

Metal extractions using water in carbon dioxide microemulsions

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Water in supercritical carbon dioxide microemulsions are examined as a new medium for the extraction of metal ions from contaminated surfaces, and are shown to extract >99% of the copper from a spiked filter paper with as little as a two-fold excess of surfactant.

Supercritical carbon dioxide (scCO₂) has many advantages as a solvent for extractions in environmental remediation including enhanced diffusivity (mass transfer), chemical stability, and pressure-dependent solvation properties that facilitate simple separations. The absence of a liquid–vapor interface above the critical temperature (31 °C) results in zero surface tension, and is particularly advantageous for extraction from solid surfaces since scCO₂ may easily penetrate the pores of solid matrices. The challenge for extracting metal ions comes from the fact that supercritical carbon dioxide has no permanent dipole moment and a low dielectric constant (*ca.* 1.5). Hence, hydrophiles and metal salts typically have near zero solubility. Ligands such as β -diketones, dithiocarbamates, and organophosphorus reagents have been used to solubilize metals into scCO₂.¹ The solubility of the ligands is quite good in some cases, but solubility of the metal–ligand complexes remains low, limiting practical applications. Solubility of the metal complexes can be enhanced with highly fluorinated ligands,² but complexes that have moderate CO₂ solubility often require a large excess of ligand for efficient extraction.^{1e,g,i,2e} Yazdi and Beckman have shown that attaching ‘CO₂-philic’ tails, consisting of either highly fluorinated or polysiloxane groups, to ligands increases the solubility of the metal complexes and results in moderately efficient metal extractions (up to 87%) in liquid CO₂.³ The approach of designing specific fluorinated ligands has the drawback that efficient extraction depends on the metal being present as a simple metal salt in a specific oxidation state.

Our approach differs significantly from strategies to date in that we solubilize the metal ion with water in CO₂ microemulsions. Johnston *et al.*⁴ and Eastoe *et al.*⁵ first demonstrated that a perfluoropolyether ammonium carboxylate surfactant was effective in forming water microemulsion droplets (< 10 nm in diameter) in supercritical carbon dioxide. We report here on using these water-based microemulsions as a new medium for metal extraction from contaminated surfaces. The nanodroplets 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 are inaccessible to bulk water. The pressure-dependent solvent strength of CO₂ can be used to control formation and disruption of the nanodroplets. 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 μ L of water.

Water in carbon dioxide microemulsions were formed in a stainless steel variable volume view cell.⁶ The standard amounts of material added for microemulsion formation were

0.2 g PFPE-NH₄, 10 g CO₂ and 60 μ L water. Selected experiments were done with 0.122 g PFPE-NH₄, 10 g CO₂ and 42 μ L water (data in Table 1). All extractions were conducted at 207 bar and 45 °C. Filter paper was spiked by two different methods. A 42.5 mm diameter filter paper was submerged in aqueous 1 M copper nitrate for at least 48 h (method 1). After drying, the filter paper was cut into quarter sections and extractions were conducted on one section of the paper. For method 2, 5–6 mg of Cu(NO₃)₂ was dissolved in 30 μ L of water and the entire solution was added dropwise to a piece of filter paper. Each filter paper was dried for at least 24 h and placed in a small extraction cell (ISCO, 3 mL cell). The microemulsion was recirculated through the extraction cell at a flow rate of 10 mL min⁻¹. The kinetics of extraction from the filter paper were followed with UV–VIS spectroscopy (Hewlett–Packard model 8453). At the completion of the extraction, at least 50 mL of neat CO₂ was passed through the extraction cell (207 bar, 25 °C) to remove residual fluorinated surfactant from the filter paper. The filters were digested and copper concentrations were determined by ICP-AES.

The extinction coefficient for the 733 nm band of Cu(NO₃)₂ in the water/CO₂ microemulsion was determined to be 59.3 M⁻¹ cm⁻¹.⁷ The low energy absorption band is blue shifted compared to copper nitrate in nitric acid (810 nm) at ambient conditions (Fig. 1). We attribute this shift to two factors: copper binding to the surfactant head groups and a decrease in the polarity of water in the micelle core. The maximum solubility of copper in the microemulsion was found to be 3 M.

Extractions of copper from spiked filter paper were conducted to examine the effectiveness of the microemulsion in removing metal contaminants from solid surfaces (Table 1). More than 99% of the copper is extracted in one step from smaller pieces of filter paper. Extraction efficiency decreases when a larger piece of filter paper is used, but following with a second extraction improves the efficiency to 82–99%. The kinetics of extraction from a spiked filter paper (method 1) were followed by UV–VIS spectroscopy (Fig. 1). The absorption from copper reached a maximum after 60 min of exposure to the microemulsion, with no further increase after an additional 90 min. The kinetics of extraction with microemulsions are much

Table 1 Extraction of copper from filter paper at 45 °C and 207 bar for 1 h, using 122 mg surfactant and 42 μ L water

Number of extractions	Weight of filter paper/g	Concentration, initial/ppm	% Extracted
1 ^a	0.018	81400	99.65
1 ^{a,b}	0.019	81400	99.53
1 ^c	0.384	3430	58.5
2 ^c	0.386	4090	98.0
2 ^c	0.238	6630	82.8
2 ^c	0.096	16400	99.7

^a Extraction from Whatman No. 3 filter paper; % extracted based on measured value from an unextracted piece of spiked filter paper; method 1 spiking procedure (saturated solution). ^b Using 50 μ L water. ^c Extraction from Whatman No. 5 filter paper; % extracted based on a calculated value for 5 and 6 mg Cu(NO₃)₂; method 2 spiking procedure.

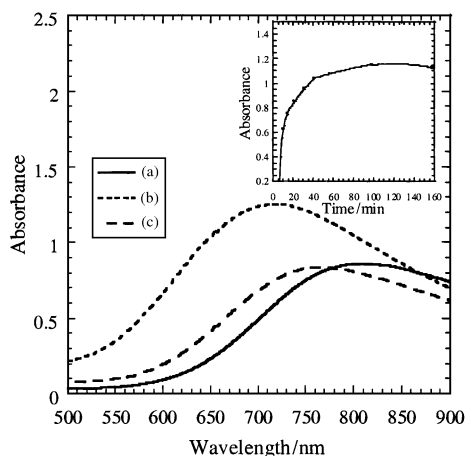


Fig. 1 The absorption spectra of copper(II) from: (a) copper nitrate dissolved in nitric acid at ambient conditions, (b) copper nitrate dissolved in the water/CO₂ microemulsion, and (c) aqueous copper acetate at ambient conditions. The inset shows the intensity at 733 nm vs. time for extraction of copper.

faster than those observed recently with CO₂-soluble polymers that required many hours to days for extraction.⁸ In addition to improved kinetics, the microemulsions have improved efficiency compared to previous studies with CO₂-soluble chelating agents. In general, past extractions have required a tremendous excess of ligand to achieve reasonable metal extractions (>1000 fold).¹ By comparison, at the maximum solubility of copper, the molar ratio of surfactant to copper in the microemulsion is approximately 3.

Europium fluorescence lifetimes and emission spectra were examined to probe ion solvation in the water in CO₂ microemulsions. The relative heights of the europium emission bands at 593 and 615 nm provide information on the first solvation sphere around the europium ion.^{9,10} In the microemulsion, the 615 nm band gains in intensity, indicating that the center of inversion around europium is removed by displacement of water in the first hydration sphere by another ligand.¹¹ Two possible ligands are available in the microemulsion core: the carboxylate head group of the surfactant or carbonic acid, formed by CO₂ dissolved in the aqueous phase. As a control, europium chloride was dissolved in D₂O and the headspace over the solution was pressurized to 3000 psi with carbon dioxide to introduce bicarbonate with no surfactant present. The europium emission spectra appeared the same as in water at ambient conditions, suggesting that the carboxylate head group of the surfactant is solely responsible for the changes in the emission spectra of europium ion dissolved in the microemulsion.

Further evidence for surfactant binding comes from lifetime experiments using H₂O- and D₂O-based microemulsions. The isotope effect provides a way to determine the number of water molecules surrounding the europium ion using the equation: $n = C*(1/\tau_H - 1/\tau_D)$, where n is the number of water molecules, C is a constant (1.05 for Eu), τ_H is the fluorescence lifetime in H₂O, and τ_D is the fluorescence lifetime in D₂O (lifetimes in milliseconds).⁹ The lifetime of europium(III) ion in the water in supercritical CO₂ microemulsion was found to be 120 μ s and increased to 274 μ s when the microemulsion was formed with D₂O. Using the above equation with the measured lifetimes gives ca. 5 water molecules in the first hydration sphere of the europium ions. As the fully hydrated ion has 8 to 9 water molecules,¹² this result suggests that the surfactant displaces 3 or 4 water molecules from around the europium ion.

Radioactive and heavy metal contaminants are often present as water-insoluble metal oxides in heterogeneous waste. To demonstrate the versatility of the microemulsion in metal extraction, the microemulsion was formed with a 20 wt% nitric acid solution instead of pure water. The increase in acidity was confirmed by dissolving methyl orange indicator in the microemulsion. The indicator appeared bright red when the

microemulsion was formed with 20% nitric acid as opposed to orange when distilled water was used. The ability of the acidic microemulsions to extract metal oxides was examined with europium oxide. Based upon visual observation, 10 mg of europium oxide completely dissolved into a microemulsion formed with 20 wt% nitric acid after stirring for 1 h.

Water in supercritical carbon dioxide microemulsions are effective for extraction of metals from solids. At maximum solubility, a 3 M solution of copper can be obtained within the microemulsion core. The nanodroplets offer the advantages of rapid and efficient extractions with a versatile environment. Making the microemulsion with 20 wt% nitric acid rather than pure water allowed europium oxide to be solubilized. Agents that oxidize low valent metal oxides or water-soluble chelating agents could also be introduced into the microemulsions to expand the types of metals that may be extracted and to provide selectivity in mixed metal extractions. Metal is readily recovered by simply dropping the CO₂ pressure below the cloud point, causing the water to coalesce into a single droplet with all of the metal and some surfactant. Initial experimental work has indicated that surfactant recycle should be possible by adding excess water and reducing pressure to destabilize the microemulsion while maintaining surfactant solubility. An additional 270 μ L of water was added to a copper-saturated microemulsion at 207 bar, and then pressure was reduced to 101 bar. At 101 bar, phase separation occurred and the aqueous phase settled to the bottom of the cell, while a significant fraction of the surfactant remained in the upper phase. No copper was observable in the upper phase by UV-VIS. The ability of the microemulsion to concentrate the metal into a small volume of water makes it particularly attractive for extractions from contaminated solids that often have small amounts of metal dispersed over a large volume of solid waste.

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