Colloids and Surfaces
Prof. Basavaraj Madivala Gurappa
Department of Chemical Engineering
Indian Institute of Technology-Madras

Lecture-20
Colloids Polymer Mixtures

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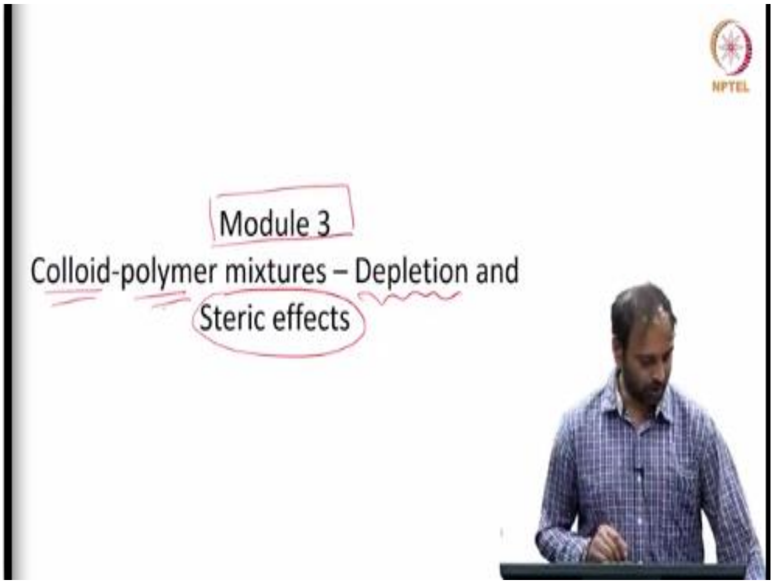

Module 3

Colloid-polymer mixtures – Depletion and Steric effects

Ok, so this is module 3 we are going to look at what are called as colloid polymer mixtures. We are goanna talk a lot about in effect called depletion effects or depletion interactions and then I will briefly touch upon steric effects you know towards the end, ok. So, before we go into colloid polymer mixtures you know we could.

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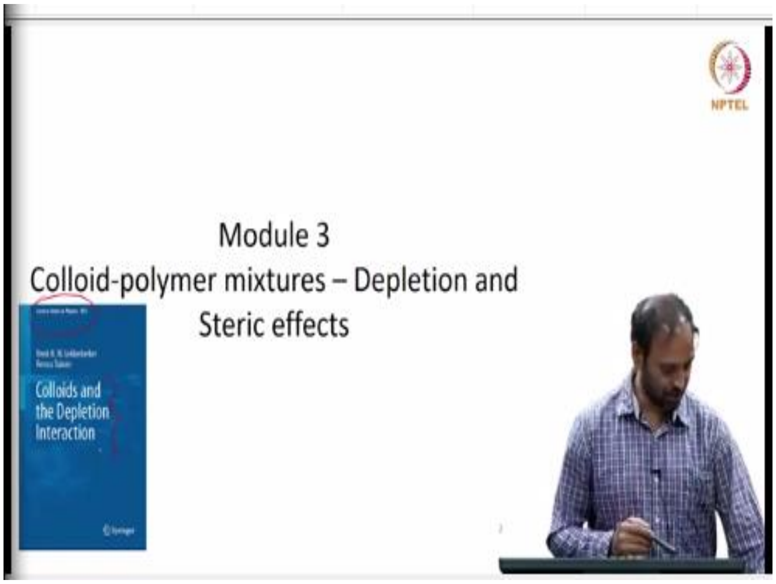

Module 3

Colloid-polymer mixtures – Depletion and Steric effects

Colloids and the Depletion Interaction

So, you will see that the lot of contents from in this particular module or taken from lecture notes in physics. There is a book or notes dedicated to you know depletion interactions if you are interested in know more you should read of this book.

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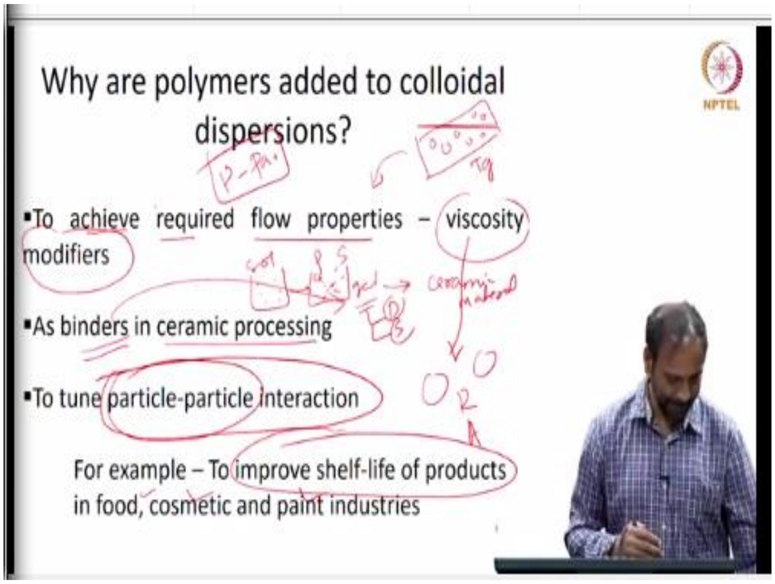

Why are polymers added to colloidal dispersions?

- To achieve required flow properties – viscosity modifiers
- As binders in ceramic processing
- To tune particle-particle interaction

For example – To improve shelf-life of products in food, cosmetic and paint industries

So, the again motivation ok, why are polymers added a colloidal dispersions. So, there are you know you can think about as many motivations as possible, some of the common ones are to achieve required flow characteristics ok. In that sense they are used as what are called as viscosity modifiers, if you look at lot of products like paints for example you know or a shampoo you know or any you know material like that.

Or even you know the oral suspension that you know syrups and all that right. So, the way they flow of the bottle ok becomes important, ok, so to achieve the right you know flow properties people do add certain amount of polymer. In a sense then it will affect it is viscosity and it will affect the way it comes out of you know the containers and things like that. We have talked about ceramic processing when you start with a nice dispersion of particles ok.

And then I just mentioned that you know from that you can actually go to interconnected network called as a gel I said there is a sol gel transition. And from the gel you can make ceramic materials, ok, after you take this gel dry it up and then you do what is called sintering right. Now during drying or during sintering it so you know often what happens is that you know because of the drying induce stresses these material there would not hold together they may lead to this could be some crack you know there could be you know there maybe defects in the material that you develop.

So, what binders do is they kind of provide you know the right amount of adhesive forces between the particles. So, you will see lot of applications where polymers are added as binders in ceramic processing you know which could be which is a method for obtaining porous materials or dense you know porous material so. Other motivation to look at polymer addition is you can use polymers for tuning particle-particle interactions, ok.

Again if you look at lot of products you know like you know in food, cosmetic or paint industries you would like to have a product which has a very high shelf life you know you want to keep it in the shelf for a year or 2 year you know you do not wanted to go bad . So, one of the ways of doing that would be to add polymers when you do that what you are actually doing is of course you are increasing viscosity which will kind of you know help you in you know dealing sedimentation effects, right.

Because if the things become more viscous, they will take a little longer to settle, right. And on the other hand you can also tune what is called as particle-particle interactions you know I can make the particle-particle interaction either repulsive or attractive depending upon you know what product that I am trying to look at, ok. So, these are some you know different fields where you know you will come across polymer colloid mixtures.

And it is also known that if you take like say a polymer film, right and if peoples are trying to look at you know it is Tg that is a glass transition temperature the polymer it is know that the addition of particles to such a films will also alter the Tg of the film, ok. So, therefore there are several you know cases where you will see that the polymer and the particles they coexist, ok. And therefore it will be interesting to look at what happens to the interactions between particles when the polymers are present, ok.

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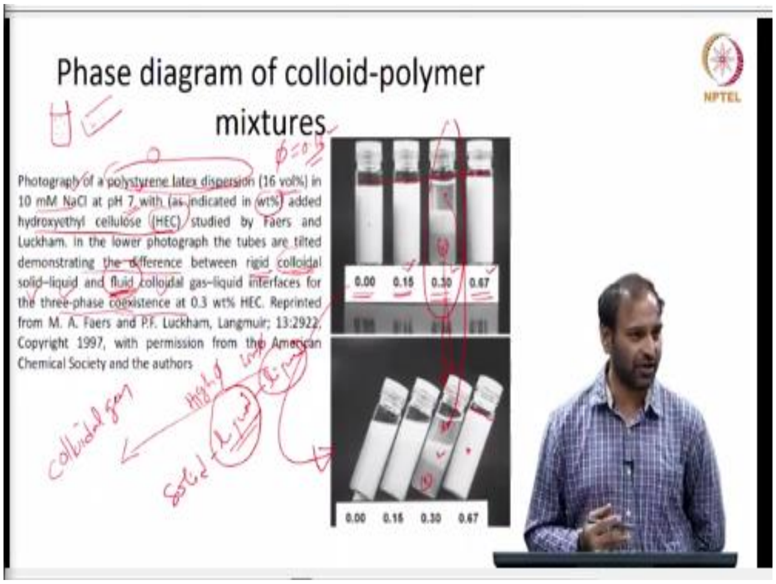

Phase diagram of colloid-polymer mixtures

Photograph of a polystyrene latex dispersion (16 vol%) in 10 mM NaCl at pH 7 with (as indicated in wt%) added hydroxyethyl cellulose (HEC) studied by Faers and Luckham. In the lower photograph the tubes are tilted demonstrating the difference between rigid colloidal solid–liquid and fluid colloidal gas–liquid interfaces for the three-phase coexistence at 0.3 wt% HEC. Reprinted from M. A. Faers and P.F. Luckham, Langmuir; 13:2922, Copyright 1997, with permission from the American Chemical Society and the authors

These are some examples from literature again I have taken from the book that I will just mentioned. This is a photograph of polystyrene dispersions you know this is polystyrene particles they are spherical particles, ok. And they have 16% particles in volume ok, I talked about this phi right, phi is the volume fraction, the volume fraction is going to be 0.16 in this case, right.

They are in 10 millimolar NaCl, ok there is a you know some salt in the system. And everything is at pH 7, ok. To this what is been done is they were added a polymer which is called hydroxyethyl cellulose HEC, ok. And they are add in different weight percentage ok which is indicate here, that is 0.15, 0.3, 0.67, ok. And what they done is that you know picture ok of the vials which contain these dispersions, ok.

So, the concentration the particles are same pH conditions are same you know salt is a same. The only thing that is different in these 4 vials is a presence of polymer, that is right. Now so this is a the what you see below is the same picture, ok, in which what is being done is all these vials have been slightly tilted, ok. So, I was mentioning that you know this is one of the nice way of seeing whether something else become you know gel like or you know solid like right, ok.

So, now what they do is they have tilted the vials and what it does is it demonstrates the difference between rigid colloidal solid liquid and colloidal fluid, gas liquid ok maybe let me explain a little bit. So, let us look at this particular vial ok, so what can you say about the bottom phase. So, there are 3 phases right, ok, this one phase here, one phase here and other phase here, ok.

The bottom phase is this is straight right, that means it is become gel like ok I can say it is a solid, ok, what about the next one, it is liquid like right. So, right, it is liquid like, ok, the upper one is also liquid like, right. But however if you look at the liquid that is this liquid there is a the concentration of the particles there is higher, right. Because that is evident from the turbidity right, typically I mean turbidity can mean different things.

But if you look at this vial, right, this contains only particles and the salt and you know and the pH is 7, ok. So, because this is turbid, so I can say that this is a dispersion of if you take any latex dispersion, dispersion of polystyrene particle it will appear you know white ok**.** So, this looks very similar to I will come back to your question, this looks very similar to this, right. But the only thing the only difference between this liquid and this liquid these two is that the concentration of the particle is higher here, higher phi I will say and it is low phi.

So, whenever you see a liquid ok with a low concentration of particles you refer to that as a colloidal gas, ok. The analogy is you know if you look at gas like state right I mean you know typically if you look at number of molecules per volume, ok. In a gas like it is goanna be lower compare to what you are see for the liquid and you know and lower much lower than what you see would for the solids right. So, in that context whenever you have fluid which lower concentration of particles it is called a colloidal gas, ok. Therefore if you ok, so if you look at this second vial here, so you have a fluid that is actually a colloidal fluid, ok.

That is colloidal fluid and you have a colloidal so let us look at the first one, right. So, the difference between the rigid colloidal solid right, that is a rigid colloidal solid was this, right. And liquid, ok, colloidal fluid or colloidal liquid, right, and of course there is also a transition between the gas like region and the liquid like region, ok. So, this is one way of you know visually telling something about the phase transitions, right.

Visually telling something about what is happen to your colloid you know colloidal solutions after you added polymer. And if you look at the again the third vial right, so here they talk about the coexistence of 3 phases, right, ok, this phase 1, phase 2 and phase 3, right. So, there is a ok for 0.3 concentration 3 phase coexistence occur, ok any question you had a question. It is just like a lamella classifier, what is it, what do you mean lamella classifier, sir it is a instrument sir, when we tilt the bottle the normal in color solution what happens the rate of settling is faster in that sir.

So, amount of the when it straight when it tilted when the amount of liquid is still same as in the top sir. I have a doubt because these things we have done at our lab scale. Also here the amount of liquid on the top is still same, because you have a same. See if you look at these vial, right on the average I was say that the volume of the fluid in all of them are the same. Now if I tilt it also why would the volume be different, right.

So, I mean you right, I mean you know volume of the fluid whether you take volume of the fluid you know in this particular vial in this state or the volume of the fluid in this container I mean it is tilted, the volume has to be same you know. Why would there will be a difference in the volume. I yeah I mean do not know in what context you are asking yeah, see you said I mean yeah the sedimentation, right, yeah.

There is work which shows you know if you have sedimentation you know carried out in the vial like this was a sedimentation in a vial which is carried like that. There are differences, ok, that is a different aspect, so you know here what you doing is you are really not looking at sedimentation problem the whole idea is look I prepared a solution with whatever composition. And I would like to have a rough idea has to what is happen to you know the contents of the vial, ok or if something is solidified if something is remaining as liquid.

So, when you want to get a quick you know kind of a inference you can just tilt it and then look up you know what happen that is all, ok, yeah. HEC yeah, so this is a the hydroxyethyl cellulose a polymer, ok. So, this experiment essentially shows that depending upon the concentration of the polymer that you added, ok, your solutions can behave very differently, ok. And phase separation is occurring you know things are becoming gel like here, right.

So, this looks like a more or less a solid right you know it is not perfectly flat but you know there is a, ok, right. So, yeah so this is to illustrate that the addition of polymers can significantly change the appearance of the fluid itself you know to begin with, ok.

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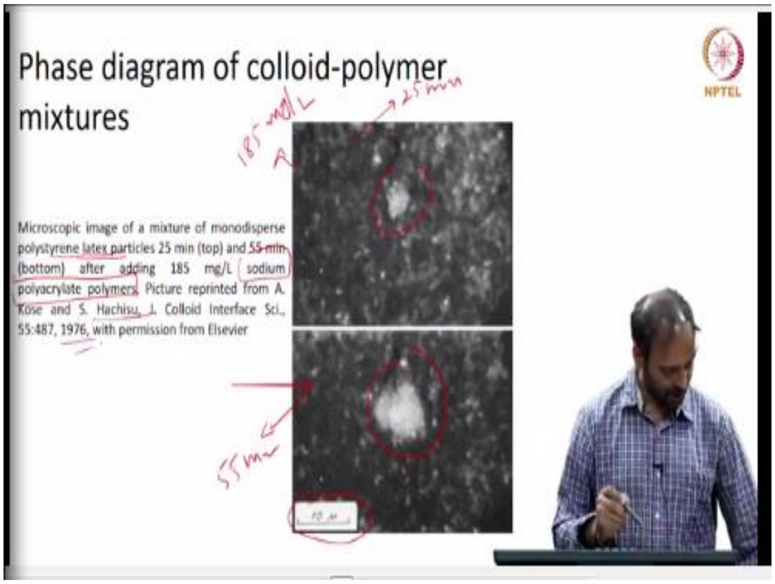

Phase diagram of colloid-polymer mixtures

Microscopic image of a mixture of monodisperse polystyrene latex particles 25 min (top) and 55 min (bottom) after adding 185 mg/L sodium polyacrylate polymers. Picture reprinted from A. Kose and S. Hachisu, J. Colloid Interface Sci., 55:487, 1976, with permission from Elsevier

These are some experiments where what is done is, so it is a mixture of polystyrene particles, ok and a polymer. In this case it is sodium polyacrylate, ok and so that is and a different concentrations. And this is ok same concentration 185 milligrams ok per liter, the same concentration the polymers added. However one is taken at 25 minute then second one is taken at 55 minute, ok. And if you take a sample like this and if you observe them under microscope, ok you know you will see images like this.

And you know these white dots are mostly the particles, ok. And you know there is you can think that you know there is some kind of a particle clustering or you know or there some you know phase that occurs right. So, this is to show that there is a macroscopic change in the you know the appearance itself. But that is because microscopically also things are changing, ok, so that is a the scale bar is about 10 micrometer, if you want to know more you can just read this up, ok .

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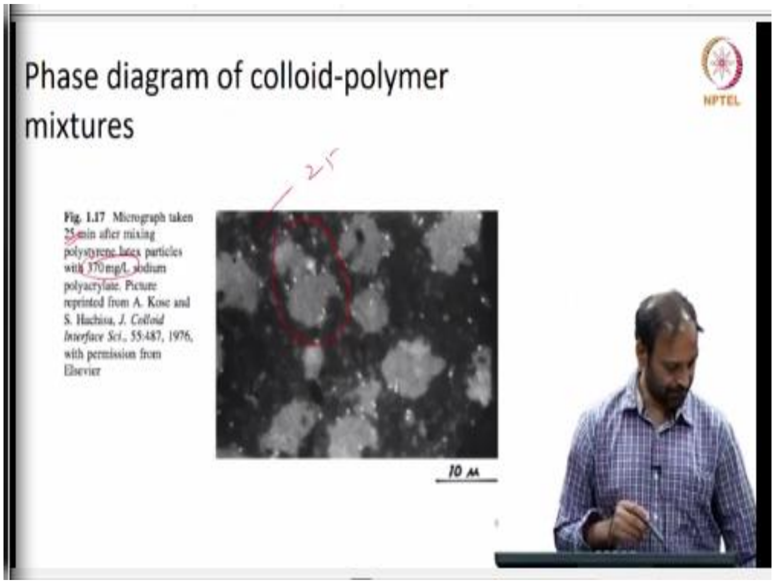

Phase diagram of colloid-polymer mixtures

Fig. 1.17 Micrograph taken 25 min after mixing polystyrene latex particles with 370 mg/L sodium polyacrylate. Picture reprinted from A. Kose and S. Hachisu, *J. Colloid Interface Sci.*, 55:487, 1976, with permission from Elsevier

And again another example this is at a higher concentrations, so if you look at these 2, right this was it a low concentration 185 milligrams per liter and this is at you know 370 milligrams per liter which is 25 minutes after the addition, ok. If you compare this with this, right, this is exactly at the same time this is at 25 minute but 185 milligrams per liter concentration, this is at 25 minute but however at a higher concentration.

You can clearly see that means quite different, ok. That means you are able influence that you know this domain formation and that seems to you know the kinetics of domain formations seems to have increased if you have higher concentration of you know the polymer, ok.

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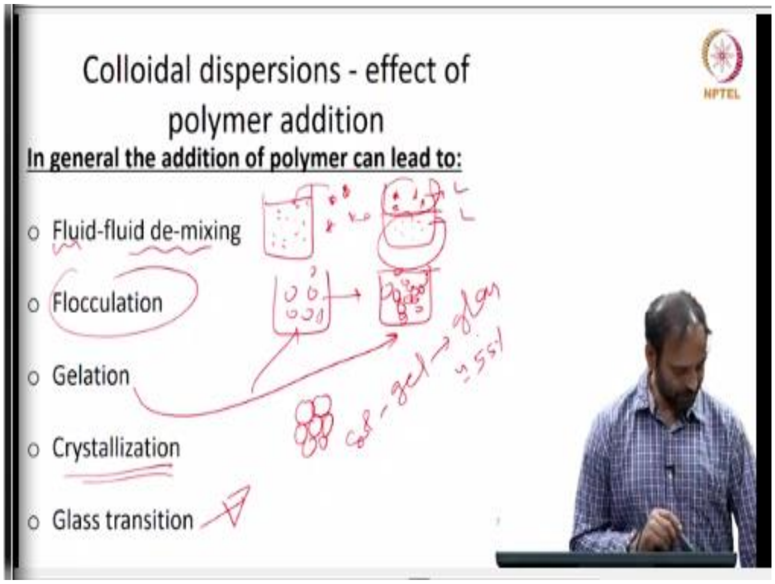

Colloidal dispersions - effect of polymer addition

In general the addition of polymer can lead to:

- Fluid-fluid de-mixing
- Flocculation
- Gelation
- Crystallization
- Glass transition

So, ok, so this is ok these are few examples to show that both macroscopically and microscopically the colloid polymer mixtures behave differently from a pure colloidal dispersions, ok. Now in general the addition of polymer can lead to some of these things, ok. There is fluid-fluid de-mixing, ok, what I mean by that is you could have you know dispersion of particles, ok.

And I could add a little bit polymers ok**,** then this could essentially phase separate, ok in which there could be you know maybe a particles in one region and maybe polymer in one region. And both of them you know could be liquid like ok, both the regions could be liquid-liquid ok and the polymers could go to one region polymer could be you know something like could happen, right.

So, you know the addition of polymer can lead to fluid-fluid de-mixing , it can lead to flocculation. That means if you have particles like this, ok, it can form you know aggregates right. And if the concentration of the particles is high enough you know these aggregates could form a space spanning network. That means it could gel, ok, it could lead to crystallization, ok. So, say that you know the particles are kind of randomly arranged in a dispersion I add polymer it could bring in these particles together.

And it could form you know maybe nice hexagonal lattice some things like that, right. And further lead also lead to what is called as glass transition, ok, so it can you know make, so typically when people talk about the behavior of colloids in general you have sol then there is gel, ok. At some concentration it becomes a glass, ok typically at very high concentration maybe of the order of you know 55% by volume and more something like that, ok. They can mix what is it, they can mix like in a stable form yeah, yeah, yeah it can yeah, yeah, ok.

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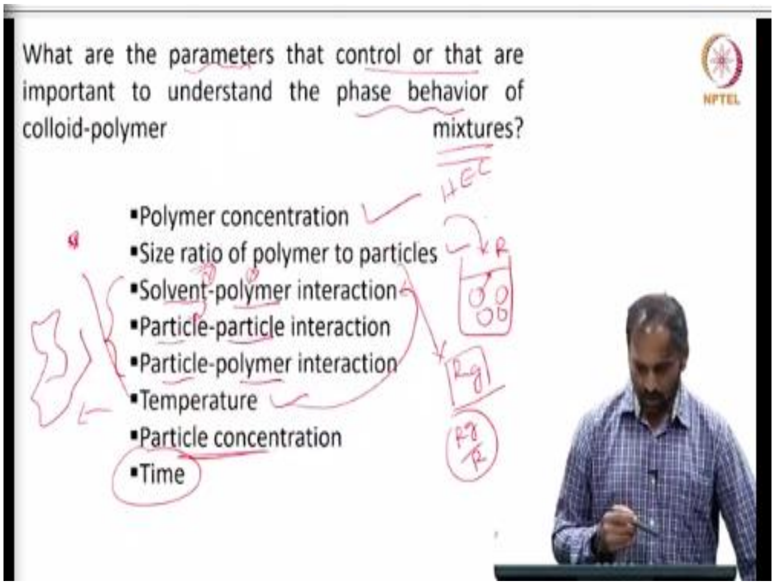

What are the parameters that control or that are important to understand the phase behavior of colloid-polymer mixtures?

- Polymer concentration
- Size ratio of polymer to particles
- Solvent-polymer interaction
- Particle-particle interaction
- Particle-polymer interaction
- Temperature
- Particle concentration
- Time

So, now what are the parameters that control or that are important to understand the phase behavior of colloid-polymer mixtures, ok. So, we looked at you know the polymer concentration, right. As we said that the first example that I gave you this was you know HEC right, a polymer it was at a different concentrations. We saw that the polymer concentration does influence the phase behavior.

The second parameter that would become important is the size ratio of polymer to the particle, ok. So, when I what I mean by that is I could have a particle**,** right in a dispersion, particles in a dispersion. When they add polymer to it typically people characterize you know these polymer the size of the polymer by a quantity called Rg ok the radius of which gyration of the polymer. If R is the size of the particle, your Rg by R becomes an important factor, ok.

So, whether Rg by R is very, very small or Rg by R is very, very large, so depending upon the size ratio of the polymer to the particles become important, ok. And of course the interactions are important and when we talk about colloid polymer mixture we have a solvent-polymer interaction, particle-particle interaction and particle-polymer interactions, right. So, this would again be you know depending upon the type of the solvent that you are working with depending upon the type of the polymer and the type of particle each of them could be very different, ok.

And of course temperature because temperature can both affect you know the polymer-polymer you know interaction as well as the polymer-solvent interactions, right. You could have a condition or you could have particular temperature where the polymer would in a crude sense be happy in a solvent. That means you know it want to stretch out more or you know and there could be cases where the polymer does not like to be in you know a particular fluid at a particular temperature you know it would like to coil up, ok.

So, therefore the temperature becomes important of course the particle concentration, right you know. So, we saw an example where you know the particle concentration was fix at 0.16 but however if I were to have a different concentration of particles. So, these whatever these changes that we see there could either be shifted to lower concentration or higher concentration, ok or at lower polymer concentration you know or higher polymer concentration depending upon the concentration of particle that you have, ok.

And of course time, right, that was listed in this particular example where we saw that the same mixture. But if you look at different time you know it would microscopically it will be very different. And at the same would also be true in terms of the macroscopic behavior as well, ok.

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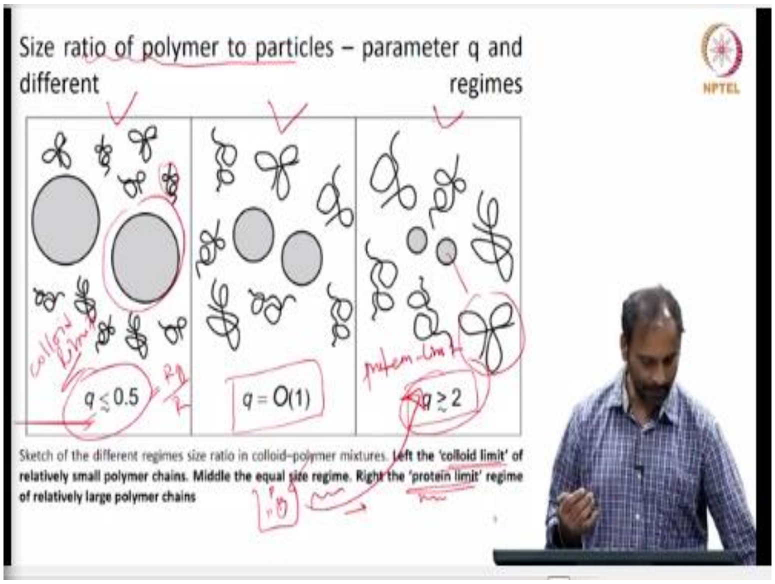

Size ratio of polymer to particles – parameter q and different regimes

Sketch of the different regimes size ratio in colloid–polymer mixtures. Left the 'colloid limit' of relatively small polymer chains. Middle the equal size regime. Right the 'protein limit' regime of relatively large polymer chains

So, we will again this is a cartoon which tells you something about the size ratio of the polymer to particle. Typically this people refer to a quantity called q, ok which is as I said is a ratio of the size of the polymer divided by the size of the particle itself, ok, you could have a case where you know q could be you know very small, ok, you could have a case where the q could be of the order of 1, ok and q could be much larger than 1, right.

So, when people talk about typically q less than 1, ok people use a term called colloid limit, ok. That means I have added a polymer whose size is much smaller than the size of the particle that I have in the dispersion, ok, that is what is called as a colloid limit. And when you have the q is larger than 1, ok, people use a term called protein limit in which case the size of the polymer that you have added is much larger than the size of the particle itself, ok.

The reason why a thing is called protein limit is because I think when you add people have used polymer for crystallization of proteins, ok. That means I have a solution of protein, ok I add a polymer and I would like to crystallize protein out of the solution, ok when that happens the protein molecule size of the protein molecules are much smaller compare to the size of the polymer that I had, ok.

Therefore it will invariably fit into q much, much larger than you know 1 or 2 you know larger than one case, ok. So, therefore if you have cases where the size of the polymer is much larger than the size of the particle which is what is depicted in this cartoon, ok, what is called as a protein limit, ok. If you have a case where the size of the particles are much larger than this is a polymer, ok, it is called a colloid limit, ok.

So, whenever you know you are trying to look at colloid polymer mixture, ok, it is good to identify whether you are working in this regime, this regime or this regime, ok depending upon you know any of these regimes you are colloidal interactions going to be different, the phase behavior is going to be different, ok.