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Formation and characterization of emulsions consisting of dense carbon dioxide and water: Ultrasound

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ABSTRACT

In this work, we studied ultrasound formation of surfactant-free emulsions consisting of water and dense carbon dioxide (CO_2). Emulsions with limited kinetic stability were formed after approximately 2 min of pulsed ultrasound at 20 kHz and above a critical power density of at least 0.05 W cm^{-3}. Emulsion stability and formation were studied using a variety of techniques. In situ microscopy using a high-pressure microfluidic reactor indicated that the water/CO_2 emulsion consisted of finer droplets of about 5 μm compared to the CO_2/water emulsion which consisted of droplets with average diameters of about 12 μm. A partially miscible tracer technique was used to measure the dispersed phase content of the two emulsions to be about 4 vol% and up to 9 vol% for the CO_2/water and water/CO_2 emulsions, respectively. Engineering analysis and complementary experiments indicated that the water/CO_2 emulsions formed via a two-step mechanism consisting of surface wave break-up to form a coarse emulsion followed by cavitation to form a fine emulsion. We use KI oxidation as a probe reaction to examine ultrasound-induced chemistry in the dense CO_2/water system, finding that KI oxidation was suppressed by the presence of a high pressure CO_2 phase. Through the combination of formation, stability, and KI oxidation experiments and analyses, we suggest that the dense CO_2 cushioned cavitation bubble collapse, damping ultrasound chemical effects while permitting physical effects such as emulsification. Engineering analysis suggests energy efficient scale-up might be achieved in a carefully designed flow reactor.

Notation

$\langle d_N \rangle$ number averaged droplet diameter
$\langle d_S \rangle$ surface area averaged droplet diameter
$\langle d_V \rangle$ volume averaged droplet diameter
$\langle d_{32} \rangle$ "Sauter diameter", determined as the volume-area average
L settling path length
r droplet radius
g gravitational constant (9.8 m s^{-2} at sea level)
$U_{unhindered}$ unhindered settling velocity, used for dilute emulsions
$U_{hindered}$ hindered settling velocity, used for concentrated emulsions
$\tau_{observed}$ observed time required for emulsion breaking
$\tau_{unhindered}$ calculated time required for emulsion breaking by unhindered settling
$\tau_{hindered}$ calculated time required for emulsion breaking by hindered settling
$\tau_{coagulation}$ calculated time required for emulsion breaking by coagulation
ϕ_{water} volume fraction of water phase
$\phi_{carbon\ dioxide}$ volume fraction of CO_2 phase
ϕ_d volume fraction of dispersed phase, irrespective of it being CO_2 or water
λ length scale of the critically unstable wave
μ dynamic viscosity
ρ density
$\Delta\rho$ density difference
γ surface tension
ω driving frequency (radians)

1. Introduction

Homogeneous catalysis has potential advantages over the heterogeneous variety for many applications yet its potential has not yet fully been recognized due to challenges in the design of industrial-scale chemical reactors employing homogeneous

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catalysts [1–3]. Catalyst retention, recovery, and reuse is the source of most failed attempts at commercialization [1]. Use of homogeneous catalysts under biphasic conditions [4], in which separate, immiscible phases are used for different reaction, separations, and catalyst applications, has been shown as an attractive approach in synthetic chemistry [4], commodity chemicals [5], and fuels [6] applications.

A chief consideration in biphasic reaction design is selection of the immiscible solvents; careful selection can benefit product yields and selectivity [7]. In addition to performance considerations, environmental and process considerations must be factored into the decision. For this reason, biphasic reaction mixtures consisting of water and a supercritical fluid (SCF) have substantial promise [8–11]. At conditions typical of process chemistry (25–350 °C and 0.1–20 MPa), many commonly used SCFs, including CO_2 [12], ethane, and propane are immiscible with water–an obvious requirement for biphasic reactions. Near the critical point, modest changes in operating conditions can be used to tune physiochemical properties [13], including diffusion coefficients [14–16], viscosity, partition coefficients [17–19], and even aqueous phase pH within a modest range [20,21]. Additionally, the use of SCFs such as $scCO_2$ provides means for easy catalyst separation and product recovery by depressurization without requirement for further processing steps.

When CO_2 is selected as the SCF in conjunction with water, both solvents in the biphasic system are environmentally benign, non-toxic, inexpensive, and abundant. In fact, $scCO_2$–water mixtures as both emulsions [22–31] and microemulsions [32] have been used for a wide variety of chemical reactions including Diels–Alder cycloaddition [33], olefin epoxidation [34], hydrolysis reactions [35–37], polymerization reactions [38], Barbier reaction [39], oxidation [40], hydrogenation [41,42], hydroformylation [43], biomass pretreatment [44], hydrogen peroxide synthesis [45,46], and particle and materials synthesis [47]. Beyond the chemical process industries, $scCO_2$/water mixtures – including emulsions – are likely important in geological systems and potentially of interest for geological CO_2 sequestration and CO_2 enhanced oil recovery [48].

Finite mass transfer rates are a challenge that can limit efficiency in biphasic reaction mixtures, especially for rapid chemical reactions [35,36]. Increasing the mixing rate and $scCO_2$–water interfacial area, either as microemulsions or emulsions, is an effective strategy for overcoming mass transfer limitations [33]. For process efficiency, the energy costs of surface area generation can be an important consideration. The use of surfactants may decrease the energy required to generate surface area, and surfactant addition can be a viable economic option in some cases.

Unfortunately, use of surfactants incurs additional environmental and economic costs associated with surfactant synthesis, recovery, and reuse. The costs are especially problematic for surfactant-stabilized water–$scCO_2$ biphasic mixtures as these have required boutique or highly fluorinated surfactants [49]. The costs of fluorinated surfactants suggests a search for surfactant-free emulsions [50] consisting of water and $scCO_2$ phases.

Ultrasound has been demonstrated to be an additive-free method to generate short-lived emulsions consisting of water and $scCO_2$ [33,35,36,51] or to improve the effectiveness of low-cost hydrocarbon surfactants stabilizing water and $scCO_2$ emulsions. Timko et al. [36] found that short-lived, surfactant-free emulsions could be generated consisting of $scCO_2$ and water and used them for hydrolysis [35] and Diels–Alder reactions [33]. More recently, Cenci et al. [37,39] used pulsed ultrasound to generate water–$scCO_2$ emulsions, studied their stability, and used them for a hydrolysis [37] and Barbier reactions [39]. In addition to surfactant-free emulsions, Cenci et al. investigated the use of an inexpensive hydrocarbon surfactant, Tween 80, to increase the volume fraction of $scCO_2$ dispersed in the water phase from approximately 5% to 35% and to extend the apparent breaking time from 15 min to 60 min.

These two sets of ultrasound studies [18,33,35–37,39,51] indicate the potential for ultrasound to generate emulsions consisting of water and $scCO_2$ phases. Unfortunately, characteristics of emulsions consisting of water and dense CO_2 phases have been incompletely published, the mechanism of ultrasound formation of water–$scCO_2$ emulsions is not fully understood, and the energy and scale-up requirements are poorly understood. Here, we present new data and analysis to examine the emulsification mechanism of power ultrasound of CO_2–water mixtures. The focus is on ultrasound emulsification process in a batch reactor and we present new data on the emulsion volume fractions, droplet distributions, and stability. We couple this with experiments and analysis of cavitation and surface wave formation. These contributions advance the state of knowledge of emulsification of dense CO_2–water mixtures and provide an engineering basis for reactor design.

2. Experiment

2.1. Experimental system

The complete experimental system consisted of a high-pressure ultrasonic reactor, used to generate the emulsions, and a high-pressure microfluidic reactor, used to image emulsion droplets. The Supporting Information contains a simple schematic of the complete system.

2.2. Ultrasonic reactor

The high-pressure ultrasonic reactor used in this work was described previously in the literature [35,51] and only the most relevant details are provided here. The main body of the reactor was a 316-stainless steel block. Into this block, were bored two cylinders that intersected (diameter = 1.9 cm) at the center of the block. A titanium probe (o.d. = 0.80 cm) was sealed into one of the 4 main reactor openings so that the tip of the probe was approximately 1 cm offset from the intersection point. The other 3 reactor openings were sealed using α-Al_2O_3 (sapphire) windows and stainless steel glands. Additional entry ports were machined into the reactor to measure pressure and temperature. With all ports sealed, the reactor volume was $87.2 \pm 0.4\,cm^3$ and, except where noted, the reactor was filled 50/50 vol/vol with water and CO_2 during all experiments.

2.3. Emulsion imaging

The stability of ultrasonically formed emulsions was determined visually by recording the time required for the emulsion to clear after ultrasound had been terminated. A video camera (Sanyo, VCB 3524) equipped with telescopic lenses (Tiffen) was used to record images. The camera was focused on the center of the reactor, which corresponded to a working distance of roughly 7 cm. A fiber optic light source (Fostec, 8375) with a maximum power output of 150 W provided indirect lighting by reflection off a PTFE sheet placed behind the reactor. A standard video recorder was used to archive demulsification. The video tape was digitized using commercial software (FinalCut) and still images were extracted from the digitized movies.

2.4. Volume fraction measurement

A chemical tracer technique was used to measure dispersed phase volume fractions [35]. A known quantity of tracer was added to the reactor before filling with CO_2 and water. To take advantage of near-quantitative partitioning in the desired phase, octane