VISCOSITY EFFECTS IN DYNAMIC LIGHT SCATTERING MEASUREMENTS

Dynamic light scattering measurement of particle size is strongly influenced by the viscosity, both in the calculation and in how the sample behaves. Care must be taken to provide correct values for viscosity and to prepare the sample so that the viscosity does not unduly influence the results.

Dynamic light scattering (DLS) actually measures the translational diffusion of particles due to Brownian motion. The relationship between the diffusion coefficient and particle size can be expressed by the following Stoke-Einstein equation: $D = kT / (3\pi\eta a)$ where k is the Boltzmann constant, T the absolute temperature, η the viscosity coefficient of the solvent, a the particle size, and D the diffusion coefficient.

If a particle is free to exhibit Brownian motion, its size can be related to the viscosity of the fluid, as indicated in the above formula. When the temperature at the time of measurement and the viscosity of the dispersant are known, it is possible to determine the particle size by measuring the diffusion coefficient.

The viscosity required is the dynamic viscosity at zero shear rate.

<u>Limits to Dispersant Viscosity</u>
However, if the Brownian motion of a particle is restrained, i.e., the viscosity of a solvent is high enough to prevent the particle from moving under the force exerted by the thermal movement of any surrounding solvent molecules, the particle size can no longer be accurately correlated to the viscosity of the solvent.

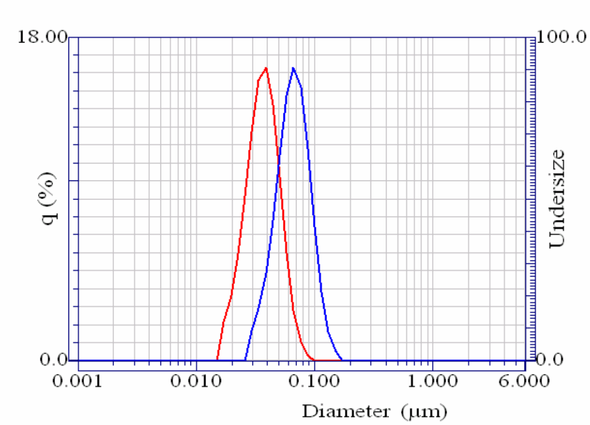
Although it varies depending on the type of dispersant employed, the fluid viscosity up to which these variables can be related to each other is empirically considered to be 3mPa/s (milli pascal/sec) (cP centipoise). Samples with higher viscosities can be measured and calculated, but consideration must be given to how higher viscosity affects the Brownian motion of the particles.

Fluids having a viscosity of 3 mPa.s or greater are frequently fluids known as non-Newtonian, in which the particles are placed in such a suppressive condition that they are not allowed to exhibit free Brownian movement. As a result, findings obtained from samples measured in this condition may not be reliable. The software of the viscometer version of the LB-550 is programmed in such a manner that, when the viscosity reading exceeds 3 mPa.s, a message will be displayed indicating that it has reached the critical viscosity. However, data collection and processing can be continued at higher viscosities.

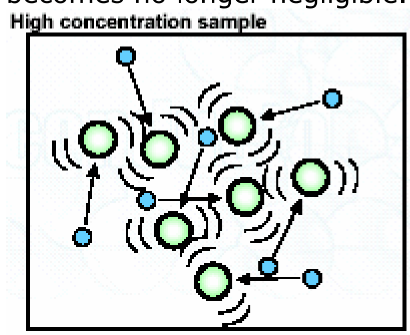
Horiba LB-550V Dynamic Light Scattering Particle Size Analyzer

What is a Newtonian fluid?
Newtonian fluid can be defined as a fluid in which the rate of strain (shear velocity) is proportional to the shear stress. Samples which indicate the same viscosity at the same temperature and pressure, irregardless of the magnitude of the rate of stress and shear strain, are classified as Newtonian fluids.

Importance of accurate viscosity values
The effect of an error in measurement or entry of the viscosity value in the equation can be quite significant. The example below shows the results of an analysis of a pigment dispersed in water. The data was analyzed using a viscosity of 1.0 (blue graph) and 2.0 mPa·s (red). The data can be seen to shift from a median value of 350nm to 700nm, a 100% difference due solely to changes in the viscosity. Accurate measurements require accurate viscosity information.



Effects of Particle Concentration
Calculations based on the dynamic light scattering theory assume an ideal system in which there are no substances around a particle that hamper its motion. In this case, the use of the pure dispersant viscosity would give accurate results. In reality, however, the probability of collision between particles increases proportionately with increasing concentration of the sample. It has been determined empirically that in most cases, when the concentration reaches percent order, the influence of this interparticle bombardment becomes no longer negligible.



The higher the concentration of a sample becomes, the less negligible does the presence of any other particles become. When this particle congestion occurs in the presence of other particles, it results in a decrease in the rate of movement of the particle and an increase in the viscosity of the dispersion.

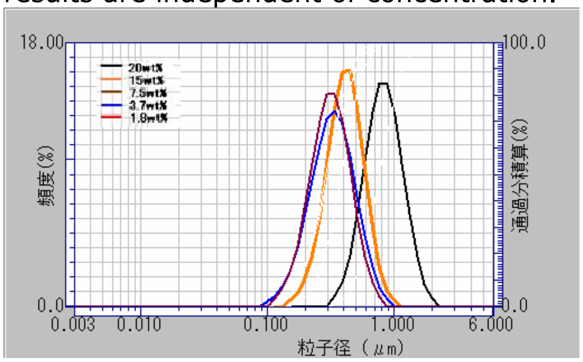
In this regime of high concentration, the dispersion behaves as a non-Newtonian fluid. It is difficult to analyze high concentration dispersions in their natural states, without either diluting them to reduce the viscosity to a level at which their particles exhibit Brownian motion, or increasing the temperature.

For this type of system, the results of calculation based on measured viscosity have proven closer to the true size distribution than when the viscosity of the pure dispersant fluid is used for analysis.

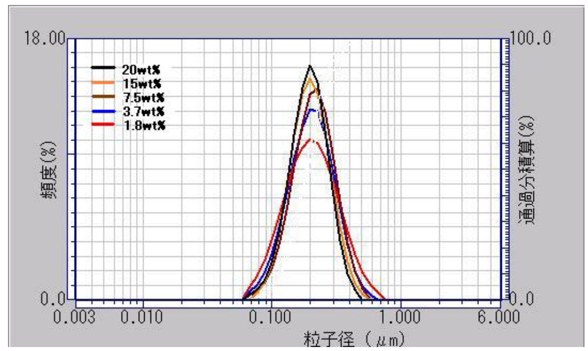
At higher concentrations or viscosities where we can no longer completely correct for these effects, the results will suffer from some error, but the results still serve as a relative measure of changes in the sample.

Example of measurement at different concentrations

Half-and-half (dairy) sample measured at concentrations from 20 wt% to 1.8 wt%. If the pure dispersant (water) viscosity is used, the reported results are dependent on concentration. When the viscosity of the dispersion is used to correct the results, the results are independent of concentration.



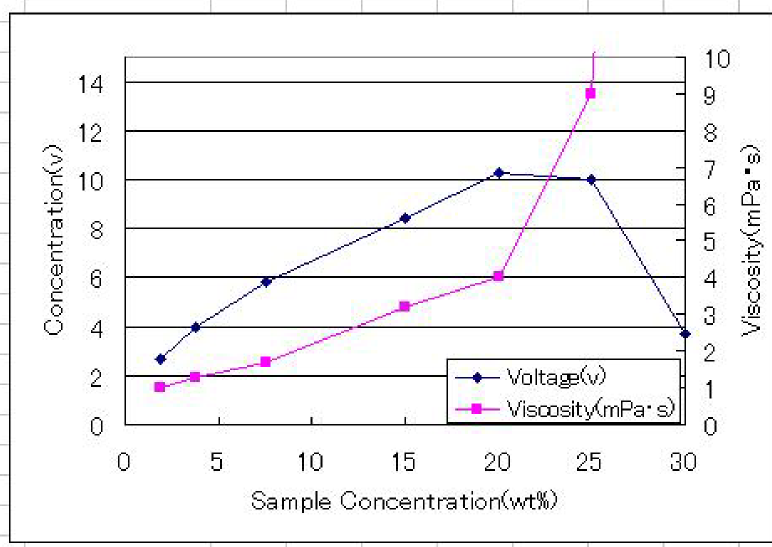
1. Viscosity of water



2. Dispersion viscosity

A comparison of sample concentration versus sample signal strength (voltage) and viscosity shows that above 20 wt%, the voltage increases non-linearly. This is the non-Newtonian region and measurements from this area can not be accurately completed. The signal strength increases with increasing concentration up to this same point. As the particle-particle interactions start to damp the Brownian motion, the particles are less able to scatter light.

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



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