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Title: MICELLE FORMATION AND SURFACE INTERACTIONS IN
SUPERCRITICAL CO₂ FUNDAMENTAL STUDIES FOR
THE EXTRACTION OF ACTINIDES FROM
CONTAMINATED SURFACES.

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Project Title: Micelle Formation and Surface Interactions in Supercritical CO₂.
Fundamental Studies for the Extraction of Actinides from Contaminated Surfaces.

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Graduate Students: Mary Campbell worked on the project for most of the year as a GRA and made significant contributions to the extent that she appears as the first author on a paper just accepted to Langmuir. We already have interests from another GRA to work next year if the renewal that we submitted is accepted.

Research Objective: We are examining the potential of water in CO₂ microemulsions as a new medium for the extraction of metal ions from contaminated surfaces with the ultimate goal of extracting actinides from heterogeneous waste to aid in decontamination and waste reduction.

Research Progress and Implications:

This report summarizes the third year of work on a 3 year program. We report here on using water in CO₂ microemulsions as a new medium for metal extraction from contaminated surfaces. The nano-droplets of water suspended in CO₂ take advantage of both the high solubility of metal ions in water and the high diffusivity of CO₂ to penetrate pores that might be inaccessible to bulk water. The pressure-dependent solvent strength of CO₂ can be used to control formation of the nano-droplets. As the CO₂ pressure is dropped, a cloud point is reached where the nano-droplets coalesce into a water phase that is no longer suspended in the CO₂, allowing easy separation of the metal solution. This extraction scheme is particularly attractive for remediation of heterogeneous waste in which small amounts of metal contaminants are dispersed throughout a large volume of solid waste. Typically, such extractions require an amount of water or solvent proportional to the volume of solid material. With microemulsions, CO₂ is effectively used as a diluent and the amount of water need only be proportional to the amount of metal to be extracted, making it possible to decontaminate grams of waste with μL of water.

Intracellular Structure/ Localization of Metal Ions

We have characterized the interactions of metal ions with the surfactant head group by using both absorbance spectroscopy in the case of Cu²⁺ and luminescence spectroscopy in the case of Eu³⁺. The maximum solubility of Cu²⁺ was determined to be 11 mM in 15 mL of CO₂ or 0.66 moles Cu²⁺ per mole of surfactant. This corresponds to an effective concentration of 2 M Cu²⁺ within the water phase. The λ_{max} for copper in a w/c microemulsion was found to vary from 732 nm to 761 nm, based on the concentration of copper in the microemulsion. Control experiments with copper dissolved in glacial acetic acid demonstrated that the copper absorption shifts rapidly toward the red as water is added. In glacial acetic acid $\lambda_{\text{max}} = 684$ nm, in a solution of 95 % acetic acid $\lambda_{\text{max}} = 710$ nm and in a solution of 90 % acetic acid $\lambda_{\text{max}} = 770$ nm; the λ_{max} continues to shift to 808 upon further dilution. At low concentrations of copper, λ_{max} is closer to that of copper(II) dissolved in 95% acetic acid, implying that copper is strongly interacting with the carboxylate end group. These results suggest that copper experiences an environment similar to 90 % acetic acid. To further probe metal ion interactions in the microemulsion, emission spectra and luminescent lifetimes were obtained for anhydrous europium chloride in a microemulsion with $n = 3$ PFPE-COO⁻NH₄⁺ and water, $n = 3$ PFPE-COO⁻NH₄⁺ and D₂O, and PFPE-PO(OH)₂ alone. The increase in emission intensity of the 615 nm band indicates that the

center of inversion which is present for the fully hydrated europium ion is gone due to displacement of water from the first hydration sphere. The symmetry around the europium ion can only be broken by direct binding of the carboxylate head groups of the surfactant. Further evidence for such interactions comes from comparing the lifetime of europium in w/c microemulsions formed with H₂O and D₂O. The lifetime of europium in the w/c microemulsion was found to be 120 μs; when D₂O is used, the lifetime increases to 274 μs. Using the equation: $n = C^*(1/\tau_H - 1/\tau_D)$, where n is the number of water molecules in the first hydration sphere, C is a constant (1.05 for Eu), τ_H is the lifetime in H₂O, and τ_D is the lifetime in D₂O, the observed isotope effect indicates that approximately 5 water molecules are present for the europium ion in the w/c microemulsion as compared to 8 or 9 for the fully hydrated ion. This again supports the idea that at least two surfactant molecules are bound to the europium ion. When no water is present, as in the case of a dry micelle formed with PFPE-PO(OH)₂, the lifetime increases to 2100 μs. The extended lifetime in the absence of an aqueous-based microemulsion indicates that there is deactivation in the microemulsion in addition to that provided by the O-H or O-D stretch. The deactivation could be due to stretching of the PFPE-surfactant end group or to Eu-Eu effects in the forced proximity of the microemulsion.

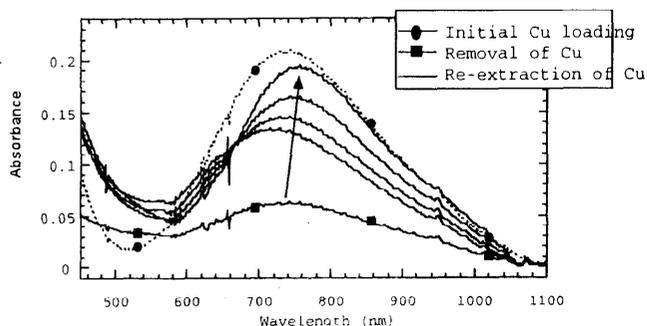
Extractions: Filter Paper and Wood

Almost complete extraction of both copper and europium from filter paper is accomplished with PFPE-COONH₄⁺. The amount of metal spiked onto the filter paper was approximately one-tenth of the capacity of the microemulsion, resulting in a 0.3 M solution of copper in the microemulsion core. Extraction is complete in less than one hour, demonstrating excellent kinetics of contact between the water core and the paper substrate. This is in contrast to polymer-based ligands in CO₂, which have very slow extraction kinetics, on the order of hours to days. Remarkably, the water of the micelle core can interact with metals on the cellulose acetate filter, yet the water is not adsorbed into the filter matrix. All components of the w/c microemulsion are required for complete extraction. Not surprisingly, no copper is extracted in the absence of surfactant and water, as copper is not soluble in carbon dioxide. Only a small amount of copper, 26 %, is extracted in the absence of water. In this case, the surfactant serves simply as a ligand, solubilizing small amounts of copper in the CO₂ phase. The best extraction percentages are achieved in the presence of water and surfactant, when a droplet of water formed in the microemulsion generates a micro-environment that is compatible with high metal loading. Roughly the same extraction amount is seen for a w₀ of 2 as compared to a w₀ of 5. These results suggest that water is important for extraction from a solid matrix although only a minimum is required. The surfactant length did not influence extraction percentages. Extraction is unchanged at 99 % with the n = 3 or n = 4 ammonium carboxylate as compared to the undistilled surfactant. As long as a stable microemulsion forms, extraction seems to be limited only by the number of charged species in the water core and the number of ligand sites.

Wood represents a challenging substrate based on its porous nature and is a realistic substrate to encounter in potential applications. A w/c microemulsion removed 84 % of the Eu³⁺ from the wood in 2 hours. Leaching an identical sample in 5 % nitric acid or water for the same amount of time yielded only 26 % – 32 % extraction. This result dramatically demonstrates the potential advantages of the w/c microemulsions for extraction. The w/c microemulsion required only 60 μL of acid to extract more material than 10 mL in a bulk system. Clearly the microemulsions are able to penetrate the porous wood structure much more effectively than a bulk solution.

Regeneration and Reuse of Surfactant

Surfactant recycle was demonstrated by generating a w/c microemulsion in the presence of copper and then using pressure changes to precipitate out the water droplet, allowing removal of the copper. By following the absorbance of the copper at 750 nm, the amount of copper in the cell could be determined. The initial trace (closed circles) shows copper dissolved in a w/c microemulsion. When the pressure within the cell was dropped to 1514 psi, copper-containing water droplets precipitated onto the sides of the cell, removing 90% of the copper from the bulk solution (closed squares). At this point, the cell was manually turned so that the water droplets were near the vent of the cell, and the water, with the copper, was vented from the cell. The same



cell was again loaded with CO_2 and water (no additional surfactant) to generate a microemulsion and used to extract a second amount of solid $\text{Cu}(\text{NO}_3)_2$. UV-Vis shows that eighty one percent of the original copper uptake was obtained, indicating excellent recovery. The majority of the loss is likely due to engineering problems, as our cells are not designed to vent in this fashion. The likelihood of using the surfactant for multiple extractions is high.

Conclusion

We have demonstrated that w/c microemulsions with two types of polyperfluoro-surfactants are capable of extracting copper and europium from a variety of solid substrates. The extractions are facile and result in high ion loadings within the water core. Regeneration of the surfactant without loss of capacity is possible through controlling the pressure of the system. The system has slight selectivity for metals that bind to the surfactant relative to alkali metals, future research will focus on improving this selectivity through modifications of the surfactant head group. This new technique offers promise in remediation of solid materials contaminated with heavy metals or radioactive waste.

Planned Activities:

During the remainder of the year we plan to:

- 1) Control the pH within the microemulsion by changing the surfactant head group.
- 2) Characterize and determine pH of microemulsions with newly synthesized sulfonic acid, hydroxamic acid, and histidine based surfactants.
- 3) Determine if the CO_2 water equilibrium to form carbonic acid is affected by the size of the microemulsion.