SOLUBILITY OF LIGATED GOLD NANOPARTICLES AT ROOM TEMPERATURE IN VARIOUS HYDROCARBON SOLVENTS

by

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Abstract

Gold Nanoparticles (AuNP) 5nm in diameter, ligated with n-dodecanethiol, were dissolved in various hydrocarbon solvents including normal alkanes from n-hexane to n-hexadecane as well as two aromatics, toluene and para-xylene. These solutions were centrifuged at room temperature under 12000g acceleration for one hour to separate larger clusters from AuNP monomers dissolved in the supernatants. UV-Vis absorbance data were taken on the supernatants and were then converted to concentrations in moles of Au atoms/L. These concentrations correspond to the saturated concentration of dissolved AuNP monomers in equilibrium with a precipitate at room temperature. For the alkanes, we discovered a non-monotonic functionality of saturated concentration vs. solvent chain length with a maximum corresponding to n-dodecane. This agreed with predictions made of the ligands' interactions with the solvents based on comparisons of solubility parameters where the n-dodecanethiol ligands were approximated as n-dodecane. The concentrations of AuNPs when dissolved in the aromatics did not follow the trend predicted by solubility parameters.

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CHAPTER 1 - A Background of Nanoscience

The Impact of Gold

From the discovery of metals between 7000-5000 BCE [1], mankind has been fascinated by gold. Indeed, this infatuation can be best expressed by miscellaneous writer Charles Caleb Colton (1780-1832) with the following aphorism, "Gold is worshipped in all climates, without a single temple, and by all classes, without a single hypocrite" [2, 3]. Humankind's admiration for gold has contributed to its venerated position as a medium of exchange throughout history, but this inherent value also derives from gold's use as a commodity in art, sculpture and jewelry-making as well as for other important industrial uses such as those in the electronics industry.

Most of us have some familiarity with metallic gold, its uses and its impression on the human condition, yet another less well-known form of gold has found applications throughout the ages. Soluble gold or "colloidal gold" is a form in which small nanometer sized particles of gold are suspended in a fluid. This form of gold was discovered in antiquity and has been used in various applications well into the present. The Romans added gold salts to sand and soda ash in the manufacture of glass and unbeknownst to them, the formation of gold nanoparticles was responsible for the unique red coloring of the resulting glass [4]. This technique was used into the Middle Ages to produce bright red stained glass windows for churches [4]. Gold colloids had also been used to dye silk by 1794 [5]. Humankind's faith in the power of gold had even led colloidal or "drinkable" gold solutions to be used as curative elixirs through the Middle Ages and beyond to the 20^{th} century as a diagnosis of syphilis [5]. Gold, in all of its forms, has been influential in industry and the sciences.

The first truly scientific study of gold nanoparticles was conducted by Michael Faraday in 1857 in which he reported the reduction of a solution of $AuCl_4^-$ resulted in a red solution of gold colloid [5]. Gold colloids have been shown to have "qualitative" applications such as in the coloring of glass. Smaller nanoparticles take on a pink or reddish color, larger clusters are purple and even larger aggregates take on a more yellowish or golden color. These ideas were suggested in 1818 by Jeremias Richters [5], and have been verified in our own group by dynamic light scattering experiments. It would appear that the properties of the colloid solutions depend upon the size of the nanoparticles involved. During the time of Faraday, engineering the

particles to have specific properties proved very difficult due to the polydispersity of the particle sizes. Recently discovered techniques such as **digestive ripening** (discussed in Chapter 2) allow us to control the size of gold nanoparticles during their synthesis with narrow size distributions. The advent of these techniques has enabled material scientists to systematically study the properties of these nanogold solutions. These size-control techniques producing monodisperse materials pave the way for a new realm of novel materials with adjustable size-dependent properties. Truly, these new discoveries have rekindled the allure of gold as it propels us forward into the age of nanotechnology.

On Stoichiometry

Nature has been very kind to us by providing a wide variety of elements with an almost endless number of combinations yielding a plethora of different molecules. This vast array of materials and their properties are used for specialized roles in construction, medicine, science, engineering and virtually every other endeavor of human labors. A unique property of a molecule is its **stoichiometry**, that is, its constituent elements' atoms always appear in the same proportions [6]. For example, a water molecule is always composed of one oxygen atom and two hydrogen atoms. Water molecules found anywhere in the universe are chemically equivalent and made of the same constituent elements in the same proportions. These ratios are discrete because the elemental atoms are chemically identical.

The effect of digestive ripening in producing monodisperse nanoparticles with a narrow size distribution is that they can be considered stoichiometric entities. A typical dodecanethiol ligated gold nanoparticle with a 5nm diameter can be expressed as a "molecule" with the following chemical formula.

$$Au_{3850}(C_{12}SH)_{350}$$

Typically the standard deviation of the number of atoms is around 10% [7]. This means that the 5nm nanoparticles are approximately equivalent in stoichiometric properties. Further, we can treat the nanoparticles as new types of "atoms" or "molecules," or even further, a new type of matter called a "stoichiometric particle compound" [7]. Nanoparticles of different species (different metal cores as in the case of silver nanoparticles, different species of ligand shells, different monomer sizes) offers an opportunity to create structures analogous to "supermolecules" with any number of new properties and applications.

Whereas all the combinations of elements on the periodic table have a definite and discrete stoichiometry, the size-dependence of the nanoparticles allows them to have a broad and continuous stoichiometry [8]. The implication is that the immense number of materials available from the periodic table is expounded on an inconceivable scale with the addition of a size-dependence. Moreover, the continuous stoichiometry of these novel materials can be "tuned in" to specific desired properties by controlling the final particle size.

Academic and Industrial Applications

The words "nanoparticle" and "nanotechnology" invoke futuristic images of tiny robots infecting our blood to turn us into zombie-like cyborgs. In reality, "nanoparticles" simply refer to particles that are on the length scale of nanometers across. These particles are important to physical science because they lie between the chemical realm of quantum mechanical effects and the condensed matter physics realm of bulk materials. Indeed this dichotomy can be inferred from the chemical formula for a dodecanethiol ligated AuNP of 5nm size given above. The thousands of gold atoms and hundreds of ligands per particle illustrate the particles' aggregate or bulk properties while the convenient stoichiometric form reflects their "molecular" nature. The nanoparticles' position between these two distinct realms of science makes them very interesting subjects for study in an emerging new field of research.

Due to the nanoparticles' small size, the surface area to volume ratio is very large compared to pulverized powders of the same materials. A result of this is that a significant portion of the atoms are located at the surface of the particle (as much as 50%) making them very reactive [9]. A consequence of this high reactivity is that the nanoparticles can be used as catalysts in purification or detoxification applications. Potential uses lie within the pharmaceutical community where a high surface to volume ratio can aid in the effectiveness of drug delivery. The particles could also find themselves in electrodes to make better batteries as our technology has been evolving much faster than power supply systems [10]. Our speculation for potential uses for these seemingly "magical" materials can go on ad infinitum.

CHAPTER 2 - Synthesis of Nanoparticles

Gold nanoparticles (AuNPs) must be synthesized before they can be studied. A systematic study of the AuNPs' properties requires the particles to be uniform in size. A few techniques exist in the literature, but our group primarily works with two, the SMAD method and the Inverse Micelle Method. As-prepared particles are polydisperse in nature and thus must be subjected to digestive ripening in order to make them monodisperse. Once digestively ripened, the particles are precipitated out of solution by ethanol, decanted, and vacuum dried. The vacuum dried particles represent a **gold lot** (discussed in Chapter 3) and are ready for experimentation.

SMAD

Solvated Metal Atom Dispersion (SMAD) is a synthesis procedure in which gold is evaporated and deposited on a surface to form small nanosized particles, separated from each other by an organic solvent with a keen interest in halting the aggregation process of the gold as soon as possible [11]. The general procedure is as follows.

1) Capping agents (ligand) and organic solvent is placed in the bottom of a glass reactor and metallic gold is placed in a crucible in the reactor.
2) The solvent is frozen with liquid nitrogen, then the reactor is evacuated to milli-Torr pressures in order for the gold to be evaporated at a temperature low enough that the solvent does not decompose.
3) Solvent is evaporated into the reactor which then condenses on the wall of the frozen reactor near the bottom leaving a thin layer.
4) The crucible is heated and the metal is evaporated. Atoms condense onto the walls on top of the layer of solvent.
5) More solvent is released resulting in highly reactive nanoparticles sandwiched between two layers of organic solvent.
6) The frozen pool of solvent and ligand is heated back to a liquid phase.

7) The highly reactive nanoparticles come into contact with the dissolved capping ligand and are surface ligated. They are now shielded from aggregation with other nanoparticles.
8) Polydisperse product is digestively ripened to narrow the size distribution [12].

Inverse Micelle

The inverse micelle method involves the reduction of a gold metal salt to slowly grow nanocrystals in an inverse micelle environment. The growth rate of the particles is about two orders of magnitude slower than simple aggregation in a single liquid phase [13]. Growth to the final size involves diffusive interactions between the inverse micelles which contain only a few atoms. The slow growth of nanoparticles (that depends on the inverse micelle size) results in narrow size distributions. Ligand can also be added to the micelle solution, altering the growth rate of the clusters. An interesting result of the process is that the size distribution narrows with age as the inverse micelles grow larger. For our experiments, digestive ripening is performed to further narrow the size distribution

1) A gold salt like $AuCl_4^-$ is dissolved into a solution with a solvent like toluene.
2) A surfactant is added to the solution to promote inverse micelle formation.
3) A stabilizing ligand is added to the solution and is present in the inverse micelle environment.
4) A reducing agent such as $NaBH_4$ is added to the solution to reduce the dissolved gold ions into atoms.
5) Micellar diffusion is responsible for a slow growth rate of particles giving rise to nanocrystalline structures instead of disordered clusters [14].
6) The product of inverse micelle synthesis is digestively ripened.

Digestive Ripening

For the nanoparticles to be useful for any systematic study or size-dependent application, they must be monodisperse in size distribution. Digestive ripening is a simple procedure first described by Xiao-Min Lin and coworkers in which the polydisperse ligated gold nanoparticles are heated anaerobically in the presence of excess ligand [15]. The procedure for digestive ripening is poorly understood, but involves the nanoparticles trading their constituent atoms or

groups of atoms back and forth until an equilibrium size is reached. A driving force for this favored equilibrium size can be a consideration of the competition between the surface energies of the particles favoring large size and the interaction of ligand with the metal surfaces favoring small sizes [16].

Final Product

A typical transmission electron micrograph of the gold nanoparticle solutions is provided below in Figure 2-1. These particles were digestively ripened by the inverse micelle method in toluene. The particles were vacuum-dried and redissolved in hexane. A 20nm scale bar is provided near a few AuNP monomers to show that the gold cores are ~5nm on average across and separated by a ligand shell. The TEM picture was taken from a precipitate with large superclusters and a few sporadic monomers. The repeated array of AuNPs is evident in the superlattice.

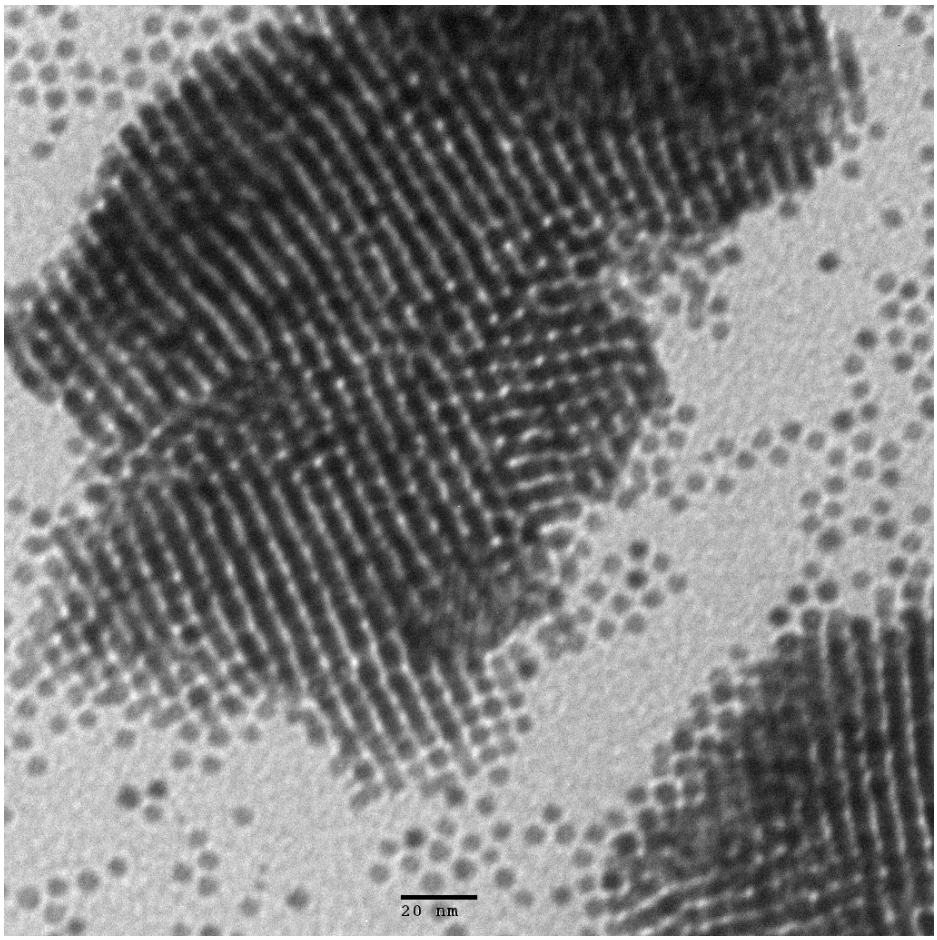

Figure 2-1: TEM picture of an AuNP supercluster and some monomers

CHAPTER 3 - Methodology

The experimental goal was to determine solubility behavior of the gold nanoparticle (**AuNPs**) monomers with respect to alkane solvent carbon chain length in a **two-phase system** in equilibrium at room temperature. The solubility behavior can be inferred by comparing the monomer concentration in a supernatant in equilibrium with the precipitant phase for the various solvents. Concentration can be found easily from UV-Vis absorbance data provided a valid calibration curve is known. Although experimental techniques vary in the minutia between batches of gold particles tested, all experiments follow the same basic procedure:

1) Undissolved dry nanoparticles are dissolved into various solvents.
2) The resulting solutions are sampled and spun under 12000g centrifugation.
3) Supernatants containing only monomers are transferred to a washed cuvette.
4) UV-Vis absorbance data are taken from the supernatants.
5) The absorbance data are finally converted and expressed as concentrations.

Preparation

The gold nanoparticles of a particular **gold lot**—a batch of AuNPs synthesized by the chemists—must be dissolved into a number of selected solvents for study. An arbitrary mass (about 1mg) of AuNPs is measured on a Mettler AE200 0.0001g scale and placed in a 20mL glass bottle for each solution studied. Each solution is prepared by adding 1000μL (1mL) of solvent to the milligram masses of AuNPs. Care must be taken to ensure the **nominal concentration**, i.e. the total moles of gold in total volume of solvent, is greater than the concentration of monomers in equilibrium with any precipitates. If the nominal concentration is less than the equilibrium monomer concentration, the solution will be in a **one-phase system** where all particles are dissolved and suspended in an unsaturated solution. One-phase systems yield no useful data regarding solubility behavior. The solutions *must* be in the two-phase regime in order for the solvents' ability to hold AuNP monomers in equilibrium with the precipitate to be revealed without ambiguity. After AuNPs and solvents are combined in the collection of small bottles, they were sonicated for 5-10 minutes to aid and accelerate dissolution. These **stock solutions**—the sources from which samples are taken— are ready for

study and should be protected from light and oxygen by wrapping with parafilm and storing in a dark box.

Experiment

Prepared gold nanoparticle solutions can be a very dark, opaque mixture of precipitates, monomers, clusters and abnormally large monomers. Each solution must be centrifuged to isolate the AuNP monomers from heavier undesirable particles or clusters. A small sample (150-300μL) of each solution was pipetted into **centrifuge vials**, small plastic containers compatible with the centrifuge and designed to withstand high (1000s of g's) acceleration. The vials were loaded into a Thermo Legend14 centrifuge and spun for 60 minutes at 12000g acceleration. After centrifugation the solutions appear to have a transparent, colored supernatant of monomers above either a thick opaque liquid or a compacted solid pellet at the bottom of the centrifuge filler. A comparison between the turbid solutions before spinning with the separated supernatants above precipitates after spinning is provided in Figure 3-1. Because the darker liquid of clusters at the bottom has a tendency to creep upward into the supernatant with time after the high acceleration is removed, the supernatants were pipetted away and sequestered in different containers immediately after centrifugation to prevent contamination by unwanted non-monomeric species.

Figure 3-1: AuNP Sample Before (Right) and After (Left) 60 min of 12000g Spin

A Cary 50Bio UV-Vis spectrophotometer was employed to take absorbance data. The spectrophotometer must be calibrated before use with samples. Calibration was accomplished by taking a baseline measurement on a cuvette filled with some solvent transparent in the visible

range. Some experimental setups used ethanol while others used toluene or hexane as the transparent solvent. The choice of solvent did not appear to make any difference as long as it was colorless and transparent. The software will automatically subtract away any baseline contributions from the measurements of gold solutions, leaving absorbance data relevant to the AuNPs only. Throughout the experimental process, absorbance data should occasionally be taken from a standard sample to ensure the background doesn't vary. It's possible that the baseline could drift away from zero with time. By measuring the absorbance of a standard sample before the experiment and comparing it to later data taken during the experiment, we could confirm the AuNP absorbances aren't varying due to problems with the apparatus. In our case an ampoule of Holmium Oxide solution assayed by the US Department of Commerce, National Institute of Standards and Technology served as this absorbance standard.

Standard disposable cuvettes are convenient because they are of a standard 10mm path length and their one-time use nature precludes any need for cleaning; however, 1mL volume standard cuvettes are wasteful of sample. A smaller volume cuvette was thus required for pragmatic reasons. A Cary Brand quartz cuvette of 1mm path length and 100μL nominal volume was available for this experiment. Unfortunately, because only one cuvette was available, it required appropriate cleaning between data collections for the various solvents. The cuvette was cleaned via varying techniques for each experiment. It was first rinsed with a pure solvent—either hexane or the solvent corresponding to the solution being examined. After a pure solvent rinse, the cuvette was either dried in an oven to evaporate away residual solvent or it was rinsed with a portion of the sample. For longer-chain solvents that don't readily evaporate, a rinse with a portion of sample provides an excellent means for flushing away residual solvent that could dilute the sample of interest. Any residual waste from the gold solution rinse that was adhered to the cuvette's walls would dilute and contaminate the sample of interest less than residual pure solvent. Once the cuvette was satisfactorily cleaned, the AuNP sample was transferred from its isolated container into the cuvette.

The cuvette was loaded into the spectrophotometer and absorbance data were taken three times consecutively per sample. The UV-Vis spectrometer displays absorbance plotted against the illuminating light's wavelength and is presented in a manner similar to the typical set of data from an early experiment provided in Figure 3-2. Use of the term "prototypical" signifies that

the experimental procedure was in an exploratory state of development for this particular set of data.

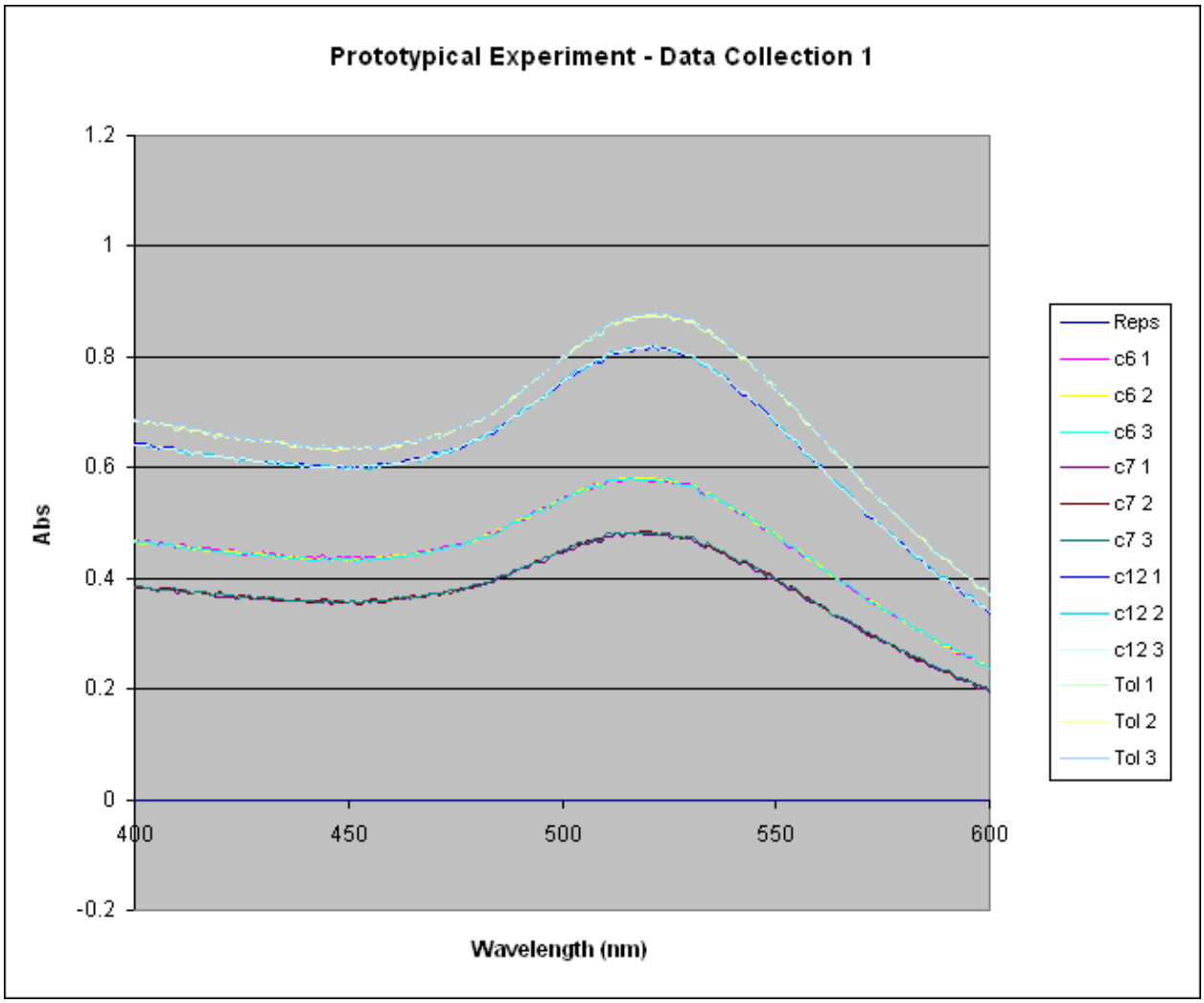

Figure 3-2: Typical data as provided by the UV-Vis apparatus for an early experiment

Manipulation

Figure 3-2 contains data for a single trial run of an early exploratory experiment. The plot for just one solvent contains a wealth of data points. Some point of reference must be chosen to make comparisons of data between different solutions. The maximum absorbance at the **plasmon** near 520nm was chosen as a reference point. The location of the plasmon (in wavelength of absorbed light) may drift; therefore, the reference point was chosen as the peak and not at a fixed wavelength. This is illustrated by the slightly redder peak for toluene solution in Figure 3-2. The plasmon is a property of the illuminating light's interaction with a free

electron gas in the nanoparticles [17] and thus the plasmon itself serves as a landmark that corresponds directly to the AuNPs in solution. A greater absorbance *at the plasmon* for one solution containing AuNP means a greater concentration of nanoparticles suspended in solution. We take a "cross section" of the raw data at the plasmon (as in Figure 3-3) to select only plasmon absorbances, then plot those representative points for each data run or trial as shown in Figure 3-4.

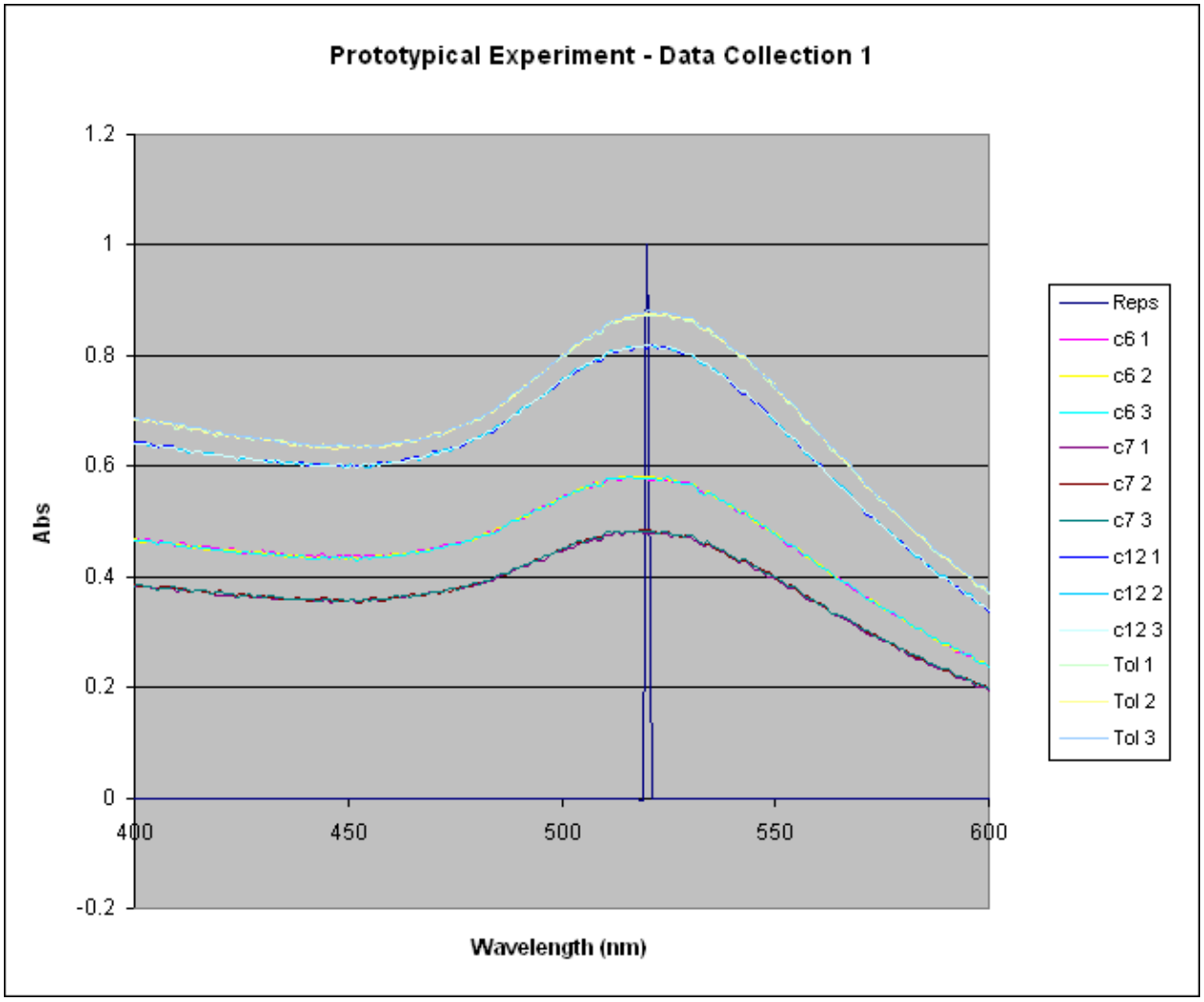

Figure 3-3: Plasmon peak selected for typical raw data

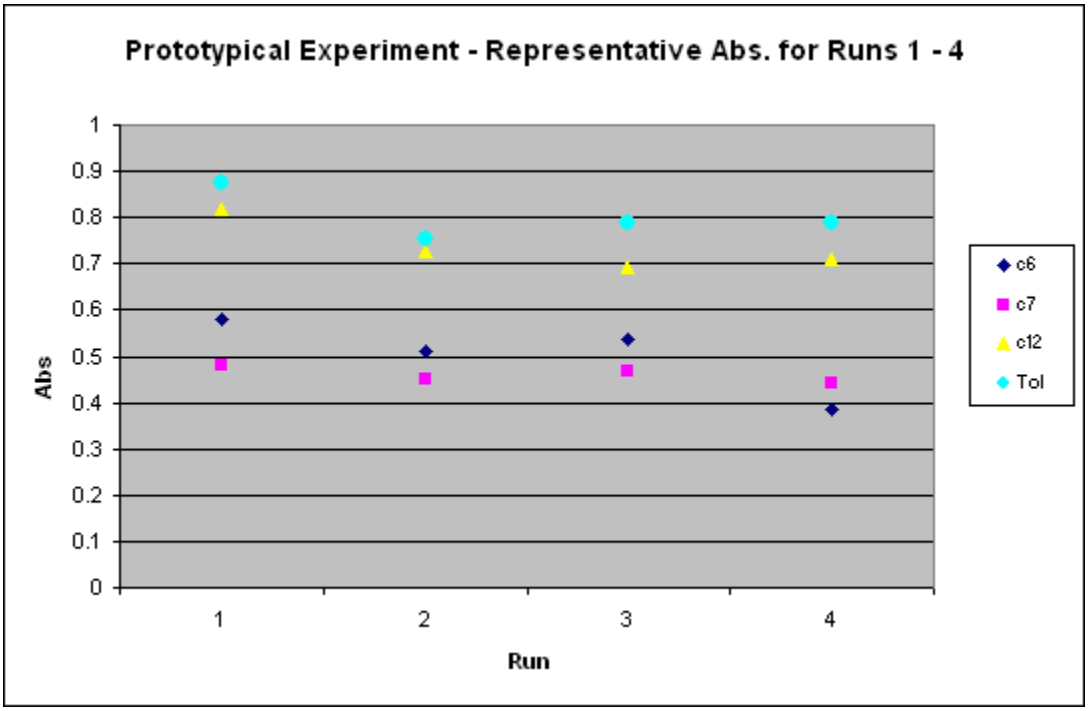

Figure 3-4: Typical plasmon absorbances for different solvents over a number of trials

Plotting absorbance vs. trial run in the manner of Figure 3-4 allows us to gauge consistency at a glance. Data for each solvent should make a horizontal line across all trial runs. Extreme outliers such as the data for C_6 in Run 4 on Figure 3-4 are obvious and the ability to readily identify this point with a particular trial run aids in nominating potential sources of error in experimental technique. Outliers are present in a concentration vs. solvent chain length plot, but information related to run number is slightly more obscure.

Absorbance data tell us relative behavior between the solvents, but absorbance data does not offer any quantitative information about the concentration of monomers in a centrifuged solution's supernatant. These data must be converted from absorbance to concentration of gold. A calibration curve is available for plasmon absorbances corresponding to known nominal concentrations of one-phase systems. Because all of the solute is fully dissolved when the system is one-phase, a known nominal concentration represents the true concentration of monomers dissolved. The calibration curve is provided in Figure 3-5. Notice the plasmon wavelength indicated in the figure is at 535nm, whereas the plasmon was located at 520nm for the prototypical data. The difference in plasmon location is related to the difference between one-phase and two-phase systems.

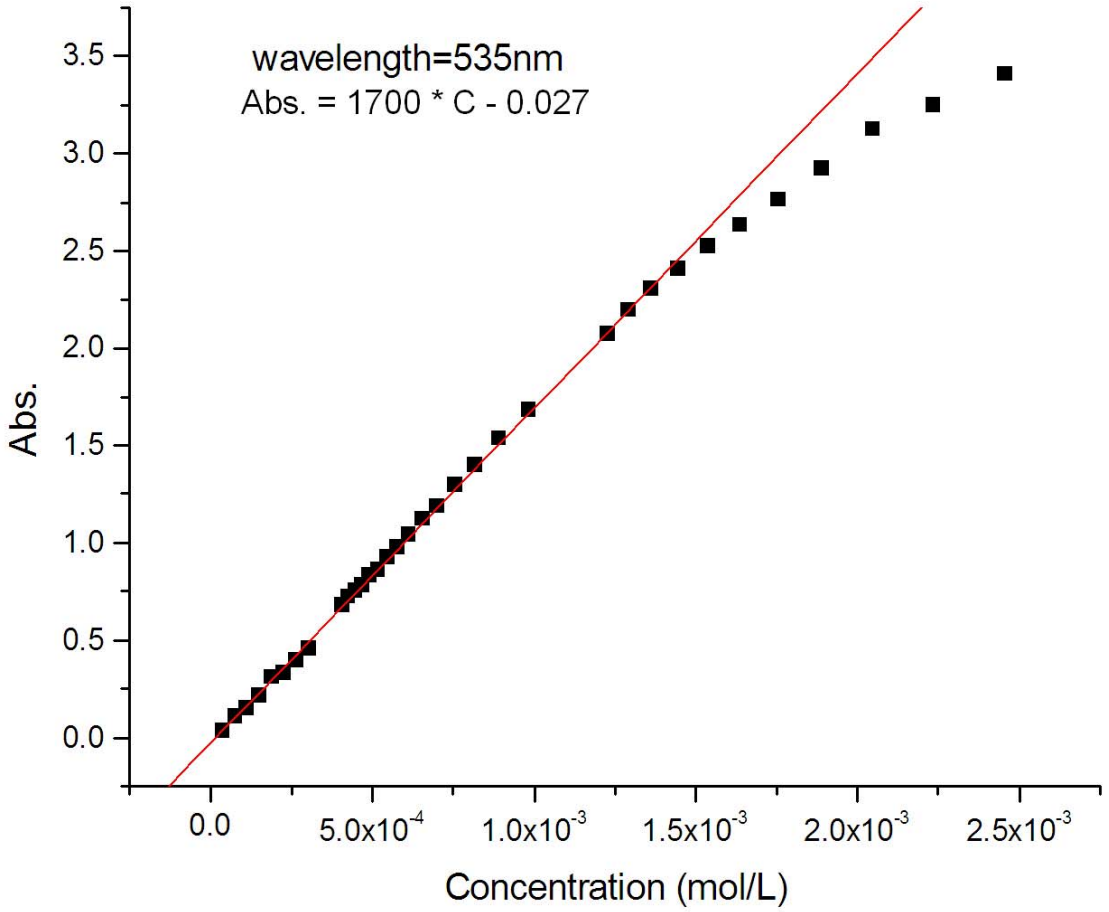

Figure 3-5: Calibration curve for absorbance and concentration in mol Au atoms/L Provided courtesy of Dr. Ben Scott, personal communication [18]

Lambert's Law provides an exponential decay relationship between incident light and transmitted light passing through a sample of absorbers such as a solution of particles. Lambert's Law is provided in Equation 3-1 [19].

$$T = \frac{I}{I_0} = e^{-\varepsilon l c} \qquad \textbf{Equation 3-1}$$

An interesting feature of Lambert's Law is the linear extinction in the argument of the exponent. As long as the molar absorptivity of the system (ε) and the sample's concentration (c) remain constant, an increase in the path length (l) for the light will result in a linearly increasing

extinction argument. Instead of dealing with exponentially varying transmissions T or %T, we exploit this linearity to work in terms of absorbance. **Beer's Law**, which follows from Lambert's Law, expresses a direct relationship of absorbance to the molar absorptivity of the system (ε) in L/(mol-cm), the sample's concentration (c) in mol/L, and the path length of illuminating light through the sample (l) in cm. Beer's Law is provided in Equation 3-2 [20].

$$Abs = -\ln[T] = \varepsilon l c \qquad \textbf{Equation 3-2}$$

Calibration data in Figure 3-5 were obtained from samples held in a standard 10mm path length cuvette, but our experiments were performed in a 1mm cuvette. In order to make the data in Figure 3-4 comparable to the calibration, it must be converted to an equivalent 10mm path length. Beer's Law proves very useful in this manipulation. By moving the gold nanoparticle solution to a different path length cuvette, we change none of its intrinsic properties. The molar absorptivity and the solution's concentrations are constant. By passing the light through ten times the path length, ten times more light is absorbed by the solution. We can therefore "correct" the Figure 3-4 absorbance data to a standard cuvette by applying a tenfold multiplication. Typical "corrected" absorbance data are presented in Figure 3-6.

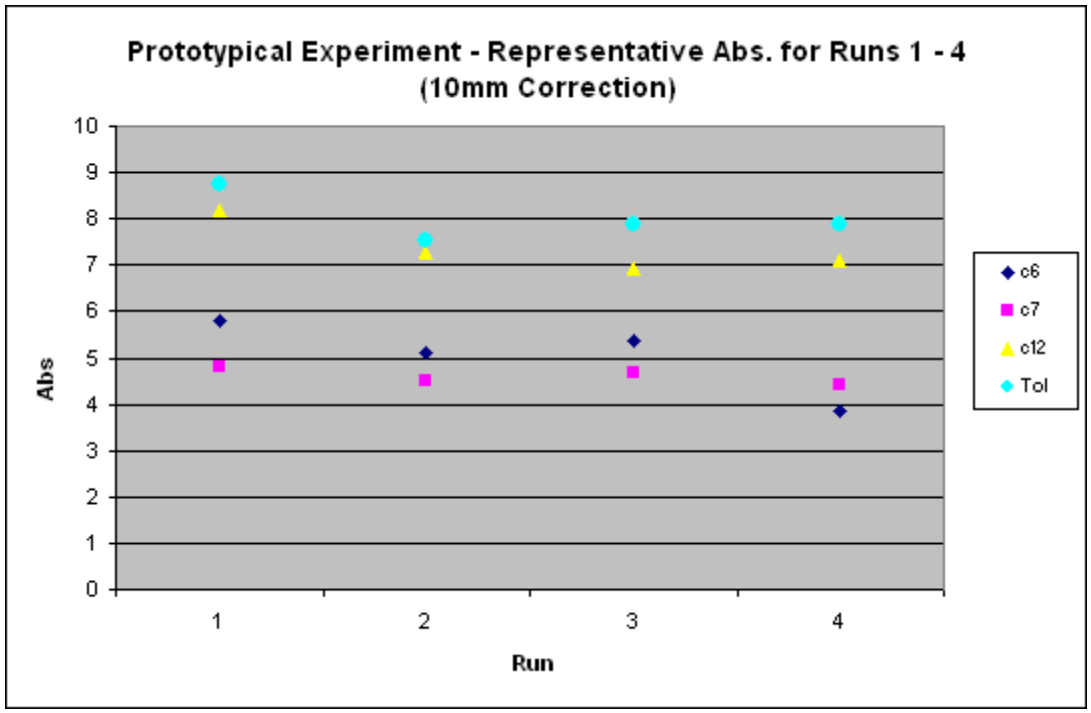

Figure 3-6: Typical absorbance data corrected for a standard 10mm path length

Beer's Law is a linear relationship of absorbance with increasing solution concentration; however, as the system's turbidity increases the linear relationship breaks down. Figure 3-5 illustrates this phenomenon at concentrations greater than 1.5×10^{-3} mol/L. The linear relationship from the calibration data is valid for concentrations up to 1.5×10^{-3} mol/L, and for absorbances up to about 2.5. An average absorbance for the n-heptane solvent of 4.9 in Figure 3-6, for example, is clearly outside that linear range of validity. A question of trustworthiness in this absorbance-to-concentration treatment is unavoidable. This treatment is in fact sound because the *raw data point* of 0.49 absorbance units (Figure 3-4) taken from the solutions is indeed within the range of validity for Beer's Law.

Concentrations of monomers in the supernatant are found by manipulation of the slope of the linear relationship in Figure 3-5, discovered by Dr. Ben Scott [18], provided in Equation 3-3.

$$Concentration = \frac{Abs + 0.027}{1700\,L/mol} \qquad \textbf{Equation 3-3}$$

Typical concentrations vs. trial run are plotted in Figure 3-7. We also plot concentration vs. solvent chain length in order to recognize any solvent-dependent functionalities and infer solubility behaviors of the nanoparticles in solution. These data are presented in Figure 3-8.

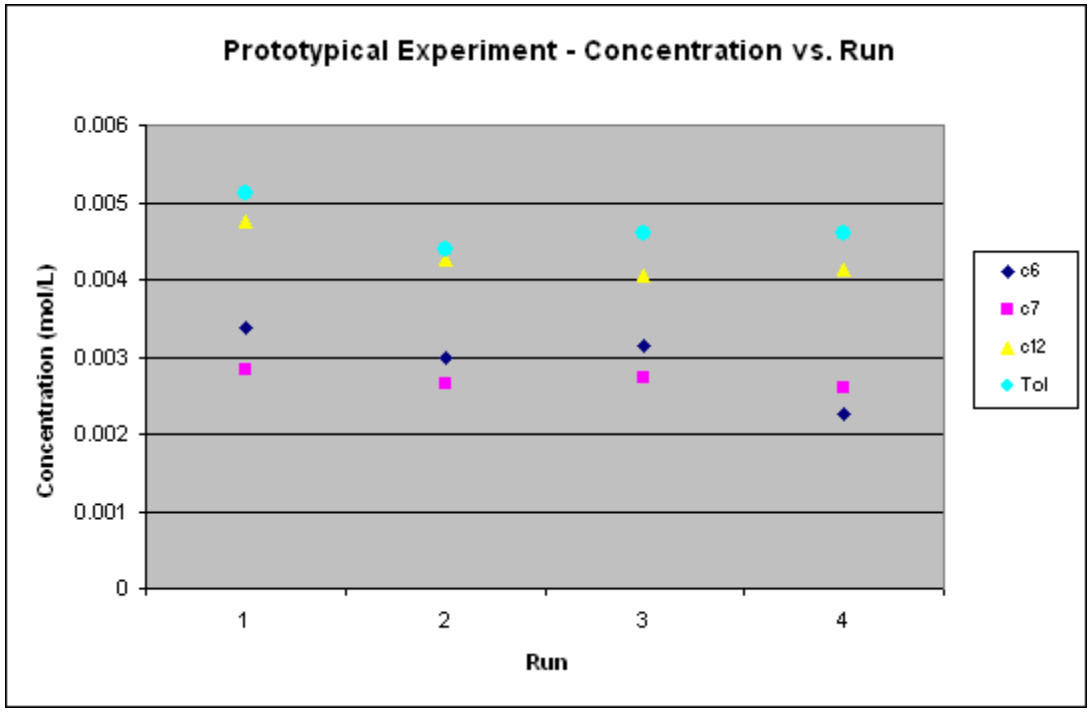

Figure 3-7: Typical concentration of Au atoms with experimental trial

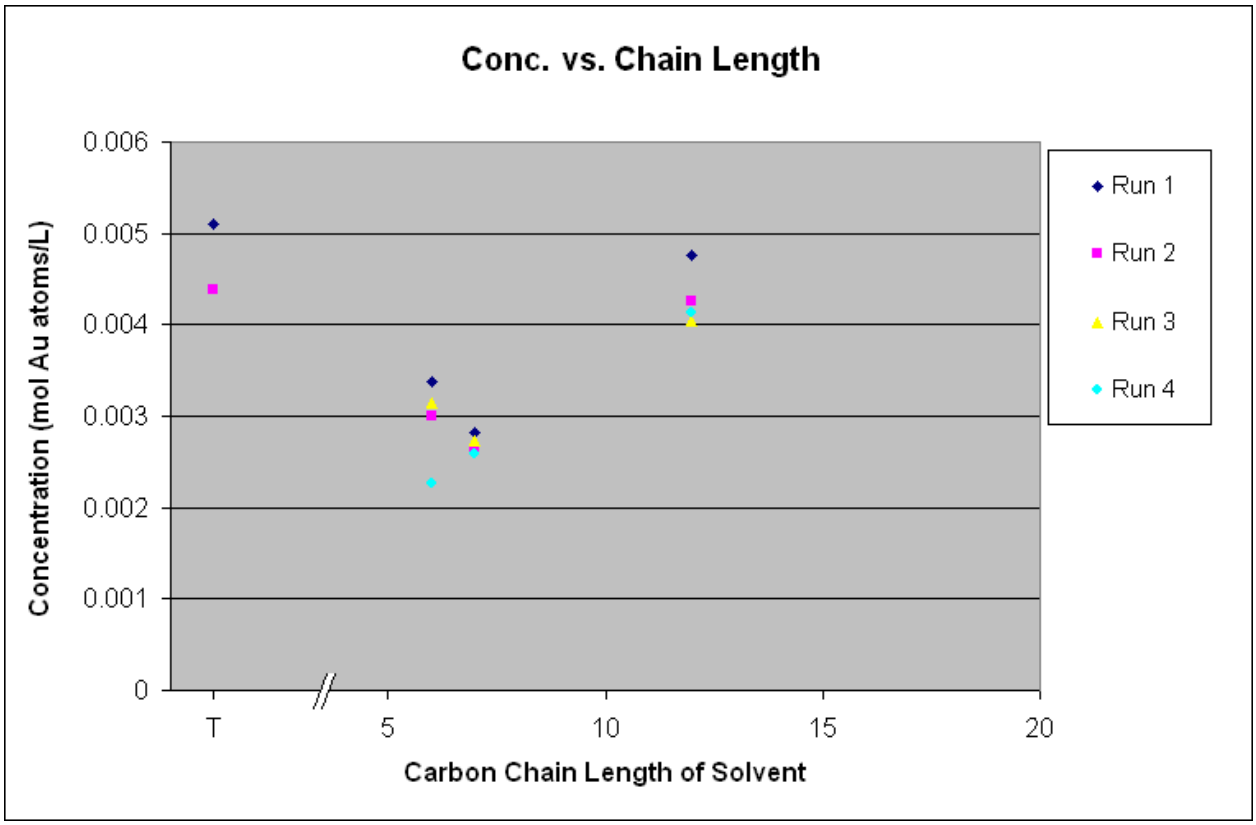

Figure 3-8: Typical concentration of Au atoms with respect to solvent chain. Notice non-alkane toluene is removed from the carbon length parameter.

Once the concentration data are available as a function of chain length, we must estimate the error bar. The simplest error bar estimate comes from finding the mean average for concentration at a given solvent chain, then fixing the error to be from the minimum to the maximum recorded values. As experimental technique became more sophisticated, more sophisticated types of error estimates became apparent and vary from experiment to experiment. Certain questions can be answered to gain insight on the experimental errors.

- How much noise is present in the UV-Vis spectrophotometer's raw data? A plot of zero absorbance should yield a horizontal line, but we noticed some fluctuations about zero. The band of absorbance for this "fuzzy zero" propagates through the 10mm correction and into the concentration data.
- If the cuvette is cleaned by rinsing with solvent, either pure solvent or n-hexane, some volume of solvent adheres to the glass. An estimate of how much solvent remains can be achieved by weighing the wet cuvette and comparing to a dry cuvette or by visually observing the meniscus's height in the cuvette after some time of settling. Knowing the

cuvette has a capacity of 100μL, we can see proportionally how much of the cuvette's empty column is occupied by solvent and estimate quantitatively the amount of residual pure solvent. Because the aliquot of sample being examined is about 25-50μL, we then know by how much the sample is contaminated and diluted by rinse-solvent. If the cuvette is rinsed with a portion of supernatant before the sample is introduced, the same type of error analysis can be done twice to estimate the contamination of rinse-supernatant that will be passed along to the sample.

- Was the supernatant contaminated by clusters in the dark turbid liquid underneath the supernatant after spinning? Care was taken as reasonably as humanly possible when the supernatant was pipetted away from the undesirable clusters, but unfortunately contamination happened when the spun clusters remain liquid (for shorter chain length solvents) instead of pelleting out to a solid precipitate. Sometimes a ribbon of this liquid can be observed caught in the pipette's suction and entering the supernatant. A quantitative error for these points is difficult to ascertain, but data for these contaminated solutions can be qualitatively identified and treated with skepticism in the final plot.

Error was estimated for our prototypical data by the minimum-maximum recorded point method and is presented finally in Figure 3-9.

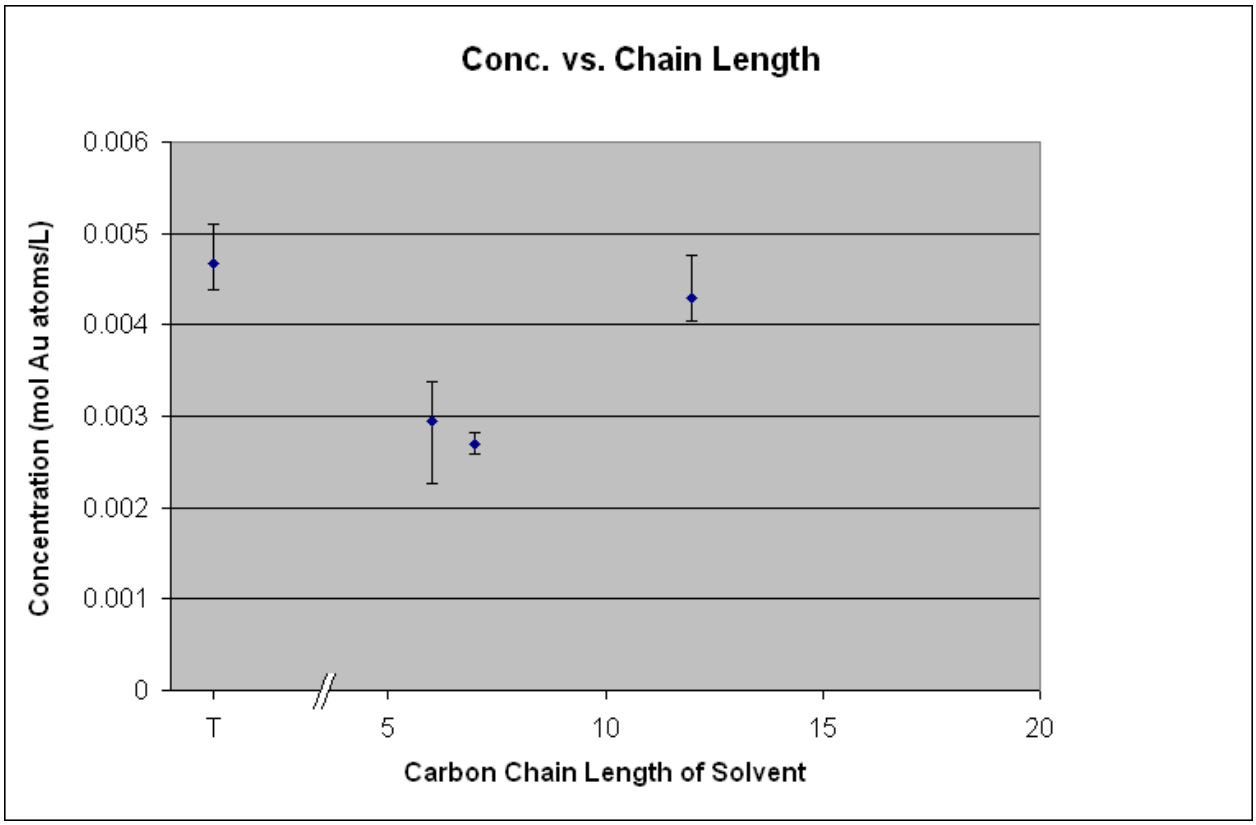

Figure 3-9: Final plot of saturated concentration vs. solvent chain with error bars for typical data

CHAPTER 4 - Data and Findings

Prototypical Data – The *"Renaissance Series"*

The data available in Figure 3-9 were acquired from a set of stock solutions prepared from a gold lot nicknamed "*Renaissance*." The particles were provided predissolved in solvent at a very exploratory stage of the experiment. The synthesis procedure (SMAD or Inverse Micelle?) is unknown as well as the nominal concentrations of AuNPs in the solvents n-hexane, n-heptane, n-dodecane and toluene. The data in Figure 3-9 paints a very incomplete picture of any monotonic behavior of solubility with increasing solvent chain length and the quantitative values of concentration of gold atoms per liter cannot be trusted with confidence unless the *Renaissance* data is considered collectively with other gold lots.

Although the data may not be reliable, much was learned from the *Renaissance* gold. A systematic technique was developed which yielded the reproducible data retained in Figure 3-9. Moreover, qualitative assessments of the AuNP solutions were made. For example, the long-chain solvent n-dodecane precipitated AuNPs after a few hours under a normal 1g gravitational acceleration, whereas solutions in the short chain solvents n-hexane and n-heptane remained very dark and turbid after days of storage under 1g. A colored transparent supernatant was isolated only after one hour of centrifugation under 12000g acceleration.

During centrifugation, it was noticed that a very heterogeneous separation of transparent colored supernatant from dark turbid remainders occurred. If the supernatant is a solution of pure monomers and the dark liquid is a mixture of several species of clusters with a continuous distribution of cluster sizes (dimers, trimers, tetramers, etc. out to *n*-mers), we should have seen a "fuzzy" transition from transparent supernatant on top to more translucent or turbid clusters on bottom. Instead we observed a discrete plane separating the monomers from the clusters that descended linearly with increasing centrifugation time. This discrete change implies that the dark liquid may be composed of a single specie of cluster that can be considered a "solution" of clusters in its own right. We can measure the terminal velocities of these particles as they fall and make a prediction about their size. Raw data on the depth of the binary liquid layer in the

centrifuge vials with time was used to compute the layer's speed. These speeds are given in Table 4-1.

Table 4-1: Speeds of descending liquid-liquid layer

	hexane	heptane	
Vmin	7.1	4.3	um/s
Vavg	7.8	6.6	um/s
Vmax	8.7	8.3	um/s

The terminal velocity of a spherical mass falling through a viscous liquid can be calculated by setting the net force on the sphere equal to zero.

$$F_{drag} + F_{buoyant} = mg \qquad \textbf{Equation 4-1}$$

The drag force comes from Stoke's Law [21], provided in Equation 4-2, where the drag depends on the drag coefficient C (6π for a sphere), the medium's viscosity η, the sphere's radius r and its terminal velocity v.

$$F_{drag} = 6\pi\eta r v \qquad \textbf{Equation 4-2}$$

In our case, the mass of a gold nanoparticle can be found by taking its density times its volume. Equation 4-1 can be tailored to our system in the following manner.

$$6\pi\eta_{solvent} r v + \frac{4}{3}\pi r^3 \rho_{solvent} g = \frac{4}{3}\pi r^3 \rho_{AuNP} g$$

The solution of which leads to a formula for terminal velocity in Equation 4-3.

$$v = \frac{2}{9}\frac{(\rho_{AuNP} - \rho_{solvent}) r^2 g}{\eta_{solvent}} \qquad \textbf{Equation 4-3}$$

The average density of the AuNPs with a 5nm diameter gold core and dodecane ligand shell comes to 3.56g/mL. Using the viscosities of n-hexane as 0.294cP (1 cP = 10^{-3} Pa-s) and n-heptane as 0.386cP, we can solve for the effective radius of these clusters treated as spheres. The speeds in Table 4-1 were used with the above data and Equation 4-3 to produce radii. Because the gold particles are ligated with dodecanethiol, the nanoparticle radius is 4.2nm, more than only the 2.5nm of the gold core. A ratio was found between the measured effective radius of clusters and the radius of the monomers. A table of these ratios of $r_{cluster}/r_{monomer}$ is presented below in Table 4-2.

Table 4-2: Ratios of cluster radius to monomer radius

	hexane	heptane
Rmin/Rmonomer	1.2	1.1
Ravg/Rmonomer	1.3	1.4
Rmax/Rmonomer	1.4	1.5

The cluster volume is proportional to the effective cluster radius cubed. If we were to compare the volume of clusters to the volume of monomers using a relation such as $V_{cluster}/V_{monomer}$, we recognize we can simply cube the ratio of radii $r_{cluster}/r_{monomer}$. The ratios of volumes are provided in Table 4-3.

Table 4-3: Ratios of cluster volume to monomer volume

	hexane	heptane
Min Vol/Monomer Vol	1.9	1.4
Avg Vol/Monomer Vol	2.2	2.6
Max Vol/Monomer Vol	2.6	3.7

The depths of the liquid-liquid layer were measured with the centrifuge vials held vertically, but the vials sat in the centrifuge at an angle. This means that the total vertical depth covered during the centrifugation was less than what was measured. The raw values of depth were overestimated by failing to preserve the orientation of the vial. Overestimated distance translates into an overestimated speed and thus, an over estimated radius and volume. It is probable that the true average ratios of cluster volume to monomer volume in Table 4-3 are much closer to 2.0. Because the clusters are composed of monomers, a cluster with twice the volume of a monomer has twice as many monomers in its composition. The clusters are probably dimers!

A continuous size distribution would result in a gradual gradient in turbidity or absorbance between monomers in the supernatant and clusters in the lower region of a colloid undergoing centrifugation. Because the liquid-liquid layer exists and is discrete, there is an implication that the AuNP colloid is composed of a solution of monomers and a solution of specially sized clusters with no allowed sizes in between. If the clusters are to be considered dimers, this observation of a liquid-liquid layer becomes obvious. There are no cluster sizes possible that exist between monomers and dimers. A further implication of this find is that the monomer solution could be in equilibrium not only with the precipitate, but also with perhaps a monodisperse “solution” of dimers.

Stock Solutions Made 1/30/2009 – Gold Lot *"Enlightenment"*

Preparation

The second set of stock solutions was made via the inverse micelle method followed by digestive ripening in toluene by S. Cingarapu, graduate student with Professor K. Klabunde, Department of Chemistry, Kansas State University. The series of solvents was expanded from the *Renaissance* data set to include toluene, n-hexane, n-heptane, n-decane, n-dodecane, n-tridecane, and n-hexadecane. Because the gold nanoparticles were delivered in a vacuum-dried state and may have been damaged due to ligands breaking from the gold surface, the NPs must not only be redissolved in a volume of solvent, but also re-ligated by adding a "drop" (50μL or 5% by volume in a 1mL sample) of dodecanethiol (DDT) to the solution. *Renaissance* data from Figure 3-9 for the most soluble solvent (toluene) was used to guide us in choosing a safe minimum gold mass to ensure the nominal concentrations are high enough to push the solutions into a two-phase system. After dissolution the stock solutions were sonicated for ten minutes. A table of AuNP masses chosen, the volumes of solvents, and nominal concentrations is provided in Table 4-4.

Table 4-4: Stock solution data for "Enlightenment" samples

	Au mass (mg)	Au (mol)	Solvent (μL)	DDT (μL)	Nom. Conc. (mol Au/L)
n-hexane	2.7	1.4E-05	3000	50	0.00457
n-heptane	2.5	1.3E-05	1000	50	0.0127
n-decane	2.8	1.4E-05	1000	50	0.0142
n-dodecane	2.8	1.4E-05	1000	50	0.0142
n-tridecane	3.1	1.6E-05	1000	50	0.0157
n-hexadecane	3.1	1.6E-05	1000	50	0.0157
toluene	2.8	1.4E-05	1000	50	0.0142

Because of hexane's volatility, 20-30% of the sample is lost due to evaporation during the standard 60 minute spin under 12000g acceleration. To compensate for this evaporative loss, larger samples of hexane solution were taken. Anticipating a potential shortage of stock solution in future runs, the hexane solution was tripled in volume with no regard for the relative proportion of gold mass or excess DDT. This careless volume expansion resulted in the hexane solution's nominal concentration being dangerously close to the concentration of Au-toluene solution from the *Renaissance* set in Figure 3-9. The *Renaissance* Au-toluene concentration is a benchmark for the *Enlightenment* experiment for estimating a critical minimum nominal

concentration before the monomer solution completely dissolves the precipitate and slips into an unsaturated (one-phase) state. The nominal concentration of *Enlightenment*-hexane however is still ~150% of the *Renaissance*-hexane supernatant's monomer concentration, so the monomer solution should still be in equilibrium with the precipitate for this particular stock solution. These facts may or may not contribute to potential sources of error in the final concentration vs. carbon chain plot for this gold lot.

Examining Raw Data

The experimental procedure follows the generalized rubric of Chapter 2. Typically a 125μL aliquot of sample was spun for 60 minutes and the resulting supernatants were transferred to a clean cuvette. The cuvette was cleaned by rinsing with pure solvent corresponding to the sample solution, followed by another single rinse with some of the supernatant sample. The resulting absorbance data were manipulated and plotted in Figure 4-1.

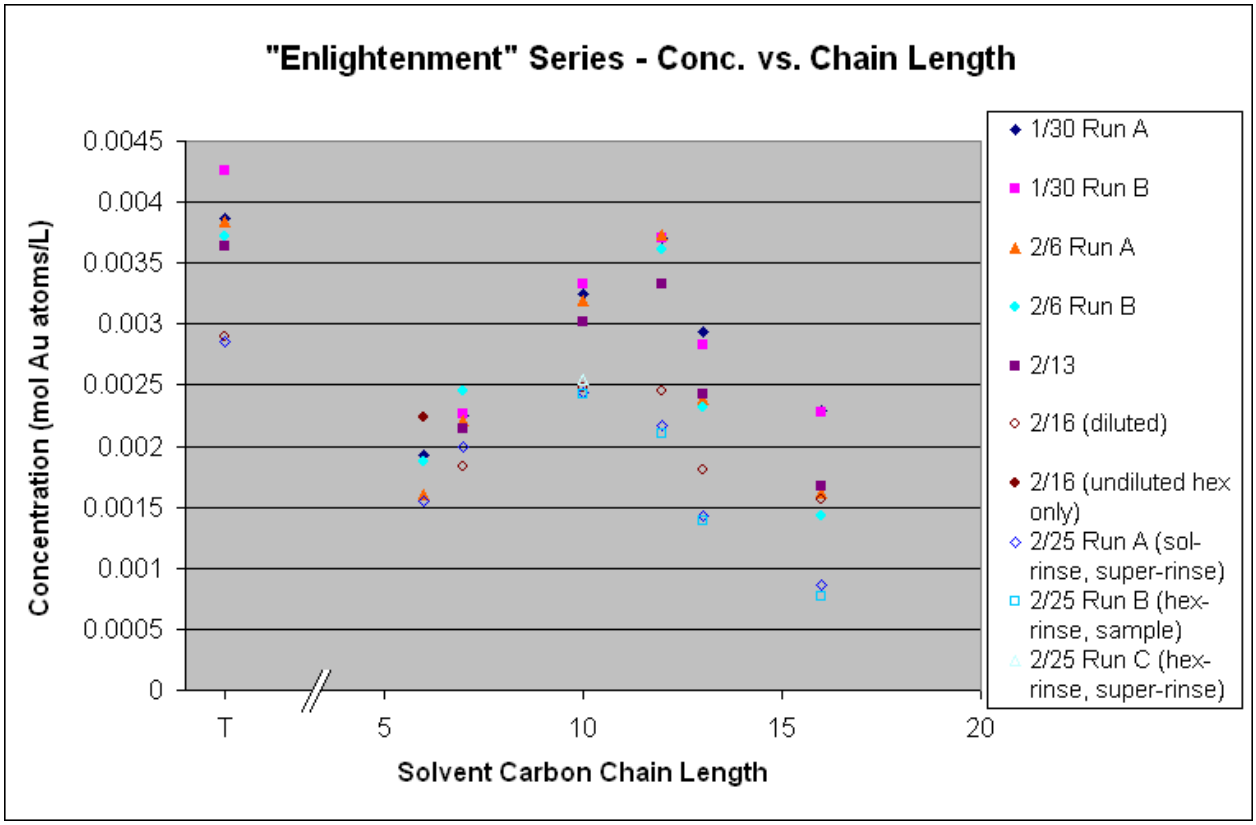

Figure 4-1: Saturated concentration vs. solvent chain length for "Enlightenment" experiment

Data were taken over five total runs spanning three sessions on 1/30, 2/6 and 2/13. After the 5th run on the 3rd session (2/13) all stock solutions except hexane ran low. Undissolved precipitates were observed in all of the stock solutions. With the exception of Au-hexane—which was diluted and increased in volume threefold at the onset of the experiment—500μL of additional solvent was added in order to obtain more data from the nearly depleted stock solutions. Data from these newly volume-increased solutions are displayed in the two "2/16" runs. Data points taken from diluted solutions are represented by hollow markers in Figure 4-1, whereas undiluted data are represented by filled markers. If enough excess AuNPs exist in the precipitate, the addition of solvent should dissolve it until the new "diluted" solution is saturated with monomers, leaving behind a remaining undissolved portion of the precipitate and a monomer solution with the same concentration as that observed before dilution. Still, the distinction between the two experimental regimes—before and after dilution—should be noted in the figure. Because the hexane sample in the 2/16 run was undiluted, it was appropriate to pull that single datum out of the collective 2/16 data.

There is some concern over the approximate 50% drop in concentration between data before dilution and the 2/16 (diluted) data series. Perhaps the dilution *does* play a hand in changing the equilibrium monomer concentration? Although, if the systems *did* slip into a one-phase or unsaturated solution, we should expect the different solutions to have roughly the same concentration (within about 25%), implying their equal starting masses (within about 25%) have been completely dissolved. This evidence for dilution effects is absent from the data in Figure 4-1. A very important control was absent from the 2/16 (diluted) data. The ratio of solvent to dodecanethiol (DDT) was *not* 5%. Only 500μL of solvent was added to the nearly-empty stock solutions. The corresponding 25μL of DDT to help coat the NPs with ligand was omitted. We have observed from experience a strong importance of DDT on the solubility of the gold nanoparticles. Bare un-ligated gold spheres have no solubility in these solvents. By coating the particles with a bristling ligand shell, we provide a means for the NPs to interact with the surrounding solvent. This experiment may have been defeated when the DDT/solvent ratio was fouled at the dilution step.

Three sets of data were produced during the 2/25 session. Run A was conducted normally on the solutions which had been diluted *and* ligated with a 25μL drop of DDT. The cuvette was rinsed first with a pure solvent corresponding to the sample solution. It was then

decanted and rinsed with a portion of supernatant to flush away residual solvent wetting the glass surface. Finally the rinse solution was discarded and a sample was inserted into the cuvette and examined under UV-Vis. Run B was performed with a single rinse of pure hexane. It was decanted leaving a very thin wetting layer of residual hexane followed by insertion of the sample. If the sample was diluted by the hexane layer, it was diluted by much less than it would be by pure solvent because the hexane's thin wetting layer contains less volume than a solvent with a thicker, more voluminous residual layer. Run C was intended to be a continuation of Run B. After Run B's sample was discarded, it could be considered a "supernatant rinse" for the sample in Run C. Because a single 150μL aliquot of gold solution was spun yielding ~100μL of supernatant, not much supernatant was available for two rinses and two samples. Only one solution (Au-decane) had enough supernatant solution by the fourth portion to gather any data.

Based upon the data for Au-decane in Figure 4-1, the pure hexane rinse yielded higher absorbance (less contamination via dilution by pure solvent) than the solutions' natural solvents. The difference between pure hexane rinse and pure solvent rinse is only a few percent and is within a range of skepticism as to whether the hexane treatment is significantly better; however, an argument based on reason will tell us that less hexane adheres to the glass surface, thus there is less contamination of the first supernatant rinse, thus there is less contaminated supernatant adhered to the glass, thus there is less contamination by dilution in our final sample. Further justification for the hexane treatment comes from practical considerations. The hexane's volatility helps it to dry out more than a heavy nonvolatile long-chain alkane when briefly exposed to air during sample preparation. Hexane is inexpensive in bulk and is much cleaner to deal with in the laboratory. These lessons learned from the 2/25 Runs in Figure 4-1 were carried on as improved technique in the next experiment.

Further Manipulation and Pattern Recognition

Considering all of the data in Figure 4-1 collectively is difficult, as discrete "regimes" seem to have developed within the data. Instead of lumping together all data points for a single solution, the old adage of "comparing apples to apples" comes to mind. A more appropriate treatment is to consider all data series with common elements. For example, Runs 1/30 A and 1/30 B were performed on the same day. It is logical to condense these two together while exploring, say, diluted samples from three weeks later separately. These plots are displayed in

Figure 4-2 with error bars varying between the maximum and minimum measured concentration. The two series that had no multiple runs lack error bars. The lone hexane datum for undiluted 2/16 run was folded into the 2/13 series. The 2/13 series lacked a value for hexane and it was the most comparable data run for the lone hexane point.

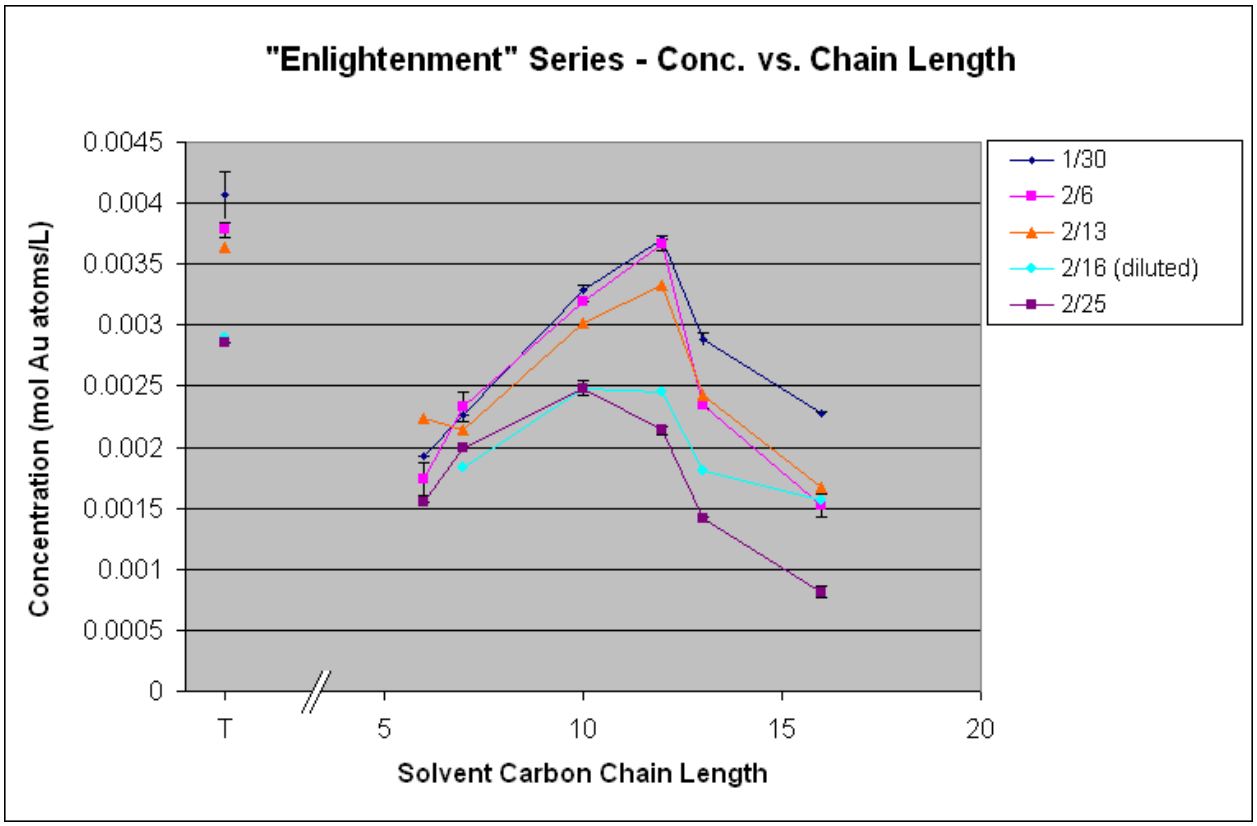

Figure 4-2: "Enlightenment" data condensed into single day data series

There appears to be a time dependence implying that the nanoparticles have an effective lifetime. This is noticed most prominently in the longer chain solvents (dodecane, tridecane, hexadecane). To feature this time dependence, concentration data were plotted against stock solution age in days in Figure 4-3 with notation identifying undiluted, diluted –DDT, and diluted +DDT regimes.

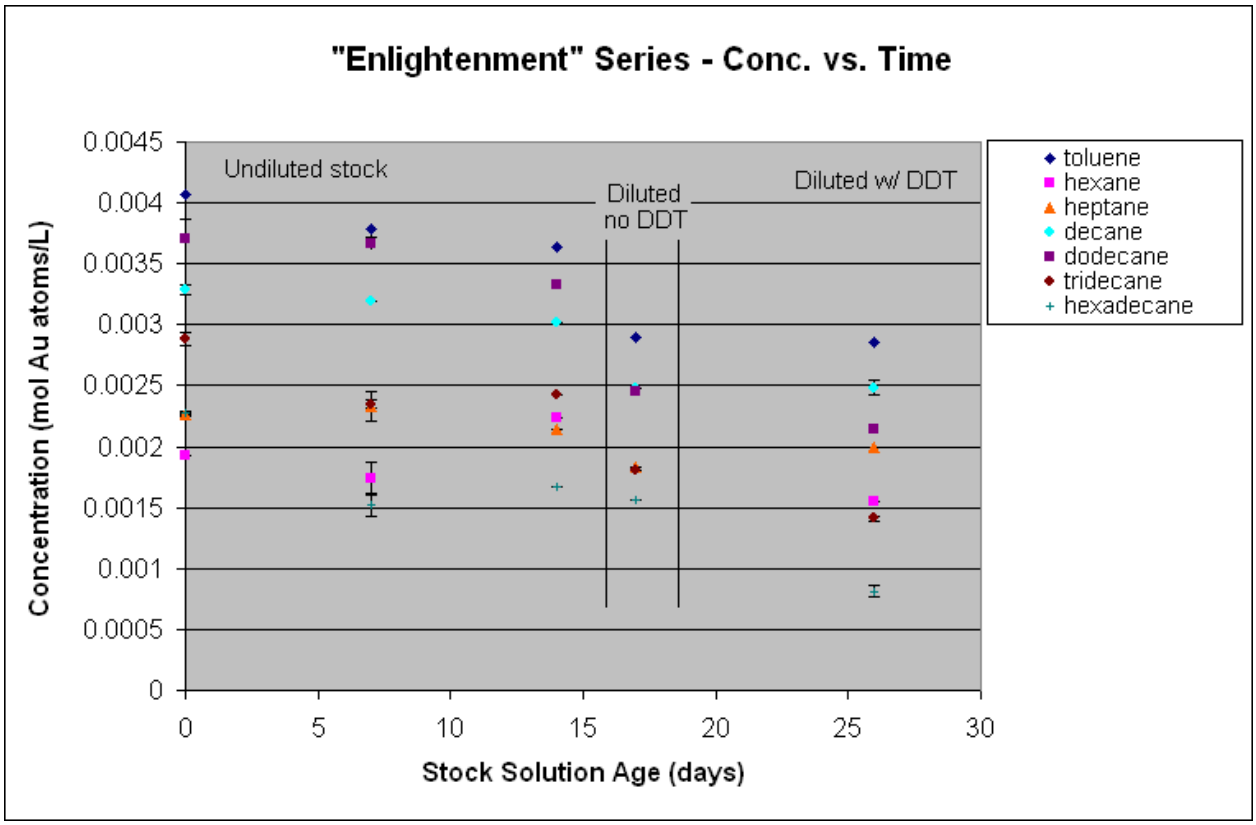

Figure 4-3: Concentrations plotted against solution age with dilution regimes noted

Because the Day 17 (diluted with no DDT added to maintain excess ligand/solvent ratio) data has been identified as erroneous, excluding it from further analysis is appropriate. Furthermore, if we can assume the addition of DDT in the Day 26 sample makes it a comparable data set to the pre-diluted data, a very clear decreasing trend of concentration with respect to time develops. The question is to the functionality of this decrease. For solvents with chain lengths greater than heptane, the functionality could either be a linear or an exponential decay. Plots with trendlines are displayed below in Figure 4-4 and Figure 4-5.

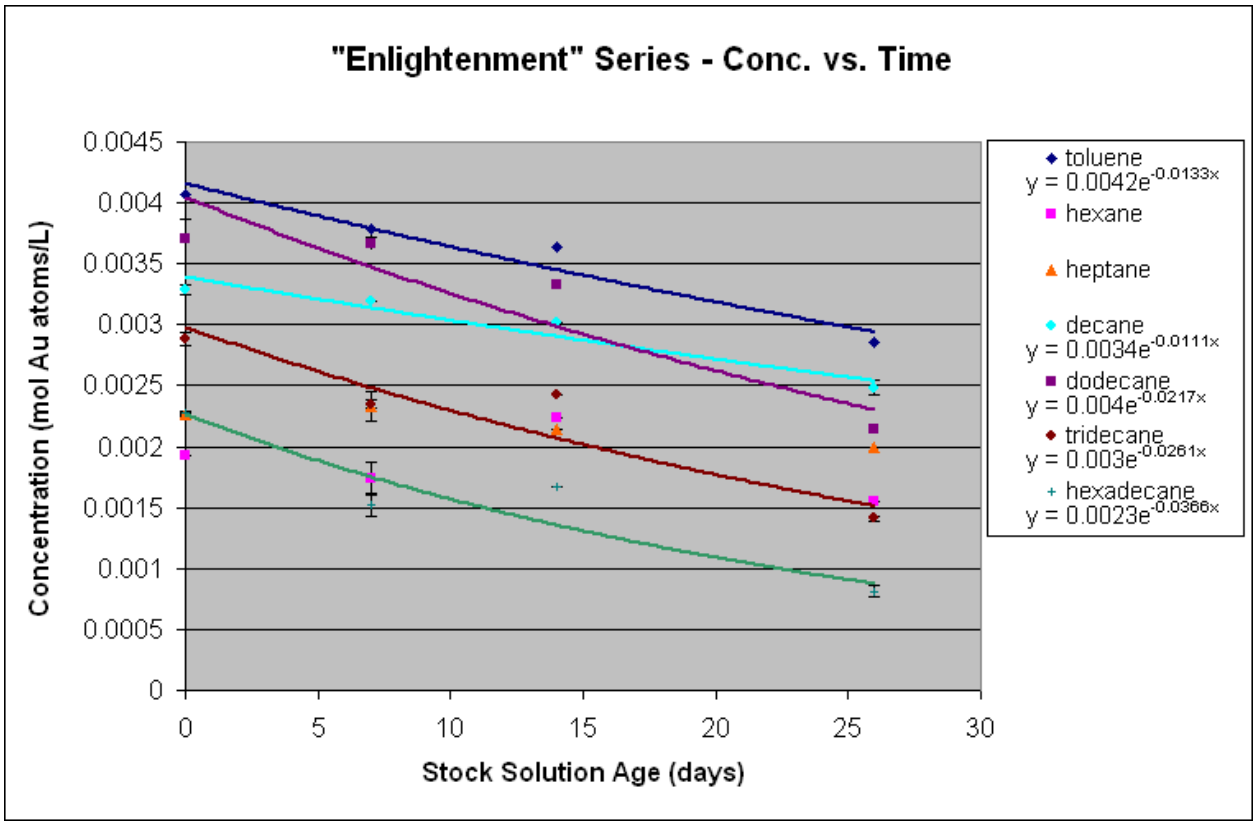

Figure 4-4: "Enlightenment" saturated concentration vs. time with exponential trendlines

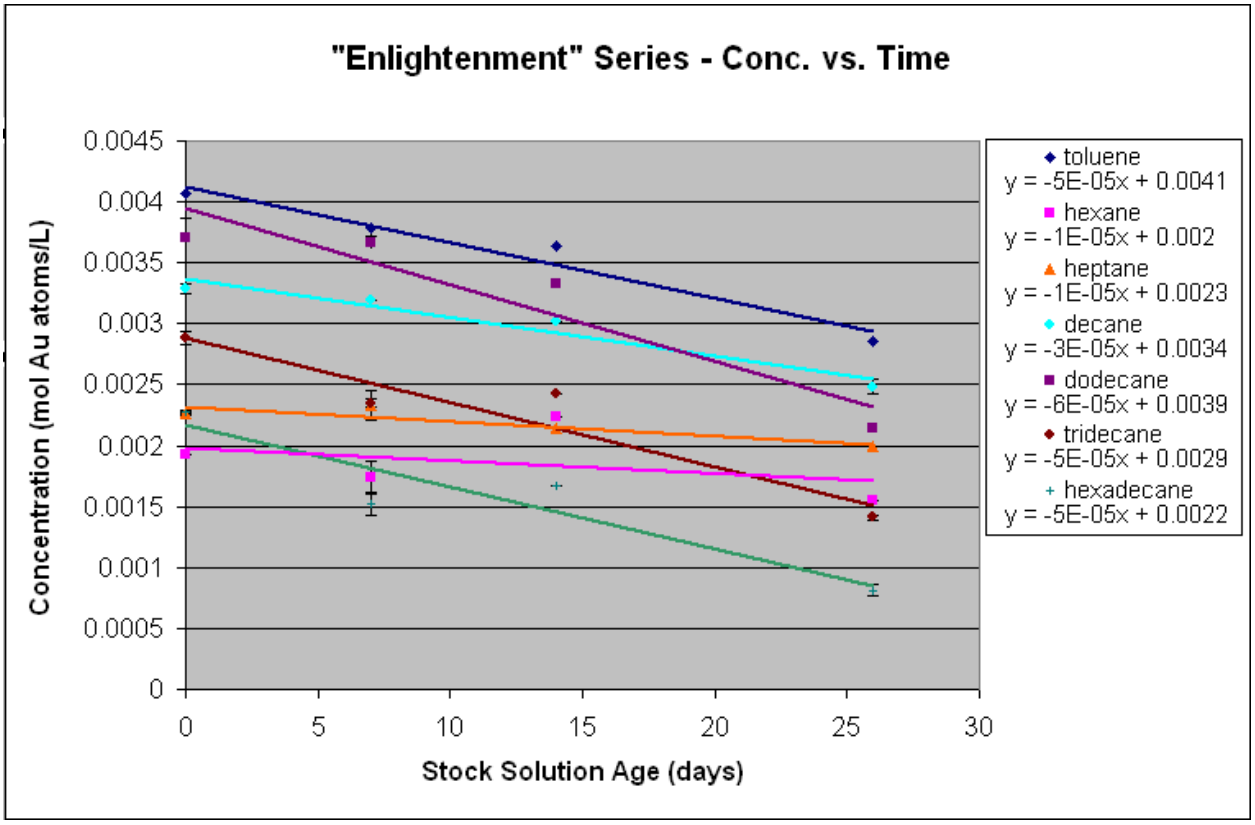

Figure 4-5: "Enlightenment" saturated concentration vs. time with linear trendlines

Stock Solutions Made 2/23/2009 –Gold Lot *"Modern Era"*

A vacuum dried lot of gold nanoparticles was prepared via the inverse micelle method and it was digestively ripened in toluene. A total mass of 49.2mg of AuNP was available for the preparation of a new set of stock solutions dubbed the *"Modern Era"* series. More data was required to fill in the gaps in the solvent carbon chain length functionality from the *Enlightenment* experiment. The alkane solvents used includes the complete homologous series between n-hexane and n-hexadecane. At the onset of the experiment, neither n-tetradecane nor n-pentadecane was considered for study, but these solvents were included in later data collections. In addition the solvent list includes toluene and p-xylene. Strict comparisons of only solubility parameters predicts toluene should be a bad solvent with respect to DDT-ligated gold, yet the data from both *Renaissance* and *Enlightenment* experiments suggest toluene is an even better solvent than dodecane—the location of the peak concentration of gold with respect to alkane chain. We suspected some effects beyond the solubility parameters contributed to this

increase. Perhaps a dipole moment due to the methyl group connected to toluene's benzene ring contributes to this effect? To test this hypothesis p-xylene was added to the list of solvents. Para-xylene has the same structure as toluene with the exception that a second methyl group is situated across the benzene ring from the first. A molecular comparison is provided in Figure 4-6. Because p-xylene has a solubility parameter similar to toluene, it should also be a bad solvent. If the good solvent nature of toluene is due to some kind of dipole moment effect, p-xylene's symmetry should negate it, thus a very low concentration of AuNP monomers should result. Further discussion of the predictions and solubility parameters is reserved for Chapter 5.

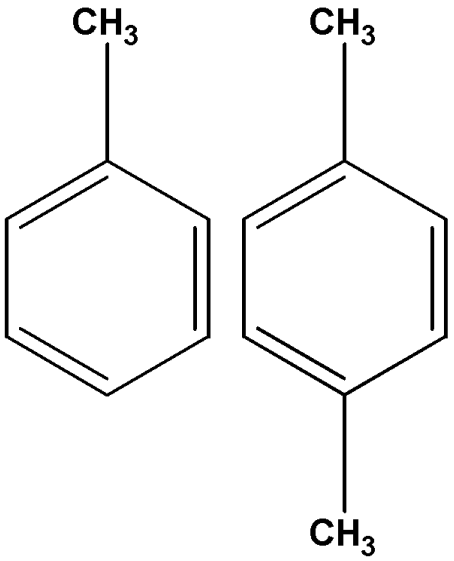

Figure 4-6: Structural comparison of toluene (left) with p-xylene (right)

First-String Players – The Starting Lineup of Solvents for Study

Stock solutions were made from the gold with nominal concentrations twice as high as the most concentrated points from *Enlightenment* data. The gold masses were dissolved into the solvents and 5% (by volume) DDT was added. The stock solutions were sealed with parafilm and sonicated for fifteen minutes. Typical sample sizes for the centrifuge were 125μL with the exception of hexane. The solvents chosen, masses, solvent volumes, DDT volumes and nominal concentrations are available in Table 4-5 below.

Table 4-5: Stock solution data for first set of "Modern Era" samples

	Au mass (mg)	Au (mol)	Solvent (μL)	DDT (μL)	Nom. Conc. (mol Au/L)
n-hexane	3.8	1.9E-05	2000	100	0.010
n-heptane	2.6	1.3E-05	1000	50	0.013
n-octane	1.8	9.1E-06	1000	50	0.0091
n-nonane	2.0	1.0E-05	1000	50	0.010
n-decane	2.1	1.1E-05	1000	50	0.011
n-undecane	2.3	1.2E-05	1000	50	0.012
n-dodecane	2.4	1.2E-05	1000	50	0.012
n-tridecane	2.5	1.3E-05	1000	50	0.013
n-hexadecane	2.4	1.2E-05	1000	50	0.012
toluene	3.1	1.6E-05	1000	50	0.016
p-xylene	2.8	1.4E-05	1000	50	0.014

Several measures were employed to improve consistency and confidence in the data after failures were identified in the *Enlightenment* experiment.

- Foreseeing the need to use larger aliquots of Au-hexane for centrifugation because the volatile nature of the hexane will evaporate away too much supernatant leaving too little sample for the UV-Vis apparatus to function properly, the Au-hexane volume was doubled. Unlike the *Enlightenment* experiment, the mass was doubled in order to maintain a similar nominal concentration to the other stock solutions and the amount of DDT added was doubled to keep its DDT/solvent ratio at 5%.
- *Enlightenment* data suggested a time-dependence affecting the solubility of the nanoparticles. This chemical instability could be due to exposure to light, heat or oxygen. The plastic box containing the stock solutions was able to block most of the ambient light in the room. The inside was lined with aluminum foil in order to increase the box's opacity to block all room light. Also, the stock solution bottles in the *Enlightenment* experiment were closed "hand-tight" with a screw-on cap. The solutions are only exposed to open air for about 30 seconds during each data collection and the caps should be tight enough to seal out continued exposure to atmosphere after the bottles are closed. Nevertheless, parafilm was used for the *Modern* series to further exclude oxygen when the stock solutions were not being sampled.
- An improved experimental technique was learned from the *Enlightenment* experiment. Instead of rinsing the cuvette with pure solvents that could leave a thick layer and larger volume behind after decanting, all cuvette rinses were performed with pure hexane. Because the hexane leaves behind only a thin layer, less residual solvent is present to

dilute the supernatant rinse. Also, because of hexane's volatility, a more substantial portion of that residual layer may evaporate off before the following supernatant rinse—contaminating it even *less*. The new cleaning technique involves two rinses with pure hexane followed by one rinse with a portion of supernatant before the introduction of sample for testing.

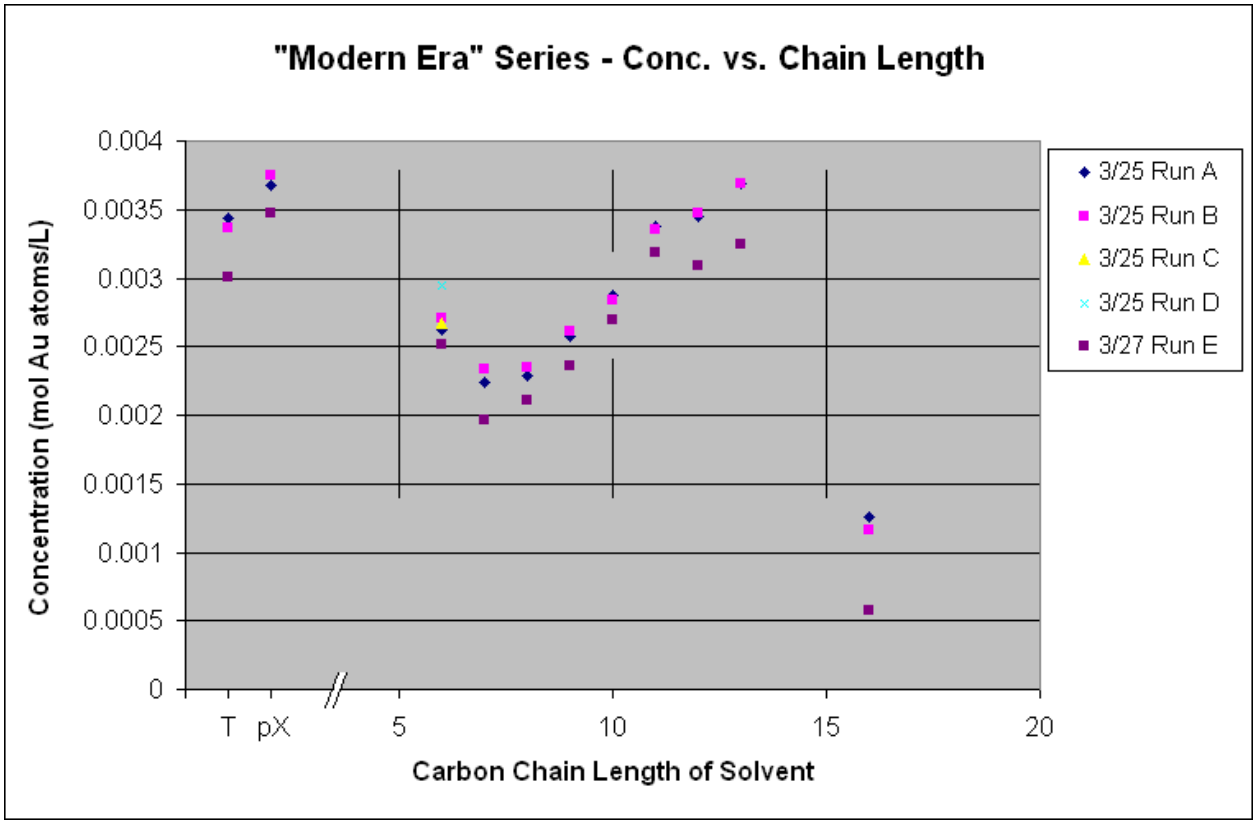

Figure 4-7: "Modern Era" saturated concentration data from two separate days of experimentation with respect to solvent chain length

The results from two experimental sessions (3/25 and 3/27) are provided above in Figure 4-7. Several notable features are present.

- The peak concentration appears to occur at n-*tri*decane, not n-dodecane; however, the true peak may be obscured within experimental error.
- The hypothesis that p-xylene would perform poorly as a solvent for gold nanoparticles ligated with an alkane solvent is false. The plot shows p-xylene to hold a greater concentration of gold monomers than toluene. Whatever force is responsible for this phenomenon is *not* related to a dipole moment due to the asymmetry of toluene's structure.

- A "tail" on the functionality—that is, an increase in the solubility in n-hexane compared to n-heptane—seems to have developed near the short-chain solvents. This feature is implied by *Renaissance* data of Figure 3-9 but is absent from *Enlightenment* data in Figure 4-2. We should recall though that the controls in the *Enlightenment* n-hexane stock solution were compromised in the DDT re-ligation at the initial dissolution stage, so the absence of evidence for the "tail" is not necessarily the evidence of absence. Both *Modern* and *Renaissance* data suggest there is a break from the increasing concentration with increasing chain length trend at n-hexane.

  We should recall that the hexane's volatility was a constant nuisance during the experimental technique because the volume of solution available after centrifugation was often insufficient to fill the cuvette enough to take UV-Vis data, so the total volume of hexane solution was tripled with a corresponding tripling of DDT. *Modern* solutions contain 5% DDT by volume, and DDT does *not* evaporate as hexane does. A strong correlation between the DDT/solvent ratio and solubility of AuNPs has been observed (see discussion on *Enlightenment* sample run "2/13 diluted"). We could postulate that as the hexane evaporates the relative concentration of DDT in the solvent increases, thereby potentially increasing the concentration of monomers in equilibrium with the precipitate in the centrifuge vials. Once the supernatant is pipetted off of the precipitate, it has been transformed into a solution of monomers with different solubility properties than the stock solution from which it came. Heptane solutions do not exhibit such evaporative losses during the 60 minute centrifugation. This potential "contamination" of the hexane solution by "excess DDT" and resultant increase in monomer concentration could explain why the data shows a "tail" at n-hexane while the concentration for n-heptane is lower and in agreement with the trend of solubility parameter comparisons.

  One could argue that this postulate is contradicted by the absence of the "tail" for both *Enlightenment* runs. We should recall that the volume of *Enlightenment* hexane stock solution was tripled without an appropriate tripling of DDT. In order for enough hexane to evaporate in the *Enlightenment* centrifuge filler such that the DDT/solvent ratio is elevated to that of the other "tail" hexane solutions, *three times as much evaporation would have to occur in the same amount of time!* In fact, the absence of the tail in *Enlightenment* runs seems to confirm the role DDT plays in the solubility of DDT-ligated

NPs as well as confirm the hypothesis that the hexane "tail" is a consequence of experimental error from using non-airtight centrifuge vials with a volatile solvent.

The Backup Team – A More Complete Homologous Series of Alkane Solvents

The *Modern Era* experiment was partially modified after preliminary data suggested the concentration peak may not have been centered at dodecane. Is the greater concentration at tridecane just due to run-to-run variation and error, or does the concentration *continue* to increase at tetradecane or pentadecane? This void in the solvent data demands attention. Stock solutions for n-tetradecane and n-pentadecane were made with leftover dry gold from the *Modern Era* gold lot. A new stock solution was made for n-hexane as well. Even though the nominal concentration and relative DDT/solvent ratio were preserved in the larger-volume solution of n-hexane, the differences in absolute amounts of mass, volume, and DDT are still potential lurking variables. A new stock solution of n-hexane was prepared to the same nominal concentration as the other solutions, but with only 1000µL of solvent and 50µL of DDT. Preparation data for the new solutions are available in Table 4-6.

Table 4-6: Stock solution data for second set of "Modern Era" samples

	Au mass (mg)	Au (mol)	Solvent (µL)	DDT (µL)	Nom. Conc. (mol Au/L)
n-hexane (new)	3.0	1.5E-05	1000	50	0.015
n-tetradecane	1.7	8.6E-06	1000	50	0.0086
n-pentadecane	1.8	9.1E-06	1000	50	0.0091

With the addition of two more solvents, the total list of stock solutions includes n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, toluene and p-xylene for a total of 13 solvents. The centrifuge rotor is equipped with 12 bays. Because the solutions are spun for 60 minutes, it is not feasible to break the experiment into two sessions. One of the solvents must be cut from the study and that solvent was p-xylene. Para-xylene was only included to test a hypothesis about toluene's solubility properties. It is evident that there is a more complicated mechanism governing the aromatic solvents. Though data on the entire aromatic series would be interesting, it goes beyond the scope of this study on alkanes and would be best left for a future project.

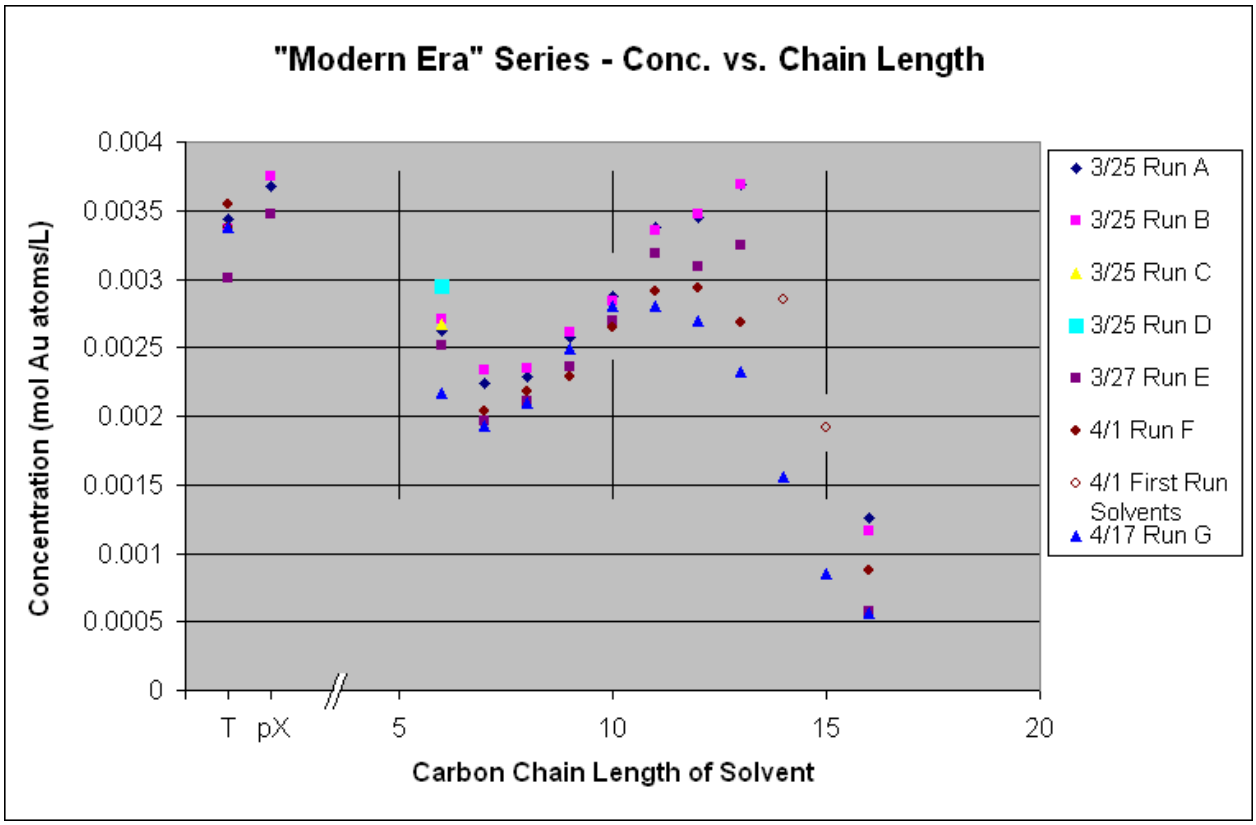

Figure 4-8: "Modern Era" saturated concentration data with respect to solvent chain length

The concentration data for *Modern Era* gold is provided above in Figure 4-8. Run F taken on 4/1 contained some of the new stock solutions. Because it has been observed that a potential chemical instability or "lifetime" exists for the particles, it was appropriate to discriminate particles experiencing their first data collection from older "veteran" samples. The time dependence does not appear as prominent (or present at all) for solvents from heptane to decane, while the longer alkanes vary greatly over time. This implies that the parafilm is somewhat successful in stabilizing the solutions over time, or it implies that that the long chains solutions are more susceptible to changing with age. The apparent "hexane tail" is still present. The hexane tail appears to be anomalous, but it has been confirmed with better controls in *Modern* data, recognition of errors made in *Enlightenment*, and an initial sighting in *Renaissance.* Finally, data taken on the new solvents n-tetradecane and n-pentadecane drastically fall from their initial 4/1 Run F values. Similarly strange behavior is manifested for initial "Day 1" data in some of the other *Modern* solutions, as well as previous *Enlightenment* solutions. A potential variable could lie in the fact that the solutions were sonicated when they

were initially prepared. Because the sonicator generates heat, the solutions were inadvertently heated gently on the preparation date until they were lukewarm to the touch. The solutions were left to settle for several hours during which they would have cooled back to room temperature. Because the solutions returned to room temperature before being examined under UV-Vis, this should not have been an issue, yet the observed gentle heating is worth mentioning. In any case, confidence is lacking in the same-day-as-preparation samples and they should be excluded from data analysis for these systems overall.

The final analysis of data is provided below in Figure 4-9. Mean average concentrations were based on data excluding 3/25 Run A and 4/1 First Run Solvents. The error bars are estimated as a range between the minimum and maximum observed concentrations. These error bars *do* include the "first day" data because although we discounted the initial runs due to some kind of anomalous behavior, these concentration values *were* measured and it is possible that the true concentrations could be valid between the average and the higher maximum recorded value.

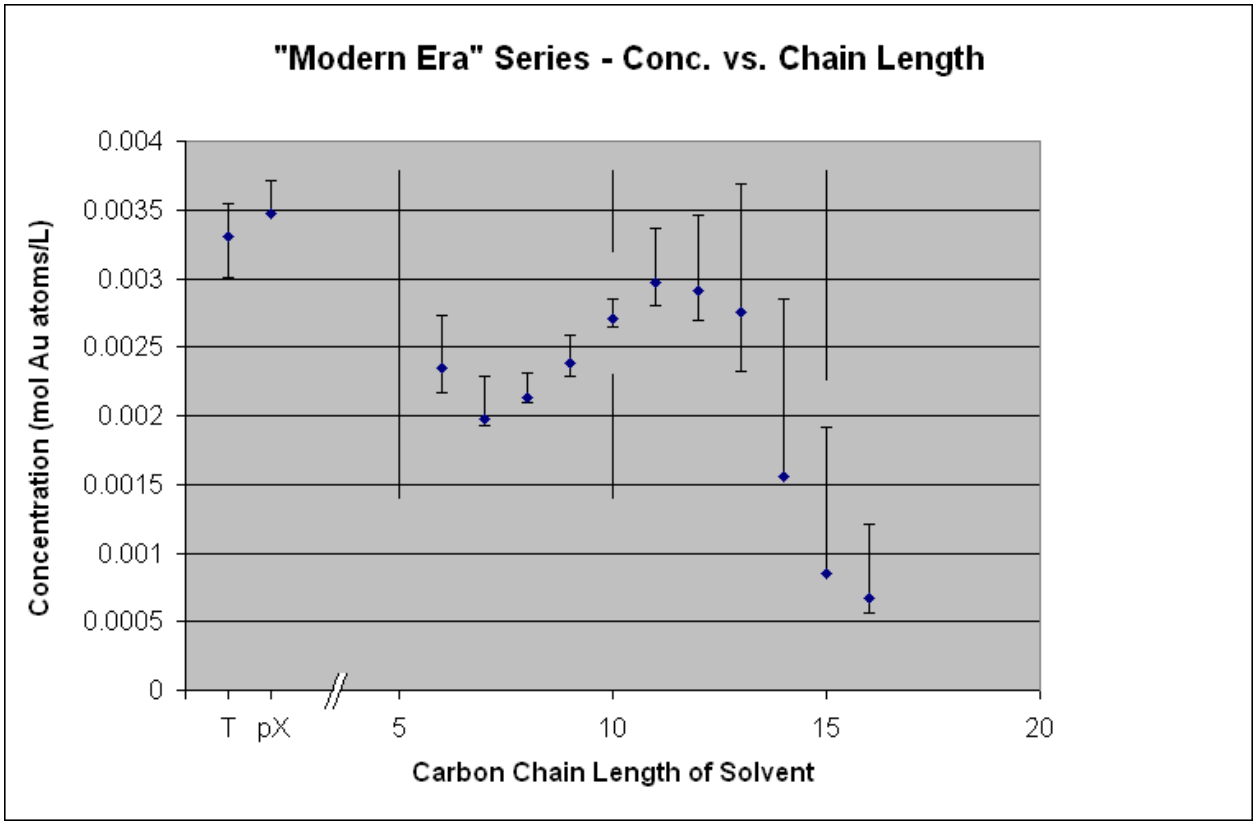

Figure 4-9: Final "Modern" saturated concentration vs. solvent chain length

CHAPTER 5 - Analysis and Theoretical Considerations

Critical Analysis of All Data

Data from *Renaissance, Enlightenment* (before dilution and after dilution) and *Modern* experiments is provided in Figure 5-1. It should be noted that first-day data series have been omitted from *Enlightenment (Before Dilution)* and *Modern* data in computing average concentrations. First-run data was considered in estimating the error bars for *Modern* data but was not considered in the error bar estimates for *Enlightenment (Before Dilution)*. The *Enlightenment* experiment was separated into two regimes: before and after dilution to expand the total volume of stock solution. It should be noted that sample "2/16 Diluted" in Figure 4-1 that was diluted without addition of extra DDT to compensate for the increase in volume was excluded from the mean average computation as well as the error bar estimates for *Enlightenment*. Also, the lone undiluted "2/16" data point above in Figure 4-1 was used in the average and error bar computations for *Enlightenment Before Dilution* in Figure 5-1 below. The error bars in *Enlightenment (After Dilution)* for toluene, hexane and heptane are absent because only one data point was acquired for these solvents. Because run-to-run variations of a range of about 10% greatly overshadow error due to noise in the detector and residual solvent present after a supernatant rinse, modest error bars of 2 or 3% are misleading for these solvents and have been omitted. Moreover, data for the other solvents with multiple points were all taken on the same day. Significant run-to-run variation seems to be present between data sets taken in different experimental sessions. The error bars on the solutions in decane, dodecane, tridecane and hexadecane have modest error bars estimated from minimum recorded concentration to maximum recorded concentration; however, because the multiple runs were conducted on the same day, these error bars may not reflect run-to-run variation but instrumental noise and lab error. For this reason, the error bars on all solutions in *Enlightenment After Dilution* could be misleading and should be treated with skepticism. Finally, all data series were plotted with a slight offset to one another to aid in distinguishing overlapping error bars. For example, concentration data at carbon chain lengths of 6.9, 7.0, and 7.1 all correspond to n-heptane.

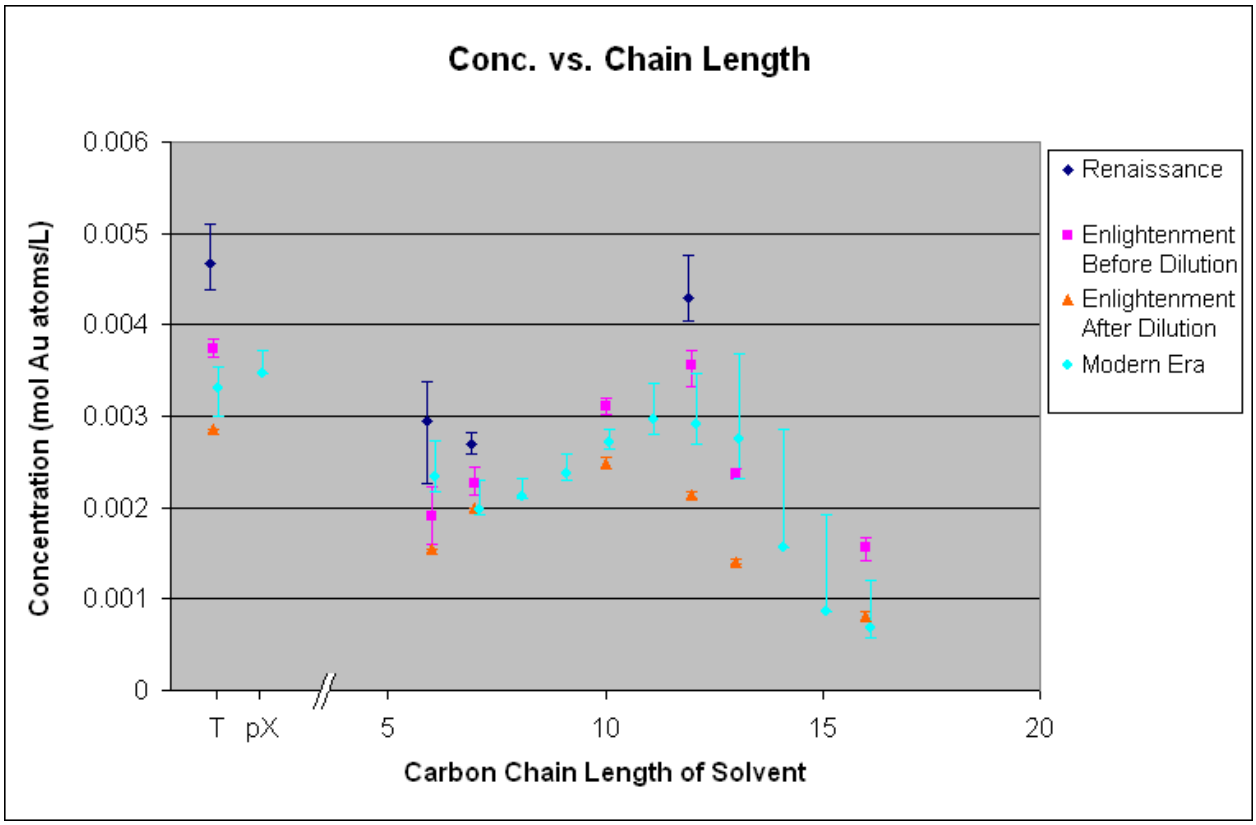

Figure 5-1: Saturated concentration vs. solvent carbon chain length for all three experiments.

Though the different data sets appear to have a scalar or multiplicative offset in absolute concentration relative to one another, there is a clear trend showing a functionality of concentration of gold nanoparticle monomers ligated with dodecanethiol and dissolved at room temperature in alkane solvents with varying carbon chain lengths. We can infer from the data and the error bars that the peak concentration for the alkane series is located at a carbon chain length of 12. This means that AuNPs coated in dodecanethiol are most soluble in n-dodecane as compared to other alkane solvent*s*. It should be noted however that for all four data sets presented, toluene is the best solvent overall in solubility of AuNPs. This is an interesting observation, but because toluene is an aromatic and not an alkane a comparison of toluene alone to the alkane series is inappropriate. Implied from the miniscule amount of data acquired from p-xylene, a more appropriate hypothesis to make is that aromatic solvents dissolve aklanethiol ligated gold nanoparticles better than normal alkane solvents. Verification of this hypothesis is better left to a separate future project.

Is the conclusion that n-dodecane dissolves dodecanethiol ligated nanoparticles reasonable? Dodecanethiol differs from n-dodecane in that a sulphur containing thiol (S-H) group is affixed to one end of the carbon chain. The DDT ligands are attached to the AuNP by the sulphur atom. As far as the solvent is concerned, it only "sees" the dodecane chain in the DDT because the sulphur is too "busy" interacting with the gold surface. In our simple model, we think of the NPs as being coated in n-dodecane. Knowing that "like dissolves like," it is perfectly reasonable that n-dodecane has the greater solvent properties on *itself* than any other alkane solvent.

Solubility Parameters

Solubility parameters provide an estimate of the interactivity of a particular solvent with another. The **Flory-Huggins** parameter χ is found from the following relationship between the molar volume of the solvent and the solubility parameters of the two alkanes (ligand and solvent) [22].

$$\chi = \frac{V_{molar}}{RT}(\delta_{solvent} - \delta_{ligand})^2 + 0.34 \qquad \textbf{Equation 5-1}$$

In Equation 5-1, R is the gas constant, V_{molar} is the molar volume, T is the absolute temperature and $\delta_{solvent}$ and δ_{ligand} are the solubility parameters of the solvent and ligand, respectively. The Flory-Huggins parameter is a gauge for how well a solvent can dissolve another liquid material. A better gauge for the solvent's effectiveness is the parameter $(1/2 - \chi)$. A plot of $(1/2 - \chi)$ for all solvents tested with the exceptions of n-tetradecane and n-pentadecane (these solubility parameters were not available) and with the addition of n-pentane is provided below in Figure 5-2.

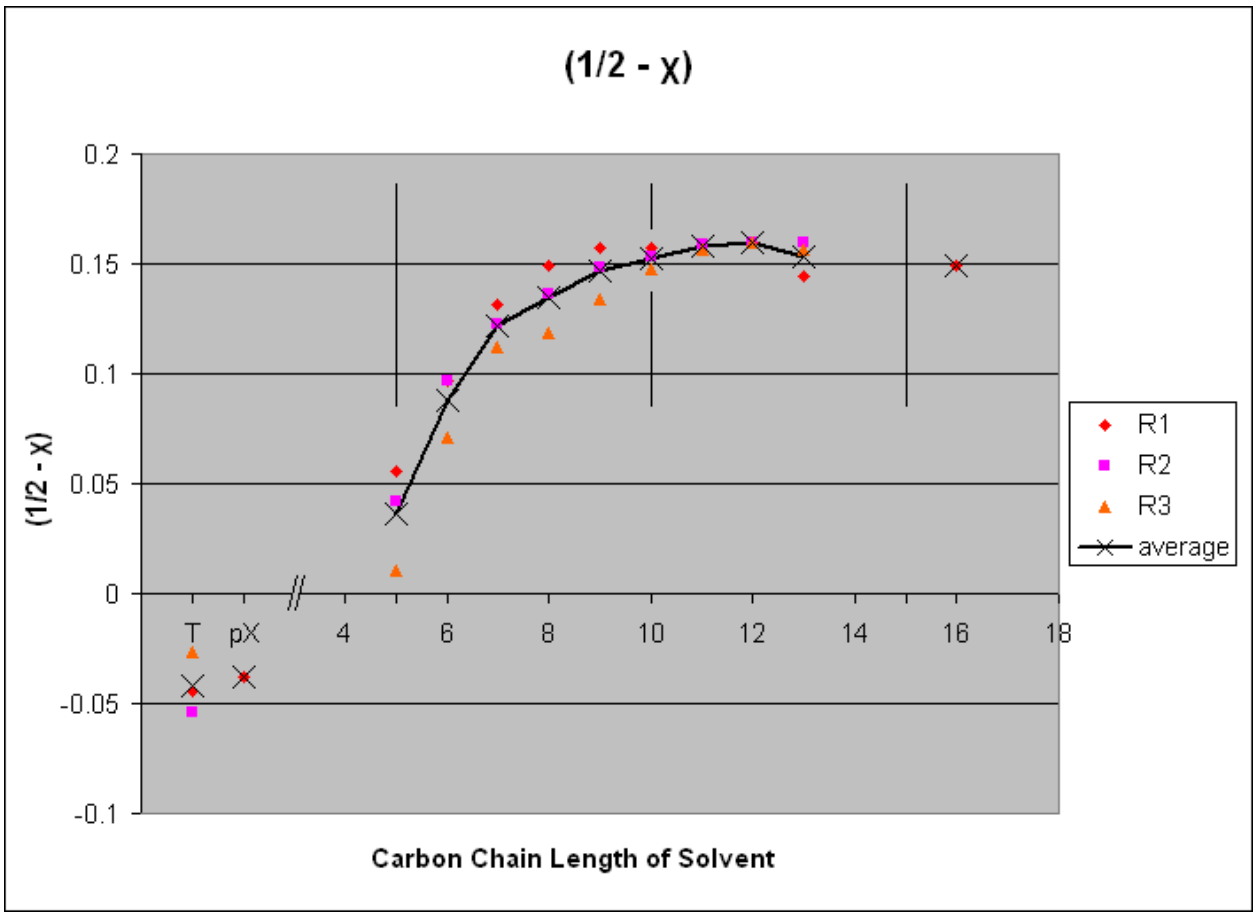

Figure 5-2: Comparisons of solubilities based on Flory-Huggins parameters

Solubility parameters vary between sources, so three sources of data were taken. In Figure 5-2, R1 corresponds to parameters computed using solubility data from [23], while R2 and R3 came from [24] and references therein. The molar volumes are provided in [23].

We superimposed the average values from Figure 5-2 over monomer concentration data acquired throughout experimentation to create Figure 5-3 below. The figure is essentially Figure 5-1 with $(1/2 - \chi)$ plotted against a secondary axis. The scales of the y-axes in Figure 5-3 were manipulated such that the concentration scale equals 0.02 of the $(1/2 - \chi)$ scale with both scales sharing a common zero. This allowed the calculated parameters to be positioned in the midst of the measured data. No normalization techniques or other manipulations of the data were employed. These are simply two overlapping charts.

We could have imposed a scalar or multiplicative correction (or both) onto the $(1/2 - \chi)$ plots in order to "force" it to fit the measured concentration data at one or two points. This method was not used because such a correction would have meant the maximum value of 0.16 for $(1/2 - \chi)$ at dodecane would be transformed into a concentration of 0.0032 mol Au/L. Had we plotted these "newly transformed" $(1/2 - \chi)$ values in terms of concentration in units of mol/L, we may be confused into believing these values are predicted or calculated absolute concentrations of monomers when in fact $(1/2 - \chi)$ is only a general estimate of how well the pure solvents can dissolve pure n-dodecane with no regard to the AuNPs whatsoever. Plotting the concentration data and calculated $(1/2 - \chi)$ values on two separate y-axes was more appropriate because the two sets of data retain their distinctive nature and we are simultaneously able to see the trend of solubilities and the trend of concentration data without falsely correlating the two.

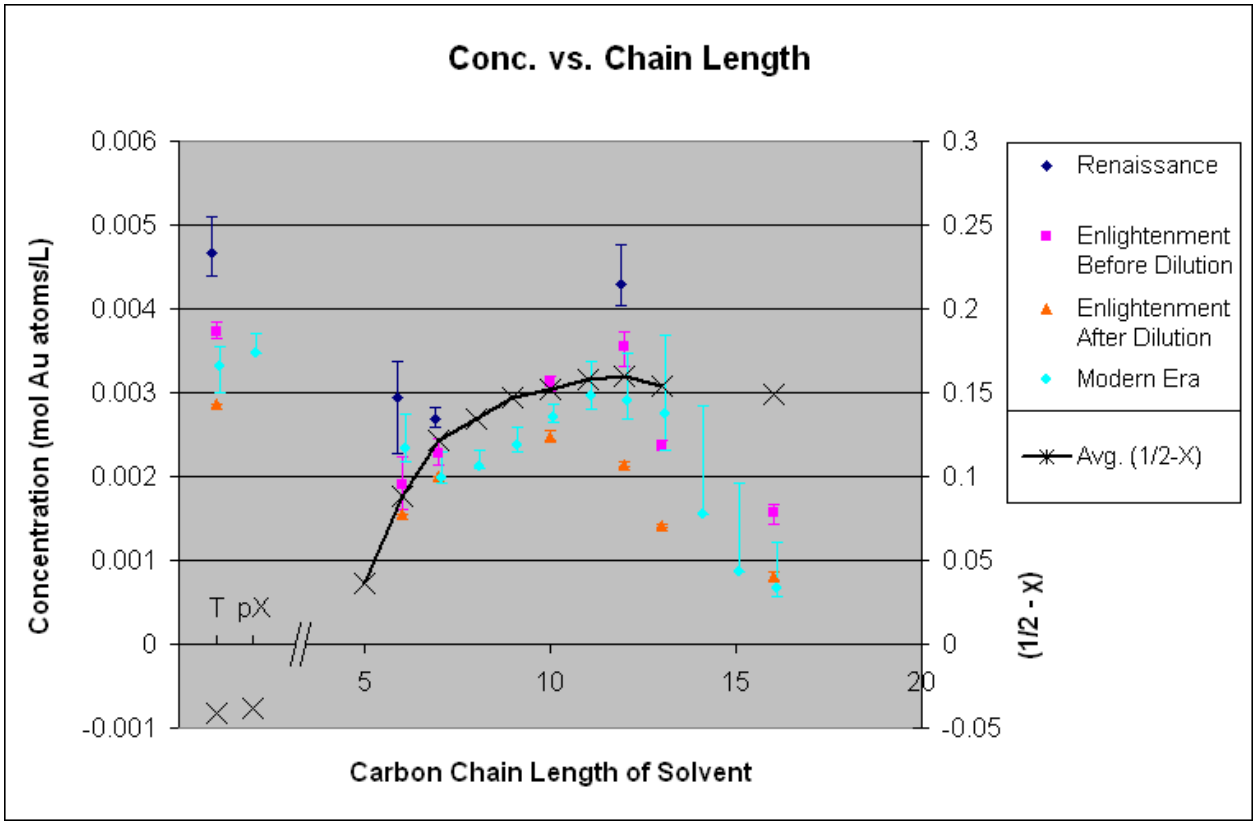

Figure 5-3: $(1/2- \chi)$ superimposed on concentration data

The figure shows a clearly increasing trend of solubility parameters that corresponds to our increasing trend of monomer concentration in equilibrium with a precipitate with peaks at n-dodecane. The prediction of solubility for our simple model works well between n-heptane and

n-tridecane. Some important features are noted in the comparison of solubility parameters to the measured concentrations.

- A "tail" was noticed around n-hexane corresponding to a brief decrease in solubility followed by an increase with increasing chain length up to the n-dodecane peak. This phenomenon was not predicted by the solubility parameter comparisons for n-pentane (of which AuNP monomer concentrations were not measured experimentally) through n-heptane. We had established above in Chapter 4 in the analysis of *Modern Era* data that the "tail" is most likely a product of experimental error caused by evaporation of the hexane in the solution resulting in the relative concentrating of DDT in the solutions. The "tail" in the measured concentration data seems to run counter to the trend of increasing concentration with increasing chain length until the peak at n-dodecane. It would appear that the solubility parameter analysis supports the idea that this anomalous increase in concentration for hexane solutions is not to be expected and is most likely an erroneous result.
- The parameter $(1/2 - \chi)$ describes the interaction between the solvent and the polymer ligand. If $(1/2 - \chi)$ is a positive value, we can say the solvent is a "good solvent." From that, the greater the relative value of $(1/2 - \chi)$, the better the solubility. Normal hexadecane was observed to behave as a weaker solvent than n-dodecane, yet the $(1/2 - \chi)$ value for n-hexadecane predicts that it should be a good solvent.
- If $(1/2 - \chi)$ is a negative value, we say the solvent is a "bad solvent." The calculations then predict that the aromatic solvents should not dissolve the gold nanoparticles. The data tells us though that the toluene and p-xylene are much better solvents for AuNPs than the n-dodecane. The aromatics' much greater solubility properties must be due to some more complicated mechanism than is described by the solubility parameters.

CHAPTER 6 - Conclusions

We make the following conclusions.

1) A non-monotonic functionality exists between the saturated concentration of dodecanethiol ligated gold nanoparticle monomers, dissolved at room temperature in an n-alkane solvent, in equilibrium with a precipitate and the carbon chain length of the solvent.
2) The gold nanoparticles are most soluble in n-dodecane compared to other normal alkane solvents.
3) The nanoparticles appear to be more soluble in aromatics than normal alkanes. Verification of this hypothesis should be performed in a future work.
4) The solutions of AuNPs appear to have a useful lifetime. Some chemical instability is observed that diminishes the nanoparticles' solubilities over time.
5) The presence of excess ligand in the solution greatly affects the particles' solubilities in the solvent.
6) A turbid mixture exists under normal room gravity for shorter chain solvents. Apparently the shorter chain solvents hold not only a solution of monomers in equilibrium with the precipitate, but also a solution of dimers. This phenomenon is not present in longer chain solvents.
7) A simple model was used to estimate the solubility properties of the solvents by approximating the dodecanethiol ligands as pure n-dodecane dissolved in various solvents. Flory-Huggins parameter comparisons correctly predict the trend of the measured concentrations for the most part, albeit with very important discrepancies. The simple model is good, but due to these discrepancies at n-hexadecane and the aromatics, it is inadequate to fully describe the system.

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Appendix A - Glossary of Terms

Beer's Law: A linear relationship between the absorbance of light to a solution's concentration, molar absorptivity and path length.

Digestive ripening: A procedure in which gold colloid solution is heated near the boiling point of its solution's solvent under reflux. Digestive ripening results in nearly monodisperse nanoparticles.

Flory-Huggins parameter: A numerical estimate of the degree of solubility between two polymers.

Gold lot: A batch of gold nanoparticles. A series of stock solutions may derive from the same gold lot. Typically a gold lot arrives from the chemists in a vacuum-dried state where it can be divided and dissolved in various solvents to make the stock solutions used for experimentation.

Lambert's Law: An exponentially decaying relationship of the transmitted intensity compared to the initial intensity of light passed through a sample of absorbers.

Nominal concentration: Concentration of solution "in name only." The nominal concentration is strictly based upon the amount of gold nanoparticles mixed in a known amount of solvent. Nominal concentration should not be confused with the actual concentration of dissolved monomers that the solvent is capable of holding at a given temperature.

One-phase system: An unsaturated solution in which all nanoparticle monomers are fully dissolved.

Plasmon: A quantum of plasma oscillation of the free electron gas at the surface of the gold nanoparticle.

Reflux: A situation in which vapors from a boiling liquid are collected, condensed and returned to the boiling sample. A system heated without reflux would be boiled to dryness.

Stock solution: A bottle or jar of AuNP solution from which small samples are taken for study.

Stoichiometry: A property of compounds in which their constituent atoms always appear in the same definite proportions.

Two-phase system: A saturated solution in which the concentration of nanoparticle monomers is at a maximum value for a given temperature. The monomers suspended in solution are in equilibrium with undissolved precipitates.