

Interfacial Engineering

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Lecture-12

Work of cohesion, adhesion, and spreading coefficient

Inter and intramolecular forces of attraction; spreading coefficient of droplets on the surface

Welcome back.

In today's video lecture, we will look at the role of surface tension in determining the work of cohesion, adhesion and the spreading coefficient. So, these things will be very important whenever we deal with, you know, application like lubricants additives, right, because the adhesion is going to be very crucial, you know, in such application. Sometime when you are preparing the waterproof material, there you need to understand what is the spreading coefficient and things like that, okay, because, you know, there we do not want the you know, wetting property to be enhanced, right? So depending on the application, these aspects one has to look into in very detailed matter. So in today's lecture, we are going to look at, you know, these topics, you know, with somewhat more insight, right Okay, so let us begin, right Yeah. So as just now we mentioned the work of cohesion, adhesion and spreading coefficient, these parameters are going to be very crucial in coating applications.

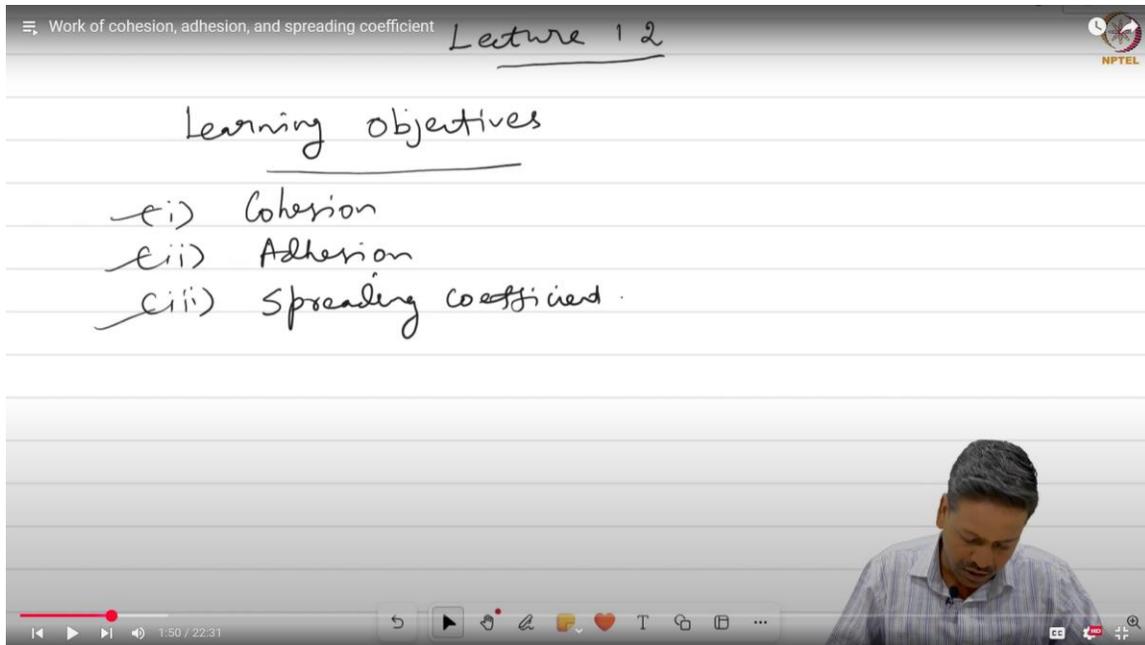
So we look at them in detail. Let's first start with the cohesion and we also have what is known as adhesion. Whenever we talk about cohesion, one thing that we should understand is that it involves the interaction between the identical molecules. This is more of an interaction between the identical molecules.

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Work of cohesion, adhesion, and spreading coefficient Lecture 12 NPTEL

Learning objectives

- i) Cohesion
- ii) Adhesion
- iii) Spreading coefficient.



Whereas this one is between dissimilar type, interaction between dissimilar type. So in actual one can call cohesion as intramolecular, one can relate cohesion as intramolecular interaction. Whereas adhesion as intermolecular right I think this difference is very clear now right so we talk about cohesion or work of cohesion I denote work of cohesion as W_{AA} which means that interaction between the like molecules right so so so We are going to follow a slightly different strategy. Let's say I want to understand the work of cohesion of, you know, a column of liquid, right? This is the column of liquid type A. Now, how do I understand this? I'm going to use a strategy, right? Using which I can calculate the work of cohesion.

So what I can do is, what if I you know, break this or pull this column of liquid, okay, pull this liquid column apart into two, into two equal parts. Let's say if I, you know, break them into two equal parts, let's say I have A and A, right But whether you are breaking them into two equal parts or not, what is more interested, more important is the surface. So when you do so, you create two new energy surfaces, right This is one energy, this is another energy, right Or you can say you got two new surfaces, right Now the question is, the work required to pull them apart, is same as the work required to put them back, right Okay, let's say if I know what is the work required to pull them apart, if I know that it is easy for me to calculate or understand what is the energy or work required to put them back, right Okay, it will be safe, correct So in this way, I can, so using this strategy, I can calculate work of cohesion So if I denote that as W_{AA} , you know, AA stands for the cohesion between identical molecules. Right. So remember now, if I want to put them back, OK, whether they may combine to form, you know, the column of liquid as they were originally.

It depends on whether the process is spontaneous or not. So for that, we will have to associate this workup cohesion with what is known as ΔG , which is change in Gibbs free energy. In such case, we know that my final, the energy at final configuration minus energy at initial configuration should be negative only then this process of combining can happen right spontaneously otherwise it is very difficult one has to pay the energy penalty right so now we know this that what is the energy at the final configuration what is the energy at the initial configuration we spend what is energy we spend To arrive at the final. So these two things should be clear. Now this configuration that is final minus initial.

Now we know that this energy here is associated with the surface tension, right So we have γ_A , γ_A here. Since energy is associated with the energy, since we have the final configuration, this is my final configuration, this is my initial configuration, right? Initially I started from this configuration, this is my final configuration. So what is my final configuration is, so it should be, you know, two γ_A , right So I have got γ_A , γ_A plus γ_B minus initial configuration is zero because remember, there is no interface here, right There is no interface here. So when you put them back, it is completely homogenized There's no new surface in this. There is no interface there.

No interface exists in this case. So you will not have any energy at the, when you talk about initial configuration. So, in this case, I can, sorry, it should be γ_A , right, because both are identical molecules. In this case, it will be simply γ_A itself.

Okay. So, this is nothing but work of cohesion. Now, similar way, let's say we have a column of liquid where I have got two type of molecule, which is A and B. Now, If you want to understand the work of addition in this case, what if I pull them apart into two? So, which means that I will have A and I will have B separately, right? Right. Now, if I use this similar strategy, γ_{AB} , subscript AB represents interaction between molecule A and molecule B. So, which is supposed to be, so I have to associate this with the ΔG , which is again final minus initial.

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Work of cohesion, adhesion, and spreading coefficient

Initial

$$\Delta G = W_{AA} = \text{Final} - \text{Initial} = (\text{ve})$$

$$= \gamma_A + \gamma_A - 0 = 2\gamma_A$$

W_{AB}

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Okay. So this has to be negative. So my final configuration is going to be gamma A plus gamma B. Okay. My initial, remember here interface do exist, right? In this configuration, you have boundary A and boundary B in between you have got interface right so that you have to take into account right in the previous case there was no interface so you don't have any interface over this so the energy at the initial configuration we have taken as zero but in this case it do exist I mean the interface do exist so you have to take that into account so this energy here the interface the interface the energy at this point is nothing but gamma AB right. So this is going to be my you know the work of adhesion.

So similar strategy you can also use let's say you have a solid surface and liquid. In this case you have used this approach for a liquid column where you have got A molecule and B molecule. What if I have to do the same exercise where I am spreading liquid on surface like solid now what is going to be my adhesion right in this case so you have got A and B here too Now, can we understand what is the work of adhesion? Can we write a work of addition for this case? Yes, you can write. So, this you will have to write in this way, right So, because we have got liquid, right Which is, in this case, gamma A is going to be my L, liquid, right So, it should be Lg. I am going to write explicitly because this is associated with the surrounding, that is gas, right So, Lg.

Thank you. And the gamma B has to be this one. So this is supposed to be SG because this is associated with the surrounding. So it has to be gamma SD minus gamma AB in this case will be, you know, so gamma SL, right? In this case it will be gamma SL. So you can write this also as, if I remember, if I have to use the, if I borrow from Young-

Dupré equation, I know what is these things, right? γ_{lg} minus γ_{sl} explicitly. So in that case, γ_{lg} , I can replace this as $\gamma_{lg} \cos \theta$.

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Work of cohesion, adhesion, and spreading coefficient

$\Delta G = W_{AB} = \text{Final} - \text{Initial}$

$= \gamma_A + \gamma_B - \gamma_{AB}$

$\Delta G = W_{AB} = \gamma_{LG} + \gamma_{SL} - \gamma_{SL}$

$= \gamma_{LG} + \gamma_{LG}$

So one would know that one would get gamma, I mean work of addition for this case as γ_{lg} into $1 + \cos \theta$. So, this is very compact equation borrowing from Young-Dupré. So, let us look at now spreading coefficient. So, whether spreading coefficient is just like a quick guideline So by knowing the number, one can quickly say whether liquid right, will spread nicely on the solid surface, given solid surface or not.

Okay. To say that, what you do is, what people generally followed is, you know, the same approach that we have used just now, ΔG approach. But instead of ΔG approach, what the convention that people followed was minus ΔG . So that more positive favors the wetting and less positive doesn't favor the wetting. Okay. So which means that if spreading coefficient is negative, it will de-wet.

Whereas spreading coefficient, if it is very high positive, then it will wet, right? Spontaneously it will wet. So that is the idea. So So for that, we have to use the minus ΔG approach, which means that you have to reverse this at the approach that we have used just now. So it should be in that case, initial minus final, right Because you want it to be more positive, right So that is the idea. So if I use this approach, let's say this is going to be my scenario where you have a surface Okay, and you have a liquid droplet.

If I spread this, if I place this droplet on the solid surface, whether it will wet or not, right So remember, we are taking, we are considering the complete wetting, right This is very

important to understand. We are taking the case of complete wetting. So unlike the partial wetting that we have seen so far, in complete wetting case, you don't have theta, right? Theta doesn't exist. Contact angle doesn't exist. So that is the condition we are using here.

So in this case, what is going to be my spreading coefficient? Let's say if I call this as A and this one as B, what is the spreading coefficient of liquid A spreading on surface B? Right? In this case, it is initial minus final. My initial configuration says that it is simply:

$$\gamma_{SD}$$

because this surface is associated with the surrounding. And my final configuration says that it is supposed to be:

$$\gamma_{SL} + \gamma_{LG}$$

So you can also express this as:

$$S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG}$$

Now, by borrowing from Young-Dupré, you can also write:

$$S = \gamma_{LG}(\cos\theta - 1)$$

So in this way, you can define the spreading coefficient. Remember, you can also rewrite this spreading coefficient as:

$$S = W_{AB} - W_{AA}$$

because we know:

$$W_{AB} = \gamma_{LG}(\cos\theta + 1)$$

If I write:

$$W_{AA} = 2\gamma_{LG}$$

Then,

$$S = \gamma_{LG}(\cos\theta + 1) - 2\gamma_{LG}$$

which simplifies to:

$$S = \gamma_{LG}(\cos\theta - 1)$$

This matches the spreading equation as expected.

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Work of cohesion, adhesion, and spreading coefficient

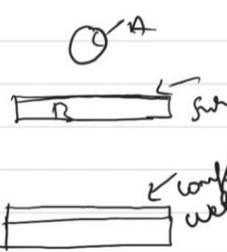
$\gamma = \gamma_{LV} (1 + \cos \theta)$

Spreading coefficient:

$-\Delta G = \text{Initial} - \text{Final}$

$-\Delta G = S_{A/B} = \gamma_{SG} - [\gamma_{SL} + \gamma_{LV}]$

$= \gamma_{SC}$



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If I compare this, this, this is going to be the same, right? If you compare this equation and this equation, both are same. So it is also, you can also say that spreading coefficient is same as the work of adhesion, right? W_{AB} minus work of cohesion, right? So this is the relation that we have. So spreading coefficient in terms of work of addition and work of cohesion also one can define. So we have seen so far the cohesion, adhesion and spreading coefficient. Now we will look at some example tutorial based on these concepts.

(Time:15:55)

Work of cohesion, adhesion, and spreading coefficient

$= \gamma_{SG} - \gamma_{SL} - \gamma_{LV}$

$= \gamma_{LV} (\cos \theta - 1)$

$S_{A/B} = W_{AB} - W_{AA}$

$= \gamma_{LV} (\cos \theta + 1) - 2\gamma_{LV}$

$= \gamma_{LV} \cos \theta - \gamma_{LV}$

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Okay. Right. All right. So let's look at the problem. Right. So this problem nicely describes the spreading coefficient concept, right? So you can see that in this problem, you know, so the work of adhesion data has been found out by these authors, right? So here it involves carbon black. So here one of the component is carbon black. The other is these organic liquids, okay Right.

(Time:16:45)

Work of cohesion, adhesion, and spreading coefficient **Tutorial** 

Bartell and Osterhof describe an experimental procedure for measuring the work of adhesion between liquids and solids. With carbon (lampblack) as the solid, the following values for the work of adhesion were obtained:

Liquid	Benzene	Toluene	CCl ₄	CS ₂	Ethyl ether	H ₂ O
W _{AB} (mN/m)	109.3	110.2	112.4	122.1	76.4	126.8

Use these data together with the surface tensions of the pure liquids to calculate the spreading coefficients for the various liquids on carbon black. Use your results to interpret and justify the authors' observations: "About equal quantities of water and organic liquid were put into a test tube with a small amount of the finely divided solid and shaken. It was observed that the carbon went exclusively to the organic liquid phase."

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

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So, use this data together with the surface tensions of the pure liquids, okay The surface tension of these liquids are not given in this problem, but we can supply that, right, as we saw, right To calculate the spreading coefficients for the various liquids on carbon black. sorry, carbon black, right, carbon black. So this is the kind of nanoparticle they use. So in this problem, they want us to interpret and justify the observation, which means that What is observation? So they say that when they mix equal quantity of water and organic liquid, which means that one face is water and the other face is different organic liquid in a different set of experiments, they understood, they observed that after some time, they observed that after shaking the mixture, they observed that the carbon particle, right, the carbon particle went exclusively to the organic liquid phase what does it mean is the if we know the spreading coefficient okay if spreading coefficient is more positive which means that this carbon with respect to a given organic liquid If the spreading coefficient between carbon and this organic liquid is more positive, then it will prefer a particular phase only, organic phase only.

Right. So that is observation. So they're asking us to justify this observation, which means that this carbon block, black, carbon black went exclusively into the organic phase, which means they don't want to wait. they don't want to be associated with water

phase. That's why this carbon particle went into the organic phase. So we have to first calculate what is the spreading coefficient in these cases for different cases. Then if the value is so high, then we can say that yes, this observation is correct.

Otherwise, the observation is invalid, right So we will look at that now. So we have got this problem. I hope this excel sheet is very clear to you. So for different organic liquid we have benzene, toluene, carbon tetrachloride, carbon disulfide, ethyl ether, water.

This work of adhesion has been, you know, reported by the authors. And this is the value I supply to you. This is taken from the textbook for, you know, surface tension of liquids, for these liquids. Now, we know the spreading coefficient is simply nothing but work of adhesion minus work of cohesion, right? So, work of cohesion is nothing but $2 \gamma_{LG}$ So, γ_{LG} value we have reported here. So, we just have to simply subtract γ_{AB} minus $2 \gamma_{LG}$.

So, in that way you can say that. So, these things is very clear. So, we will just simply you know minus right $2 \gamma_{LG}$ this one, correct? Yeah. So then we will get the spreading coefficient in this case. So we have got this as, okay, so if I simply control C, you can see that the values are changing here.

Look at the value for the water case. Look at this one, right? This is negative. In the case of spreading coefficient for water with the carbon black, spreading coefficient is negative that's why a carbon particle doesn't want to stay in the water phase they went extrusion to the organic phase so in the rest of the case spreading coefficient is highly positive so it is encouraging that i mean it is justified that the observation made by the authors is correct So, one can say that it is because of the high spreading coefficient. That is why the carbon particle went exclusionary to the organic phase. So, I think this is clear now.

(Time:22:20)

Work of cohesion, adhesion, and spreading coefficient

9-(2*H9))

E	F	G	H	I
		Work of adhesion	Surface tension of liquids	Spreading coefficient
✓	Benzene	109.3	29	51.3
✓	Toluene	110.2	28.5	53.2
✓	CCl ₄	112.4	26.9	58.6
✓	CS ₂	122.1	32.3	57.5
✓	Ethyl ether	76.4	17	42.4
✓	H ₂ O	126.8	72.8	-18.8

WAB - (W_{DA}) 272m ↓

We will stop here. We can continue from the next lecture.

Thank you.