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Transporting metal ions using reverse micelles in alcohol modified supercritical carbon dioxide

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Abstract

Metal species including Cd, Co, Cu, Pd and Zn can be extracted from solid materials using reverse micelles (microemulsions) formed by sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and dissolved in supercritical carbon dioxide ($ScCO_2$) containing an alcohol. The cloud-point pressure (CPP) of the microemulsion decreases with increasing amount of alcohol in $ScCO_2$. Below the CPP, two phases co-exist in the system with the bottom phase containing alcohol and the metal loaded microemulsion. After removing the alcohol/microemulsion phase from the high-pressure system, the extracted metal species are recovered by adding a small amount of water and the surfactant can be recycled. The amount of water used to destabilize the microemulsion for metal recovery is much less than that used in solvent-based extraction and acid leaching processes. This solvent-assisted microemulsion dissolution method does not require expensive fluorinated surfactants and may provide an economic and effective method for extraction of metal species from different matrices with minimum liquid waste generation.

Keywords: Transporting; Metal ions; Supercritical carbon dioxide; Water-in-CO_2 microemulsion; Octanol

1. Introduction

Water-in-supercritical CO_2 (W/C) microemulsions can be considered as a new type of green medium for dissolving polar compounds or metal species in supercritical carbon dioxide ($ScCO_2$) [1–4]. Microemulsions are thermodynamically stable aggregates of amphiphilic surfactants, resulting in a hydrophilic head group region surrounding nanosized water cores with hydrophobic tails that are extended into a non-polar CO_2 continuous phase. Polar and ionic species can be dissolved in the water core and dispersed in the CO_2 phase. The size of the micelle core is determined by the molar ratio of water to surfactant molecules in the solution, i.e., $W = [H_2O]/[\text{surfactant}]$.

One of the common surfactants used in the formation of microemulsion is the anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT), which unfortunately is not soluble in CO_2. The first report of AOT reverse micelles in supercritical fluid–AOT–water systems was in 1987 by Gale et al. using colored azo dyes, methyl red and a protein (cytochrome *c*) by visual observation for the phase behavior investigation [5]. The supercritical fluids investigated were ethane and propane [5]. In 1990, Consani and Smith tested over 130 commercial surfactants for their solubilities in CO_2 at 50 °C and the pressure range of 100–500 bar and found that only a few of them were soluble in $ScCO_2$ [6]. So far, most reported surfactants [7–10] which are capable of forming W/C microemulsions without using a co-surfactant are fluorinated ones. Campbell and co-workers in 2001 extracted metal species from different matrices, including filter paper, wood, activated carbon and cement, using W/C microemulsions by a one-surfactant system, ammonium carboxylate perfluoropolyether phosphate (PFPE-$COO^-NH_4^+$) [2,3]. Erkey and co-workers evaluated phase behaviors as a function of temperature, pressure and *W* values of a laboratory synthesized fluorinated AOT [bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)-2-sulfosuccinate] [8]. Ji et al. used AOT and a fluorinated co-surfactant perfluoropolyether-phosphate ether (PFPE-PO_4) to synthesize Ag^0 nanoparticles in a W/C microemulsion [4]. Wang et al. removed a number of metal ions from lab coat samples using a W/C microemulsion made of two surfactants (AOT + PFPE-PO_4) [1]. Ohde et al. separated hydrogenated products dissolved in $ScCO_2$ from an octanol solution containing AOT microemulsion with Pd nanoparticles by phase separation accompanied by reduction of CO_2 pressure [11]. Compared with conventional water-based extraction methods, removing

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metal species from solid matrices using W/C microemulsions can significantly minimize wastewater generation.

Because of high cost and potential toxicity of fluorinated surfactants, other approaches for stabilizing W/C microemulsions, such as using alternative co-surfactants (to modify interfacial properties of surfactant monolayers) or co-solvents (to improve surfactant solubility), have been developed by a number of research groups [12–15]. For example, addition of 7.5% (v/v) ethanol to supercritical CO_2 can make the AOT surfactant soluble in the fluid phase [16]. The dielectric constant of the $ScCO_2$ phase increased almost a factor of 2 when 12% (v/v) of ethanol was added [16]. To make 10% (v/v, co-solvent/CO_2) of AOT soluble in $ScCO_2$, Jackson and Fulton showed that the dielectric constant of the solvents must be greater than 1.6 in supercritical conditions [17]. McFann et al. reported that alcohols with medium chain lengths could act as co-surfactants and increase the size and solubility of the W/C microemulsions [18]. They chose *n*-pentanol as a co-surfactant to enhance the formation of micelles and water uptake. Studies suggest that this effect is due to the insertion of the alcohol between the surfactant tails reducing tail–tail and micelle–micelle interactions [19,20].

Solubilities of alkyl alcohols (n-$C_nH_{2n+1}OH$) are usually high in CO_2. Using alkyl alcohols or alkanes as co-solvents can increase the analyte's solubility in CO_2 [15,21,22]. At 60 atm and 35 °C (near critical region), methanol, ethanol, octanol, nonanol and decanol can be dissolved in CO_2 at 0.50, 0.53, 0.48, 0.45, and 0.48 molar fractions, respectively. When pressures increased to the supercritical region, e.g., at 80 atm and 35 °C, solubilities of octanol, nonanol and decanol increased quickly to the molar fractions of 0.6, 0.63 and 0.6, respectively. It was reported that hydrogen bonds of some organic acids in $ScCO_2$ with a polar co-solvent (e.g., alcohol) can be formed even at low concentrations of the co-solvent. Because of their high solubilities in $ScCO_2$, alcohols, acting as co-solvents and co-surfactants, can make AOT microemulsions soluble in $ScCO_2$. It is also known that alkyl alcohols can reduce the cloud-point pressure (CPP) of an AOT microemulsion considerably [23]. Cloud-point pressures usually increase with rising temperatures and decrease with increasing alkyl alcohol concentrations [24].

In a previous report [1], we showed that by using a W/C microemulsion made of a commercially available surfactant, AOT, and a fluorinated co-surfactant, PFPE-PO_4, cobalt and other transition metal ions can be removed. In this paper, a solvent-assisted dissolution of microemulsion method for transporting metal species in $ScCO_2$ is reported. Octanol, in this study, acts as a co-surfactant and a co-solvent for the formation of W/C microemulsions. Using this method, phase separation can be achieved, i.e., as the octanol-modified CO_2 density is reduced, a single reversed micellar phase becomes unstable and two phases are formed consisting of an AOT-octanol-rich liquid phase and a predominant-CO_2 upper phase. The extracted metal species can be collected from the AOT-octanol-rich liquid phase on the bottom. We found no report in the literature regarding this metal extraction method using solvent-assisted dissolution of microemulsion. The advantages of this method for extraction of metal species from solid materials are discussed.

2. Experimental

2.1. Reagents and apparatus

Instrument grade carbon dioxide (99.99% purity) (Oxarc, Spokane, WA) was used in all experiments. Sodium bis(2-ethylhexyl)sulfosuccinate (Aldrich Chemical Co., Milwaukee, WI), perfluoropolyether phosphate (PFPE-PO_4) (KDP-4413, Lot No. E88576-64, DuPont Co.), ethanol, *n*-octanol and heptane (all ACS reagent grade) were purchased from Aldrich and used as received. A fluorinated AOT $\{[H(CF_2)_4CH_2OCO]CH_2CH(SO_3{}^-Na^+)$-$[COOCH_2(CF_2)_4H]$, $C_{14}H_9F_{16}O_7SNa$, MW: 648.25 g/mol$\}$ was synthesized in our laboratory. The details of the synthetic procedure were reported by Ohde et al. [25]. Standard solutions of cobalt chloride and nitrate solutions of Cu, Cd, Pb and Zn were prepared from atomic absorption spectroscopy standards (EM Science, a Division of EM Industries, Inc., Cherry Hill, NJ). An ionic dye, methyl orange, was obtained from Aldrich and used as received. Sea sand (washed, S25–500) was purchased from Fisher Scientific and used as received. All other reagents and solvents used in this study were of analytical grade. De-ionized water (Millipore Milli-Q system, Bedford, MA) was used for the preparation of all aqueous solutions.

The high-pressure apparatus for supercritical fluid extraction of metal species with microemulsions are described in the literature [1]. The phase behaviors of CO_2 with surfactant and co-solvent were studied by a high-pressure view cell with a 20 mL volume, 5 cm path length and quartz windows as shown in Fig. 1. The view cell was pre-heated to a fixed temperature with a hot plate which was controlled and monitored by a thermocouple. The view cell was wrapped with glass wool except the windows and covered with a layer of paper towel outside the glass wool. After reaching a desired temperature, the cell was allowed to stand for 20 min for thermal equilibrium before introducing the CO_2 fluid. The temperature could be controlled within ±2 °C. The view cell allowed visual observation by a video camera and a TV monitor through which phase behaviors of W/C microemulsions were monitored and recorded.

Metal extraction experiments were performed using a specially designed porous stainless-steel extraction vessel (internal volume: 5.2 mL) with a conduit (1 mL volume) underneath as

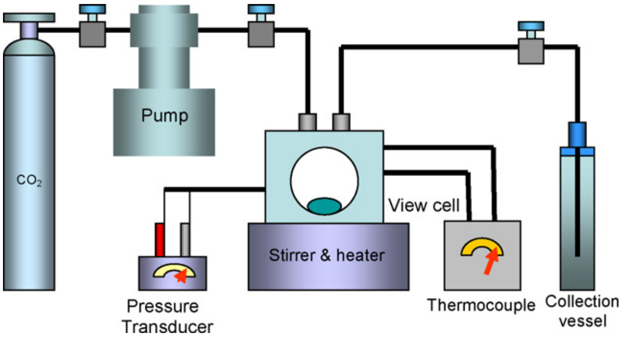

Fig. 1. Apparatus of the high-pressure view cell system used in phase behavior measurements.