

pH SWITCHES FOR THE SELECTIVE EXTRACTION OF METAL IONS FROM BIPHASIC WATER-CO₂ SYSTEMS

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ABSTRACT

Supercritical fluids are quickly becoming a realistic alternative to conventional organic media used in the extraction of metal ions from aqueous phases. However, supercritical fluid extraction (SFE) is complicated by the inherent low pH (~ 3) associated with CO₂ in contact with water. However, we have recently shown that selective extraction of the metal ions can be achieved through the control of the aqueous phase pH and the use of a hydrocarbon surfactant. Furthermore, we demonstrate that pressure-induced pH switches of the aqueous phase can be utilized for the selective separation of metal ions from an aqueous metallic broth. SANS results show that this metal ion extraction occurs through the formation of reverse micelles using the hydrocarbon surfactant Triton X-100 eliminating the use of fluorinated surfactants and the uptake of water.

INTRODUCTION

Over the last ten years, an increased awareness of the problems associated with metal ions in the environment has resulted in demands for more selective and effective separation processes. Supercritical fluid extraction (SFE) [1, 2] is an increasingly popular alternative to conventional liquid-liquid extraction from contaminated samples. Supercritical carbon dioxide (sc-CO₂) is the most utilized supercritical fluid for SFE as it is non-toxic, non-polar, non-flammable, inexpensive, and easily recyclable [3].

SFE from an aqueous phase is made possible through the use of metal chelating agents. Fluorinated chelating agents have been highly successful in the extraction of metal ions from aqueous matrices by SFE [4, 5] due to high solubility in CO₂ [2] and can be engineered for the targeted extraction of a specific metal ion [6, 7]. However, fluorinated molecules are often costly and time consuming to synthesise. Additionally, the extraction of a specific metal ion from a broth of metallic ions typically requires the use of multiple chelating agents limiting their usefulness in SFE.

Although hydrocarbons are soluble in CO₂, [8] their larger cohesive energy densities compared to fluorinated surfactants has made it challenging to form hydrocarbon reversed micelles in CO₂. Recently, several researchers have utilised hydrocarbon surfactants in CO₂ for stabilising emulsions and microemulsions by minimising the cohesive energy density of the hydrocarbon surfactant [9-12]. The use of hydrocarbon chelating agents in SFE, [13-17] is clearly appealing as they are easier to synthesise and cheaper to produce than their fluorocarbon analogues.

Extraction of metal ions from an aqueous phase into CO₂ is complicated by the presence of carbonic acid which lowers the pH of the aqueous phase to approximately 3 [18, 19]. While some metals are extracted efficiently at pH ~ 3 [18, 20], other metal ions, cannot be efficiently extracted at such an acidic pH. Under these conditions, a large excess of ligand is often required to achieve complete extraction of the targeted metal limiting the practical application and economic feasibility of large-scale extractions from contaminated soils and wastes. Recently, Holmes et al [21, 22] have demonstrated that the pH of the aqueous phase in a biphasic water–CO₂ system can be altered from pH~3 to values approaching 7 expanding the pH region available for the SFE of metal ions. In addition, pH ‘switches’ of 1-2 pH units can be readily obtained [23] by taking advantage of the fact that modest changes in pressure and temperature result in large changes in the solubility of CO₂ in the aqueous phase. In the presence of a buffer, these changes in the solubility of CO₂ can then be manipulated to affect the extent of neutralisation of carbonic acid.

Here we describe an extraction process for the selective removal of metal ions into supercritical CO₂ using reversed micelles. This extraction process overcomes the inherent low pH problem associated with water in contact with CO₂ and utilizes a cheap, commercially available hydrocarbon surfactant as a micellar complexing agent with no uptake of water into the micelle core. The aggregation behaviour of these surfactants as well as their metal analogues were investigated by the direct method of small angle neutron scattering. Other indirect spectroscopic methods are also utilized to suggest aggregation into micelles.

EXPERIMENTAL

Materials and Reagents. The non-ionic surfactants Triton X-100 (n = 9.5), Triton X-114 (n = 7), and Triton X-45 (n = 2) are based on a polyethylene oxide (PEO) repeating unit with an average molecular weight of 625, 536, and 426 (g mol⁻¹), respectively. The metal ion sources used for extraction were obtained from cobalt (II) nitrate, gold (III) chloride (prepared in approx. 0.5 M hydrochloric acid), copper (II) nitrate, chromium (III) nitrate, and nickel (II) nitrate. Sodium hydroxide was used to vary the pH of the aqueous phase. All reagents were used as received. De-ionised water was used in all experiments and carbon dioxide was used as received. All surfactant metal salts were prepared by mixing a known volume of metal salt with 10 mL of Triton X-100 solution. The quantity of salt added was the maximum possible soluble in that quantity of surfactant.

pH measurements. All experiments were carried out in a 25 mL stainless steel view cell fitted with two UV-grade sapphire windows. Extraction temperatures were controlled by isopad heating tape (Type ITW//SS-M) and thermostated to ± 0.2 °C using a platinum resistance thermometer and a temperature controller. Pressure was controlled to ± 0.2 bar using an ISCO (Lincoln, NE) syringe pump. An external magnetic stirrer drove a PTFE coated magnetic stirrer bar. For each extraction, an aqueous sample of metal ions was carefully loaded into the cell using a Pasteur pipette (typically 2.5 mM gold (III) chloride, 70 mM copper (II) nitrate, 80 mM cobalt (II) nitrate, 30 mM nickel (II) nitrate, and 30 mM chromium (III) nitrate). A known volume of surfactant was introduced into the cell using a 1 mL syringe. 15 mL of CO₂ was then introduced into the cell at ambient temperature. Extractions were carried out at various temperatures between 22 and 60 °C for approx. 2 hr and monitored *in-situ* using a HP 8453 UV-vis spectrometer. The pH of the aqueous layer was controlled by the addition of NaOH and/or the temperature and pressure. The aqueous layer pH was calculated using a Newton-Raphson method to solve a set of non-linear equations based on a thermodynamic model. This model had been previously used to predict the pH of the aqueous layer in a water–CO₂ biphasic system. [23]

UV-vis data for the extraction of metals from the aqueous phase was monitored by the disappearance of the characteristic metal ion species peak. Concentrations were related to the peak height using the Beer-Lambert law. Each Triton-metal complex had a characteristic UV-vis peak (due to a ligand metal charge transfer band) different from that of the metal ion species. This characteristic LMCT peak appeared in the CO₂ phase and not in the aqueous phase confirming that the surfactant-metal species resides in the CO₂ phase and not the aqueous phase. The appearance of the characteristic nitrate peak was witnessed in the CO₂ phase for all extracted metals, except gold(III), suggesting that the nitrate ion is also extracted with the metal ion. Control experiments were performed without the presence of Triton X-100 to ensure that metal ion species were being extracted and not precipitating from solution. The maximum error attributable to precipitation occurred at basic conditions (pH ~7.8) and was no larger than 5%.

Phase Behaviour. Phase behaviour was studied by immersing the view cell in a water bath and controlling the temperature to ± 0.1 °C by a water circulator. Each sample was loaded into the cell using a 1 mL syringe. CO₂ was loaded into the cell at ambient temperature using a 260 mL ISCO syringe pump. The mixture was stirred using a PTFE coated magnetic stirrer bar driven by an external stirrer. The pressure was raised to the point where a clear, single phase solution was obtained (after the collapse on an initial unstable emulsion). The phase boundary or cloud point was found by subsequently lowering the pressure until the solution became cloudy. Such transitions, measured at constant temperature (allowed to equilibrate for 10 min) with decreasing pressure, are clearly visible and highly reproducible to within ± 10 bar. The rate of pressure decrease (7 bar per min) could be controlled with the ISCO pump using a gradient program.

Small-angle neutron scattering. SANS measurements were performed on the LOQ spectrometer using the ISIS pulsed neutron source of the CLRC Rutherford Appleton Laboratory, UK using a stirred high-pressure optical cell (maximum pressure 500 bar, path-length 12 mm) as described previously. [24] The magnitude of the transfer vector Q is given by $Q = 4\pi/\lambda \sin(\theta/2)$ where λ is the incident wavelength (2.2-10 Å), determined by time of flight, and θ is the scattering angle. The intensity of the neutrons was recorded on a position sensitive 64 × 64 pixel 2-D detector at a fixed sample to detector position (4.43m) providing an effective Q range from 0.01 to 0.2 Å⁻¹ in a single measurement. The data was corrected for transmission and incoherent background scattering and normalised to absolute scattering probabilities using standard procedures. $I(Q)$ data were analysed using the multi-model FISH program. [24]

THEORY

For small particles (or micelles) of volume V_p present at a number density n_p , the normalized SANS intensity $I(Q)$ (cm⁻¹) may be written as $I(Q) = n_p(\rho_p - \rho_m)^2 V_p^2 S(Q)P(Q)$ where ρ_p and ρ_m are the mean coherent scattering length densities of the dispersed phase (e.g. particles) and solvent medium, respectively. $P(Q)$ is the single particle form factor describing the angular distribution of the scattering owing to the size and shape of the particle. Expressions for $P(Q)$ representing various particle shapes, such as spheres, rods, disks, ellipsoids, etc., can be used to model SANS data in order to determine particle shape and size. $S(Q)$ is the structure factor which arises from spatial correlations between particles. For reversed micelles far removed from phase boundaries, i.e., in the absence of attractive interactions between micelles, and at low micelle concentration $S(Q) \approx 1.0$. Under these conditions, $I(Q)$ is a direct measure of $P(Q)$, i.e. $I(Q) = n_p(\Delta\rho)^2 V_p^2 P(Q)$. For reversed micelle systems at fixed volume fraction, the $S(Q)$ contribution becomes increasingly significant as

the aggregation number (micelles size) decreases. Theoretical models are then available for $S(Q)$ when the micelles are spherical but as yet no simple formalism exists to account for interactions between anisotropic rod or disk-shaped structures. However, since the aggregation number is then appreciable, the $S(Q)$ contribution will be less significant than for spherical micelles formed at the same surfactant concentration. Since $P(Q) = 1$ when $Q = 0$ and the $I(Q)$ data are fitted in absolute units, the value of the scale factor $(n_p(\Delta\rho)^2V_p^2)$ is a self-consistency check on the model since both $n_pV_p (=F)$ and $??^2$ are known. The fitting program we have developed allows us to examine a wide range of models from which physically unrealistic solutions can be eliminated using, in part, the scale factor criteria.

RESULTS AND DISCUSSION

pH effects. Despite the obvious importance, pH dependent SFE has not received much attention and any attempts to do so has been limited to controlling the aqueous phase pH *before* the addition of CO_2 . However, the effects of the aqueous phase pH on the extraction efficiencies of various metals are clearly demonstrated in Figure 1a for a biphasic water- CO_2 system using Triton X-100 as the extractant. Selective metal ion extraction can be achieved by simple pressure-induced pH switches as seen in Figure 1b. These changes in the extraction efficiency for the different metal ions as a function of pH can be attributed to changes in the speciation of the metal complexes as the aqueous phase pH changes. However, pH and speciation effects may also affect the formation and stability of micelles formed in CO_2 [25].

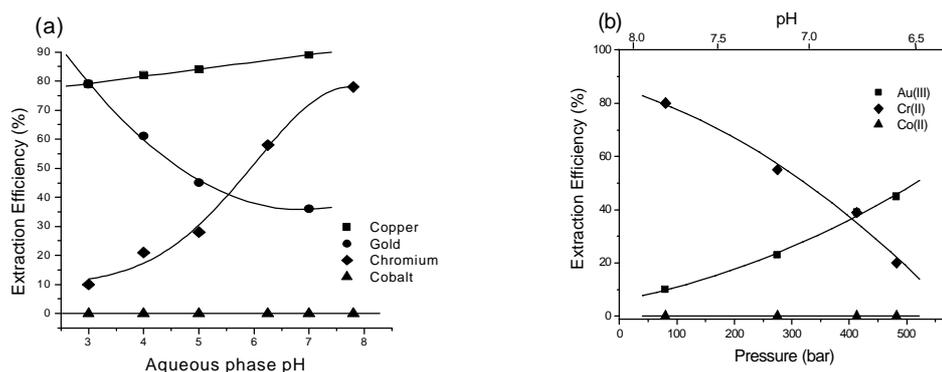


Figure 1. (a) pH effect of metal ion extraction in biphasic water- CO_2 systems using TX-100 as the extractant; and (b) pressure-induced pH switches for selective metal ion extraction.

Triton reversed micelles in CO_2 . Although Triton X-100 is widely believed to form reversed micelles in CO_2 , [17, 26, 27] direct evidence of micelle formation has not been presented. Phase behaviour measurements for pure Triton X-100 in CO_2 over a wide range of concentrations show that Triton solubility is favoured at higher pressures and lower temperatures due to the increased solvent strength of CO_2 . SANS data of pure Triton X-100 in CO_2 in the one phase region is shown in Figure 2. The scattering intensity is very weak but clearly indicates the presence of small aggregates. Reasonable fits were given using a polydisperse spherical form factor model with a Schultz polydispersity function index (σ/R_{mean}) of 0.2. [28] The mean radii, R_{mean} , representing the overall micelle dimensions were obtained as 11 Å for Triton X-45 and 13.5 Å for Triton X-100. The absolute intensity of the scattering is at least a factor of four lower than would be expected from a solution of Triton X-100 at this composition assuming complete aggregation into unsolvated reversed micelles. This attenuation in absolute intensity and small size suggest loosely packed reversed micelles of low aggregation number with significant CO_2 solvation of the aggregate structure. It is also

likely that the $c_{\mu c}$ for the surfactants in CO_2 is significant at the concentration levels employed leading to a relatively high monomer:micelle ratio. Tests using a more parameterised core-shell model did not alter the above conclusions but the statistical resolution of the data does not merit such detailed analysis at this stage.

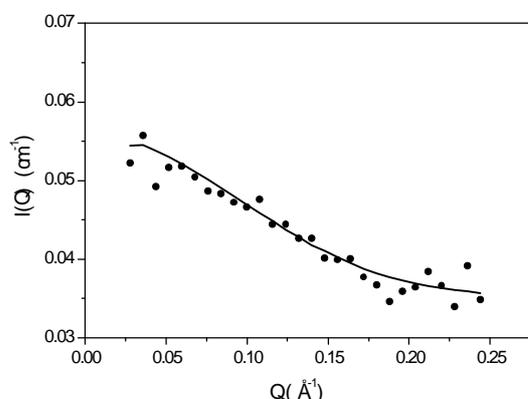


Figure 2. Small angle neutron scattering data for TX-100 in pure CO_2 .

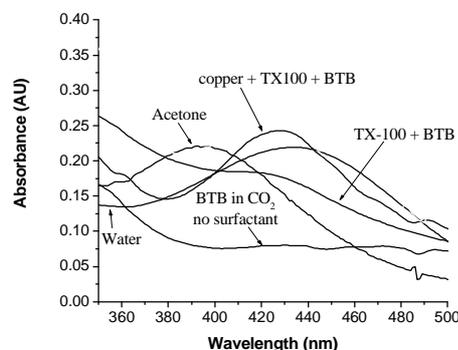


Figure 3. UV-visible spectra of thymol blue in various solvent environments.

UV-vis dye solubilization measurements were also carried out to confirm the presence of reversed micelles as seen in Figure 3. No thymol blue absorbance was detected in pure CO_2 . However, with the addition of Triton X-100, a spectrum characteristic of thymol blue is obtained. The shift in λ_{max} for thymol blue in pure water compared to that in Triton and CO_2 seen in Table 1 is indicative of a change in the polarity of the environment surrounding the dye suggesting the incorporation of the thymol blue into Triton X-100 aggregates.

Table 1. The wavelength shift of thymol blue in various solvent environments.

Substance	λ_{max}
Water	438nm
Acetone	396nm
Triton X100	414nm
Triton X100 + Copper	427nm

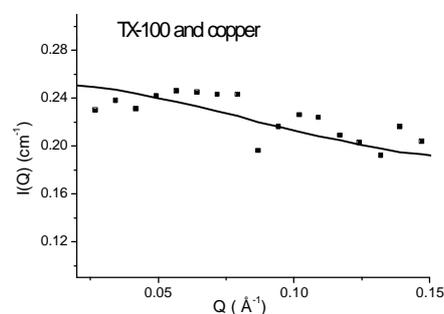


Figure 4. Small angle neutron scattering data for TX-100-copper complex in pure CO_2 .

Triton-complex reversed micelles in CO_2 . SANS data of Triton X-100-copper complex in pure CO_2 is shown in Figure 4. Once again, the scattering intensity is very weak but clearly indicates the presence of small spherical aggregates. The mean radius representing the overall micelle dimensions was 6.5 \AA . UV-visible dye experiments appear to confirm that Triton-copper complexes form dry micelle aggregates as characterized by the shift in λ_{max} . This data suggest that the mechanism of metal ion extraction in aqueous matrices using Triton X-100 proceeds via the formation of reversed micelles. The formation of reversed micelles offers several advantages over w/c microemulsion-mediated metal ion extraction since there is no uptake of water into the micelle core eliminating the need for further treatment of the contaminated water.

CONCLUSIONS

Here we describe a simple and environmentally benign route for the extraction of heavy metal ions from aqueous matrices using the cheap, commercially available hydrocarbon surfactant Triton X-100 as an extractant in lieu of expensive, fluorinated chelating agents. Triton and Triton-metal complexes are shown by both SANS and dye solubilization to form reversed micelles in pure CO₂ and is believed to be the mechanism for metal ion extraction in biphasic water–CO₂ matrices. The formation of reversed micelles in lieu of microemulsions offers the additional advantage of expulsion of water from the core eliminating the need for further processing of the water after extraction.

ACKNOWLEDGEMENTS

We acknowledge financial support from Enterprise Ireland for a postgraduate studentship for JPH and a postdoctoral research fellowship for KJZ. Financial support from EPSRC (GR/L05532 and GR/L25653) is also acknowledged.

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