

FINAL PROGRESS REPORT

Project Title: Physicochemical Processes Controlling Source Term from Tank Residuals

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Executive Summary: The research carried out under this EMSP program was aimed at developing spectroscopic probes for measuring diffusion of O₂ and H₂O in porous media and simulated waste samples. The focus was on the preparation of silica and metallic based nanoparticles with reporter molecules or ions incorporated or attached as systems that could effectively probe diffusion of the systems of interest. During the research program we developed many new synthetic procedures for the production of nanoscopic silicas and metals. In fact we published a research article focused on the preparation of metallic nanoparticles using a completely green chemistry method. This paper literally started a novel area of research that other researchers are now following, namely, a totally green approach to the synthesis of metallic nanoparticles. This had not previously been accomplished although others had envisioned a method such as this, previous systems always relied on a passivation agent, a reducing agent or a solvent that was not environmentally benign. The particular system used metal ions, starch as a nanoparticle stabilizer and glucose as a metal reducing agent. This approach or modifications of it to prepare other nanomaterials will have a positive impact on the environment as nanomaterials become more widely used in consumer products. The metallic nanoparticle preparation, in particular is robust and produces particles that are dispersible in aqueous systems for years. To our knowledge this also is a significant accomplishment since the shelf-life of many nanoparticle systems is days

to months. Additionally, the research provided insight into many of the fundamental physical and chemical parameters that control the preparation of nanomaterials, in particular silica and metallic particles.

Project Objective: The primary goal of the UNC portion of this EMSP project was the development of new spectroscopic probes to monitor diffusion and permeation in systems relevant to long time scale transport. The methods should allow an accurate determination of H₂O and O₂ diffusion coefficients in simulant systems relevant to radionuclide wastes stored at DOE facilities.

Summarize project activities for the entire period of funding, including original hypotheses, approaches used, problems encountered and departure from planned methodology, and an assessment of their impact on the project results. Include, where applicable, facts, figures, analyses, and assumptions used during the life of the project to support the conclusions; and

Project Activities: The goal in the initial phases of this EMSP project was to incorporate luminescent and paramagnetic species into a porous silica nanoparticles for the development of NMR, luminescent and other spectroscopic probes for the measurement of H₂O, aqueous solvated ions and O₂ diffusion coefficients in single phase, sludge simulant samples. Desired characteristics of the porous particle probes are: 1) A spherical shape; 2) A size ranging from 5-150 nm with low polydispersity; and 3) Surfaces and interiors that are accessible to the surrounding environment, i.e. porous and/or high surface area. Control of the particle morphology isn't critical although the necessity of having discreet particles in the desired size range is important. The particle size is important in terms of providing a dispersible, noninterfering probe of diffusion within a small enough length that the transport can be monitored on a reasonable laboratory timescale. The last criterion concerning the porosity is absolutely necessary since it is the physical interaction between the diffusing species (aqueous species or oxygen) and the probe that ultimately allows detection of that species' transport properties. These characteristics of the particles are important for diffusion tracer probes since the quenching of the luminescent system or perturbation of the NMR relaxation should occur in a consistent manner throughout the sample that the probe is dispersed in. This is important to minimize errors in the diffusion measurement.

The synthetic procedure chosen was based on a reverse microemulsion process that involved performing a sol-gel reaction in the interior H₂O pool of a microemulsion system. An example of the type of silica particles that are typically produced in a microemulsion confined reaction are shown in **Figure 1**. The incorporation of luminescent Eu³⁺ or Fe³⁺ was accomplished through the processing of EuCl₃ or Eu(NO₃)₃ or FeCl₃ in basic solution to produce a hydrated precipitate that was peptized with acid and yielded a sol that was incorporated into the reverse microemulsion sol-gel silica synthesis. A typical preparation was:

- 1) Add 5M NH_4OH solution dropwise to 10.0 ml of a 0.1 M probe salt solution, until $\text{pH} = 8.5$.
 - 2) Centrifuge precipitate and wash 3-4 times with deionized water.
 - 3) Add 0.25M HNO_3 solution until a homogeneous clear solution is formed ($\text{pH} = 1.5$ -2.0).
 - 4) Sol-gel nanoparticles
6.3 ml Triton-N101
2.0 ml hexanol
50.0 ml cyclohexane
1.1 ml probe salt solution
0.6 ml NH_4OH
3.3 ml tetraethylorthosilicate (TEOS)
- Mix all components and stir until the solution turns white.
- 5) Rotavap the solution to remove the solvent.
 - 6) Wash with EtOH and centrifuge twice.
 - 7) Dry in vacuum oven.

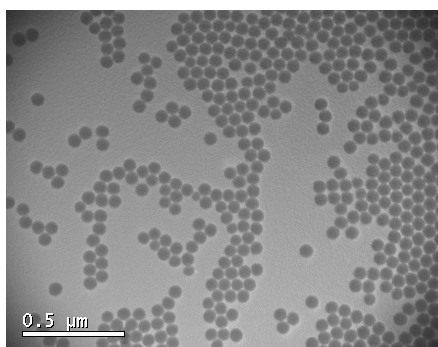


Figure 1 Typical sol-gel silica nanoparticles produced in a reverse microemulsion

As indicated above the initial surfactant utilized was Triton-N101 dissolved in a water-in-oil reverse microemulsion with cyclohexane as the continuous phase. The incorporation of the luminescent probes, e.g. Eu^{3+} , Fe, was problematic. Water in cyclohexane reverse microemulsions using Triton-N101 were shown to have limitations with respect to the size and polydispersity of the nanoparticle reporters produced. Additionally, the distribution of the probe ions was not homogeneous across the silica particles produced. Therefore, experiments were undertaken to determine possible solvents that could allow the production of nanoparticles with the desired properties.

A series of continuous phase solvents was examined using the Eu^{3+} ion in the Triton-N101 surfactant. These included benzene, toluene, isooctane and hexane. Results indicated that in both the presence and absence of a Eu^{3+} reporter, the particles lacked the desired physical characteristics described above. Therefore, efforts with this surfactant were halted and another surfactant system was considered.

This led us to consider the use of the most popular reverse microemulsion forming system, Aerosol-OT (AOT), sodium di(ethylhexyl) sulfosuccinate), since it had been successful at forming many varieties of nanoparticles in the past decade.[1, 2] In the investigation of this surfactant, primarily with isooctane as the solvent, it was also discovered that the incorporation of the luminescent probe was problematic in these systems as well. Similar results to those obtained with the Triton-N101 system were observed. Although the probe was incorporated into the particles synthesized, the

particle morphology was again problematic. The particles were clustered in large micron-sized aggregates with irregular morphology. One proposed solution to this was to utilize a cosolvent in the continuous phase system that would modify the interior of the micelle and stabilize the exchange of material in such systems preventing the aggregation behavior observed. In this approach, CH_3CN was chosen based on the knowledge of its complete miscibility with H_2O and previous results from our group and others concerning the microheterogeneity of this mixed solvent system in which it has been shown that on a microscopic scale H_2O and CH_3CN exist as discrete solvent clusters of each of the individual solvents.[3] The use of such a cosolvent on the interior of the micelle was hypothesized to lead to well separated particles that would be prevented from aggregating.

Concurrently, we utilized pulsed field gradient (PFG) NMR diffusion measurements to examine diffusion of H_2O in simulant sample sent by PNNL. However, the NMR technique was not sensitive enough to allow us to examine the H_2O which was loaded at various levels in the simulants. The primary problem in the solid sample was the severe line broadening due to the presence of the solid and difficulty in shimming i.e. making the magnetic field homogeneous.

A mixed CH_3CN - H_2O -AOT-isooctane reverse microemulsion system did not produce useful silica particles again in the presence or absence of a probe ion. A new strategy was hypothesized to produce diffusion probes. The success of the production of nanoscopic coinage metal particles[1] led us to consider potential spectroscopic methods based on these systems. This direction was analogous to our original quenching approach with the luminescent system in which the sol-gel support would be replaced by a metallic nanoparticle with a luminescent compound attached through a thiol, amine or other surface. We chose to utilize the CH_3CN - H_2O reverse

microemulsion system. An example of the surface plasmon bands of Ag nanoparticles produced using various amounts of CH_3CN are given in **Figure 2**. The results indicated there was an upper limit to the use of CH_3CN to produce Ag nanoparticles with the size of the CH_3CN system's core of approximately 13 nm. These results led us to begin investigation of the physical environment of the CH_3CN in the AOT reverse microemulsion system. Contrary to many recent reports[4-7] that indicate the formation of AOT-isooctane reverse microemulsions containing CH_3CN in

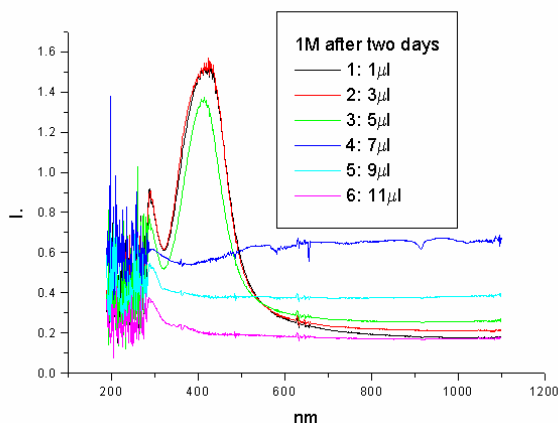


Figure 2 The UV-VIS absorption spectrum showing the surface plasmon band of Ag nanoparticles for CH_3CN added to 1 mL of a 0.1 M AOT solution.

the micelle interior the present results seem to indicate that the CH_3CN does not partition into the core of the reverse micelle unless sufficient amounts of H_2O are present.

A Raman spectroscopic analysis of the CH_3CN $\text{C}\equiv\text{N}$ symmetric stretching mode, ν_2 , was used to investigate CH_3CN dissolved in neat isooctane, 0.1M AOT in isooctane containing CH_3CN and mixtures of CH_3CN and H_2O (**Figure 3A, B and C**). The pure CH_3CN system was investigated as a function of CH_3CN content up to the maximum solubility. The spectral properties of the ν_2 mode are highly dependent on the environment surrounding the CH_3CN and change dramatically upon coordination of the CH_3CN to Na^+ . Though the $[\text{Na}^+]$ in the micelle interior in this system is very high, similar spectral responses are observed in the presence and absence of AOT at a concentration well above the critical micelle concentration (cmc). There is no indication of CH_3CN coordination to Na^+ in the micelle interior, indicating that CH_3CN does not form reverse microemulsions. Similar Raman spectroscopic studies for AOT-isooctane solutions containing increasing W values (where $W = \text{moles H}_2\text{O}/\text{moles AOT}$) and a small, constant amount of CH_3CN were also reported. Deconvolution of the ν_2 spectral region points to the presence of a band corresponding to CH_3CN in the isooctane continuous phase, and a second band corresponding to CH_3CN bound to H_2O in the micelle interior. These spectroscopic studies allow the calculation of the relative concentrations of CH_3CN in both environments and the partition coefficient (K) as a function of W in this system. The data indicate that CH_3CN does not partition into the micelle interior until $W \geq 10$, and that partitioning steadily increases with W up to

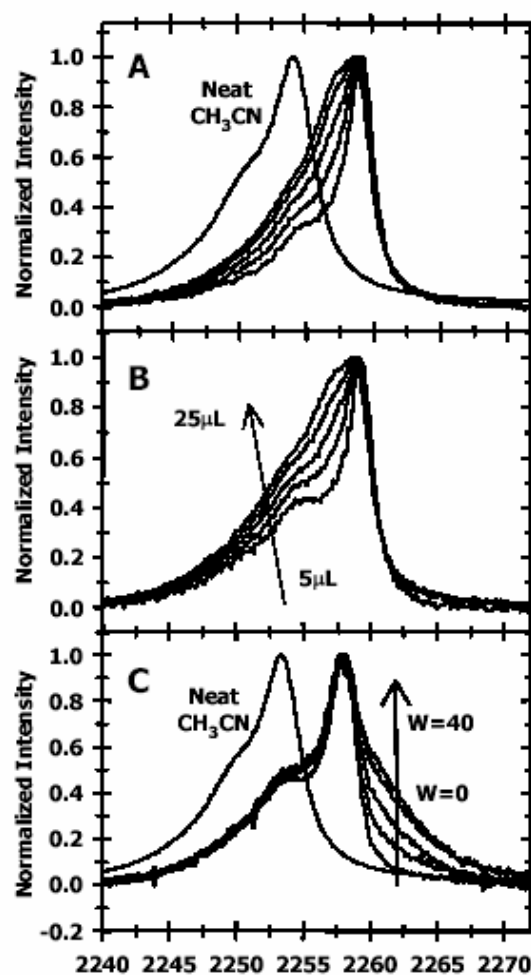


Figure 3 The Raman spectra of the ν_2 region of CH_3CN for (A) pure CH_3CN (labeled) and 5.0 μL – 25.0 μL of CH_3CN added in 5.0 μL increments to 1.0 mL of pure isooctane, (B) 5.0 μL – 25.0 μL of CH_3CN added to 1.0 mL of 0.10M AOT in isooctane. Arrow shown in B denotes direction of increasing 5 μL increments of CH_3CN for both A and B and (C) CH_3CN in samples containing constant 5.0 μL $\text{CH}_3\text{CN}/\text{mL}$ of AOT in isooctane and variable W of H_2O

the maximum H₂O solubilization. Even at high W values, approximately half of the total CH₃CN is still found in the continuous phase.

An NMR spectroscopic investigation of the same system involved measurement of the ¹H chemical shift and deuterium (²H) spin-lattice (T₁) relaxation times for CH₃CN as a function of the volume of CH₃CN added in CH₃CN-AOT-isooctane. Similar measurements were performed as a function of [AOT] at a fixed CH₃CN content. These measurements showed that CH₃CN is able to effectively interact with the nonpolar AOT tails, and that CH₃CN can be used to probe the aggregation behavior of the anionic surfactant in this system. Using the CH₃CN resonance as a probe, the critical micelle concentration (cmc) was determined to be 4.1 mM. The populations of the rotational conformations around the C1-C1' bond of AOT in both CH₃CN and H₂O-containing AOT-isooctane systems were determined as a function of the polar solvent added. These results indicate a decrease in the preference for the most amphiphilic conformer in the CH₃CN-AOT-isooctane system compared to the H₂O-containing system, indicating that CH₃CN facilitates more conformational flexibility due to interactions with the AOT tails. Additionally, measurements of the ¹H chemical shifts and ²H T₁ relaxation times of both CH₃CN and H₂O in a system containing a small, fixed amount of CH₃CN and a variable amount of H₂O in AOT-isooctane were performed. A linear correlation between the H₂O and CH₃CN data exists above W=10, corroborating the previous Raman spectroscopic evidence that indicates CH₃CN is unable to partition into the micelle interior until sufficient H₂O (W=10) is added to fully hydrate the ions in the micelle interior. These combined results not only further support that CH₃CN does not partition into the micelle interior without the presence of H₂O, but additionally indicate that CH₃CN interacts with the tails of the AOT surfactant.

This study was followed by a dynamic light scattering (DLS) and NMR relaxation study (²³Na and ²H) of the same systems. It was observed that subtle changes in the mixed polar solute composition could dramatically tune the intermicellar potential. This is illustrated in **Figure 4** in which the effective diameter calculated by DLS analysis is plotted as a function of W (H₂O-to-AOT mole ratio). Results from other studies of the pure H₂O system show that the micelle diameter for scales linearly with W.[8-12] The present results were interpreted in terms of a changing intermicellar potential which DLS also senses. This tuning of the intermicellar potential with changes in solvation is the first report of its kind. Results showing an increase in the intermicellar potential have been reported for a single solute as a function of pressure near the phase separation boundary.[13,14] A neutron scattering study of these same systems was performed at the NIST Neutron Scattering Facility. Preliminary analysis supports the fact that CH₃CN does not partition into the micelle interior without assistance from H₂O and that the DLS results showing an increase in the effective diameter are not actually micelle diameter increases but as hypothesized above a change in the intermicellar potential. Full analysis of this neutron scattering data is being carried out by a collaborator.

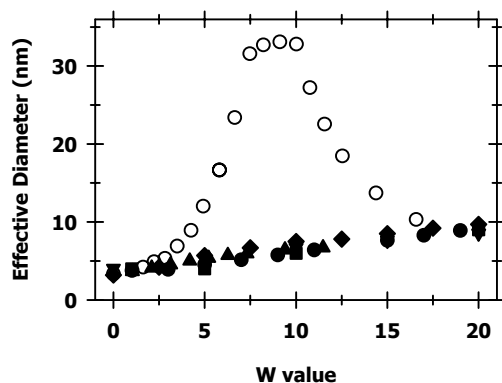


Figure 4. Effective diameter of CH₃CN-H₂O-AOT-isooctane reverse micelles in the 30 μ L constant total volume of CH₃CN and H₂O system as determined by DLS measurements (\circ). Diameters of H₂O-AOT-isooctane system from (\blacksquare) Bohidar and Beboudnia,[9] (\blacklozenge) Keh and Veleur,[10] (\blacktriangle) Zulauf and Eicke,[8] (\bullet) Amar-arene et al.,[11] and (\blacktriangledown) Dunn et al.[12].

Another aspect of the nanoparticle approach was to investigate the production and stabilization of such materials in an aqueous host system using environmentally benign synthetic methods, i.e. green chemistry. The ultimate goal of green chemical processing is the total elimination or at least the minimization of generated waste and the implementation of sustainable processes. Preparation of nanoparticles generally involves the harsh reduction of metal ions in solution or in high temperature gaseous environments. The high surface energy of these particles makes them extremely reactive and most systems undergo aggregation without protection or passivation of their surfaces. Some of the commonly used methods for surface passivation include protection by self-assembled monolayers, the most popular being thiol-functionalized organics; encapsulation in the H₂O pools of reverse microemulsions; and dispersion in polymeric matrices.

The three main steps in the preparation of nanoparticles that should be evaluated from an environmental perspective are the choice of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent and the choice of a non-toxic material for the stabilization of the nanoparticles. Most of the synthetic methods reported to date rely heavily on organic solvents. This is mainly due to the hydrophobicity of the capping agents used. We developed the first completely green processing method to produce metallic nanoparticles. This method involves the dissolution of AgNO₃ in a aqueous starch solution followed by addition of glucose and gentle heating. Typical examples of the particles produced in this environmentally benign manner are shown in **Figure 5**. The mean particle diameter = 5.3 nm with a σ = 2.6 nm. The solutions of dispersed silver nanoparticles in these systems are highly stable and show no signs of aggregation even after more than a year of storage. The present results represent the first completely green synthesis of metallic nanoparticles

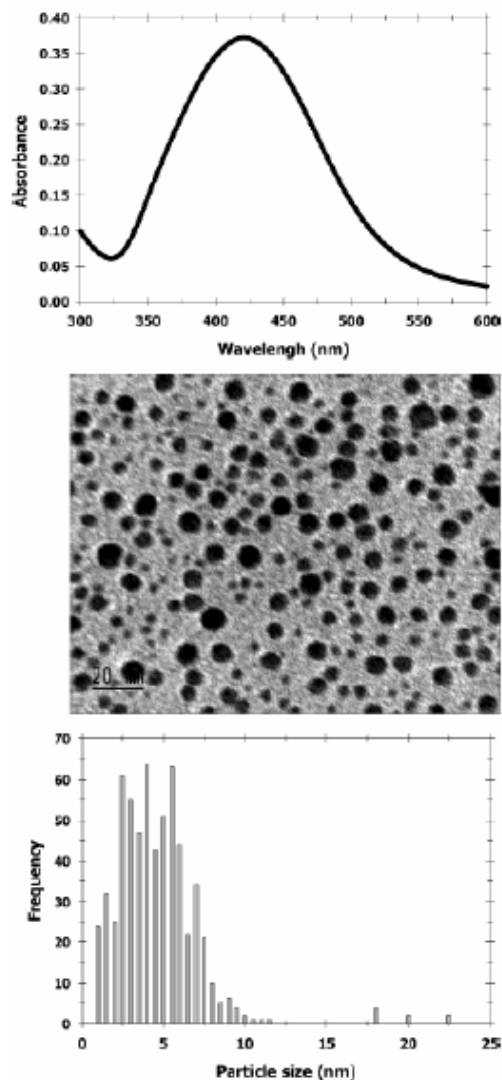


Figure 5 (A) The surface-plasmon absorption spectrum with $\lambda_{\max} = 419$ nm, (B) a typical TEM image and (C) a histogram showing the size distribution of the Ag nanoparticles formed using a green processing method.

and have opened a new approach to the synthesis of metallic nanomaterials.

This work has motivated other researchers to take this approach. In addition to the synthesis of Ag nanoparticles by this route we also developed a similar strategy for the synthesis of true Au-Ag alloys.

Although the ultimate goals of this research were not met the overall program has made significant progress on the development of synthetic procedures for the desired probes and a better fundamental understanding of such systems.

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Journal Articles (Published and In Preparation)

- “Locating Acetonitrile in AOT-Isooctane Solutions: The Importance of Water for the Partitioning of Acetonitrile into the Micelle Core?”, Dawson, E. D.; Wallen, S. L., *J. Am. Chem. Soc.*, **in preparation**.
- “Nuclear Magnetic Resonance Investigation of CH₃CN-AOT-Isooctane Solutions: Evidence for CH₃CN-AOT Interactions”, Dawson, E. D.; Wallen, S. L., *J. Phys. Chem. B*, **in preparation**.
- “Synthesis of Silver Nanocrystals in Mixed CH₃CN-H₂O Micelles”, Fu, J.; Dawson, E. D.; Wallen, S. L. *Mat. Lett.*, **in preparation**.
- “Tuning Intermicellar Potential Through Solvation Changes”, Dawson, E. D.; Wallen, S. L., *J. Am. Chem. Soc.*, **in preparation**.
- “A Raman Spectroscopic Examination of Microscopic Structure and Dynamics in CH₃CN-H₂O Binary Mixtures: Validation of a Two-State Model”, Wallen, S. L.; Dawson, E.D.; Blatchford, M. A. *J. Am. Chem. Soc.* **in preparation**.

“Neutron Scattering Studies of CH₃CN-H₂O Reverse Microemulsions”, Wallen, S. L.; Dawson, E.D. *J. Phys. Chem.*, **in preparation**.

“Completely “Green” Synthesis and Stabilization of Metal Nanoparticles”, Raveendran, P.; Fu, J.; Wallen, S. L. *J. Am. Chem. Soc.* **2003**, 125, 13940-13941.

Highlighted Articles

“Completely “Green” Synthesis and Stabilization of Metal Nanoparticles” highlighted in *Chemical and Engineering News* as a Science & Technology Concentrate (**2003**, 81, 44); *Materials Today Research News Nanotechnology Fabrication and Processing* (**2004**, 7, 10); *Process Engineering*, Chemical & Process Business News, 2/19/05 (<http://www.e4engineering.com>); *Nanotechweb* (<http://nanotechweb.org/articles/news/3/1/1/1>); Nanotechnology Now (<http://www.nanotech-now.com/2004-february-news.htm>); *News.NanoApex* (<http://news.nanoapex.com/modules.php?name=News&file=article&sid=4296>); NSFSTC Newsletter (<http://www.nsfstc.unc.edu/Newsletter/August2002.pdf>).

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