Colloids and Surfaces
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Lecture - 44
Colloidal Particles at Interfaces: Introduction

So we are going to start with the module 6 today. And so, this concerns colloidal particles at interfaces.

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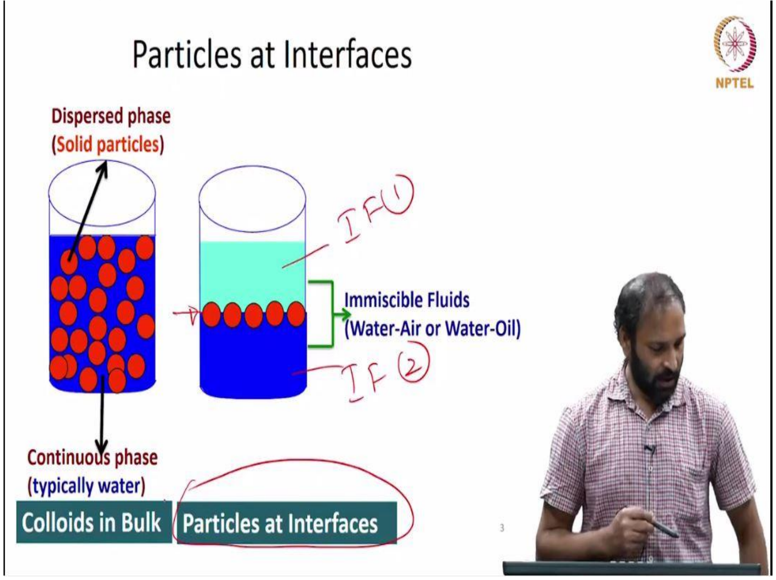

Particles at Interfaces

Dispersed phase
(Solid particles)

Immiscible Fluids
(Water-Air or Water-Oil)

Continuous phase
(typically water)

Colloids in Bulk

Particles at Interfaces

So, far what we have looked at is when we have particles dispersed in a continuous medium, so, these are the, the solid particles and that is the continuous medium and you have solid particles dispersed in a fluid medium, fluid medium could be typically water or any other liquid for that matter or gas. And so, we have looked at colloids in the bulk, as against that, what we are going to do today is to look at a colloids that are sitting at an interface between two fluids. So what you are looking at here is immiscible fluid 1 and you know another is immiscible fluid.

So, once you have any combination of immiscible fluids, you will have an interface that separates the two particles. So, we will deposit particles right at the interface between the two fluids. And we look at some important consequences of particles at interfaces.

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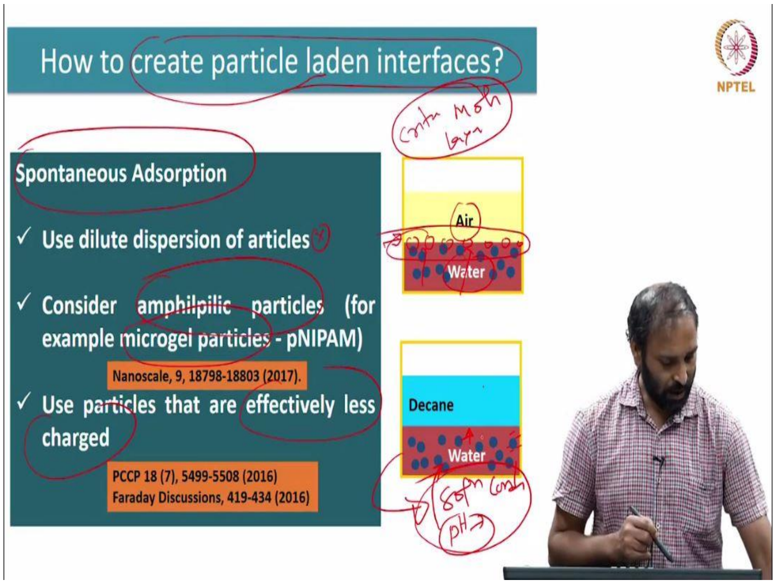

How to create particle laden interfaces?

Spontaneous Adsorption

- ✓ Use dilute dispersion of articles
- ✓ Consider amphilpilic particles (for example microgel particles - pNIPAM)

Nanoscale, 9, 18798-18803 (2017).

- ✓ Use particles that are effectively less charged

PCCP 18 (7), 5499-5508 (2016)
Faraday Discussions, 419-434 (2016)

Now, before we move on further, I just want to spend maybe a few minutes to talk about how do we create interfaces with particles or how do we create particle laden interfaces, there are two typical strategies one could use one is based on what is called as a spontaneous adsorption. So, in such a case what you do is you consider a system of immiscible liquids. So, this could be like say water air or like say decane or any other oil in contact with water.

So, then you create an interface now, then what you do is you take dilute dispersion of particles this portion could be either in the aqueous phase, or the particles could as well be dispersed in the decane phase as well. But the schematic that you see here, it contains these particles that are colored blue, and they are disposed in water medium. And so, if you take very dilute dispersions that is the one of the requirement and we will talk a little bit about why little later.

Then, if the particles are amphiphilic that means they are surface active example could be micro gel particles or pNIPAM or any micro gel particles which are known to be amphiphilic and in spite of dispersing these particles in the bulk. If there are sufficient low concentration, you will see that all the particles migrate to the interface and then they decorate the interface, that is one way of creating interface with particles and the concentration at which the entire monolayer entire interface is populated with particles is what is called as critical monolayer concentration.

And, for any concentration above that critical monolayer concentration, the particles are going to be in the bulk as well as at the interface. Therefore, one has to work at sufficiently low concentration to have particles positioned only at the interface and nothing at the bulk. The second method of achieving this particle laden interfaces is to use a particle that are effectively less charged that means, if you have a system like this and if you have the particle that are disposed in water.

And if the charge density whether if the particles are either positively charged or negatively charged, and if the surface charge density is lower, and they have a tendency to adsorb spontaneously at the interface and their adsorption can be tuned by changing solution conditions. For example, one could consider a pH whether the particles are have a low charge or you could add a small amount of electrolyte and the fact that the addition of electrolyte reduces the electrical double layer interaction.

That enables this spontaneous adsorption of particles at interface. In other words, whenever the particles are trying to approach an interface there is an energy barrier for the absorption and this energy barrier can be either completely removed or reduced by changing the solution conditions that as such as manipulation of pH or the addition of salt. So, therefore, the spontaneous adsorption can be achieved by considering amphilpilic particles in the aqueous phase at sufficiently low concentration or by using a dispersion where the particles are less charged.

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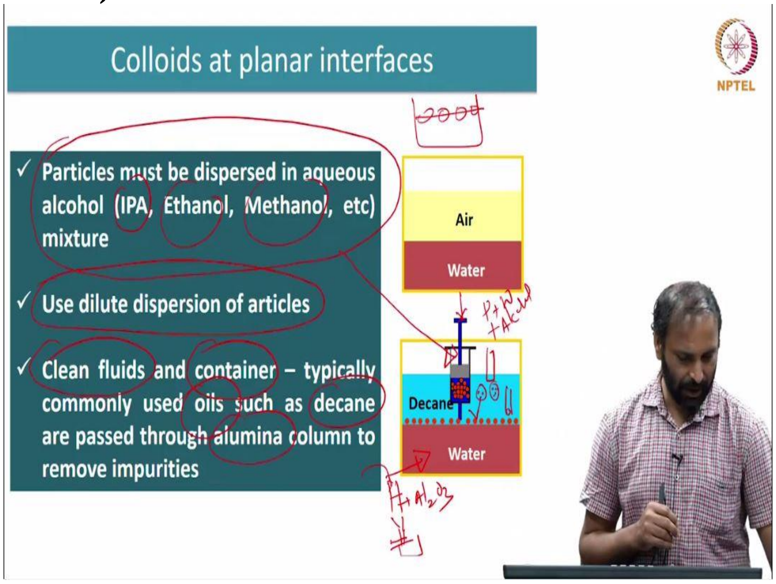

Colloids at planar interfaces

- ✓ Particles must be dispersed in aqueous alcohol (IPA, Ethanol, Methanol, etc) mixture
- ✓ Use dilute dispersion of articles
- ✓ Clean fluids and container – typically commonly used oils such as decane are passed through alumina column to remove impurities

The second method of you know achieving a particle laden interface you know or the interface is containing particles is by deposition of particles at the interface. So, for that what is done is the particles must be dispersed in an aqueous alcohol solution. So, what you should do is you should take a micro syringe for example, and this should contain particles plus if it is an aqueous dispersion of course, you will have water along with that you would have to add a small amount of alcohol.

And this alcohol could be isopropanol alcohol, ethanol, methanol or any you know standard alcohol. And once you have an aqueous alcohol dispersion of particles, so, what you could do is you can position the micro syringe either in the decane phase or you can position it right close to the interface. And when you inject these dispersion so, what we will have is you will have small droplets containing particles that form and the moment these droplets touch the interface.

Because of the presence of alcohol these droplets break and that essentially enables the spreading of particles the interface and of course, one has to work with very dilute dispersions and another important consideration is that the fluid that are being used for these experiments have to be extremely clean and the container also has to be extremely clean. What I mean by that is that it is a good practice to consider water.

That is double distilled and which does not have any ions present plus the oils that are typically used you know usually ensure that there are no surface active additives in these oils. For example decane is passed through a column that contains alumina to remove any surface active impurities that may be present in the system. The arrangement could be as simple as you consider a burette and fill the burette with aluminum particles and then you add a small amount of decane.

And then let it pass through this column and then you collect the clean decane at the bottom and you can use such you know treated oil for further experiments. So, these are couple of different ways by which one could create interfaces with particles or the particle laden interfaces.

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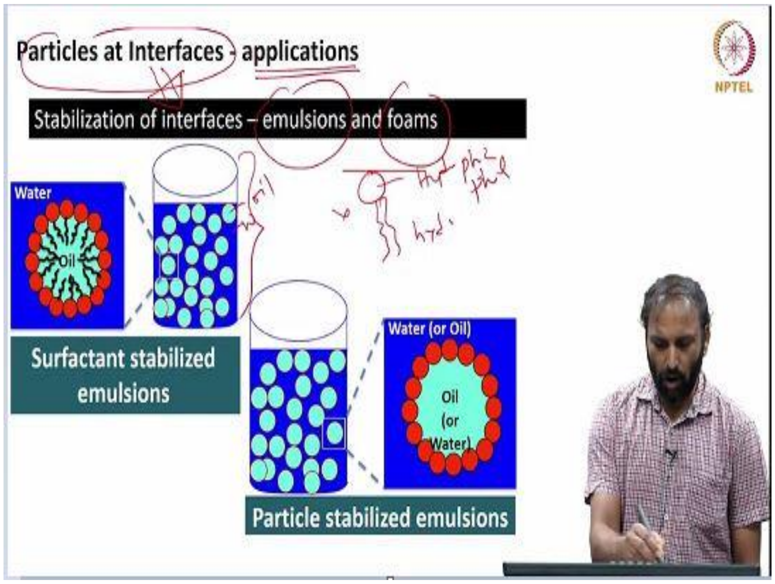

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

Surfactant stabilized emulsions

Particle stabilized emulsions

Now, before we discuss further on the particles or interfaces concept, I would like to talk a little bit about some applications of such systems and the particles or interfaces concept has been used for stabilization of interfaces, in that means for obtaining emulsions and foams. The schematic that you see here is a is an example where you have a system of water and an oil and then you add a little bit of surfactant that is a surface active agent which is designated you know as a something that is a circular head group and a tail group.

And that is the hydrophilic part of the surfactant and the hydrophobic part of the surfactant and we know that this effect surface surfactants are surface active and they are known to go and sit at the interface and you can get what are called as surfactant stabilized emulsions in a similar way.

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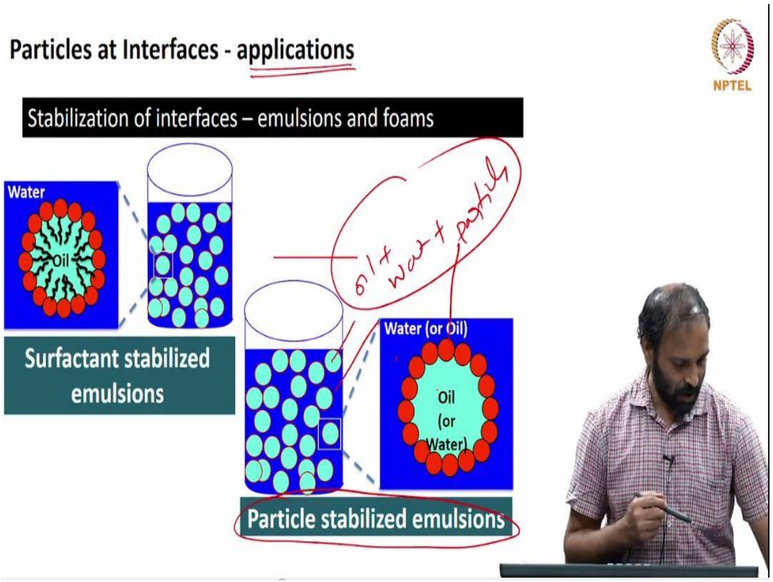

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

Surfactant stabilized emulsions

Particle stabilized emulsions

There has also been a lot of interest in what are called as particle stabilized emulsions, in such a case the emulsions are prepared by taking an oil and water plus some particles. And these particles again have a tendency of going and adsorbing at the interface between the 2 immiscible liquids and then they can act as a as stabilizers.

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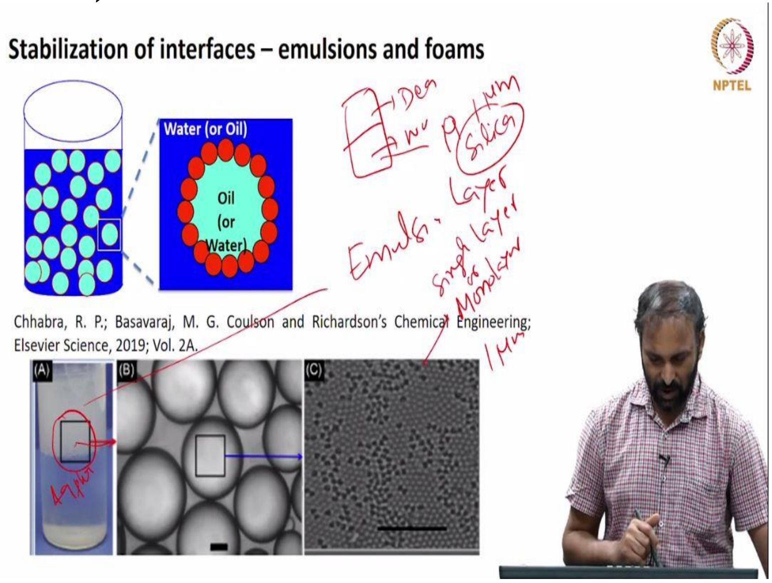

Stabilization of interfaces – emulsions and foams

Chhabra, R. P.; Basavaraj, M. G. Coulson and Richardson's Chemical Engineering; Elsevier Science, 2019; Vol. 2A.

This is a an example in which what you are seeing here is this is the aqueous phase and what do you see at the top which is which appears turbid it is an emulsion layer that has been created by taking water and decane and what is also present in water is a 1 micro meter particle and these particles are of silica particles. And, and so you can do microscopy of the emulsion layer that is formed and he will see that you know, it contains large droplets.

And if you focus if you use an optical microscope and if you focus on the droplet surface, you see that you know there is these droplets are decorated with a single layer or a monolayer of 1 micrometre particle that is present on the surface of these droplets and the presence of these droplets give a very good stability for the such emulsions.

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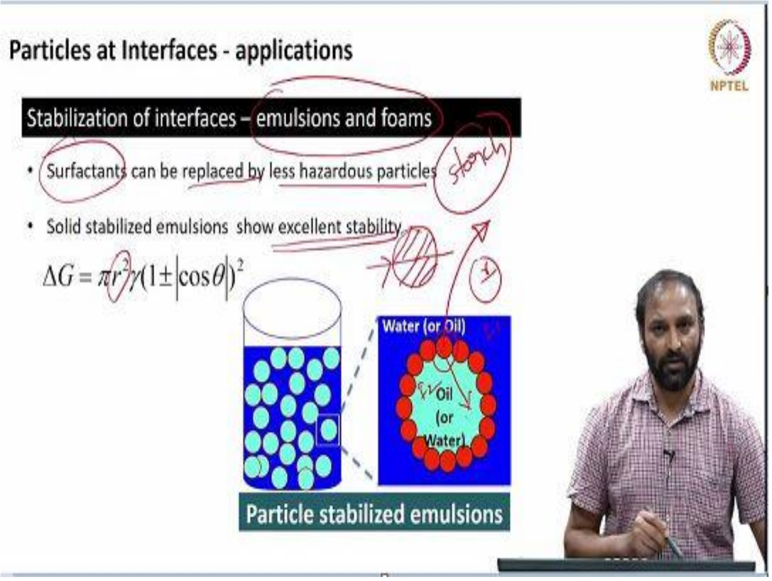

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

- Surfactants can be replaced by less hazardous particles
- Solid stabilized emulsions show excellent stability

$$\Delta G = \pi r^2 \gamma (1 \pm |\cos\theta|)^2$$

One of the advantages of looking at there are several advantages of producing particle stabilized emulsions, and foams. So, they are the surfactants that are typically used for this purpose, they can be replaced by less hazardous particles. So, for example, one could look at using inorganic particles or for example, starch particles of starch, which therefore, one could design edible Pickering emulsions, you know, without the need of using any hazardous surfactant molecules.

So, the other important consequence of stabilization of emulsions with particles is that solid stabilized emulsions, they show excellent stability and that is because, once the particles are sitting at the interface of the two fluids to remove it from the interface to dislodge the particles in the interface either into the aqueous phase or into the oil phase, it requires a lot of energy and this energy that is the surface free energy that is required for removing a particle either into the continuous phase or into the oil phase is given by pi r square.

Where pi r square is the radius of the particles that are being used for stabilization of emulsion and gamma is the interfacial tension between the two particles, the two fluids that is fluid 1 and fluid 2 and this term 1 plus or minus cos theta whole square this and that multiply by pi r square will give you what is the area that the particle is replacing when it is at the interface or essentially if there is a particle that is sitting at the interface.

If the particle is exactly situated the interface is that you know half of the particle is in one phase and half of the particle is in other phase, then this term becomes pi r square essentially it is what is called as a contact area that is the area that is obtained by the intersection of the interface and the particle. So, and the reason why so, this delta G which is the energy that is required to detach a particle either into the aqueous phase or into the oil phase it goes as the square of the particle size.

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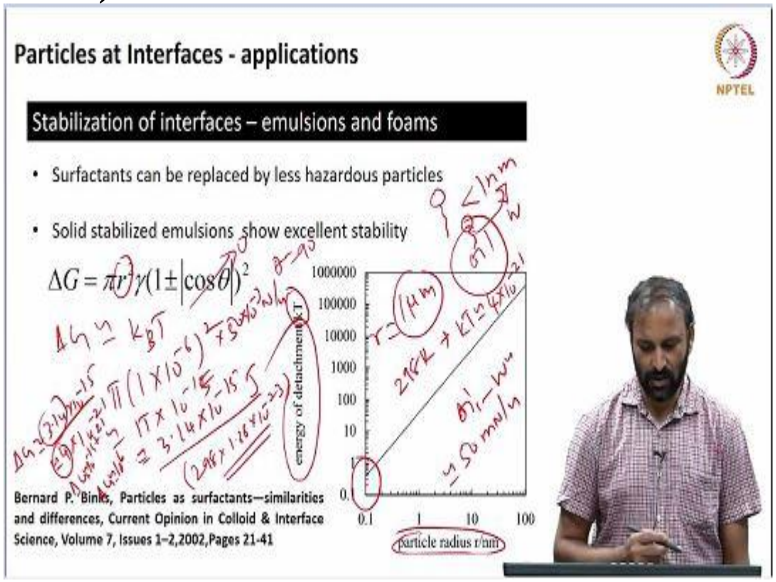

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

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$$\Delta G = \pi r^2 \gamma (1 \pm |\cos\theta|)^2$$

Bernard P. Binks, Particles as surfactants—similarities and differences, Current Opinion in Colloid & Interface Science, Volume 7, Issues 1–2,2002,Pages 21-41

So, therefore, what you see here is the energy of detachment that is plotted that is a scaled with k_BT and that is plotted as a function of particle radius. Now, if you consider surfactant molecules which are in a sub nanometer in size, so, if I substitute for r to be sub nanometer it turns out that this delta G that we calculate it would be of the order of k_BT itself that is, you know somewhere here and now, when the surfactant molecules have energy, which is of the order of k_BT.

What they could do was once even though they could be absorbed in interface, they can easily detach from the interface and go either into the aqueous phase or the continuous phase or into the oil phase. However, in contrast, if you look at particles that have an energy of radius 1, this is the radius is in nanometer. Now, if you take particles that are larger in dimension for example, if you take 1 micrometer particle, so, therefore, if the radius is 1 micrometer.

So, let us calculate quickly so, that is pi multiplied by 1 micrometer is 1 to 10 power minus 6 whole square and let us assume that the theta is equal to like say 90 therefore, this term becomes not important. So, therefore, and if we consider the surface if you consider an oil water interface with the interfacialtension of say for example, 50 millinewtons per meter. So, therefore, this becomes 50 into 10 power minus 3 newton per meter, therefore, what we have is pi into 10 power minus 12 and as minus 3 here.

So, that is minus 15 that is approximately 3.14 into 10 power minus 15. That is going to be in joules. Now, if you divide this by thermal energy at for example, say 298 Kelvin, turns out that thermal energy k_BT at 298 Kelvin, so, is of the order of 4 into 10 power minus 21. So, that is if I take 298 that is the temperature multiply by 1.38 into 10 power minus 23. So, that is the k_BT. So, therefore, this delta G becomes of the order of 3.14 10 power minus 15 divided by 4 approximately into 10 power minus 21. So, if I say that these are of similar magnitude, therefore, delta G becomes 10 power minus 15 plus 21 therefore, delta G is of the order of 10 power 6.

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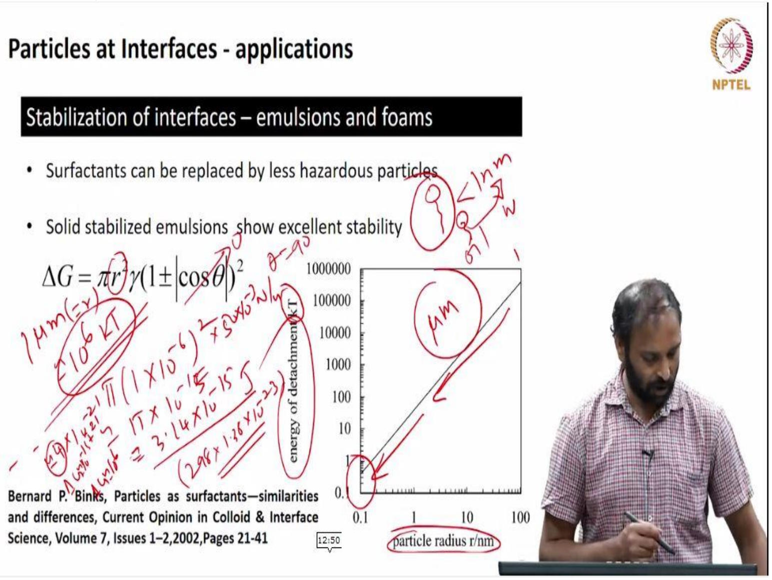

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

- Surfactants can be replaced by less hazardous particles
- Solid stabilized emulsions show excellent stability

$$\Delta G = \pi r^2 \gamma (1 \pm |\cos\theta|)^2$$

Bernard P. Binks, Particles as surfactants—similarities and differences, Current Opinion in Colloid & Interface Science, Volume 7, Issues 1–2,2002,Pages 21-41

Therefore, the simple calculations show that if you have a 1 micrometer particle of radius 1 micro meter and if that is situated at the interface with the interfacial tension 50 millimeter per meter. So, the energy that is required to dislodge a particle into one of the phases is of the order of 10 power 6 kT. And this energy is much larger when you consider a surfactant molecule which is sub nanometer in size.

And of course, this energy decreases with decreasing the particle size. So, what you are seeing here is you know, a plot of this detachment energy is a function of dimension, therefore, it has the particle size become smaller and smaller, the energy that is required to dislodge the particle into one of the phases becomes smaller that means, they can easily escape the interface and such emulsion would not be highly stable on the contrary, if you use particles which are micrometer in dimension, the energy of detachment is of the order of 10 for 6 $k_B T$ that gives excellent stability for particle stabilized emulsions.

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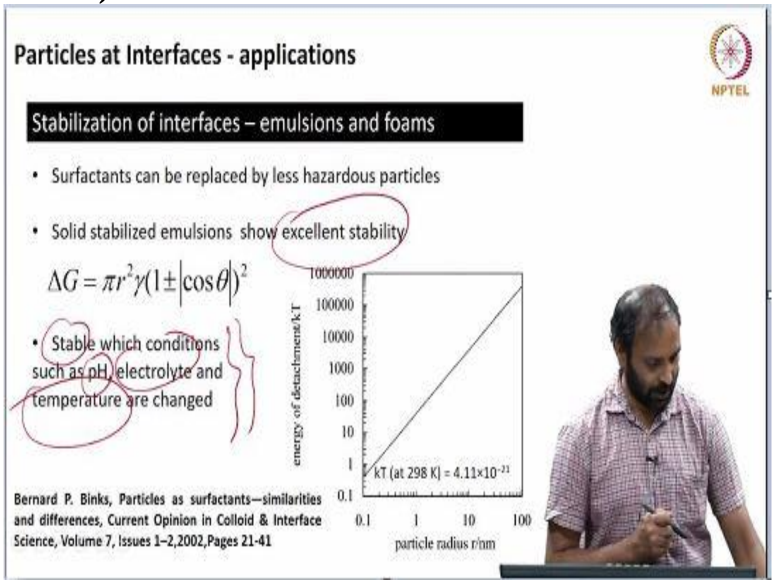

Particles at Interfaces - applications

Stabilization of interfaces – emulsions and foams

- Surfactants can be replaced by less hazardous particles
- Solid stabilized emulsions show excellent stability

$$\Delta G = \pi r^2 \gamma (1 \pm |\cos\theta|)^2$$

- Stable which conditions such as pH, electrolyte and temperature are changed

Bernard P. Binks, Particles as surfactants—similarities and differences, Current Opinion in Colloid & Interface Science, Volume 7, Issues 1–2,2002,Pages 21-41

And other important aspect of these emulsions is that they are stable under conditions where surfactant stabilized emulsions, may destabilize that could be they are stable under harsh pH conditions in the presence of electrolyte as well as when the temperature of the emulsion that are prepared when they are changed, they still continue to remain stable as well. So, therefore, they show excellent time stability and they also show excellent stability under various solution conditions such as changes to pH, electrolyte concentration and temperature.

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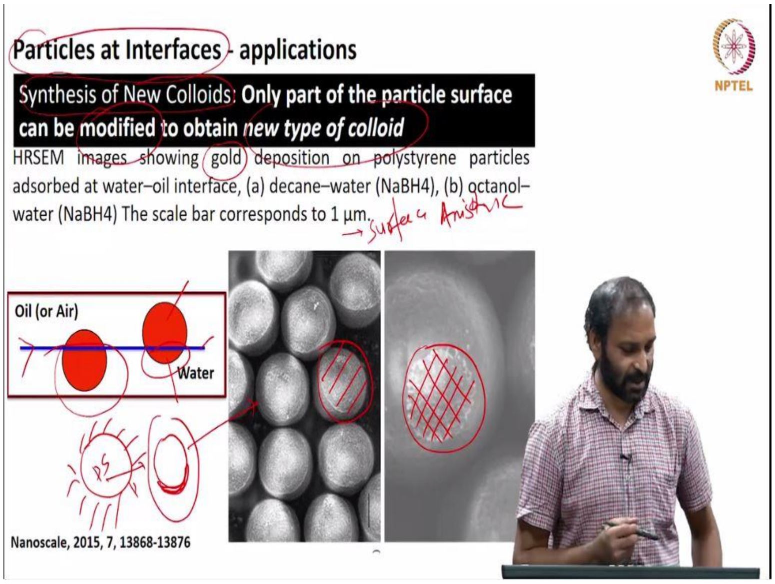

Particles at Interfaces - applications

Synthesis of New Colloids: Only part of the particle surface can be modified to obtain *new type of colloid*

HRSEM images showing gold deposition on polystyrene particles adsorbed at water–oil interface, (a) decane–water ($NaBH_4$), (b) octanol–water ($NaBH_4$) The scale bar corresponds to 1 μm.

→ Surface Anisotropic

Nanoscale, 2015, 7, 13868-13876

So, the particles or interfaces concept can also be used to make new colloids and if you look at a schematic here, what you have is if this is interface, that the blue line and you have two cases where the particle is immersed more in the water phase and in the second case it is immersed less in the aqueous phase. And because, and the fact that the part of the surface is in contact with oil and the part of the surface in is in contact with water.

In this case, it can be exploited to make new type of colloids by what is called as a selective surface modification of the part of the particle either in contact with water or the one that is in contact with oil. And what is shown here is an example where a part of the surface that is in contact with water for example, what is circled here and here they have been coated with gold particles gold nanoparticles and depending upon how much of the surfaces in contact with water.

I can either have a smaller region coated with gold or a larger fraction of the particle surface coated with gold and this brings about a novel way of making colloids which are not isotropic that means, if I take a parent particle for example, say polystyrene surface chemistry would be same everywhere. However, on the contrary, if you do this treatment, what you have is exactly a similar particle however, the part of the particle is now coated with gold therefore it this is a nice way of making new type of colloidal particles.

And such particles which have part of the surface coated with gold, the example of what are called surface Anisotropic particles because the bulk of the particle is exactly same, what is different is the surface of the particle and there are ways by which one uses what is called as the fractional surface area that is coated with gold as a method for characterizing such particles.

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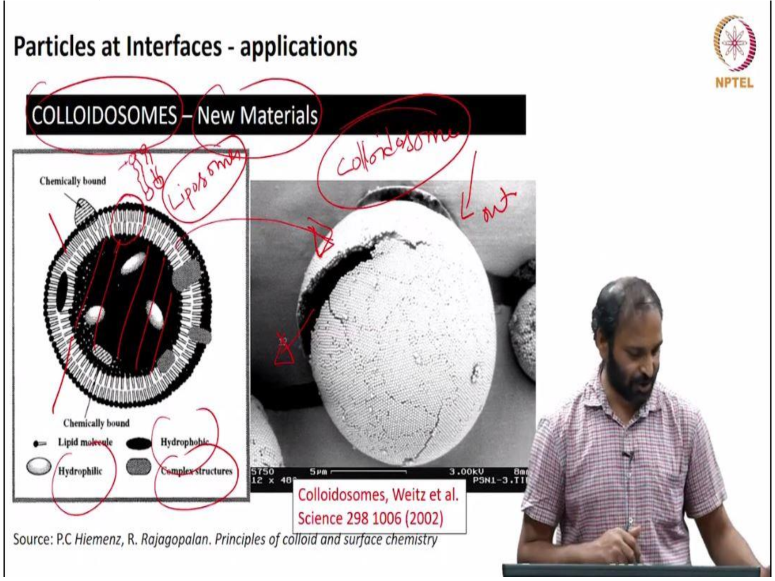

Particles at Interfaces - applications

COLLOIDOSOMES – New Materials

Colloidosomes, Weitz et al. Science 298 1006 (2002)

Source: P.C Hiemenz, R. Rajagopalan. *Principles of colloid and surface chemistry*

And the next application comes in the form of making what are called as colloidosomes again a new class of materials. So, we are talked about what are called as liposomes and these liposomes are containers which are stabilized by lipids so, what you are looking at is here his lipid molecules which have a 1 head group and a 2 tailed group and they are arranged in a particular fashion to give what are called as surfactant by layers, that is one layer of particle one layer of surfactant.

And the second layer this is a curved by layer and, these contain fluid inside and this fluid can be used for as cargo carriers in terms of incorporating either hydrophobic or hydrophilic as well as complex structures in these containers and they can be used for drug delivery applications. So, similarly, when you replace lipids with colloidal particles and you make similar structure and because of analogy with the liposome, they are what are called as colloidosomes. And these colloidosomes are hollow structures.

So, what you do is you make particle stabilizer emulsion and you can cross link the particle that means, you know you can join the particular on the surface and you can remove you can evaporate both the inner fluid and the outer fluid to get a shell like structure called colloidosomes and there is been a lot of interest in making such materials from different particles and exploiting them in some controlled release applications.

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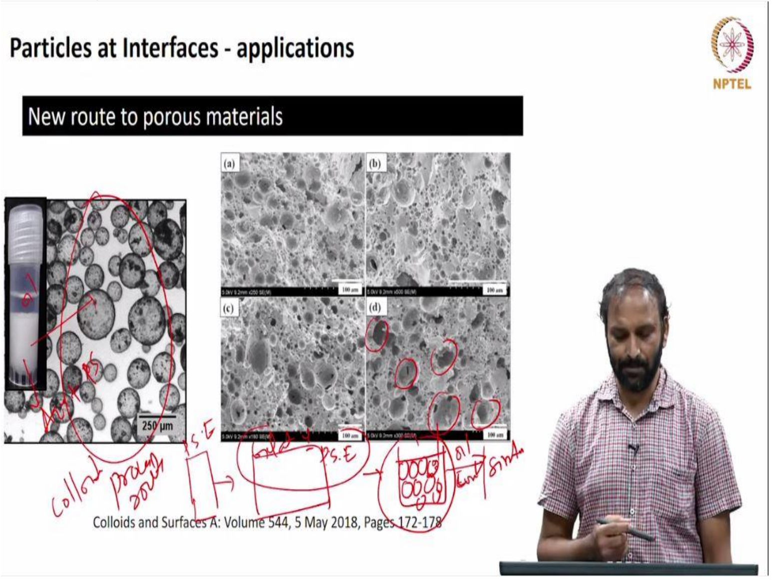

Particles at Interfaces - applications

New route to porous materials

Colloids and Surfaces A: Volume 544, 5 May 2018, Pages 172-178

And just to make a final note, these particles stabilize emulsions. So, what you are seeing here is a container where you have an oil and aqueous phase with polystyrene particles and this was emulsified to get you know a particle stabilized emulsion and one could start with such emulsion as a starting material. And you can use what is called as a colloidal processing route in which you make a particle stabilized emulsion you induce gelation in such systems gelation of particle stabilized emulsion.

Which can be simply done by using a higher concentration of colloidal particles you know when you prepare emulsion and once you have such a gel, what you can do is you can evaporate the 2 fluids that are in the emulsion, both the oil phase and the continuous phase and to obtain a green body which is which has only the these hollow structures which are with particles and both the fluids removed. And you can start with this material.

And you can actually sinter it, which is a method of heating this screen body to a temperature close to the melting point of the particles that are used for making these green body and the emulsion and you can end up with a porous material. What you are looking at here is a structure which has a lot of pores and these pores arise because of the oil that was present in the emulsion and one could use these porous materials in several applications as well.