Detection of the Onset of Aggregation as a Function of pH of Iron Oxide Nanopowder by Dynamic Light Scattering

By Lauren Szwast, Applications Specialist

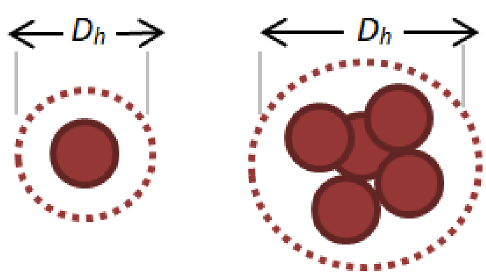
The automated measurement of particle size as a function of pH is fast and easy with the Brookhaven Instruments NanoBrook Omni and BI-ZTU autotitrator. Here, we demonstrate the effectiveness of these instruments to measure aggregation of Iron Oxide nanopowder with a change in pH.

Introduction

Industrial and academic applications that use iron oxide nanoparticles are vast. Of the nanomaterials, iron oxide has been recently drawing much attention from researchers due to its stability, low toxicity, and magnetic properties.[1] Given the great potential for applications using iron oxide, it is beneficial to understand the effect of chemical changes to the surface of the nanoparticle. The aim of this study was to determine the onset of aggregation due to a change in pH.

Aggregation can occur due to changes in pH or temperature. When nanoparticles coalesce, they appear larger as shown in Figure 1. The hydrodynamic diameter, sometimes referred to as the effective diameter, is the diameter of a sphere that diffuses at the same rate as the particle being measured. The hydrodynamic diameter is not only dependent on the size of a particle core, but also the ionic strength of the medium. Outer layers such as surfactants on the surface of the particle will also change a particle's apparent size. The apparent size of the particle will also change with any change to the surface of the particle that affects the diffusion rate.

Figure 1 Representative increase in Hydrodynamic Diameter as Nanoparticles Aggregate



Materials and Methods

A suspension was prepared by adding 5.8 mg of commercially available iron oxide nanopowder Fe_3O_4 from Skyspring Nanomaterials to 20 mL of filtered MilliQ water. A 0.2 µm filter was used to filter the MilliQ water 3 times. The suspension was then sonicated in a Branson 2800 low energy sonic bath for five minutes. A Brookhaven Instruments BI-ZTU Autotitrator was loaded with four reagents: Fluka Analytical 0.1 M nitric acid, 1 mM nitric acid, 0.1M potassium hydroxide, and 1 mM potassium hydroxide.

The suspension was tested from a pH of 2 to 12 in 2 pH unit steps. The solution was analyzed at each pH, 5 times, each, for 5 minutes per run using dynamic light scattering (DLS).

Measurements were made using Brookhaven Instruments NanoBrook Omni Particle Size Analyzer and BI-ZTU Autotitrator and were analyzed using Particle Solutions, version 3.5 software. The effective diameter of iron oxide nanoparticles was determined from pH 2 to 12 in 2 pH unit steps in a suspension of MilliQ water. Iron oxide nanoparticle aggregates in suspension were examined by plotting the measurements collected over the ranges of tested pHs.

Results and Discussion

Dynamic light scattering (DLS) technique can detect the effective diameter or size of a nanoparticle and an autotitrator can help automate the process so that changes in particles' apparent size can be detected as a function of pH. Table 1 demonstrates the average effective diameter of iron oxide nanoparticles was in the size range of 1023 to 1029 nm on an intensity weighted basis, in acidic solution. The effective diameter of iron oxide nanoparticles was in the size range of 4258 to 4520 nm on an intensity weighted basis, in basic solution.

Table 1 Representative Effective Diameter with Change of pH

Effective Diameter with Change of pH	
pH	**Effective Diameter**
2	1029 nm ± 102
4	1023 nm ± 143
6	1157 nm ± 200
8	4258 nm ± 1463
10	3243 nm ± 740
12	4520 nm ± 2316

Brookhaven Instruments
750 Blue Point Road
Holtsville, NY 11742
Phone: +1 (631) 758-3200
Fax: +1 (631) 758-3255
E-mail: info@brookhaveninstruments.com
Web: brookhaveninstruments.com

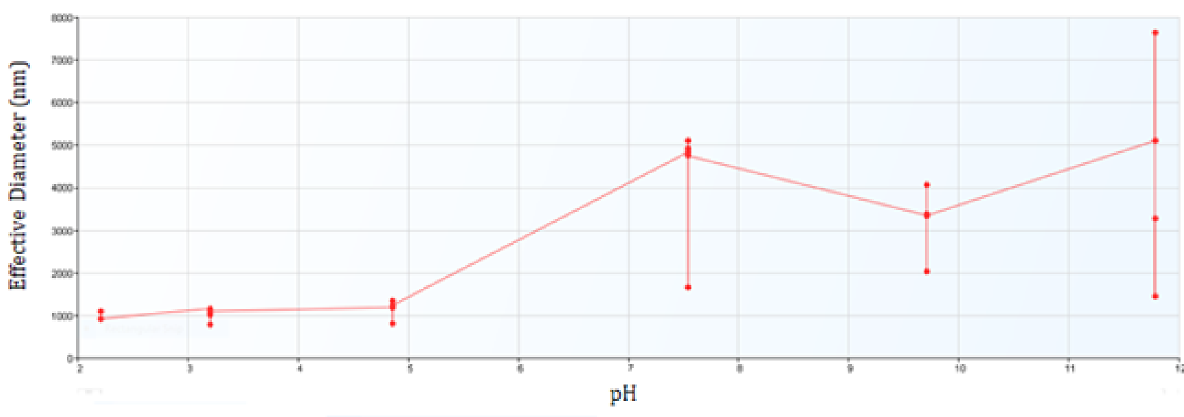
Table 2 shows that the average polydispersity of iron oxide nanoparticles was 0.329 to 0.361 in acidic solution. The polydispersity was 0.315 to 0.334 in basic solution. Therefore, the change in the width of the distribution is fairly constant.

Table 2 Representative Polydispersity with Change of pH

Polydispersity with Change of pH	
pH	**Polydispersity**
2	0.329 ± 0.044
4	0.361 ± 0.035
6	0.329 ± 0.043
8	0.315 ± 0.055
10	0.297 ± 0.069
12	0.334 ± 0.107

Figure 2 shows the results of all measurements of the prepared suspension at different pH values. This suggests that as the pH value increases, the effective diameter increases and the stability decreases. The stability decreases as the particles approach the isoelectric point. The onset of aggregation is apparent for iron oxide between pH 4 and 8, the same region where the zeta potential nears zero.

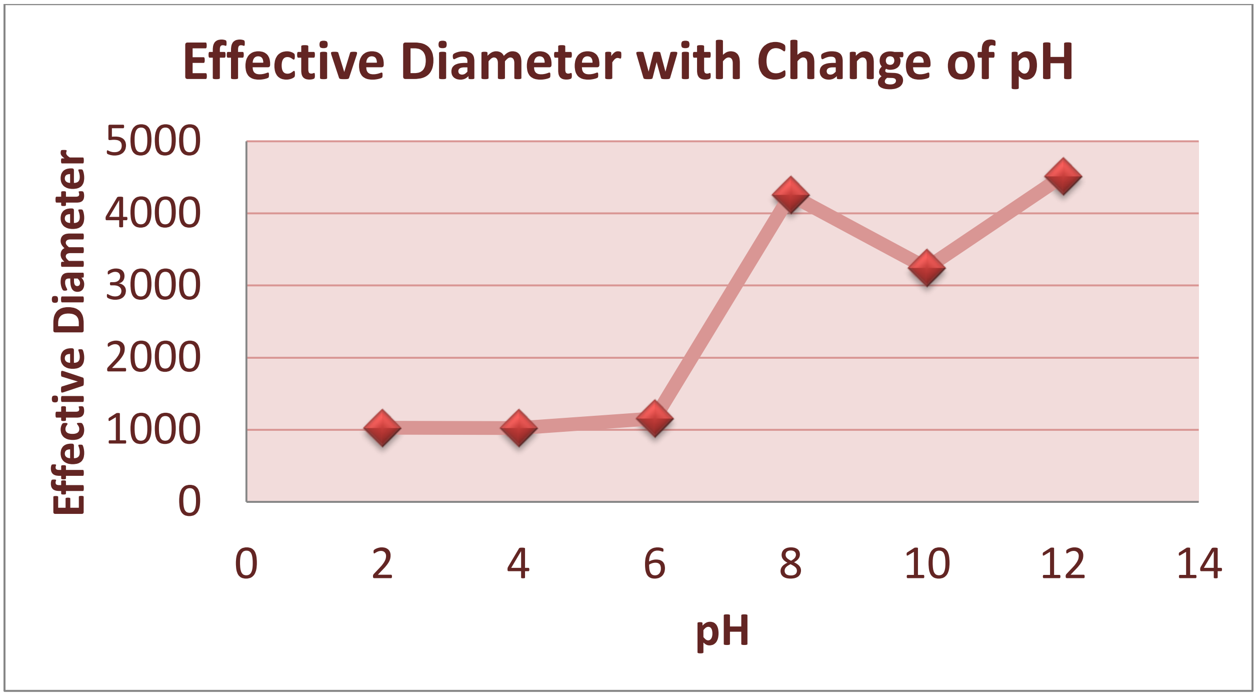
Figure 2 Effective Diameter of Iron Oxide from pH 2 to 12



Brookhaven Instruments
750 Blue Point Road
Holtsville, NY 11742
Phone: +1 (631) 758-3200
Fax: +1 (631) 758-3255
E-mail: info@brookhaveninstruments.com
Web: brookhaveninstruments.com

Figure 3 shows that as the pH increases, the effective diameter of the particles becomes larger.

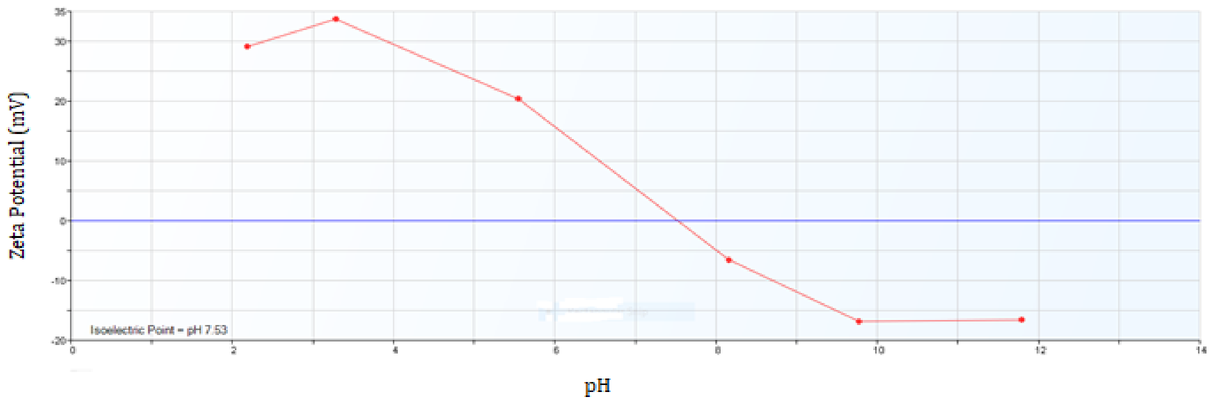
Figure 3 Average Effective Diameter with Change of pH



The isoelectric point for iron oxide is at pH 7.5. This is the range where particle aggregation occurs due to low charge on the particle surface. Measurement of zeta potential with change of pH further supports particle aggregation at the same pH range and can be done using the same Brookhaven Instruments Omni and BI-ZTU.

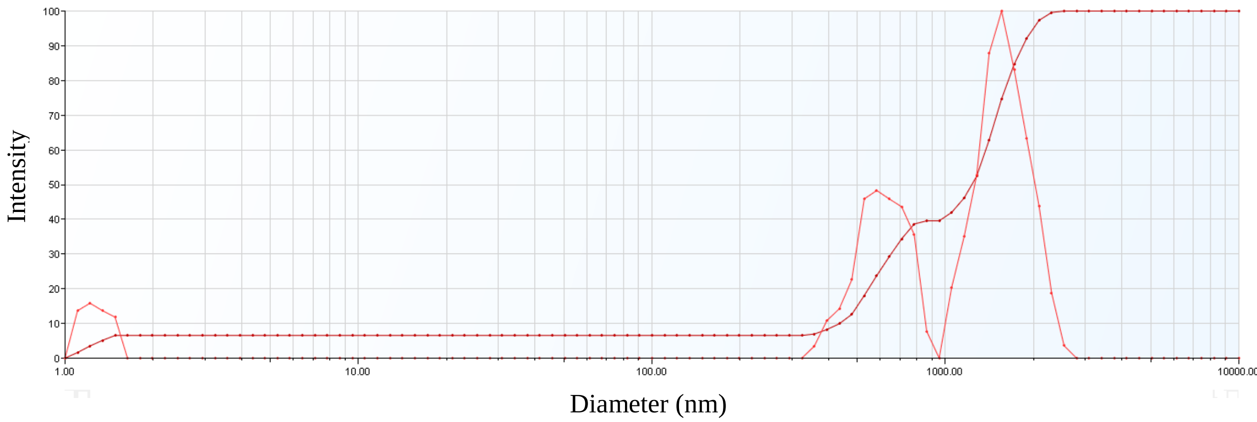
Brookhaven Instruments
750 Blue Point Road
Holtsville, NY 11742
Phone: +1 (631) 758-3200
Fax: +1 (631) 758-3255
E-mail: info@brookhaveninstruments.com
Web: brookhaveninstruments.com

Figure 4 Zeta Potential of Iron Oxide from pH 2 to 12

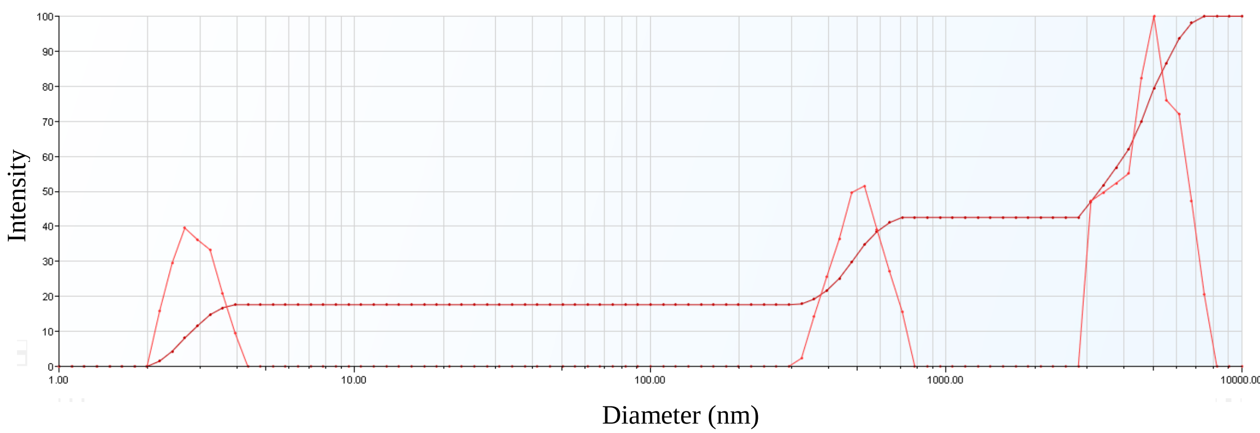


The multimodal size distribution shows multiple particle populations in the sample. The iron oxide nanopowder had 3 particle size populations. The particles shifted in size as they aggregated, and 3 populations remained from pH 2 to pH 12. As shown in Figure 5, the multimodal size distribution shown in the upper graph is at pH 2 and the multimodal size distribution in the lower graph is at pH 12.

Figure 5 Multimodal Size Distribution Comparison at pH 2 and pH 12



pH 2



pH 12

Conclusion

The Brookhaven Instruments NanoBrook Omni Particle Size Analyzer and autotitrator are useful tools to detect the onset of aggregation of iron oxide nanoparticles because of their ease of use and quick sample preparation. This general method can be applied to many types of nanomaterials and can be customized to particular applications. Different parameters such as time dependence or additive titrations like salts or dispersing agents can be incorporated. Many industries can benefit from the ease of use and efficiency of the NanoBrook Omni together with the ZTU.

1. Wu, Wei, et al. "Designed Synthesis and Surface Engineering Strategies of Magnetic Iron Oxide Nanoparticles for Biomedical Applications." *Nanoscale*, vol. 8, no. 47, 2016, pp. 19421–19474., doi:10.1039/c6nr07542h.