Phase Behavior and Spectroscopic Characterization of CO_2-Expanded Fluorinated Microemulsions

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The formation of water-in-CO_2 emulsions and microemulsions overcomes the limited solvent power of CO_2 for polar compounds while maintaining the advantages of processing in a pressure-tunable environment. The aqueous core of these reverse microemulsions provides a polar environment for synthesis, extraction, and materials processing. This study examines the preparation of fluorinated reverse microemulsions in a CO_2-expanded fluorinated solvent. At constant concentration in these fluorinated surfactant/CO_2/water/fluorinated solvent systems, moderate pressure (46 – 189 bar) provides a "switch" for the formation of nano-sized water droplets dispersed in CO_2-expanded fluorinated solvent.

The formation of reverse microemulsions is examined for the system of perfluoropolyether surfactant (ClPFPE-NH$_4$, MW = 632) and PFPE oil as a function of temperature, pressure, CO_2 concentration, and water to surfactant ratio. Visual observations of one-phase behavior consistent with reverse microemulsion formation are further supported by spectroscopic experiments that establish the existence of an aqueous core. The phase behavior of this system is compared to conventional water-in-oil microemulsions as well as CO_2-continuous reverse microemulsions. These results suggest the potential to combine synthesis and subsequent separation steps in a single process system at significantly lower pressures than traditional CO_2-continuous microemulsions.

INTRODUCTION:

The recent interest in CO_2-expanded media for chemical synthesis [1, 2] and separation [3] is based on their pressure-tunable solvent properties, their enhanced mass transfer characteristics (relative to organic solvents), and the reduced operating pressures relative to supercritical fluid processes. The use of CO_2-expanded media addresses the limited ability of pure CO_2 to solvate a variety of polar species. An alternative approach to increase the solvent power of compressed CO_2 is the formation of reverse microemulsions using CO_2-philic surfactants [4, 5]. The aqueous core of these reverse microemulsions provides a polar environment for synthesis, extraction, and materials processing. Similar efforts to enhance the poor solvation characteristics of fluorinated hydrocarbon solvents, which are neither hydrophilic nor hydrophobic, have demonstrated the application of water-in-CO_2 fluorinated emulsions for chemical syntheses [6] and drug delivery [7, 8].

Recently, Zhang and coworkers successfully dispersed water into gas-expanded organic solvent systems using a triblock copolymer (Pluronic P104; $PEO_{27}PPO_{61}PEO_{27}$). The expansion fluids used were compressed CO_2 [9] and ethylene [10]. They concluded that dissolution of the gas changed the solvent quality of the organic solvent to induce formation of reverse micelle aggregates [10] at significantly lower pressures (< 57 bar) than traditional supercritical solvent approaches. This study extends the formation of reverse microemulsions to CO_2-expanded fluorinated solvent systems, an approach that maintains CO_2's benefit of processing in a chemically inert media. This novel approach to fluorinated microemulsions formation avoids the use of fluorinated cosolvents, which are expensive and difficult to recover, to induce microemulsion formation. The use of pressure as a phase switch to induce microemulsion formation highlights the potential to combine synthesis and subsequent separation steps in a single solvent system.

MATERIALS AND METHODS:

The fluorinated surfactant (ammonium carboxylate perfluoropolyether; $Cl(CF_2CF(CF_3)O)_m$-CF_2-COO^- NH_4^+; m ~3) and perfluoropolyether oil (HT110; MW = 580; BP = 110 ^{o}C) were obtained from Ausimont USA. The surfactant was prepared from the PFPE carboxylic acid form according to published procedures [11]. Methyl Orange (MO) [$(CH_3)_2NC_6H_4N=NC_6H_4SO_3Na$], obtained from Aldrich Chemical Co., was used without further purification. Deionized ultrafiltered water (Fisher, PA) was used in preparing the microemulsions. CO_2 (99.99%) was obtained from Scott-Gross Co. Inc. (Lexington, KY).
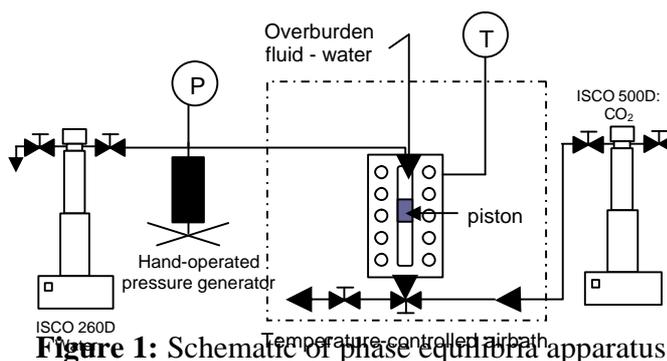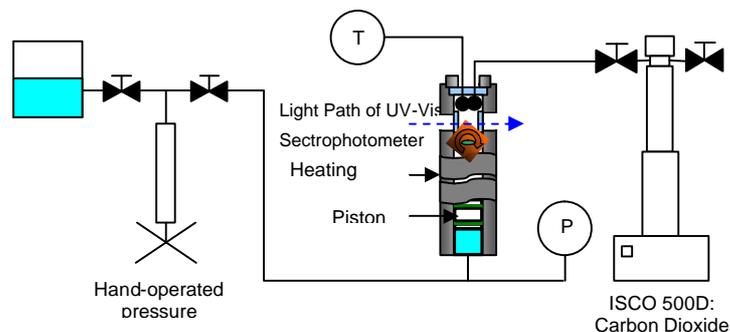

Figure 1: Schematic of phase equilibria apparatus

Phase equilibria observations. Microemulsion phase behavior was studied in a Pressure Volume Temperature (PVT) apparatus from DB Robinson Design & Manufacturing Ltd. (Edmonton, Canada) (Figure 1). The detailed set up of the apparatus was reviewed elsewhere [12]. During each run, 10 mL of PFPE oil, 5 wt% of the ClPFPE-NH_4 surfactant, and water required to form the desired W_o (water to surfactant molar ratio) was loaded into the cell. After the system was thermally equilibrated, CO_2 (125 bar, 22 ^{o}C) was injected to make a mixture with an overall initial CO_2 composition of 10 mole % (with respect to total amount of materials) and stirred vigorously for 15 minutes. After the phase observation for the equilibrated system (settling time > 15 minutes), more CO_2 was injected to raise the CO_2 composition to 30, 50, 70, 80 and 90 mole%. The phase observations were conducted at 25, 35 and 45 ^{o}C, and W_o's of 10, and 20. Phase observations were confirmed with duplicated experiments.

High-pressure UV-Vis Characterization of Water Cores. The UV-vis measurements were performed in a custom-designed high pressure, variable-volume, spectroscopic cell (Thar Designs Inc., PA) (Figure 2), described previously [13].

The solvatochromic behavior of the probe molecule MO was determined for

Figure 2: High pressure view cell for spectroscopic studies of microemulsion systems.

microemulsion samples at two conditions: 25 ^oC and $W_o = 20$; and 35 ^oC, $W_o = 10$. The PFPE oil, surfactant and MO aqueous solution (4.7 x 10^{-4} M) were loaded into the variable volume cell. After the desired amount of CO_2 was injected into the view cell and the mixture was equilibrated, duplicate spectra were

taken. Additional CO_2 was then injected to raise the concentration of CO_2 in the view cell. The equilibration and spectral acquisition steps were then repeated.

RESULTS AND DISCUSSIONS:

Similar to CO_2, fluorinated hydrocarbon solvents are neither lipophilic nor hydrophilic. In addition, phase equilibria [12, 14, 15], *ab initio* calculations [16] and spectroscopic investigations [17] suggest that there is are favorable interaction between CO_2 and fluorinated compounds. The favorable interaction between fluorinated moieties and CO_2 is explored in this study as a potential 'switch' to induce microemulsion formation.

The cloud point transition pressure (CPP) of water-in-CO_2 microemulsion systems has previously been used to characterize the effectiveness of fluorinated surfactants at promoting microemulsion formation for a given water-to-surfactant ratio [18, 19]. Below the CPP, the solvent power of CO_2 is insufficient to stabilize the microemulsion droplets. The homogeneous mixture undergoes phase separation, and turns cloudy or opaque. In this study, phase observations of the fluorinated surfactant/CO_2/water/fluorinated solvent systems were used to identify the conditions at which an optically clear and thermodynamically stable CO_2-expanded, fluorinated microemulsion exists as a function of temperature, pressure, CO_2 concentration, and water to surfactant ratio.

The CPPs for a 5 wt% ClPFPE-NH$_4$ surfactant in PFPE oil (W_o =10) at 25, 35, and 45 ^oC is presented in Figure 3a. CO_2 compositions greater than 80 mol% were required to form microemulsions at 25 and 35 ^oC. However, at 45^oC, microemulsion formation was observed at a CO_2 composition as low as 70 mole%. The CPPs increased with increasing dissolved CO_2 and temperature. For example, at $x(CO_2) = 0.8$, the CPPs for the microemulsion samples were 49, 76.1, and 91.8 bar at 25^oC, 35^oC and 45^oC,

respectively. At 25°C, the CPP was observed at 49 bar, well below the pressure at which a CO_2-rich liquid phase is observed to condense in this system (64.3 bar).

With an increase in system water content (W_o = 20, Figure 3b), the pressure required to stabilize the droplets also increased. For example, at 80 mol% CO_2 and 25°C, the CPP were 49 bar and 52.8 bar at water to surfactant ratios 10 and 20, respectively. At W_o = 20, microemulsion phase behavior was observed at x_{CO2} > 0.7 at 25 ^{o}C and at x_{CO2} > 0.8 at 35 and 45 ^{o}C. The CPPs increased with system temperature and CO_2 composition. However, the CPPs for the CO_2-expanded microemulsion at 45 ^{o}C are relatively constant.

The CPPs observed in these CO_2-expanded fluorinated solvent systems are comparable to the lowest reported CPPs for fluorosurfactants in water/CO_2 microemulsions at similar conditions [19, 20]. Eastoe and coworkers have demonstrated that a fluorinated, dichained sodium sulfosuccinate, (di-CF4) could stabilize a water/CO_2 microemulsion ([surf.] = 0.05 mol dm^{-3}; W_o = 10; T = 20 ^{o}C) at ~50 bar [20]. Furthermore, a phosphate analogue of the fluorinated dichained sulfosuccinate surfactant (di-HCF6-P) was also shown to stabilize a water/CO_2 microemulsion ([surf.] = 0.05 mol
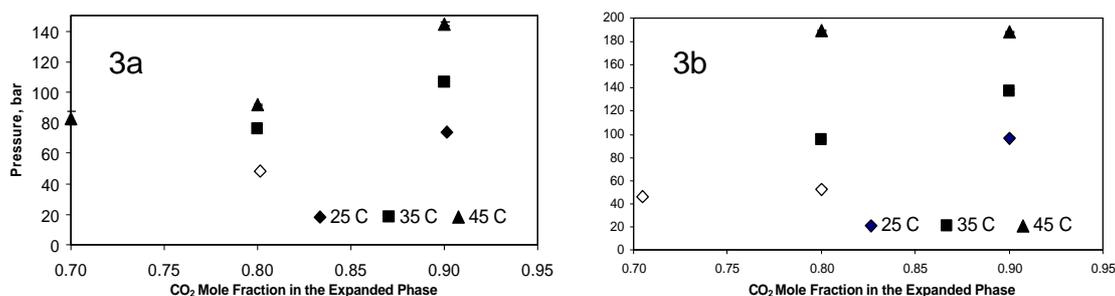
Figure 3: CPP of microemulsion systems as a function of temperature, CO_2 mole fraction in the expanded phase (a) at W_o, =10; and (b) W_o, = 20 (3b). Unfilled data points indicate bubble point pressures of samples at 298 K.

dm^{-3}; W_o = 10; T = 15 ^{o}C) above a similar cloud point pressure [19].

The nature of the water droplets dispersed in the CO_2-expanded fluorinated solvent was explored using a solvatochromic probe, MO, previously used to verify the aqueous environment in reverse microemulsions [4, 21]. Our measured values of the absorption maxima of MO in the CO_2-expanded PFPE microemulsion, as well as relevant solvent systems, are provided in Table 1. The shoulder (at 540 nm) observed in the CO_2-saturated aqueous solution and CO_2-expanded is consistent with the presence of carbonic acid [4, 22]. Pure methanol and PFPE surfactant/PFPE oil /CO_2 mixture (125 bar, 35 ^{o}C, x_{CO2} = 0.8; no added water) have similar maxima (422 and 421 nm, respectively). This suggests that, in the absence of added water, MO is solvated in an environment whose polarity is similar to methanol. In the presence of water (W_o = 10), the CO_2-expanded microemulsion had a absorption maximum at 457 nm with a distinct shoulder at 540 nmn, indicating that MO resided in an acidified water environment, or an aqueous core.

Table 1: Maximum absorption wavelengths of MO in different solvent environments.

Solvent Environment	λ_{max}, nm
Water	464.5 nm
Methanol	422.8 nm
CO_2-saturated aqueous solution, 125 bar, T=35 °C	501.3 nm; shoulder ˜ 540 nm
CO_2-expanded PFPE microemulsion, W_o = 10, xCO_2 = 0.80; T=35 °C, P = 125 bar	457 nm; shoulder ˜ 540 nm

With increasing CO_2 content (W_o = 19.8), the absorption maximums underwent a shift from 473 nm (x_{CO2}= 0.7) to 465 nm (x_{CO2}= 0.9) (Figure 4). The shift suggests that the water molecules surrounding the dye inside the droplets behaved increasingly like bulk water.
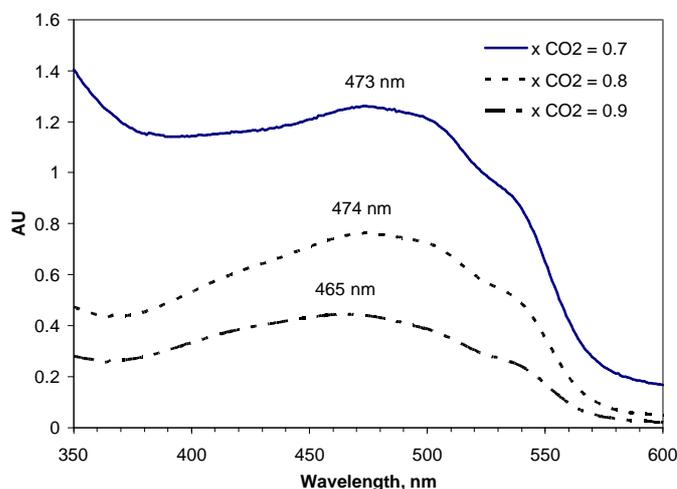
Figure 4: Spectra of Methyl Orange in CO_2-expanded PFPE microemulsion, W_o = 19.8, 25°C. Solid line: spectra at x_{CO2} = 0.7; Dashed line: spectra at x_{CO2} = 0.8; (— - —) spectra at x_{CO2} = 0.9.

CONCLUSIONS:

A new method for preparing pressure-tunable fluorinated microemulsion using CO_2 expansion is demonstrated. Transparent, thermodynamically stable microemulsions were formed at water to surfactant molar ratios as high as 20 and at temperatures up to 45 °C. Moderate cloud point pressures were observed throughout the process conditions investigated. The lowest transition pressure observed was recorded at 46 bar, 298 K (5 wt% ClPFPE-NH_4, W_o = 20, x_{CO2} = 0.7). The cloud point pressures increased with temperature, water loadings, and CO_2 content. Absorption dye studies using methyl orange support the existence of water molecules dispersed in the cores of the microemulsion droplets. Further, these water molecules behave like bulk, free water. The lowest CPPs observed compare well to other reported CO_2-continuous reverse microemulsion systems, further validating this technique as an alternative to preparing a pressure-tunable microemulsion system at moderate CO_2 pressures.

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