Fluid Mechanics
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Lecture – 36
Colloidal aggregates - Introduction

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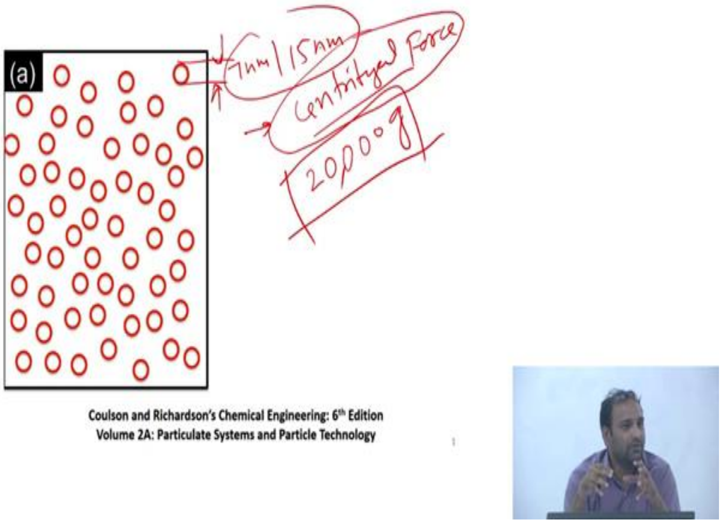

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Today's class we are going to kind of talk a little bit about again aspects of settling. But I just want to post this problem by just saying that say that I have a container, and it has particles ok. Now, if I want to and say that these dimensions of these particles are very small ok, ok. Say that I have the dimensions of these particles, say they are very tiny ok, like say sub micron size, say 7 nanometre particle or 15 nanometre particle, when the particles are very small ok. It so happens that you know even if you want to use external force like say we talked about centrifugal force right ok.

If of course, we know that for smaller sized particles, gravity is not good enough to settle the particles down ok. However, you can say that look I am going to go for centrifugal forces. We know that you know I can generate you know if you look at commercially available centrifuges, you know you can use like say centrifugal force which is of which is of the order of you know maybe even to 20,000 times g ok. It turns out that you know even such high centrifugal force, it will be very difficult to sediment particles of you know smaller dimension ok.

Now, in such cases what do we do? Ok, because, because when people work with you know particularly dispersions, now that there is a lot of interest in going to smaller and smaller sized particles right the nano domain ok. Therefore, there comes a case you know where you are basically interested in looking at you know separating out such small particles from solution, and it turns out that you know external forces you know kind of become you know not very applicable in such cases ok.

So, what do we do in such cases? So, I have smaller sized particles. I would like to separate them out or sediment them out from the solution. And you know I cannot use the external forces, because the particles are too small ok. One way of doing this would be, what is that? Make these particles bigger right, how do we do the, how do you make the particle bigger? Not the particle bigger.

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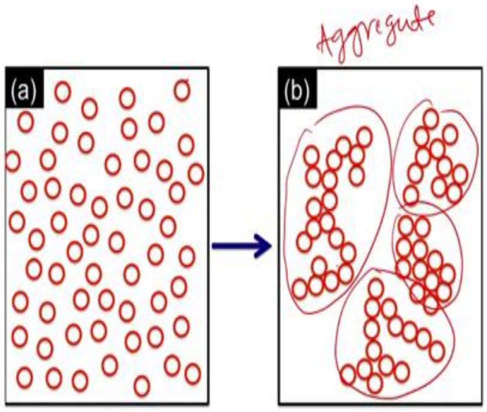

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But what I can do is I can actually make the particles large enough in terms of you know what I can do is, I can start with this case if you know homogeneous dispersed particles, I can make them what is called as aggregate right ok. I can make the particles come together, so that they form what are called as multi particle clusters ok, also called as aggregates.

Now, these aggregates you know if they are sufficiently big they could contain you know many number of particles depending upon the size of the aggregate. And now when the particles become larger in size we know that you know I can make use of the either gravity or you know or the other external forces right.

Now, how do we go from you know in a state a to state b, what do we do? Can you think of some ways by which I have a homogeneous dispersion of particles I want to go from state a to state b, where I have aggregates of particles people also called as cluster of particles people you know use term called coagulation, flocculation ok, these are different terms that you come across in the literature, but I want to go from A to B. So, can you think of some ways of doing that?

Any thoughts? Should I pick some names? How about Saurabh, is Saurabh here? Yes, Saurabh. All of you have kind of I am sure you have kind of looked at this.

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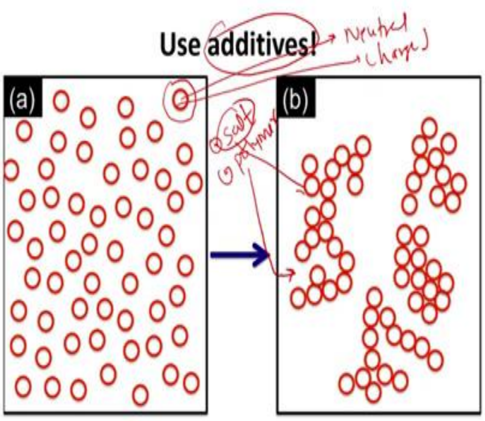
Use additives!

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So, basically use additives right ok. Do you know of some process where people use additives to make the particles aggregate or cluster together? You would have heard in the context of water purification right people put in what is called as alum which is a aluminum sulfate which is a salt that is typically added to water to ensure that whatever dirt particles that you have that is there in water, they become larger in size ok. And the moment such things are stored in a tank ok, they slowly settle down ok. Therefore, you basically you know can obtain you know water purification right or achieve water purification ok.

So, one way of doing this would be additives right. But it turns out that you know the kind of additives that you are going to use, it depends on lot of factors ok. It depends on the on the type of particle that you have in the dispersion ok, whether the particles are say neutral or whether the particles are charged. Basically the characteristics of the particles become important. And again what kind of additives you use that again depends on the particle fluid combination that you are working with ok.

Typically what is done is a two types of additives are typically used; one is basically adding a salt ok. I gave this example of alum right which is an aluminum sulfate which is a salt that is added in the water purification. And other kind of additive that people typically use is a polymer ok. And the way the, the salt helps in the aggregation, and the way the polymer helps in the aggregation, the mechanism is very different ok.

But the take home is that you know you have a dispersion of particles, very tiny particles in size, very tiny particles, and I would like to you know make them larger; that means, I want to cluster them to you know make a multi particle aggregate, and you can use additives you can either do that by adding salt or by polymers. Of course, there is a lot of other additives as well which people use, but for today's class we will just stick to these two. Now, I have added an additive, how does it work ok? So, the way all these additives work is that it basically alters ok, it basically changes what is called as inter particle interactions ok.

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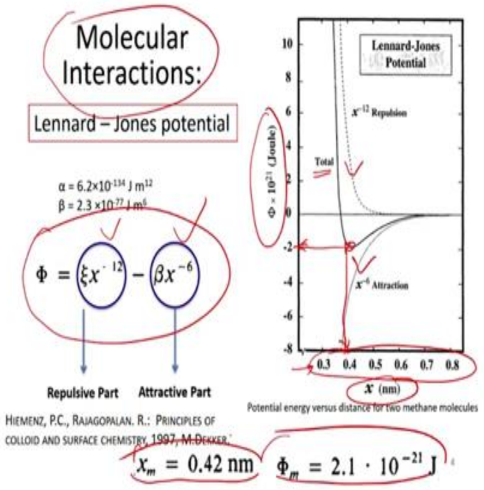
Molecular Interactions:

Lennard – Jones potential

$\alpha = 6.2\times10^{-134}\ \mathrm{J\,m^{12}}$

$\beta = 2.3\times10^{-77}\ \mathrm{J\,m^{6}}$

$$\Phi = \xi x^{-12} - \beta x^{-6}$$

Repulsive Part

Attractive Part

HIEMENZ, P.C., RAJAGOPALAN. R.: PRINCIPLES OF COLLOID AND SURFACE CHEMISTRY, 1997, M.DEKKER.

$x_m = 0.42\ \mathrm{nm}$

$\Phi_m = 2.1\cdot10^{-21}\ \mathrm{J}$

In terms of inter we talked about this intermolecular interactions right ok, where we talked about you know Lennard-Jones potential which has a repulsive part and an attractive part ok, and that is a plot of you know how the potential varies as a function of separation. This is what I was mentioning you know in the tutorial that you have to work with dimensions which are sub nanometre; otherwise any distance larger than a nanometre your you know at least for the Lennard-Jones potential, your potential of interaction is 0; that means, essentially the molecules are non-interacting right.

So, there is a repulsive part, there is an attractive part, and that is at overall potential, that is the total potential here. And there is a minima and the you know basically I can get that by just differentiating this equation, and you know you know equating to 0 right. And it turns out you know that the minimum occurs at you know that is a minimum position and that is a energy corresponding to the minimum right. So, similar to intermolecular forces, you can also play with you know interparticle forces as well ok, when you when you talk about particles in a solution.

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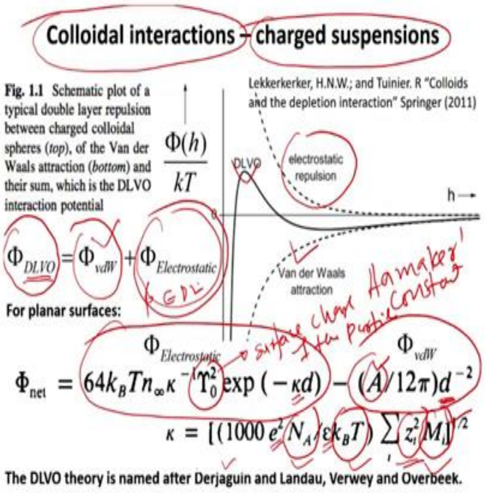

Colloidal interactions – charged suspensions

Fig. 1.1 Schematic plot of a typical double layer repulsion between charged colloidal spheres (*top*), of the Van der Waals attraction (*bottom*) and their sum, which is the DLVO interaction potential

Lekkerkerker, H.N.W.; and Tuinier. R "Colloids and the depletion interaction" Springer (2011)

$$\Phi_{DLVO} = \Phi_{vdW} + \Phi_{Electrostatic}$$

For planar surfaces:

$$\Phi_{net} = \overset{\Phi_{Electrostatic}}{64 k_B T n_\infty \kappa^{-1} \Upsilon_0^2 \exp(-\kappa d)} - \overset{\Phi_{vdW}}{(A/12\pi) d^{-2}}$$

$$\kappa = [(1000\, e^2 N_A / \varepsilon k_B T) \sum_i z_i^2 M_i]^{1/2}$$

→ surface charge

Hamaker constant

The DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek.

So, I am just going to flash a slide where we talking about in this case we are talking about colloidal interaction, that means, interaction between the particles in the case of charged particles in a solution ok. Analogous to the Lennard-Jones potential, so the total potential phi DLVO is what is called as a total potential. And DLVO actually stands for the four scientists you know who basically came up with this formalism that the total potential in the case of a charged stabilized dispersion, that means, a dispersion which contains charged particles, it basically has the Van der Waals contribution and a electrostatic contribution ok.

And this DLVO stands for the name of the four scientist Derjaguin, Landau, Verwey and Overbeek ok, these are because these are the two groups of two scientists one from Russia, one from Netherlands you know which came up with this argument ok. And like the Lennard-Jones potential, there is a attractive part which is the Van der Waals that is the one that is in the you know the below that you know zero axis right. And there is a electrostatic repulsion term ok, and that is the total potential right.

Now, I do not want you this to know a lot of details about this, but the point that I want to make is there is a Van der Waals term ok; the Van der Waals force of attraction, it depends on a parameter A which is what is called the Hamaker constant ok, what is called as a H a m a k e r - Hamaker constant ok. This basically contains all the material properties of the particle that you are dealing with ok. This takes a certain value for say polymeric particle, certain value for metal oxide particles, certain value for you know metal particles and stuff like that ok. And this d is the separation distance ok. So, it depends on the the kind of particle that you are working with and it depends on the separation distance between the particle that is the Van der Waals term.

And the electrostatic term it depends on a parameter called kappa ok. And that kappa depends on the salt concentration that people are working with I have a dispersion and I have added certain amount of salt. I know the concentration of the salt that I am you know working with ok. It only depends on the salt concentration; it depends on the the valency of the ion that I am using I am. Whether I am using a sodium chloride that is Na plus and Cl minus or whether I am using a CaCl 2 right Ca 2 plus and you know 2 times Cl minus right. So, it depends on the valency of the ions that I am working with.

And of course, it depends on thermal energy K B T, it depends on the permittivity right of the medium in which the particles are dispersed. N A is the Avogadro number; e is the charge that the electron has right the elementary charge ok, plus there is a term called capital gamma square which basically depends on the surface charge of the particle ok, whether the particle is highly charged or less charged ok, it depends on something like that ok.

So, what people do is there is a lot of work that has gone on in you know in looking at charge stabilized dispersions and their interaction. And people have come up with a way of manipulating the interaction between the particles ok. Either I can make the you know the you know the attractive forces more or I can make the repulsive forces more ok, depending upon whether I want to have a stable dispersion. What I mean by that is whether I want to have a state like this or I want to have a state like this, I can manipulate this by changing the interactions that is the point ok.

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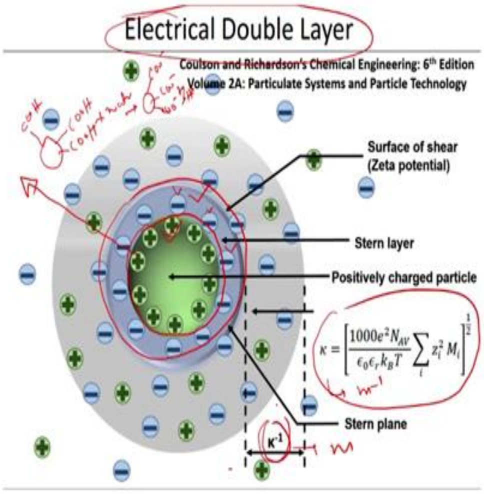

Electrical Double Layer

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$$\kappa = \left[\frac{1000e^2 N_{AV}}{\epsilon_0 \epsilon_r k_B T} \sum_i z_i^2 M_i\right]^{\frac{1}{2}}$$

And just to give you a little bit about whenever I have a, so what you are looking at is a schematic ok. What you have in the inner that is a charged particle ok. In this case, the particles are positively charged ok. And the moment you have a the moment I put in a particle in water ok, and if it acquires charges ok, and one of the ways of acquiring charges could be say that you know I have like say a particle which has say COOH groups on the surface ok. The moment I put it put this in water, what happens is that it is going to dissociate and it is going to give a particle that is negatively charged.

Similarly, I am going to have 3 H plus ions right that is the what are called as the counter ions ok. Now, that is a positively charged particle and these are the negatively charged counter ions ok. And because of the fact that you know I have a positively charged particle and there if there are negatively charged ions in the solution, the electric field that is developed because of the that the positive charges on the particle surface, it is going to attract the negative charges right. Because of which there is going to be a concentration of you know counter ions or the negatively charged particle in this case close to the particle surface ok.

So, in a way I have a picture of what is called as a charge that belongs to the particle surface and the charge that is in the solution ok. This is what is called the electrical double layer ok, that is the charges on the particle surface the constitute one type of you know charged surface ok, and there is a charge surface that is surrounding the particle, and this kind of combinations what is called the electrical double layer ok. I just want to introduce the terminology ok, this phi electrostatic ok, it is also called as phi electrical double layer because of the fact that you know the moment you have a charged particle in solution the configuration around the particle looks something like this ok.

And this is the K that I was talking about this K, if you work out the units of K, it turns out that K has a units of meter inverse ok. And therefore, this K inverse will have a unit of meter ok. This K inverse tell you something about the length scale up to which I have to worry about the electrical double layer interactions ok. I talked about the range of interactions right, in the case of you know Lennard-Jones I said that you know any distance greater than 1 nanometre, I do not have to worry about the interactions because beyond that the interactions are not you know present in essentially right.

In the case of charged stabilized dispersion, if the particles are such that the distance between the particles is more than K inverse ok, then I can practically neglect all the electrical double layer interactions or the electrostatic interactions because now the particles are far enough that the repulsive interactions do not come into picture at all ok. However, the Van der Waals force of attraction typically occurs in the size range of in the in the length scale of the order of you know a few nanometres up to about 10 nanometres that is a distance ok.

Now, what I can do is I know a little bit about Van der Waals, it depends on this type of the particle that you are working with. I know a little bit about the electrical double layer interaction, it depends on the kind of salt that I am using it depends on the concentration of the salt that I am using also the charge on the particle. What I can do is I can actually play with the double layer interactions ok.

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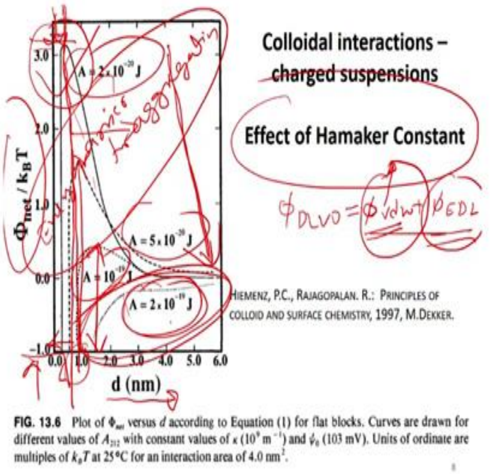

Colloidal interactions – charged suspensions

Effect of Hamaker Constant

$\phi_{DLVO} = \phi_{vdW} + \phi_{EDL}$

HIEMENZ, P.C., RAJAGOPALAN. R.: PRINCIPLES OF COLLOID AND SURFACE CHEMISTRY, 1997, M.DEKKER.

FIG. 13.6 Plot of Φ_{net} versus d according to Equation (1) for flat blocks. Curves are drawn for different values of A_{212} with constant values of κ (10^9 m^{-1}) and ψ_0 (103 mV). Units of ordinate are multiples of k_BT at 25°C for an interaction area of 4.0 nm^2.

This is a case where what is being done is this is your phi net that is a total potential plotted as a function of distance ok. What is being changed is the Hamaker constant? Ok what I mean by that is your phi DLVO has phi Van der Waals plus phi electrical double layer. What is being done is your phi electrical double layer is basically kept constant ok, the only thing that you are changing is the you know Van der Waals force of attraction ok. And that I can actually change by changing A right the Hamaker constant.

If I increase the Hamaker constant ok, if I increase the Hamaker constant, you can think about you know this barrier this barrier as a energy barrier for aggregation, that means, if the total interaction potential is negative ok. That means, if I somehow ensure that the particles do not come to a distance which is smaller than the distance that is corresponding this vertical line right. Any distance that is less than this if I ensure that the particles do not come to such sufficiently small distances, the particle would continue to remain in a well dispersed state right ok.

And for them to come to the such close separation where the attraction becomes dominant, that means, what I have to do is I should ensure that the separation between the particles never occurs you know what I mean by that is that I should ensure that the separation is sufficiently large that this energy barrier is kind of prominent that the aggregation does not occur ok.

The point is that look at the energy barrier the energy barrier is this in the case of 2.0 to 10 power minus 20 J Hamaker constant. I have reduced the Hamaker constant now; now it becomes a little smaller. I have reduced the Hamaker constant further or sorry I have increased the Hamaker constant further ok. Basically I am playing with the this barrier right, I am basically reducing the barrier by increasing the Hamaker constant. And what that leads to is a is at or some point your interaction become completely attractive ok.

Therefore if you keep the Van der Waals force of, so if you keep the electrical double layer interactions same, if I play with the Van der Waals force of attraction ok, I can actually go from a nicely dispersed state which is what is you know you would have if your Hamaker constant is lower 2 into 10 power minus 20 ok. However, if I go on you know increasing the Hamaker constant that is if I go to A into 10 power A is equal to 2 into 10 power minus 19, I have just reduced the Hamaker constant by one order of magnitude, your interaction becomes completely attractive, that means, I am going from a well dispersed state to an aggregated state just by changing the Van der Waals force of attraction ok. Any questions you have?

The point on you know note is that you know there is an energy barrier for aggregation ok. And does energy barrier occurs at sufficiently close distances right. If you look at this right, if I look at this plot, so I would say that you know the energy barrier maximum is about 1 nanometre right, it occurs at 1 nanometre. That means, if I somehow ensure that the particles approach a distance that is less than 1 nanometre, that means, I am already crossing the energy barrier then the particles are going to cluster together, and they are going to make aggregate right.

And one way of changing this energy barrier is basically I use particles of different types. Therefore, I am basically increasing the Hamaker constant going from 2 into 10 power minus 20 to 2 into 10 power minus 19 that leads to the totally attractive interactions, and you know that your particles would become unstable and aggregation kicks in ok.

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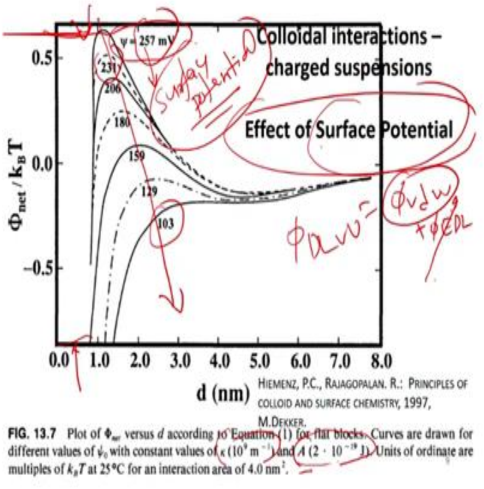

Colloidal interactions – charged suspensions

Effect of Surface Potential

HIEMENZ, P.C., RAJAGOPALAN. R.: PRINCIPLES OF COLLOID AND SURFACE CHEMISTRY, 1997, M.DEKKER.

FIG. 13.7 Plot of Φ_{net} versus d according to Equation (1) for flat blocks. Curves are drawn for different values of ψ_0 with constant values of κ (10^9 m^{-1}) and A ($2 \cdot 10^{-19}$ J). Units of ordinate are multiples of $k_B T$ at 25°C for an interaction area of 4.0 nm^2.

Second way of doing this would be if I work with particles of different charges ok. I do not want to, I do not want to get into the details, but the charge is basically measured in something called as a surface, but surface charge is basically measured in terms of what is called as a surface potential. The only thing that is important at this point is you know a higher value of psi means higher charge that is the only thing that is important at this point ok. And what I what I am doing is I am basically decreasing the surface charge or the I am decreasing the surface potential going from 231 all the way up to 103 ok.

And you can clearly see that the if this is a if this is a barrier to begin with ok. I am basically reducing the barrier by changing the surface potential right. Again this is a another way of making sure that the aggregation occurs, that means, if I am want to go from a an well dispersed state to an aggregated state, one of the way of second way of doing this would be playing with the surface potential or the surface charge.

So, in this case, what is done is you have basically kept the again phi DLVO is Van der Waals plus you know phi electrical double layer, I have kept phi Van der Waals same ok. Your Hamaker constant is kept constant, your Hamaker constant is kept constant at you know 2 into 10 power minus 19 joules ok. And you have kept the salt concentration same. As I said the salt can also influence the potential, I kept that also same. The only thing that has changed is a the surface potential and that is how you basically manipulating your electrical double layer interaction ok.

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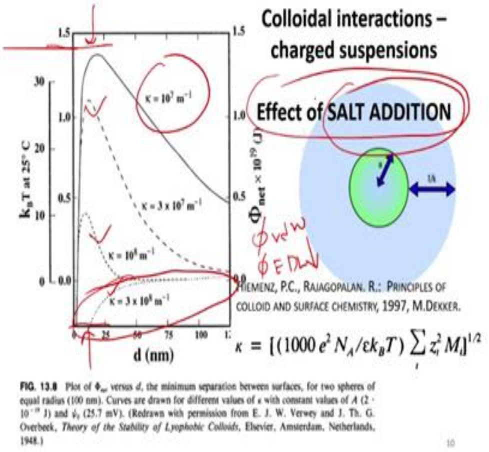

Colloidal interactions – charged suspensions

Effect of SALT ADDITION

HIEMENZ, P.C., RAJAGOPALAN, R.: PRINCIPLES OF COLLOID AND SURFACE CHEMISTRY, 1997, M.DEKKER.

$$\kappa = [(1000\, e^2 N_A/\varepsilon k_B T) \sum_i z_i^2 M_i]^{1/2}$$

FIG. 13.8 Plot of Φ_{net} versus *d*, the minimum separation between surfaces, for two spheres of equal radius (100 nm). Curves are drawn for different values of κ with constant values of *A* (2 · 10^{-19} J) and ψ_0 (25.7 mV). (Redrawn with permission from E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, Netherlands, 1948.)

And the third way of doing this would be by the addition of salt ok, which is what I said is most commonly you know followed in the in practice. That again this is the energy barrier with certain salt; certain salt correspond to certain value of kappa ok. And by increasing the salt concentration, I am basically reducing the barrier, at some point you know your electrostatic potential becomes completely the total potential completely you know becomes attractive that is because again here my phi Van der Waals is kept constant. I am basically reducing the electrical double layer interactions ok, I am reducing it by changing the salt concentration ok.

So, therefore, whenever you are working with a particle that have charge, I can play with the material properties or I can play with additives such as salt right and manipulate the total interaction. So, that your overall interaction goes from a purely repulsive a case like this to an attractive. So, there you know I basically induce the clustering of particles right.

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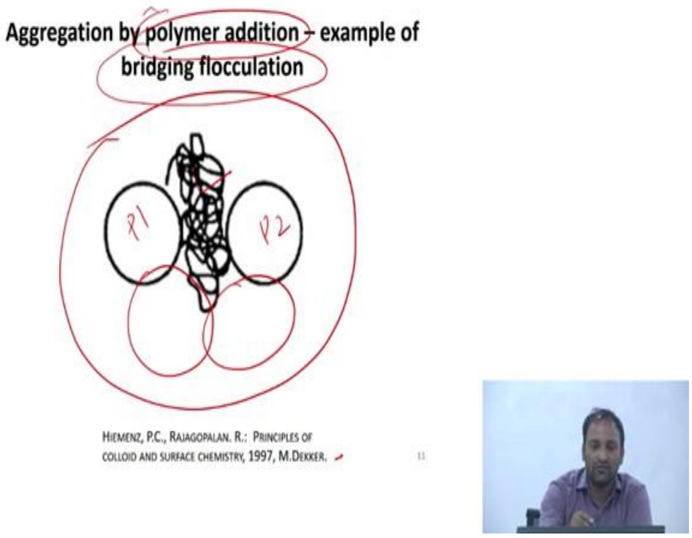

Aggregation by polymer addition – example of bridging flocculation

HIEMENZ, P.C., RAJAGOPALAN. R.: PRINCIPLES OF COLLOID AND SURFACE CHEMISTRY, 1997, M.DEKKER.

Now, other ways of doing this would be by putting other additives a polymer for example, again the use of polymers as additives to you know tune the interaction between the particles is again a is a big field. There is a lot of literature if you are interested you know I can go through it. But I just want to give you a feel for a particular term called bridging flocculation.

So, what could happen is you know if I have particles in a dispersion, I add a little bit of polymer. And if this polymer has a tendency to go and adsorb onto one of the particle surface, if this is say particle 1 and if this is say particle 2 ok. If it goes and adsorb onto the particle surface and if another particle comes in it its vicinity ok, it will also can adsorb onto other particle as well right.

So, therefore, this polymer kind of bridges the polymer bridges the two; two particles. And now if many such particles come into picture, for example, I could be one more here one more here, ok, therefore, I can again make a particle cluster. In this case, the clustering of particles is basically done by adding a polymer that goes and adsorbs onto the particle surface. And when many particles come together, so you basically get a multi particle cluster which is basically held together because of the additives that I have added ok.

Now, ok so, these are a couple of different ways of doing it. I mean again there are different mechanisms of you know how the polymer addition helps in aggregation, so that we will not talk.