Micellar Water Characterization: A Laser Light Scattering Application

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Micellar waters are the trendy new facial cleanser that boasts its ability to clean skin without irritation. We present results from dynamic light scattering (DLS), phase analysis light scattering (PALS), and microrheology measurements of commercial micellar water formulations using the Brookhaven Instruments NanoBrook Omni system. The size and charge of the micelles may impact their performance and stability. This technology may provide a new way to easily characterize these formulations.

Introduction

A popular facial cleanser on the cosmetic market right now is micellar water. Many companies carry this product and tout its ability to remove dirt, oil, and makeup while not irritating skin. As seen in **Figure 1**, micellar water is applied to a cotton pad and then wiped across facial skin to remove impurities. The main ingredients of the commercial cleanser are water, surfactant, and moisturizer, with fragrance often added.

When an aqueous solution has a certain amount of surfactant molecules, micelles are formed. The hydrophilic heads of the surfactant molecules orient themselves toward the water molecules while the hydrophobic tails orient towards each other, avoiding contact with water. These spherical aggregates are widely used in drug delivery, cosmetics, water treatment, detergents, and more. Characterization of these micelles can help qualify their performance. One common way of characterizing solutions like these is using non-invasive laser light scattering. This technique can be used to measure particle size, charge, and rheological properties. Currently, it is not clear whether a qualification or characterization method of micellar water formulations has been established. The presence of micelles and the solution's dilute nature makes it a candidate for characterization by laser light scattering.

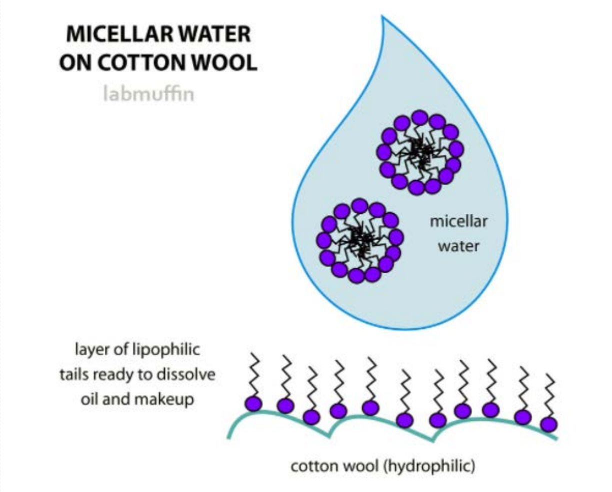

Figure 1: Micellar water behavior[1]

In this application note, four commercial micellar water formulations and one control formulation were measured by DLS, PALS, and microrheology and typical results are presented.

Material Method

Four commercial formulations of micellar water were obtained from a local retailer (Samples 1-4). One formulation was prepared with the three main ingredients of micellar water to serve as a control (Sample 5)[2]. All five

[1] Michelle. "What Is Micellar Water and How Does It Work?" *Lab Muffin Beauty Science*, 14 Sept. 2015, labmuffin.com/fact-check-what-is-micellar-water-and-how-does-it-work-an-update/.

[2] Carli, Belinda. "Creating Micellar Water." *Institute of Personal Care Science*, 28 June 2017, https://personalcarescience.com.au/free-tutorial/

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formulations were poured directly into standard cuvettes for measurement.

Analysis was performed using a NanoBrook Omni using dynamic light scattering (DLS) for particle size analysis, phase analysis light scattering (PALS) for zeta potential analysis, and microrheology for viscoelastic analysis, with the Particle Solutions software suite. Three DLS measurements, five PALS measurements, and three microrheology measurements of each sample were made to ensure repeatability and reliability of results.

Results

DLS

A baseline was established with preliminary measurements at the 90° angle and 5 µs first delay time. The measurement conditions were then improved by using the backscatter angle (173°) and 0.5 µs first delay time to be able to fully interpret particle sizes below 20 nm. The correlation function is the first graph to examine when interpreting the integrity of a DLS measurement. The decay should be smooth and flatten out to a zero slope. The presence of multiple decays in a correlation function confirms the presence of multiple size populations. As seen in **Figure 2,** all of the correlation functions have at least one smooth decay and flatten out. There is evidence of multiple decays for Samples 1-4.

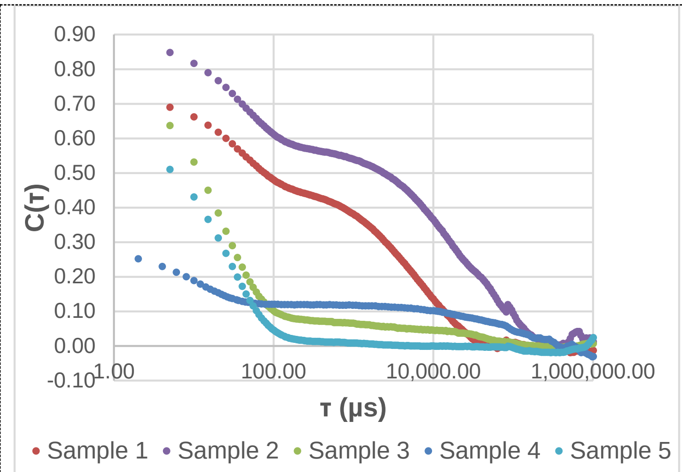

Figure 2: Correlation Function Overlay at 173° (0.5 µs first delay)

To then interpret the size populations present, the non-negatively constrained least squares (NNLS) algorithm within Particle Solutions was applied.

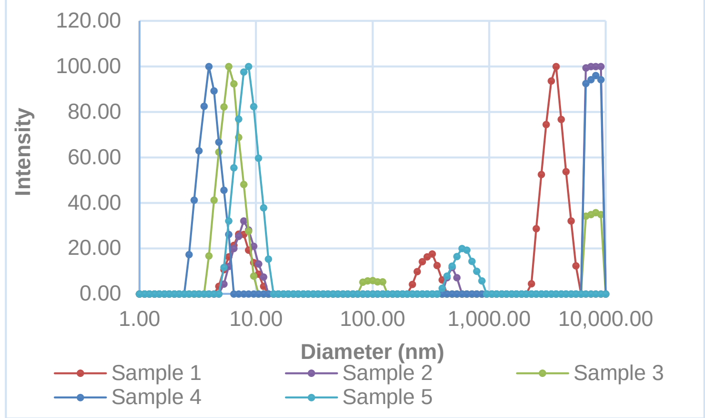

Figure 3: NNLS by Intensity Overlay

As seen in **Figure 3**, on an intensity-weighted basis, there are particles in the 10 nm range for all samples and most also have populations exceeding 1 micron. These data suggest the presence of small micelles as well as aggregates or other species.

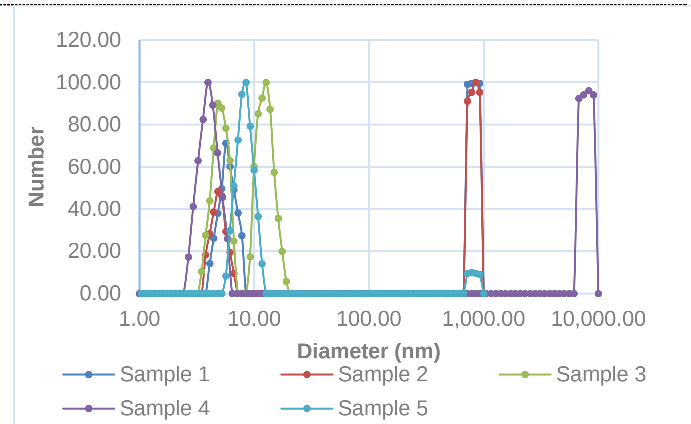

Figure 4: NNLS by Number Overlay

As seen in **Figure 4**, on a number-weighted basis, every formulation has a dominating 10 nm population. There are also fewer populations in the micron range as compared to the intensity interpretation. This suggests that these formulations have a high percentage of particles in the 10 nm range as compared to those in the micron range. Sample 3 only shows evidence of particles near 10 nm.

These data suggest the ability of dynamic light scattering to quantify size differences among micellar water formulations. This insight may be useful in the formulation process.

PALS

By applying a voltage to a suspension of charged particles, the mobility of the particles can be measured. This mobility value is then used to calculate zeta potential. Zeta potential is determined by the charge near the surface of the micelle.

Table 1 summarizes the zeta potential, mobility, and conductance results.

Sample	Zeta Potential (mV)	Mobility [(μ/s)(V/cm)]	Conductance (μS)
1	-14.12 ± 0.53	-1.10 ± 0.04	6095
2	-8.18 ± 0.90	-0.64 ± 0.07	6888
3	-0.49 ± 0.36	-0.04 ± 0.03	5851
4	-0.09 ± 0.15	-0.01 ± 0.01	1981
5	0.25 ± 0.38	0.02 ± 0.03	194

Table 1: Zeta potential results

Samples 1 & 2 are negatively-charged. Zeta potential magnitude can be used to characterize suspension stability. The larger the magnitude of the zeta potential, the more stable the suspension due to the electrostatic repulsion between particles.

The sign of the charge can also describe the behavior of the suspension and the particles. Dirt is typically positively charged; applying negatively charged micelles may improve the efficacy of the formula. Samples 3-5 are all neutrally charged. Since Sample 5 was the control that did not contain any stabilizers or additives, this suggests these additives would be useful in modifying the charge of the micelles. Either Samples 3 & 4 may not contain additives that affect the charge of the micelles, or the formulators are intentionally creating a neutrally charged suspension. In general, neutrally charged suspensions are prone to agglomeration of particles which can cause these larger particles to settle out of solution and no longer yield effective formulas.

The conductance value is directly related to the ionic strength of a solution. Samples 1-3 contain much more salt than Sample 4. Sample 5 was the control and did not have any salt added and that is reflected in the measured conductance value. Samples 1 & 2 had the highest ionic strength and the largest charge magnitude. These observations are consistent with the fact that salt concentrations affect both size and charge, as manifested by zeta potential, of micelles.

These data suggest the ability of zeta potential measurements to quantify differences across formulations that may be able to characterize stability and efficacy.

μRhe

Microrheology is used to determine the viscoelastic properties of fluids. Microrheology allows the measurement of these properties at much higher frequencies than a traditional rheometer. This experiment is simple as it uses the same principles of DLS. A probe particle of a known size is chosen and added to the solution of interest so that it dominates the scattering signal. The motion of this probe throughout the solution is tracked and used to calculate rheological properties.

An 820 nm diameter latex standard (Spherotech) was added to each sample as the probe particle. Three measurements were made for each sample. **Figure 5** shows an overlay of complex viscosity for one measurement of each sample.

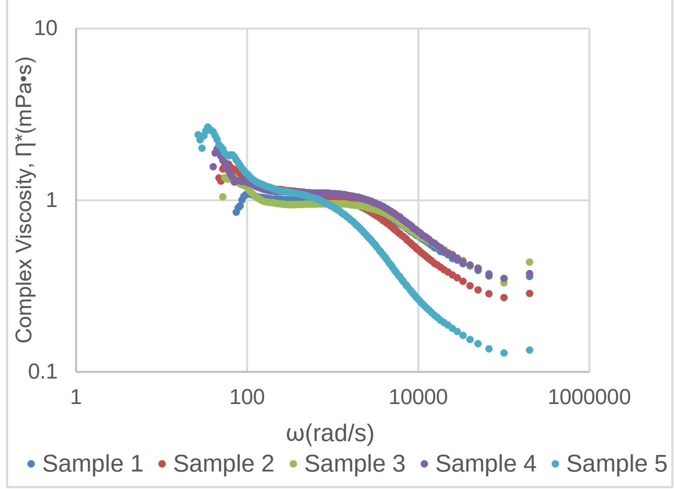

Figure 5: Complex Viscosity Overlay

The shape of the curve for all samples indicates *shear thinning*. It also supports its non-Newtonian behavior. This quality may be useful for micellar water since its method includes using force while wiping the face.

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Across all formulations, there are minor differences in complex viscosity. These data suggest the ability of dynamic light scattering measurements to characterize viscoelastic properties across formulations.

Conclusion

By performing particle size, zeta potential, and microrheological analyses, clear similarities and differences among commercial micellar water formulations were discovered. The presence of 10 nm particles along with particles in the micron size range support the presence of micelles as well as possible aggregates or other species. These size populations were easily characterized by DLS and could be useful in quality control and formulation to identify what populations are supposed to be present and what should be removed. The presence of charge differences, observed with PALS, could be useful in stability and efficacy characterization based on the expectations of the manufacturer. Consistent batch-to-batch stability could also easily be qualified with this method. The microrheological data could be used in addition to all of these methods for further qualification of formulas from batch-to-batch. Complex viscosity and other properties could play a role in the ease of application of the micellar water.

Based on this preliminary study, future work can be done to fully understand the valuable role light scattering can have for this product and industry.