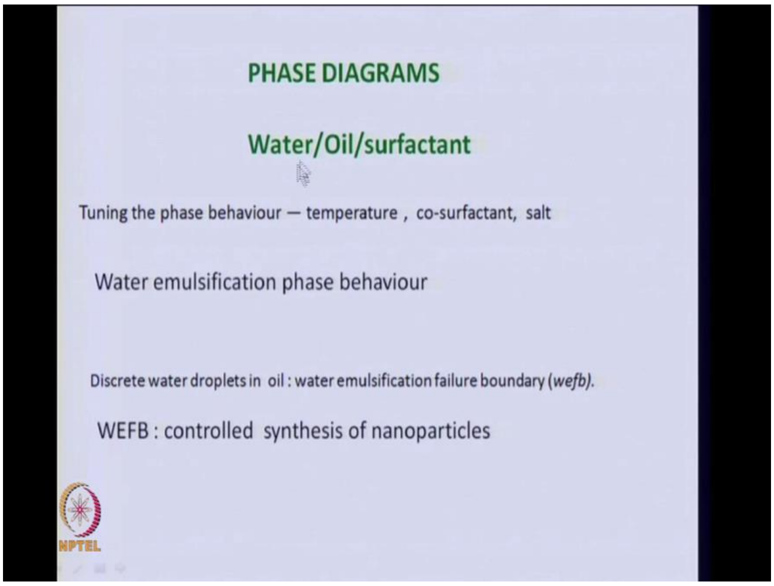

PHASE DIAGRAMS

Water/Oil/surfactant

Tuning the phase behaviour — temperature , co-surfactant, salt

Water emulsification phase behaviour

Discrete water droplets in oil : water emulsification failure boundary (*wefb*).

WEFB : controlled synthesis of nanoparticles

You have to use phase diagrams and to tune the phase behavior, you can control the temperature, the co surfactant and the salt. Then you can understand what is called a water emulsification phase behavior. So, you want to make discrete water droplets in oil and there is one term, which is called the water emulsification phase boundary. You can have this water droplets, only when you are within the boundary. Otherwise, this will fail and you will get separate droplets of oil and water.

If you know WEFB, you can do the controlled synthesis of nanoparticles. Basically, you need to know the phase diagram of the system, which will tell you where is this water emulsification failure boundary?

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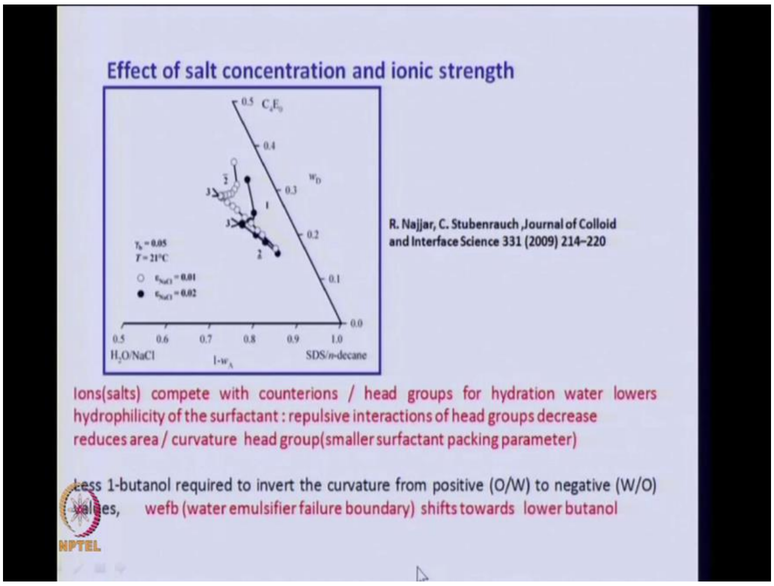

Effect of salt concentration and ionic strength

R. Najjar, C. Stubenrauch ,Journal of Colloid and Interface Science 331 (2009) 214–220

Ions(salts) compete with counterions / head groups for hydration water lowers hydrophilicity of the surfactant : repulsive interactions of head groups decrease reduces area / curvature head group(smaller surfactant packing parameter)

Less 1-butanol required to invert the curvature from positive (O/W) to negative (W/O) values, wefb (water emulsifier failure boundary) shifts towards lower butanol

The water emulsification failure boundary WEFB is also dependent on salt concentration and ionic strength. If you keep the same surfactant; oil and water, but if you change salt concentration or ionic strength, then you see, you can move to different lower amount of isooctane. Because, this is isobutanol; this is the b used as a co surfactant.

If you add more sodium chloride, which is a salt. If you add more salt, you move this side which means you move to lower concentration of butanol. So, butanol is being used in this system as a co surfactant. With less surfactant, you can stabilize the microemulsion system by adding salt. The salt actually, gives irons and these irons compute with the head groups for hydration, which lowers this hydrophilicity of the surfactant, and the repulsive interactions of the head groups decrease. That means, your interfacial tension is lower, and you need less amount of co surfactant to achieve the condition of interfacial tension go to zero.

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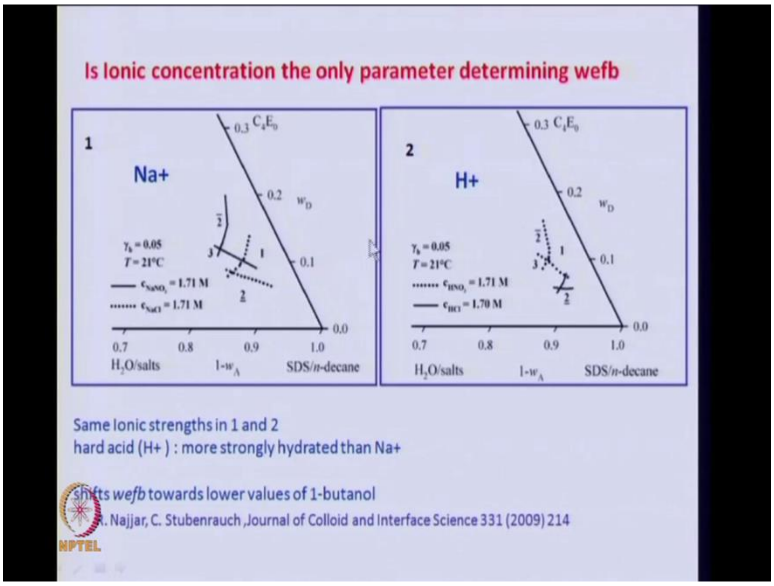

Is Ionic concentration the only parameter determining wefb

Same Ionic strengths in 1 and 2
hard acid (H+) : more strongly hydrated than Na+

shifts *wefb* towards lower values of 1-butanol
R. Najjar, C. Stubenrauch ,Journal of Colloid and Interface Science 331 (2009) 214

Is ionic concentration the only parameter determining the water emulsion failure boundary? No. Ionic concentration is one parameter, but if you change the ions, say, compare sodium ion and h plus ion. Both have one positive charge. However, h plus ion gets more hydrated than Na plus ion. So, the effect of h plus ion is more than Na plus, and you can see their shift is more, towards less butanol requirement, for stabilization of the micelles or reverse micelles, compared to sodium ion. This basically, related to the hydration ability of h plus ion which has more hydration ability compared to sodium ions. So, you can change this behavior of the WEFB or the water emulsification failure boundary to lower values of one butanol by adding salt.

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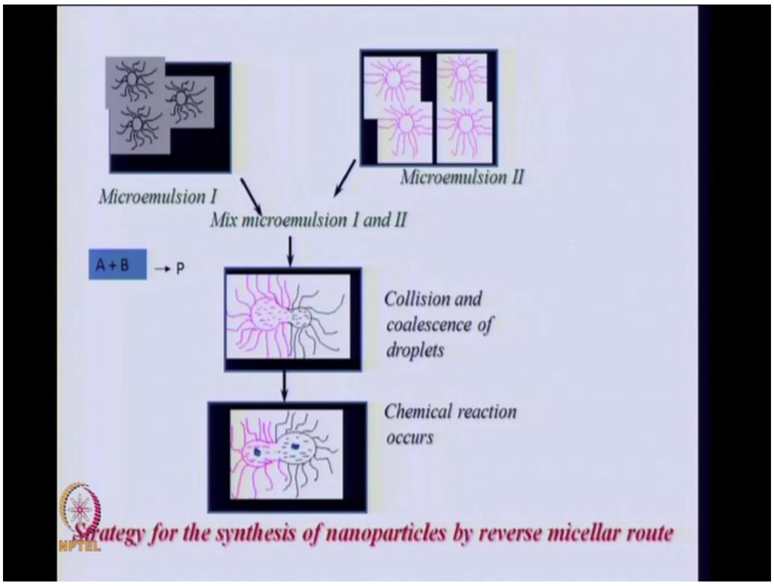

Strategy for the synthesis of nanoparticles by reverse micellar route

Typically, when you want to synthesize nonmaterials, what you do is, we make microemulsion of a metal A. If you want to make a compound AB, nano particles of the compound AB, in one of the microemulsions; that means, you take A ions and in another microemulsion, you take B ions. First, you create microemulsion by having your aqua solution; which contain the A ions, your solvent; which is non aqueous medium and the surfactant. Then in this, you have the B ions in aques medium, and then solvents and the surfactant. So, you get transparent microemulsion II and transparent microemulsion I, and you make these 2 microemulsions.

They collide and coalesce, and during this collision and coalescence, there is exchange of A ions from here, to B ions from here. Then you get the compound AB. The size of AB is controlled by the size of these droplets. However, the size of this AB is not exactly equal to the size of these droplets, but will be larger than the original size of these droplets, because two or more droplets are interacting to give these particles. So, this is how you can prepare nano particles by the reverse micellar route, using surfactants or microemulsions. The kinetics of this intermicellar exchange: this is the step where you are having the inter micellar exchange.

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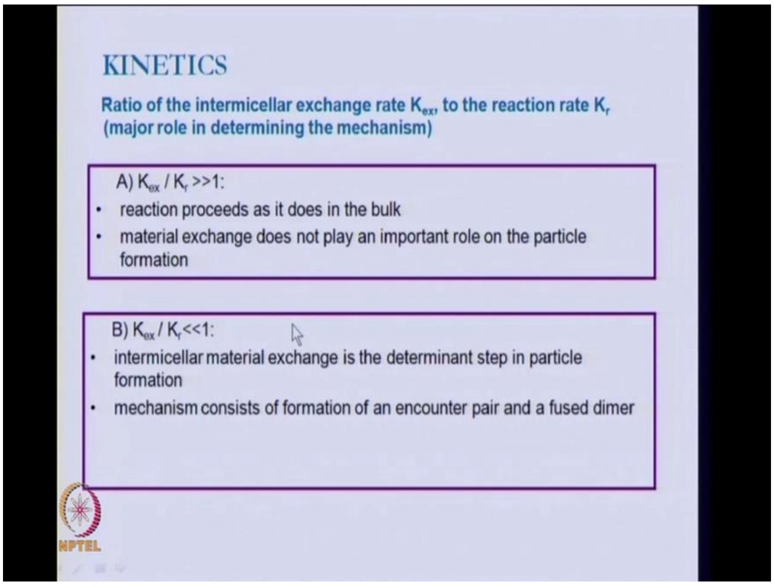

KINETICS

Ratio of the intermicellar exchange rate K_{ex}, to the reaction rate K_r (major role in determining the mechanism)

A) $K_{ex} / K_r >> 1$:

- reaction proceeds as it does in the bulk
- material exchange does not play an important role on the particle formation

B) $K_{ex} / K_r << 1$:

- intermicellar material exchange is the determinant step in particle formation
- mechanism consists of formation of an encounter pair and a fused dimer

The kinetics of the intermicellar exchange rate compared to the overall bulk reaction rate, is very important in determining the mechanism. If the exchange rate is very high compared to the bulk reaction rate, then the exchange does not have any particular roll to play on the particle formation. However, if the intermicellar exchange rate is slow, then it becomes the rate determining step in particle formation. Then the mechanism depends on the intermicellar exchange, where first, there is an encounter pair; two micellar units come together to form a pair and then a fuse dimer.

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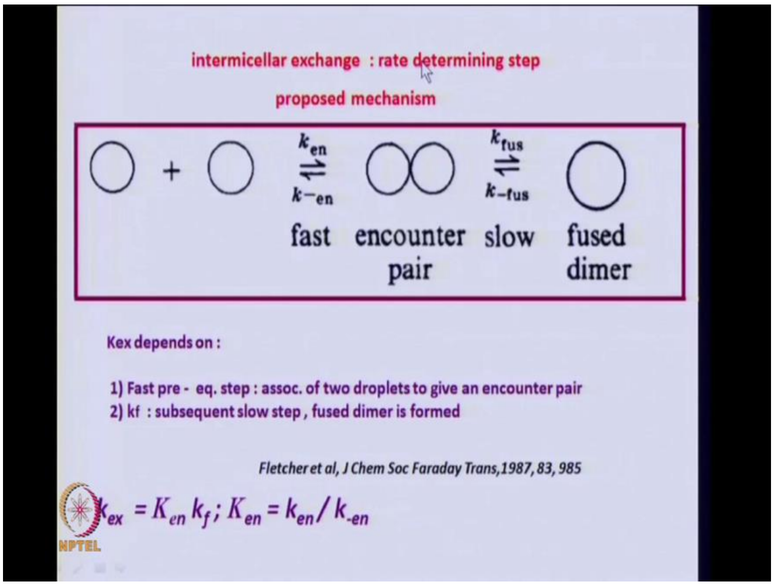

intermicellar exchange : rate determining step

proposed mechanism

Kex depends on :

1) Fast pre - eq. step : assoc. of two droplets to give an encounter pair
2) kf : subsequent slow step , fused dimer is formed

Fletcher et al, J Chem Soc Faraday Trans, 1987, 83, 985

$k_{ex} = K_{en} k_f ; K_{en} = k_{en} / k_{-en}$

In this intermicellar exchange, this is the rate determining step. This is slow compared to the bulk reaction rate. Then a mechanism has been proposed in 1987, where it is said that two interacting micelles come together to form an encounter pair, and then they fuse to form a fused dimer. This is the slowest step. There is a fast pre equilibrium step, which is the association of the two droplets to give an encounter pair and then a slow step, for the fused dimer to form. The rate constant for this exchange is given by these equations.

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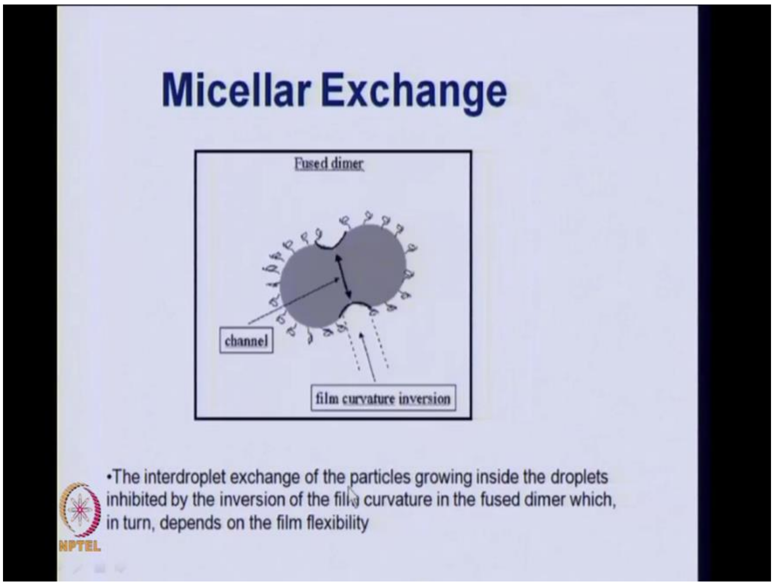

Micellar Exchange

- The interdroplet exchange of the particles growing inside the droplets inhibited by the inversion of the film curvature in the fused dimer which, in turn, depends on the film flexibility

During intermicellar exchange, when the fuse dimer is formed, the exchange rate is dependant a lot on the curvature here. If the curvature is very high then this exchange is more difficult. So, the inter droplet exchange of the particles is inhibited by the inversion of the film curvature in the fused dimer. How much this will curve inside depends on the film flexibility and that will affect the micellar exchange.

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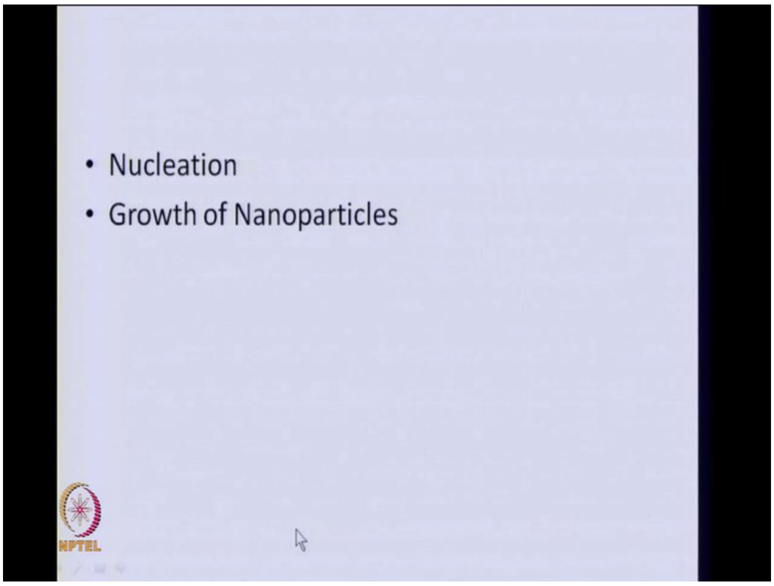

- Nucleation
- Growth of Nanoparticles

So, after the particle nucleate, that is, the nucleation stage then there is a growth of the nanoparticles.

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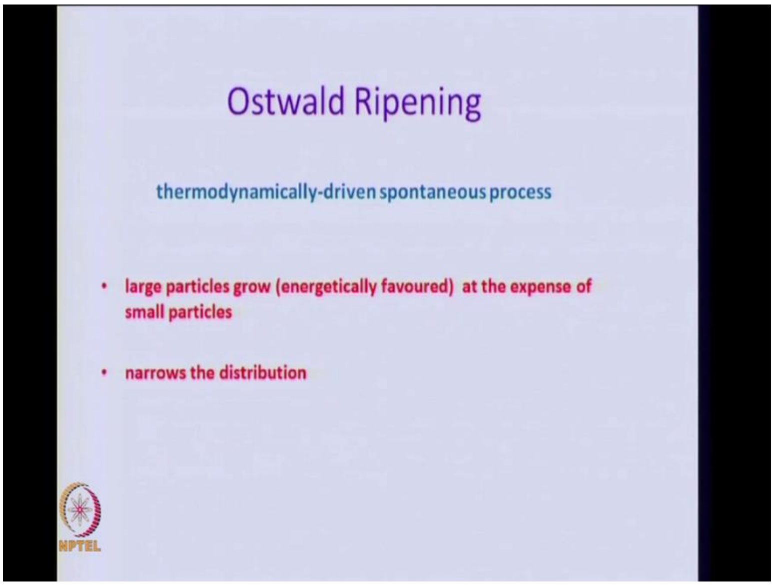

Ostwald Ripening

thermodynamically-driven spontaneous process

- large particles grow (energetically favoured) at the expense of small particles
- narrows the distribution

The growth of the nanoparticles typically, follows what is called the ostwald ripening rule. It is a thermodynamically driven spontaneous process, where large particles grow which are energetically favored at the expense of small particles. Some small particles will form and then they will dissolve, and some large particles will form, and this will continue, till the larger particles become larger and larger, and the distribution; that is, the particles size distribution will become much narrower; that means, you will have a large number of particles of one particular size, and then you will have a very few numbers of sizes, which are must smaller.

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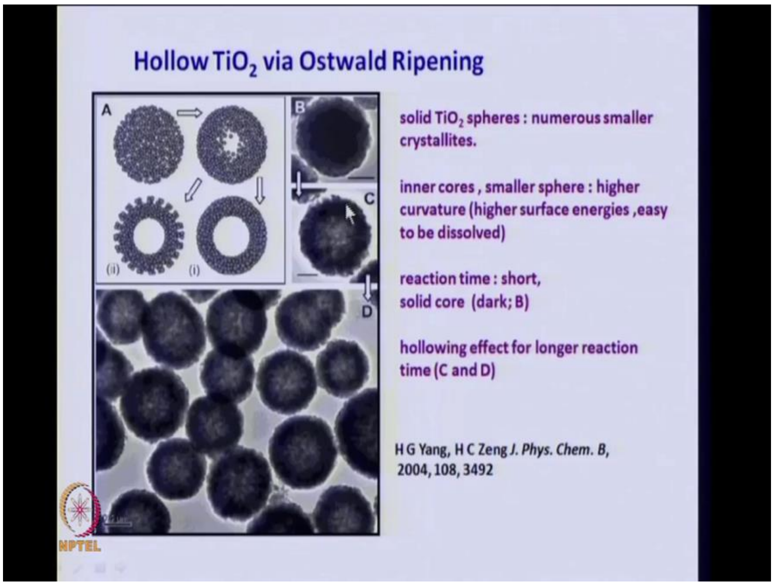

Hollow TiO_2 via Ostwald Ripening

solid TiO_2 spheres : numerous smaller crystallites.

inner cores , smaller sphere : higher curvature (higher surface energies ,easy to be dissolved)

reaction time : short, solid core (dark; B)

hollowing effect for longer reaction time (C and D)

H G Yang, H C Zeng *J. Phys. Chem. B*, 2004, 108, 3492

This is called the ostwald ripening process. This is a thermodynamically driven process. During ostwald ripening, what happens initially, you have many of these particles which are forming, many nuclei which form, and then the smaller particles dissolve becoming larger particles.

The inner core particle dissolves first, because the surface energy is higher at the inner cores. This higher curvature gives higher surface energy and easy to be dissolved. So, the inner cores dissolve first, and the outer cores are present, and this is a model, and this is what is seen in experiments. You see the inner cores; it is dark here and then it becomes lighter. So, this is the process by which you are getting this ostwald ripening to give rise to these particles. Thermodynamically, this is the process: ostwald ripening process of how the after nucleation, the particle will grow. We will stop our lecture here and we will continue the second lecture on microemulsions in the next lecture. We will continue how the particles grow using ostwald ripening, and we will consider other aspects of synthesis of nano structures by microemulsions

Thank you very much.