Solvent filtration through the use of monolayer-protected gold nanoparticles

By

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Chemical purification is typically approached by taking advantage of the constituent molecules’ sizes, densities, phase transitions, or bonding capabilities to isolate individual chemical components from one another. Here, a novel approach for solvent filtration is proposed based on localized geometric constraints and bonding capabilities through the use of mixed monolayer ligand coated nanoparticles. Gold nanoparticles were synthesized and coated with octane thiol and mercaptoproprionic acid in a 3:1 ratio. Such nanoparticles have been reported to form an interesting grooved surface morphology, and it has been shown that their solubility varies according to the ability for individual solvent molecules to penetrate these grooves. Here, a system of filtration was designed, aimed at using these nanoparticles to remove a small quantity of ethanol from a solution of methanol. Solubility tests were performed on the synthesized nanoparticles and additional possible contaminants were isolated for testing including toluene, chloroform, and trihydrofuran. Titration columns were run to test the ability of the synthesized nanoparticles to separate the candidate contaminants above from a methanol solution. NMR spectroscopy of both the filtered and unfiltered solutions was performed and the results compared. Although far from conclusive, the evidence presented in this paper indicates that it very may well be possible to remove specific solute molecules from solution by flowing them through a group of nanoparticles with very clearly defined surface morphologies.
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I would also like to sincerely thank the department’s faculty, staff, graduate students, and my undergraduate peers for making my educational experience at MIT as inspiring as it has been. Additionally, I extend my love to my girlfriend for all of her support and understanding in dealing with my frustrations while working on this project, my father for teaching me to always measure three times and cut once rather than the other way around, and most important of all, my mother, without whom I would not be here today.
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**Background and Motivation**

Chemical purification is a broad and crucial branch of engineering which serves a variety of societal needs. Purification applications span a scale ranging from the massive quantities of drinking water and petrochemical products consumed around the globe daily to the separation of specific chemicals from one another in laboratory or pharmaceutical settings. For each of these applications, a number of separation mechanisms are used depending on their suitability to the particular task at hand. Common methods of purification include distillation, filtration, evaporation, and adsorption. The work undertaken in this study seeks to validate a novel approach to chemical purification by taking advantage of the high surface area to volume ratio of nanoparticles to create a compact filter which could be used to separate miscible chemicals from one another. The proposed means of purification is a filter-inspired adsorption method which relies heavily on the enthalpic interactions between the nanoparticle surface sites and solvent molecules. Proof of the validity of this conceptual filtration method would open the doorway to further research, possibly leading to tunable filters for a variety of tasks where chemicals of similar densities, boiling points, and other chemical properties would make conventional purification methods difficult or impossible.

Monolayer-coated nanoparticle solubility has long been known to heavily depend upon the surface composition presented to the surrounding solvent by the ligands. A recent study entitled “The role of nanostructure in the wetting behavior of mixed-monolayer-protected metal nanoparticles” (Centrone et al) has shown that in certain cases, nanoparticle solubility is not only affected by the composition of the monolayer and the particular chemical groups presented, but also depends heavily on the nanostructure of the surface itself. The authors propose that the unique surface topography of their synthesized nanoparticles (shown below in a schematic
In the aforementioned study, a series of nanoparticles was synthesized using mercaptoproprionic acid (MPA) and octane thiol (OT) in varying quantities. The surface characteristics of the synthesized nanoparticles were quantified and solubility measurements were taken on the series to study variation of the nanoparticles with composition. Results suggest that in certain cases, solubility is actually highly dependent upon the ability of individual solvent molecules to interact with the nanostructured surface in different ways.¹

Since the previous work cited directly attributes the solubility of the nanoparticles to the unique nanostructured surface presented by the monolayer, one might pose the question as to why the use of nanoparticles as a substrate for the monolayer is even necessary. First of all, the monolayers presented on the surface of the nanoparticles in question were self-assembled during nanoparticle synthesis. This both simplifies the monolayer deposition process and assures the consistent synthesis of particles with the same surface characteristics. The rate of nucleation and growth directly affects nanoparticle size, which in turn affects the surface curvature likely affects the shape of surface pockets and ultimately the solubility. Furthermore the use of nanoparticles
offers the use of their surface plasmon (a wave affecting its optical properties) as a simple empirical method of determining nanoparticle solubility. Most importantly however, nanoparticles have an extremely high surface area to volume ratio. Since the solubility of the particles is directly attributed to the pockets on their surface, the most efficient means of filtering out target molecules from a solution should be to flow that solution through a network of tightly packed nanoparticles. Ultimately, could the monolayer pockets be reproduced on the surface of a more conventional, larger scale filtration medium such as a mesh, a much larger sized filter would be needed to achieve the same number of surface pockets as a small cluster of nanoparticles.

Of particular interest from the solubility studies in the work cited above was the measured solubility of nanoparticles in both methanol and ethanol. While the chemical composition of both solvents is extremely similar (with the ethanol molecule being slightly larger and containing an extra methyl group), the solubility of the nanoparticles in each was found to vary dramatically at a particular ligand concentration. When particles were synthesized using OT and MPA in a 3:1 ratio, it was found that their solubility varied in methanol and ethanol by over an order of magnitude. The paper proposes that the sites at this particular composition are able to favorably seat ethanol molecules, allowing for particle dissolution while methanol molecules would not pack the pockets in the self-assembled monolayer (SAM) surface nearly as efficiently. For this reason, particles of the same 3:1 OT:MPA ratio were synthesized for this study and a system was designed whereby a small amount of contaminating ethanol could be removed from a methanol solution. ¹

In order to separate an individual ethanol molecule from a quantity of methanol, one needs to ultimately bring the entire system to a lower energy state. In order to do this, the energy
gained by the favorable ethanol-nanoparticle interaction must outweigh the energy lost by taking the molecule out of solution. Additionally, the degree to which the pocket does not wish to interact with the bulk of solvent molecules modulates this energy exchange. A schematic diagram of the system is shown below.

![Schematic diagram](image)

**Figure 2.** Schematic surface pocket occupation. (Left) A single ethanol molecule (encircled in green) is surrounded by a group of methanol molecules while the surface site within the monolayer (encircled in red) is left empty and exposed to methanol molecules. (Right) An ethanol molecule rests within the surface pocket (encircled in blue) while the methanol molecules interact with one another in a pure solution.

Thus the interactions between the single ethanol molecule and the nanoparticle surface pocket when compared to the empty or solvent-filled state of the pocket must overcome the entropic driving force and enthalpic interactions trying to keep the ethanol molecule in solution. This statement of the change in energy associated with pulling a single ethanol molecule out of solution can be summarized in equation 1 below,

\[
\Delta E = H_{\text{filled-pocket}} - H_{\text{empty-pocket}} - T\Delta S_{\text{mixing}} 
\]  

(1)
where $\Delta E$ is the total energy change upon the removal of a single ethanol molecule from solution, $H_{\text{filled-pocket}}$ is the energy of the ethanol-pocket interaction, $H_{\text{empty-pocket}}$ is the surface energy of an empty pocket or one occupied by methanol molecules, $\Delta S_{\text{mixing}}$ is the driving force for mixing, and $T$ is the absolute temperature. Should the quantity $\Delta E$ be greater than zero, than the individual ethanol molecule should be pulled out of solution.

By examining equation 1 above, it becomes evident that in order to maximize $\Delta E$, one must maximize the favorable interaction between the molecule to be removed from solution and the surface pocket. Additionally, the entropic driving force for dissolution of that molecule should be low. The temperature of the system could be lowered as well. Lastly, the bulk solvent-pocket interaction should be as unfavorable as possible.
Procedure

Nanoparticle Synthesis

Since the most enticing test system at the beginning of the project was expected to be the methanol-ethanol system, nanoparticles were synthesized to target this system specifically. Particularly, octane thiol (OT) and mercaptoproprionic acid (MPA) ligand coated nanoparticles were synthesized in a 3:1 ratio according to the procedures outlined in Centrone et al. An image from the paper reporting the measured solubilities for a series of ligand-coated nanoparticles is shown below.

The reader should pay particular attention to the 25% MPA column and note that the reported solubility varies by an order of magnitude. The goal of the synthesis was the mimic this behavior before beginning solubility tests.

To begin the synthesis, a 500 mL flask and a 200 mL beaker were cleaned and rinsed with ethanol, and then allowed to dry. The flask was suspended within a large bowl and the bowl was packed with crushed ice. Water was added to the bowl to cover the bulb of the flask past the 400 mL mark. The entire system was assembled on top of a magnetic stirrer (VWR International – Colorsquid, VWR, spin 0-1500 rpm). A football-shaped stirbar approximately 1 inch in length was placed in the flask. Additionally, a 60 mL syringe was suspended above the flask and fitted...
with a 23 gauge needle for later use in controlling the flow rate of sodium borohydride into the flask. An image of the above setup is shown below.

Figure 4. Nanoparticle synthesis setup. A large cylindrical bowl (to later be filled with an ice-water bath) is placed on a magnetic stirrer. Suspended within the bowl is a 500 mL round-bottom flask. Above the opening of the flask is suspended a 60 mL syringe (with the upper portion removed) fitted with a 23 gauge needle.

To achieve the desired nanoparticle surface configuration, a total of 1.8 mMoles of thiol ligands were used to obtain the appropriate ratio with gold (III) chloride trihydrate and sodium borohydride. Approximately 709 mg gold (III) chloride trihydrate was measured on a scale (Mettler Toledu – Ag135) and placed in a small vial. Ethanol in the amount of 20 mL was added to the vial to dissolve the gold. The gold solution was then poured directly into the 500mL flask and an additional 180 mL of ethanol was added to the solution. The magnetic stirrer was activated. Of the 1.8 mMoles of thiolated molecules used, 1.35 were OT and 0.45 were MPA.
These molar quantities correspond to 39.15 μL of MPA and 234.3 μL OT. The MPA and OT were pipetted directly into the flask containing the gold solution and allowed to stir for 10 minutes to ensure a uniform distribution of molecules in solution.

While the solution described above was stirred, 756.6 mg of sodium borohydride was measured out and dissolved in a separate beaker with 200 mL of ethanol. The dissolution process was slow and the solution had to be agitated with the aid of a magnetic stirrer for about 7-8 minutes.

The syringe was aligned above the flask such that the needle was not directly over the stir bar to prevent nucleation on its surface. 1 mL of the sodium borohydride solution was added to the syringe and allowed to drip through into the flask. This process was repeated three more times until the gold solution changed from a yellow color to a very black color with only a slightly yellow tint. Once the solution uniformly changed color, the syringe was filled to the 60 mL mark with the sodium borohydride solution and allowed to drip into the flask. Once the level of solution in the syringe fell to the 40 mL mark, more of the sodium borohydride solution was added to refill the syringe to the 60 mL mark. This procedure was repeated until the entirety of the 200 mL sodium borohydride solution was added to the gold solution. The final solution was left to stir for at least 6 hours before it was capped and placed in a standard freezer for three days.

When removed from the freezer, it was observed that the particles had precipitated out of solution. The supernatant was pipetted from the flask and then the nanoparticle precipitate was vacuum filtered through quantitative filter paper. The particles were allowed to dry on the paper for over 24 hours before an encrusted powder was collected from its surface. The particles were
stored in a sealed vial at standard conditions until their use in solubility and filtration experiments. An image of the final synthesized product is shown below.

Figure 5. Synthesized and filtered nanoparticle product. Nanoparticles collected from a dried clump on the filter paper after synthesis and vacuum filtration. A black encrusted powder was cracked apart and removed from the filter. Particles were stored in a capped 20 mL vial.

All glassware coming into contact with the solutions was rinsed with ethanol and allowed to dry. Spatulas were rinsed with acetone. Teflon tape was wrapped around the spatula tip when handling gold (III) chloride trihydrate.

**Solubility Testing**

Solubility tests were carried out on the synthesized, filtered and dried nanoparticles using a number of solvents to characterize their behavior. In each case, a small vial was filled with 20 mL of the desired solvent. Approximately 5-10 mg of the nanoparticles were measured out and added to each vial. The vials were closed and sealed with parafilm. The samples were then sonicated for 20 minutes each. Afterwards, a small magnetic stirbar was added to the vials and they were resealed. The samples were stirred for 5 hours. The vials were allowed to rest for 5 days before 15 mL of the solution was pipetted into a separate vial (to separate it from any precipitates which had developed at the bottom or top of the vials). The solutions were allowed
to sit for several weeks to ensure that a steady-state equilibrium had been reached before solubility measurements were taken.

Control and experimental solutions were prepared and run on a UV-Vis in standard mode. Proprietary software was used for data collection and the results were exported as CSV files for later processing. A control sample of simply the solvent solution was taken as a baseline against which the experimental samples would be compared. For each experimental sample (consisting of the supernatant of the nanoparticle-solvent system after it had come to equilibrium) three data runs were taken.

**Column Procedure**

Standard laboratory pipets were used to create columns with which to conduct filtration experiments. A small piece of copper wire was washed with ethanol and allowed to air dry, and then re-washed with acetone and dried with a Kimwipe. A small torn piece of a clean Kimwipe was packed down into the pipet using the wire. The process was repeated until about 5 mm of paper were firmly packed at the necking region on the pipet. Approximately 125-130 mg of nanoparticles were measured out using a scale (Mettler Toledu – Ag135) and then added to the pipet. A small piece of Kimwipe was packed down on top of the nanoparticles and firmly pushed to create an even layer. Additional Kimwipe fragments were added to the tube until another 3 mm of firmly packed paper covered the nanoparticles. An image of a typical column is shown below.
Filtration Procedure

Based off of the solubility measurements, several candidate solvents were identified as possibilities for testing. In each case, the majority constituent of the solution was deuterated methanol. Minority constituents for testing included ethanol, chloroform, toluene, and trihydrofuran (THF). In each case, 3.5 mL of methanol was measured and placed in a small vial. To this, 25 µL of the minority constituent to be tested was added. The vial was capped and the solution mixed manually and sonicated for 2 minutes.
The columns were suspended over a small vial and 1.5 mL of the solution to be tested was added to the top of the pipet. The solution was allowed to drip slowly through the pipet and collected in the empty vial below. The entire process typically took between 30 minutes and 1 hour to complete. Typically, about 1 mL of solution was found to have flowed through the pipet (with some losses due to evaporation and absorption by the Kimwipes). From this solution, 700 μL was collected for NMR testing. The sample volume along with 10 μL dimethyl sulfoxide (DMSO) was pipetted into a NMR sample tube. The known amount of DMSO was added as a standard against which to measure the other chemical quantities during NMR data analysis.

DMSO, unfortunately, could not be a standard against which to normalize the ethanol experiments, due to its single peak location overlapping one of ethanol’s 3 characteristic peaks. Additionally, it was found that the solubility of the nanoparticles in ethanol required the presence of an acidic environment. As a result, a new procedure for ethanol experiments was developed. For the ethanol experiments, 3.5 mL of deuterated methanol was measured into a small vial. Then 25 μL of ethanol and 25 μL of acetic acid was added to the solution. From this, 1.5 mL of solution was flowed through the filter column and 700 μL of the resulting solution was added to a NMR sample tube. Another tube was filled with 700 μL of the initial solution. As a standard, 30 μL of Chloroform were used.

NMR Procedure

The prepared NMR samples were capped and boxed for transport to the MIT Department of Chemistry Instrumentation Facility. A VARIAN Mercury 300 NMR Spectrometer (with an Oxford Instruments Ltd. superconducting magnet - A 300 MHz NMR spectrometer. Software: VNMR 6.1c.) was used to conduct the NMR testing. The NMR was calibrated for use with deuterated methanol as the solvent and the standard pre-programmed manufacturer parameters.
were used. The samples were loaded, spun at a rate of 20 hz, and locked at resonance. The “bestshim” file was loaded but the shims were then manually adjusted to maximize the lock signal and minimize the lock gain.

For each experimental sample that was prepared and run through the filtration column, a control sample was taken from the remainder of the methanol solution which was not filtered through the nanoparticles. Again, 10 μL of DMSO were added to these samples and they were run on the same NMR machine on the same day as their experimental counterparts. Additionally, several other controls were prepared consisting of 10 μL of each individually tested chemical along with 10 μL of DMSO. These were run under the same NMR conditions and used as a double check on peak positions and magnitudes for the experimental samples.

After the data was collected, it was processed using the VNMR 6.1c. proprietary software. The data was loaded and the baselines were autocorrected and auto-phased. In instances where auto-phasing was obviously poor manual phasing was attempted to correct the problem. Partial integration limits were set by hand and the resulting integral values were normalized by the DMSO control peak.
Results and Discussion

Solubility Tests

Given the previous work reported in Centrone et al, it was predicted that the synthesized nanoparticles should be somewhat soluble in ethanol and less soluble in methanol. Initially, an attempt was made to suspend the nanoparticles in ethanol and methanol immediately following their precipitation out of solution during their production and before any filtration or drying. It was found that the synthesized nanoparticles were insoluble in the ethanol and would simply fall out of solution just as they did in the methanol. Both supernatants were clear indicating that there was very little chance of any particles in solution. Individual non-aggregated particles should present a surface plasmon which leads to a reddening of the solution if they are even somewhat soluble. After these initial tests, one of the leading authors on the paper indicated that she obtained a similar result when she initially synthesized the particles. She commented that after the particles had been rinsed and dried, their solubility behavior differed. Following her advice, the particles were filtered in the same method as reported in Centrone et al (outlined here under the procedural section entitled “Nanoparticle Synthesis”). The filtered and dried nanoparticles were then again placed in both ethanol and methanol and sonicated for 20 minutes followed by 5 hours of stirring. However, again the nanoparticles appeared to be insoluble in both methanol and ethanol. Several other syntheses of the nanoparticles were carried out only to observe similar results. An image of a typical pair of nanoparticle solutions is included below.
An additional series of solubility tests was carried out to determine what solvents, if any, would dissolve the synthesized nanoparticles. Solvents tested included acetone, chloroform, DMF, THF, toluene, a solution of ethanol with hydrochloric and acetic acid (discussed at the end of this section), and water. The solubility of the nanoparticles in each of the solvents was characterized qualitatively by whether or not the solution changed color. In cases where the particles are soluble, the solution should darken and redden, as demonstrated below.
Solutions found to be entirely optically transparent to the naked eye were considered to be insoluble, while the darkness of the solution was used as a relative measure to compare solvents.

A summary of the overall results is tabulated below.

Table 1. Qualitative nanoparticle solubility data.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Highly Soluble</td>
</tr>
<tr>
<td>Toluene</td>
<td>Highly Soluble</td>
</tr>
<tr>
<td>DMF</td>
<td>Insoluble</td>
</tr>
<tr>
<td>THF</td>
<td>Highly Soluble</td>
</tr>
<tr>
<td>Methanol + HCl</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ethanol + HCl</td>
<td>Soluble (unstable)</td>
</tr>
<tr>
<td>Ethanol + Acetic Acid</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

In the interests of obtaining a slightly more reliable quantification of the presence of the nanoparticle solubility, UV-Vis spectroscopy was used to confirm the presence of a surface plasmon at the expected 520 nm peak location (for gold nanoparticles). The obtained spectra are displayed below.

Figure 9. Nanoparticle solubility series (UV-Vis). UV-Vis spectra taken for absorbance form 200-1100 nm.
In the case that nanoparticles are present in solution, there should be an absorbance peak around 520 nm. By examining the plot above, it becomes evident that the only samples to present relatively high levels of solubility are the chloroform (presented in blue), the toluene (presented in purple) and the THF (presented in green). The remainder of the tested solvents were essentially equivalent to the baseline and as such their solubility is negligible. For this reason, chloroform, toluene and THF were identified as three candidate contaminants for filtration testing.

After consulting with additional graduate students working with MPA ligand coated nanoparticles, it was suggested that perhaps protinating the particles through the use of a dilute acid would change their solubility characteristics. Both hydrochloric acid and acetic acid were suggested. Ethanol solubility tests were re-performed on the nanoparticles using two drops of acetic acid and two drops of hydrochloric acid on two different trials. In both cases, the particles dissolved in solution almost instantly, giving both solutions a light rosy color. The presence of a surplus of protons in solution likely pulled electrons away from the ligands coating the surface of the nanoparticles, causing them to become charged to some extent. Obviously, since the solubility of nanoparticles is heavily dependent on their surface characteristics, this change allowed for a favorable interaction with the ethanol molecules. This would account for the increased solubility of the nanoparticles in ethanol in a slightly acidic solution when compared to one with no acid present. Adding acid to methanol did not visibly affect the solubility of the nanoparticles, whose supernatants remained clear and colorless. UV-Vis data for the ethanol and methanol acid trials taken several weeks after initial dissolution is presented below.
In the case of methanol, protination seems to have had little effect in changing its solubility when compared to the data presented in figure 9. The ethanol however, now shows a clear peak centered about 520 nm whereas earlier the ethanol was also essentially baseline. It should be noted that these data were taken after the solutions had been allowed to equilibrate for several weeks. Over that time, the optical properties of the ethanol and HCl solution had changed drastically. These stability issues with the solution will be discussed in detail below.

The coloration of each of the ethanol-acid-nanoparticle solutions was very similar at first; however the stability of the two systems varied significantly over time. While the acetic acid solution retained its rosy color for weeks, the solution containing hydrochloric acid gradually lightened and eventually cleared over a period of days. Shown below are a time series of photographs taken of the hydrochloric acid ethanol solution over the first few weeks after nanoparticle dissolution.
Figure 11. Ethanol-HCl-nanoparticle solution time series. (Left) Solution within an hour of particle addition, presenting clear optical signs of solubility. (Middle) Solution, while still tinted, has appeared to lighten three days after the addition of the nanoparticles. (Right) Nanoparticles seem to have entirely fallen out of solution after several weeks.

While specific solubility measurements were not take over the time-frame of the test, visual evidence suggests that the solubility of the nanoparticles decreased drastically over time. While we see a clear plasmon and rosy tint to the solution immediately following nanoparticle introduction, the plasmon fades with time and ultimately the solution presents itself as entirely clear. The simple explanation for this phenomenon is nanoparticles aggregating, combining, and falling out of solution.

Gold nanoparticles, when uncoated, will come into contact with one another. When this occurs, the particles combine and material diffuses creating a single larger particle. The
A thermodynamic reason for this combination and growth of nanoparticles is surface energy. A single larger particle will be more energetically favorable than two smaller particles, as its surface area per amount of volume will be lower. Surfaces tend to sit at a higher energy state than bulk materials because of surface reconstruction and decreased, strained bonds. Thus the larger particle will pay a smaller energy penalty for its surface than two smaller particles. If unprotected gold nanoparticles are placed into a solution they will aggregate and fall out of solution as time progresses.

In the synthesis method used for this research, the thiolated molecules coat the nanoparticle surfaces during synthesis, ultimately creating a physical barrier which prevents gold atoms from any two nanoparticles from coming into contact with one another. In addition to affecting the surface chemistry and solubility of the nanoparticles, the monolayer coating of thiolated molecules serves the important function of stabilizing the nanoparticles by preventing combination and growth. The thiolated molecules are capped at one end by a sulfur-hydrogen (S-H) bond before they are placed into solution with the growing nanoparticles. When the S-H bond comes into contact with a gold atom, the hydrogen is favorably expelled and a sulfer-gold (S-Au) bond is formed. However, in the presence of a highly acidic environment, the likelihood of the S-Au bond breaking is increased. Should a sufficient number of thiolated molecules by stripped from the nanoparticle surfaces by the presence of protons, it would be possible for nanoparticle surfaces to come into contact in solution. This would cause the nanoparticles to combine with one another, aggregating into larger and larger particles which would eventually become too large to stay in solution. This reasoning accounts for the shift in solubility in the hydrochloric acid ethanol system, going from initially soluble to ultimately insoluble.
NMR Tests

NMR spectroscopy was carried out on 4 chemical additive systems, ethanol with acetic acid, chloroform, toluene and trihydrofuran. In each case, deuterated methanol was used as the solvent and the total sample size (solvent plus additive) was 700 µL. Additionally, 10 µL of DMSO was added to each tube bringing the total sample volume to 710 µL. A sample of the obtained spectra, referenced, phased and integrated with values normalized to the DMSO concentration, is shown below along with the tabulated data from the series of NMR trials.

Figure 12. NMR control spectra for all solvents. From left to right: chloroform peak, toluene peak, unknown contaminant, THF peak, methanol peak, DMSO peak, second toluene peak, second THF peak. Integration values are presented below the plot and tabulated in Table 2.
Table 2. NMR solvent control data.

<table>
<thead>
<tr>
<th>Sample Volume (µL)</th>
<th>DMSO Value</th>
<th>Impurity</th>
<th>Quantity (µL)</th>
<th>Impurity Peak 1</th>
<th>Impurity Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>1</td>
<td>Chloroform</td>
<td>10</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>710</td>
<td>1</td>
<td>Toluene</td>
<td>10</td>
<td>0.36</td>
<td>0.29</td>
</tr>
<tr>
<td>710</td>
<td>1</td>
<td>Trihydrofuran</td>
<td>10</td>
<td>0.51</td>
<td>0.49</td>
</tr>
</tbody>
</table>

The obtained integration values from the filtration experiment spectra are tabulated below.

Table 3. Filtration experiment NMR results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Volume (µL)</th>
<th>DMSO Value</th>
<th>Impurity Peak 1</th>
<th>Impurity Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform Cont.</td>
<td>710</td>
<td>1</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Chloroform Exp.</td>
<td>710</td>
<td>1</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Toluene Cont.</td>
<td>710</td>
<td>1</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>Toluene Exp.</td>
<td>710</td>
<td>1</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>THF Cont.</td>
<td>710</td>
<td>1</td>
<td>0.2</td>
<td>0.23</td>
</tr>
<tr>
<td>THF Exp.</td>
<td>710</td>
<td>1</td>
<td>0.17</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The data presented is fairly consistent across the various trials. In the initial NMR impurity control, 10 µL of each impurity was placed into the sample volume. Later, in the individual filtration experiments, a concentration of 5 µL / 700 µL (about half the original control value) was used. There is strong agreement between the initial NMR controls and individual experimental controls presented in the charts above. For example, a concentration of 10 µL / 700 µL in Toluene yielded integrated peak values of 0.36 and 0.29. The later experimental control, expected to have a concentration half that of the initial control, was found to have normalized integrated peak values of 0.18 and 0.14. The expected relative integral values holds for the other solvents as well, confirming that normalization by DMSO is a reliable method for determining the relative concentration between two samples.

The data presented in Table 3 above appears to show a decrease in the contaminating chemical concentration in all three cases. This would suggest that the experiment has been at least partially successful in removing some amount of the undesirable species through the filtration process. It should be noted that the measured difference in integration values is heavily
dependent upon the phasing of the spectra and the NMR parameters used during data collection. Regardless, the evidence tabulated above does warrant future investigation and perhaps a more exhaustive statistical approach to the analysis. Theoretically however, only a small change in concentration was expected to be seen as a result of the filtration, thus as a proof of concept the data is quite strong.

The analysis of the ethanol experimental data, on the other hand, was not particularly promising. Two trials were conducted on the ethanol sample, one normalized by DMSO and the other by chloroform. In the case of the DMSO sample, little useful data could be extracted due to the peak overlap between the single DMSO peak and ethanol’s central peak. The second ethanol experiment produced almost as unexpected results. The amount of ethanol in the experimental sample was found to have actually increased rather than decreased or stayed the same. Additionally, the ratios of the three ethanol peaks between the experimental and control samples was not uniform, and varied from a factor of 2 to 3.5. One would expect that in the case of a successful experiment, the amount of ethanol in solution should decrease, while in an unsuccessful experiment the amount of ethanol should stay the same.

There are two possible solutions for the reason that this difference may have been observed. The first, and more improbable explanation, is that during the nanoparticle synthesis there is actually an amount of ethanol trapped on the particle surfaces. This ethanol would have to have been released as a result of contact with the methanol, ethanol, and acetic acid solution. Additionally, the quantity would have to have been sufficiently large to account for nearly a doubling of the concentration of ethanol in solution (a fact that is highly unlikely considering only 125 mg of nanoparticles were used, and we would expect only a small amount if any to be trapped on the surface during synthesis). Another factor against this explanation is that if there
was a substantial amount of ethanol trapped on the nanoparticle surfaces, some of the other NMR tests, which did not contain any ethanol, would have shown at least some small ethanol peak. There was no such peak present in any of the samples. One could suggest that it's the presence of the acid which allows for the release of the trapped ethanol, however a simple way to test this would be to re-perform the tests using only a methanol and acetic acid solution and check for released ethanol.

A much simpler explanation for the inconsistent results observed in the case of the ethanol system is evaporation of chloroform. In both cases, 30 µL of chloroform were pipetted directly into the NMR tube (a procedure developed to minimize the total number of vials and pipettes through which the sample solutions would need to be passed). However, chloroform readily evaporates in air. As such, even leaving the sample tube uncapped a few more seconds in one case could have resulted in the loss of several microliters of chloroform. As such, the normalized amounts of ethanol in the experimental could appear larger than in the control, simply because this is less chloroform in the experimental sample. However, this does not explain the peculiar trend observed in the data where the peak values were off by different ratios.
Conclusions and Future Work

Although far from definitive proof, the experiments described in this essay provide evidence of an enticing possibility for new approaches to solvent filtration and purification. In the performed work, two miscible solvents were chosen based on their ability to dissolve a particular type of nanoparticle. The majority solvent was chosen to have unfavorable interaction with the nanoparticles while the minority solvent, the contaminant meant to be taken out of solution, was chosen such that it expressed a favorable interaction with the nanoparticles. For systems of two miscible solvents, nanoparticles should be able to interact with the minority constituent and coat the molecules of that solvent onto their surfaces. When removed from solution (in this work mechanically affixed within the column through which the solution was flowed), a number of the favored molecules should remain and coat the surfaces of the nanoparticles. As such, the concentration of the contaminating chemical should decrease in solution. This effect should be multiplied as the exposed surface of the nanoparticles is increased, such that using 1 gram of nanoparticles instead of 100 milligrams should express improved filtration results.

One should remind the reader that the extent to which molecules can be pulled out of solution in this method is limited by the enthalpies of interaction between the two solvent molecules and between the solvent molecules and nanoparticles, as well as by the entropic driving force for mixing which grows extremely strong at very small concentrations of solute. An extremely favorable interaction between the nanoparticles and one of the chemicals, with a highly unfavorable interaction with the other chemical is preferred when choosing solvents for filtration. Furthermore, the less driving force for mixing there is between the two solvents, the more pronounced the effect of filtration should be per unit of exposed surface area.
Further work should be performed in this area to explore a variety of interesting possibilities and characterize possible trends. Three experiments which were considered, but not performed due to unavoidable constraints, were a series of filtrations at different temperatures, at different nanoparticle quantities, and at different contaminant concentrations.

1. The free energy gain associated with mixing is primarily entropic, and therefore should be temperature dependent. Since it is predicted that for the filtration to work, the enthalpy of the nanoparticle-molecule interaction must compete with the driving force for that molecule to remain in solution, lowering the temperature should increase the number of molecules which associate with the nanoparticles at any given mass of nanoparticles (assuming a fixed size and density). One could then use this data and study the effect of temperature on the concentration of the contaminating species in the filtered solution and ultimately try to calculate energies associated with the interaction between the two solvents and the nanoparticles.

2. The second interesting project would be to perform a series of filtrations at a fixed temperature and fixed starting contaminant concentration, but with a varied amount of nanoparticles. One would imagine that such an experiment would show an almost linear decrease in the presence of the contaminating species in the filtered solution for smaller nanoparticle amounts, with a diminishing effect at high nanoparticle quantities. The expected diminishing effect would be due to the high entropic driving force for mixing when only small quantities of the contamination species remained in solution.
3. Lastly, one could fix the temperature and nanoparticle quantity but vary the concentration of the contaminating species in solution. This test would be essentially the same as the second one proposed above. One would expect the nanoparticles to remove roughly the same absolute amount of the contaminating chemical from solution at higher concentrations of the species, but as the concentration of the contaminant was lowered, entropy would play a higher roll and it would statistically become less and less likely that the nanoparticles would pull the same absolute amount of contaminating molecules out of solution.

The set of three experiments described above would open the door for interesting modeling and statistical analysis of any particular solvent-contaminant-nanoparticle system. One could explore the entropic and enthalpic dependencies of the various interactions involved. Even without any theoretical modeling or analysis, one could use the data to find an optimum set of operating conditions for nanoparticle filtration of a particular system by determining the temperature, concentration range and solution to nanoparticle ratio at which the effect is most pronounced.

Before jumping into any further work in the area however, there are two tasks which should be undertaken by potential researchers. First, the experiments above should be reproduced rigorously and analyzed using statistical methods. Since only a few trials were performed, the reported integral peak values in this paper could vary heavily depending on the way the NMR spectrum was phased. For consistency, auto-phasing was used in most spectra and spectra were manually phased only where it was blatantly evident that auto-phasing was producing erroneous (such as negative) results. By performing dozens of trials, one would be more certain that the reported behavior is in fact due to the nanoparticle-contaminant interaction and not simply due to human error during filtration, sample preparation, or data analysis. Secondly, should further
work in the area be pursued, increased instrumental precision would be of benefit to the project. Currently, the observed changes in the spectrum are so small that integral values between trails would vary by +/- 0.02, when the total difference in integration values between the control and experimental trials tended to be from 0.03 to 0.05. The variance here is obviously quite large when compared to the magnitude of the measured change.

This project has presented, at best, a glimmer of promise at a novel and possibly very useful means of filtration. While not definitive, the argument can be made that initial tests show that nanoparticle-molecule interactions can be used to remove a measurable, if small, amount of a contaminating species from solution. The future of this method would be most pronounced if particle-molecule interactions could be very fine tuned. For example, perhaps a similar system to the ones demonstrated here could be developed to separate a pair of chiral molecules from one another. Ultimately, the long term usefulness of this method would depend on the extent to which the nanoparticles could be used to purify solvents, and the ability to tune nanoparticle surfaces to particular, useful chemical systems.
References