The Effects of Water on the Size of Gold Nanoparticles

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Abstract

One of the big problems facing the gold nanoparticle industry is that size is hard to control. However size is important when it comes to gold nanoparticles as size is part of what makes them useful. Deep Eutectic Solvents (DES) are an emerging solvent for the synthesis of the gold nanoparticles as DES act as a cheaper and easier to make stabilizer for the shape of the nanoparticles. The DES that was used was reline, a molecule made of chlorine chloride and urea in a 1:2 molar ratio. This research was conducted to analyze how increasing the water concentration of reline solutions would affect the size of the gold nanoparticles during synthesis. It was hypothesised that increasing the concentration of water in the reline solution will increase the average size of the gold nanoparticles because the lack of the stabilizer in the synthesis solution would allow the gold to aggregate into larger nanoparticles. The idea being that with more water there is less of the stabilizing agent in the solution and so the particles will grow bigger. The results of the four trials that were done of the water reline solutions were gathered from a coulometric titrator, UV-Vis, and AFM. The different concentrations of the water used in testing was 2.5mL of water and 7.5mL of reline, 5mL of water and 5mL of reline, 7.5mL of water and 2.5mL of reline, and 10mL of water and 0mL of reline. In the end the results showed that gold nanowires may have been created or nanospheres could have been created. The nanoparticles that were created aggregate and this was seen in the AFM. During synthesis of the 7.5mL of water and 2.5mL of reline the gold aggregated into a macro form leaving none in solution which can be seen in the UV-Vis. With this evidence the hypothesis can be minimally supported but further research would need to be done to better support the hypothesis.

Intro

The need and use of gold nanoparticles (Au NPs) has grown greatly in the last couple decades as Au NPs have been regarded as the new generation of catalyst. A problem of the synthesis process of AuNPs is that the size of the AuNPs is unpredictable and with their uses needing precise sizes this can be problematic. The purpose of this research is to test whether the water concentration, in percent weight, in the reline solution will affect the size of gold nanoparticles. The hypothesis was, increasing the concentration of water in the reline solution will increase the average size of the gold nanoparticles because the lack of the stabilizer in the synthesis solution would allow the gold to aggregate into larger nanoparticles. The results will be found using, first instrument that will be used the UV-Vis spectrophotometer to show if gold is even in the solution after synthesis. Then instrument is the Scanning Electron Microscope (SEM) which can be used to determine the elemental composition of the nanoparticles. And finally the Atomic Force Microscopy (AFM) which can be used to determine the sizes and shapes of the synthesized nanoparticles.

Literary Review

Understanding Gold Nanoparticles and deep eutectic solvents from ionic liquids

The need and use of gold nanoparticles (Au NPs) has grown greatly in the last couple decades as Au NPs have been found to be a very good catalyst, and have been regarded as the new generation on catalyst[1]. Au NPs have also found uses in other fields of science as they have many purposes because of the wide variety of Au NPs that can be created due to the use of them being dependent on the size and shape of the Au NPs. However the size and shape is determined during synthesis and the conditions of the synthesis, for example the water concentration may have control of the size, type of solution, and the time in the solution. However size cant be fully controlled but semicontroled in certain conditions. The focus of recent experiments in nanostructures have gone away from ionic liquids (IL) which are liquids made from a salt in which the ions are poorly coordinated, and more towards deep eutectic solvents (DES) a liquid formed from a halide salt and a hydrogen bond donor. Two solids that have higher melting points and when mixed become a liquid, the DES have been the focus of the liquids that are used during synthesis. Both DES and IL are low-transition-temperature mixtures (LTTM) which are combinations of two or three components which are able to establish hydrogen bond interactions, however DES are a newer class of LTTMs that has grabbed the attention of research because of its unique properties during synthesis[2].

Understanding DESs and Their Uses

With research moving towards DES rather then IL the first thing was understanding the use and application of DES to AuNPs. DES has advantages over IL as they are easy to make and the components are easily attainable and inexpensive to get. DESs also aren't flammable, exhibit low vapor pressure, and have a wide liquid range[3]. This allows them to be used in many different types of synthesis with different metals. The use of DES in this experiment would be a reaction medium and a shape-directing agent for the AuNPs. The DESs being cheap also allows them to be used in industrial purposes. One DES that is used is called reline and is made from chlorine chloride and urea in a 1:2 molar ratio. This is because the chlorine chloride has two places that the urea will create a hydrogen bond due to the valence electrons on the Chlorine and so it will make a structure that can control the shape of the Au NPs.

Gold Nanoparticle Synthesis in Reline

The DESs is only part of synthesis, as the second part is adding and creating the AuNPs. The next thing is adding $HAuCl_4$ the gold salt and then adding $NaBH_4$ the reducing agent to the Reline. This causes a chemical reaction where the Au(III) is isolated and becomes neutrally charged this also makes the reline a pink red to a dark purple, this is caused by the light reflecting off the gold. This reaction and neutralization allows the gold to clump and grow into a crystal form, this form determined by the solution that the synthesis was carried in. After this the gold nanostructures will need to be observed using instruments, the first one being a UV-Vis Spectrophotometer to test if there is even gold within the solution and to see their average size, Scanning Electron Microscope which will show what was made, and finally the Atomic Force Microscope to show the size and shape of the AuNPs[2].

Methods and Materials

Using a 50 mL beaker and an analytical balance, 34.523g of urea was measured out and placed under the fume hood. At this time the heat plate was set to 80°C. A 100 mL beaker was placed on the balance and zeroed out, then used to measure out 40.117g of Chlorine Chloride. The 100 mL beaker containing Chlorine Chloride was placed on the heat plate and a small stir rod was added. The Urea was added to the Chlorine Chloride after waiting a little for the heat plate to warm up and warm the beaker up. The stir rod was turned on at this point, and then the Urea was added to the Chlorine Chloride. After moving the mixture around and pushing the solids closer to the stir rod with a spatula the mixture became a liquid solution and became very viscous so the rpm of the stir rod was upped. After sitting a while the solution was colorless and clear except for the small air bubbles in the solution. The mixture of the two solids had now turned into the desired solution of reline.

After the reline had time to cool a coulometric titrator was used to test the percent mass of water in the reline solution. This was done by setting coulometric titrator was turned on and put into data collection mode. A small sample of the reline was put into the titrator by using a pipet that was put on a balance. This was used to determine the mass of the sample used so it could be input into the instrument. The reline was dropped into the titrator and the mass of the sample was recorded and put into the instrument so that the titration could start. After a little the percent water by weight was given and recorded.

With the reline made, the heat plate was turned on once again and set to 40°C. 8.4mg of $HAuCl_4$ was measured out on a balance in a 50 mL beaker and added to 5 mL of reline until it was dissolved. This was placed on the heat plate and stirred.While that was warming up 4.4mg of NaBH4 was added to another 50 mL beaker and also given 5mL of reline and placed on the heat plate next to the other beaker with the gold. After stirring both mixtures until homogeneous, the $NaBH_4$ reline solution was slowly dripped into the $HAuCl_4$ reline solution. This caused the color of the $HAuCl_4$ reline solution to go from a yellow clear liquid to a dark purple or black solution. The solution was stirred for several minutes to ensure the reaction had completed.

The gold nanoparticle solution was extracted from the beaker using a micropipette and put into six 1.5 mL centrifuge tubes, each tube getting 1 mL of the solution. Once each tube was filled they were placed into the centrifuge that was set to 10000 rpm for 5 min. The centrifuging was repeated till the gold nanoparticles came out of solution and became stuck on the walls of the tube or collected on the bottom of the tube. The solution was clear and colorless rather then dark purple at this point. The gold nanoparticles were then out of solution, so the reline was able to be taken out of all but two of the tubes with normal pipet. The other two tubes that still had reline were removed and placed in storage for later, this was because one of the tubes is needed for UV-Vis and the other as backup or a second point for the UV-Vis. The other four tubes with no reline were going to go through a process of cleaning the gold nanoparticles of the reline, as this was required for the AFM. This cleaning process consists of first adding one mL of ethanol to the tubes. Then the gold was put back into solution with the ethanol that was added, this was done when the tubes were vortexed and sonicated, and when the gold was back into solution they were put but back into the centrifuge for 10 min at 10000rpm or till they came back out of solution. The ethanol was removed and one mL of new ethanol was added. On the third run through new ethanol was added and the gold was put back into solution in prep for the tests. Two carbon stickers were placed on the SEM plate and two mica plates were prepped. The preparation process for the mica plates were to hole punch circles of mica from a mica sheet and use tape to remove the first few layers and then placing them in a petri dish. One drop from one of the tubes was added to one of the carbon plates and then the rest of the tube was set aside for storage. This was repeated on the rest of the carbon and mica plates. All four of the plates were covered and given time to allow the ethanol to evaporate.

The two tubes that were left over were taken and drained of three fourths or 0.75 mL of the reline in both the tubes using a micropipette. Then 0.75 mL of ethanol was added to both of the tubes. Both of the tubes were sonicated and vortexed so that a homogeneous mixture is created between the reline and ethanol. Four more tubes were pulled out and one mL of ethanol was added to each of the tubes. Once the UV-Vis was turned on and the ethanol background was set, using a pipet, the tube with the reline ethanol solution was put into the quartz cuvette. The other two tubes filled with ethanol were squeezed into the cuvette and the solution was mixed by sucking the solution into the pipet and squeezing it back into the cuvette multiple times. After this the UV-Vis was used to test the solution and the results which would be a bump in the 500-600 range. The AFM was also tested after it was confirmed that something was made.

This process was repeated except the synthesis of reline but with different concentrations of water, 2.5 mL of water, 5 mL of water, and 7.5mL of water from the same batch of reline that was made at the beginning.

Results

The UV-Vis results are shown below in figures 1-4.

2.5 mL of Reline to 7.5 mL of Water Solution UV-Vis Graph

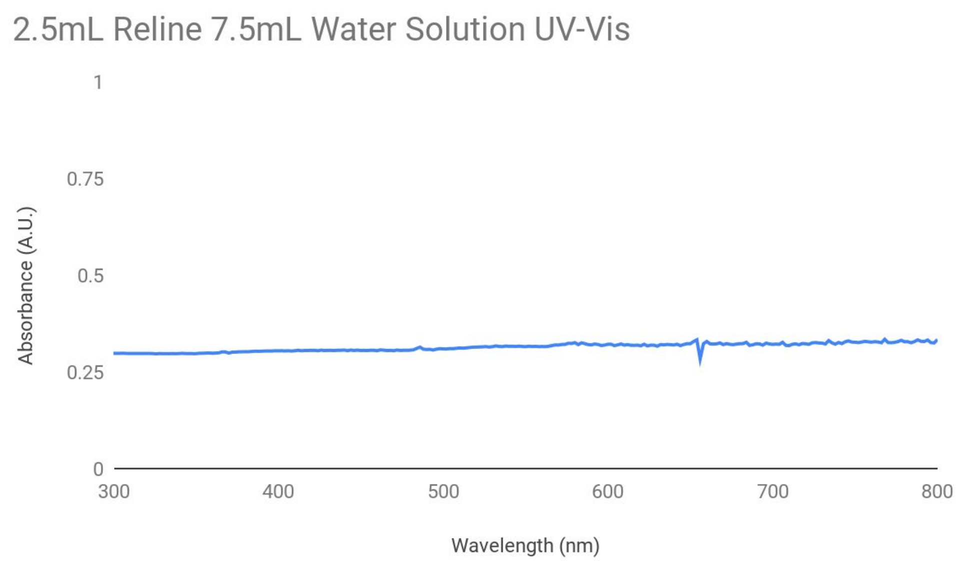

Figure 1: 2.5 mL Reline 7.5 mL Water Solution UV-Vis

The graph of 2.5 mL of reline has no curved peak on the graph showing no presence of gold nanoparticles in solution. To get this result 1ml of the solution was used with 2ml of ethanol.

5 mL of Reline to 5 mL of Water Solution UV-Vis Graph

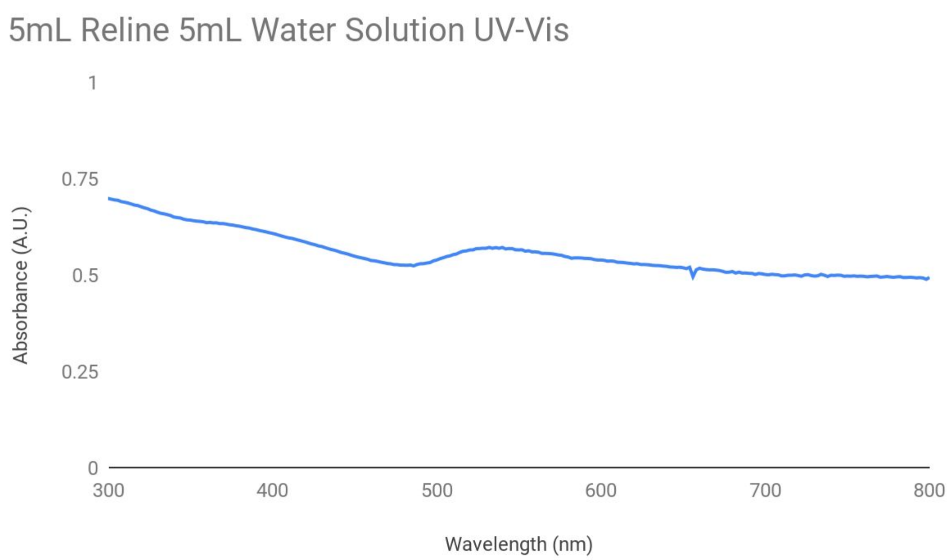

Figure 2: 5 mL Reline 5 mL Water Solution UV-Vis

In the 5 mL graph there is smooth peak from 500 nm to 600 nm that has a max absorbance of about 0.6. This shows that there are nanoparticles in the solution. To get this result 1ml of the solution was used with 2ml of ethanol.

7.5 mL of Reline to 2.5 mL of Water Solution UV-Vis Graph

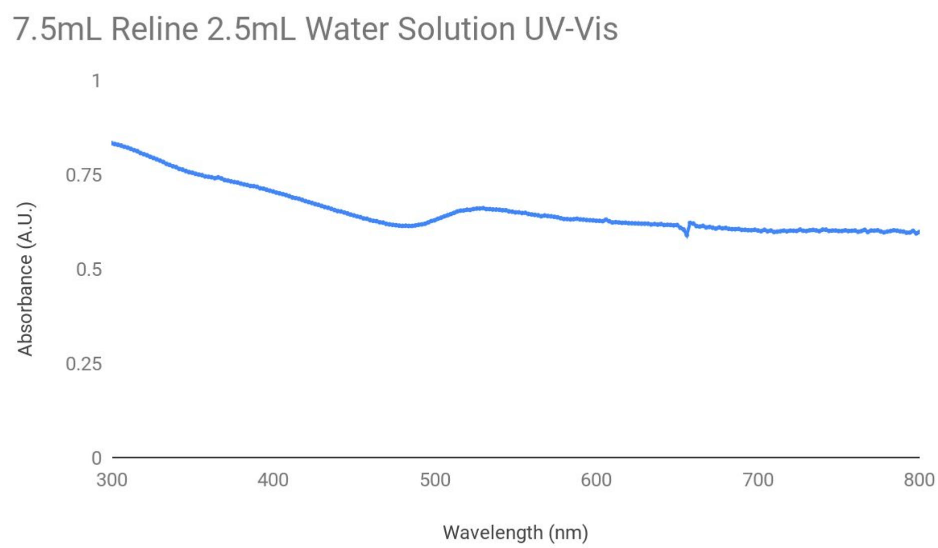

Figure 3: 7.5 mL Reline 2.5 mL Water Solution UV-Vis

The graph of 7.5 mL of reline shows relatively similar peak at 500nm to 600nm as 5mL and 10mL with once again a max height of about 0.6 and a broad rather then sharp peak.

10 mL of Reline to 0 mL of Water Solution UV-Vis Graph

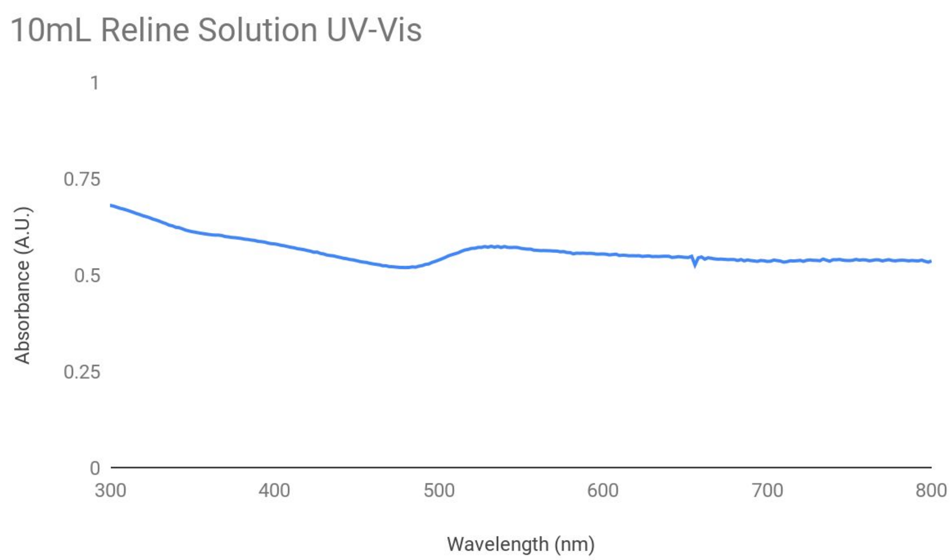

Figure 4: 10 mL Reline Solution UV-Vis

The graph of 10 mL of reline shows relatively similar peak at 500nm to 600nm as 5mL and 7.5mL with once again a max height of about 0.6 and a broad rather then sharp peak.

Figures 5-7 are from the AFM and are all of the 10 mL reline sample.

AFM 10µm by 9.98µm

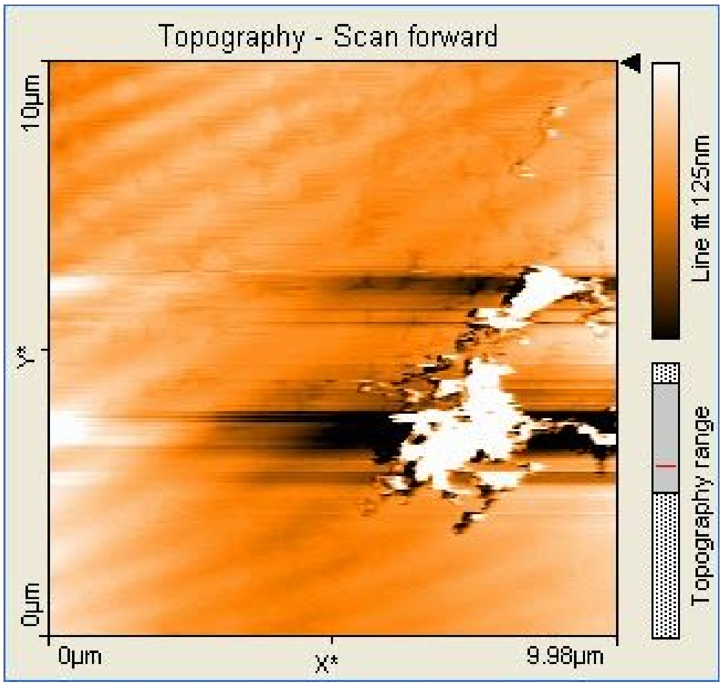

Figure 5: AFM image at 10 nanometers

AFM 6.64µm by 6.62µm

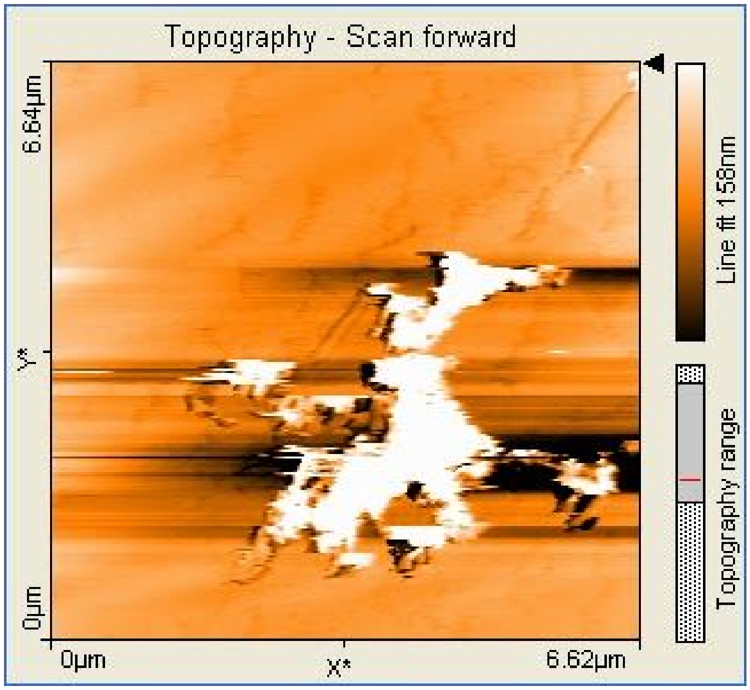

Figure 6: AFM image at 6 nanometers

AFM 2.36µm by 2.35µm

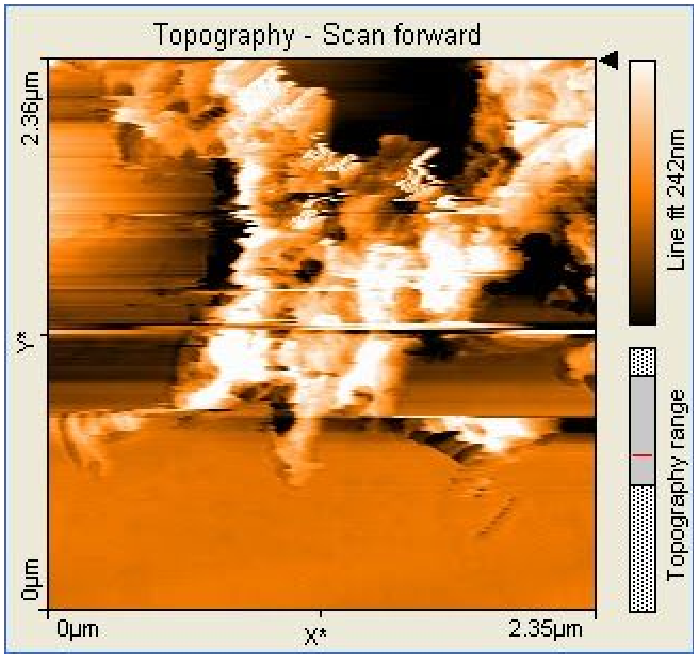

Figure 7: AFM image at 2 nanometers

In figures 5-7 shows the formation of gold nanoparticles in the 10 mL reline solution. The size shows that the reline wasn't great at making nanostructures and created nanowires that aggregated together. Other images were not taken as the particles were big even with 10 ml of reline and would only get bigger and messier when the concentration of the reline decreased.

Water Percent in Each Solution by Mass

Ratio of Reline to Water	Water Percent Trial 1	Water Percent Trial 2	Water Percent Trial 3	Water Percent Average
10mL reline 0mL water	2.765%	2.767%	2.451%	2.661%
7.5mL reline 2.5mL water	23.830%	22.170%	23.272%	23.091%
5mL reline 5mL water	52.472%	50.873%	x	51.673%
2.5mL reline 7.5mL water	72.459%	76.010%	x	74.235%

Figure 8: The water percent by mass was measured using the coulometric titrator. For the 5mL and 2.5mL reline solutions a third trial was not taken due to a lack of time.

Discussion

The results of the research done has given evidence to strongly support but not quite prove the hypothesis that was proposed. The hypothesis was, increasing the concentration of water in the reline solution will increase the average size of the gold nanoparticles because the lack of the stabilizer in the synthesis solution would allow the gold to form into larger nanoparticles.The data doesn't fully support the hypothesis because for one the formation of gold nanoparticles and gold nanostructures was somewhat unsuccessful as nanostructures were created just not in the shape wanted and then they created aggregates. What is thought to be created is gold nanowires rather then small circles or other shapes. This is supported through the AFM images, the shapes of the gold, while also being an aggregate rather than singular nanostructure have what can be seen as a wire like structure within the aggregate. The wires was also supported with the UV-Vis having a more curved peak then sharp ones normally indication larger sizes of particles. The creation of what seems to be nanowires and then the nanowires aggregating together delegitimize the data that was collected as the aggregates made it so . The AFM wasn't taken for the others as taking away the stabilizing agent, the reline, would cause the aggregate to grow. This was shown in figure 1 in that there was no curve of absorbance around 500-600 nm, and to further that point during the synthesis of the 2.5 mL reline the gold precipitated into a macro from that could be seen with the eye. These things show that the increased water concentration would increase particle size but not prove it as that would require an AFM of multiple particles and an average of their sizes taken for each of the concentrations. The limitations of time made it so that the process of taking multiple images and looking at all the samples not possible. Now knowing that reline isn't a great stabilizer to start with, which is supported by the 10 mL reline solution creating aggregates rather then nanoparticles, then decreasing the concentration of the reline would cause larger particles to grow which is shown by the data retrieved, the hypothesis then can be minimally supported. A better alternative or further testing could go into use a different DES to create nanoparticles. This would explore how other DES react in an aqueous solution and if size can be controlled with water in other DESs.

References

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