

Importance of surface; Application of interfaces

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Lecture-2

Nano and micro-sized particles; Application based on drug delivery and metal-organic frameworks (MoF)

Welcome back. So, in today's lecture, we will look at, we will highlight the importance of surface, you know, by taking, let us say, one particle which radius is one centimeter. We will try to cut this particle or object into several halves down and we will demonstrate how by cutting this sphere into several logs down, how we can increase the surface area, how we achieve or how we obtain the larger surface area, that aspect we will show in this video lecture. And apart from that, we will also discuss something about what is specific surface area for a given object, and how we can calculate. And we'll also try to, you know, highlight on the importance of surface chemistry from various applications, right?

(Time: 1:36)

Importance of surface for small particles

Radius (cm)	Volume per sphere (cm ³)	No. of spheres	Area per sphere (cm ²)	Total area (cm ²)
1	4.186667	1	12.56637	12.566371
0.5	0.523333	8	3.141593	26.305602
0.25	0.065417	64	0.785398	50.265482
0.125	0.008177	512	0.19635	100.53096

↓ ↓

0.00012207	7.62E-12	5.49756E+11	1.87E-07	102943.71
1.9073E-06	2.91E-17	1.44115E+17	4.57E-11	6588397.3
1.1921E-07	7.09E-21	5.90296E+20	1.79E-13	105414357
7.4506E-09	1.73E-24	2.41785E+24	6.98E-16	1.687E+09

Total area increases by several fold just by cutting the spheres into several halves down

Surface-volume ratio increases



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So now we will move on to the first topic, that is surface, you know, importance of surface, right? As you can see here, we are going to do one simple exercise. Let's say we

take a simple object, a spherical object, which is one centimeter in radius, right? If you want to calculate what the volume is, because we have only one spherical object, the volume of it we can calculate, okay? Using the formula four by, you know, four by three, π , r^3 . And then we now know that we have only one sphere, okay? So, area per sphere can be calculated for this one sphere, that is what we are asking. Now, by multiplying this number of spheres into area per sphere, we can actually calculate what the total surface area or total area is.

Now, in the second step, what I am going to do is, I am going to cut this spherical object into two. Instead of one radius, I mean one centimeter, you know, radius, we will now have the radius as 0.5 centimeter, in this way, you will achieve number of spheres as 8 because your volume per sphere goes down drastically now when you calculate the area per sphere it is again less lesser than what we obtained in the previous case but if we have to achieve total area, we need to multiply this area per sphere into number of spheres. You look at this one, because the number of spheres has gone here. So, when we multiply these two values, you get, the total surface area, which is at least, you know, two times higher than the previous one, right? So, the same exercise, if we have to do keep cutting this object 7 arcs down, you will achieve, you will reach some point wherein you will go from a macroscopic object into a microscopic object and even sometimes you will go up to the nano, the dimension nanometer in size.

(Time: 4:09)

Importance of surface for small particles



Radius (cm)	Volume per sphere (cm ³)	No. of spheres	Area per sphere (cm ²)	Total area (cm ²)
1	4.186667	1	12.56637	12.566371
0.5	0.523333	8	3.141593	26.305602
0.25	0.065417	64	0.785398	50.265482
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Total area increases by several fold just by cutting the spheres into several halves down

Surface-volume ratio increases



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Interfacial Engineering
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So you can see that, although the number of the volume which is nothing but the volume per sphere and the number of spheres is same in this case, because the number of spheres have gone up too high, right? And although the area per sphere is significantly smaller in this case, you can see that when you multiply these two, we get the surface area, which is at least 900 higher than the original one, right? So we started with, surface area as 12.56-centimeter square, but now we have at least 2 into 10 power 9, right? So, which is, I mean, at least 9 orders greater than what we have had initially, right? So, what it comes to say is that when we, you know, when we go, I mean, when we cut this sphere into several arcs down, when we approach the size almost nanometer or micron size your, the surface to volume ratio goes up, you know, significantly, okay, so this comes to say that for small particles the surface is very key right it is a key aspect, right,

(Time: 5:23)

Specific surface area



$$A_{sp} = \frac{A_{total}}{m_{total}} = \frac{n4\pi R_s^2}{\frac{n4\pi R_s^3 \rho}{3}} = \frac{3}{R_s \rho} \quad \text{For Spheres}$$

Variation of specific surface area with geometry. A material of density ρ exists as uniform cylindrical particles of radius R_c and length L . Derive an expression for A_{sp} for this material and examine the limiting forms when either R_c or L is very small.



Paul C. Hiemenz et al. Principles of colloid and surface chemistry, Marcel Dekker Inc., New York, 1997

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so here look at a simple, you know, exercise for a specific surface area, how do we calculate specific surface area for a given object Let us say we start with spherical particle, right. So, specific surface area is defined like this. It is a ratio of total surface area to the total mass of the sample. Let us say if you collect handful of samples containing spherical objects, okay, you need to know what is the radius of the particle, okay, and what is the mass of the sample.

So once we know that, we can actually calculate what is the specific surface area of a given geometry.

$$A_{SP} = \frac{A_{total}}{m_{total}} = \frac{n \cdot 4\pi R_s^2}{n \cdot \frac{4}{3}\pi R_s^3 \cdot \rho} = \frac{3}{R_s \rho}$$

Now, just to appreciate the, you know, the difference in surface, we will now deal with, let us say, cylindrical particle. Maybe you are, you know, working with, let us say, carbon nanotube particles or rod and silica rod, various particles you may be dealing with. Let's take an example of cylindrical object, right? In this case, how do we calculate the specific surface area? Remember, this cylinder is not hollow, okay? When you synthesize this kind of particle, you will also have, you know, the, this surface also will be filled, right? So in this case, you will have the surface that is coming out of the, as part of, I mean, you know, as the length and both radius will be taken into account in this case. So, you can see that the specific surface area we can calculate for this case in this way, okay. So, let us say I have to calculate the specific surface area for this case.

Now, all I need is, I need to know what is the surface, you know, along the length, right,

$$\begin{aligned} A_{SP} &= \frac{[2\pi r l + 2\pi r^2]n}{[\pi r^2 l \rho]n} \\ &= \frac{2\pi r[l + r]}{[\pi r^2 l \rho]} \\ &= \frac{2[l + r]}{[r l \rho]} \end{aligned}$$

This is my compact equation for cylindrical particles. If you want to calculate the specific surface area, you can use this approach, right. In this case, we need to know what is the radius of the particle and what is the length. You know, for example, if you are dealing with a thin rod, maybe a, you know, wire, cylindrical wire, there the length will be important compared to the radius, right, because radius will be too smaller. In that case, you can ignore this one. For a thin rod, this is for thin rod and, this one is for disk.

$$\begin{aligned} A_{SP} &= \frac{2}{\rho} \left(\frac{1}{r} + \frac{1}{l} \right) \\ &= \frac{2}{\rho l} \\ \text{or} &= \frac{2}{\rho r} \end{aligned}$$

(Time: 11:10)

Specific surface area





$$A_{sp} = \frac{[2\pi r \times l + 2\pi r^2] \times \rho}{[\pi r^2 \times l \times \rho] \times \rho}$$
$$= \frac{2\pi r [l + r]}{\pi r^2 l \times \rho} = \frac{2[l + r]}{r \times l \times \rho}$$
$$\Rightarrow \frac{2}{\rho} \left[\frac{1}{r} + \frac{1}{l} \right] \Rightarrow \frac{2}{\rho l} \rightarrow \text{thin rod}$$
$$= \frac{2}{\rho} \times \frac{1}{r} \rightarrow \text{disc}$$



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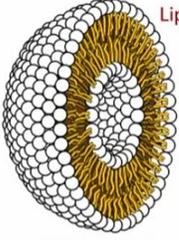
So, in this way you can calculate the specific surface area.

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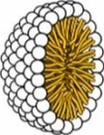
Impact of surface chemistry in science, engineering, and technology



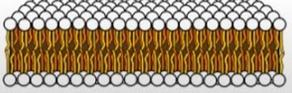
Biological and life sciences: Biological membranes and cells



Liposome



Micelle



Bilayer sheet

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- ❖ Surfactant capsule known as liposome was discovered in 1960s.
- ❖ Drugs administered in free form cause side effects because of their toxicity to areas of the body that are not affected by the disease.
- ❖ Encapsulating the drugs in liposomes and delivering them efficiently and specifically to the affected organs will reduce the side effects.
- ❖ It is possible to design liposomes that avoid detection by hunters such as macrophages in the body so that the drugs can be delivered to the cells effectively.



Paul C. Hiemenz et al. Principles of colloid and surface chemistry, Marcel Dekker Inc., New York, 1997

11:16 / 23:51 Interfacial Engineering

Now, we move on to the impact of surface chemistry. maybe from different perspectives, different applications' point of view. So, let us first take an example of the biological and life sciences applications. For example, biological membranes and cells.

Now, we know what is known as liposome, micelle, bilayer sheet. These are self-recentral structure of lipid You may have seen this term, micelle, whenever you dealt with a surfactant, right? Surfactants are going to form micelles, okay? When they form micelle, because surfactant has got two components into it. One is a hydrophilic group and another one is hydrophobic part. Now, this tail, which basically is nothing but hydrophobic part, whereas the head group is hydrophilic, right? So, if I look at this micelle, a simple structure, it has got at the center, it can actually entrap organic molecules which are, you know, which are not water loving, right? The affinity towards oily like substances will be very high in the case of micelle. So, it can trap organic molecules, right? Example, you can use this kind of I mean this kind of structure is very useful in, you know, oil recovery by enhanced oil recovery and things like that.

Then the liposome, liposome are also called as you know surfactant capsule okay. This was discovered way back in 1960 okay. Both liposome and bilayer sheet, both are actually bilayer structure ok they self assemble to form bilayer assembly whereas in liposome this is spherical in shape whereas this one is sometimes cylindrical or rectangular ,now if I look at this structure it has got a unique way of ,you know , encapsulating the cargo molecule the cargo is, is a vehicle that carries the drug, right, along with it. Uh, so, liposome can be used as a drug delivery vehicle because it can actually, uh, encapsulate the drugs, uh, uh, you know, in three different ways. One is the, you can encapsulate the drug molecules into the core, uh, which means that hydrophilic-like drug molecule or, or cargo can be, uh, trapped in this, uh, core part, whereas outer side again you can actually you know get this cargo molecule attached to this outer the exterior part as well of this liposome and then inside between interior and exterior part you also have the tail group which is basically nothing but a hydrophobic part, it can also trap hydrophobic cargo or drug molecules In this way, you can encapsulate drug and deliver, use it as a drug delivery vehicle.

One of the advantages of using liposome is that, it can deliver the drug into the targets area, selectively. The advantage of that is, it can help us, you know, prevent from the side effects generally when you consume drug in the free form in a conventional way what happens is because it is also creating some sort of toxicity to the areas of the body that are not affected by the disease so it not only delivers the drug into the conventional drug delivery system ,works, I mean doesn't work effectively because it is also delivering the drug into the area which are not affected by the disease, right? Whereas this liposome, it is possible to employ liposome as a death delivery vehicle which will not be, which

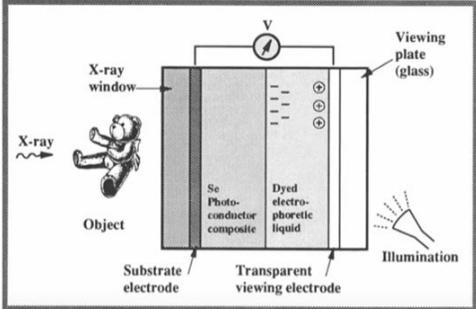
will not be detected by the hand test or you can say macrophages in the body so that the test can be delivered to the sense effective manner, okay? This is one of the important applications from the biological and life sciences point of view. Here, surface is very important because hydrophobic, hydrophobic interaction between the liposome and drug molecules okay or even hydrophilic the affinity between hydrophilic part and hydrophobic part is very important because when we deal with surface so these interactions also very important that we will study as we move on, right,

(Time: 16:35)

Impact of surface chemistry in science, engineering, and technology

Colloid based electrophoretic imaging devices





- ✓ EPIDs, e.g., *Flat panel device*, contain submicron-size particles of pigments (TiO_2) dispersed in a liquid along with a dye that provides contrast.
- ✓ When an electrical potential is applied to the system, pigment particles are driven to the interface between the suspending liquid and a viewing plate.
- ✓ EPIDs have the potential of providing an image that has extremely high optical contrast under normal lighting, that is legible over a wide range of viewing angles.

EPID combined with x-ray imagers

- **Liquid dispersion of pigment particles and dye is very crucial aspects in this technology.**
- **Dispersion must be stable even when particles are concentrated to form an image at the viewing plate.**

Nanoparticle technologies

Paul C. Hiemenz et al. Principles of colloid and surface chemistry. Marcel Dekker Inc., New York, 1997

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so next is the surface chemistry from the imaging device point of view, so gone are the days ,where we used you know picture tube in TVs right nowadays those picture tubes are replaced by liquid crystal device, okay, LCD and another example of flat panel device I can give you is this one, electrophoretic imaging devices, okay, it contains, I mean, it contains simply, you know, the TiO_2 nanoparticle, submicron size nanoparticle, along with it, there is also a dye molecule, which is spread in the matrix, right, so the TiO_2 is basically help in providing the, you know, a good contrast when we weave it through the weaving plate, right, and the dye molecule absorbs some light so that it can it can provide perfect balance between, you know ,the light that I mean between, you know, that has more brightness and it can also tune the contrast of the image right So the dye molecule here is to provide the contrast whereas the TiO_2 is to provide the high optical contrast under even normal lighting. So the reflective properties as well as the absorbing properties both are coupled together in this application. So together they provide a very high optical contrast even under normal lighting.

So, this technology is nowadays used extensively. So, it has replaced the conventional system of picture tube, right? But still, we do have some challenges when we deal with this kind of technology. Like, for example, when we use, you know, higher concentration of particles, you know, there may be, the stability is an issue. They will aggregate. There's a tendency, you know, for these particles to, you know, come together and aggregate.

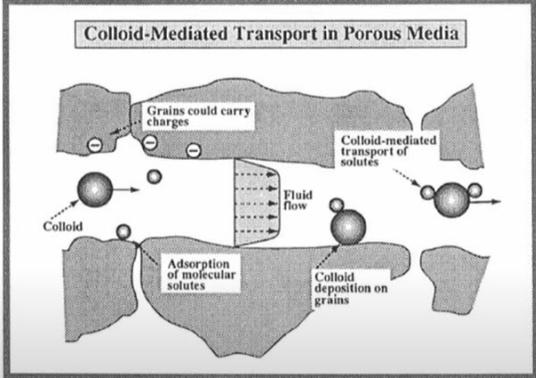
And so then stability is a big question that one has to address when we deal with this kind of an application. Here, surface chemistry plays a very important role. When we talk about stability, the interaction between the particle and dye molecule, right, their electrophoretic mobility also is affected by the TiO_2 . the property of TiO_2 . So, all this becomes very important when we deal with such applications.

(Time: 19:30)

Applications: Colloid-Mediated Transport in Porous Media


NPTEL

- The sketch illustrates the transport of molecular solutes by colloidal particles.
- Colloids are known to have a large capacity to bind hydrophobic compounds.



- The bed sediments contain many hydrophobic organic compounds and metal ions.
- These sediments act as sources of pollutants of the overlying aqueous phase.

Paul C. Hiemenz et al. Principles of colloid and surface chemistry. Marcel Dekker Inc., New York, 1997

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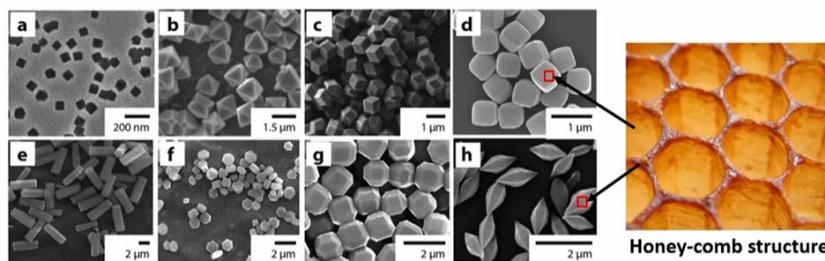
So, this is from the, again, we have another application from the, you know, the groundwater perspective. Let's say, we know that a groundwater table is often refreshed, I mean, by, I mean, often treated using some you know reagent, you know, to remove the, the contaminants from the bed, right, so let's take an example of in the water table we have rock, right, porous media right into this porous channel there will be contaminants sometime right they settle down over the period of, you know, the application. Now, this colloid, sometimes people use this, you know, for example, if you want to remove the contaminant, which is hydrophobic in nature, people can, people often use colloidal particle, which is, you know, also hydrophobic, so that when we use it to, you know, chart the the porous channel, porous media. So, this colloidal particle can, you know,

combine with the pollutants, right, combine with pollutants and then they can, these pollutants can attach, get attached with the colloidal particle and then, then it can, the solid, I mean, the pollutant molecules can be easily transported, okay, removed from this bed, right. So, this is a very important application based on colloidal nanoparticles or colloidal particles, right.

(Time: 21:29)

Applications: Metal-Organic-Frameworks (MOFs)

- It is desirable to produce lightweight and compact materials that can rapidly adsorb and desorb large amounts of hydrogen.
- MOFs are very attractive for hydrogen storage due to their high surface to volume ratio.



Examples of colloids synthesized from metal-organic frameworks: (a) cubes, (b) octahedra, (c) rhombic dodecahedra, (d) truncated cubes, (e) hexagonal rods, (f) hexagonal discs, (g) truncated rhombic dodecahedra, and (h) bipyramidal hexagonal prisms

- ❖ Exhibits greater capacity for gas storage due to ultra-high surface area

M. Sindoro et al. Acc. Chem. Res., 2014, 47, 459-469

So, the next application that we will see is metal-organic frameworks. Here also, you know, we will look at the application from the point of surface to volume ratio. So, basically this MOFs, which is metal-organic framework, is often used I mean, it took a center stage in recent time because of its capacity to absorb the hydrogen or CO₂ molecules in a significant amount. For example, the advantage that we have here is it produces lightweight and compact materials.

We can use this material to absorb or dissolve large amounts of hydrogen. because it contains three-dimensional network porous structures. These structures are formed by what is known as metal and organic framework. The metal atoms are linked with organic ligands and this structure provides a greater capacity for storage. and it offers a high surface to volume ratio.

These MOFs can be prepared in a different shape as well. But what is so unique about this structure is, it forms honeycomb like structure, wherein these metal atoms are connected with the organic ligand. And because it provides, you know, a three-

dimensional porous structure, I mean, the storage capacity, the absorption capacity is also increased several fold, okay, so these are various applications considering the surface chemistry from different perspectives we have seen biological perspective and we have seen from the metal organic framework perspective okay and imaging devices perspective and water treatment perspective, right, so there are I mean we can even go on listing many such applications but we will stop here We will continue from the next lecture. Thank you.