Controlling the Swelling of Polymer Coated Gold Nanoparticles

Impact of temperature and ionic strength on the cloud point, measured with a Cary 3500 Multizone Peltier UV-Vis spectrophotometer

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Introduction

Nanoparticles have been incorporated into an enormous number of technologies and industries over the last few decades, including cosmetics, electronics, and biomedical applications (*1,2*). The extensive use of such materials highlights the importance of understanding the properties and key influencing factors dictating the use of nanoparticles.

Gold nanoparticles (GNPs) have been explored extensively, with many exciting and novel technologies, and strategies emerging (*1-3*). The surface properties and suspension stability of GNPs are important for both application development and manufacturability. As such, techniques that facilitate the study of the stability mechanisms of nanoparticle and colloidal particle suspensions are highly relevant for researchers in this field.

In this study, the impact of both temperature and ionic strength on the swelling state of poly N-isopropylacrylamide (PNIPAM)-coated gold nanoparticles was examined. Note that the gold nanoparticles are referred to as AuPNIPAM in this document. Temperature and ionic strength are two parameters that can influence the swelling state of the polymers. The swelling state can dictate the extent of the steric stability imparted by the PNIPAM polymer coating. The polymers may become more strongly attracted to other neighboring polymer chains than to the surrounding water molecules (they become more hydrophobic) at a certain temperature or ionic strength. This effect is referred to as the cloud point of a polymer. If the cloud point is met or exceeded, the polymer coating resides closer to the gold nanoparticle, decreasing the hydrodynamic radius. This results in closer interactions with neighboring particles and aggregation due to the overwhelming Van der Waals (VdW) forces.

As the polymer-coated particles aggregate, they attenuate incident light. Therefore, the cloud point can be measured as a function of iconic strength or temperature using UV-Vis spectroscopy. This measurement is done by monitoring the transmission of light (measured as absorbance) at a specific wavelength.

Experimental

Sample and standard solutions

The AuPNIPAM was synthesized by seeded precipitation polymerization. This process consists of two steps:

1. The synthesis of spherical gold nanoparticles by citrate reduction (*3*).
2. The seeded growth of a PNIPAM/cross-linker shell on the surface of the nanoparticles to form a core-shell particle (*4*).

The procedure for each step is outlined in each of the respective references, indicated earlier.

The polymer was synthesized with 15 % N,N'-methylenebisacrylamide cross-linking monomer. Its deswelled diameter is ≈ 220 nm and its swelled diameter is ≈ 340 nm (*3, 4*).

A concentration of a stock solution was set to 0.05 %m/v by diluting a known mass of freeze-dried particles in Milli-Q filtered water, following synthesis, and purification. A background potassium chloride (KCl) concentration of 0.100 M was also established, unless otherwise stated.

Instrumentation

Cary 3500 Multizone Peltier UV-Vis spectrophotometer was selected for this study due to its unique capabilities in accurately controlling and measuring the sample temperature. The Cary 3500 has temperature ramping capabilities with highly accurate monitoring of sample temperature. A thin and flexible temperature probe can be positioned in the sample solution, next to the instrument light beam. The light beam is being used to measure the light attenuation (reported as absorbance) of the sample at that point. The position of the temperature probe ensures that the reported temperature of the sample accurately represents that of the portion of the sample being measured. The temperature accuracy of the temperature probe is ± 0.25 °C, allowing a high level of confidence to be attributed to the data collected.

The Cary 3500 can measure seven samples simultaneously, allowing several parameters to be explored at the same time, under identical conditions. Using the multiple temperature zone (multizone) capabilities of the Cary 3500, it is possible to perform four individual experiments at different set temperatures, simultaneously.

Identifying the wavelength to use for monitoring cloud point

To determine the optimum wavelength for monitoring the change in light attenuation of the sample, the absorbance of the sample was measured across a wavelength range at 10 different temperatures. The settings shown in Table 1 were used. 2.5 mL of AuPNIPAM was transferred to a 3.5 mL quartz cuvette and a temperature probe was fitted into the cuvette.

Table 1. Instrument parameters.

Parameter	Setting
Wavelength Range (nm)	1000 - 200
Spectral Bandwidth (nm)	2
Signal Averaging Time (s)	0.02
Data Interval (nm)	1
Stirring Speed (rpm)	None
Temperatures (°C)	30, 31, 32, 34, 35, 36, 37, 38, 39 and 50

Identification of the temperature-induced cloud point of AuPNIPAM

To determine the cloud point induced by temperature change, 2.5 mL of AuPNIPAM was transferred to a 3.5 mL quartz cuvette and fitted with a temperature probe. The absorbance of the sample was measured at 450 nm as the temperature of the sample was increased from 25 -45 °C, using the instrument parameters shown in Table 2.

Table 2. Instrument parameters.

Parameter	Setting
Wavelength (nm)	450
Spectral Bandwidth (nm)	2
Signal Averaging Time (s)	0.02
Data Interval (nm)	1
Start Temperature (°C)	25
End Temperature (°C)	45
Temperature Interval (°C)	0.2
Temperature Ramp Rate (°C/min)	1
Stirring Speed (rpm)	500

Ionic strength influence on cloud point

To determine the cloud point induced by ionic strength, six AuPNIPAM suspensions at 0.0500 (%m/m) were prepared with KCl concentrations set to 0.0000, 0.0100, 0.0500, 0.0020, 0.0274 and 0.1000 M.

A temperature probe was fitted inside the cuvette holding the sample solution. The absorbance of the sample at 450 nm was measured as the temperature was increased from 25 to 45 °C, using the parameters shown in Table 3.

Table 3. Instrument parameters.

Parameter	Setting
Wavelength (nm)	450
Spectral Bandwidth (nm)	2
Signal Averaging Time (s)	0.02
Data Interval (nm)	1
Start Temperature (°C)	25
End Temperature (°C)	45
Temperature Interval (°C)	0.2
Temperature Ramp Rate (°C/min)	1
Stirring Speed (rpm)	500

Results and discussion

Effect of temperature on nanoparticle swelling

The optimum wavelength to determine the cloud point was identified by performing wavelength scans of the AuPNIPAM particles at incremental static temperatures (Figure 1). These scans were performed from 1000 to 200 nm to allow any variations in the swelling state due to temperature changes to be identified (Figure 1). The extinction was plotted, determined from the absorbance data collected via the Agilent Cary UV workstation software.

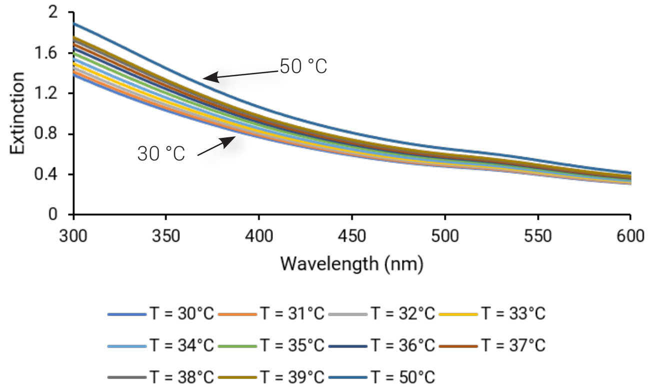

Figure 1. Wavelength scans of AuPNIPAM suspensions at incremental temperatures. The absorbance signal increase with temperature indicates the polymer coatings deswelling. Only 300 to 600 nm shown for clarity.

From Figure 1, it is clear the extinction of the AuPNIPAM samples increases as the temperature increases. The AuPNIPAM suspension has no salt (KCl) present, removing the possible influence of ionic strength and isolating the thermal changes as the only variable. At 0 M KCl, no nanoparticle aggregation is occurring. Any increased absorbance is due solely to thermally induced deswelling events. As the nanoparticles deswell, they become denser and hence scatter light to a greater extent.

Identification of the temperature-induced cloud point of AuPNIPAM

From the scans presented in Figure 1, 450 nm was selected as an appropriate wavelength to observe for further experiments. By observing a single wavelength, a clear signal can be used to observe response to changes to thermal conditions, allowing easy identification of changes in light attenuation (Figure 2).

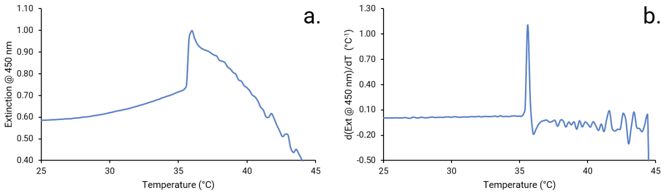

Figure 2. The (a.) thermal spectrum of 0.0500 % AuPNIPAM with a fixed KCl concentration of 0.1000 M with (b.) the corresponding first derivative plot.

To characterize the swelling and aggregation properties of the thermo-responsive AuPNIPAM nanoparticles, the sample temperature was increased, with absorbance being monitored at 450 nm. As the temperature increased from 30 to 35 °C, the polymer deswelled as it underwent a volume phase transition - directly proportional to the extent of scattering of visible light.

Figure 1 shows a slow increase in the absorbance reading, caused by an increase in light scattering due to the increased density of the AuPNIPAM nanoparticles. The dramatic change at 35.7 °C, as shown by the first derivative plot (Figure 2), indicates aggregation of the nanoparticles. The optical design, and close proximity of the Cary 3500 detectors to the sample allows the measurement of a large proportion of the light scattered by the nanoparticles. Gathering much of the scattered light improves the signal-to-noise ratio, allowing accurate measurements.

Ionic strength influence on cloud point

The influence of salt concentration on nanoparticle swelling was explored by measuring the absorbance of samples of differing ionic strengths while slowly increasing the temperature of the samples (Figure 3). Seven samples of different ionic strength could be analyzed at the same time (without moving the samples) due to the Cary 3500 capability for measuring multiple samples simultaneously. This capability offers considerable time savings, and ensures that no data points are missed, when compared to measuring each sample sequentially.

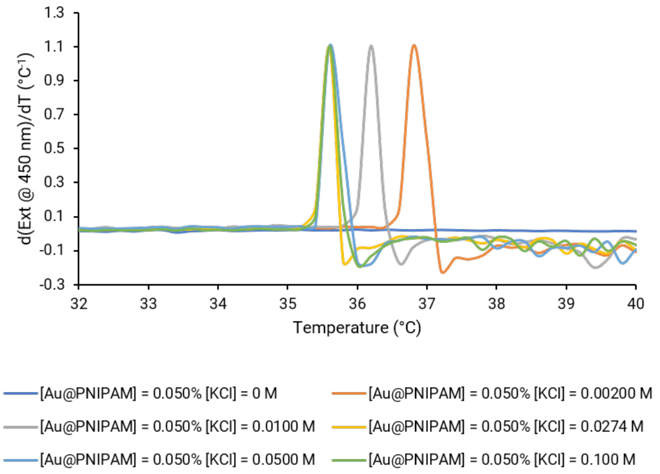

Figure 3. AuPNIPAM thermal ramp first derivatives of samples with differing salt (KCl) concentrations.

The peaks in the derivative of the thermal gradient curve can be used to determine the onset of particle aggregation. At 0 M KCl concentration, there is no aggregation (dark blue line in Figure 3). With salt concentration of 0.002 M (orange line in Figure 3), particle aggregation can be observed at 36.8 °C. Aggregation can be seen to occur at lower temperatures as the salt concentration is increased (Figure 3). At salt concentrations of 0.027 M and above, the onset of aggregation remains at 35.7 °C.

Understanding of the thermally induced aggregation point at different ionic strengths allows further exploration of the effects of salt and temperature on swelling state as well as the stability of the nanoparticles (Figure 4).

The ionic strength influence can be observed in Figure 4a to increase the density of the particles, resulting in the increased light attenuation, supporting the data shown in Figure 1. The extinction of the different salt concentration suspensions over a temperature range was measured. The temperature range used was known to be below the aggregation point. The influence of both the salt- and thermally- induced deswelling events can then be monitored and a linear model observed.

Further, as the salt concentration is increased, the extent of deswelling follows two distinct trends. For [KCl] < 0.03 M, the particles deswell with increasing salt. For [KCl] > 0.03, the particles become more swollen with increasing salt (Figure 4b).

At low salt concentrations, any further addition of salt may cause the release of water molecules from the polymer. This release aims to maintain the ionic strength of the bulk solution and could result in deswelling of the particles, and an increase in light scattering. At high salt concentrations, any addition of KCl disrupts the hydrogen bond networking of water. This disruption makes it more thermodynamically favorable for the water molecules to hydrogen bond with the polymer. This results in polymer swelling, and less scattering.

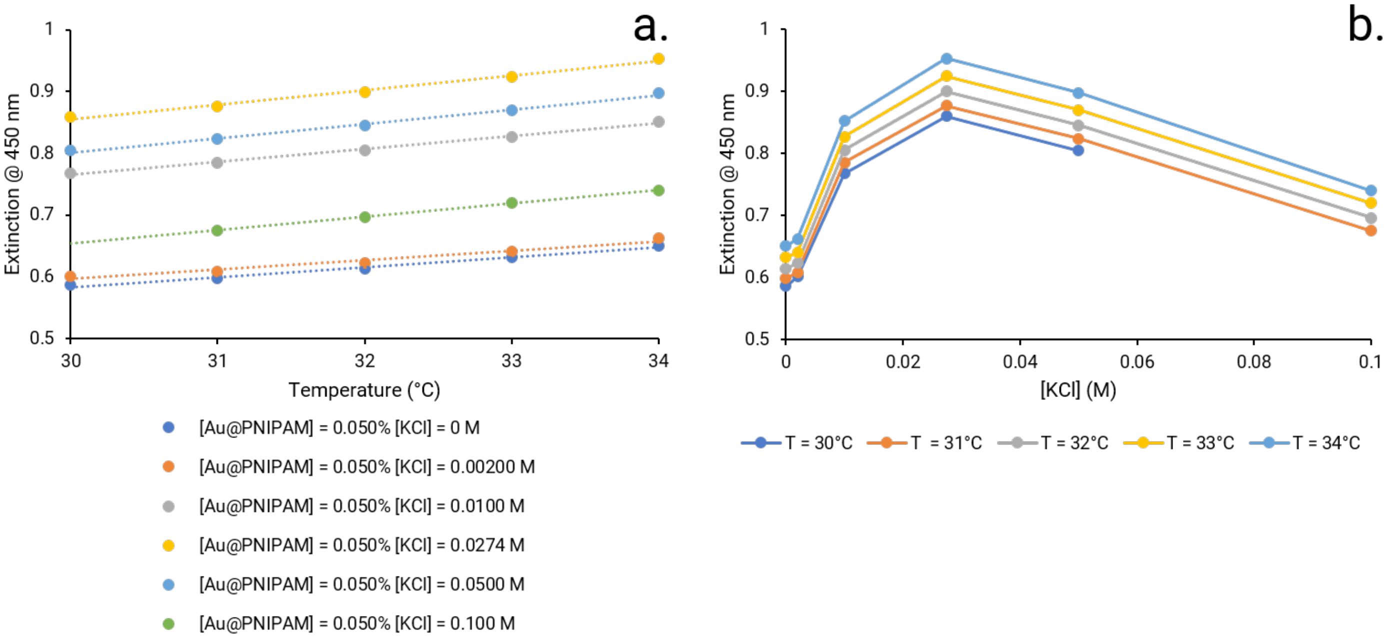

Figure 4. The (a) extinction at 450 nm over a subaggregation inducing temperature range as a function of salt concentration, highlighting the linear relationship with temperature. (b) The relationship between salt concentration, temperature, and extinction at 450 nm shows that as the salt concentration increases from 0 to 0.03 M the nanoparticles deswell. As the salt concentration exceeds 0.03 M, the nanoparticles swell and thus they scatter less light (the extinction decreases).

Conclusion

The thermally- and ionically- induced swelling of AuPNIPAM nanoparticles was explored and measured using the Cary 3500 Multizone Peltier UV-Vis spectrophotometer. Changes in temperature and ionic strength caused the polymer coating of the nanoparticles to deswell and thus reside closer to the surface of each particle. This deswelling resulted in an increased light scattering, measured as increased absorbance.

When the nanoparticles were in a solution of 0 M KCl concentration the swelling state changed as the temperature changed, but the particles did not aggregate under these conditions. However, when the salt concentration was equal to or higher than 0.02 M, nanoparticle aggregation was induced from 36.8 °C. This aggregation was observed by measuring the absorbance at 450 nm while increasing the temperature of the sample. These measurements clearly identified the aggregation points, which in turn allowed differences in ionic strength to be explored and identified.

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