

Interfacial Engineering

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Lecture-38

Steric (Polymer-mediated) forces

Influence of polymer concentration on the stability of dispersions; Structure of polymer chains in bulk solution and near a solid surface; Thermodynamic considerations

Welcome back. In this video lecture, we will look at what is known as steric forces. It is also called polymer-mediated forces. So far, we have looked at different forces, such as Van der Waals and electrostatic forces. And what we have not covered in this module is steric forces. These are polymer-mediated forces.

Whenever we deal with both polymer and colloidal particle mixtures, we will have to encounter, you know, interactions, right? Polymer and, you know, polymer-mediated interactions that will take place between the polymer molecule and the colloidal particle surface. Okay. We will look at them in detail. Okay.

Let's begin. Right.

Time: 1.16 mins

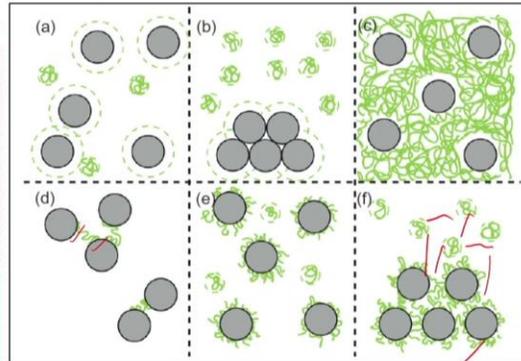
Introduction to polymer-colloid mixtures



Mixtures comprising colloidal particles dispersed in polymer solution

Common in paints, food products, and biological systems

- ❖ Negative adsorption occurs when the affinity between polymers and colloids is poor (Repulsive). As a result, polymers are excluded (depleted) from the vicinity of the colloidal particle surfaces.
 - ❖ The depletion layer thickness depends on R_g and Mwt. $R_g \propto Mwt^{1/2}$. Higher Mwt polymers form larger coils and lead to thicker depletion layers.
 - ❖ The presence of depletion zones leads to an effective attraction between the colloidal spheres.
- ❖ Positive adsorption occurs when the affinity between polymers and colloids is great (Attractive). As a result, polymer molecules adsorb onto the surfaces of the colloidal particles.
 - ❖ Small amount of positively adsorbing chains induce bridge flocculation.
 - ❖ When the amount of polymers added is sufficient to completely cover the particle surface, steric repulsion takes place which makes the dispersion more stable.



A-C → Negative adsorption

D-F → Positive adsorption

10:04 / 23:15 (10) Polymer-mediated colloidal stability: on the transition between adsorption and depletion. *Advances in colloid and interface sc*

So first, let us look at the polymer-mediated forces. Nothing but I mean, what kinds of interactions occur when we deal with polymer colloidal mixtures? Right. That is precisely what we are looking at.

Whenever we deal with this kind of system, we often encounter two kinds of scenarios, right? Two possibilities will emerge. One is nothing but what is known as negative adsorption, okay? The other one is favorable adsorption. So the figures A, B, and C illustrate the negative adsorption phenomena, whereas the figures D, E, and F describe favorable adsorption. Right. So, negative adsorption occurs when the affinity between the polymer molecule and particle surface is not great.

When it is very poor, you expect the negative adsorption. In such scenario, what will happen is polymer molecules will be excluded from the vicinity of the particle surface, which means that you know, you can see that they get segregated themselves into a separate phase, okay, because they don't share a great affinity between particle surface and polymer, I mean, among themselves. So you can expect that these polymer molecules get excluded from the vicinity of the particle surface, such that each, you know, will be segregated into different phases. So what is the consequence of that? First, they generate a depletion layer. So, the depletion layer, meaning specific volume, will not be accessible by the polymer molecule.

Say, for example, because they don't share a great affinity, around the particle surface these molecules cannot freely move around okay because they share very poor affinity right so in such scenario you can expect that the polymer molecules will you know will create a

depletion layer okay from the vicinity of the particle surface okay and what is the consequence of that so in such case what will happen is because some of the volume is not accessible to the polymer molecule, so they will try to push this particle, compress this particle, so that they get more free volume. So this process is spontaneous, and this is driven by entropy. I mean, this is an entropy-driven energy minimization process. In this case, what happens is that they don't share a great affinity and create a depletion layer around the particle surface, so there will be a pressure imbalance, okay? There will be an osmotic pressure imbalance because of this condition. So to get more accessible volume, this polymer molecule will be pushed by these colloidal particles so that they get more, you know, free volume, right? More freely accessible volume. So this will happen whenever you deal with a non-absorbing polymer molecule. Remember, this scenario is applicable when you deal with a non-absorbing polymer molecule. So when the affinity between them is not great, right? So the consequence of that will be, as I said, a depletion zone.

This will lead to an attractive force between the particles. So, how do we control this depletion layer thickness? So it depends basically on the size of the polymer molecule. As the size of the individual polymer molecule goes up, the depletion zone itself will grow, right? So the size of the polymer molecule is characterized by what is known as the radius of gyration. That is nothing but R_g . R_g is nothing but radius of gyration, which is again, you know, affected by molecular weight, right? So, because the radius of gyration is proportional to molecular weight, it is equal to the power of one and a half. Again, molecular weight is an important parameter controlling the depletion layer thickness.

So, both R_g , which is the radius of gyration, and molecular weight, are essential parameters in this depletion layer thickness, right? So, as a result, what happens is that because of these depletion zones, I mean, the presence of these depletion zones, it leads to an effective attraction between the colloidal space. This is clear now. There is something called favorable adsorption, right? The other one is positive adsorption. In this, the affinity between the particle and polymer will be great, okay, in such a scenario. uh so what will happen is uh uh they will get absorbed onto the polymer molecule and particle surface nicely right so this is happen when the affinity between the polymer molecule and particle surface is great right so uh what are the consequences so let's say uh you have you know three scenario I mean three cases right one is you have got affinity is good. Still, polymer concentration is low in such a scenario. What will happen is that they cover the particle surface partially, not completely. In such a case, what will happen is that they will lead to bridging between the adjacent neighboring particles, right? This polymer molecule, which is anchored to one particle surface, will also be anchored to the neighboring particle surface.

In this way, they will form a bridge, right? So this phenomenon is nothing but bridging

flocculation. So in this case, the particle, they get bridged, right? And they will exhibit, you know, elastic characteristics because of this bridging. And it can be regarded as, you know, spring-like objects as well, right? On the other hand, let's say if you have polymer concentration, sufficient concentration, I mean, if you have concentration sufficient to cover the entire particle surface, in such a case, what you would expect is the steric stabilization, right? So, the steric stabilization occurs because the polymer molecules cover the surface of the particle, and the entire surface of the particle is now covered with the polymer molecules. The adjacent molecule is the same case, right, because when these two particles, you know, approach each other, there will be steric hindrance because the polymer molecules will act as a physical barrier. They will not allow the particle, you know, to, you know, penetrate any further, right, beyond some center-to-center distance.

So in such a case, you would expect steric stabilization. There is something this scenario figure F corresponds to case when you deal with you know higher concentration of polymer in such case what will happen because when you have concentration which is slightly higher than what is required to completely cover the surface this free molecule will go in between the the neighboring particles so they will form more like a network like a structure okay because this free molecule can now get anchored to another polymer molecule so they will form a network like structures right this scenario is You know, this is more likely to happen when you deal with, you know, when you have a higher concentration of polymer in the mixture. Right. Right.

Time: 10.14 mins

Influence of polymer concentration on the stability of dispersions

NPTEL

Mixtures comprising colloidal particles dispersed in polymer solution

Common in paints, food products, and biological systems

Low concentration	Bridging flocculation
Moderate Conc.	Steric stabilization
High concentration	Depletion stabilization

Crowding effect

In good solvents, the demixing process is thermodynamically unfavourable, hence, one can have depletion stabilization.

Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC press.

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Now, let's look at different phenomena.

Right. So we just looked at what is known as bridging flocculation, steric stabilization, and depletion stabilization. Right. Okay so as you see as we just now described when at low concentration of polymer you expect bridging to take place that will lead to bridging flocculation okay because this happens because there are I mean when there is no sufficient number of polymer chains to cover entire surface because only because the polymer molecules adsorbed on the surface partially not fully so they will lead to bridging flocculation right on the other hand when you have sufficient number of molecules to cover the entire surface we expect you know steric stabilization to occur okay so in this case, these polymer molecules will act as brushes, right? So when they approach each other very closely, they cannot penetrate further, okay? Unless.

The, you know, force is applied from outside, I mean, from outside the particle, right? So these two particles cannot penetrate further because of the physical barrier or steric hindrance. So this is nothing but steric stabilization. When you have polymer concentration, okay, from, you know, moderate to high, so that you can expect depletion flocculation or stabilization. So depletion stabilization occurs, you know, whenever in a good solvent, okay. Because these molecules are not adsorbing molecules, right? This molecule, you know, can be readily, will be readily, I mean, can be easily dissolved in the good solvent. So when you have a higher concentration of adsorbing polymer molecules, because these molecules, you know, can move around freely around the particle surface, they, you know, So these particles, I mean, these molecules will move around freely around the particle surface. So they will act as a, you know, you know, shield for the particles.

Right. So they will create some sort of, you know, crowding effect. OK. So, because of this, depletion stabilization can be expected. Right. On the one hand, we saw that there is something called depletion attraction that is due to a non-absorbing polymer molecule.

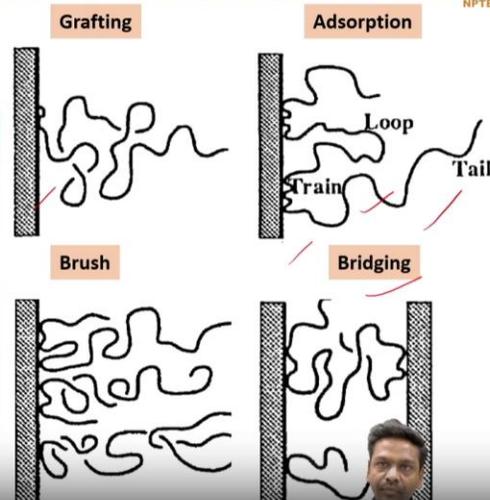
Time: 13.25 mins

Structure of polymer chains in bulk solution and near a solid surface



Mixtures comprising colloidal particles dispersed in polymer solution

Adsorption	Grafting
Non-covalent (reversible)	Covalent (Permanent)
High chain flexibility	Low chain flexibility
Loops, tails, and train configuration	Brush-like structure
Energy minimization is entropy-driven	No energy minimization
Sensitive to pH and ionic strength	Less responsive to environment.
Bridging is favoured	Steric repulsion is favoured due to brush-like structure



16:41 / 23:15

Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC press.

The depletion stabilization is caused by the absorbing polymer molecule. So this happens in good solvent because in good solvent the demixing process is thermodynamically unfavored right so hence you can expect depletion stabilization because here the polymer molecule will have a good affinity okay between themselves and the particle surface they can easily move around the particle so they will these molecules will surround the particles so they act as a shield right or crowding effect right so what is good solvent so good solvent meaning the polymer molecule is highly soluble. They remain expanded rather than collapsing or aggregating, rather than being collapsed or aggregated. So here, let us look at the difference between grafting and adsorption. So, grafting is due to the covalent bonding, which is permanent. The adsorption is due to the non-covalent interaction or physical interaction.

Whenever the affinity between the polymer molecule and the surface is good, they will be anchored. In the case of grafting, it is purely due to the covalent interaction. So, because it is a covalent interaction, the chain doesn't offer good chain flexibility. However, in the case of adsorption, it offers good chain flexibility. So when it comes to adsorption, because it is an adsorption process, it is, you know, due to energy minimization, and energy minimization is, you know, entropy driven.

The energy minimization process is entropy-driven in the case of adsorption. Why? It undergoes different configurations, like loop-like configuration, train-like configuration, and tail-like configuration. In this scenario, the energy minimization is because of the entropy, okay, uh. In contrast, in the case of grafting, you don't expect any energy minimization because this is already anchored onto the surface due to the covalent bonding.

So, because this is, you know, that there is a chain flexibility, and all that, in the case of adsorption, can be controlled by the fact that it is sensitive to pH and ionic conditions. Conditions in the solution whereas the in the case of grafting it is less responsive to environment so you can expect bridging in the case of adsorption especially when tail like configuration is you know favored and concentration is too low okay in such scenario you expect bridging in the case of grafting, it produces brush-like structure, okay?

Time: 16.35 mins

Comparison of Configurations



Configuration	Attachment Points	Orientation Relative to Surface	Role
Loops	Two or more points	U-shaped, extends into solution	Steric stabilization and surface coverage
Tails	Single point	Extends freely into solution	Long-range interactions, bridging, and flocculation
Trains	Continuous segment	Lies flat on the surface	Strong adhesion and anchoring

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And this brush-like structure will always lead to steric stabilization, provided the grafting density is meaningful, okay? Right.

So here, we will look at the... The configurations and their various configurations are detailed. So, as we described just now, the loops and the trains are the same. But in the case of a train, you know, the polymer molecules anchor onto the surface, you know, in a continuous fashion, okay, such that they orient themselves in parallel to the surface or lie flat on the surface. Which will ensure stronger adhesion and anchoring, right? So this will always lead to steric stabilization, and both train-like configuration and loop-like configuration lead to steric stabilization, okay? So in the case of a loop, you know it, it leads to, I mean, the polymer molecules anchored at multiple points on the surface. It will exhibit u-shaped orientation okay and this will also lead to steric stabilization okay but in the case of tails um in contrast to loops and trains uh you know when uh when it assumes tail leg configuration okay basically this is nothing but you know, configuration, you know, when it anchors onto the surface at a single point, but extends freely into the surface, the solution, which means that the rest of the segments will, you know, protrude outward from

the surface into the bulk solution.

In such a scenario, you expect bridging and or bridging flocculation, I mean flocculation, because this tail can again get anchored onto the surface, neighboring particle, or neighboring surface. So these are various configurations. So we expect steric stabilization when it comes to loop-like or train-like. And we hope to bridge flocculation, you know, when it assumes tail-like configurations, right? Yeah.

Time: 19.20 mins

Thermodynamic considerations

Mixtures comprising colloidal particles dispersed in polymer solution

Overlap occurs when polymer-coated particles come into close proximity.
- As lens volume increases, repulsion or attraction occurs depending on the configurations, concentrations of polymers

Loops and trains provide a physical barrier when layers overlap, causing steric repulsion.

Effect on polymer overlap:

- Low concentration – Promotes bridging flocculation
- High concentration – Promotes steric stabilization
- High grafting density (Brushes) – Prevent overlap and aggregation
- Longer chains create thicker layers, increasing steric repulsion

Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC press.

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So here we look at interaction energy a little bit more.

See, whenever the particle surface is covered with a polymer molecule using covalent interaction, you always expect steric stabilization. But provided the grafting density is too good. If grafting density is poor, we can't always expect steric stabilization, okay. But on the other hand, whenever the particle surface is covered uniformly with polymer molecules via adsorption, okay, in such a scenario, one would get either steric stabilization or, you know, bridging flocculation, okay, depending on the concentration of the polymer chains on the surface.

Okay. If the concentration of the polymer segments on the surface is too high, we expect, you know, good stabilization due to steric endurance. Whereas, if the concentration is too low, we expect bridging flocculation. Okay. Right. Sometimes, you can also tune the bridging flocculation by increasing the steric repulsion and tuning the molecular weight of the polymer.

So let's say if you choose a slightly higher molecular weight polymer, the longer chains create thicker layers on the surface. So this will ensure that there is more steric repulsion. In such a case, you would expect steric repulsion to be more dominant than the bridging flocculation. So you can see the interaction energy between the particles as a function of surface-to-surface distance. So in the absence of the depletion attraction and bridging flocculation when there is a steric hindrance you would only expect you know repulsive force okay in this plot the positive y direction represents the repulsive force and negative y direction represents the attractive force so in the case of the steric hindrance you will only get the repulsive force okay right whereas on the other hand in the absence of steric interactions especially when there is a depletion attraction or bridging flocculation you the interaction energy follows the dotted line right so the interaction energy varies as a function of surface to surface distance as shown in the dotted line so there will be attraction will as well okay because of the absence of steric interactions right so this is all about the steric forces or you can say polymer mediated forces. What is very important for us is when you can expect steric stabilization, when we can expect bridging flocculation.

I think these examples would have given you enough insight into the steric forces and polymer-mediated forces of interaction. We will stop here. We will continue from the following lecture. Thank you.