Macroemulsions of Liquid and Supercritical CO$_2$-in-Water and Water-in-Liquid CO$_2$ Stabilized by Fine Particles

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Liquid and supercritical carbon dioxide-in-water (C/W) and water-in-carbon dioxide (W/C) macroemulsions (Pickering emulsions) stabilized by fine particles were created in a high-pressure batch reactor. C/W macroemulsions form when hydrophilic particles, such as pulverized limestone, sand, flyash, shale, and lizardite, a rock rich in magnesium silicate, are used as stabilizers; W/C macroemulsions form when hydrophobic particles, such as Teflon powder, activated carbon, carbon black, and pulverized coal, are used as stabilizers. C/W macroemulsions form with both liquid and supercritical CO$_2$. C/W macroemulsions consist of dispersed droplets of liquid or supercritical CO$_2$ sheathed with particles in water; W/C macroemulsions consist of droplets of water sheathed with particles dispersed in liquid CO$_2$. The sheathed droplets are called globules. The globule diameter is largely dependent on the shear force imparted by mixing the two fluids, CO$_2$ and H$_2$O. The particle size needs to be adjusted to the dispersed droplet diameter; a practical ratio was found to be 1:20. In a batch reactor with a magnetic stir bar rotating at 1300 rpm, liquid CO$_2$ produced typical globule diameters in the 200−300 μm range, whereas supercritical CO$_2$ produced smaller globules, in the 100−150 μm range.

Introduction

Liquid and supercritical carbon dioxide are poorly miscible with water. However, CO$_2$-in-water (C/W) and water-in-CO$_2$ (W/C) emulsions can be created with various surfactants.[1−3] In a previous publication, we described that a C/W macroemulsion, also called a Pickering emulsion, can be created both with liquid and supercritical CO$_2$ using finely pulverized limestone as a stabilizer.[4] Dickson et al. reported on the stabilization of C/W emulsions with silica nanoparticles.[5] Here, we report that C/W macroemulsions can be formed with several hydrophilic fine particles, including pulverized beach sand, flyash, shale, and a magnesium silicate rock, while W/C macroemulsions can be formed with hydrophobic fine particles, including Teflon, carbon black, and pulverized coal. Emulsion stabilization with fine particles may prove particularly attractive because particles are low in cost, easy to recover, and can be tailored for each specific application, e.g., by adjusting the chemical properties (pH, ionic strength, and solubility) and physical properties (density, viscosity, and rheology) of the emulsion. These emulsions may find applications in ocean and geologic sequestration of CO$_2$, enhanced oil recovery, coal beneficiation, and binary solvent extraction. For deep ocean sequestration, the release of a C/W emulsion stabilized with pulverized limestone may be desirable because the emulsion will not acidify the ambient seawater.[4] For geologic sequestration, the injection of a C/W emulsion stabilized with pulverized limestone or sand may be useful because the emulsion is dense; therefore, it will not buoy upward ("finger") from the injection point as pure liquid or supercritical CO$_2$ would.[6] For enhanced oil recovery (EOR), a W/C emulsion stabilized by carbon black or pulverized coal particles may be advantageous because the emulsion would serve a dual purpose. Upon disintegration in the pores of the oil-bearing stratum, the external-phase CO$_2$ would dissolve in the heavy crude oil, reducing its viscosity. The remaining slurry of fine particles in water (which can be brine or seawater) would sweep out the CO$_2$-diluted crude oil. In this case, the particles must be ultrafine, so they will not clog the pores. Liquid CO$_2$ has been proposed for coal beneficiation.[7] Because of different surface properties, coal and mineral materials are separated into two streams. Coal is separated in the form of a coal−CO$_2$ slurry, while mineral matter remains in the aqueous phase. A W/C emulsion stabilized by pulverized coal particles may also prove to have a dual purpose. The external-phase liquid or supercritical CO$_2$ may form a coal−CO$_2$ slurry, and the dispersed-phase water (which could be sea- or wastewater) may form a gravity-separated mineral-matter slurry. For binary solvent extraction, a C/W or W/C emulsion may be attractive because of preferred wettability of the substrate by water or carbon dioxide, respectively. The particles can be recovered from the remaining slurry by depressurization and evaporation.

The basic mechanism of emulsion stabilization with fine particles rests on the fact that a particle sheath forms at the interface between the two immiscible fluids, CO$_2$ and H$_2$O, preventing their coalescence into a bulk phase. (The term *fluid* is used deliberately, because both liquid and supercritical CO$_2$ can form particle-stabilized emulsions.) The particle-sheathed droplets are called *globules*.[8] Hydrophilic particles are mostly wetted by water, forming a C/W emulsion, where CO$_2$ is the dispersed phase and H$_2$O is the continuous phase. Hydrophobic particles are mostly wetted by CO$_2$, forming a W/C emulsion, where H$_2$O is the dispersed phase and CO$_2$ is the continuous phase.[9]

Materials

Carbon Dioxide. Industrial-grade liquid carbon dioxide was supplied from 50 lb siphon cylinders (Northeast Airgas). Water was either water that was deionized and filtered in a laboratory still (Millipore Milli-RO), municipal tap water, or artificial seawater (3.5 wt % reagent-grade NaCl). The following particles were used:

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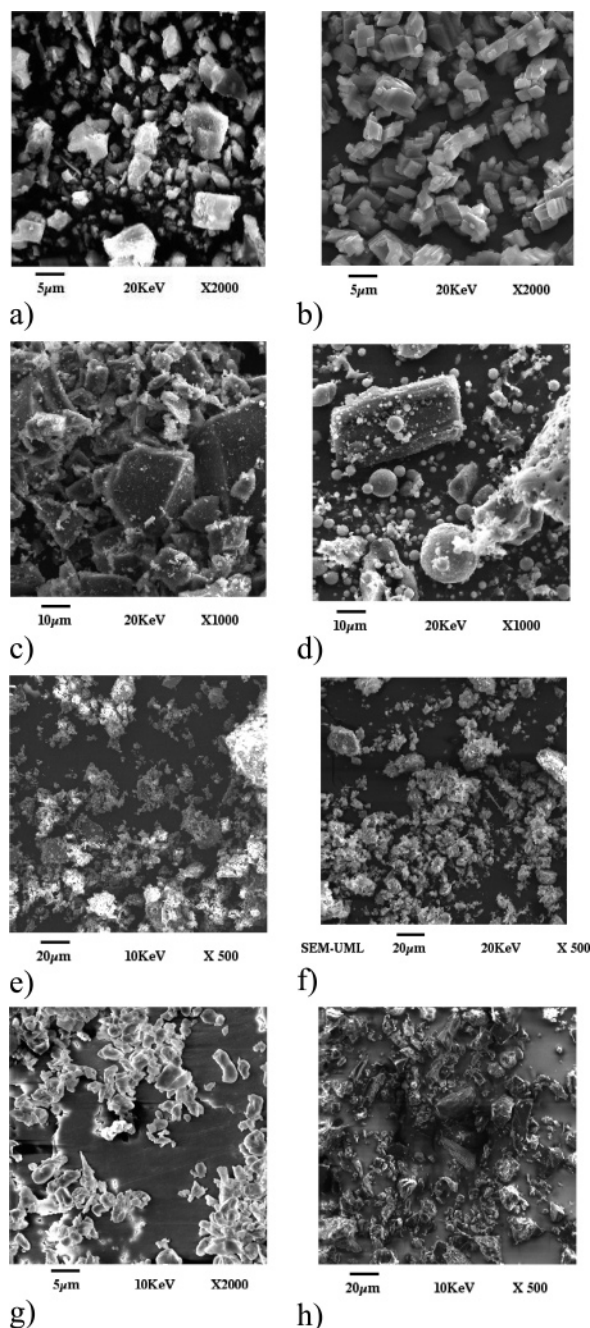
Figure 1. Scanning electron micrographs (SEM) of particles used for stabilizing C/W and W/C type emulsions: (a) Hubercarb Q6 pulverized limestone; (b) Fisher Chemical reagent-grade CaCO₃; (c) pulverized beach sand; (d) unprocessed flyash; (e) pulverized shale; (f) pulverized lizardite; (g) pulverized Teflon; and (h) pulverized coal.

1. Hydrophilic Particles. 1.a. Limestone. Mined pulverized limestone (96.5% $CaCO_3$, 2% $MgCO_3$, 1% silica and silicates, and 0.5% others) supplied by Huber Engineered Materials, Quincy, IL, was used with a bulk specific gravity of 2.7 and a solubility of 0.0035 g/(100 mL of H_2O) at 100°C. The pulverized samples can be purchased with different size distributions. In this study, Hubercarb Q1 and Q6 with nominal median particle sizes of 1 and 6 μm, respectively, were used. A scanning electron microscope (SEM) image of sample Q6 is given in Figure 1a. It can be seen that some particles are crystalline (rhombohedral) and others are irregular. For some runs, reagent-grade $CaCO_3$ was used, obtained from Fisher Scientific. An SEM image of the reagent-grade $CaCO_3$ particles is given in

Figure 1b. These particles appear to be mostly rhombohedral calcite crystals.

1.b. Sand. Ordinary beach sand was brought to the laboratory, ground in a Patterson-Kelley V-shaped wet/dry blender charged with ~200 g of sand, 500 mL of water, and 200 g of ~1 cm silicon nitride grinding pebbles. After about 24 h, the pulverized sand was recovered by Buechner filtration, and the filter cake was air-dried and then sieved through a U.S. mesh 325 sieve. An SEM image of the sand particles is given in Figure 1c. Most particles appear to be crystalline, probably quartz. Energy dispersive X-ray (EDX) spectroscopic analysis shows the most abundant element in the sand is Si with some trace metals, Ca, Mg, Fe, and Al.

1.c. Flyash. Flyash collected by an electrostatic precipitator (ESP) at the Salem Harbor, Massachusetts, coal-fired power plant was used without further processing. An SEM image of the flyash particles is shown in Figure 1d. Some particles are crystalline, some are amorphous, and there are a fair number of glassy spheres. EDX analysis shows the major elements are Si and Al, with minor elements Ca, Fe, and Mg and trace elements K, S, and Ti.

1.d. Shale. A piece of shale was ground to a fine powder in a rotary pulverizer using hardened steel plates and then sieved through a U.S. mesh 325 sieve. An SEM image of the shale particles is shown in Figure 1e. The particles appear rather amorphous. Most shales are composed of clay minerals and quartz, 60–65% SiO_2, 16–18% Al_2O_3, with the rest being Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, and other trace metal oxides.[10]

1.e. Magnesium Silicate. Pulverized lizardite, a rock rich in magnesium silicate, was obtained from the U.S. Department of Energy Albany Research Center, Albany, Oregon, and used as received. An SEM image of the lizardite particles is shown in Figure 1f. The particle shape is irregular.

2. Hydrophobic Particles. 2.a. Teflon. Teflon powder is commonly used for lubricating purposes. We purchased several grams from a local hardware store and used it without further processing. An SEM image of the Teflon powder is shown in Figure 1g. The particle shape is irregular.

2.b. Activated Carbon. Norit Darco G-60, -100 U.S. mesh size was used without further processing.

2.c. Carbon Black. Carbon black was obtained from the Cabot Corp., Billerica, Massachusetts. It is composed of 100% carbon. It was used without further processing.

2.d. Coal. Pulverized coal was obtained from the Salem Harbor, Massachusetts, coal-fired power plant. The coal is of Colombian origin, bituminous, dried, 65% carbon, and 6.6% ash. The coal was pulverized in a ball mill at the power plant and used without further processing. An SEM image of the coal particles is shown in Figure 1h. Most particles are irregular in shape, although some are crystalline, possibly due to sand and other crustal materials excavated together with the carbonaceous coal, commonly referred to as ash.

Apparatus

The investigations of the formation and properties of particle-stabilized CO_2-in-water (C/W) and water-in-CO_2 (W/C) macroemulsions were performed in a high-pressure batch reactor (HPBR) with view windows. The reactor, the auxiliary equipment for introducing the reactants into the reactor, and the monitoring instruments are depicted in Figure 2. The reactor consists of a stainless steel pressure cell of 85 mL internal volume equipped with tempered glass windows (PresSure Products G03XC01B). The windows are placed 180° apart, with
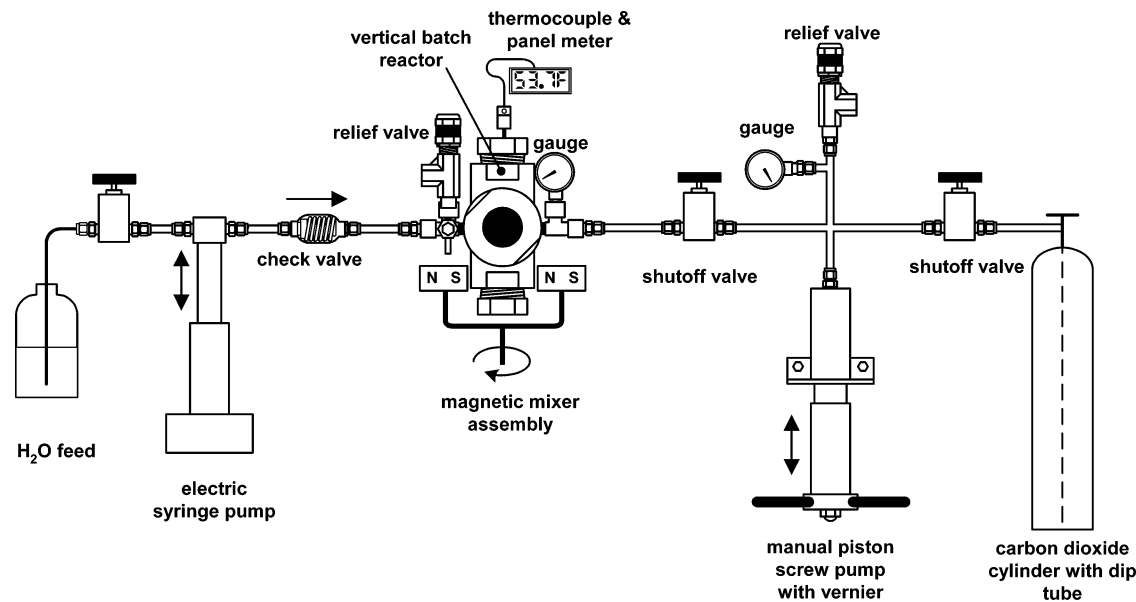
Figure 2. Schematic of high-pressure batch reactor with view windows and auxiliary equipment.

Table 1. Mean Particle Size and (Standard Deviation) in μm of Pulverized Materials Used for Stabilizing C/W and W/C Type Emulsions

			(a) Hydrophilic				
particle	limestone (Q6)	limestone (Q1)	$CaCO_3$ (Fisher)	sand SiO_2	flyash	shale	lizardite
mean size, μm	2 (1.7)	0.55 (0.4)	3.1 (1.6)	4.3 (5.7)	2.5 (3.4)	4.2 (6.0)	4.8 (3.9)

		(b) Hydrophobic	
particle	carbon black[a]	coal	teflon
mean size, μm	0.12	4.2 (4.4)	1.8 (1.0)

[a] Manufacturer data.

one illuminated with a 20 W, 12 V compact halogen bulb and the other allowing observation with a video camera. The view window diameter is 25 mm. The window diameter is used as a scale for determining droplet and globule diameter sizes. The reactor is equipped with a pressure-relief valve (Swagelok R3-A), a thermocouple (Omega KMQSS-125G-6), a pressure gauge (Swagelok PGI-63B), a bleed valve (Swagelok SS-BVM2), and a 3.2 mm port for admitting CO_2. A cylindrical magnetic stir bar with a cross shape on top (VWR Spinplus) is utilized for internal mixing. Unless otherwise indicated, the stir bar rotated at 1300 rpm. Reactor temperature was adjusted by application of hot air from a heat gun or solid dry ice chips.

For preparation of C/W macroemulsions, the usual procedure was to prepare a slurry of the hydrophilic particles in water, add a measured volume of the slurry to the HPBR through an opening, close the opening, and then add a measured volume of liquid or supercritical CO_2 by means of a syringe pump. Unless otherwise indicated, the proportions of the ingredients were as follows: 10 g of particulate matter suspended in 65 mL of water and ~18−20 mL (balance) of liquid CO_2. The pressure in the HPBR was 17.2 MPa and the temperature was 15 °C.

For preparation of W/C macroemulsions, the procedure was reversed. First, the dry matter was added to the HPBR, followed by injection of liquid CO_2. After agitation, a high-pressure syringe pump was used to inject water to a set pressure of 17.2 MPa. For the W/C emulsions, a proportion of ~65 mL of CO_2/ (20 mL of H_2O) was used.

Particle and Globule Size Determination

For most particles used in this study, the particle size was determined from SEM images. In each frame, nearly all particles were counted and measured. For spherical particles, their diameter was measured; for crystalline or irregular particles, the average of two dimensions was taken, one along the long axis and the other along the short axis. The mean diameter was estimated as

$$(d_p)_{mean} = [\sum n_i(d_p) \times d_p]/N_t \tag{1}$$

where $n_i(d_p)$ is the number of particles counted that have a size d_p, and N_t is the total number of particles counted. The mean size, $(d_p)_{mean}$, and standard deviation of the particles used in this study are tabulated in Table 1.

For globule size determination, the HPBR window diameter (25 mm) is used as a scale. The diameter of globules near the window is measured under magnification and compared with the window diameter.

Results

1. Hydrophilic Particles. 1.a. Limestone. Both Hubercarb as mined pulverized limestone and Fisher Chemical reagent-grade $CaCO_3$ gave stable C/W macroemulsions. Figure 3a presents a video camera picture of a C/W macroemulsion formed with Hubercarb Q1 particles with mean particle size of 0.55 (0.4) μm, where the number in parentheses is the standard deviation. A nonuniform macroemulsion was formed, with heavier globules settling at the bottom of the water column, median-size globules being neutrally buoyant, and large globules floating on top of the water column. The large globules appear to be only partially covered with a sheath of particles. Figure 3b shows a C/W macroemulsion stabilized by Hubercarb Q6 particles with mean particle size of 2 (1.7) μm. After thorough
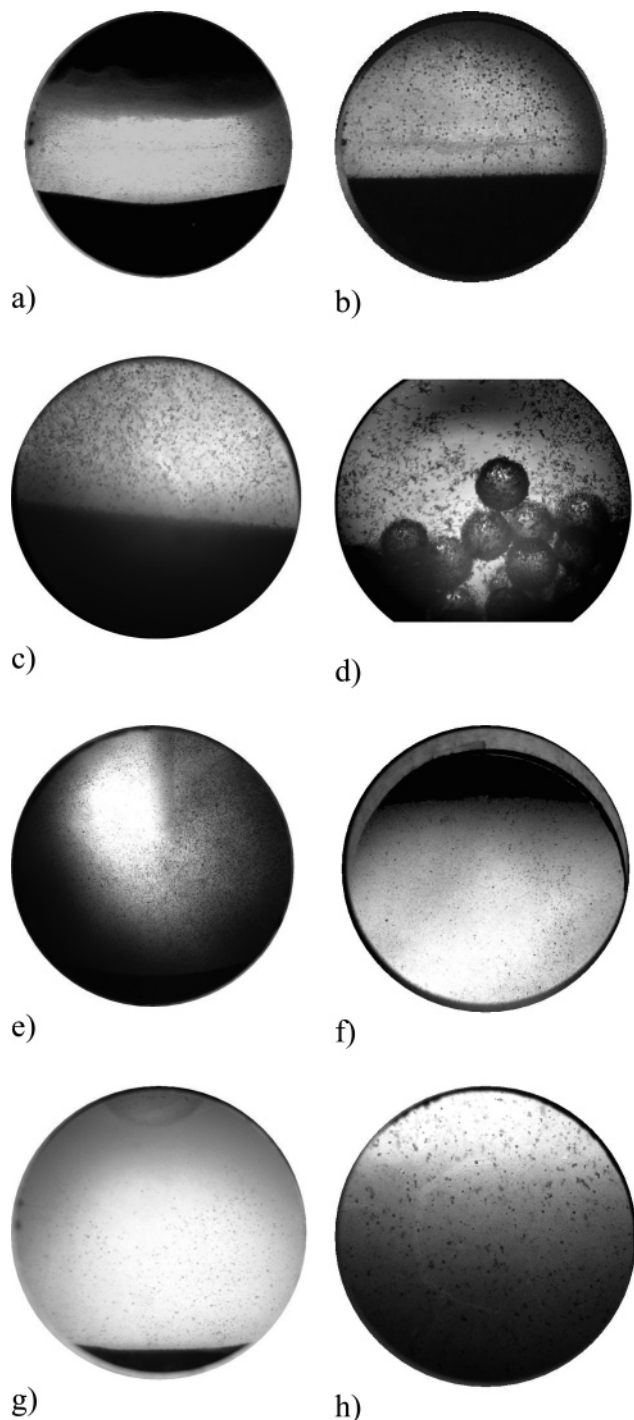
Figure 3. C/W emulsions stabilized by hydrophilic particles: (a) Hubercarb Q1 pulverized limestone; (b) Hubercarb Q6 pulverized limestone; (c) Hubercarb Q6 pulverized limestone with supercritical CO_2; (d) Fisher Chemical C-65 reagent-grade $CaCO_3$—photo taken through horizontally mounted microscope, magnification 40×; (e) pulverized sand; (f) unprocessed flyash; (g) pulverized shale; and (h) pulverized lizardite.

mixing and a rest period, most globules settled in the bottom of the pressure cell, indicating that the globules are heavier than the surrounding water. The globule diameter is in the 200–300 μm range.

Figure 3c presents a photograph of a macroemulsion formed with supercritical CO_2 and Q6 particles. The pressure in the cell was 17.2 MPa at a temperature of 45–47 °C. A stable macroemulsion formed with a globule diameter in the 100–150 μm range, smaller than that with liquid CO_2 under the same pressure and mixing conditions. Most globules settled in the

bottom of the cell. Even though the density of supercritical CO_2 (~800 kg m^{-3}) is smaller than that of liquid CO_2 (~930 kg m^{-3} at 17.2 MPa and 15 °C), the gross density of the supercritical globules is greater than that of the surrounding water.

Limestone particle-stabilized macroemulsions were also formed in a solution of 3.5 wt % NaCl in deionized water. The globule diameter is similar to that formed in deionized water alone, and all the initially present liquid CO_2 was emulsified. However, no systematic measurements were performed on emulsion yield as a function of NaCl concentration. In a study by Tambe and Sharma of decane/water emulsions stabilized by barium sulfate particles, it was found that increasing NaCl concentration decreased the yield of the emulsions, indicating that high ionic concentration tends to decrease the thickness of the double layer around the emulsion droplet. Furthermore, the emulsification potential of particles may decrease because the particles tend to coagulate with increasing ionic concentration.[12]

Figure 3d shows a microscopic image of a macroemulsion formed with Fisher Chemical C-65 reagent-grade $CaCO_3$ (mean particle size 3.1 (1.6) μm). The magnification is ~40×. Under mild mixing conditions (400–500 rpm), rather large globules formed, in the 500–800 μm diameter range. The sheath of crystalline particles adhering to the surface of CO_2 droplets is clearly visible. The micrograph is a vivid illustration of how the sheath of particles prevents coalescence of the CO_2 droplets into a bulk phase.

1.b. Sand. The milled and sieved sand particles have a mean particle size of 4.3 (5.7) μm. The large standard deviation indicates a wide distribution of particle size. The sand particles produced a stable C/W macroemulsion, probably due to the hydrophilic silica content of sand. The globule diameter is in the 200–300 μm range (Figure 3e).

1.c. Flyash. The unprocessed flyash particles have a mean particle size of 2.5 (3.1) μm. The large standard deviation indicates a wide distribution of sizes, but most particles are in the submicron to a few μm size range. The size of the particles, plus their hydrophilic character (similar to sand), is conducive for the formation of a stable C/W macroemulsion. The globule diameter is in the 80–150 μm range (Figure 3f).

1.d. Shale. Pulverized shale has a mean particle size of 4.2 (6.0) μm with a wide distribution of sizes. Pulverized shale produced a stable C/W macroemulsion, probably due to the hydrophilic character of shale's major ingredients, clay minerals and quartz. The globule diameter is in the 80–150 μm range. Because of the small bulk density of shale (2.0–2.2 g/cm^3), most pulverized shale-sheathed globules float on top of the water column (Figure 3g).

1.e. Magnesium Silicate. Pulverized lizardite has a mean particle size of 4.8 (3.9) μm. The appropriate particle size and the hydrophilic character of magnesium silicate produced a stable C/W macroemulsion. The globule diameter is in the 80–130 μm range (Figure 3h). It is noteworthy that we tried to form a C/W emulsion with pulverized olivine, a magnesium–iron silicate. The pulverized mineral did not produce a stable emulsion; an opaque mixture was formed, probably due to gelation of the particles or to a chemical reaction between liquid CO_2 and the mineral.

2. Hydrophobic Particles. 2.a. Teflon. Teflon powder is strongly hydrophobic. One gram of the powdered resin produced a water-in-carbon dioxide (W/C) macroemulsion, where water is the dispersed phase and CO_2 is the continuous phase. Water droplets sheathed with Teflon particles are evident, and no phase separation occurred during several hours of observation, which
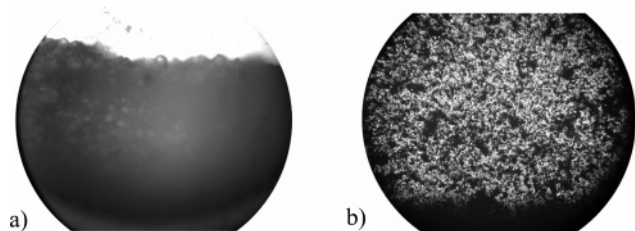
Figure 4. W/C emulsions stabilized by hydrophobic particles. Photos taken through horizontally mounted microscope, magnification 40×: (a) pulverized Teflon and (b) pulverized coal.

indicates that a stable W/C macroemulsion was formed. A microscopic image of the macroemulsion is given in Figure 4a.

2.b. Activated Carbon. When activated carbon (AC) was dispersed in liquid CO_2 under pressure, the AC agglomerated into clumps. Upon addition of water and stirring, a black mass ensued in which it was difficult to discern distinct globules.

2.c. Carbon Black. Carbon black (CB) did disperse in liquid CO_2 without agglomeration. Upon addition of water with stirring, a black, inscrutable liquid ensued. However, no phase separation occurred after several hours of observation, suggesting that a stable W/C emulsion was formed.

2.d. Coal. Pulverized coal also dispersed readily in liquid CO_2 without agglomeration. Upon addition of water with stirring, a W/C macroemulsion was formed where water droplets are sheathed with coal particles dispersed in CO_2. A magnified image of the macroemulsion is given in Figure 4b.

Mass Ratio

While in most experiments 10 g of pulverized particles were used for the creation of C/W emulsions, this amount is excessive, and a portion of the particles accumulated in the bottom of the batch reactor. The proper amount of particles necessary for macroemulsion formation can be estimated from a monolayer particle sheath model. A typical example is given for $CaCO_3$-sheathed liquid CO_2 droplets. Taking a droplet diameter of 100 μm, a sheath thickness of 2 μm (corresponding to a monolayer of Hubercarb Q6 particles with mean size 2 μm), a liquid CO_2 density at 15 °C and 17 MPa of 0.93 g/cm^3, and a $CaCO_3$ bulk density of 2.7, the mass ratio of $CaCO_3/CO_2$ is estimated at 0.2:1. Because not all particles have a uniform size (some are too small to adhere to the interface and some are too big), a practical ratio might be 0.4:1, that is, for every 1 kg of CO_2 we need 0.4 kg of pulverized limestone.

Stability

Both the C/W and W/C emulsions were stable for several hours of observational periods. Because of the pressurized content of the batch reactor and its reuse for subsequent emulsion formation, the emulsions could not be kept in the reactor for prolonged periods. However, surrogate oil-in-water (O/W) and water-in-oil (W/O) macroemulsions formed at atmospheric pressure were proven to be stable for prolonged periods. For example, Figure 5 presents a photograph of a macroemulsion formed when sebacic acid (diethylhexyl) ester, deionized water, and Hubercarb Q6 were mixed in an ultrasonic bath. The $CaCO_3$-sheathed oil globules of 0.5−1 mm diameter are clearly visible. Kralchevsky et al. concluded that oil-in-water and water-in-oil Pickering emulsions can be very stable owing to the steric drop−drop repulsion provided by the adsorbed particles.[11] These authors also predict a "catastrophic" phase inversion (i.e., from O/W to W/O emulsions) by varying the
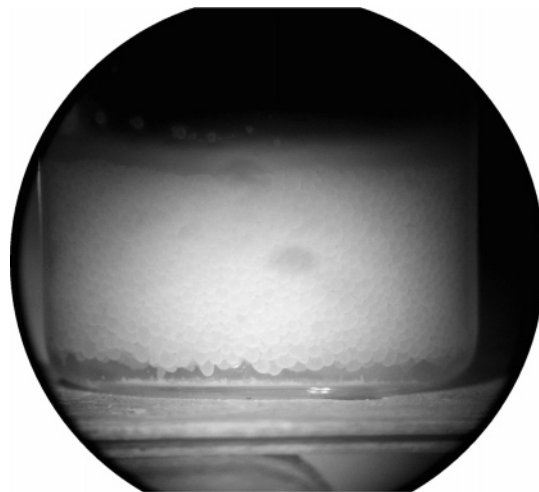
Figure 5. Pickering emulsion formed by vigorously shaking deionized water and sebacic acid (diethylhexyl) ester stabilized with Hubercarb Q6 particles. This sample has been kept on the shelf for several months.

volume fractions of oil and water, respectively. In future work, we shall experiment with phase inversion of C/W and W/C emulsions.

Discussion

Very finely pulverized particles can act as stabilizers for emulsifying two immiscible fluids, called a Pickering emulsion.[9] The presence of fine particles enables the three-phase system, two fluids and the solid particles, to reach an equilibrium state of minimal free energy.[11] The only work that needs to be applied for the formation of the emulsion is the energy for the dispersion of the three phases. The particles are held at the interface between the two fluids by van der Waals forces. Once the particle sheath forms around the dispersed droplets, steric factors prevent the globules from colliding and coalescing.[1] The particle wettability determines whether an oil-in-water (O/W) or water-in-oil (W/O) emulsion is formed,[9] or as in the work described here, a carbon dioxide-in-water (C/W) or a water-in-carbon dioxide emulsion. Hydrophilic particles (e.g., $CaCO_3$, SiO_2, flyash, shale, and magnesium silicate) are preferentially wetted by the water phase; hence, they promote C/W-type emulsions. Hydrophobic particles (e.g., Teflon, activated carbon, carbon black, and pulverized coal) are preferentially wetted by the carbon dioxide phase; hence, they promote W/C-type emulsions. Very fine particles may be dislodged from the surface of large droplets by Brownian motion, whereas large particles may not be able to pack onto small droplets.[12] The particle size needs to be adjusted to the dispersed droplet diameter. From our experiments, we conclude that, for creating a stable macroemulsion, a practical particle size-to-droplet diameter ratio is 1:20. The diameter of the globules is largely determined by the shear force of the mixing mechanism. However, the particle characteristics and size also affect the globule diameter. Using the same rotational speed of the magnetic stir bar, Hubercarb Q6 pulverized limestone and pulverized sand produced globule diameters in the 200−300 um range, whereas flyash, pulverized shale, and lizardite produced smaller globules, in the 80−150 um range. Using Hubercarb Q6, liquid CO_2 produced larger globules (200−300 um), whereas supercritical CO_2 produced smaller globules (100−150 um). The formation of smaller globules with supercritical CO_2 is likely due to the fact that the interfacial tension between supercritical CO_2 and water is smaller than that between liquid CO_2 and water.[13] We noticed that, when

applying the same shear force, supercritical CO_2 dispersed in water forms smaller droplets than those formed when liquid CO_2 is dispersed in water.

Summary

Carbon dioxide-in-water (C/W) and water-in-carbon dioxide (W/C) macroemulsions (Pickering emulsions) can be readily formed using fine particles as stabilizers. Hydrophilic particles, such as pulverized limestone, sand, flyash, shale, and a magnesium silicate rock, promote C/W-type macroemulsions; hydrophobic particles, such as pulverized Teflon, activated carbon, carbon black, and coal, promote W/C-type macroemulsions. The C/W macroemulsions consist of tiny CO_2 droplets sheathed with a layer of hydrophilic particles dispersed in water; the W/C macroemulsions consist of tiny water droplets sheathed with a layer of hydrophobic particles dispersed in carbon dioxide. Both liquid and supercritical CO_2 can be emulsified in water when stabilized by fine particles. Because of steric factors, the sheath of particles prevents the coalescence of droplets of the dispersed fluid. C/W- and W/C-type emulsions may find applications in deep-ocean and geologic sequestration of CO_2, enhanced oil recovery, coal beneficiation, and solvent extraction.

Acknowledgment

Literature Cited

(1) Lee, C. T.; Psathas, P. A.; Johnston, K. P. Water-in-CO_2 emulsions: Formation and stability. *Langmuir* **1999**, *15*, 6781−6791.

(2) da Rocha, S. R. P.; Harrison, K. L.; Johnston, K. P. Effects of surfactants on the interfacial tension and emulsion formation between water and CO_2. *Langmuir* **1999**, *15*, 419−428.

(3) Fremgen, D. E.; Smotkin, E. S.; Gerald, R. E.; Klingler, R. J.; Rathke, J. W. Microemulsions of water in supercritical CO_2: An in-situ NMR investigation of micelle formation and structure. *J. Supercrit. Fluids* **2001**, *19*, 287−298.

(4) Golomb, D.; Barry, E.; Ryan, D.; Lawton, C.; Swett, P. Limestone-particle stabilized macroemulsion of liquid and supercritical CO_2-in-water for ocean sequestration. *Environ. Sci. Technol.* **2004**, *38*, 4445−4450.

(5) Dickson, J. L.; Binks, B. P.; Johnston, K. P. Stabilization of CO_2-in-water emulsions with silica nanoparticles. *Langmuir* **2004**, *20*, 7976−7983.

(6) Golomb, D. S. Carbon dioxide/limestone/water emulsion for ocean and geologic sequestration of CO_2. In *Greenhouse Gas Control Technologies, Volume I*; Gale, J., Kaya, Y., Eds.; Elsevier Science Ltd.: New York, 2003; pp 683−688.

(7) Feng, Y.; He, D.; Chiang, S. H. Liquid carbon dioxide based agglomeration process and its application to coal beneficiation. *Adv. Filtr. Sep. Technol.* **1992**, *6*, 458−461.

(8) Ramsden, W. Separation of solids in the surface layers of solutions and suspensions. *Proc. R. Soc. London* **1903**, *72*, 156−165.

(9) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilized solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503−546.

(10) Boggs, S., Jr. *Principles of Sedimentology and Stratigraphy*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 2001.

(11) Kralchevsky, P.; Ivanov, A. I. B.; Ananthapadmanabhan, K. P.; Lips, A. On the thermodynamics of particle-stabilized emulsions: Curvature effects and catastrophic phase inversion. *Langmuir* **2005**, *21*, 50−63.

(12) Tambe, D. E.; Sharma, M. M. Factors controlling the stability of colloid- stabilized emulsions. *Adv. Colloid Interface Sci.* **1994**, *52*, 1−63.

(13) Tewes, F.; Boury, F. Effect of $H_2O−CO_2$ organization on ovalbumin adsorption at the supercritical $CO_2−H_2O$ interface. *J. Phys. Chem. B* **2005**, *109*, 1874−1881.