Powder Metallurgy
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Lecture-25
Dynamic Light Scattering -2

Hi everyone and welcome back. In the previous class, we were talking about the Dynamic Light Scattering Technique for the particle size analysis. We have seen the basic principle of this technique and we have discussed how the data is collected and how it is analyzed.

This technique is based upon the Brownian motion of particles in a suspension. And, due to the Brownian motion, when the particles come in the path of the light, the scattered intensity which is collected on the detector varies and this variation in the intensity is related to the size of the particles.

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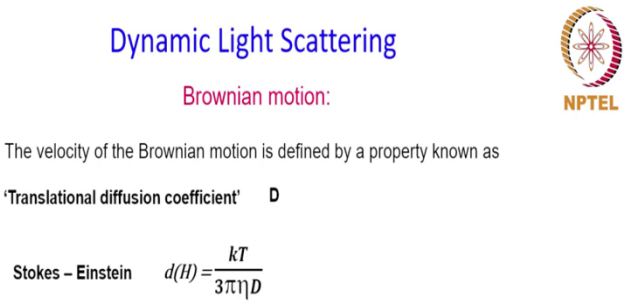

We have seen that this motion can be defined by a parameter called translational diffusion coefficient, which is related to the particle size D by the Stokes-Einstein equation.

$$d(H) = \frac{kT}{3\pi\eta D}$$

And, if we could derive the parameter D, we will be able to get the particle size from this particular equation.

So, that is what the dynamic light scattering technique does, in terms of measuring those intensity fluctuations which contain the time scale information of the Brownian motion and from that the diffusion coefficient can be obtained, and it can be used in the Stokes-Einstein equation to derive the particle size.

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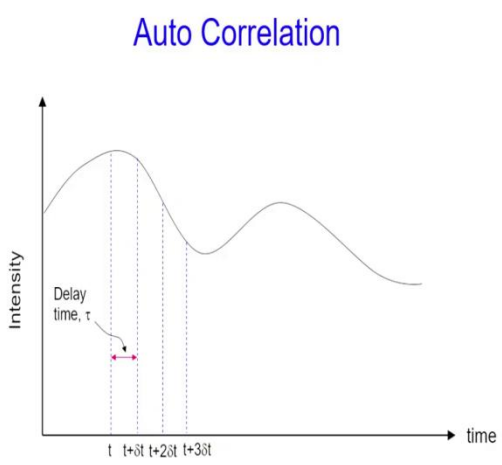

But, in order to do that, the data has to be analyzed and for that, we have seen about a method called auto correlation, which is used to derive the diffusion coefficient from the intensity fluctuation data.

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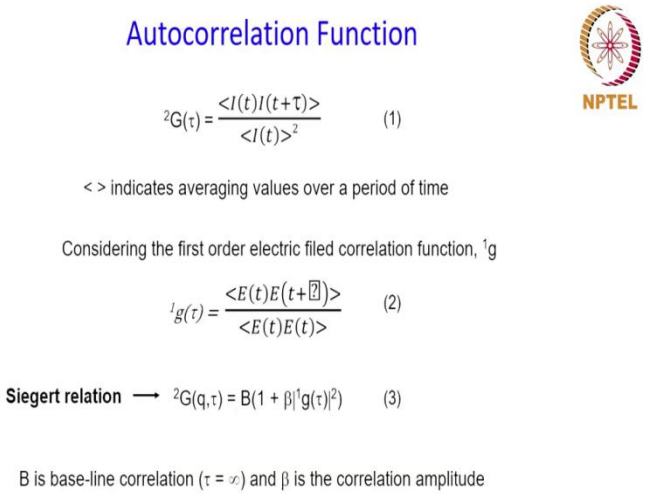

So, once you do this auto correlation with the help of a second order autocorrelation function, which basically correlates the intensity of signal with respect to the time, you can derive the diffusion coefficient and from that the particle size can be obtained.

So, now in this class we are going to see about the instrumentation and how the experiment is actually carried out in the DLS instrument to measure the particle size and size distribution.

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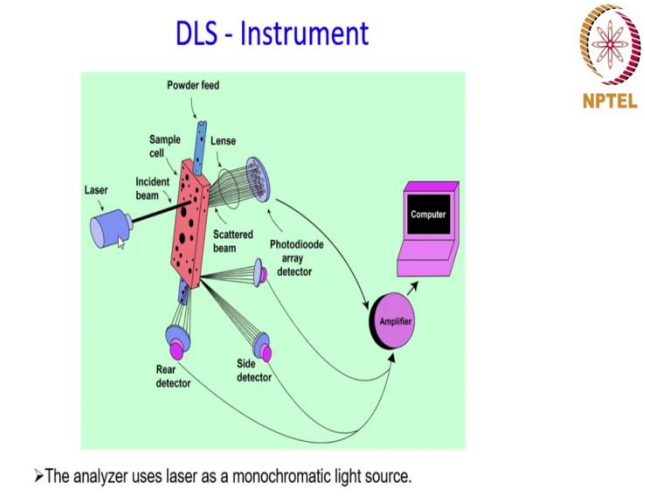

So, here is this schematic of the instrument (slide below), where you can see the vital parts. The instrument uses a laser as a monochromatic light source.

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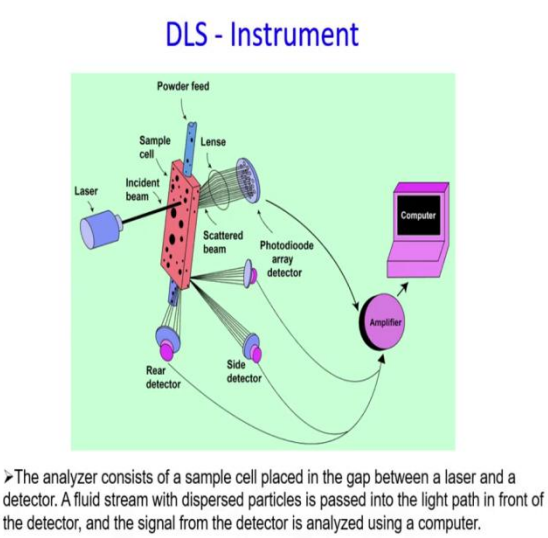

It also consists of a sample cell. The sample cell is placed in the gap between the laser and a detector. The detector is a photodiode array detector, which captures the scattered intensity.

A fluid stream with dispersed particles is passed through this sample cell. And, as the particles come in front of the light beam it gets scattered and the scattered intensity is captured by the detector. There are lenses, which help in focusing the scattered intensity onto the detector.

The signal is collected by the detector and sent to the computer, where it is being analyzed with the help of the autocorrelation function, and the particle size is derived from that data. There could be more than one detector which allows more flexibility and also helps expand the dynamic ratio (ratio of largest to smallest particle size), which essentially means that it can analyze a wide range of particle size

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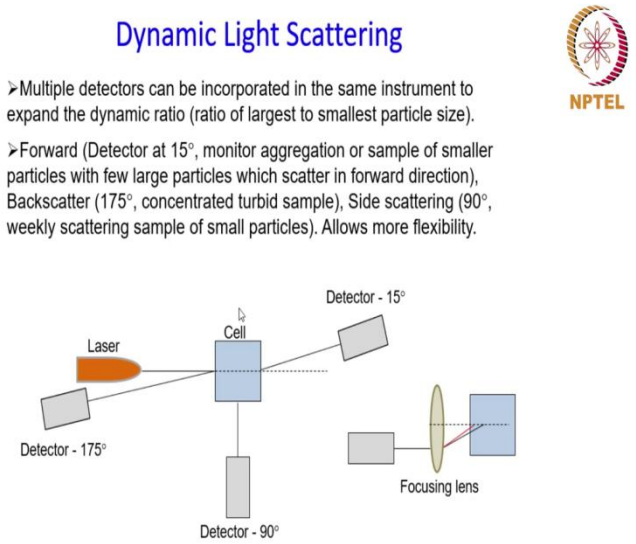

And, the way the detectors are arranged when you have multiple detectors is shown in the diagram (slide above), where you can see a detector at 15° which is to capture the forward scattering. And, apart from that you can also see two more detectors one at 175° which is basically to capture the backscattered signals that come out from the front wall of the sample cell. And, there is one more detector at 90° which is to capture the scattered signals from the sidewalls. And, now which detector to be used and how the signal will be captured, that will depend on the kind of sample you have.

For example, when the detector is kept at 15°, it is primarily for capturing the forward scattering light. And, this kind of forward scattering happens for samples, which will typically have smaller particles with few large particles, which scatter in the forward direction. And, this detector at 15° is also used to monitor aggregation in the sample.

And, the other two detectors are there basically to capture the backscattered signal from the front wall of the optical cell, and the one at 90° is used to capture the backscatter signals from the sidewalls. So, which one to be used to capture the backscatter signals will again depend on the type of sample. For example, the 175° detector is used for concentrated turbid samples where the particle concentration is high. And, the 90° detector is useful for weekly scattering sample of small particles.

With the help of the multiple detectors the instrument allows a range of sample types to be analyzed. And, therefore, it allows more flexibility to the system. Now, when you talk

about back scattering, the path length of the scattered light can be reduced, because the scattering volume is close to the front wall of the sample cell. And, therefore, the path that the light has to travel to reach the detector is reduced. And, this will in turn reduce the multiple scattering, which might interfere with the actual signal. Multiple scattering is the scattering of the light beam by more than one particle before it reaches the detector. And, if that happens it might interfere with the signal, and the data may be skewed compared to the data, which would have been received through single scattering.

Now, in order to control the light path, focusing lenses can be used with the help of which the focus point can be varied. As the path length is reduced the multiple scattering is also reduced and depending on the sample type this focus length can also be increased, if there is a need.

For example, if there is a dilute sample of small particles there may be a need to have more scattering from each of these particles. And, therefore, it may be beneficial to increase the path length and therefore, the focus point can be changed to a larger distance.

On the other hand if you have large particles or samples with high concentration. In those cases it will be good to have the focus point closer to the front wall of the sample cell to minimize the path length and in that case, the position of the focus point can be brought closer to the front wall of the cell.

So, that was all about the DLS instrument, but there is one more thing which is very important in case of DLS measurements and that is the sample preparation.

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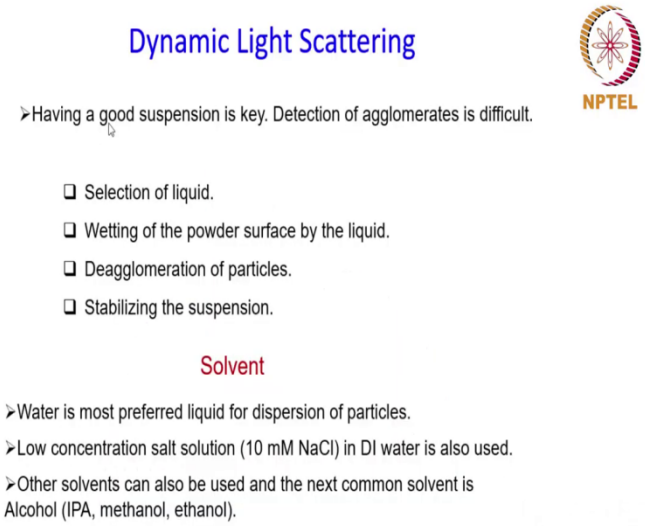

Having a good suspension is the key to the success of the DLS technique. Because, if the particles are not uniformly dispersed in a liquid and if they agglomerate, then obviously, the particle size data which is obtained is not at a true representative of the actual particle size. In addition, the detection of agglomerate is difficult by this technique. And, therefore, it is essential that a good suspension is made before the measurement is carried out.

The four vital things that one has to keep in mind in order to make a good suspension are as follows:

1. **Selection of an appropriate liquid** in which the particles are dispersed is very important, because every particle may not disperse in every liquid. And, therefore, depending on the type of particles, a particular type of solvent has to be chosen.
2. Once the liquid is chosen and the particles are added to the liquid to make the suspension, it is essential that the powder particle surface is wetted by the liquid; that means, the particles surface would be entirely covered by the liquid. Otherwise a good suspension will not form. So, **wetting of the particle surface** is also very important.
3. And, then as I said agglomerations are not good for this measurement and therefore, the particles need to be **de-agglomerated**, once they are added to the liquid.

4. And, in fact, a **stabilizing agent** is added to make sure that the particles do not agglomerate and a uniform suspension is obtained where the individual particles are dispersed without forming clusters.

So, talking about the solvent which is used to disperse the liquid, water is the most preferred solvent for dispersing most of the particles unless they are soluble in water. And, many times a low concentration salt solution is used instead of pure de-ionized (DI) water because DI water can reduce the charge on the surface of the particles. And, as a result the repulsion between the particles will decrease and that would lead to agglomeration.

Addition of trace amount of an ionic compound such as sodium chloride can overcome that problem. For example, a 10 milli molar solution of sodium chloride can be used instead of pure DI water to make sure that the particles do not form agglomerates. Other solvents can be also used apart from water and the next best solvent is alcohol. For example, Iso-propyl alcohol, methanol, ethanol can be used to disperse particles.

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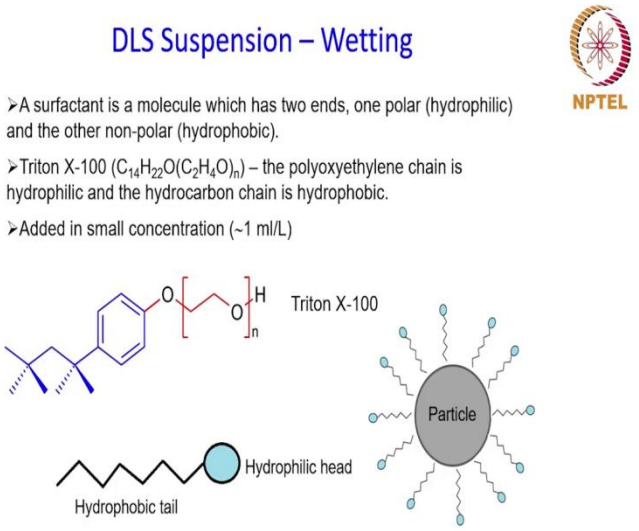

Wetting of the particles by the liquid is very important, otherwise they will not be suspended and a good dispersion cannot be obtained. So, in order to do that you will have to make sure that the particle surface is conducive towards water; that means, it should not be hydrophobic and expel water, rather it should be water loving or hydrophilic. So, that the water can spread over the surface and coat it uniformly and

wetted. For this reason, a compound known as a surfactant is used. Surfactant stands for surface active agents. And, these molecules have two ends; one end is polar or hydrophilic and, the other end is non polar or hydrophobic.

For example, Triton X-100. Here you can see these two ends (slide above), which are in different colors. The red end is the polar hydrophilic end and the hydrocarbon chain that you see on the other end is the non polar hydrophobic part. So it has hydrophilic head, or the polar head, and a non polar or hydrophobic tail.

Now, when you add the surfactant in small concentrations, the surfactant molecules can get attached to the particle surface. And, now that this surfactant is present over the surface of the particles, the water can easily get attached to the particle surface with the help of this hydrophilic heads which are extended towards the water. So, this is how the surfactant will help in wetting the particles with the liquid in which they are added.

Now, one thing you must remember here is the concentration of the surfactant that is to be used, because this is a very key parameter to ensure that there is no overdose of the surfactant.

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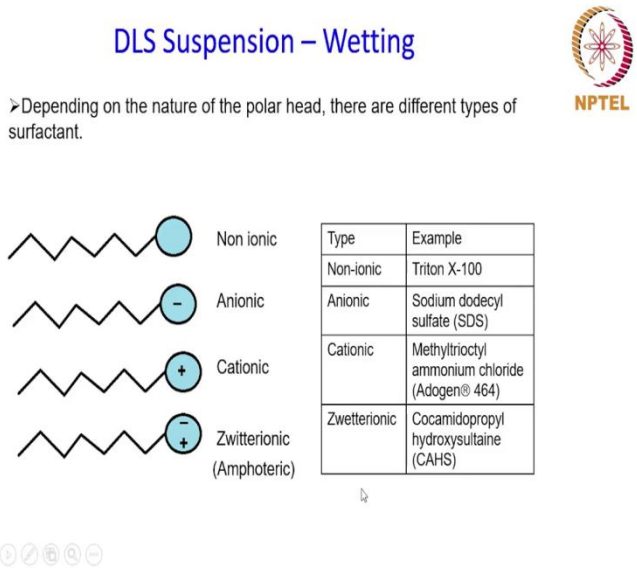

Let us see the different types of surfactants. Depending on the nature of the polar head, there are primarily four types, these are as follows.

1. Non ionic where there is no charge in the polar head.

2. Anionic where the polar head has negative charge.
3. Cationic where it has positive charge at the polar head.
4. Zwitterionic or amphoteric, which can have both positive and negative charge depending on the pH of the solution.

So, here are some examples of different types of surfactants. Triton X-100 is a non ionic surfactant. Sodium dodecyl sulfate or SDS is anionic. The compound which goes by the trade name Adogen 464 is cationic. Similarly CAHS is zwitterionic.

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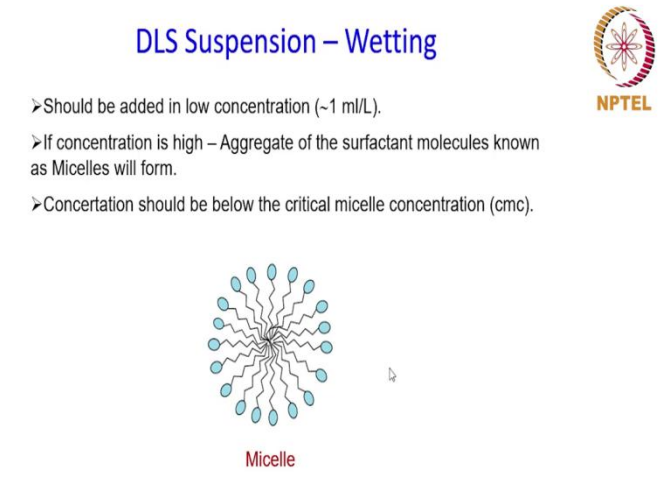

I mentioned about the importance of the concentration that you need to maintain when the surfactants are added. They should be always added in low concentrations. For example, a typical concentration could be 1 ml per liter of the solution.

So, what is going to happen if you have high concentration? That can be understood from this particular image over here (above slide), where you can see lot of the surfactant molecules coming together and forming an aggregate. If the concentration is high, instead of attaching to the particle surface, the surfactant molecules would rather attach to each other and form an aggregate. And, such aggregates are known as micelles. In which the hydrophobic tail of the surfactant molecules orient towards the centre and these heads are oriented outward.

So, this kind of aggregates will form in the solution and it is not good for the particles as far as their wetting is concerned. So, therefore, the concentration should be always low when surfactant is added. And, there is a critical concentration beyond which these micelles form and that particular concentration is known as the critical micelle concentration or CMC.

So, CMC is the concentration of surfactant above which the micelles will form. And, therefore, when the surfactants are added in the DLS suspension, the concentration should be always below the critical micelle concentration. So, this is something that you need to keep in mind when you are preparing DLS suspension using surfactants.

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Now, once added into the solution the particles would tend to form aggregates, because of the attractive Vander Waal forces between them. And, therefore, the next important thing in making DLS suspension is to ensure that the particles are suspended without forming agglomerates to be able to scatter effectively.

So, in order to break these agglomerates, energy has to be applied. For example, the suspension can be subjected to ultrasonication, for a particular period of time with certain amount of energy which will ensure that the agglomerates, if there are any, will break and the particles will be suspended in the liquid individually and many modern instruments are equipped with in-line ultrasonicators to do the job and when you do the

ultrasonication, the applied energy has to be optimized and some instruments can even do that as well.

So, now, we are done with three important things out of the four that we listed in the beginning. That is selection of an appropriate solvent, then wetting of the powder particles by the solvent and then de-agglomeration of the particles in the suspension. Now, even if you do this de-agglomeration by ultrasonication, there are chances that the particles will agglomerate again, because the Vander Waal forces are always there to attract the particles to each other or them to form aggregates.

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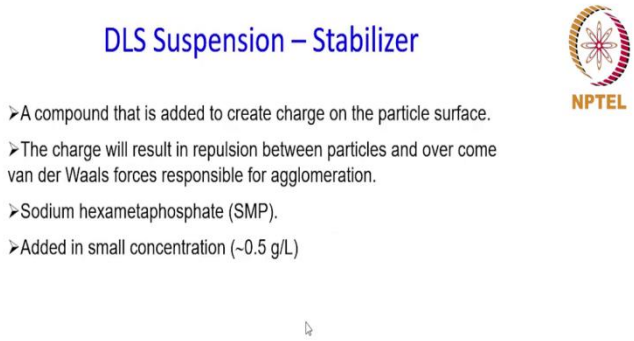

So, in order to avoid that, a compound is added to the suspension, to stabilize the dispersion and prevent de-agglomeration of the particles. Such compounds are known as stabilizers. Stabilizers are compounds which can create charge on the particle surface. And, due to the increased charge on the surface, the particles will now repel each other. This repulsive force can now overcome the Vander Waal forces, which are responsible for forming the agglomerates and as a result of that, the agglomeration of the particles will be prevented.

Sodium hexametaphosphate or SMP is a very commonly used stabilizer for making DLS suspension. And, the stabilizer is also added in small concentrations. For example, 0.5 gram in a liter could be a typical concentration. So, these are the four important things

that have to be followed in order to make a good suspension which can be used for DLS experiments to do particle size analysis.

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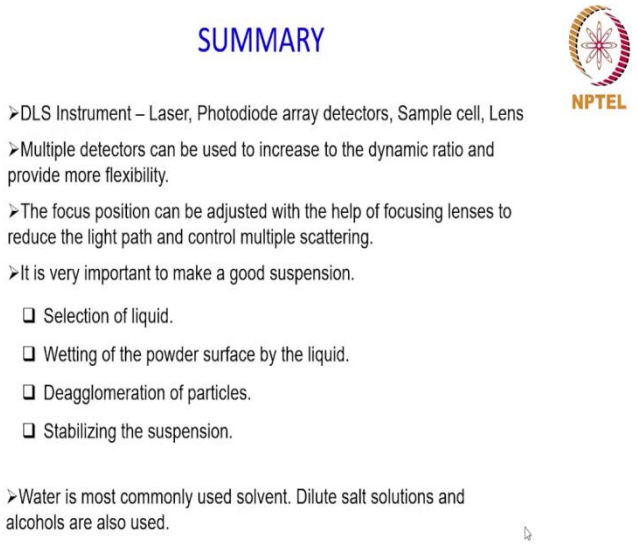

Let us take a moment to summarize this lecture. In this lecture we have learned about the DLS instrument, which basically consists of a laser as a monochromatic light source. And, then there are detectors (photodiode array detectors), which are used to capture the scattered light beam intensity.

And, then the sample which is a fluid containing the dispersed particles is send through the sample cell, which is placed in between the laser and a detector. And, as the particles come in the path of the light, it gets scattered and the scattered intensity is recorded on the detectors, and are sent to the computer to analyze that data using the autocorrelation function and from that the particle size is derived.

And, we have also seen that there can be multiple detectors in the same instrument. And, this will increase the dynamic ratio, which is the ratio of the largest particle size to the smallest particle size.

And, we provide more flexibility to the instrument in terms of handling different types of samples. And, we have also seen that the focus position from where the data is collected or the scattering volume can be adjusted with the help of focusing lenses. And, this can also be used to reduce the light path and control multiple scattering if there is a sample

where there are chances of multiple scattering. And, one thing that we have learned today is that it is very important to make a good suspension, because this is a key to the success of this particular technique.

If there is agglomeration or clustering of particles in the suspension, then the accuracy of the results will not be good. And, therefore, it is always recommended that these things are followed:

1. Selection of a particular liquid, which is good for suspending the particles.
2. Wetting of the particle surface by the liquid which is used for dispersing them and to make sure that there is no agglomeration of the particles.
3. Provisions to de-agglomerate the particles.
4. And, finally, the suspension has to be stabilized to make sure that the particles do not de-agglomerate again, and form those agglomerates.

So, these are the four important things that one has to follow in order to ensure that a good suspension is made.

Now, as far as the solvent or the liquid is concerned water is the most commonly used solvent, because it can disperse a wide range of particles as long as the particles do not dissolve in water. And, apart from water, dilute salt solutions and alcohols are also used. And, at times, in fact, salt solutions are better than pure DI water, in order to prevent agglomeration of particles. And, alcohols like IPA, ethanol, methanol etcetera can be used as the solvent for dispersing a variety of particles.

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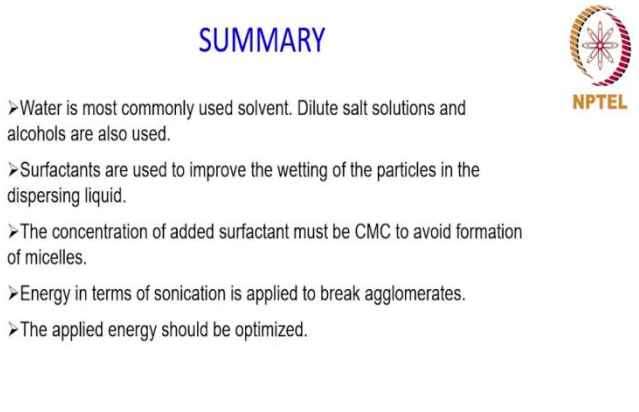

And, we have also seen that surfactants are used to improve the wetting of the particles in the dispersing liquid. Surfactants are actually surface active agents which help in wetting the particles with the help of the two ends; the hydrophilic and the hydrophobic ends. When the surfactants are added, you have to ensure that they are added in low concentrations, because if added in higher concentrations, they can form aggregates known as micelles.

And, there is a particular concentration beyond which these micelles form and this is known as the critical micelle concentration or CMC. And, therefore, the surfactant which is added in DLS suspension has to be below the CMC concentration.

And, in order to make sure that there are no agglomerates, energy is applied to break the agglomerates and most often this is done with the help of sonication. And, we have seen that most of the modern instruments are equipped with in-line sonicators which help in breaking the agglomerates.

Such equipments are also capable of optimizing the energy that is to be applied, because when you try and break the agglomerates with the help of energy like sonication, it is also important to optimize the energy that has to be applied to a particular type of sample. So, with that we come to the end of this class.

Thank you for your attention.