Homework 1: SOLUTIONS

1. Qualitatively sketch the titration curve for the titration of citric acid with 0.05M NaOH. Note the pKa values and the equivalence points. Why did the pH jump so radically when Shane added a drop too much NaOH?

The pH jumps rapidly at the end of the titration because the difference between pK3 (6.4) and the pH of the titrant (13) is very large.

2. How many atoms, on average, are expected in the Ag and Au clusters that you prepared?

   - Au - 2950 atoms (Table 3, Hostetler et al. Langmuir 1998, 14, 17-30)
   - Ag – ca. 200,000 (Lee and Miesel J. Phys. Chem. 1982, 86, 3391-3395)
3. What average Au and Ag cluster diameters do you expect to have made?
   
   Au – 4.4 nm (Table 1, Hostetler et al. *Langmuir* 1998, 14, 17-30)
   
   Ag – 20 nm (Lee and Miesel *J. Phys. Chem.* 1982, 86, 3391-3395)

4. For the Au monolayer protected clusters (MPC’s), how many alkanethiols per cluster do you think you have?
   
   Au – 371 (Table 2, Hostetler et al. *Langmuir* 1998, 14, 17-30)

5. What is the structure of the thiol that you used to prepare your clusters?

6. Sketch a ‘cartoon’ picture of the Au MPC’s that shows the relative size of the thiol molecules and the core.

7. Why is it possible to prepare and re-dissolve MPC’s, but not the Ag clusters that you prepared?
   
   The Ag colloids have a bare Ag surface that has unsatisfied (dangling) bonds projecting out from the Ag atoms. When two Ag colloids come into contact, such as when they are dried, they will tend to bond together and form a bulk Ag phase.
8. Describe the metathesis (ion exchange between aqueous and toluene phases) reaction that you did in the Au MPC prep.

\[
\text{Tetraoctylammonium} = \text{TOA}^+ \\
\text{TOA}^+_{(\text{Tol})} + \text{Br}^-_{(\text{Tol})} + \text{K}^+_{(\text{Aq})} + \text{AuCl}_4^-_{(\text{Aq})} \rightarrow \text{TOA}^+_{(\text{Tol})} + \text{AuCl}_4^-_{(\text{Tol})} + \text{K}^+_{(\text{Aq})} + \text{Br}^-_{(\text{Aq})}
\]

9. Why was it important to use highly purified water in the Ag cluster preparation?

Starting with a dilute AgNO\textsubscript{3} solution means that the small amount of Ag\textsuperscript{+} present could be severely depleted by only a small concentration of Cl\textsuperscript{−} in the water.

10. Why was I worried when it appeared that the boiling AgNO\textsubscript{3} solutions scattered light from my laser pointer?

If AgCl (s) had formed, it would scatter light and I would see the laser pointer beam.