Determining Dispersant Viscosity Using Dynamic Light Scattering

PARTICLE SIZE

Introduction

Dynamic Light Scattering (DLS) is a non-invasive technique for determining the size of particle suspensions or molecular solutions. The technique measures the translational diffusion coefficients of the particles or molecules as they undergo random, Brownian motion [1-3]. The diffusion coefficients are converted into hydrodynamic sizes 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 and η = viscosity.

The direct relationship between the viscosity value defined in the measurement set up and the hydrodynamic size obtained highlights the importance of the accuracy of the viscosity value used.

For dilute sample concentrations, the viscosity value can be considered to be that of the dispersant. However, if the dispersant viscosity is modified by, for example, the addition of polysaccharide or polymer, the increased viscosity of the modified dispersant needs to be accurately determined for accurate size results to be obtained.

The viscosity of the dispersant can be measured on an appropriate viscometer. However, an alternative method is to use dynamic light scattering measurements. As the DLS technique measures the diffusion speed of molecules or particles undergoing Brownian motion, which depends on the viscosity of the medium, a useful method of determining the appropriate viscosity value is to dope a dispersant with a known size of polystyrene latex standard, then instead of calculating the latex size using a known viscosity, calculate the viscosity from the known latex size.

This application note summarizes measurements made on a series of sucrose solutions of increasing concentration where a polystyrene latex of known size was doped into each sample. Comparison of the results obtained allows for the determination of the dispersant viscosity.

Experimental

Sucrose solutions of 5, 10, 15, 20, 25, 30 and 35% w/v respectively were prepared in ultra pure water and filtered through Whatman Anotop 0.02µm pore size filters.

10µl of a 150nm polystyrene latex obtained from Duke Scientific (Palo Alto, US) was added to 990µl of the appropriate sample. Comparison of the size obtained for the latex dispersed in sucrose (using the viscosity of water in the measurement set up of the instrument software) with the size obtained for the same latex dispersed in 10mM NaCl (the true hydrodynamic diameter), allows for the determination of the viscosities of the sucrose solutions. Measurements were made in 10mM NaCl in order to suppress the electrical double layer according to the International Standard ISO22412 [2].

Measurements of all samples were made on a Malvern Zetasizer Nano S at a detection angle of 173°. The Nano S uses a 4mWHe-Ne laser operating at a wavelength of 633nm. All measurements in this study were taken at a temperature of 25°C. At least 3 repeat measurements on each sample were taken to check for result repeatability.

Results and Discussion

The success of the method discussed in this application note is dependent upon the amount of excess scattering produced by the latex compared to the dispersant. The choice of a suitable size for the latex used is important in ensuring that the scattering intensity is sufficiently increased above that of the dispersant.

In addition, it is important to check that the polydispersity index (PdI) of the latex dispersed in the dispersant does not significantly change as any increase in the PdI value would indicate that the probe particles are aggregating and that the dispersant is not compatible with the polystyrene latex being used as a doping agent. The polydispersity index values are very sensitive to the presence of aggregates or dust. A monodisperse sample such as the polystyrene latex used in this study would be expected to give a PdI value of less than 0.05.

Table 1 summarizes the derived count rates (the normalized count rates) in kilo counts per second (kcps) obtained for 10mM NaCl and the various sucrose concentrations with and without latex. These results illustrate that the small aliquot of latex doped into the samples (10µl of latex into 990µl of sample) has greatly increased the scattering intensities obtained by orders of magnitude, hence the scattering from the sucrose will have no effect on the result.

Table 1: A summary of the derived count rates (the normalized count rates) in kilo counts per second (kcps) obtained for the various sucrose concentrations with and without latex.

Sample	Derived Count Rates (kcps)	
	Without Latex	With Latex
10mM NaCl	23.5	446703
5% sucrose	107.7	535243
10% sucrose	159.0	495978
15% sucrose	228.3	454304
20% sucrose	238.5	469424
25% sucrose	258.2	401375
30% sucrose	289.6	446398
35% sucrose	297.0	453577

The results obtained for the 150nm polystyrene latex sample doped into 10mM NaCl and the various sucrose concentrations are summarized in table 2. Please note that the z-average diameters were obtained using the viscosity of water in the measurement set up of the instrument software. All the PdI values reported in table 1 are less than 0.05 indicating that the latex was not affected at any of the sucrose concentrations.

Table 2: The results obtained for a 150nm Duke Scientific polystyrene latex standard doped into 10mM NaCl at various concentrations of sucrose. The table contains the z-average diameter in nanometers (using the viscosity of water as the viscosity parameter), the polydispersity index values and the calculated viscosities.

Sample	Z-Average Diameter (nm)	Polydispersity Index	Calculated Viscosity (mPa.s)#
10mM NaCl	151.5	0.011	0.8872 (measured)
5% sucrose	180	0.015	1.054
10% sucrose	200.1	0.028	1.172
15% sucrose	222	0.017	1.300
20% sucrose	248.9	0.021	1.458
25% sucrose	283.2	0.014	1.658
30% sucrose	317.2	0.025	1.858
35% sucrose	359.9	0.017	2.108

The calculated viscosities for the various sucrose concentrations were determined according to the following equation:

$$\eta = \eta_{NaCl} \Big/ \left(D_{H(NaCl)} \Big/ D_{H(X)} \right)$$

Where η = calculated viscosity, η_{NaCl} = the viscosity of 10mM NaCl, $D_{H(NaCl)}$ = the z-average diameter of the latex in 10mM NaCl and $D_{H(X)}$ = the apparent z-average diameter of the latex in the appropriate sucrose concentration.

The viscosity required for DLS measurements is the viscosity that the particle being studied experiences as it undergoes Brownian motion. This is the most appropriate way of obtaining this information and is a valid technique as long as the latex being used is not being affected by the dispersant it is doped into and as long as the introduction of latex does not significantly alter the sample viscosity. In this study, such a small aliquot addition to each sucrose concentration would not be expected to affect the viscosity of the solutions.

Conclusions

This application discusses how dynamic light scattering measurements can be used to determine dispersant viscosities. The success of this method depends on using a suitable sized polystyrene latex to generate enough excess scattering and also to ensure that the polydispersity index values obtained are not increased due to the aggregation of the latex in the dispersant.

References

[1] R. Pecora (1985) Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy. Plenum Press, New York.

[2] International Standard ISO22412 (2008) Particle Size Analysis: Dynamic Light Scattering (DLS). International Organization for Standardization (ISO).

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