Colloids and Surfaces
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Lecture - 21
Colloid Polymer Mixtures: Colloid-Solvent Interactions & Colloid - Polymer Interactions

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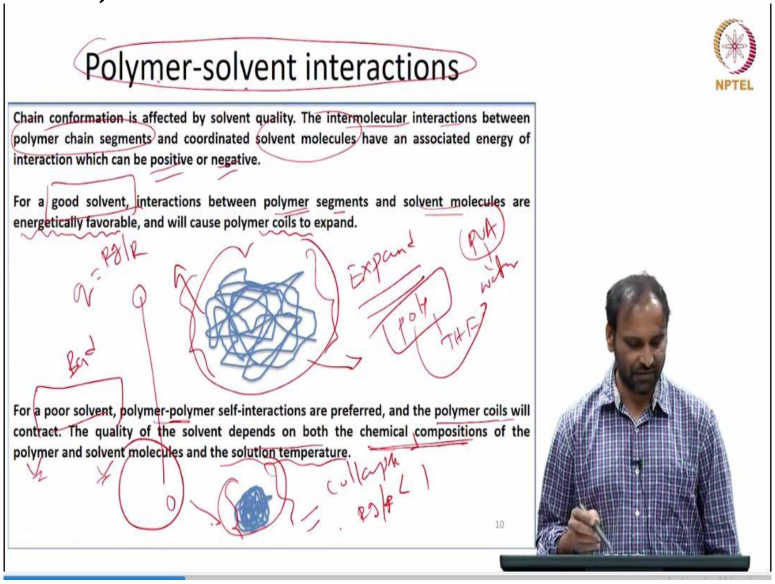

Polymer-solvent interactions

Chain conformation is affected by solvent quality. The intermolecular interactions between polymer chain segments and coordinated solvent molecules have an associated energy of interaction which can be positive or negative.

For a good solvent, interactions between polymer segments and solvent molecules are energetically favorable, and will cause polymer coils to expand.

For a poor solvent, polymer-polymer self-interactions are preferred, and the polymer coils will contract. The quality of the solvent depends on both the chemical compositions of the polymer and solvent molecules and the solution temperature.

So, the polymer solvent interactions so it is what is known is that the conformation the polymer takes what you are looking at is 2 confirmations one case is what is calls expanded you know configuration is more like a collapse configuration. So, whether the polymer is in this state or in this state in a solution depends on the, polymer solvent interaction in a crude sense you can say that if the interaction the intermolecular interaction between the polymer chain and the solvent depending upon if the energy associated with this interaction is.

You know either positive or negative depending upon that it like this take this configuration or it will take this configuration people typically something called as a good solvent and a poor solvent or a bad solvent. So, in the case of good solvent the interaction between the polymer segments and the solvent molecules are energetically favorable. And therefore, it will cause the polymer coil to expand.

On the other hand, when some polymers are put in a solvent what are called as poor solvents, the polymer-polymer self interactions of preferred the polymer would like to be in contact with its own molecule rather than being in contact with the fluid. Therefore, the polymer coils and it will contract or it will you know, it will collapse. And of course the quality of the solvent that means you know whether the solvent is good solvent or bad solvent depends on the chemical composition of the polymer and the solvent and also the solution temperature as well.

If you look at when people study polystyrene polymer the good solvent for polystyrene is THF you know, and then if you look at like say PVA polyvinyl alcohol a good solvent for PVA is water. And the same time if I take this you know, polystyrene if you put in water will collapse, we know the water is a poor solvent for polystyrene.

So, depending upon the composition of the polymer and the solvent and the solution temperature, the polymers can either take this configuration and this configuration. Now, if it takes this configuration if I am working with like say the particles of certain size if the particle size is same in both the cases. Now, you can as you can imagine, your q is going to be different, because q is a the size of the polymer divided by the size of the particle.

Now, if the polymers in expanded state it will be more likely that you know, if the particles are very small it could be a protein limit. However, in this case, you know, if of course, I have drawn very small particle if I take a particle like that. So, you know, if I have a case where you know, the your Rg / R could be less than 1. So, therefore, the polymer solvent interactions become important both in terms of deciding on. You know, maybe which regime you are in in terms of the size, particle size to polymer ratio.

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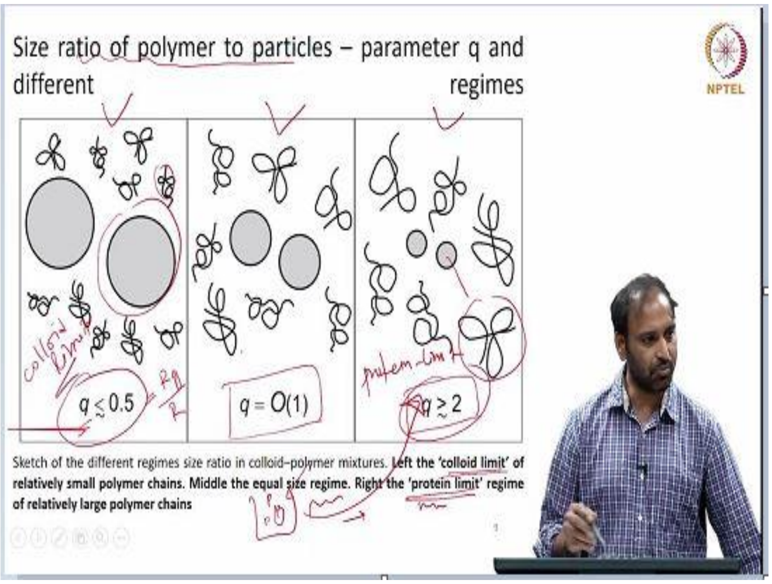

Size ratio of polymer to particles – parameter q and different regimes

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

And of course, it will also influence you know, the, other kind of interaction in the system.

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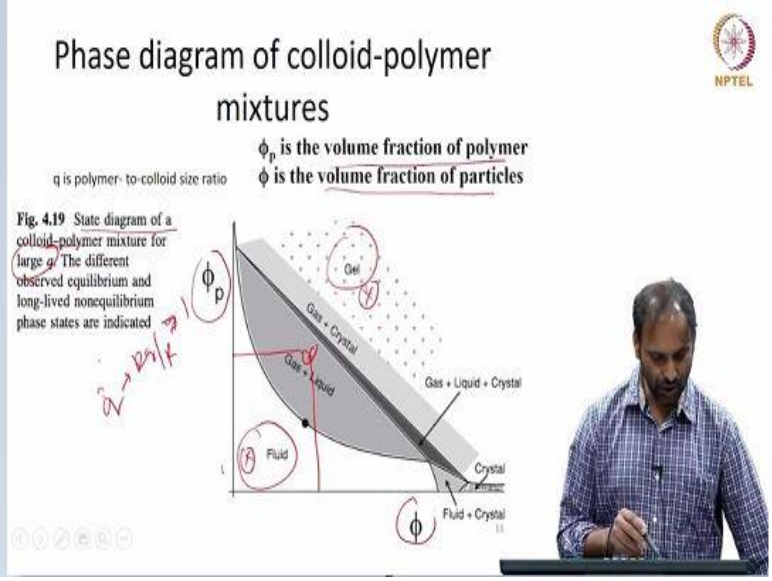

Phase diagram of colloid-polymer mixtures

ϕ_p is the volume fraction of polymer

ϕ is the volume fraction of particles

q is polymer- to-colloid size ratio

Fig. 4.19 State diagram of a colloid-polymer mixture for large q. The different observed equilibrium and long-lived nonequilibrium phase states are indicated

Now, so, these are 2 phase diagrams. This is for the cases where q is large, so, this is a state diagram for a colloid polymer mixture, for large q when I say large q, this is going to be the protein limit q large q is for the protein limit that means q is you know Rg / R This is you know it is much you know larger than 1 or larger than 1 And what is drawn here is you know phi p that is the volume fraction of the polymer in the solution and phi which is the volume fraction of particles in the solution.

And again we mentioned this. So, you could typically when the concentration of the polymer is very low state like this if I take a point like this the concentration of the particle is low and the concentration particle both the polymer the particles are low, you know, you will expect you know the state of the you know mixture can be fluid like however, if I am at an appreciable concentration of polymer and particles, you could have a gas liquid kind of coexistence and if I again go to higher concentration of particle in the polymer I could have a gel like system.

So, therefore, this kind of gives you know, depending upon it is not a I mean, you know, what you can do what has been done here is people have done experiments with a variety of polymer colloid mixtures. And you know, you can think about the different phases that come about when you work with colloid polymer mixture can be broadly classified into these, you know, states and it will tell you what is the typical concentrations that which, you know, each of these phases may come about. So, that is for the large q case.

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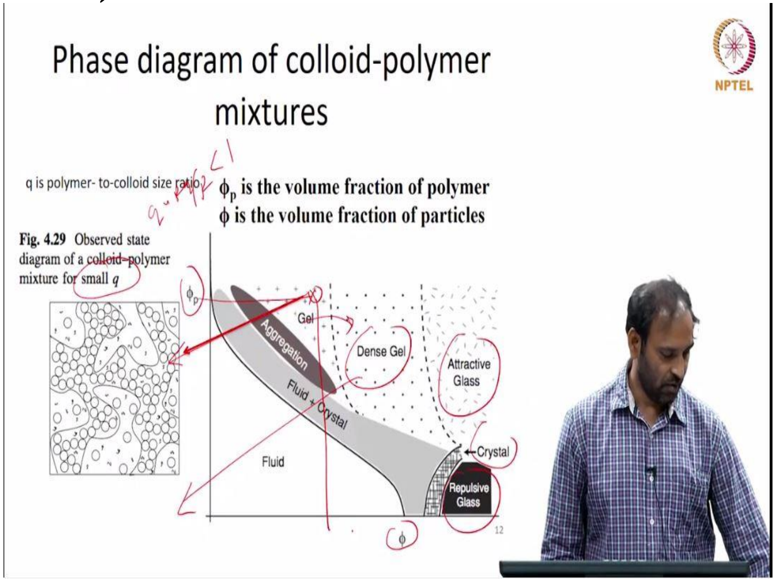

Phase diagram of colloid-polymer mixtures

q is polymer- to-colloid size ratio

$q = R_g/R < 1$

ϕ_p is the volume fraction of polymer

ϕ is the volume fraction of particles

Fig. 4.29 Observed state diagram of a colloid-polymer mixture for small *q*

And this is for a small q case, where, you know, this q that is Rg / R. Yes, is smaller than 1, in the same similar plot phi P versus phi and so, again, there is a range of at particular you know, the polymer particle concentration you have a gel like behavior. And then you could have a case where I know it could be a dense gel, it is a space spanning network, but with more concentration of particles, maybe it will have a higher modulus compared to these gels.

And of course, at sufficiently high concentration of particles, you can have a glasses crystals or repulsive glasses and things like that. So, this is basically gives you a broad picture of you know, what is the different states that people observe in colloid polymer mixtures. Any questions so far? Before we go further? So, phase separation, any experimental technique that you can use it for?

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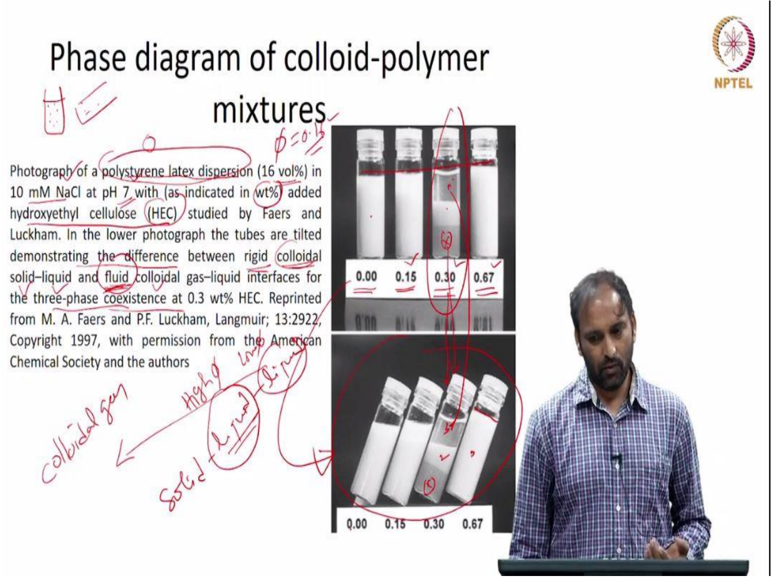

Phase diagram of colloid-polymer mixtures

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

One simple would be just, I mean, first, of course, it is a visual observation method? That is a simplest one that you can think of. What people see, there are lot of I mean, of course, one could be that you know, you can microscopy could be good technique. You can take you can start with you know, one fluid system and you basically take a small sample sandwich them between 2 plates for a microscope and then keep observing, you record you know, that is one way to look at.

I mean, people have kind of looked at onset of phase separation by light scattering as well you know, you can you know, depending upon whether the if I take 2 fluid mixtures say that these fluids are miscible at a particular temperature and then if you just heat it up they become you know, they de-mix, they become 2 individual phases as you do a temperature you know, either heating or cooling cycle.

I can put a small sample and I can shine a beam of light I can look at you know, what will happen to the scattered intensity, there are other there ways by which you can you know extract out phase separation by experiment like that, I will say these are the 2 techniques you know, that comes to my mind at this point.

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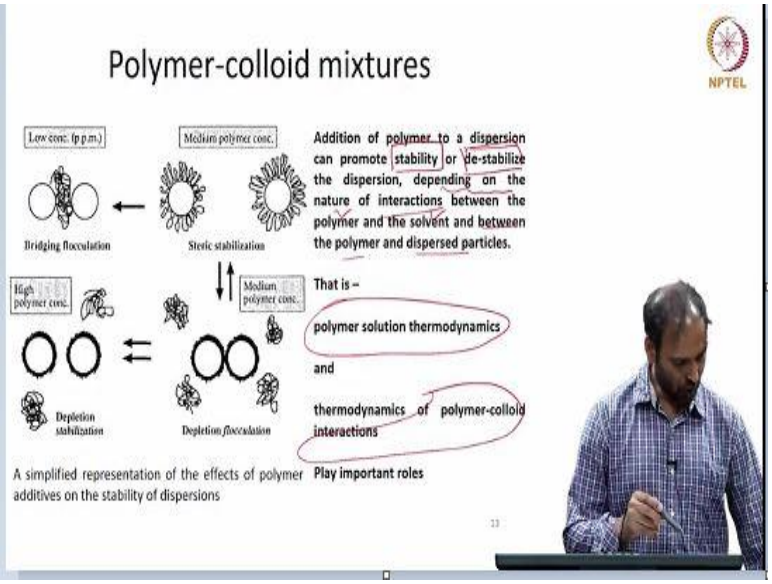

Polymer-colloid mixtures

A simplified representation of the effects of polymer additives on the stability of dispersions

Addition of polymer to a dispersion can promote stability or de-stabilize the dispersion, depending on the nature of interactions between the polymer and the solvent and between the polymer and dispersed particles.

That is –

polymer solution thermodynamics

and

thermodynamics of polymer-colloid interactions

Play important roles

So, this is a kind of picture which tells you what will happen, what are the different mechanisms that people have proposed, in order to understand what happens to a dispersion of colloids, when you add polymers to them. So, the addition of polymer to dispersion can promote stability or it can also destabilizes dispersion both is possible. That means I have dispersion which is inherently not stable at polymer it can become stable or I could have a dispersion is already stable then add polymer it becomes no unstable.

It can be destabilized and that depends on the nature of interaction between the polymer and the solvent and between the polymer and the dispersed particles it depends on lot of factors that I mentioned can be listed several parameters it depends on all of that. So, other way to think about this problem would be you know what is also important is the polymer solution thermodynamics that is when you know the conformation of the polymer you know, whether it is in a coil state expanded state or that becomes picture very important.

Also, you should also worry about you know, the typical interactions that exists between you know, the different components that you have in the solution.

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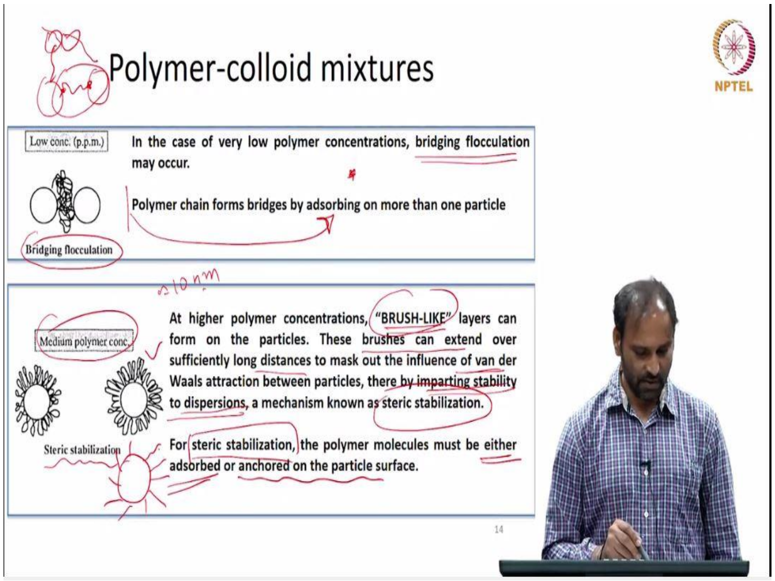

Polymer-colloid mixtures

Low conc. (p.p.m.)

In the case of very low polymer concentrations, bridging flocculation may occur.

Polymer chain forms bridges by adsorbing on more than one particle

Bridging flocculation

~10 nm

Medium polymer conc.

At higher polymer concentrations, "BRUSH-LIKE" layers can form on the particles. These brushes can extend over sufficiently long distances to mask out the influence of van der Waals attraction between particles, there by imparting stability to dispersions, a mechanism known as steric stabilization.

Steric stabilization

For steric stabilization, the polymer molecules must be either adsorbed or anchored on the particle surface.

So, typically when the concentrate of the polymer is low people have observed what is called is a bridging flocculation this will happen in cases where the polymer could adsorb on the surface of the particle I have 2 particles in the solution I add a polymer one end of the polymer gets attached to the you know on the surface the other end kind of attaches to the other you know the polymer. So, therefore there is a bridging.

And when you when many such particles and polymers come together, you could have this you could have bridging flocculation. And this typically happens in cases where the polymers are adsorbing, that is one of the requirements for the bridging to occur. If the adsorption does not occur, then the polymer continues to be the solution. And continues to be in the solution as maybe individual molecules therefore, the bridging will not be a possibility.

So, at certain concentration people have seen what is called a steric stabilization. In which case what will happen is the polymer that are added it adsorbs onto the polymer. And it forms brush like layers, which is depicted here it forms brush like layers and these brushes can extend over sufficiently long distance, when I mean, but what I mean by that sufficiently long distance. So, we said that the van der Waal force of attractions I know can be operative almost up to about 10 nanometer.

Now, if you somehow make sure that the particles never approach a distance which is less than 10 nanometer then you can actually get rid of the influence of van der Waals forces what these brush likes layer do. They extend you know they basically mask the influence of van der Waals force of attraction and therefore, they can impart stability to the dispersion and this mechanism is what is called a steric stabilization people also call it what is called a steric hindrance.

So, for steric stabilization what are the 2 things should happen? Either the polymer molecules must adsorb on the particle surface or they can be anchored on the particle surface that means what you have seeing is an example where the polymer is adsorbed onto the particle surface, I could have a case where I could have a particle and these polymer molecules are coherently bonded onto the surface both in this case and this case you will have steric stabilization.