THE EFFECTS OF SAMPLE LOADING ON DYNAMIC LIGHT SCATTERING

When using dynamic light scattering (DLS) to measure particle size, the sample viscosity plays an important role in particle behavior and measurement calculation. In order to obtain the most accurate size results, high concentration viscosity effects need to be understood and corrected.

Introduction

When a particle is dispersed in a liquid medium, the solvent molecules will bump into and, if small enough, move it. To an observer the particle will appear to migrate randomly. This random behavior is called *Brownian motion*. Mathematically, Einstein determined that the motion is dependent on the size of the particle and the viscosity and temperature of the liquid. This dependence is described by a variable that contains all the information about the particle's movement: the diffusion coefficient. The diffusion coefficient is described by the Stokes-Einstein equation:

$$R_H = \frac{kT}{6\pi\eta D}$$

In the equation, *k* is a constant, *T* the absolute temperature, *η* the viscosity coefficient of the solvent, R_H the particle size expressed as hydrodynamic radius, and *D* the diffusion coefficient.

The temperature and viscosity are controlled parameters. The only unknowns are the diffusion coefficient and the particle size. The diffusion coefficient can be measured using dynamic light scattering. Therefore, once the diffusion coefficient is measured, the Stokes-Einstein equation can be solved for particle size.

Diffusion is inversely proportional to viscosity. For sample loading (i.e. particulate concentration), viscosity increases as the concentration of particles increases. Therefore, diffusion slows as the concentration increases.

Figure 1: LB-550V Dynamic Light Scattering Nanoparticle Size Analyzer

If *sample viscosity* affects diffusion, and diffusion provides particle size, then an accurately known viscosity is needed to accurately measure particle size.

Restricted Diffusion

Sample loading can change the physical properties of the sample. For example, when the concentration is increased, the viscosity of the sample will increase. When the concentration is increased, particle agglomeration can be induced. Or, when the concentration is increased, particle-particle interactions may increase. Each of these changes in physical properties can be measured and interpreted.

Imagine a particle in an infinitely dilute environment - it will diffuse freely and demonstrate random Brownian motion. As the concentration increases, the particle will begin to interact with other particles that have been loaded into the sample. As sample loading

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increases and as the concentration increases, the diffusion of individual particles is effected because of these interactions with neighboring particles.

These particle-particle interactions hamper the free random Brownian motion. In fact, the particles will begin to diffuse as an ensemble. This is known as *restricted diffusion* and is a property of high concentration samples.

There is proportionality between the increase in particle-particle interactions and the increase in viscosity from sample loading. Since the viscosity can be measured, it is easy to interpret the effects of sample loading on the Brownian motion of the particle.

Typically, no change in the polydispersity (distribution width) occurs with restricted diffusion – only the mean size will increase. This increase in mean size is a result of not properly determining the viscosity changes from sample loading. When the correct measured viscosity is used during the analysis, the dilute and concentrated results overlay perfectly. This measurable viscosity is the correct viscosity to be used for high concentration analysis.

This viscosity can be measured with the LB-550V (Figure 1) in real-time. There is no need for an external viscometer or messy rheological analysis. A quick and easy viscosity measurement can be performed and used for a subsequent size analysis.

Example of Restricted Diffusion and Sample Loading Limits

The particle size analysis for a lipid emulsion measured from 20 to 1.8 wt% provides an example of the importance of viscosity.

An inappropriate assumption that viscosity remains constant with changing concentration can lead to very poor size results. The multiple analyses shown in Figure 2 imply that particles either grow larger or agglomerate as concentration increases. However, Figure 2 hints at a viscosity problem as the multiple PSD appear to maintain a constant width

though the average size changes. This is a classic indicator of viscosity affecting the particle size measurement.
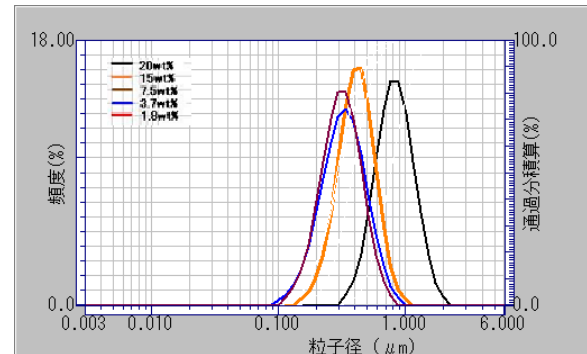

Figure 2: Multiple PSD using identical viscosity values, in this case the viscosity of pure water

Performing the same particle size analyses using the LB-550 with viscometer attachment shows a dramatic difference. The highest concentration sample has a viscosity four times larger than the lowest concentration sample. When the correct viscosities are used for the analysis, the results in Figure 3 show more physically realistic size values.
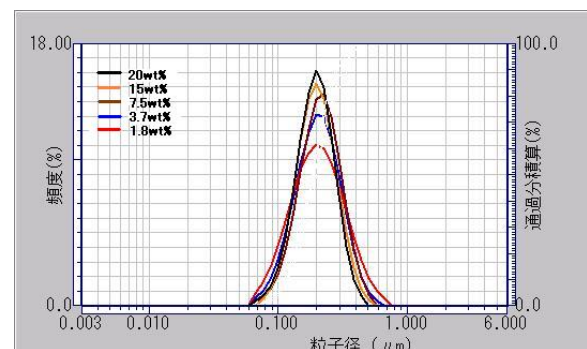

Figure 3: The same measurements, with bulk viscosity corrections, show the ideal result of a near perfect overlay

Example of Multiple Scattering and Sample Loading Limits

Restricted diffusion is not the only effect sample loading has on a measurement. The viscosity correction is a matter of interpreting the sample's scattered light signal, but sample

loading also affects the quality of the measured signal. There is an upper limit to particulate concentration before multiple scattering begins. The effect may be seen by plotting concentration against the detector's voltage (incident light induces a voltage via the photoelectric effect).

Figure 4 shows a comparison of concentration (x-axis), signal strength (1st y-axis) and viscosity (2nd y-axis). The graph shows that voltage decays and viscosity spikes above 20 wt%. This is the multiple scattering region and measurements from this region can not be completed. When light is lost into the system because of multiple scattering, the limits of concentration have been reached.
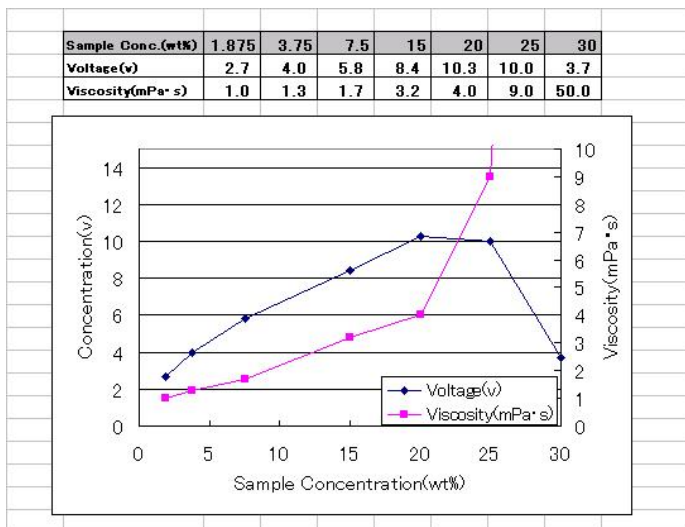

Sample Conc.(wt%)	1.875	3.75	7.5	15	20	25	30
Voltage(v)	2.7	4.0	5.8	8.4	10.3	10.0	3.7
Viscosity(mPa·s)	1.0	1.3	1.7	3.2	4.0	9.0	50.0

Figure 4: The relationship between sample loading and viscosity, and sample loading and signal strength. Multiple scattering begins above 20%

The signal strength increases with increasing concentration up to this same point. Accurate, high quality size measurements may be acquired at any concentration below the multiple scattering threshold so long as the change in viscosity with sample loading is included.
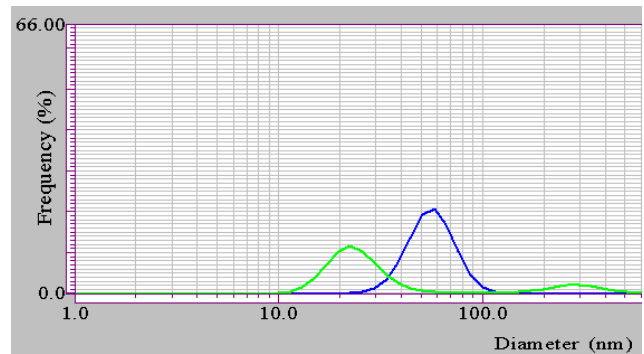

Figure 5: Colloidal silica measured at maximum sample loading (green) and diluted (blue). The green result suffers from multiple scattering. Note how the peak both shifts locations and broadens. Multiple scattering is always interpreted as a smaller size.

Summary

The HORIBA LB-550 nanoparticle size analyzer uses the dynamic light scattering method to measure the diffusion coefficient of a system. The diffusion coefficient may be affected by sample loading conditions.

Sample loading alters the viscosity which, in turn, requires a measurement of its own to correctly interpret the scattered light signal. This measurement may be performed with a viscometer accessory for the LB-550.

Sample loading also has a natural upper limit where multiple scattering begins and the scattered light signal is lost into the system. Simple tests can be performed to identify the concentration limit and remove that as a possible source of error.

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