

# THE IMPORTANCE OF SAMPLE VISCOSITY IN DYNAMIC LIGHT SCATTERING MEASUREMENTS

Dynamic Light Scattering (DLS), sometimes referred to as Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering, is a technique for measuring the size of particles typically in the sub micron region.

DLS is usually applied to the measurement of particles suspended within a liquid. The technique measures particle diffusion due to Brownian motion and relates this to the size of the particles. Brownian motion is the random movement of particles due to the bombardment by the solvent molecules that surround them. The parameter calculated is defined as the translational diffusion coefficient (usually given the symbol,  $D$ ).

The particle size is then calculated from the translational diffusion coefficient by using the Stokes-Einstein equation;

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

where:

$d(H)$  = hydrodynamic diameter

$D$  = translational diffusion coefficient

$k$  = Boltzmann's constant

$T$  = absolute temperature

$\eta$  = viscosity

In this equation the viscosity is required. This means that the temperature needs to be known accurately and be stable during the measurement because the viscosity of a liquid is related to its temperature.

The viscosity required for this technique is the *dynamic viscosity* of the sample at zero shear rate.

The accuracy of the particle size determined is directly related to the accuracy of the viscosity

measurement. This means that an appropriately accurate viscometer must be available for the accuracy of the particle size required.

## SAMPLE CONCENTRATION

The upper limit of sample concentration where DLS will give a concentration independent result, is determined by two effects; multiple scattering and particle-particle interactions.

To ensure that these effects are not present, many samples are routinely highly diluted. In such circumstances, the viscosity that is used can be assumed to be that of the diluent.

However such high dilutions are often not ideal and can affect the size distribution of many types of samples.

The Malvern High Performance Particle Sizer (HPPS) enables the measurement of much higher sample concentrations when compared with conventional 90° DLS instruments. This is because the HPPS uses non-invasive backscatter (NIBS®) detection optics. This optical configuration reduces the path length the light has to travel through the sample. This in turn reduces multiple scattering and absorption and hence, much higher concentrations can be measured.

## PARTICLE-PARTICLE INTERACTIONS

One of the effects of particle interactions in a sample is an increase in viscosity. Using the sample viscosity rather than the dispersant viscosity will compensate for these interactions to give a concentration independent result up to usually 1vol% and sometimes much higher.

Use of the dispersant viscosity will give an incorrect answer.

## EXAMPLES

### 1) MICROEMULSIONS

Microemulsions are thermodynamically stable dispersions of one liquid phase in another. As their refractive indices are usually so similar, and their size is under 100nm, they are optically clear. They are typically prepared at high concentrations and it is often assumed that the viscosity of these samples should be that of the disperse phase. For example, if the continuous phase of the microemulsion is water, then it is incorrect to assume that the viscosity of the sample is that of water as it will usually be higher.

Table 1 shows the Z-average diameters obtained for a microemulsion sample at 25°C assuming the viscosity of water (i.e. 0.89cP) and the corrected z-average diameter obtained with the actual sample viscosity (1.85cP).

As can be seen from the Stokes-Einstein equation, there is a direct relationship between viscosity and particle size. In the example discussed here, there is a 48% error in the viscosity used for the measurement and this gives a 48% error in the z-average diameters obtained.

## 2) PIGMENTS

Table 2 summarises the results of measurement of a magenta pigment dispersed in toluene at 2%w/v, at least 100 times the concentration where measurement is possible with conventional 90° DLS systems. The first set of results with an average of 420.6nm, assumed that the viscosity of the sample was that of toluene. (0.557cP at 25°C).

However the concentration of particles in the sample resulted in an increased sample viscosity and this was measured to be 2.185cP at 25°C.

The result of 107.3nm using this viscosity is within 1% of the measurement made at the high dilutions required for conventional DLS measurements.

The error of a factor of four in the size is seen to track the four fold error in assuming that the dispersant viscosity could be used.

## CONCLUSIONS

Using the dynamic viscosity at zero shear rate will extend the range of sample concentrations that can be measured, giving a concentration independent size.

At higher concentrations, where inclusion of the sample viscosity no longer compensates for particle/particle interactions, the result can be used as a monitor to track changes in the sample.

<i>Run Number</i>	<i>z-Average Diameter Assuming Viscosity of Water (nm)</i>	<i>z-Average Diameter obtained with correct sample viscosity (nm)</i>
1	92.5	44.5
2	91.6	44.1
3	91.8	44.2

**Table 1:** Results obtained for a microemulsion sample showing the effect of using the incorrect viscosity value

<i>Run Number</i>	<i>z-Average Diameter Assuming Viscosity of Toluene (nm)</i>	<i>z-Average Diameter obtained with measured sample viscosity (nm)</i>
1	420.1	107.1
2	422.5	107.7
3	419.3	106.9

**Table 2:** Results obtained for a magenta pigment dispersed in toluene showing the effect of using the incorrect viscosity value

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