Tangential Flow Filtration of Colloidal Silver Nanoparticles: A Novel "Green" Nanotechnology Laboratory Experiment

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Introduction

- The National Science Foundation has recently indicated that there is a growing need of trained personnel in the nanotechnology and nanoscience sectors.[1,2]

Main Objective

- To introduce undergraduate and graduate students to the "green" tangential flow filtration method for the fractionation and purification of colloidal silver nanoparticles (AgNPs).

Tangential Flow Filtration (TFF)

- In contrast to normal flow filtration methods, TFF operates via the *tangential* flow of a liquid suspension/solution across a size-selective membrane[3] (Figure 1).
- TFF is an alternative, "green" process for nanomaterial manipulation[3,4] as it reduces the amount of axillary chemical modifiers and allows for real time analysis of constituent components.

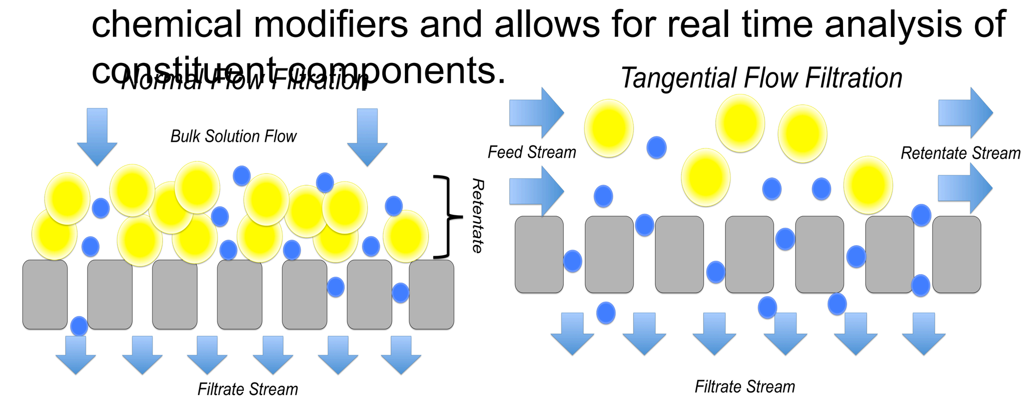

Figure 1. Schematic representations of normal and tangential flow filtration. Yellow and blue spheres correspond to particles with diameters larger and smaller, respectively, than the pore diameter of the membrane.

Surface Plasmon Resonance (SPR)

- When an incident electromagnetic (EM) field crosses the boundary of a dielectric and a thin metallic film, a secondary EM wave may propagate along the surface interface[5] (Figure 2A).
- The case is satisfied for AgNPs at optical frequencies, resulting in a localized SPR, namely LSPR (Figure 2B & C).
- The LSPR is heavily dependent upon the size and shape of colloidal AgNPs[6].

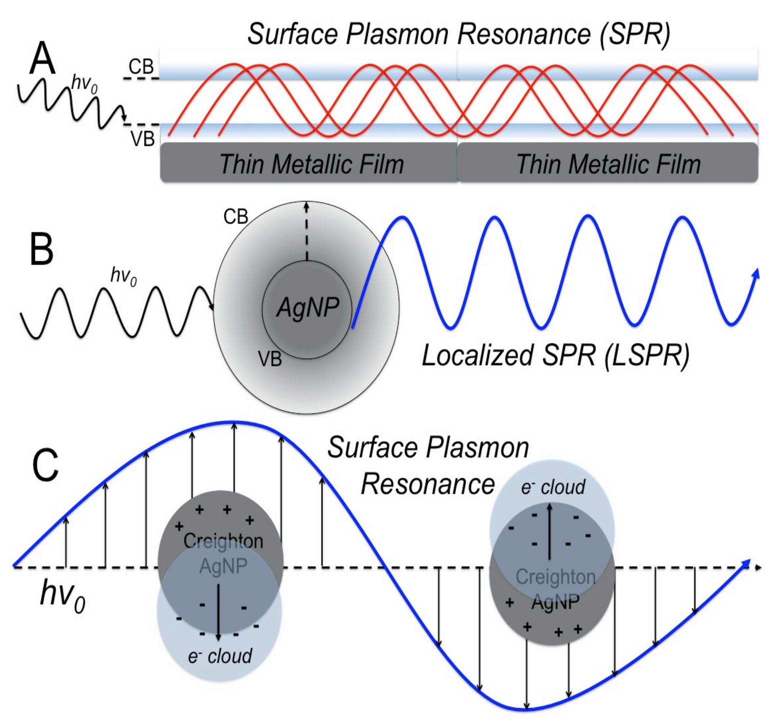

Figure 2. (A) Depiction of the SPR effect for metallic surfaces.(B) Schematic of the LSPR exhibited by AgNPs. (C) "Classical" depiction of the LSPR in Creighton AgNPs. [7]

Experimental Methods

Synthesis of Creighton Colloidal AgNPs

- A large volume of polydisperse colloidal AgNPs was synthesized via a modified Creighton method[8] utilizing the reduction of silver nitrate ($AgNO_3$, 1 mM) with sodium borohydride ($NaBH_4$, 2 mM) in water, at ice-cold temperature (Figure 3A & B).

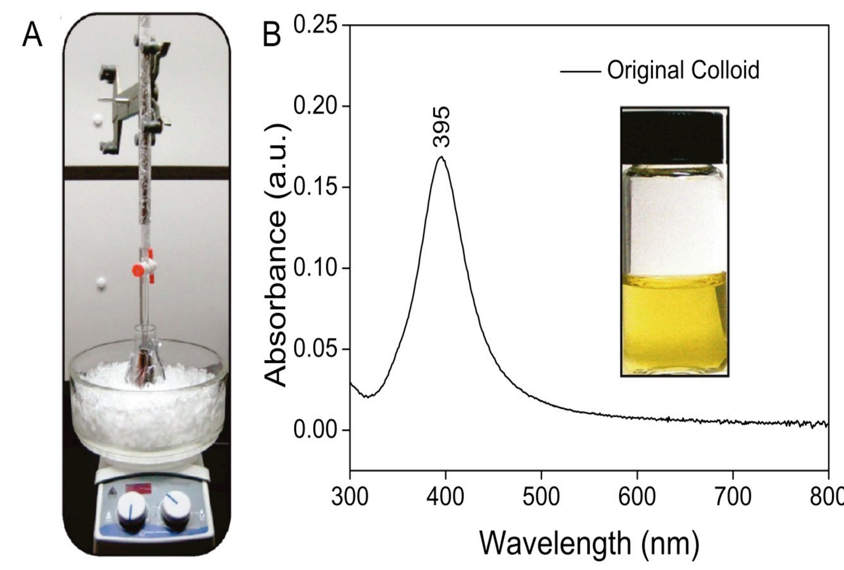

Figure 3. (A) Experimental set up for the synthesis of Creighton colloidal AgNPs. (B) LSPR absorption at 395 nm for the original colloid, giving the colloid its characteristic yellow color[6].

Ultraviolet-Visible Absorption Spectrophotometry (UV-VIS) Measurements

- The retentates and filtrates collected at each step in the TFF procedure were quantified using UV-VIS absorption spectrophotometry to determine the resonant absorption of the LSPR.
- The TFF fractionation process was quantified by investigating the extinction profile of the LSPR peak.

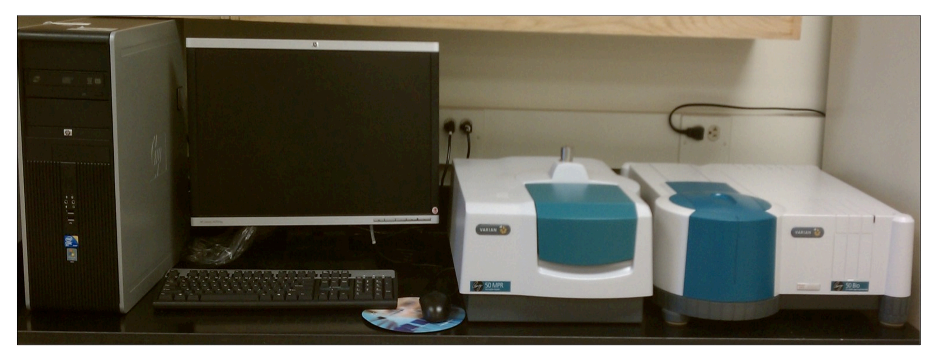

Figure 4. Cary Bio 50 UV Visible Spectrophotometer (Varian, Inc.)

Three-step TFF of Creighton AgNPs

- TFF was employed to concentrate, purify and size-select the original Creighton colloid (Ori.) using hollow fiber filter modules of varying pore diameter and surface area (a 50 nm polysulfone filter of S.A. 390 cm², and two 30 kDa polyethersulfone filters of S.A. 860 cm² and 20 cm², respectively).
- Students assembled two TFF systems in order to physically manipulate the Ori. colloid using commercial and "home-built" TFF ensembles (Figure 4 AI & II).
- The Ori. solution was fractionated by the TFF process into seven distinct suspensions of varying AgNP size and concentration, according to the proposed scheme (Figure 4B).

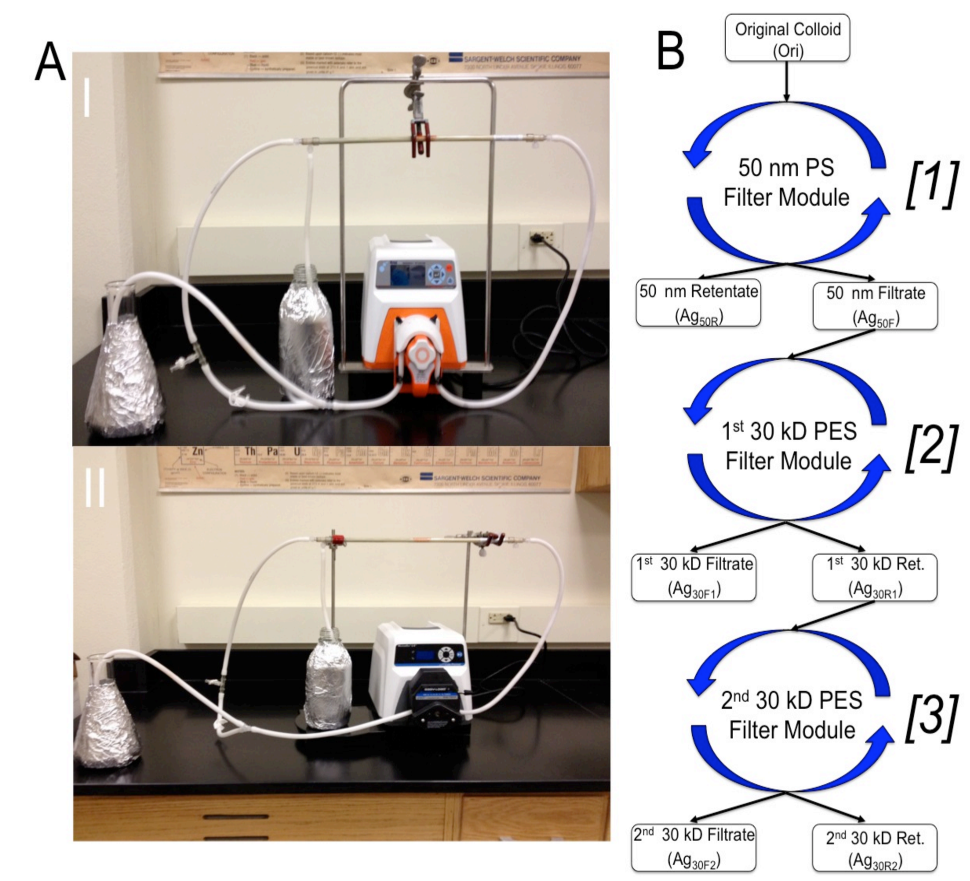

Figure 5. (AI) KrosFlo Research II*i* system (Spectrum Labs). (AII) Home-built version of the TFF system in (AI).(B) Proposed TFF scheme for the original Creighton colloid.

Results & Discussion

Fractionation and Concentration of the Original Creighton Colloid via TFF

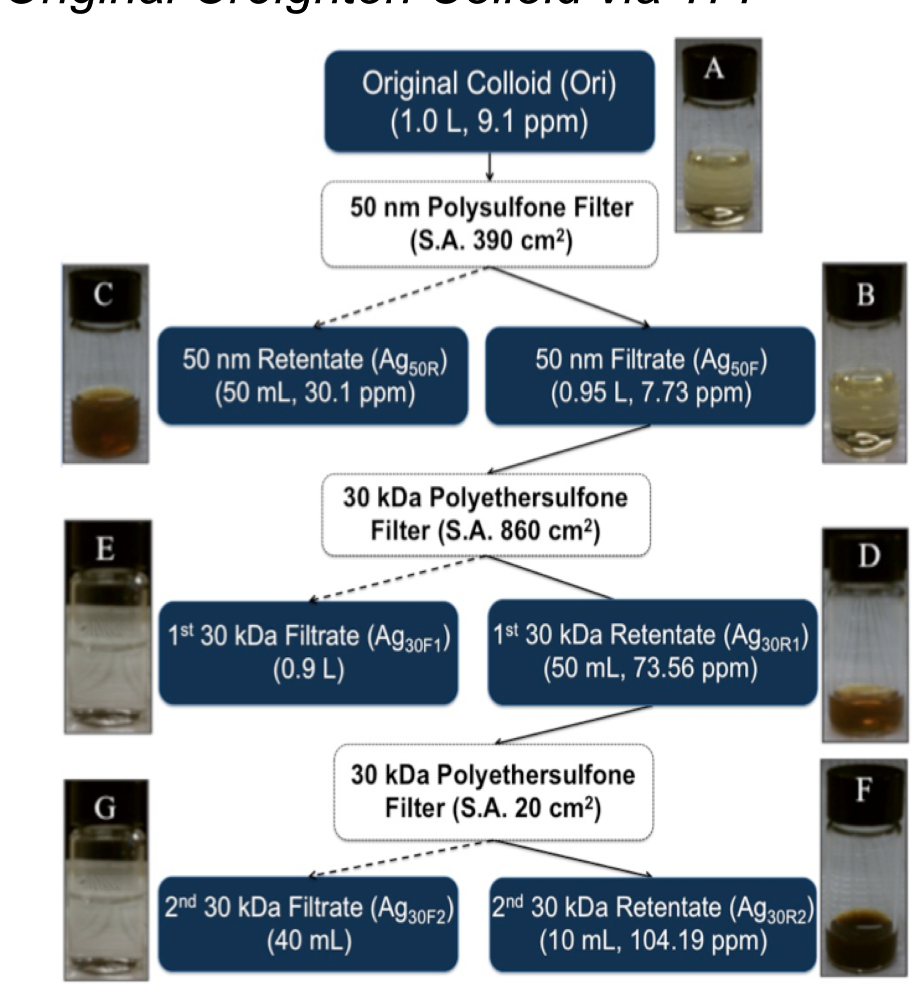

Figure 6. Schematic of the proposed three step TFF process utilized to size-select and concentration the Ori. solution.

- Students collected small aliquots from the filtrate and retentate suspensions at each step in the TFF process for further analysis.
- The three step-TFF sequence resulted in three concentrated solutions (Figure 6A,C,D and F); a 50 nm retentate (Ag_{50R}, 100- 50 nm in diameter), and two 30 kD retentates (Ag_{30R1} and Ag_{30R2}, 49- 6 nm in diameter).
- The proposed TFF procedure was successfully implemented to obtain six fractionated colloidal AgNP suspensions (Figure 6), with an overall yield of 91%.

Quantification of the AgNP Size and Concentration via UV-VIS

- The Lambert-Beer Law provides a direct relationship between the LSPR absorption of incident radiation and the concentration of AgNPs in a colloidal suspension[6]

$$A = -\log(\%T) = \varepsilon \cdot b \cdot C \qquad [1]$$

- A is the absorbance of incident radiation (related to the percent transmittance, $\%T$, via the negative logarithm).
- ε is the molar extinction coefficient for silver clusters (1.9×10^4 dm³ mol⁻¹ cm⁻¹)[5].
- b is the cuvette path length (1 cm in this experiment).
- C is the concentration of AgNPs in each TFF suspension.
- Mie's solutions[7] provide an exact result to the Maxwell equations for the scattering of an incident EM field by an arbitrary, uniformly shaped sphere.

$$D_{ave} = \frac{\lambda_{max}^2 \cdot V_f}{c \cdot \omega \cdot \pi} \qquad [2]$$

- D_{ave} is the average diameter of AgNPs in each concentrated TFF solution (in nm).
- λ_{max} is the absorbance maximum of the LSPR extinction peak profile (in nm).
- V_f is the velocity of electrons at the Fermi level of silver (1.4×10^6 m s⁻¹)[6].
- c is the speed of light (2.99×10^8 m s⁻¹).
- ω is the full width at half maximum (FWHM) of the LSPR extinction peak (in nm).

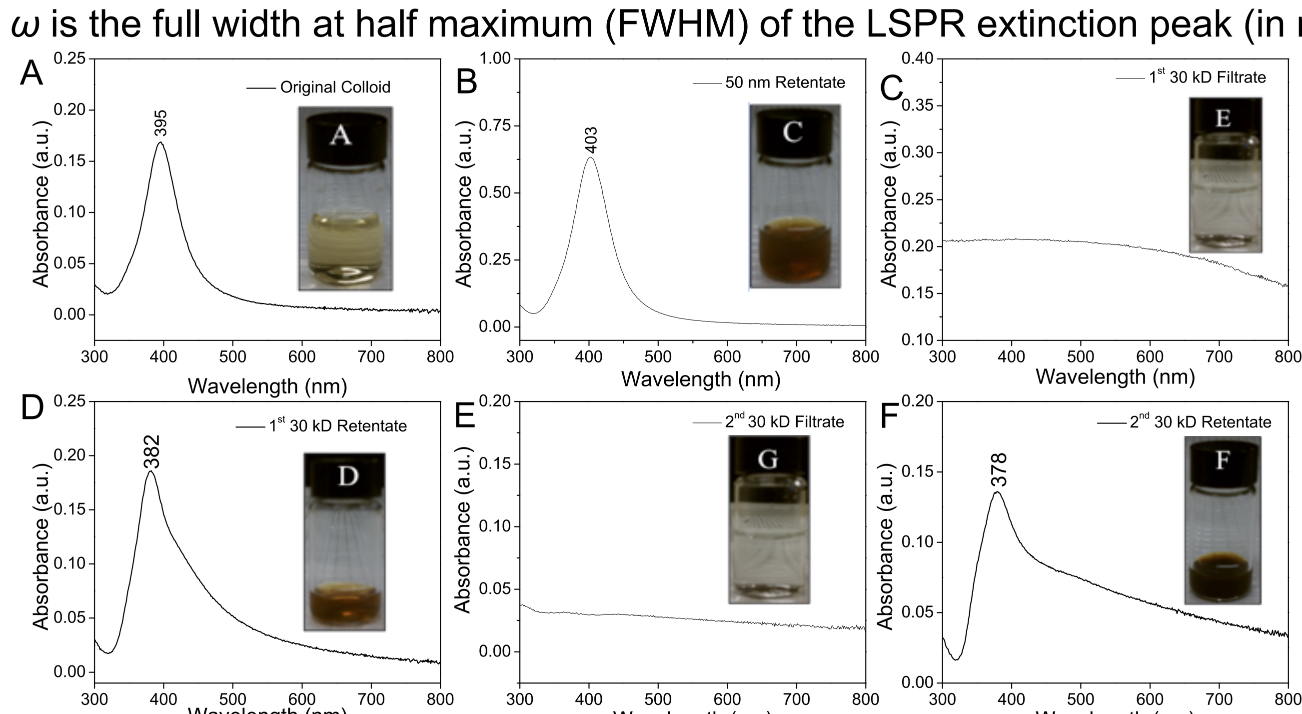

Figure 7. Ultraviolet-visible absorption spectra of the six fractioned AgNP suspensions obtained by students in the TFF process.

Student Evaluations:

- The experiment was rated by students pre- and post-laboratory (Figure 8A).
  - *Q1: Overall interest prior to performing the laboratory.*
  - *Q2: Overall interest after completing laboratory experiments.*
  - *Q3: Overall experience in the laboratory experiment.*
  - *Q4: Overall rating of the laboratory experiment.*
- An evaluation form for laboratory skills was developed and utilized by the instructors to assess students' lab performance and understanding of key concepts (Figure 8B).

Seven key skills were utilized in the evaluations:

- *S1: Proper assembly of TFF apparatuses.*
- *S2: Thorough understanding of the dynamic TFF process.*
- *S3: Ability to accurately follow and apply the TFF scheme.*
- *S4: Proper collection of all TFF solution for analysis.*
- *S5: Determination of dilution factors for UV-VIS analysis.*
- *S6: Proper operation of UV-VIS absorption spectrophotometer.*
- *S7: Application of "green" chemistry principles.*

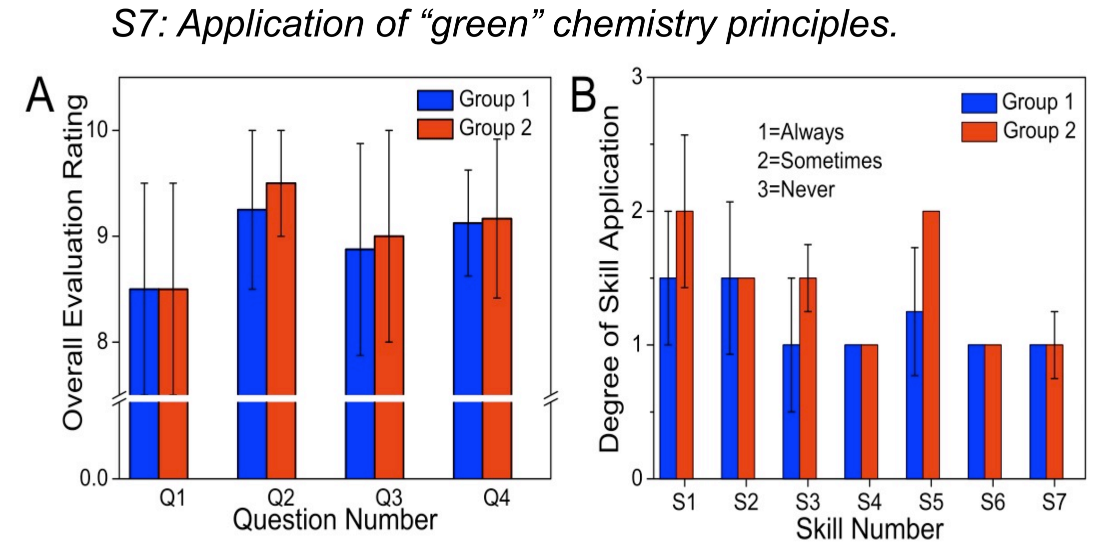

Figure 8. (A) Histogram depicting the results of the pre- and post-laboratory student evaluations (1 being the lowest, 10 being the highest). (B) Histogram summarizing the results of the laboratory skill evaluations performed by instructors. Absence of error bars indicates no deviation of instructor scoring. Group 1 and 2 refer to the two laboratory sections.

Conclusions

Figure 9. Students assembling the "home-built" TFF apparatus.

- The proposed laboratory experiment was successfully implemented in a *Experimental Nanomaterials and Nanoscience* laboratory course.
- In this laboratory, students became familiar with the fundamental aspects of TFF and its "green" applications for the manipulation of colloidal nanomaterials.
- Student evaluations indicated that the TFF experiment was perceived as a very positive educational experience.

Acknowledgments

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References

[1] 1. Roco, M.C.; Bainbridge, W.S. "Societal implications of nanoscience and nanotechnology." *Kluwer Academic Publishers*, The Netherlands, 2001.
[2] Roco, M.C. *J. Nanopart. Res.* **2011**, *13*, 427-445.
[3] Millipore Corporation. *Protein Concentration and Diafiltration by Tangential Flow Filtration*; Lit. No. TB032 Rev. C.; Billerica, MA, 2003.
[4] Sweeney, S. F.; Woerhle, G. H.; Hutchison, J. E. *J. Am. Chem. Soc.* **2005**, *128*, 3190-3197.
[5] Lütz, H.; Ibach, H.*Solid State Physics: An Introduction to Principles of Materials Science*. 4th Ed. Springer, 2009.
[6] Pavel, I. E.; Alnajjar, K. S.; Monahan, J. L.; Stahler, A.; Hunter, E.; Waever, K. M.; Baker, J. D.; Meyerhoefer, A. J.; Dolson, D. A. *J. Chem. Educ.* **2012**, *89* (2), 286-290.
[7] Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., *The Journal of Physical Chemistry B* **2002,** *107* (3), 668-677; Joshua D. Baker's master thesis at http://etd.ohiolink.edu/view.cgi?acc_num=wright1344523437.
[8] Creighton, J. A.; Blatchford, C. G.; Grant, A. M. *J. Am. Chem. Soc., Faraday Trans. 2.* **1979**, *75*, 790-798.